CHEMISTRY

INORGANIC CHEMISTRY
ORGANIC CHEMISTRY

Blocks 1 – 4

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COURSE TEAM

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PREFACE

This book deals with the topics in Inorganic Chemistry and Organic Chemistry included in the syllabus for the Second year of the B.Sc. course offered by the Andhra Pradesh Open University. These topics cover the *core area* of the subject to be sudied to be studied in the Second Year of the Three Year Degree Course in Science. The syllabus is for the sake of convenience divided into blocks, each of which comprises a number of *units*. Each block generally covers a specific area of the subject. The units are prepared by specialists in accordance with a format so designed as to enable the student read and understand them without much difficulty. Each unit begins with a statement of its aims and objectives. fEach unit has two short answer questions (as check your progress) and has at its end examination questions intended to test the student's comprehension of its subject matter. Generally technical terms with which the student may not be familiar are given at the end of each block under the head, Glossary.

First book (section A), of this course - II delaing with *Inorganic Chemistry*, it is attempted to explain the properties of chemical elements and their compounds in terms of the electronic configuration of the atoms of the elements. This section seeks to compare in groups the properties of those elements which have similar electronic arrangements. It is hoped that this will help the student to use known facts about one element to deduce probable facts about an unfamiliar element.

The second book (section B), dealing with *Organic Chemistry*. Efforts are made to describe the preparation, properties adn structure of carbon compounds. Attempts are made to explain the reaction mechanisms in terms of modern electronic theories. The University hopes that this course material will help the student to get acquainted with the concepts and princples of *Chemistry* in general and of *Inorganic chemistry* and *Organic chemistry* in particualr.

CONTENTS

SECTION – A

INORGANIC CHEMISTRY

Block - 1

CLASSIFICATION OF ELEMENTS

The inquisitive man over the ages gathered a large mass of knowledge about many things, say in our context the chemical elements. With increase in the number of chemical elements and their compounds discovered, man found it difficult to retain and remember this vast knowledge he gained. He found that certain groups of elements behave similarly and differ from others. Accordingly, he classified the known elements on the basis of their similarities in behaviour. The earliest classification was into *metals* and *non-metals*. A majority of the known elements had properties generally spoken of as *'metallic'* - metallic lustre, metallic sound, conductivity (thermal and electrical), electropositive character, etc. they were called *metals*. The rest were called *non-metals*. But a few had properties of both metals as well as non-metals, and were known as *metalloids*.

Hence to avoid this confusion and study systematically the properties of varios elements on their compounds, the classification of elements was necessary.

UNIT - 1 PERIODIC TABLE

Contents

1.1 AIMS AND OBJECTIVES

The main aim of this unit is to present you a comprehensive view of the classification of elements and observe the various tends either in groups or periods of the periodic table.

When you have completed the reading and understanding of the various aspects covered in this unit you must be able to

- Appreciate the need of a classification of elements
- Describe the construction of the long form of the periodic table
- Reason out the basis for the classification of elements into s, p, d and f blocks
- Know the meaning of ionization energies of elements and satisfy the various trends in their values
- Account for the variations in atomic and ionic radii both in groups and periods
- Appreciate the great significance attached the electronegativity concept and thereby classifying compounds as ionic or covalent.

1.2 INTRODUCTION

The above classification was not very helpful for a large number of elements under metals and non-metals categories. Classification of elements had become more meaningful and really useful in the 19th century. With the advancement of atomic theory by **Dalton**, the atomic weight drew the attention of scientists. **Dobereiner's** *law of triads*, **Newland's** *law of octaves and* **Lother Mayer's** *atomic volume curve* were among the notable contributions in the field of classification of elements. In spite of faulty atomic weight data **newland** observed the periodicity in properties. More correct atomic weights of elements helped **Mendeleeff** to arrive at a better classification which is followed even today with little modification.

1.3 PERIODIC TABLE

Mendeleeff arranged the elements in a tabular form in the ascending order of their atomic weights while placing the elements with similar properties one below the other. The resulting *table of elements*

came to be called the *periodic table*. His observation about the periodicity in properties was known as the *periodic law*. It may be stated as follows. *The elements with similar physical and chemical properties appear at regular intervals when they are placed in the ascending order of their atomic weights.* Alternatively it can be stated as follows. *The physical and chemical properties of elements are a periodic function of their atomic weights.* The law held sway for some time. But as more and more elements were discovered the earlier table had to be expanded to give the new elements their appropriate places.

The modified Mendeleeff's periodic table (Fig 1.1) has nine groups ranging from I to VIII and O. Ordinarily one element is placed in a square under its group as in periods 1,2, and 3. But periods 4, 5 and 6 two elements were placed in a square, one at the top left and another at the bottom right corner in the square. Those at the top left are designated as A-subgroup and those at the bottom right as B-subgroup elements in their respective groups. This placement of two elements together in a square shows that they have some properties in common. Writing them apart and somewhat up and down indicates that they also differ in many of their properties. Besides this at certain places in the table the sequence of increasing order of an atmic weight was reversed. The periodic table had therefore to be modified again. After Moseley showed the *atomic number* to be a more fundamental property than the atomic weight the elements were assigned their respective atomic numbers. The atomic numbers of elements in the periodic table agreed well with their positions in the table. Further, the B-subgroup elements were separated from the A-subgroup elements resulting in the long form of the table.

Check your progress - 1

1. Why is an atomic number of an element considered more important than atomic weight?

The long form of the periodic table that is currently in use (Fig 1.2) gives a square for each of the elements. Normally, one expects the long form of the talbe to be composed of 32 vertical columns, but for compactness it is restricted to 18 columns, the remaining 14 columns relating to the *lanthanide* and *actinide* elements are placed at the bottom of the rest of the table.

The long form of the table clearly brings out the gradation in properties of elements not only along a period but also down a group. The so-called demerits of Mendeleeff's table no longer appear in the long form of the table.

1.4 LONG FORM OF THE PERIODIC TABLE

The first quarter of the twentieth century had made great strides in the advancement of science. The atom was no longer the ultimate indivisible particle of **Dalton.** Discharge tube experiments showed the atom to be a composite particle of electrons and protons. **Rutherford** discovered the nucleus of an atom and proposed the planetary model of the atom. **Bohr** enunciated his revolutionary theory of hydrogen atom based on the quantum theory. It was later modified by **Sommerfeld. Moseley** discovered the atomic number which is a better fundamental property of elements than the atomic weight. Soon the electronic configuration of atoms of elements came to be known. The relation between atomic structure (electronic configuration) and the chemical properties of elements was observed. These paved the way for the emergence of the present day long form of the periodic table (Fig. 1.2) and its justification in regard to *the periodicity in properties of elements as a function of atomic number.*

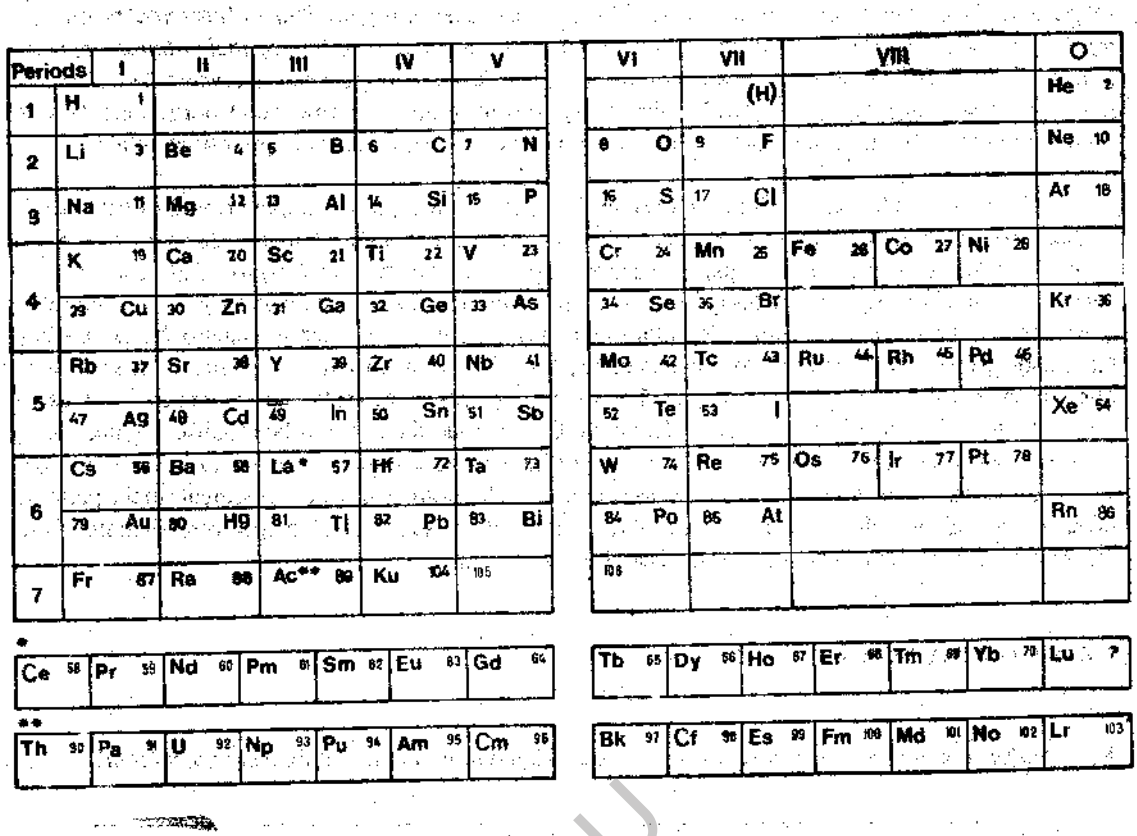

Fig. 1.1 - Mendeleeff's Periodic Table

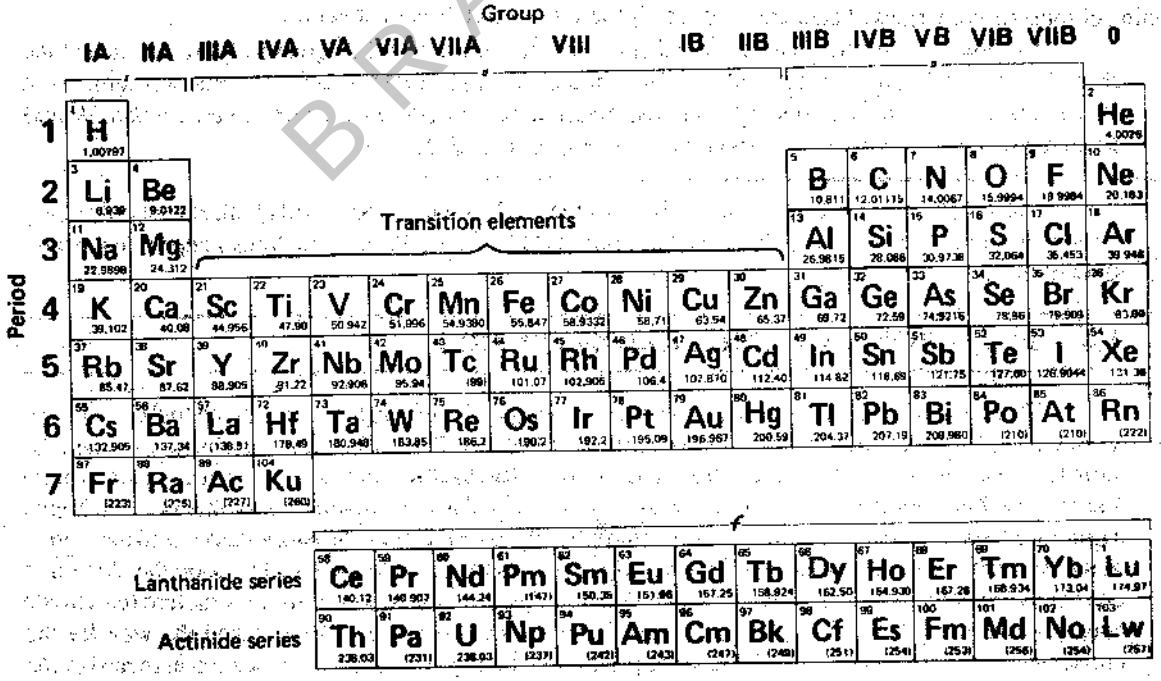

Fig. 1.2 - Long Form of the Periodic Table

The atomic number is a fundamental property of an element. The electronic configuration is a direct consequence of the atomic number. The electronic shells (orbits) around a nucleus have definite composition and capacity for electrons. These vary from shell to shell. The shells comprise one or more but a definite number of component sub-shells. Each sub-shell has again a definite capacity for electrons. The energies associated with the shells and sub-shells or more correctly the electrons residing therein denoted by quantum numbers determine the actual electronic configuration of the atom.

All elements in a group (vertical column) will have similar outer electronic configuration. Thus ns^1 is the outer electronic infiguration for Group I-A elements and ns^2 for Group II - A elements, $ns^2\ np^1$ is for Group III-B elements and so on. The sum of the superscripts indicate the number of electrons in the outermost shell and agree with the group number. This reveals the relation between outer electronic configuration and properties of elements. The minor differences in chemical behaviour are attributable to the differences in their inner electron configuration. Having found such a relation between the electronic configuration and the position of elements in the periodic table, one is apt to go a step further in founding an electronic basis for the classification of elements.

1.5 ELECTRONIC CONFIGURATION

The *Aufbau principle*, *Pauli's exclusion principle* and *Hund's rule of maximum multiplicity* laid the foundations for assigning electronic configuration for the atoms of elements. It may be recalled here that the atomic number gives the number of electrons in the atom or of the protons in the nucleus of the atom. Very often one arrives at the correct electronic configuration. But in certain cases other factors which contribute to greater stability of the atom play an important role. The spectroscopically observed electronic configuration would be slightly different from the expected electronic configuration.

A close study of the electronic configurations of elements reveals that electronic configurations with half-fielled and completely filled sub-shells (with their attendant symmetry) render the atoms more stable than when they are otherwise. Chromium and copper may be cited as examples of such cases, chromium, Cr(Z=24) has $3d^5\ 4s^1$ instead of $3d^4\ 4s^2$, and copper, Cu(Z=29) has $3d^{10}\ 4s^1$ instead of $3d^9\ 4s^2$. In these examples the 3rd-orbitals are either half-filled (5 electrons only) as in Cr or completely filled (10 electrons) as in Cu.

The long form of the table is thus in conformity with the electronic configuration of the elements. The electronic configuration in turn has its basis in Bohr's concept of atom. It is for this reason that the long form is said to be Bohr's *long form of the Periodic table*. But it is not correct to say that Bohr has devised the periodic table.

1.6 'DIFFERENTIATING' ELECTRON AS BASIS FOR CLASSIFICATION OF ELEMENTS

As the atomic number increases by unity from one element to the next, the latter element has one extra electron in addition to those in the preceding element. Here it is assumed that the arrangement of the electrons remains as such. This additional electron enters the available lowest energy orbital. In doing so it makes all the difference between this and its preceding element. It is therefore rightly called the *differentiating electron*. It is thus evident that the differentiating electron has a special significance. The classification of elements is thus designated according to the orbital into which the differentiating electron enters. The elements are thus designated as s, p, d and f-, blocks of elements based on the type of orbital.

1.6.1 s-Block elements

Elements of group I-A for example, Li (Z=3), Na (Z=11) and K (Z=19) have (He) $2s^1$, (Ne)$3s^1$ and (Ar)$4s^1$ configurations respectively. From this it can be readily seen that ns^1 is the general outer electronic configuration for elements of group I-A. Similarly, elements of group II-A, namely Be (Z=4), Mg(Z=12)

and Ca (Z=20) having (He) $2s^2$, (Ne)$3s^2$ and (Ar)$4s^2$ for their electronic configurations can be assigned ns^2 as their general outer electronic configuration. Since in elements of groups I-A and II-A the differentiating electron enters into 's' orbital, they are classed together as s-block elements.

1.6.2 p-Block elements

As in the above case the elements of groups III-B to VII-B and 'O' have their differentiating electrons entering into the p-orbital of the outer most shell. They are accordingly known as *p-block* elements. Each p-orbital can hold two electrons. Therefore the three p-orbitals can hold six electrons. Hence there are six groups of elements in this block. The group III-B element has $ns^2\,np^1$ configuration while group O element has ns^2np^6. The elements of the intermediate groups reflect the gradual filling up of the p-orbitals to completion ($ns^2\,np^2$, $ns^2\,np^2$ ..... $ns^2\,np^5$).

1.6.3 d-Block elements

The elements in groups III-A to VII-A and VIII have in general their differentiating electron entering into the d-orbitals of the penultimate or the inner shell. They are therefore referred to as *d-block* elements. To these eight elements in a given period are added elements of group I-B and II-B to make a total of 10 elements corresponding to the 10 electrons filling the five *d-orbitals*. The inclusion of I-B and II-B elements in the d-block is justified by a consideration of certain of their properties like formation of coloured compounds, formation of complexes and catalytic activity which are similar to those of the elements in group III-A to VII-A and VIII. There are four series of d-block elements relating to the 3d, 4d, 5d and 6d orbitals.

Sc (Z=21) ..... to.....Zn(Z=30).....3d series
Y (Z=39)..... .....to .....Cd(Z=48).....4d series
La (Z=57), Hf(Z=72).....to.....Hg(Z=80).....5d series
Ac(Z=89), Ku (Z=104) and Hn (Z=105) .....6d series
The 6d-series is incomplete.

1.6.4 f-Block elements

The elements bearing atomic numbers 58 to 71 Cerium to Leutecium, and elements with atomic numbers 90 to 103, Actinium to Lawrencium have their 'differentiating' electrons entering into the pre-penultimate (n-2)f orbitals. Hence they are called *f-block* elements. Corresponding to the 14 electrons filling the seven f-orbitals there are 14 elements in each of the 4f and 5f series of the *f-block* elements, corresponding to the 4f and 5f orbitals.

A closely related classification of elements is that based on the electronic configuration of their atoms. Elements with similar outer electronic configuration are grouped together as belonging to one type. This metod of classification distinguished four different types of elements. i. the *noble gas elements*, ii. the *representative elements*, iii. the *transition elements* and iv. the *inner transition elements*.

1.6.5 The noble gas elements

These are formerly known as inert gas elements and are the group O elements (from helium to radon). They are all characterized by their outer electron configuration $ns^2\,np^6$ except for helium ($1s^2$). In common, their outermost shell of electrons is filled to capacity. All the inner shells are also completely filled.

1.6.6 The representative elements

These are elements with ns^1 to $ns^2\,np^5$ outer electronic configuration. It is thus apparent that the outermost shell is incomplete. The inner orbits are completely filled with electrons. Elements belonging

to groups I-A, II-A, and III-B to VII-B are classified as the representative elements.

1.6.7 The Transition elements

These conform to the $(n-1)d^{1-9}$ ns^2 outer electron configuration. It is thus apparent that they have not only the outermost shell but also the penultimate shell incompletely filled with electrons. That is, two outer shells are incomplete. Cu ($3d^{10}4s^1$) and Zn ($3d^{10}4s^2$) and their related elements are considered transition elements although they have the completely filled (n-1) d orbitals. The reasons for such a consideration are the same as those already given for the classification of *d-block* elements. These mark a transition from the representative elements of *s-block* to the representative elements of the *p-block*, i.e., from group II-A to group III-B. Corresponding to the filling of 3d-, 4d-, 5d and 6d- subshells there are four transition series each consisting of ten elements. All these series begin with a group III-A element.

1.6.8 The inner transition elements

These are the elements with $(n-2)f^{1-13}(n-1)d^1$ ns^2 outer electronic configuration. These have three outer shells incomplete. The f-orbitals appear only in shells for which the principal quantum number is 4 or more. The energy of (n-2)f orbital is comparable to that of (n-1)d orbital. Hence the differentiating electrons flow into the (n-2)f orbitals (from Ce to Lu) only after an electron enters into the (n-1) d-orbital (at La). When the (n-2)f-orbitals are completely filled, the electrons begin to flow into the (n-1)d-orbitals to completion. Because of the similarity in properties the elements with $(n-1)d^1ns^2$ (La and Ac) are also sometimes considered as members of the f-series of elements. The first series of inner transition elements appear in the 6th period and the second series in the 7th period corresponding to the 4f- and 5f- orbital filling. These are called inner transition elements as they show a transition among the transition elements. The 4f-series are called *lanthanides* and 5f- series *actinides*.

La (57) $5d^16s^2$ Ce (58) $4f^2\,5d^0\,6s^2$ ..... Lu (71) $4f^{14}\,5d^1\,6s^2$
Ac (89) $6d^17s^2$ Th (90) $5f^0\,6d^2\,7s^2$ ..... Lr (103) $5f^{14}6d^17s^2$

1.7 PROPERTIES OF ATOMS AND THEIR PERIODICITY

The validity of law lies in its universal applicability or correctness in a majority of cases. Before one accepts a law as valid beyond doubt it is put to proof. In the present context let us see how far the arrangement of elements in the periodic table corresponds to the periodicity in their properties.

The properties like colour, state, density, hardness, melting point, boiling point, thermal and electrical conductivities of elements are not the properties of their individual atoms but are of the molecules of the elements. A molecule is a collection of atoms. It is not possible to isolate an individual atom and study its properties. Properties of atoms like atomic size, ionic size, ionisation potential or energy, electron affinity and electronegativity, however, govern the chemical behaviour of elements they compose. Our objective is to study these properties of atoms.

Check your progress - 2

2. What is meant by periodicity ?

1.7.1 Atomic radius

For a rigid spherical body its radius can be measured with accuracy.. But an atom is far from being rigid and is very diffuse. The probability of finding the electrons never becomes zero even at great distances from the nucleus. But, there is a limit where it tends to obe zero allowing a boundary line to be drawn. X-Ray and electron diffraction studies permit measurement of internuclear distances. In the case of noble gas elements composed of *monoatomic molecules* one can imagine a situation where at least two atoms come closest as to touch one another. Half of the internuclear distance then is the *atomic radius*. But many elements are composed of aggregates of atoms called *molegules*. In the case of an element containing molecules composed of two atoms (diatomic), two different values for the closest approach of atoms are obtainable. Half of the smaller value is the *covalent radius* (Fig. 1.3) and half of the larger value is the *Van der Waal's radius* (Fig.1 .3). Covalent radius is half the internuclear distance between covalently bonded atoms. The Van der Waal's, radius is half of the internuclear distance between

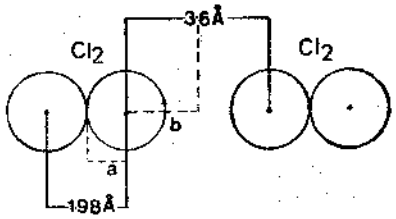

Fig. 1.3 (a) Covalent radius (b) Van der Waal's radius

atoms not bonded to one another, but happen to be at closest approach due to Van der Waal's forces of attraction.. Similarly in the case of metals in the solid state where atoms are in closest packing, half of the internuclear distance is called the *metallic radius*. Note that this is some what larger than the radius measured in their covalent compounds. Generally covalent radius is taken as a measure of the atomic radius. These are measured in angstrom units (1 angstrom = 1.0×10^{-8} cm)

1.7.2 Atomic and covalent radii of some elements

Element radius (A°)	Atomic radius (A°)	Covalent	Element radius (A°)	Atomic radius (A°)	Covalent
Li	1.55	1.23	B	0.98	0.82
Na	1.90	1.54	A1	1.43	1.18
K	2.35	2.03	C	0.92	0.77
Be	1.12	0.90	Si	1.32	1.11
Mg	1.60	1.36	N	0.92	0.75

The covalent radius of elements changes with the multiplicity of the bond and remains almost constant for a given multiplicity of bond (Tabel 1.7.2) in any compound.

1.7.3 Covalent radii of carbon in some compounds

Compound	Bond arrangement	Covalent radius (A°)	Bond multiplicity
Diamond	C - C	0.77	Single
Ethane	C - C	0.77	"
Propane	C - C	0.77	"
Ethylene	C = C	0.67	Double
Acetylene	C ≡ C	0.60	Triple

1.7.4 Periodic trends in atomic radii

As the atomic number increases along a period there is a decrease in their atomic (covalent) radii. The differentiating electrons of elements in a period flow into the same outermost shell as in periods 1,2 and 3. Sometimes they also go into the penultimate shell as in periods 4,5,6 and 7 and even into the prepenultimate shell as in periods 6 and 7. They never go into a new shell of higher principal quantum number. The increasing nuclear charge of elements along a period then pulls not only the outermost electronic shell but the inner shells as well nearer and nearer to the nucleus causing a decrease in size. This decrease is very large between elements of groups I-A and II-A as an s-electron is involved. The decrease in atomic size amongst elements of the p-block (groups III-B to VII-B) is small where p-electrons are involved. This variation in decrease in size reflect the greater penetrability of an s-electron (orbital) towards the nucleus than that of a p-electron (orbital) (Fig. 1.6).

1.7.5 Covalent radii of atoms of some elements (A°) of period 2

Element	Li	Be	B	C	N	O	F
At. No.	3	4	5	6	7	8	9
Elec.confgn	$2s^1$	$2s^2$	$2s^22p^1$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2s^22p^5$
Cov. radius	1.23	0.90	0.82	0.77	0.75	0.73	0.72

Further the decrease in size of atoms from Group II-A to those of Group III-A (the first element in each of the d-series) is quite appreciable. In this case that is in group III-A element, the additional electron enters not into the same outermost shell as in the previous element of group II-A but into the d-orbital of the penultimate (or inter) shell.

1.7.6 Covalent radii of some of elements of groups IIA - and III-A

Gr. II-A	Ca	Sr	Ba
Elec. confgn.	$4s^2$	$5s^2$	$6s^2$
Cov. radius (A°)	1.27	1.54	1.98
Gr. III-A	**Sc**	**Y**	**La**
Elec. confgn.	$4s^23d^1$	$5s^2\,4d^1$	$6s^2\,5d^1$
Cov. radius (A°)	1.44	1.62	1.69

Within the transition (*d*) series of elements the decrease in size from element to element is very small. This is due to the entry of the differentiating electrons into the same (n-1) d-subshell of the inner (penultimate) shell.

1.7.7 Covalent radii of elements of 3d series

3d series	Sc	Ti	V	Cr	Mn	Fe	Co
Elec.confgn Cov. radius(A°)	$3d^14s^2$ 1.44	$3d^24s^2$ 1.32	$3d^34s^2$ 1.22	$3d^54s^1$ 1.18	$3d^54s^2$ 1.17	$3d^64s^2$ 1.17	$3d^74s^2$ 1.16

Among the inner transition series of elements the decrease in size is of particular interest. For example, in the lanthanide series (4f-series) for an increase in fourteen units of nuclear charge from cerium (Z-58) to leutecium (Z-71) the decrease in size is only about 0.1 A. This is due to the entry of the differentiating electrons into 4f-orbitals.

1.7.8 Covalent radii of some elements of 4f series

4f series	Ce	Pr	Gd	Tb	Yb	Lu
Elec.confgn Cov. radius(A°)	$4f^25d^06s^2$ 1.65	$4f^35d^06s^2$ 1.65	$4f^75d^16s^2$ 1.61	$4f^95d^06s^2$ 1.59	$4f^{14}5d^06s^2$ ---	$4f^{14}5d^16s^2$ 1.56

The effect of increased nuclear charge in these elements is nearly counterbalanced by the electrons filling f-orbitals of the prepenultimate shell. Thereby it adds to the shielding effect of inner shell electrons. Because of the specially small decrease in atomic size among these elements it is given a name *'Lanthanide contraction'*. A similar contraction is noticeable in the Actinide series (5f-series) and is known as *Actinide contraction*.

In passing from one period to the next period the differentiating electron enters into a new outer shell of higher principal quantum number. As the new shell is farther from the nucleus, there is an abrupt increase in the size of atoms of elements of Group I-A over their preceding elements of Group 'O'.

In a periodic group the atomic size increases appreciably with atomic number as the electron is added to an outer higher principal quantum level.

1.7.9 Covalent radii of some elements of group I-A

4f series	Li	Na	K	Rb	Cs
Elec.confgn Cov. radius(A°)	$2s^1$ 1.23	$3s^1$ 1.54	$4s^1$ 2.03	$5s^1$ 2.16	$6s^1$ 2.35

The increase in nuclear charge in these elements is insufficient to overcome such an expansion. However, the increase in atomic size from one element to the next is less than expected, since the inner shells are greatly attracted towards the nucleus, while the outermost shell is also somewhat drawn inwards. This is amply evidenced by the example of Group II-A and Group III-A elements.

Among the transition groups although an increase in atomic size is noticed in passing from a 3d-sseries element to a 4d-series element there is practically no change between a 4d-and a 5d-element of the same periodic group. This is a consequence of the inclusion of the fourteen lanthanide elements and the lanthanide contraction they exhibit.

17.10 Covalent radii of some elements of 3d, 4d and 5d series

Group	III-A	IV-A	V-A	VI-A	VII-A
3d-series	Sc	Ti	V	Cr	Mn
Elec.confgn. Cov. radius(A°)	$3d^1 4s^2$ 1.44	$3d^2 4s^2$ 1.32	$3d^3 4s^2$ 1.22	$3d^5 4s^1$ 1.18	$3d^5 4s^2$ 1.17
4d-series	Y	Zr	Nb	Mo	Tc
Elec.confgn. Cov. radius(A°)	$4d^1 5s^2$ 1.62	$4d^2 5s^2$ 1.45	$4d^3 5s^1$ 1.34	$4d^5 5s^1$ 1.30	$4d^5 5s^2$ 1.27
5d-series	La	Hf	Ta	W	Rc
Elec.confgn. Cov. radius(A°)	$5d^1 6s^2$ 1.69	$4f^1 5d^2 6s^2$ 1.44	$4f^1 5d^3 6s^2$ 1.34	$4f^{14} 5d^2 6s^2$ 1.30	$4f^{14} 5d^5 6s^2$ 1.28

1.8 IONIC RADIUS

An ion is formed when an atom gains or loses one or more electrons. Like an atom, an ion is also not a rigid body because of its diffuse electron cloud. Measurement of ionic radius is more difficult. It is never half of the interionic (inter-nuclear) distance measurable in an ionic compound, since two like atoms do not combine together to form an ionic compound. Pauling has evolved a method of determining the ionic radius in the case of ionic compounds containing isoelectronic ions (Na^+F^-, K^+Cl^-, Rb^+Br^-, Cs^+I^-). Here he made the assumption that the size of the ion is inversely proportional to its *Effective nuclear charge*, $Z^*=Z-S$, where Z is the nuclear charge and S is the *shielding (Screening) constant*. Pauling thus determined the ionic radii as Na^+ 0.95 A°, K^+ 1.33 A°, Rb^+ 1.48 A°, Cs^+ 1.69 A°, F^- 1.36 A°, Cl^- 1.81 A°, Br^- 1.95 A°, and I^- 2.16A°. Assuming the constancy of ionic radii in their compounds the radii of other ions can readily be obtained from the measured inter-ionic distances.

When an atom gains or loses one or more electrons the nuclear attractive forces redistribute themselves about the new electron population. When an atom loses electrons forming a *cation* the effect or attractive force of the nucleus on these electrons becomes more. This is because the number of electrons in the cation is less than in the neutral atom. As a result the electronic shells are pulled inwards, i.e towards the nucleus. This inward pull causes an appreciable contraction in the size. A *cation* is thus smaller than its corresponding neutral atom.

When an atom gains an electron or electrons forming an *anion*, the effect of the attractive force of the nucleus becomes less than in the neutral atom. This is so because the number of electrons around the nucleus has increased. As a consequence there is an expansion of the electron cloud. An *anion* is thus larger than the correspoonding neutral atom (Table 1.8.1).

1.8.1 Atomic and ionic radii of some elements (A°)

Element	Elec. configuration		Radius	
	Atom	Ion	Atom	Ion (charge)
Li	(He) $2s^1$	(He)	1.23	0.61 (+1)
Na	(Ne) $3s^1$	(Ne)	1.54	0.95 (+1)
Mg	(Ne) $3s^2$	(Ne)	1.36	0.65 (+2)
O	(He) $2s^2\ 2p^4$	(He) $2s^2\ 2p^6$	0.73	1.40 (- 2)
F	(He) $2s^2\ 2p^5$	(He) $2s^2\ 2p^6$	0.72	1.40 (- 1)
Cl	(Ne) $3s^2\ 3p^5$	(Ne) $3s^2\ 3p^6$	0.99	1.81 (- 1)

The size of the cation decreases as the number of electrons it loses increases for reasons already stated.

Fe	Elec. Confgn.	$3d^6\ 4s^2$	1.26 A°
Fe^{2+}	" "	$3d^6\ 4s^0$	0.76 A°
Fe^{3+}	" "	$3d^5\ 4s^0$	0.64 A°

1.8.2 Periodicity in ionic radii

The ionic radius as already indicated changes with the number of electrons lost or gained. Unless the elements involved form ions of the same charge, no useful purpose is served in explaining the changes in how the ionic size changes with atomic number. In a periodic group all elements form M^{n+} ions of the same charge. Parallelling an increase in atomic number the ionic radius also increases. This is similar to that observed in their atomic radii. Among the transition series of elements which are capable of forming ions with identical charge, the ionic radius decreases steadily with increase in atomic number (Table 1.8.3)

1.8.3 Sizes of atoms and ions of some 3d- series of elements (A°)

Metal	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
M	1.44	1.32	1.22	1.18	1.17	1.17	1.16	1.15
M^{2+}	-	0.90	-	-	0.80	0.76	0.74	0.72
M^{3+}	0.81	-	0.74	0.69	-	.640	0.63	0.62

The decrease in size of the ions of the inner transition elements of similar charge is far less (Table 1.8.4)

1.8.4 Sizes of atoms and ions of some elements of 4f- series (A°)

Metal	Ce	Pr	Nd	Pm	Sm	Tb
M	1.65	1.65	1.64	1.63	1.62	1.56
M^{3+}	1.11	1.09	1.08	1.06	1.04	1.00

Among the isoelectronic ions the size decreases as the nuclear charge increases (Table 1.8.5).

1.8.5 Decrease in size of some isoelectronic ions (A°)

Element	C	O	F	Na	Mg	Al	Si
Elec. Confgn. Cov. rad.(A°)	$2s^2\ 2p^2$ 0.77	$2s^2\ 2p^4$ 0.73	$2s^2\ 2p^5$ 0.72	$3s^1$ 1.54	$3s^2$ 1.36	$3s^23p^1$ 1.18	$3s^2\ 3p^2$ 1.0
Ion	C^{4-}	O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}	Si^{4-}
Elec. Confgn. Ion. radius (A°)	$2s^2\ 2p^6$ 2.60	$2s^2\ 2p^6$ 1.40	$2s^2\ 2p^6$ 1.36	$2s^22p^6$ 0.95	$2s^2p2^6$ 0.65	$2s^22p^6$ 0.50	$2s^2\ 2p^6$ 0.41

What is said of atomic radii of the transition and inner transition series of elements is also true in the case of their ions of similar chrge.

1.9 IONIZATION POTENTIAL

An electron in an atom is constantly under the attractive influence of the nucleus. Only on absorbing energy from the surroundings or from an external source of energy an election jumps into a higher energy orbital. This is possible when the quanta of energy absorbed (nhv) equals the difference in energies (E_2 -- E_1) associated with the orbitals involved. Here E_2 and E_1, refer to the energies of the higher and lower orbitals involved. This outward movement of the electron continues with continued absorption of energy. At one stage the electron escapes from the atom, or comes out of the attractive influence of the nucleus. The *amount of energy just sufficient to pull a loosely held electron out of the attraction of the nucleus of an isolated atom in its lowest (ground) state of energy is known as the ionization potential.* This is also called ionization energy. The electron thus pulled out first from the atom is necessarily the one which is most loosely held by the nucleus. It is also the one to come into the atomic orbitals as the differentiating electron in the atomic build. By loss of an electron the atom is transformed into a *caton. The ionization potential is thus the minimum energy required to remove the most loosely held electron from an isolated (gaseous) atom in its ground state to form a unipositive ion.*

$$M + \text{Ionization energy} \rightarrow M^+ + e^-$$

The ionization energy is of hydrogen graphically represented in Fig. 1.4. The figure shows that 13.6 eV or its equivalent 313.6 kilocalories per mole atoms is the energy required to pull out the 1s electron from the hydrogen atom. The ionization potential is measured in electron volts (eV) and the ionization energy is expressed in kilocalories per mole of atoms. It is nowadays expressed in SI units (KJ/mole) kilojoules per mole.

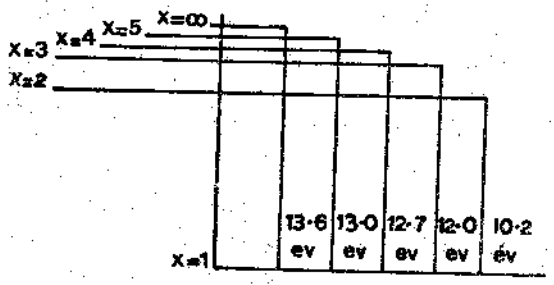

Fig. 1.4 Graphic representation of ionization energy of hydrogen

It amounts to saying that it is the energy with which the 1s electron is held by the nucleus of hydrogen in the atom in its ground state. Ionization potentials are obtained from discharge tube experiments.

Unlike the hydrogen atom, atoms of other elements contain more than one electron and are said to be multi-electron atoms. It is possible to remove all the electrons one by one through continuous supply

of energy. The minimum energies necessary to remove successive electrons from the increasingly positively charged ion in its lowest energy state are called the second, third, fourth and so on ionization potentials. The magnitudes of the energies required for pulling out an electron increases steadily from the first ionization potential (IP_1) to the second (IP_2), to the third (IP_3) and so on. This increasing magnitude of successive ionization potentials can be accounted for by considering that a unipositive ion is smaller than a neutral atom, a dipositive ion is still smaller than a unipositive ion so on. Also an electron is held more tightly in a unipositive ion than in a neutral atom, and an electron in a dipositive ion is still more strongly bound to the nucleus than in a unipositive ion and so on. Thus, the successive ionization potentials increase in the order $IP_1 < IP_2 < IP_3 < IP_4 <$ ..... IP_n

1.9.1 Periodicity in ionization potentials

Ionization potential (or first ionization potential) is commonly observed in elements including hydrogen which have one electron. The ionization potential increases with atomic number along a period and reaches a maximum at the noble gas element (Table 1.9.2). This may be related to the decrease in the atomic size and increase in nuclear charge. On passing to the next element, viz., an alkali metal of the next period, there is a steep drop in the ionization potential. Once again it increases along the period till the next noble gas element is reached. Down a periodic group of elements although the atomic number increases largely, the ionization potential decreases. This reflects the increase in size of atoms down a periodic group inspite of increase in nuclear charge.

1.9.2 Ionization potentials of some elements (ev)

Element	Atomic number	Atomic radius (A)	Ionization potential		
			IP_1	IP_2	IP_3
H	1	0.32	13.595		
He	2	0.93	24.581	54.403	
Li	3	1.23	5.390	75.619	122.419
Be	4	0.90	9.320	18.206	153.850
B	5	0.82	8.296	25.149	37.920
C	6	0.77	11.256	24.376	47.864
N	7	0.75	14.540	25.593	47.426
O	8	0.73	13.614	35.146	54.934
F	9	0.72	17.418	34.980	62.646
Ne	10	0.71	21.559	41.070	63.500
Na	11	1.54	5.138	47.290	71.650
Mg	12	1.36	7.644	15.031	80.120

A plot of the ionization potentials of elements against their atomic numbers (Fig 1.5) shows a periodic rise and fall all along with discontinuities here and there. The alkali metals occupy the lowest positions while the noble gas elements occupy the peaks. The discontinuities observed cannot be explained on the basis of the atomic size and nuclear charge alone. Certain factors besides those which influence the ionzation potential need be considered here.

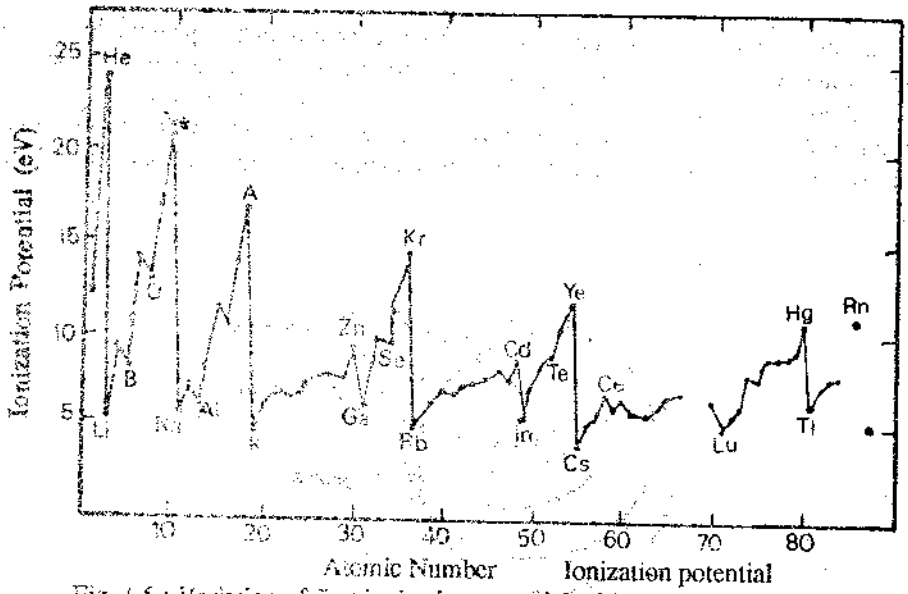

Fig. 1.5 : Variation of first ionization potential with atomic number

1.9.3 Factors influencing the magnitude of ionization potential

The magnitude of ionization potential is influenced by a number of factors chief of which are *(a)* nuclear charge, *(b)* atomic radius, *(c)* shielding effect, *(d)* extent of penetration of an electron, *(e)* stable electronic configuration and *(f)* electrostatic repulsion within an electron pair.

1.9.3.1 Nuclear charge

An increase in nuclear charge tends to increase the attractive pull of the nucleus for the electrons in the same shell. The ionization potential correspoondingly increases.

1.9.3.2 Atomic radius

The larger the atomic radius (the distance between the nucleus and the most loosely held electron in the atom) the less is the attraction for the electron and so the ionization potential is lower and vice versa.

1.9.3.3 Shielding effect

The most loosely held electron in an atom is shielded by other electrons from the attraction of the nucleus. This shielding is specially more efficiently offered by the electrons in the inner filled shells. As the nucleus pulls the loosely held electron towards itself the electron is repelled by the other electrons. As such the electron does not feel the full charge of the nucleus. The larger the number of these other electrons the greater is the shielding they offer. The influence of the nucleus effectively felt by the loosely held electron is called the *effective nuclear charge*, Z*. It is given by the relation Z* = Z--S where Z is the nuclear charge and S the total shielding (screening) constant offered by all other electrons. The shielding effect varies from electron to electron depending upon its orbital occupancy and the principal quantum number of the shell it belongs to.

1.9.3.4 Extent of penetration

In the atomic build it is said that electrons enter into atomic orbitals following the *aufbau* principle. It does not mean that an electron entering into a higher energy orbital remains in its principal quantum level alone revolving about the nucleus. It does not remain outside the domain of the inner filled shells. Actually it can penetrate towards the nucleus to an extent depending upon the eccentricity of its orbital governed by its azimuthal quantum number, l. The less the value of l the greater is its penetration towards the

nucleus. Thus the degree of penetration of an electron in a given principal quantum level is in the order $s > p > d > f$. In other words, *s*-electrons penetrate more closely towards the nucleus than *p*-electrons of the same principal quantum level. The *p*-electrons penetrate more closely than the *d*-electrons which in turn are superior to *f*-electrons in this respect (Fig.1.6). It is clear from the above that the ionization potential of an s-electron is larger than that of a *p*-electron which in turn is greater than that of a *d*-electron and so on.

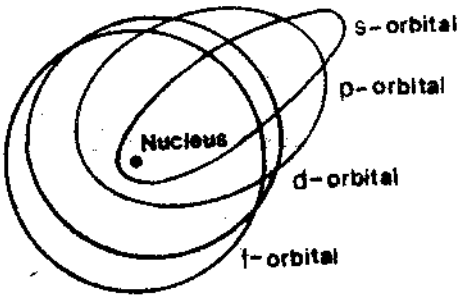

Fig. 1.6 : Penetration of atomic orbitals

1.9.3.5 Stable electronic configuration

Half-filled and completely filled subshells with the attendant symmetry in the arrangement of electrons offer extraordinary stability to an atom. And that anyother arrangement of electrons results in a less stable atom. This is also known from the examples of chromium and copper and noble gas elements.

1.9.3.6 Electrostatic repulsion within an electron pair

Pauli's principle allows two electrons of opposed spin to pair up and occupy a given orbital but not electrons of the same spin. Irrespective of the spin an electron, it carries unit negative charge. Therefore it is not unreasonable to expect a certain repulsion between the electrons in a pair. When it is a question of removal of an electron from a pair, it is the one that enters last that is loosely held by the nucleus. It is the one with spin opposite to that of the others. By loss of that electron the residual atom (unipositive ion) attains stability. This repulsion within a pair and the forthcoming stable configuration (half- filled state)allows the removal of the electron with ease.

Referring to the ionization potential curve pertaining to elements in periods 2 and 3 and later periods as well, omitting the transition and inner transition series for the present, the ionization potential in general increases from the alkali metal to the noble gas element. But at two places that is, at Group III-B and Group VI-B elements it drops to a lower value.

In the atoms of a Group III-B element ($ns^2\ np^1$) a p-electron appears for the first time in the outermmost shell. The p-electron is less penetrating than the earlier s-electrons. These latter shield the p-electron with the result that it becomes easier to remove p-electron than an s-electron. Also the removal of the p-electron leaves a filled and so stable ns subshell. The ease of removal of the p-electron becomes greater with increasing atomic number specially in the case of elements immediately following the transition series. This is due to the increased shielding effect of the inner filled shells.

The drop in ionization potential at the group VI-B elements is due to a different cause. The outer electronic configuration $ns^2\ np^4$ shows only one pair of electrons in the p-subshell. This reverts to the stable $ns^2 np^3$ (half-filled subshell) structure by loss of one electron. It may now be said that electrostatic repulsion within the pair of p-electrons is one of the reasons for the low ionization potential. The stability of the half-filled state that occurs by loss of an electron from the pair is another reason. In addition, the full shielding effect of the other electrons in the atom aids the elements of Group VI - B to have a lower ionizatiion potential.

Among the transition series of elements the ionization potential is nearly constant due to firstly unchanged outermost electronic configuration. And secondly, the size of their atoms remains almot the same. But for a small decrease in the size of atoms there is a correspondingly small increase in ionization potential. Similar is the case with the inner transition series of elements.

The importance of the concept of ionization potential lies in predicting the electropostive or electronegative character of the element concerned and so its ability to form ionic compounds. Further the normal oxidation state an element attains in its compounds can also be predicted. A low value for ionization potential indicates highly electropositive character of the element and a high value a highly electronegative character of the element. Elements with very low or very high ionization potentials (except the noble gas elements) are capable of forming ionic compounds. Again elements with low ionization potentials are good reducing agents in as much as they readily give electrons and those elements with high values are good oxidizing agents because of their ability to take up electrons readily. As energy changes involved in chemical reactions are not of a high order, the oxidation state of an element normally attains can be guessed correctly by reference to the successive ionization potentials of the element. It corresponds to that number of the ionization potential beyond which there is a sudden large jump in the value. For example,

IP_1 of Na is 5. 138; IP_2 of Na is 47.29; Oxidn. state of Na= +1
IP_1 of Mg is 7.644; IP_2 of Mg is 15.03; IP_3 of Mg is 80.13, hence the oxidation state of Mg is +2.

1.10 ELECTRON AFFINITY

In the process of ionization an atom absorbs (accepts) energy and gives out an electron. In a sort of reverse operation one can expect an atom to accept an electron and give out energy. In this process it sforms an anion with unit negative charge. **The energy released when an electron is taken up by a neutral gaseous atom in its lowest energy(ground) state is called the electron affinity.** Corresponding to the addition of second, third and fourth electrons successive second, third and fourth electron affinities may be thought of. The second and third electron affinities will have negative values owing to the repulsion between the negatively charged ion and the electron (Table 1.10.1). Taking up an electron or electrons and the extent to owhich the outermost electronic configuration is short of octet (ns^2np^6). Small atoms with nearly filled outermost shells (halogens) have high electron affinity. Atoms with outermost shells sparsely filled (like the alkali and alkaline earth metals) have very low electron affinities. The atoms of noble gas element with an octet (ns^2np^6) of electrons for their outermost shell have no electron affinity.

Unlike the ionization potential the electron affinity cannot be measured directly by experiment. However the electron affinity of an atom can be determined as the de-ionization energy of its uninegative ion, but with the sign reversed. The electron affinity is also measured in electron volts or kilocalories or kilojoules per mole of atoms.

$$X^- + \text{Energy} \longrightarrow X + e^-$$

For most elements the electron affinity values cannot be so determined. In such cases the electron affinities are obtained through an application of Born- Haber cycle to thermodynamic data for their ionic compounds. Elements with high electron affinity have a high tendency to form negative ions and ionic compounds.

1.14 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Atomic number of element was considered to be the fundamental property of it as the properties depend upon atomic number.

2. The repetetion of Physical and Chemical Properties of elements in regular manner is called periodicity.

1.15 GLOSSARY

Atomic number: This gives the number of electrons in an atom or the numbr of protons in the nucleus of the atom. It is also the position of the element in the periodic table.

Atomic weight: It is the weight average of the isotopic masses. It is expressed in atomic mass units.

Effective nuclear charge : This is the attractive influence felt by an electron. It is equal in magnitude to the nuclear charge of the atom less the shielding constant offered by all other electrons except the one under question.

Electron affinity: It is the tendency of an atom to attract electrons (bonding) to itself, this is a mere number.

Heat of hydration or hydration energy: It is the energy released when a gram-mole of a substance gets hydrated in aqueous solution at infinite dilution by attracting the polar water molecules around it. This is measured in kilocalories per mole or kilojoules per mole.

Heat of Vaporization: It is the energy required to vaporise a mole of substance. It is measured in kilocalories per mole or kilojoules per mole.

Ionization potential: It is the energy required to pullout the most loosely held electron from a neutral gaseous (isolated) atom at its ground state. This is measured in electron volts or kilocalories or kilojoules per mole of atoms.

Oxidation state or number : This denotes the number of electrons lost (or apprently lost) or gained (or apparently gained) by an atom in the formation of a compound. Loss of electrons confers a positive oxidation state and gain of electrons a negative oxidation state.

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Block - 2

STUDY OF ELEMENTS OF GROUPS O, IA AND IIA.

The first two vertical rows in the long form of the periodic table are called alkali metals (IA) and alkaline earth metals (IIA). These are 'S' block elements. The last vertical row of elements in the periodic table is 'O' group. These elements are referred to as inert gases or noble gases. They are 'P' block elements.

UNIT - 2 STUDY OF ELEMENTS OF GROUPS O, IA AND IIA

Contents:

2.1 AIMS AND OBJECTIVES

This unit aims to rationalize the physical and chemical properties of elements based on their electronic configurations and to account for the similarities and differences in the properties of the elements.

After completing the reading and understanding the various aspects presented in this unit you must be able to:

- Account for the existence of zero group elements as monoatomic gases devoid of chemical reactivity.
- Envisage the possibility of the formation of some compounds particularly with fluorine and oxygen of xenon and krypton.
- Explain the close similarities of alkalimetals and their high electropositive character..
- Account for the diagonal relationship of lithium with magnesium.
- Explain the equivalent character of beryllium in group II elements and its resemblance to aluminium of group III.
- Observe and account for the trends in the various physical and chemical properties of group II elements.
- Explain the trend in the properties of oxides halides and oxysalts of alkaline earth elements.
- Note the differences in the properties of group I and group II elements and rationalize them.

2.2 INTRODUCTION

Elements of the periodic group O are characterized by $ns^2 np^6$ electronic configuration for their outermost shell. All the inner shells of their atoms are filled to capacity with paired up electrons. This electronic configuration renders them chemically inert. Hence they were called 'inert' elements (gases). As their heavier members were found to form true chemical compounds they are now called '*noble*' gas elements. The term 'group O' refers to their general zero valency (absence of chemical activity). The elements of groups IA and IIA have super-structures over those of the previous noble gas elements forming the core for their general outer electronic configuration with electrons entering into a higher energy principal quantum shell. Thus the outer electronic configurations for elements of groups O, IA and IIA are $ns^2 np^6$, $ns^2 np^6 (n+1) s^1$ and $ns^2 np^6 (n+1)s^2$ respectively. The $ns^2 np^6$ outermost electronic configuration renders the noble gases chemically inert or inactive heavier elements with large atoms under special conditions. The $(n+1)s^1$ and $(n+1)s^2$ structures of groups IA and IIA elements make them active. In chemical reactions these elements of groups IA and IIA lose their outermost shell electrons forming cations, since their atoms are relatively large and have low ionization potentials.

2.3 ELEMENTS OF GROUP 'O'

Group 'O' comprises of helium, neon, argon, krypton, xenon and radon. The group number indicates the valence of the elements there in. Their valence is zero. This is in conformity with their chemical inactivity. As the first principal quantum shell contains only an 's' orbital helium has the electronic configuration $1s^2$. All other members of this group have $ns^2 np^6$ outer most electronic configuration. Radon, the last of these elements, is radio-active and little is known about it. The physical characteristics of these elements are given in 2.3.1.

Paralleling an increase in atomic number of elements, their atomic weight and atomic radius (covalent radius) increase. The increase in atomic size is due to increase in the number of protons and so of neutrons, two massive particles contributing to the atomic mass. The increase in atomic radius is due to a new shell of electrons of higher principal quantum number appearing with each next element down the group.

The noble gas elements are composed of monoatomic molecules (or isolated or uncombined atoms) with only weak van der Walls forces operating between them in the liquid and solid states. This is indicated by the ratio of their specific heats (Cp/Cv) which is nearly equal to 1.66. They have low melting points and boiling points too. Their densities show an increase as a consequence of the increase in atomic weight.

2.3.1 Some physical characteristics of group O elements

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic No.	2	10	18	36	54	86
Elec. confgn.	$1s^2$	$2s^2p^6$	$3s^23p^6$	$4s^24p^6$	$5s^25p^6$	$6s^26p^6$
Atomic wt.	4.00	20.17	39.95	83.86	131.8	(222)
Ratio of sp. hts.	1.65	1.64	1.65	1.69	1.67	-
Cov.radius(A°)	0.93	0.71	0.98	1.12	1.31	-
Density (g/cc)	0.178	0.90	1.78	3.71	5.85	-

Melting Point (°C)	-272.1	-245.8	-187.1	-169	-140	-
Boiling Point (°C)	-268.0	-245.8	-185.6	-151.7	-109.1	-
heat of vapouri sation (Kcals/mole)	0.02	0.422	1.56	2.16	3.02	-
IP (Kcals/mole						
Promotion energy $ns^2np^6 \rightarrow ns^2np^5$	567	497	363	323	280	-
(n+1)s'	20.0	16.6	11.5	9.9	8.3	-

The ionization potentials or energies decrease as the atomic radius increases with atomic number.. Since the increased nuclear charge is insufficient to overcome the effect of increase in atomic size, the attraction of the nucleus for the outermost electron decreases. Their high ionization energies together with the filled electronic shells are responsible for their inability to participate in chemical reactions.

Promotion energies also decrease with increase in atomic number. These promotion energies for krypton and xenon are somewhat low. These low values reveal the possibility for these elements to form compounds under suitable conditions. We will have occasion to learn about these elements in detail in a later unit (unit 4).

2.4 ELEMENTS OF GROUP IA

Lithium, sodium, potassium, rubidium, caesium and francium belong to this group. They have the characteristic ns^1 structure for their outermost electronic configuration. Hydrogen has $1s^1$ electronic configuration and is justifiably placed under this group. Because of many differences in its physical and chemical properties it is not treated as one among the alkali metal elements. The reasons for such a consideration are given in the next unit where a detailed study of the position of hydrogen is taken up. The last of these elements namely *francium* is a radioactive element and very little is known about it. The physical characteristics of these elements are given in table 2.2

2.4.1 Some physical properties of Gr. IA elements

Property	LI	Na	K	Rb	Cs	Fr
Atomic No.	3	11	19	37	55	87
Elec. confgn.	$2s^1$	$3s^1$	$4s^1$	$5s^1$	$6s^1$	$7s^1$
Atomic wt.	6.94	22.99	39.10	85.47	132.91	
Cov.radius (A°)	1.55	1.90	2.35	2.48	2.67	
Ionic radius (A°)	0.60	0.95	1.33	1.48	1.69	
Density(g/cc)	0.53	0.97	0.86	1.48	1.87	
Melting pt. (°C)	180.5	97.8	63.2	39.0	29.6	
Boiling pt. (°C)	133.1	890	768	701	605	
Heats of vapou-risation (Kcals/mole)	26.4	26.0	21.5	20.5	18.8	
Heat of hydration (Kcals/mole)	121	95	76	69	62	

IP_1 (eV)	5.39	5.14	4.39	4.17	3.89	
IP_2 (eV)	75.61	47.9	31.81	27.5	25.7	
Electronegativity	1.0	0.9	0.8	0.8	0.7	
Oxidation state	+1	+1	+1	+1	+1	
Std. Oxidn. potential(V) $M \rightarrow M+ + e^-$	+3.05	+2.71	+2.93	+2.93	+2.92	

All the elements are characterized by the same outermost electronic configuration ns^1. With increase in atomic number, a new outer shell of higher principal quantum number is added at each next element. As a result, the atomic (covalent) radius and the corresponding ionic radius increase for element to element down the group. Of course the cation is much smaller than the corresponding neutral atom. This is because an electron is stripped off in the formation of cation (ionization process) from the outermost shell.

The atomic weight increases as the atomic number increases. This is due to the increase in the number of protons (and neutrons) as the atomic number increases. The density increases steadily from lithium to caesium but potassium is lighter than sodium. This is due to the sudden increase in size of the atoms from sodium to potassium perhaps to make provision for 3d-orbitals in the elements that follow it.

Check your progress - 1

1. Why is the density of potassium lower than that of sodium?

As their outermost electronic configuration (ns^1) suggests, they are the first elements in each of the periods with largest atoms. This together with their crystal structures (body centred) make these metals soft enough to be cut with a knife.

Unlike hydrogen with its $1s^1$ electronic configuration these elements possessing the same outermot electronic configuration (ns^1) are solids. This reflects the absence of discrete molecules in these metals. The nature of bonding between atoms is different. The atoms in the solid elements are bound by metallic bonds. Their melting points and their heats of vaporization are low. They decrease with increase in atomic number showing that the interatomic attractions are sufficiently weak. This is true of an atom with *one valence electron* having to bond with *eight nearest neighbouring atoms* at appreciable but same distance. It is a case of delocalisation of bonds. Caesium with the largest atoms has a melting point as low as 29.6°C.

The *ionization potentials* decrease with increase in atomic number. This is because a new outer shell formed farther away from the neuleus. Their second ionization potentials are very high denying the elements the existence of +2 oxidation state. All of them have low ionization potentials. This is responsible for their strong reducing ability.

Their ability to lose electrons is further evidenced by their high positive oxidation potentials. In spite of its small sized atoms and high ionization potential, lithium has the highest oxidation potential. This is because of the small size of lithium ion and its large heat of hydration. These counter balance the effect of higher ionization potential. Lithium is the most powerful reducing agent. The small size and high hydration energy of lithium ion also explains the formation of hydrated lithium salts. Some sodium salts are also hydrated for a similar reason.

The *high positive oxidation potentials* coupled with low ionization potentials pose a problem in the extraction of the metals from their ores. They have to be obtained by electrolysing their fused salts free from water. They react with water. They are therefore kept under an inert liquid like kerosene. The increasingly low ionization potentials down the group reflect their reactivity with many dry reagents. With oxygen lithium forms its oxide Li_2O, sodium, potassium, rubidium and caesium form peroxides. Potassium, rubidium and caesium also form superoxides. This is in accordance with the greater ease of loss of electrons by larger atoms.

Lithium, among the alkali metals combines with nitrogen. This is attributed to the large attractive forces operating between their small atoms. All these metals combine with hydrogen to form ionic hydrides. With halogens they form halides. They react with water and acids to form the hydroxides (which are strong bases) and salts respectively. Their chemical properties are listed in 2.4.2.

2.4.2 Chemical behaviour or Gr. IA elements.

S.No.	Reagent	Reaction	Remarks
1.	Halogens (X)	$M+1/2\ X_2 \rightarrow MX$	All elements
2.	Oxygen	$2M + 1/2\ 0_2 \rightarrow M_2O$	Lithium only
		$2M + O_2 \rightarrow M_2O_2$	Na, K, Rb and Cs
		$M + O_2 \rightarrow MO_2$	K, Rb and Cs
3.	Nitrogen (N_2)	$3M + 1/2\ N_2 \rightarrow M_3N$	Lithium only
4.	Hydrogen	$M + 1/2\ H_2 \rightarrow MH$	All elements
5.	Acids	$M + H+ \rightarrow M+ + 1/2\ H_2$	All elements
6.	Water	$M + H_2O \rightarrow MOH + 1/2\ H_2$	All elements

2.5 ELEMENTS OF GROUP IIA

Beryllium, magnesium, calcium, strontium, barium, and radium constitute group IIA.. These metals are called the alkaline earth metals. The outermost electronic configuration is ns^2. They are known as alkaline earth metals since their oxides are only slightly soluble (*like earths)* in water and the resulting solutions are strongly basic (like solutions of alkali metal). They resemble the alkali metals in many respects. They show certain differences owing to their differences in electronic configuration.

The physical characteristics of these elements are given in 2.5.1.

All the elements have ns^2 outermost electronic configuration. A new higher principal quantum level with two electrons is added with increase in atomic number. The atomic (covalent) radius therefore increase down the group. So are their ionic radii.

The atomic weight increases down the group consequent on the increase in atomic number (inclusion of more and more protons and neutrons).

The density decreases from beryllium to calcium but thereafter it increases. The decrease in density is due to the rapid increase in atomic size upto calcium. Beyond calcium the increase in size of atoms is less.

The atoms of these elements have two valence electrons. These are utilized to form (metallic) bonds with *twelve* (coordination number, 12) *nearest neighbouring atoms in* the solid state. This results in a face centred cubic crystal structure. Their atoms also are relatively large next only to those of alkali metals. As a result they are somewhat soft and can be cut with a steel knife. Their melting pioints are high but decrease as the atomic number increases.

2.5.1 Physical characteristics of Gr.IIA elements

Property	Be	Mg	Ca	Sr	Ba	Ra
Atomic no.	4	12	20	38	56	88
Elec. confgn.	$2s^2$	$3s^2$	$4s^2$	$3d^{10}\ 5s^2$	$4d^{10}\ 6s^2$	$4f^{14}5d^{10}7s^2$
Atomic wt.	9.01	24.32	40.01	81.62	137.36	226
Cov.radius (A°)	1.12	1.60	1.97	2.15	2.22	--
Ionic radius M^{2+}(A°)	0.31	0.65	0.99	1.13	1.35	--
Density(g/cc)	1.86	1.75	1.55	2.6	3.59	--
Melting pt. (°C)	1280	657	845	757	710	--
Boiling pt. (°C)	2477	1120	1490	1370	1638	--
Heats of vapourisation (Kcals/mole)	73.9	32.52	36.74	33.8	35.7	--
Heat of hydration (Kcals/mole)	--	460	395	355	305	--
IP_1 (eV)	9.3	7.64	6.11	5.69	5.21	--
IP_2 (eV)	18.2	15.03	11.98	10.89	9.95	--
IP_3 (eV)	153.9	80.1	51.2	43	36	--
Electronegativity	1.5	1.2	1.0	1.0	0.9	--
Oxidation state	+2	+2	+2	+2	+2	--
Std oxidn. potential(V) $M \rightarrow M^{2+} + 2e$	1.7	2.34	2.87	2.89	2.90	--

The *ionization potentials* decrease as the atomic number increases. The second ionization potentials are nearly twice the first ionization potentials as eexpected from their electronic configuration. However, the third ionization potential is many times greater than the second. This indicates that these elements are capable of losing the two valence shell electrons and form dipositive ions or exhibit+2 oxidation state in their compounds.

The smaller atoms with large ionization potentials hardly lose their electrons so that they form predominantly covalent compounds. This is true of beryllium and magnesium. The same is revealed by their electronegativities which decrease from beryllium. Sufficiently high electronegativity of beryllium essentially permits it to form covalent compounds. The elements with larger atoms (Ca to Ba) and lower electronegativities form ionic compounds. Magnesium forms compounds which are intermediate, but more ionic, in character.

All these elements have high oxidation potentials which increase with increasing atomic number. This suggest their good reducing ability. Calcium, strontium and barium are powerful reducing agents.

The chemical behaviour of these elements is governed by their relatively low ionization potentials, low heat of vapourization, high heats of hydration and high positive oxidation potentials. Although their low first ionisation potentials appear to favour the formation of their unipositive ions they are known to form dipositive ions only. This is due to their high heats of hydration together with high lattice energies of their compounds. The latter outweighs the unfavourable effect of the high ionization potentials (IP_1 + IP_2). Their chemical properties are given in table 2.5.2.

2.5.2 Some chemical properties of gr. IIA elements

Reagent	Reaction	Remarks
1. Halogens (X_2)	$M + X_2 \rightarrow MX_2$	All elements
2. Oxygen (O_2)	$M + 1/2\ O_2 \rightarrow MO$	All elements
	$M + O_2 \rightarrow MO_2$	Ba and Ra (Sr under Pressure)
3. Nitrogen (N_2)	$3M + N_2 \rightarrow M_3N_2$	All elements (on heating)
4. Hydrogen(H_2)	$M + H_2 \rightarrow MH_2$	Ca Sr and Ba (on heating)
5. Acids(H^+)	$M + 2H^+ \rightarrow M^{2+} + H_2$	All elements
6. Water	$M + 2H_2O \rightarrow M(OH) + H_2$	Ca, Sr and Ra with cold water, with steam Be and Mg give oxides.

2.6 COMPARISON OF GROUPS IA AND IIA ELEMENTS

Elements of both the groups (the alkali and alkaline earth metals) belong to the s-block. The alkaline earth metals (ns^1). As such the atoms of the alkaline earth metals are smaller than the corresponding alkali metals. With decrease in size of toms and increase in the number of valence electrons the alkaline earth metals are relatively hard (though still soft) and have high melting and boiling points, high heats of vaporization and large heats of hydration. The alkaline earth metals are denser due to the availability of two valence electrons and large co-ordination number (12) in their crystals. The co-ordination number in alkali metals is only 8.

The ionization potentials of alkaline earth metals are higher than those of the alkali metals of comparable atomic weight. But the standard oxidation potentials of alkaline earth metals are less than those of the alkali metals. Thus the alkaline earth metals are not as powerful reducing agents as the alkali metals.

The basic character of these elements increases down each group but it is less in the case of alkaline earth metals than those of the corresponding alkali metals. The chemical properties of alkaline earth metals are similar to those of the alkali lmetals, but are less active.

2.7 ANOMALOUS BEHAVIOUR OF LITHIUM AND BERYLLIUM

Lithium and beryllium are the first members of their respective groups. Their atoms are relatively smaller than those of the elements of their groups. Their ions are too small. They have $1s^2$ configuration in their inner shell. These properties make them behave differently from the rest of the elements of their groups. The smaller the size of the atom, the shorter is the bond length and higher is the bond energy. Because of the small size they have higher melting and boiling points and also higher ionization potentials. Thus lithium and beryllium exhibit anomalous properties. Further, they show diagonal relationship to the elements belonging to the next group but of a later period. This is due to comparable ionic charge to radius ratio. Thus, lithium resembles magnesium and beryllium resembles aluminium.

Lithium like magnesium is harder and ductile. It is not easily attacked by oxygen. Unlike the other alkali metals but like magnesium it combines with nitrogen when heated to form the nitride. Like magnesium it does not form a peroxide. Like magnesium, lithium forms a monoxide which is less basic and less soluble in water. Due to the small size of its ions it generally forms covalent compounds and its compounds are mostly hydrated. Lithium chloride is soluble in organic solvents and is deliquescent.

Beryllium differs from the other members of the alkaline earth metals because its atoms are small and because it has high electronegativity. It forms predominatly covalent compounds. Like aluminium, beryllium forms an oxide which is insoluble in water. Beryllium halides dissolve in organic solvents as do aluminium halides. Thus they show their covalent character. They undergo hydrolysis.

Check your progress - 2

What is the reason for the diagonal relationship obsrved between lithium and magnesium?

2.8 SUMMARY

A general discussion of elements in groups, zero IA and IIA has been presented. Zero group elements have ns^2 np^6 configurations that suggests almost negligible chemical reactivity and their existence as mono atomic gases. Group IA elements have ns^1 configuratioin and are highly electropositive and metallic in character. Group IIA elements are characterized by ns^2 configuration which reveals their metallic nature and many subsequential properties.

Elements of both the groups IA and IIA, popularly known as alkali and alkaline earth metals respectively belong to the 'S' block and their chemical behaviour is governed by their relatively low ionization potentials low heats of vapourisation, high heats of hydration and high positive oxidation potentials. And again compared to alkali metals alkaline earth metals are relatively harder and denser because of large cohesive energies of their crystal lattices. They are milder reducing agents and their chemical reactivity is admittedly lower than the corresponding alkali metals.

Being first members of the respective groups lithium and beryllium show anomolous behaviour. In some of their compounds they display pronounced covalent character can see a clear case of diagonal relationship in lithium resembling magnesium and beryllium to alluminium.

2.9 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines.

1. How is zero valency of noble gas elements explained?
2. Account for the decrease in the first ionisation energies with increasing atomic number of IA elements.
3. Explain the chemical bonding in alkali metals.
4. Account for the anomolous behavour of lithium in the group of alkali metals.
5. Why does beryllium resemble aluminium in many chemical properties?

II. Answer the following in 30 lines.

1. a) Justify the inclusion of alkali metals in group I on the basis of electronic configuration.
   b) What are the important characteristic features one can predict from the electronic

configuration of noble gases.

2. a) Discuss the trends observed in ionisation energies and ionic raddii of alkali metals.
   b) Comment on the variations observed in oxidation potentials, densities, melting points of alkaline earth metals.

3. Examine critically the cause and consequences of diagonal relationship observed in I & II group elements.

2.10 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. The density of potassium is lower than of sodium due to the sudden increase in size of the atoms from sodium to potassium.

2. The reason for the diagonal relationship between lithium and magnesium is their comparable ionic charge to ionic radius ratio. Similarly beryllium resembles aluminium.

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UNIT - 3 : HYDROGEN

Contents

3.1 AIMS AND OBJECTIVES

The purpose of this unit is to understand the position of hydrogen in the periodic table and to account for the proprties of hydrogen on the basis of its electronic configuration.

After making a study and understanding the various aspects of chemistry of hydrogen you must be able to:

- Appreciate the unique position of hydrogen in periodic table in terms of its electronic configuration.
- Describe how it resembles group IA metals as well as halogens.
- Explain the ortho and para hydrogens with respect to their existence and differences in properties.
- Discuss the various isotopes of hydrogen.

3.2 INTRODUCTION

In unit-2 you have studied certain typical families of groups of elements which bear ample evidence in support of the periodic law. In this unit you will now learn about the primordial substance of the universe, namely hydrogen. It is not only the first element but the first of its kind as well. It is a unique element. It cannot be placed in any specific group inview of the similarities to alkali metals and halogens.

Hydrogen does not occur as such in the free state. It, however, is a common constituent of all living matter. In combination with hydrogen it occurs in plenty in the form of water. And life on earth had its origin in water. Natural gas is another rich source of hydrogen.

3.3 APPLICATIONS OF HYDROGEN

Hydrogen is one of the most useful elements. Large quantities of it are used in the production of vanaspati (a substitute for butter) prepared by hydrogenation of edible oils. It finds the applications in the preparation of ammonia and nitrogenous fertilizers. It is also used in the manufacture of synthetic methyl alchol and synthetic petrol. Among other uses of hydrogen may be said the atomic hydrogen torch and oxyhydrogen flame which are used for welding purposes. It is also used for inflating military signal baloons. Through its use in fuel cells it is becoming a promising source of energy. In fact the stars owe their energy to the process of fusion of hydrogen nuclei into relatively heavier nuclei. Man is trying hard to control the fusion reaction on this planet to solve the energy problem.

3.4 POSITION OF HYDROGEN IN THE PERIODIC TABLE

The electronic configuration of hydrogen ($1s^1$) gives it the first place in the periodic table. 1*s* orbital can take up 2 electrons. Hence hydrogen atom can attain the helium (inert gas) configuration ($1s^2$)by gaining an electron. In this process it forms the hydride (H^-) anion. It can also lose its electron leaving the tiny unipositive hydrogen cation H^+ (proton). However small size of its atom and high ionization potential render it impossible to form the hydrogen (H^+) ion easily. But the hydrated hydrogen ion ($H+H_2O$) or (H_2O) is formed when a hydrogen halide is dissolved in water. Formation of hydride ion is possible when hydrogen reacts with highly electropositive elements such as alkali or alkaline earth metals. In the hydride ion it is in – 1 oxidation state. Normally, hydrogen atom shares its electron with atoms of other elements forming covalent compounds. The oxidation state of hydrogen in such compounds is 1.

Like the alkali metals it has only one electron in the outer shell ($1s^1$). It combines with most non metals to form compounds in which it shows electropositive character. Some of these compounds, when dissolved in water, produce hydrated hyrogen ions. These are generally known as hydronium $(H_3O)^+$ ions. Hydrogen is liberated at the cathode during electrolysis of aqueous solutions of salts and other electrolytes. This behaviour is similar to the electrolytic reduction of alkali metal ions to the corresponding metals at the cathode. But unlike the atoms of the alkali metals, hydrogen atom is relatively small with high ionisation potential. It generally forms polar or pure covalent compounds.

In spite of its resemblances to alkali metals, it bears still greater resemblance to halogens in the following aspects. Its atoms are small (covalent radius 0.32 A°). It has high ionsation potential or energy (13.1 eV or 313 kcals) more similar to that of halogens. It forms diatomic molecules like halogens. It has least tendency to lose its electron but shares its electron with other elements forming covalent compounds. Its electronic configuration ($1s^1$) is one electron short of the next noble gas (helium) structure ($1s^2$). This is similar to halogens. The halogen configuration ($ns^2\ np^5$) is one electron short of the next noble gas

configuration (ns^2np^6) . Like the halogens which form halide ions, hydrogen combines with alkali and alkaline earth metals to form the uninegative hydride (H^-) ion. Electrolysis of molten alkali metal or alkaline earth metal hydride yields hydrogen at the anode. This is similar to the liberation of halogens at anode in the electrolysis of halides of alkali metals in the fused state. But it does not form the hydride (H^-) ions with ease while the halogens readily form halide ions. Like the halogens it forms covalent compounds with many elements.

Check your progress - 1

Where does hydrogen collect during the electrolysis of molten alkali hydrides? Why?

The normal oxide of hydrogen is water and it is neutral, it is neither alkaline as the oxides of alkali metals nor acidic like the oxides of halogens.

The above discussions show that hydrogen is family by itself. However, the electronic configuration assigns it a place on top of the alkali metals in group 1A although it is non-metalllic.

3.5 ISOLATION OF HYDROGEN

Although hydrogen occurs in nature in combination it can be readily prepared in the laboratory by the action of active metals on dilute acids.

$$Zn + H_2SO_4 \rightarrow Zn\,SO_4 + H_2$$

It is manufactured on a large scale by electrolysis of water, or of aqueous solutions of electolytes. It is also prepared by chemical reduction of water by passing steam over red hot iron.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

3.6 MOLECULAR HYDROGEN

Hydrogen gas consists of diatomic molecules. All the component atoms of hydrogen are not alike. In contradiction to the Dalton's atomic theory it has two naturally occurring stable isotopic atoms which differ in their mass. One type of atoms has *unit* atomic mass and the other *two* units of mass.

The lighter one called *protium* (ordinary hydrogen) is most abundent (99.9844%) and the heavier one known as *deuterium* (heavy-hydrogen) is available in a meagre amount (0.0156%) in natural hydrogen. These two isotopes are always present in this ratio in hydrogen gas obtained from any source and by whatever method it is produced. Besides these two forms there is yet another still heavier form with three units of atomic mass. It is called *tritium*. It occurs only in traces, one part in $10^{17\text{-}18}$ parts of ordinary hydrogen. Thus ordinary hydrogen is a mixture of mostly H_2 and D_2 molecules.

3.7 ISOMERS OF HYDROGEN: ORTHO AND PARA HYDROGENS

In 1927 Heisenberg predicted the possibility of existence of two isomeric forms of molecular hydrogen. These isomeric forms differ in the spin of the two nuclei in their molecule (Fig. 3.1) Bonheffer and Harteck discovered para-hydrogen possessing markedly different properties. Para-hydrogen was obtained when hydrogen gas was cooled to liquid air temperature in contact with activated charcoal. In the para hydrogen spins of the two nuclei are opposed, in the ortho-form the nuclear spins are *parallel.*

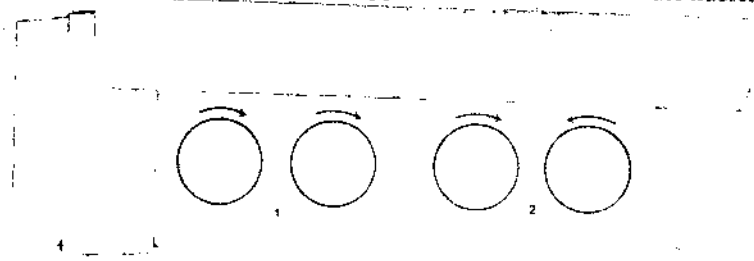


FIG. 3.1. (A) ortho hydrogen (b) Para hydrogen

However, the two electrons in these two types of molecules have opposite spins (spin paired) as is expected of any pair of electrons forming the covalent bond. At normal temperatures ordinary hydrogen is a mixture of orthoform and para- form in the ratio 3:1. Even at higher temperatures this ratio remains practically unchanged. But on cooling in the proportion of the ortho-form decreases. It is possible to prepare 99.5% pure para-hydrogen by cooling hydrogen at liquid air temperature in contact with a catalyst like activated charcoal for several hours. In the absence of catalyst the conversion is very slow.

Ortho-hydrogen has magnetic moment since the spins of its nuclei are not neutralised. Since the contribution of nuclear spin to the total magnetic moment is only very small compared to that of the electron spin contribution, ordinary hydrogen is nearly diamagnetic. The physical properties of ortho and para hydrogens are given in table 3.7.1.

3.7.1 Some physical properties of ortho-and para hydrogen

Property	Para hydrogen	ortho-hydrogen
Melting point (°K)	13.82	13.95
Boiling point (°K)	20.26	20.39
Vapour pressure at 200 °K	708.2 mm of Hg	732.9 mm of Hg.

3.8 ISOTOPES OF HYDROGEN

Three isotopes of hydrogen are known. As already stated the isotopes differ in their masses due to different number of neutrons associated with the proton in their nuclei (3.8.1). These isotopes are *hydrogen* (protium), *deuterium* (heavy hydrogen) and *tritium.* They are given the symbols H, D and T respectively being the first letters in the names. They are also represented by the symbol H with mass numbers written as superscripts. Thus they are ^{1}H, ^{2}H, and ^{3}H.

3.8.1 Some atomic characteristics of isotopes of hydrogen

Property	Protium	Deuterium	Tritium
Atomic number	1	1	1
Electronic confgn.	$1s'$	$1s'$	$1s'$
Nuclear composition	1 proton	1 proton 1 neutron	1 proton 2 neutrons
Atomic weight (amu)	1.0081	2.0147	3.0171

3.8.2. Protium

As natural hydrogen is essentially protium (99.9844%) the preparation and properties of protium are those of hydrogen gas.

3.8.3. Deuterium

It is commonly referred as heavy hydrogen. It was discovered by Urey and his coworkers in 1931. This discovery was the result of spectroscopic studies of a small residue left over after careful evaporation of a large volume of liquid hydrogen. He could prepare a nearly pure sample of deuterium by evaporating a large volume of liquid hydrogen at 13.9 °K. A cheap source of heavy hydrogen is water which contains very small amounts of heavy water (D_2O). Deuterium is isolated from heavy water by the action of sodium metal or by electrolysis of heavy water containing disolved sodium carbonate.

$$2D_2O + 2Na \rightarrow OD + D_2$$

$$2D_2O \xrightarrow{\text{Electrol}} 2D_2 + O_2$$

Deuterium is best prepared from heavy water. Heavy water is obtained by stepwise electrolysis of about 20 litres or more of water to a very small volume. Caustic soda is added to water to make it a good conductor of electricity. This process depends upon the readiness with which the 'lighter hydrogen' is liberated (about 6 times more readily than the heavy hydrogen) at the cathode leaving the residual water richer in 'heavy hydrogen'. When the volume is reduced greatly it is treated with carbon dioxide to convert the caustic soda into sodium carbonate. The resulting solution is later distilled. The distillate is again treated with caustic soda and electrolysed. This process is repeated a number of times till volume of water is reduced to about one millilitre. This sample is nearly pure heavy water. Heavy water is being produced in our country at Tuticorin in Tamilnad and Talcher in Orissa. Heavy water is nowadays produced on a commercial scale as it is a very valuable moderator in nuclear reactors (atomic piles). A moderator reduces the kinetic energy a neutron released in the nuclear fission reactions.

Check your progress - 2

What is the function of heavy water in nuclear reactor?

Heavy hydrogen differs from ordinary hydrogen in most of its physical properties 3.8.2. It takes part in all chemical reactions of the ordinary hydrogen. But those reactions are slow and sometimes incomplete. This difference in properties among the isotopes due to their relative mass differences is known as *isotope effect.* It is worthwhile noting that the mass of the heavy hydrogen is double that of ordinary hydrogen.

3.8.2 Some Physical properties of Hydrogen and Deuterium

Property	Hydrogen	Deuterium
Melting Point (°C)	-- 259.2	-- 254.5
Boiling point (°C)	-- 252.6	-- 249.4
Latent heat of fusion (Cals/mole)	28.0	52.3
Latent heat of vaporization (cals\ mole)	216.0	293.0
Vapour pressure at -- 259°C (mm of Hg)	54	58

3.9. HEAVY WATER

It is a colourless, odourless and tasteless liquid like the ordinary water. Because of its higher molecular weight its properties are slightly different 3.9.1 from those of ordinary water.

3.9.1 Some physical properties of heavy water and ordinary water.

Property	Heavy water	Ordinary water
Density (g/ml) at 20°C	1.1059	0.9982
Density of solid at m.pt.	1.107	0.917
Freezing point (°C)	3.802	0
Vapour pressure at 20°C (mm of Hg)	15.2	17.535
Temperature of maximum density	11.2	4
Dielectric constant at 20°C	80.5	82
Ionic product at 25 °C	0.3×10^{-14}	1×10^{-14}
Latent heat of fusion at m.pt. (Kcals/mole)	1.522	1.435
Latent heat of vaporisation (Kcals/mole)	9.960	9.719
Solubility of Na Cl at 25°C (g/100 g water)	30.5	35.9

Heavy water enters into all reactions of water and is the source for all deuterium compounds.

$Na_2O + D_2O \rightarrow 2NaOD$ (Sodium deuteroxide)

$SO_3 + D_2O \rightarrow D_2SO_4$ (Deuterosulphuric acid)

$Mg_3N_2 + 6D_2O \rightarrow 3\ Mg(OD)_2 + 2ND_3$ (Deuteroammonia)

Just as certain salts form hydrates with ordinary water, so also they form deuterohydrates with heavy water. $CuSo_4 . 5D_2O$; $Na_2SO_4 . 10D_2O$ are some examples of these hydrates.

3.10 TRITIUM

This is the radioisotope of hydrogen. It is produced in upper strata of the atmosphere by neutron bombardment of atmospheric nitrogen. The nuetrons required for this reaction are released by cosmic rays interacting with atmospheric molecules.

$$^{14}N_7 + {}^1n_o \rightarrow {}^3H_1 + {}^{12}C_6$$

nitrogen + neutron → tritium + carbon

It is prepared artificially by neutron bombardment of lithium and its compounds.

$$^6Li_7 + {}^1n_o \rightarrow {}^3H_1 + {}^4He_2$$

Lithium-6 + nuetron → tritium + helium

or by bombardment of beryllium with deuterons (nuclei of deuterium atoms.)

$$^9Be_4 + {}^2D_1 \rightarrow {}^3H_1 + 2\ {}^4He_2$$

beryllium + deuteron → tritium + helium

3.11 ACTIVE FORMS OF HYDROGEN

The hydrogen gas is not normally reactive at ordinary temperatures. A current of hydrogen gas passed through an acidified solution of ferric chloride is without action. But if the gas is produced *in situ* by adding a piece of zinc metal to ferric chloride solution containing acid, the solution is decolourised (reduced). This gas produced in situ is the reactive form. This reactive form is called *nascent hydrogen* (nascent, means just born). Nascent hydrogen produced by the action of sodium amalgam (NaHg) on water does not however , decolorise ferric chloride. Similarly the nacsent hydrogen from zinc and sulphyric acid reaction reduces the cholrate ion to chloride ion while that from sodium amalgam and water does not reduce the chlorate ion. These instances show that the activity of hydrogen depends upon the reaction and manner of its production *in situ* or otherwise. Since chemical reactions are attended with release of energy, the chemical energy released differ from reaction to reaction. The difference in activity of hydrogen may therefore be attributed to the energy associated with it. Further, at the moment of its production hydrogen gas in the form of minute bubbles which enlarge as they shoot up the solution. This is an indication of the gas being under pressure. It has been found that hydrogen under high pressures reduces metallic salt solutions like silver nitrate to the metal. Although nascent hydrogen is believed to be composed of atomic hydrogen this hypothesis is untenable as the reversion to molecular form of hydrogen is highly exothermic. The nature of nascent hydrogen is not yet clearly known.

3.11.1 Atomic hydrogen

Atomic hydrogen is the most reactive form of hydrogen. It is produced by breaking the bond holding the two atoms together in a diatomic molecule by homolytic fission.

$$H:H \xrightarrow{\text{Bond energy}} H + H$$

Langmuir studied this reaction extensively. It was found that it requires very high temperatures like 2300 °K to produce atomic hydrogen even in small quantities. At 10,000 °K it is found to dissociate nearly quantitatively. But as the atoms have no free existence (due to the existence of an unpaired electron in their electronic shell), two atoms with electrons of opposed electron spins readily combine to form

molecular hydrogen releasing enormous energy (98-105 Kcals/mole).

The best method of production of atomic hydrogen is due to Langmuir. It is prepared by passing a stream of hydrogen gas through an electric arc struck between two ltungsen electrodes. As the gas passes through the arc the molecules are broken into atoms or atomic hydrogen. These atoms being unstable recombine as they emerge out. This combination is catalysed by a metal surface on to which it is directed. As a result very high temperatures (4300-5300 °K) are produced. The atomic hydrogen torch is a convenient tool for welding. It has the additional advantage in that the hydrogen formed serves to protect the metal surface from atmosphere oxidation.

Atomic hydrogen is a very active agent. It combines with many nonmetals like sulphur, bromine and iodine rapidly forming their hydrides. With oxygen it, however, forms hydrogen peroxide. Many metal oxides and chlorides are reduced to the corresponding metal. Alkali metals are converted to their hydrides.

Another active form of hydrogen is obtained when the gas is subjected to silent electric discharge at very high voltages (300,00 volts). Like the atomic hydrogen it readily combines with many nonmetals like sulphur, arsenic, phosphorus and reduces many metal oxides to the metals.

3.12 HYDRIDES

By convention the binary componds of hydrogen with other elements are called *hydrides*. But in the strict sense of the term hydrides are binary compounds of hydrogen with more electropositive (or less electronegative) elements.

The modified Paneth's classification of hydrides considers three types of hydrides. They are (i) *ionic* hydrides (salt like) with hydride ion (H^-) (ii) *covalent* or *molecular* hydrides in which the bonding is covalent in nature and (iii) *metallic* hydrides in which the metallic structure is retained. This classification mainly concerns with the difference in the properties due to difference in the nature of the other element.

3.12.1 Ionic hydrides

These have ionic lattices. They have high melting points and conduct electric current in the fused state. These are formed by alkali and alkaline earth metals and certain lanthanides and actinides. They are formed by heating the metals in hydrogen.

$$2Li + H_2 \rightarrow 2LiH$$

These are stoichiometric compounds. The alkali metal hydrides have Na C1 type of crystal lattice. Those of the alkaline earth metals are more complex. In the fused state they liberate hydrogen at the anode during electrolysis. They do not dissolve in ordinary solvents but are soluble in molten halides. They decompose on heating to their elements. Their thermal stability decreases with increasing atomic number of the element down a periodic group. They are powerful reducing agents at high temperatures. Most of them spontaneously burn in air. They react with halogens (X_2) readily to form halides.

$$NaH + X_2 \rightarrow NaX + HX$$

They react vigorously with water liberating hydrogen. The amount of hydrogen so liberated is double that of the gas liberated by the corresponding metals from water. Hence calcium hydride is used under the name *hydrolith* as a handy source of hydrogen by the military. They are excellent desiccants in as much as they react with water readily.

3.12.2 Covalent hydrides

These are also known as molecular hydrides as they have discrete molecules. In the solid state the molecules are held by weak van der Waals attractions forming molecular crystals. They are accordngly soft, low melting and volatile. They do not conduct electricity in the fused state or even when dissolved in non-polar solvents.

Except noble gas elements all truly nonmetallic elements (of grs. IIIB to VIIB) form covalent hydrides. They are formed by many methods. These are direct combination of elements, reduction of certain compounds with (nascent) hydrogen, hydrolysis of metal borides, carbides, nitrides and halides.

The molecular hydride undergo thermal decomposition to the elements. Their thermal stability decreases with increase in atomic number in any periodic group. Also their thermal stability increases with decreasing electronegativity of the non-metal in a given period. Hydrides of highly electronegative elements (N,O,F,) with small sized atoms are characterized by association through hydrogen bonding. Accordingly ammonia, water and hydrogen flouride have higher melting and boiling points than the hydrides of the other members in their respective groups.

3.12.3 Metallic hydrides

As the name suggests these have metallic structures. They are interstitial in character. They are generally non-stoichiometric.

Transition metals form metallic hydrides. The nature of hydrogen in these compounds is not definitely known. They are formed by heating metals in hydrogen under pressure or by electrodeposition of hydrogen on metals used as cathodes. The metals take up large volumes of hydrogen gas which can be removed by strong heating under vaccum. The small hydrogen atoms appear to occupy the interstices in the metal lattices. They have strong reducing properties indicating that hydrogen is probably in the atomic state. The hydrogenation catalysis (like Pt and Ni) owe their catalytic activity to their ability to take up hydrogen.

There are some metallic hydrides like CuH_2, CoH_2, FeH_2 and CrH_2 which are stoichiometric. They are different from ionic hydrides in that their crystal structure is different from that of the metals involved. They are therefore called *border line metallic hydrides*. These metallic hydrides react with water and acids to liberate hydrogen.

3.13 SUMMARY

Because of the unique electronic configuration of hydrogen atom, it resembles both alkali metals of group IA and halogens of group VIIA. Thus it forms a family by itself.

Molecular hydrogen exists in two isomeric forms called ortho and para hydrogens, in the ortho form the nuclear species are parallel and in the para form they are opposed. The two isomers differ in some of their physical properties besides their stabilties.

Three isotopes of hydrogen are known, owing to the difference in the number of neutrons they are hydrogen, deuterium and tritium. Heavy hydrogen, deuterium is best prepared from heavy water. Tritium is a radioactive isotope of hydrogen.

The binary compounds of hydrogen with other elements are called hydrides. They are of three types, ionic, covalent and metallic hydrides. While transition metals form metallic hydrides highly electro positive metals as those of groupIA and II'A' form ionic hydrides. The rest of the elements, except noble gases form covalent hydrides. All these types have their characteristic properties.

3.14 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines.

1. In what important respects does hydrogen resemble halogens?
2. How is ortho-hydrogen different from para-hydrogen? Why is it so?
3. Account for the differences in the properties of heavy hydrogen and ordinary hydrogen.
4. How is tritium prepared? What is its special feature?
5. How is atomic hydrogen produced?

II. Answer the following 30 lines.

1. (a) Discuss the position of hydrogen in the periodic table.
   (b) Comment on the statement that"hydrogen forms a family by itself"
2. (a) Write a concise account on the isotiopes of hydrogen
   (b) What is meant by istope effect?
3. (a) Present a comparitive account of hydrogen and deuterium
   (b) What are the important features of tritium?
4. (a) How are hydrides classified? Give suitable examples.
   (b) Present a concise account of the chemistry of hydrides.

3.15 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Hydrogen is collected near cathode during electrolysis of aqueous solutions of alkali salt. But during electrolysis of molten alkali hydrides hydrogen is collected at the anode, similar to the liberation of halogens. This is due to the nature of hydrogen as hydride ion.

2. Heavy water functions as a very valuable moderator in nuclear reactors.

3.16 GLOSSARY

Isomers: Isomers are substances having the same molecular formula but possessing different properties.

Isotopes: Isotopes are atoms of the same element having different atomic masses, but have the same atomic number i.e., have the same number of protons.

Stoichiometric compound: Stoichiometric compound is one in which the proportion of the combining atoms is in simple integral (whole) numbers.

Author : *D.R. Rajeswar Rao*

UNIT - 4 GROUP 'O' ELEMENTS

4.1 AIMS AND OBJECTIVES

The main aim of this unit is to present to you a critical study of zero group elements and to explain your their unusual chemical behaviour in terms of their electronic configuration.

After reading and understanding the material presented in this unit you would be able to:

- explain why zero group elements are placed at the end of each period in the long form of the periodic table.
- give the reason for their existence as mono atom gases at room temperature
- state the main reason for their near total chemical inactivity
- describe the isolation of individual gases from liquid air
- state the principle in the separation of noble gases by absorption on charcola
- explain how rare gases combine with polar molcules like HCL or So_2
- explain the clath rate compound formation with quinol
- mention the use of noble gases
- discuss the bonding in xenon flourides.

4.2 INTRODUCTION

Helium, neon, argon, krypton, xenon and radon constitute the group 'O' elements. They were not known at the time of classification of elements by Mendeleeff. These elements came to be known

only towards the end of 19th century. In the early years of their discovery, they were not known to form compounds. Accordingly they were placed in a separate group. It is designated as group 'O' to indicate their chemical inertness or zero valency. The elements are placed at the right hand extreme of the periodic table after halogens. This position is fitting in that it bridges the gap between the most electronegative halogens (group VIIB) and the most electropositive alkali metals (Group IA). With the determination of their atomic number and electronic configuration they were found to have ns^2 np^4, outermost electronic configuration. Helium is an exception and has the configuration $1s^2$. The position of elements in the periodic table is justified in view of their electronic configuration. A completely filled outermost shell in any period marks the end of that period. The completely filled outermost shell in an element renders it chemically inert in as much as it can take up no more electrons into that shell. It cannot also easily lose electrons because removal of an electron from a completely filled shell requires very high energy. However, heavier elements with large atoms show a tendency to participate in chemical reactions because of their relatively lower ionisation potentials. Barlett, in 1962 prepared the first compound of xenon viz., xenon platinum hexafluoride $XePtF_6$. This is soon followed by the discovery of many other compounds. Thus these elements which were for a long time thought to be chemically inert ('inert' gas elements) came to be called *noble* gas elements. This is probably because of their reluctance to form compounds which is referred to as their nobility. In this unit you will learn about their occurence, isolation, properties, compounds with fluorine and uses.

4.3 OCCURENCE

As indicated earlier the elements helium, neon, argon, krypton, xenon, and radon form the group 'O' of the periodic table. With the exception of radon, all the others occur in the atmospheric air though to a small extent (about 1%). Argon itself account for about 0.9%. Radon is a radioactive element.

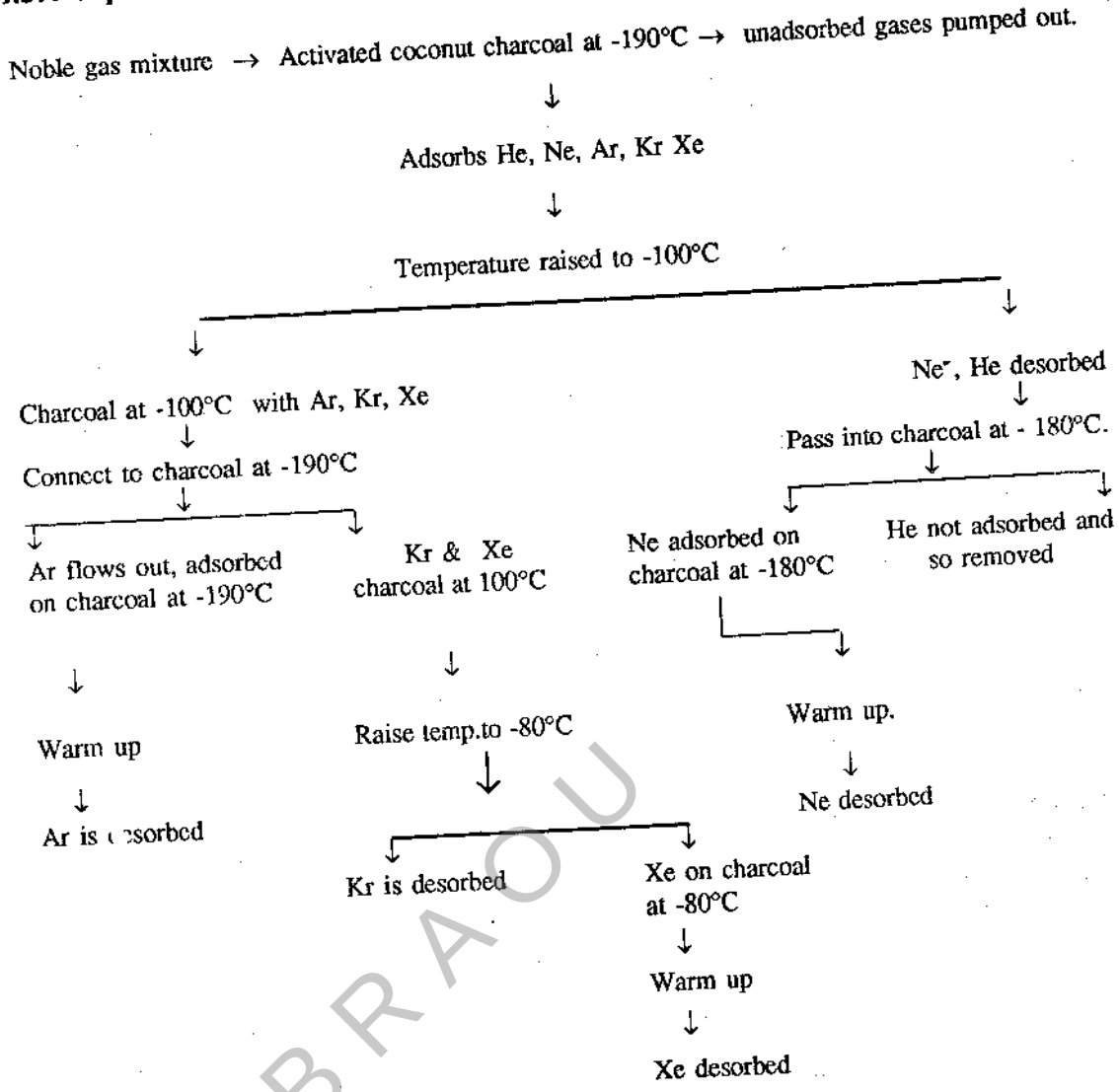
4.4. DISCOVERY

Cavendish, a well known chemist observed that atmospheric air contained about 1% of nitrogen/like inert gas. In 1892 Rayleigh experimentally observed that the density of atmospheric nitrogen is higher (0.5% more) than that of the nitrogen prepared in the laboratory. This he attributed to the presence of a heavier inert gas along with nitrogen in air. He could succeed in isolating the gas but he could not identify the same, because of its chemical inertness. Ramsay, a physicist, found this heavy inert gas to be a new chemical element by spectroscopic studies. He named it *argon* (meaning lazy) as it failed to react with metals, caustic alkalis, oxygen and dry chlorine. About the same time another inert gas was obtained from uranium minerals by Hildebrand. Ramsay took the spectrum of the new inert gas and found it to be yet another unknown element. The spectrum of this gas was identical wiht the one obtained in the spectral studies of solar corona during a total eclipse in 1868 by Janson in India and Lockyer in England. Accordingly Ramsay named it *helium* (meaning sun). The presence of helium was soon established in the atmosphere near certain springs. Discovery of these two chemically inert gas elements in the atmosphere led to further investigation for the possible existence of similar inert gas elements. In 1898 Ramsay and Travers discovered *neon* (meaning new), *Krypton* (meaning hidden) and *xenon* (meaning stranger) in the residues of liquid air. Radon was later discovered as a product of radio-active decay of elements, radium, thorium and actinium.

4.5 ISOLATION OF THE NOBLE GASES FROM ATMOSPHERE

The only source of noble gases (except radon) is the atmosphere. The isolation and separation of chemical elements or compounds are generally effected taking advantage of differences in their chemical properties. But since the noble gases are chemically inert their isolation and separation has

4.5.4 Seperation of noble gases by adsorption on charcoal



4.6 PROPERTIES OF THE ELEMENTS

The physical characteristics of these elements have already been discussed in unit 2. They are all colourless and odourless gases. They are very slightly soluable in water. They are mono-atomic gases. Their boiling points increase with increase in atomic weight. They can be liquified.

They have completely filled outer shell. They have high ionisation potentials. Because of these facts they do not show any tendency to form compounds. However there were reports that they form compound-like substances under special conditions.

Under excited conditions in a discharge tube helium is said to form He^{2+} ($He.H^{+}$) and (HeH^{2+}). Helium is also reported to react with metals used as electrodes forming WHe, Pt He_3, FeHe. It is now believed that these helides might be interstitial compounds.

The noble gases can be expected to form co-ordination compounds with powerful electron pair acceptors like boron trifluoride. The presence of pairs of electrons permits their formation of co-ordination compounds. Argon was reported to form argon-boron trifluorides ($Ar.nBF_3$, where n=1,2 or 3). It is doubtful whether they actually form such compounds, since similar compounds are not reported in the case of higher members like krypton and xenon.

Argon,, krypton, xenon and radon are known to form hydrates and deutero-hydrates of the formula $G.xH_2O$ and $G.yD_2O$ where x and y approach the value of 6 with the heavier members. Similar compounds are known to form with *phenol* C_6H_5OH, (an organic compound) conforming to the formula $G.2\ C_6H_5OH$ where G is Kr, Xe or Rn. With the exception of Rn. $2C_6H_5OH$ which melts at 50°C all other hydrates deuterohydrates and phenolates are stable only at very low temperatures. Radon also forms solid compounds at low temperatures with hydrogen chloride, hydrogen bromide, hydrogen sulphide, sulphur dioxide, and carbondioxide. The formation of the above compounds is attributed to the polarisability of large noble gas atoms by a strong dipole (like water, phenol, hydrogen chloride) inducing polarity. Then due to dipole-induced dipole forces of attraction a compound is formed. But as these forces are quite weak the compounds are unstable.

Argon, krypton and xenon are also reported to form with quinol ($CH_4\ (OH)_2$ an organic compound) *clathrate* (cage like) compounds of formula $G_3.\ C_6H_4\ (OH)_2$. These are prepared by passing the noble gases under high pressures into benzene solutions or aqueous solutions of quinol at its crystallisation temperature. This method of preparation suggests that noble gas atoms must have been physically trapped in the cavities in the crystal lattice of quinol during its crystallisation. The dipole type of compounds cited above might also be clathrates. As such any of the above compounds are not compounds in the strict sense of the word, since the noble gas atoms are not held by any chemical bond or bonds.

The first compound ever formed of noble gases is xenonhexafluoroplatinate, $XePtF_6$. It was obtained as a yellow solid by Bartlett in 1962 by making xenon react with deep red vapours of platinum hexafluoride.

$$Xe + PtF_6 \rightarrow XePtF_6.$$

Barlett could prepare xenon hexafluoroplatinate on the basis of the idea derived from the preparation of oxygen hexafluoroplatinate, O_2PtF_6.

Oxygen molecule which has an ionisation potential of 12.2 eV reacts with platinum hexafluoride to form O_2PtF_6.

$$O_2 + PtF_6 \rightarrow O_2PtF_6$$

Hence, xenon with an ionization potential of 12.1 eV is expected to behave in a similar way.

Certain other unstable hexafluorides (PdF_6, RuF_6 and RhF_6) also form similar compounds.

Xenon forms three fluorides, XeF_2, XeF_4, while krypton forms KrF_2 only. The KrF_4 reported is highly unstable. The most electronegative element, namely fluorine could induce even a noble gas element like xenon into reaction. This is understandable from the relatively lower ionization potential of xenon.

Krypton difluoride; **KrF_2** : This is prepared by passing an electric discharge through a gaseous mixture of krypton and fluorine at low temperatures. It is a white crystalline solid which sublimes well below O°C. It spontaneously decomposes at room temperature. It is a powerful flourinating agent.

Xenon difluoride, **XeF_2**: This is formed by passing a mixture of xenon and fluorine through a nickel tube heated to 400°C and cooling the out-going gas in a U-tube kept at =40°C. The xenon

difluoride, under these conditions condenses to a solid. It is a white crystalline solid which melts at 120°C. When pure and dry it can be stored in a nickel or glass container. It dissolves in liquid hydrogen fluoride without any action. It oxides hydrogen and water to hydrogen fluoride and oxygen repsectively.

$$XeF_2 + H_2 \rightarrow Xe + 2HF$$

$$2XeF_2 + 2H_2O \rightarrow 2\,Xe + 4HF + O_2$$

It is hydrolysed by aqueous solutions of alkalis.

$$2XeF_2 + 2NaOH \rightarrow 2\,NaF + 2\,HF + O_2$$

Xenon tetrafluoride, **XeF_4:** This is obtained as a colourless, crystalline solid by heating a mixture of xenon and fluorine in the ratio of 1:5 in a nickel vessel at 400°C under a pressure of 6 atmospheres for few hours and suddenly cooling the vapours. Alternatively it is prepared by passing a mixture of xenon and fluorine through a nickel tube heated to 400°C and condensing the vapours. It is a colourless crystalline solid which melts at about 100°C. It is quite stable when pure and dry and can be stored in a nickel or a glass vessel. It dissolves in liquid hydrogen fluoride. It is a good flourinating agent. It reacts with hydrogen and boron trichloride to form hydrogen fluoride and boron triflouride.

$$XeF_4 + 2H_2 \rightarrow Xe + 4HF$$

$$3XeF_4 + 4BCl_3 \rightarrow 3Xe + 4BF_3 + 6Cl_2$$

It oxidises potassium iodide, water and sulphur tetrafluoride to iodine, oxygene and sulphur hexafluoride respectively.

$$4\,KI + XeF_4 \rightarrow 4KF + Xe + 2I_2$$

$$12\,H_2O + 6Xe\,F_4 \rightarrow 2\,XeO_3 + 4Xe + 24HF + 3\,O_2$$

$$2SF_4 + XeF_4 \rightarrow 2\,SF_6 + XeF_2$$

Xenon hexafluoride, **XeF_6:** It is formed by heating together a 20:1 mixture of fluorine and xenon at 200° – 250°C under a pressure of 50 atomosphere and cooling the gases. It is a colourless crystaline solid which melts at 47.5°C. It is the most volatile of xenon fluorides. Its vapor is yellow. It is stable at room temperature. It can be stored in a dry nickel vessel but as it attacks silica it cannot be stored in a glass bottle.

$$2XeF_6 + SiO_2 \rightarrow 2\,XeOF_4 + SiF_4$$

It dissolves in liquid hydrogen fluoride but forms $[XeF_5]^-$ and $[HF]^-$ ions.

$$XeF_6 + HF \rightarrow [XeF_5]^- + [HF_2]^-$$

It oxidises hydrogen to hydrogen fluoride.

$$XeF_6 + 3H_2 \rightarrow Xe + 6\,HF$$

It is hydrolysed by water in stages to give xenon trioxide.

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2\,HF$$

$$XeF_6 + 2\ H_2O \rightarrow XeO_2\ F_2 + 4\ HF$$

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6\ HF$$

However, in aqueous alkalies it forms xenate ions $(HCeO_4)^-$ which in turn is slowly transformed into the perxenate $(XeO_4)^-$ ion in which it is in + 8 state or exhibits octavalence.

4.7 USES OF NOBLE GAS ELEMENTS

Helium is lighter than air and is non-inflammable. It is therefore used in place of hydrogen for filling meteorological balloons. A mixture of helium and oxygen is used for respiration by deep sea drivers as it is less soluble in blood than nitrogen. It is employed to provide inert atmosphere to prevent oxidation of the metal surface during the welding of active metals.

Neon is used in discharge tubes for illumination and decorative lighting. Neon gas gives an orange red glow in a discharge tube and neon signs are used for advertising. A mixture of neon with argon and mercury vapour in a discharge tube emits a blue light.

Argon is used in filament (gasfilled) electric bulbs, radio valves and tubes, since it is inert and so prolongs the life of the device. It is also used in Geiger counters.

Krypton and xenon are more efficient than argon in incandescent bulbs and geiger counters. A krypton-xenon mixture is used in photo-flash tubes for instant photography.

Radon is used in the treatment of certain cancers. It is also used as a substitute for X-rays in industrial radiography.

Check your progress - 2

Mention the important uses of argon and krypton.

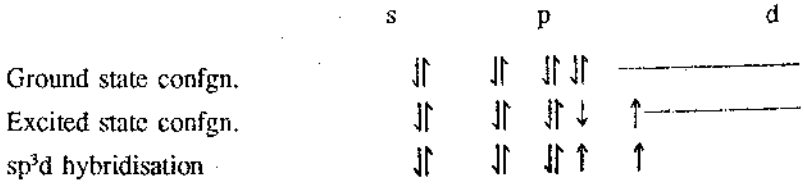
4.8 STRUCTURE OF XENON FLUORIDES

The method of arriving at the shape of these molecules is quite interesting. The highly electronegative element fluorine activates xenon so that one or more pairs of electrons in the outermost shell of the noblegas element, depending upon the need for bond formation, are unpaired and one electron from each such pair is promoted to the d-orbital. The s, p and d orbitals housing these electrons hybridise to give sp^3d^2 and sp^3d^3 hybrid orbitals as the case may be. These hybrid orbitals are then utilised for bonding. Alternatively, the shapes can also be arrived at from the *valence shell electron pair repulsion* (VSEPR) theory proposed by Gillespie and Nyholm. From a knowledge of the total number of electrons the central noble gas atom attains through bond formation, the number of pairs they form, the number of bonding pairs (from the number of unicovalent atoms bonded) and the number of lone pairs, the shape of the molecule can be readily arrived at as detailed below (4.9).

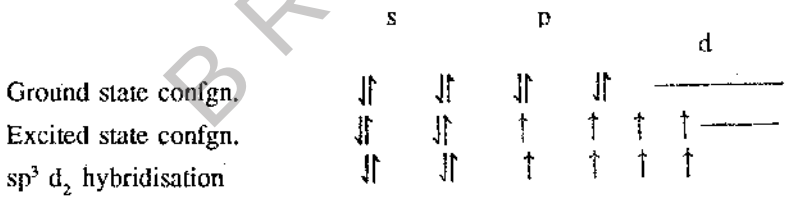
4.9 SHAPES OF XENON FLUORIDES

Molecule	Total electrons	Electron Pairs	Orientation of electrons	Lone pair	Shape
XeF_2, KrF_2	8+2=10	2+3=5	Trigonal bipyramidal	Equatorial	Linear
XeF_4	8+4=12	4+2=6	Octahedral	Axial	Square Planar
XeF_6	8+6=14	6+1=7	Pentagonal bipyramidal	Equatorial	Distorted octahedron

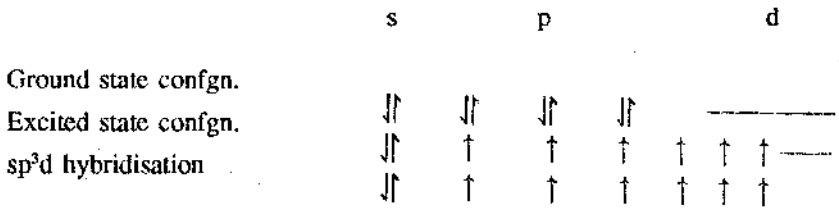
XeF_2. In this there are two Xe-F bonds which require two unpaired electrons. They can be obtained by unpairing one of the outer pairs of electrons in the p-orbital and promoting one electron into the d-orbital. The atomic orbitals undergo trigonalbippyramidal (sp^3d) hydridisation. The two axial hybrid orbitals are used in bonding with the two fluorine atoms and the other three equatorial hybrid orbitals are filled with lone pairs. Accordingly the shape of the molecule is linear. (Fig. 4. 1 a)

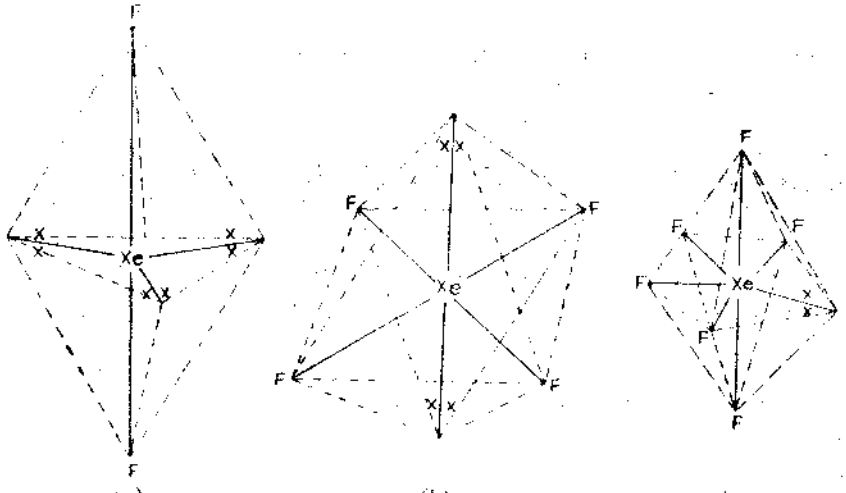


Xe F_4. There are four Xe-F bonds in this molecule. They require four unpaired electrons. They are obtained by unpairing two electron pairs in the ourter p-orbital and promoting two electrons into the d-orbital. The orbitals hybridise in the *octahedral pattern* (sp^3d^2). The four equatorial hybrid orbitals are utilised for bonding with the four fluorine atoms and the two axial hybrid orbitals houses the lone pairs. The result is a square planar arrangement of atoms and the molecule is square planar.



XeF_6. The six Xe-F bonds in the molecule require six unpaied electons. They result from unpairing all the three electron pairs in the outer p-orbital and promoting three electrons into the d-orbital. The orbitals hybridise in the sp^3d^3 type resulting in a pentagonal bipyramidal spacial orientation. The lone pair occupies one of the equatorial hybrid orbitals and the remaining six hybrid orbitals are filled with six bonding pair.. The shape of the molecule appears to be some what like a distorted octahedron.. (Fig.4.1 (c) But the shape of this molecule is not yet established.





(a) (b) (c)

Fig. 4.1 (a) Xenon difluoride (b) Xenon tetrafluoride (c) Xenon hexafluoride

4.10 SUMMARY

The zero group elements with their characterstic $ns^2\ np^6$ configuration, except helium with ns^2, occupy the inevitable last position in any given period of the periodic table. This configuration also explains the near total chemical inactivity and their existence as monoatomic gases.

Atmospheric air in the chief source for all these elements except radon and the gases are isolated from liquid air based on fractional distilation and selective adsorption techniques.

Noble gas elements as against their accepted chemical inertia, have been observed to form compounds with polar substances like phenol, water etc, They form clathrate compounds with quinol. Also xenon and krypton form fluorides. These fluorides have been studied in great detail in respect of their preparation properties and structures.

4.11 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines

1. Justify the existence of noble gases as monoatomic species.
2. Why do fluorides of xenon exist while fluorides of argon are unknown?
3. How do you account for the high ionisation potentials of noble gases ?
4. What are the important aspects of the geometry of XeF_4 molecule ?
5. Write a note on clathrate compounds.

II. Answer the following in 30 lines.

1. (a) Discuss the position of zero group elements in the periodic table.

   (b) Present a brief historical account of noble gases. Examine the isolation of noble gases from liquid air by (a) fractional distillation and (b) charcoal adsorption method.

2. Write a comparitive account of the physico-chemical properties of noble gases.

3. Present a critical account of the fluorides of xenon with emphasis on their preparation and molecular geometries.

4.12 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. The isolation of noble gases by the fractional distillation method is based on the differences in the boiling points of the liquid components of a liquid mixture.

2. Argon is used in gas filled electric bulbs, radio valves and tubes since it is inert and prolongs the life of the device. It is also used in Geiger counters. Krypton is more efficient than argon in incaondescent bulbs and geiger counters. It is used in phto-flash tubes for instant photography.

4.13 GLOSSARY

Fractional distillation: A distillation process for separation of liquid components in a liquid mixture into separate fractions provided their boiling points of any pair differ by atleast 10°C.

Adsorption: A phenomenon in which gas is taken up by the surface layers of a solid, *into its pores.* Adsorption differs from absorption. In the latter, the gas is present throughout the body of the solid mass.

Clathrate compound (cage like compound) : A compound-like substance formed by physical trappin · of a molecule of one component in a cavity of a crystal lattice formed with one or more molecu ·s of another component. The crystal lattice is roughly compared to a cage. The escape of the form ·r is prevented. Melting or dissolution only permits the encloseed component to escape.

Joule-- Thomson effect : The cooling effect produced when a compressed gas is allowed to expand into a low pressure region. Generally a gas to be liquified is cooled, compressed and passed through a orifice into a large evacuated vessel. The gas suffers in the process further cooling and often condenses to a liquid.

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Block - 3

STUDY OF ELEMENTS OF GROUPS III, IV AND V

These groups of elements are characterised by a change in properties from a non-metal to metal down each group. The atoms of the first member of each group are relatively small in size and those of the last element are quite big. Therefore the tendencyt to form cation is well marked in the last elements. Thus the metallic characters of elements increases down each group. Bismuth, the heaviest memnber of the elements of group V B is the last of the naturally occurring

UNIT - 5 THE CHEMISTRY OF ELEMENTS OF GROUP III-B.

Contents

5.1 AIMS AND OBJECTIVES

This unit is to acquire chemical knowledge in order to justify the inclusion of elements boron, aluminium, gallium, indium etc in III'B' group of the periodic table and to account for the changes in their physico-chemical properties in terms of their electronic configuration.

After an intensive study and understanding of various aspects presented in this unit you should be able to:

- Account for non metallic character of boron
- Explain how the metallic character progressively increases from boron to thallium
- Describe the amphoteric character of aluminium oxide
- Discuss the lewis acid character of boron trihalides in particular
- Explain the inert pair effect
- Discuss the bonding in boron hydrides.

5.2 INTRODUCTION

Boron, aluminium, galllium, indium and thallium form group IIIB of the periodic table. They are all characterized by the outermost electronic configuration $ns^2\ np^1$. Except in the case of boron

and aluminium they have $ns^2 np^6 nd^{10}$ configuration for their penultimate shell. They therefore belong to th p-block. By virtue of its small sized atoms boron is non-metallic but all others are metallic. The physical characteristics of the elements are listed in 5.3.

5.3 SOME PHYSICAL CHARACTERISTICS OF GROUP IIIB ELEMENTS

Property	B	Al	Ga	In	Tl
Atomic no.	5	13	31	49	81
Elec. confgn.	$2s^2 2p^1$	$3s^2 3p^1$	$3d^2\ 4s^2\ 4p^1$	$4d^{10} 5s^2\ 5p^1$	$4f^{14} 5d^{10} 6s^2 6p^1$
Atomic wt.	10.81	26.98	69.72	112.40	204.37
Cov. radius (A°)	0.82	1.18	1.26	1.44	1.48
Ionic radius (A°)					
M^3+	0.20	0.50	0.62	0.81	0.98
M +			1.13	1.32	1.40
Density (g/cc)	2.34	2.7	5.9	7.31	11.85
Melting pt. (° C)	2030	660	29.8	156.2	303
Boiling pt. (°C)	3930	2450	2237	2000	1457
Heat of vaporization (Kcals/mole)	128	67.9	61.2	53.7	38.8
Heat of hydration (Kcals/mole)	--	1121	1124	998	984
Ionization potential(cV)	803	5.98	6.00	5.79	6.11
Electronegativity	2.0	1.5	1.6	1.7	1.8
Oxidation states	+3, (-3)	+3	+3 (+1)	+3, (+1)	(+3), +1
Std. oxidation potential (V) $M \rightarrow M^{3+} + 3e^-$	0.73	1.67	0.52	0.34	-0.72

Parallelling an increase in atomic number their atomic weights, atomic (covalent) and ionic radii and densities also increase.

The melting point decreases from boron to gallium and later on it increases. Boron has a very high melting point showing strong bonding forces. A three dimensional network of covalent bonds bind boron atoms in the solid state. The lower melting points in others indicate the presence of metallic bonds which are delocalised and so are weak. Gallium has avery low melting point because of its special structure. The structure persists in the liquid state also. All the elements have high boiling points and these boiling points decrease with increase in atomic number and so atomic size. Heat of vaporization of boron is high reflecting strong bonding between its atoms in the solid state. The heats of vaporization are low for the other elements showing weak metallic bonding in their crystal lattices.

Check your progress - 1

Account for the high melting point of boron.

The first ionisation potentials are low indicating the possibility of +1 oxidation states for these elements. Actually +1 state is stable and important state for thallium Gallium and indium also

exhibit+1 state although+3 state is more important. Their high heats of hydration are sufficient to overcome the unfavouable effect of the total of first, second and third ionization potentials so that they exhibit +3 state. Ofcourse thallium is an exception. Their positive oxidation potentials reflect the ease of their entry into+3 state. The negative oxidation potential for thallium shows that +3 state is not reached. The high positive oxidation potential for aluminium suggests that it is a powerful reducing agent.

Because of small size and high concentration of nuclear charge and intermediate electronegativity, boron is essentially covalent. In the anhydrous state aluminium halides (except the fluoride) are covalent in character. Of the various elements in the group only boron has the ability to exhibit a negative oxidation stae (-3). This is because of its relatively small sized atoms with high ionization potentials. Actually it is known to attain -3 state in borides of highly active metals. Boron behaves like a nonmetal in its chemical reactions. It is resistant to attack by non-oxidising acids like hydrochloric acid. It reacts with many metals to form borides. It is attacked by alkalies. Aluminium is very reactive and is readily covered by a tough adherent coat of unreactive oxide. Because of this property the observed chemical activity of aluminium is less than expected of its high positive oxidation potential. The other metals, gallium, indium and thallium react slowly at ordinary temperatures. Their chemical behaviour is summarised in 5.4.

5.4 CHEMICAL BEHAVIOUR OF GROUP IIIB ELEMENTS

Reagent	Reaction	Remarks
Halogens	$2M+3X_2 \rightarrow 2MX_3$	All, but Tl gives TlX also
Oxygen	$4M+3O_2 \rightarrow 2M_2O_3$	At high temp. Tl gives Tl_2O
Nitrogen	$2M + N_2 \rightarrow 2MN$	Only B and Al at high temp.
Acids	$2M + 6H^+ \rightarrow 2M^{3+} + 3H_2$	Al, Ga, and In. Tl forms Tl +
Alkalis	$2M + 2OH^- + 2H_2O \rightarrow 2MO_2^- + 3H_2$	Al, and Ga. B gives H_2BO_3--

5.5 ISOLATION OF ELEMENTS

Boron in the amorphous form is prepared by reduction of boron trioxide by magnesium.

$$B_2O_3 + 3Mg \rightarrow 3\ MgO + 2B$$

The crystalline form of boron is obtained by heating boron tribromide vapurs with hydrogen over an electrically heated tungsten filament at 1200° C.

$$2\ BBr_3 + 3H_2 \rightarrow 6HBr + 2B$$

Alluminium is obtained by electrolysis of purified bauxite dissolved in a mixture of fused im fluoride and aluminium fluoride (cryolite) at a temperature of about 900°C.

$$2Al_2O_3 \xrightarrow{\text{electricity}} 4\ Al + 3\ O_2$$

Gallium, indium and thallium are, obtained by electrolysis of their salt solutions.

5.6 A COMPARATIVE STUDY OF THE COMPOUNDS

Hydrides: Except thallium all others form hydrides in the +3 state. None of them form the simplest hydride MH_3. Boron forms several hydrides, the simplest being $(BH_3)_3$ or B_2H_6. Gallium forms one hydride, Ga_2H_6. Aluminium and indium form polymeric hydrides $(MH_3)n$. They do not directly combine with hydrogen and their preparation involves indirect methods.

Boron hydride: is obtained by the action of a dilute acid on magnesium boride. This gives a mixture of boron hydrides. But the boron hydride B_2H_6 called *diborane* is prepared by the action of lithium hydride on boron trifluoride or by the action of lithium aluminium fluoride on boron trichloride.

$$8\ BF_3 + 6\ LiH \rightarrow 6\ LiBF_4 + B_2H_6$$
$$4\ BCl_3 + 3\ LiAlH_4 \rightarrow 3\ AlCl_3 + 3\ LiCl + 2B_2H_6$$

Alluminium hydride $(AlH_3)_n$: It is obtained as a white solid in ether solution by the action of aluminium chloride on lithium hydride or lithium aluminium hydrde in ether n. $AlCl_3$ + 3n. LiH $\rightarrow$ 3n. LiCl + $(AlH_3)_n$.

Indium similarly forms a polymeric hydride. Gallium hydride is known to form along with other compounds in a more complicated reaction.

All the hydrides are stable at lower temperatures but are decomposed to their elements at higher temperatures. They burn to yield the respective oxides. Boron hydride and aluminium hydride react with water to form their hydroxides. Thus boron hydride give boric acid, while aluminium hydride gives the basic hydroxide.

$$B_2H_6 + 6H_2O \rightarrow 2\ H_3BO_3 + 6\ H_2$$

Aluminium hydride is a powerful reducing agent.

Oxides: All the elements of the group form oxides of the type M_2O_3. Thallium forms a monoxide (Tl_2O) also. Besides being obtained by direct interacton of elements, boron trioxide is formed by thermal decomposition of boric acid.

$$2H_3BO_3 \rightarrow 3\ H_2O + B_2H_3$$

Oxides of other elements are obtained by precipitating their hydroxides followed by strong ignition.

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

Boron trioxide is essentially acidic in that it forms borates in its reaction with bases.

$$CaO + B_2O_3 \rightarrow Co(BO_2)_2$$

Aluminium oxide is amphoteric as it reacts with acids to form salts,

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$$

and also forms aluminates with alkalis.

$$Al_2O_3 + 2\ NaOH \rightarrow 2\ NaAlO_2 + H_2O$$

Gallium oxide is also amphoteric like aluminium oxide. Indium oxide is essentially basic in character. Thallium oxide is basic. Thus the acidic character of the oxides decreases. Boron trioxide

is acidic and thallium oxide is basic and the oxides of aluminium, gallium and indium are amphoteric. This is in conformity with the general trend of increase in basic (metallic) character of elements down a periodic group, due to increase in atomic size.

Thallium trioxide on heating decomposes to the more stable thallous oxide which is strongly basic, and water soluble like alkali metal hydroxides.

$$Tl_2O_3 \rightarrow Tl_2O + O_2$$

The stability of thallous oxide is due to the inert pair effect.

Check your progresas - 2

What is the trend in acidic character of the oxides of IIIB elements?

Halides. All the elements from trihalides of the formula MX_3. Boron forms B_2X_4 type of halides also. MX_3 type of halides are formed by gallium, indium and thallium but thallium monohalide, TlX, is the most stable and ionic. In the case of thallium the monohalide is stabler than the trihalide. TlI_3 is not the true thallium (III) iodide compound but is a complex being $(TlI.I_2)$ like KI_3.

Besides their formation by direct combination of elements they are prepared by special lmethods also. Boron trifluoride is obtained by heating boron trioxide with a fluoride and concentrated sulphuric acid.

$$B_2O_3 + 3\ CaF_2 + 3\ H_2SO_4 \rightarrow 2BF_3 + 3\ CaSO_4 + 3H_2O$$

Boron trichloride is prepared by passing a current of chlorine over a heated mixture of boron trioxide and charcoal.

$$B_2O_3 + 3\ C + 3\ Cl_2 \rightarrow BCl_2 + 3\ CO$$

Alluminium trifluoride is prepared by heating aluminium sulphate with sodium fluoride, Aluminium chloride is obtained by passing a stream of chlorine over a heated mixture of alumina and coke.

Trihalides of other elements are obtained by the action of appropriate acid on the corresponding metal hydroxide.

$$M(OH)_3 + HX \rightarrow MX_3 + 3H_2O$$

Boron trifluoride is the most important of oboron trihalides. The boron trihalides are soluble in organic solvents. They undergo hydrolysis forming boric acid; boron trifluoride however gives fluoroborate.

$$BX_2 + 3H_2O \rightarrow H_2BO_3 + 3\ HX$$

Boron trifluoride is expected to be a more powerful electron pair acceptor (*Lewis acid*) than the other trihalides of boron. This is because of the greater electronegativity of fluorine than the other

halogens. Experiments have shown it to be just the reverse. This is probably due to the ability of fluorine to form a (Pi) bond by donating a pair of its electrons to othe boron. This happens because the p-orbitals have similar energies. Boron trihalides are strong Lewis acids. The strength of these Lewis acids decreases from BBr_3 to BF_3. Fluorides of aluminium, gallium, indium and thallium are more ionic. They have high melting points. The other halides are covalent compounds and have low melting points. Anhydrous fluorides are soluble in non-polar solvents and are less soluble in water. Other halides are more soluble in water.

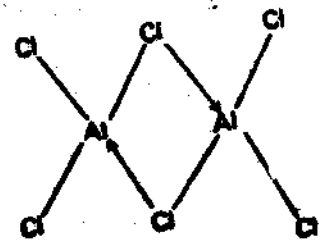


Fig. 5.1 Aluminium trichloride

Trihalides of aluminium, gallium and indium are dimeric through halogen bridges (Fig. 5.1). The dimeric formula is retained when dissolved in nonpolar solvents such as benzene. When dissolved in water the dimer is destroyed because of the high heats of hydration and ionization of the halides in solution.

$$Al_2Cl_6 + 6\ H_2O \rightarrow 2\ [Al\ (H_2O)_6]^{2+} + 6\ Cl^-$$

Biron trihalides on the other hand do not dimerise due to small size of boron atoms and large halogen atoms. Boron trifluoride exists as a monomer because of an additional bond formed between fluorine and boron, the latter accepting a lone pair into its vacant orbital. It is further stabilized by reasonance. The trihalides of boron are also monomeric and the formaion of an additional (π) bond is likely because of differnces in energies of their p-orbitals.

Stability of monohalides of thallium reflects the inert pair effect. The stability of monohalides increases from aluminium to thallium, i.e., as the atomic number increases. The stability is also enhanced by increase in size of the halogens.

The less stable monohalides of aluminium, gallium and indium are powerful reducing agents since they readily tend to revert to the more stable +3 state.

5.7 DIBORANE

As already stated diborane is the simplest of the hydrides of boron. As the name suggest it is a dimer of the hypothetical monomer BH_3, and is B_2H_6.

It is a gas which is stable at room temperature. It is spontaneously inflammable. At red heat it decomposes to its elements. It reacts with water and aqueous alkalis to form boric acid and hydrogen.

$$B_2H_6 + 6\ H_2O \rightarrow 2\ H_3BO_3 + 6H_2$$

$$B_2H_6 + 2NaOH + 2H_2O \rightarrow 2NaBO_2 + 6H_2$$

It reacts with chlorine to form boron trichloride.

$$B_2H_6 + 6Cl_2 \rightarrow 2BCl_3 + 6\ HCl$$

It reacts with dry hydrogen chloride in presence of anhydrous aluminium chloride to form a

substitution product called chlorodiborane.

$$B_2H_6 + HCl \rightarrow B_2H_5Cl + H_2$$

It reacts with ammonia at about 120°C to form an addition compound, diammoniate of diborane, $B_2H_6 \cdot 2NH_3$. The diamoniate on heating to 300°C forms borazole or borazene, $B_3N_3H_6$ known as *inorganic benzene.*

$$3\,(B_2H_6 \cdot 2NH_3) \rightarrow 2B_3N_3H_6 + 12\,H_2$$

It reacts with alkali metal hydrides to form the ionic alkali metal borohydrides which are powerful reducing agents.

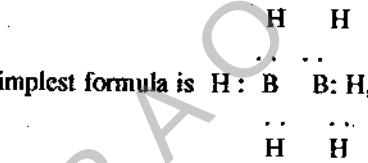
$$2LiH + B_2H_6 \rightarrow 2LiBH_4$$

5.7.1 Structure of diborane

The structure of diborane is interesting in that there are not enough valence electrons to form the required number of electron pair bonds between adjacent atoms. There are eight atoms in the molecule which require at least seven pairs of electrons, one less than the number of atoms in the molecule. For cyclic compounds the number of electron pairs required is the same as the number of atoms in molecule of the cyclic compound for bonding. Actually, there are only 12 electrons (3 electrons on each of the two borons and one electron on each of the 6 hydrogens) which make only six pairs. As such it is an *electron deficient molecule.*

Normally boron should have formed a hydride of the formula BH_3 with three B-H bonds using its three valence electrons. But the formula of diborane shows that it is dimer of the hypothetical molecule BH_3.

Let us consider it as $(BH_3)_2$. The simplest formula is



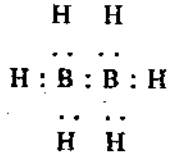
where in two BH_3 units are united together through a bond without electrons to bind them. For atoms to be bonded together atleast two electrons are required.

In the structural determination the following reactions of diborane are worth noting. Diborane reacts with strong electron pair donors which rupture the boron-boron link to form borine derivatives. For example, with trimethyl amine even at - 110°C it gives trimethl amine borine $(CH_3)_3\,N{:}BH_3$ as a white solid. On methylation of diborane only four hydrogens could be substituted by methyl groups showing that the other two hydrogens are of a different kind.

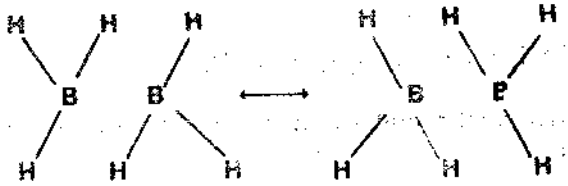
Of the many structures proposed for diborane the ethane-like structure and hydrogen bridge structure are of importance.

5.7.2 Ethane-like structure.

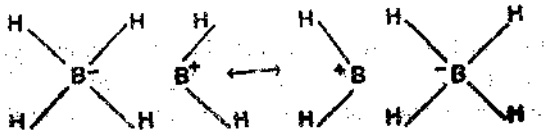
Ethane-like structures are based on Sidgwick's suggestion that two of the hydrogen atoms in diborane might be held by one electron bonds.



The one electron bond is possible because of nearly the same electronegativity for hydrogen and boron. In addition, the concept of resonance permits the one-electron bond among all six positions contributing to the stability of diborane. As diborane is not paramagnetic the existence of unpaired electrons or the one-electron bonds is ruled out. But resonance structures (Fig. 5.2) involving covalent and ionic forms with paired up electrons seem to be likely since diborane is diamagnetic. However, it is unlikely that two parts of molecule are held together by resonance stability alone without any electrons to bind them.



(a)



(b)

Fig. 5.2 (a) Covalent (b) Ionic resonance forms

5.7.3 Hydrogen bridge structure

Fitzer proposed a structure with a double bond between the two borons. In this structure two protons are embedded in the electron cloud of the double bond(Fig.5.3) in a plane perpendicular to the remainder of the molecule.

a b

Fig. 5.3 Fitzer formula

This is a modified form of a hydrogen bridge structure. But the larger boron-boron distance than is expected of a double bond rules out the protonated double bonded structure.

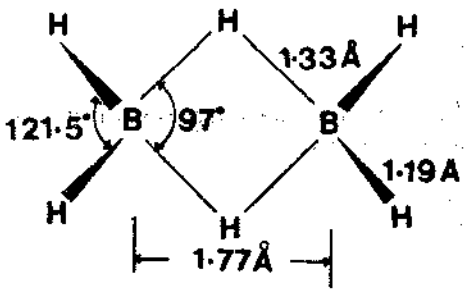


Fig. 5.4 Hydrogen bridged diborane structure

A hydrogen bridge structure is proposed in which two bridging hydrogens with their 1s-orbitals use a pair of electrons each to bind the two borons together. Of these two bridging hydrogens one atom lies above and the other below the plane of the rest of molecule so that each boron is tetrahedrally surrounded by four hydrogens (Fig. 5.4).

The hydrogen bridge structure is a better representtion that the ethane like structure in that all the six hydrogens are not equivalent (only the four coplanar hydrogens are equivalent) and the rotation of the molecule about B-B axix is hindered. The hydrogen bridge structure is supported by the electron diffracion studies of the tetramethyl diborane which shows that the four methyl groups and the two borons are coplanar. Raman spectra and infrared data are in excellent agreement with the hydrogen bridge structure.

Fig. 5.5 Hydrogen bridge (Banana bond) structure

The hydrogen bridge structure can be explained as follows. Each of the two boron atoms is sp^3 hybridised. Three of these sp^3 hybrid orbitals are singly occupied by electrons and the fourth hybrid vacant. The borons then form three B-H bonds each with three hydrogens. The Two BH groups approach each other in such a way that the vacant sp^3 hybrid of one boron overlaps one of the B-H bonding molecular orbitals of the other. As a consequence a B-H-B molecular bonding orbital forms with two electrons holding the three nuclei together. Each such bond is therefore called a three-center bond. There are two such three-center bonds one lying above and the other below the plane of the rest of the molecule. Because of the bent shape of this molecular orbital forming the hydrogen bridge it is sometimes called *banana bond.*

The coplanar B-H bond distance between the boron atoms and terminal hydrogen atoms is 1.19A° which is equal to the sum of unicovalent radii of the atoms (Fig. 5.4). The bridging B-H bond distance is 1.33 A° which is larger than the sum of the unicovalent radii of the atoms involved showing that electron deficiency lies in the hydrogen bridge bonds. The boron-boron distance (1.77 A°) is long enough to permit a B-B bond.

5.8 SUMMARY

The elements in group III B are Boron, aluminium, gallium, indium and thallium. While the first and last members are decidedly nonmetallic and metallic in nature respectively, the remaining three show a pronounced metallic character, yet with some glimpses of amphoterism.

All the elements form the oxides of the type M_2O_3, B_2O_3 is an acidic oxide and Tl_2O_3 a basic one while the oxides of remaining elements are clearly amphoteric. The nonmetallic nature changing over to metallic is inflected in the hydrolytic behaviour of their trihalides. While thallium halides hydrolyse in water to give basic solutions, boron trihalides produce acid solutions.

The hydrides of boron are of great importance from chemical bonding point of view. Diborane B_2H_6 is an electron deficient dimer and its chemical bonding involves two three centre electron pair bonds comprising hydrogen bridges.

5.9 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines.

1. Give reasons for high covalent character of of boron in its compounds.
2. In what important respects of electronic configuration boron and aluminium differ from the rest of the elements of group IIIB?
3. Explain the dimeric nature of aluminium chloride.
4. What is meant by electron deficient molecule? give an example.
5. Write a note on the ethane-like structure of diborane.

II. Answer the following in 30 lines.

1. (a) Justify the inclusion of B, Al, Ga, In & Tl in the same periodic group.
   (b) What is meant by inert pair effect? Illustrate this with reference to group IIIB elements.
2. Write a comparitive account of the oxidess and halides of group III B elements.
3. Explain the cause for the difference in the chemical behaviour of boron with the rest of the group elements. How does boron compare with silicon?
4. Write a clear account on the preparation, properties and bonding of diborane.

5.10 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Boron has a very high melting point showing strong bonding forces. A three dimersional network of covalent bonds bind boron atoms in the solid state.
2. The acidic character of the oxides of IIIB group elements decreases and basic character dominates from B_2O_3 to Tl_2O. Boron trioxide is acidic and thallium oxide is basic and the oxides of aluminium, gallium and indium are amphotenic.

5.11 GLOSSARY

Dimer . It is a molecule composed of two monomeic simple molecules chemically bound up; e.g., NO_2 is a monomer and N_2O_4 is a dimer of the hypothetical monomer BH_3.

Electron deficient molecule. It is a molecule in which there are not enough valence electrons for bonding between the atoms in the molecule. C_2H_6 {with (2 x 4) + (6 x 1) 1 = 14 -----valence electrons} has 7 pairs of electrons for 6 C-H bonds and one C-C bond. It is a normal molecule. But B_2H_6 is electron dificient. It has (2 x 3) + (6 x 1) = 12 electrons sufficient for 6 pairs for 6 bonds where as B_2H_6 requires 7 pairs normally.

Inert pair effect. The ns^2 pair in the outermost shell of heavier members in the periodic groups will not be available for bonding. This is perhaps due to larger nuclear charge and relatively smaller size of atom than expected resulting greater attraction of their nuclei on the ns^2 electrons than on the np electrons. As a result they exhibit a lower oxidation number than the oxidation number characteristic of the family. Thus thallium exhibits + 1 state while the others are essentially in +3 state.

Polymer. It is a molecule composed of a large number of monomeric molecules united together. For example $(AlH_3)n$ is a polymer of the hypothetical monomeric molecule AlH_3.

Three-centre bond. It is an electron pair bond which binds three nuclei (or atoms) together. This pair of electrons occupies a molecular orbital formed by overlap of orbitals of the three atoms bonded together. In diborane there are two such-center bonds. Molecules in which such three-center bonds are present are electron deficient molecules.

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UNIT - 6 STUDY OF ELEMENTS OF GROUP IVB

Contents

6.1 AIMS AND OBJECTIVES

This unit is mainly to discuss the chemistry of group IVB elements in terms of their electronic configurations and to account for the gradual variation from a typical non metallic to metallic character from carbon to lead.

When you have completed reading and understanding the various aspects of chemistry peresented in this unit, you must be able to:

- Justify the inclusion of C, Si, Sn and Pb in the same group of the periodic table
- Explain the amphoteric character of germanium and tin
- Account for the acidic character of the dioxides
- Explain the decreasing stability of the tetrahalides and their increasing ease of hydrolysis from carbon to lead

- Discuss the inert pair effect particularly with reference to tin and lead
- Describe the classification and reactivity of carbides
- Discuss the formation and bonding of metal carbonyls
- present a brief account of various gaseous fuels.

6.2 INTRODUCTION

Carbon, silicon, germanium, tin and lead constitute group IVB. They are characterized by $ns^2\ np^2$ configurations. Carbon with it's inner ls^2 shell behave differently from the rest of the elements as does boron (Gr/III/B), beryllium (Gr.II A) or lithium (Gr.I A). Carbon and silicon have noble gas configuration for their penultimatedshells. Germanium, tin and lead have $s^2\ p^6\ d^{10}$ configuration for their penultimate shell. In addition lead has 4f sub-shell complete with 14 electrons. This group is an excellent example for illustration of exchange in properties from non-metallic carbon and silicon to metallic tin and lead. The inert pair effect is apparent in the last two elements and is more pronounced in lead. The physical characteristics of those elements are listed in 6.3.

6.3 SOME PHYSICAL CHARACTERISTICS OF GROUP IVB ELEMENTS

Property	Carbon C	Silicon Si	Germanium Ge	Tin Sn	Lead Pb
At.no. outer Elecn. confign.	$2s^2\ 2p^2$	$3s^2\ 3p^2\ 3d^{10}$	$4s^2\ 4p^2\ 4d^{10}$	$5s^2\ 5p^2\ 4f^{14}\ 5d^{10}$	$6s^2\ 6p^2$
At wt. (amu)	12.011	28.086	72.59	118.69	207.19
Covalent radius (A°)	0.77	1.4	1.22	1.41	1.47
Ionic radius (A°)	2.6 (–4) 0.15 (+4)	2.71 (–4) 0.41 (+4)	0.93 (+2) 0.53 (+4)	1.12 (+2) 0.71 (+4)	1.20 (+2) 0.84 (+4)
Density (g/cc)	2.26	2.33	5.82	7.30	11.4
Melting pt. (C)	3727	1420	937.4	231.9	327.4
Boiling pt. (C)	4830	2680	2839	2270	1725
Heat of vapn. (Kcals/mole)	171.7	40.6	68	70	42.4
Ionization potential (ev)	11.26	8.15	8.13	7.33	7.41
Electroniegativity	2.5	1.5	1.6	1.7	1.8
Oxidation states	–4, +4	–4, +4	–2, +4	–2, +4	–2, +4
Std. oxidation potential (V) $M \rightarrow M^2 + 2e$	–	–	–	0.136	0.126

Increase in atomic number is parallalled by increase in atomic weight, atomic radius and density down the group. The decrease in melting point with increase in atomic number indicates decreasing bond strength and change in nature of bond, in the elemental solids. The unusually high melting point in the case of carbon is due to the three dimensional netowrk of strong C-C covalent

bonds in diamond giving it the characteristics of a giant molecule. Melting or vaporization requires breaking of some or all of the bonds.

The high ionization potential and high electronigativity of carbon together with its small sized atoms allow it to enter into the negative oxidation state (–4). It is energetically difficult to attain the negative (–4) oxidation state due to the necessity of taking p four electrons. Yet carbon forms ionic carbides with highly electropositive metals. Silicon has little chance for negative oxidation state because of less electronegativity and relatively large size atoms. Later elements have least tendency for the negative oxidation state. The positive oxidation states (+2, +4) are important for all elements. As the atomic number increases the elements tend to prefer lower oxidation state (inert pair) effect. The +4 state for lead is unstable. But the +2 state is stable for lead. Hence +4 state for lead is oxidizing in character. In the case of germanium and tin the +2 state is unstable and their +4 state is more stable. Thus in the +2 state they are good reducing agents. Dipositive tin and lead are ionic when dissoloved in water. They are mostly covalent in the +4 state. They are more acidic in the +4 state due to their small size in that state than in the +2 state. Thus the +4 state becomes increasingly less stable and +2 state attains stability down the group due to inert pair effect.

Carbon and silicon are nonmetals. Germanium is a metalloid. However, tin and lead are metals in their chemical behaviour. This increasing metallic character is reflected in their decreasing ionization potentials and electronegativities. Carbon is resistant to attack by non-oxidizing acids and alkalis while silicon is attacked by alkalies.

The elements of group IVB except lead from dioxides when acted upon by oxidizing acids like nitric acid. Lead forms the monoxide. Non-oxidizing acids form salts with tin and lead in their +2 state.

The low oxidation potentials show that they are not active metals. They combine with halogens and oxygen at elevated temperatures. The chemical characteristics of these elemetns are listed in 6.5, where M is any group IV B element except otherwise stated.

6.4 ISOLATION OF ELEMENTS

Carbon occurs in nature as such in the form of diamond and graphite. Graphite is prepared by electrically heating a mixture of powdered coke and using carbon conducting rods. Amorphous forms of carbon such as charcoal and activated charcoal are obtained by thermal decomposition of wood. Carbon black or soot is obtained by incompleted combustion of oils. Coke, another amorphous form of carbon, is prepared by distillation of coal in the absence of air. Elemental silicon is prepared by carbon reduction of silicon dioxide in an electrical furnace.

$$SiO_2 + 2C \rightarrow Si + 2CO$$

Germanium is obtained by reducing the dioxide with hydrogen or carbon at high temperatures. Tin metal is obntained by reducing the dioxide with carbon. Lead metal is prepared by partial oxidation of lead sulphide (galena) to the oxide which interacting with the unchanged sulphide gives lead.

$$2PbS + 3\,O_2 \rightarrow 2PbO + 2S\,O_2$$
$$PbS + 2\,PbO \rightarrow 3Pb + S\,O_2$$

6.5 SOME CHEMICAL REACTIONS OF GROUP IV B ELEMENTS

Reagent	Reaction	Remarks
Halogens	$M+2X_2 \rightarrow MX_4$	All except C; PbI_2 but not PbI_4 is formed. $PbBr_4$, $PbCl_4$ are unstable.
Oxygen	$M+O_2 \rightarrow MO_2$	All except Pb; Pb gives PbO and Pb_3O_4
Acids	$M+2H \rightarrow M^{2+}+H_2$	Sn and Pb only
Nitric acid	$3M + 4HNO_3 \rightarrow 3MO_2+4NO + 2H_2O$	All except Pb. which forms Pb^{2+}
Alkalies	$M + 2OH^- + H_2O \rightarrow MO_3^{2-} +2H_2$	Si and Ge only; Sn and Pb give MO_2

6.6. A COMPARATIVE ACCOUNT OF THE STUDY OF HYDRIDES, HALIDES AND OXIDES

A study of hydrides, halides, halides and oxides of the elements of group IV B clearly shows the gradation in their properties from nonmetallic carbon and silicon to metallic tin and lead.

6.6.1 Hydrides

All the elements of group IV B from hydrides of the type MH_4. The ease of formation and their stability decreases down the group. These hydrides are covalent in nature. Carbon forms a large number of hydrides (alkanes etc.,). Silicon and germanium form a limited number of hydrides (silanes and germanes) only. Tin and lead form one each Stannane and plumbane). Carbon forms a large number of hydrides essentially due to the strong C-C bonds unlike the Si-Si and Ge-Ge bonds which are weak (Table 6.6.1). The property to bond its own atoms so that long chains are formed is called catenation. Carbon has this property of catenation to a maximum. It is less in the case of its neighbouring elements (B, Si, Ge and N) in the periodoic table.

Bond Energies of some carbon and silicon bonds (table 6.6.1)

Bond	Bond energy (kcals/mole)
C–C	83
C–O	84
Si–Si	42
Si–O	80

Check your progress - 1

Explain the term catenation

Besides forming long chains of carbon atoms, carbon forms stable multiple bonds. Further the C–H bonds are almost non-polar because of similar electronegativities. Also the C-C bonds are not weakened by electron withdrawal by the hydrogens since hydrogen has a lower electronegativity than carbon.

Hydrides of carbon are popularly known as hydrocarbons among which alkanes are important. In them carbon exercises its tetracovalency in full. The hydrides of silicon called silanes are obtained by the action of dilute acids on magnesium silicide.

$$Mg_2Si + 4HCl \rightarrow 2MgCl_2 + SiH_4$$

silanes are also obtained by the reduction of silicon tetrachloride with lithium aluminium hydride in other solutions.

$$LiAlH_4 + SiCl_4 \text{ —— } LiCl + AlCl_3 + SiH_4$$

Germanes are prepared by similar methods. Stannane and plumbane are also prepared by the reduction of their tetrachlorides with lithium aluminium hydride in ether. All are tetrahedral in structure.

The stability of the hydrides decreases from carbon down to lead. Alkanes are quite stable. Silanes and germanes are less stable due to the weakening of Si-Si or Ge-Ge bonds by electron withdrawal by hydrogen which is more electronegative. the Ge-H bonds are weaker than the Si-H bonds which are in turn weaker than the C-H bonds. This weakness of bond is a characteristic of covalent bonds between atoms of widely differing size. This is reflected in the temperature of their thermal decomposition.

Decomposition temperature of	CH_4	800 °C
"	SiH_4	450 °C
"	GeH_4	285 °C
"	SnH_4	25 °C

Unlike silanes, germanes are not spontaneously inflammable, do not react with oxygen of air below 230° c and do not hydrolyse in water or alkalis.

$$SiH_4 + 4H_2O \rightarrow Si(OH)_4 + 4H_2$$

6.6.2 Oxides

The elements of group IV B form two types of oxides, the monoxides (MO) and the dioxides (MO_2).

Carbon monoxide (CO) is a gas. It is formed by incompleted combustion of carbon.

$$C + 1/2O_2 \rightarrow CO$$

Silicon monoxide (SiO) is obtained as a gas by heating silica with silicon at 1300 °C in vacuo.

$$Si + SiO_2 \rightarrow 2SiO$$

But being unstable it readily changes to an intimate mixture of silicon and silicon dioxide.

$$2\ SiO \rightarrow Si + SiO_2$$

Such a change is calle disproportionation (self oxidation and reduction). Germanium oxide is obtained by thermal decomposition of the hydrated oxide of of oxychloride.

$$2\ GeOCl \rightarrow 2\ GeO + Cl_2$$

Stannous oxide is formed by careful heating of stannous hdroxide formed by the action of an

alkali on a stannous salt. The stannous oxide on being heated at 300 °C in air gets oxidized to stannic oxide. But, when heated in the absence of air, the stannous oxide disproportionates to tin and stannic oxide.

Lead monoxide (PbO) is obtained as a yellow solid by oxidation of molten lead by air, or thermal decomposition of its oxysalts, or by dehydration of the hydroxide.

$$2\,Pb + O \rightarrow 2\,PbO$$
$$2Pb\,(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$
$$Pb\,(OH)_2 \rightarrow PbO + H_2O$$

Carbon monoxide is a neutral gas. Silicon monoxide is not studied being unstable. The monoxides of germanium, tin and lead are both basic and acidic. The basic character increases with increasing atomic number. This indicates the increase in metallic character down the group.

The reducing character of the monoxide decreases with increase in atomic number of the element. Carbon monoxide is a good reducing agent. Monoxides of germanium and tin have reducing property. Lead monoxide has no reducing character. This trend shows that +2 state gains stability down the group. This is a reflection of the inert pair effect.

Carbon dioxide is obtained by complete combusition or burning of carbon in excess of air. Similarly silicon dioxide is prepared by heating silicon in air. Germanium dioxide is formed when germanium is heated in air at red heat. Tin dioxide (SnO_2) is obtained by burning tin in air. But lead dioxide is produced only by electrolytic oxidation or by the action of strong oxidizing agents.

Carbon dioxide is a gas and it contains discrete molecules, In silicondioxide there are no such molecules. On the other hand there is a three dimensional network of silicon-oxygen bonds. Each silicon is tetrahedrally bonded to four osygen atoms and each oxygen bounded to two silicon atoms in adjacent SiO_4 tetrahedra. (Fig. 6.1) Even in solid carbon dioxide there are no signs of strong electrostatic forces between CO_2 units for a three dimensional net work of single covalent bonds. In silicon dioxide the high nuclear charge on a silicon atom could attract sufficiently strongly the pi-electrons away from the relatively weak Si-O double bonds. As a consequence of this, the silicon dioxide molecules polymerize forming a solid gaint molecule of composition SiO_2.

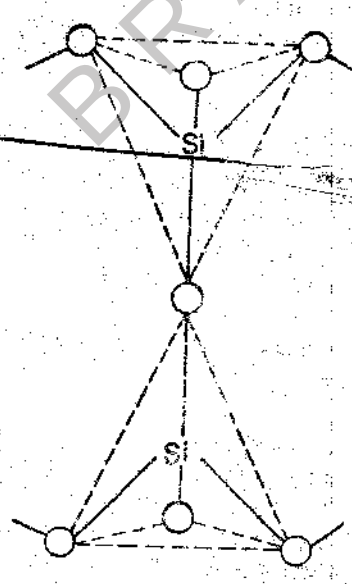


Fig. 6.1 SiO_2 tetrahedra

Carbon dioxide and silicon dioxide are acidic and form carbonates and silicates with bases, respectively. The dioxides of germanium and tin are amphoteric. The basic character of these and

that of lead is due to the ease of separation of the hydroxyl ion from larger atoms. The hydroxyacids of large atoms ionize readily as bases. However they retain their acidic properties also. Lead dioxide is predominantly acidic and forms plumbates with basic oxides. Lead dioxide is powerful oxidizing agent. This is due to its great stability in +2 state (inert pair effect).

Check your progress - 2

Why is CO_2 a gas while SiO_2 is a solid?

6.6.3 Halides

All the elements of this group from halides of the type MX_4. They are all covalent in character. Tin and lead however form the dihalides (MX_2) also. These dihalides are ionic solids.

Carbon tetrachloride is formed as a colourless liquid by the action of chlorine or sulphur monochloride on carbon disulphide.

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$$
$$CS_2 + 2S_2Cl_2 \rightarrow CCl_4 + 6S$$

Silicon tetrachloride is also obtained as a colourless liquid by heating silicon dioxide with carbon in a current of chlorine gas.

$$SiO_2 + C + 2Cl_2 \rightarrow SiCl_4 + CO_2$$

Silicon directly combines with chlorine. Germanium also directly combines with chlorine to form its tetrachloride as a colourless liquid. Stannic chloride ($SnCl_4$) is obtained as a colourless liquid by chlorination of scrap tin by passing chlorine over heated tin metal and condensing the vapours in a receiver.

Lead tetrachloride is an unstable yellow liquid. This is formed when lead dioxide is dissolved in concentrated hydrochloric acid. Lead does not form the tetrabromide or tetraiodide. This is because in the +4 lead state, lead is an oxidizing agent and the bromide or iodide ions are good reducing agents. Hence the +4 lead is reduced to the +2 state. Even lead tetrachloride is unstable unless it is kept at low temperature. It loses chlorine readily forming lead dichloride.

The tetrabromide and tetraiodide of carbon decompose on heating due to overcrowding of large halogen atoms on the small carbon atom.

Normally the melting and boiling points increase with increase in molecular weight due to van der Waal's force. But the melting points of tetrahalides decrease from carbon to silicon and later on increase. The lower melting point of silicon tetrachloride is due to the repulsion between adjacent molecules arising out of the negative charge on the chlorine atoms. This in turn is due to the greater difference between electronegativities of silicon and chlorine than between carbon and chlorine. For a similar reason the melting points of the tetrachlorides of germanium and tin are lower than that of carbon.

Carbon tetrahalides are not hydrolysed by water. But tetrahalides of the other elements are

hydrolysed. This is because carbon cannot increase its coordination number beyond four due to the absence of d orbitals.

All the halogen atoms are replaced stepwise by the hydroxyl groups in hydrolysis. Alkalies also cause hydrolisis of these halides just like water. In the hydrolic reaction, water molecules and hydroxyl groups act as electron pair donors and form a coordinate bond with the central atom. The species with a higher coordination number is unstable. It loses a molecule of HX giving the hydrolytic product. This continues till all the halogen atoms are replaced by hydroxyl groups. Silicon tetrahalides are reversibly hydrolysed since the silicic acid formed does not ionize at all as a base. But the tetrahalides of germanium and tin are reversibly hydrolysed indicating their amphoteric nature. Thus, except carbon halides the others act as electron pair acceptors or Lewis acids.

The tetrahalides of silicon, germanium, tin and lead form complex ions of the type $[MX_6]^2$ through cooordination of two halide ions. This results in an increase in the coordination number of the central atom from 4 to 6 due to the availability of 'd' orbitals in the valence shell.

The dihalides of tin and lead are well known. The hydrated stannous chloride ($SnCl_2$ $2H_2O$) is obtained by dissolving tin in hydrochloric acid and crystallizing the salt. On heating the hydrate, it undergoes partial hydrolysis forming the basic chloride.

$$SnCl_2 2H_2O \rightarrow Sn(OH)Cl + HCl + H_2O$$

Anhydrous stannous chloride can be obtained by heating in tin metal in a current of hydrogen chloride gas. It is a good reducing agent in concentrated hydrochloric acid because of its stability in +4 state.

Lead chloride ($PbCl_2$) is obtained as a colourless crystalline solid. It is formed when a solution of a soluble chloride is added to a lead salt solution. It readily forms a complex ion $(PbCl_4)^{2-}$ in presence of excess chloride ions. It has no reducing property. The +2 state is stable for lead (inert pair effect).

6.7 CARBIDES

These are binary compounds of carbon with more positive elements or elements of similar electronegativity. The carbides differ in their properties depending upon the type of linkage, which in turn, depends upon the nature of the other element. They are accordingly classified as *ionic* or *salt like*, *covalent* and *metallic* or *interstitial* carbides.

All the three types of carbides are prepared by heating the oxide of the element with carbon to a high temperature.

$$CaO + 3C \rightarrow CaC_2 + CO$$
$$SiO_2 + 3C \rightarrow SiC + 2CO$$

6.7.1 Ionic carbides

These are formed by metals of periodic groups IA, IIA and IIIA, coinage metals (Cu, Ag and Au), zinc, cadmium and some lanthanide elements. They are crystalline solids. They are non-conductors of electricity. They react with water or acids evolving hydrocarbons due to hyrolysis of their anions. Accordingly they are subdivided into three classes. Such of the carbides giving methane (CH_4) as hydrolytic product contain C^{2-} anion. They are called methanides, eg., Al_4C_3 and Be_2C. Those ionic carbides evolving acetylene gas contain C_2^{2-} anions. They are called acetylides. Most of the ionic carbides are acetylides. They crystallize in the NaCl lattice. Some examples of acetylides are CaC_2, BaC_2, BeC_2, ZnC_2, LiC_2, CuC_2, Ag_2C_2, Al_2C_6, Ce_2C_6. Allylide is the name given to a carbide which hydrolyses to give allylene ($CH_3C \equiv CH$) or methyl acetylene on hydrolysis. It

contains C_3^{4-} anion. The only example is the magnesium allylide, Mg_2C_3.

$$Al_4C_3+12H_2O \rightarrow 4Al(OH)_3+ 3\ CH_4$$

$$CaC_2+2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

$$Mg_2C_2 + 4\ H_2O \rightarrow 2Mg(OH)_2 + C_3H_4$$

Carbides of copper, silver, gold and zinc and cadmium are formed by passing acetylene through salt solutions of those metals.

Calcium carbide is used in the production of acetylene, a starting material for many synthetic products like alcohol, acetic acid, vinyl plastics. Mixed with oxygen acetylene is used in the oxy-acetylene flame for welding purposes.

6.7.2 Covalent carbides

Besides the hydrocarbons, boron carbide (B_4C) and silicon carbide (SiC) are among the covalent carbides. These carbides of boron and silicon have three dimensional network of covalent bonds. As such they come under giant molecules. In silicon carbide, silicon and carbon atoms alternate and each is surrounded by the other tetrahedrally. Boron carbide is $B_{12}C_3$ (or simply B_4C). In it 12 boron atoms forming an icosahedron cluster alternate with linear chains of three carbon atoms as C_{33} units. They are extremely hard and chemically inert. Under the name carborandum, silicon carbide is used as an abrasive and refractory. It is also used in nuclear reactors for protection against radiation and for containers of fuel elements.

6.7.3 Interstitial or metallic carbides

These are carbides of transition metals of groups IVA, VA and VIA which have atoms of radius larger than 1.3 A° . The interstices of the metal lattices of these metals are big enough to hold carbon atoms without disturbing the metal lattice. As such these metallic carbides retain their metallic lustre and most of their electrical conductance. They are harder and have higher melting points than the metals themselves. The increase in melting point and hardness is due to the additional forces of attraction due to the pesence of carbon atoms. They are chemically inert. Tungsten carbide is so hard that it is used for making cutting tools.

Transition metals with atomic size less than 1.3 A° also form interstitial type of carbides. But as the interstices in these are smaller in size they cannot hold carbon atoms without disturbing the metal lattice. This distortion in the metal lattice makes them to behave defferently from those of the aforesaid metallic carbides. They are therefore called *pseudo interstitial* carbides. Cr, Mn, Fe, Co and Ni form this class of carbides. These react with water and dilute acids to form simple hydrocarbons or mixtures of hydrocarbons with or without hydrogen and sometimes free carbon. They represent a transition between the true interstitial crbides on one hand and ionic carbides on the other.

6.8. CARBONYLS

These are coordination compounds of transition metals with carbon monoxide. They are known as metal carbonyls. Metals of group VIII and some metals of groups VIIA and VIA and IB from metal carbonyls.

They are covalent compounds formed by interaction of carbon monoxide with free transition metals or metal state. They are soluble in non-polar solvents and insoluble in polar solvents. In general they are diamagnetic, the only exceeption being $V(CO)_6$. They decompose on heating to metal and carbon monoxide. They are easily oxidized by atmospheric oxygen. They react with pyridine, bromine or iodine monochloride.

$$Cr(CO)_6 + Py \rightarrow Cr(CO)_4(Py)_2 + 2\,CO$$

$$Ni(CO)_4 + Br_2 \rightarrow NiBr_2 + 4\,CO$$

$$Fe(CO)_5 + XY \rightarrow Fe(CO)_4XY + CO$$

where Py is pyridine and XY is ICl or IBr. This indicates that in these compounds the CO groups are attached to metal atoms.

X-Ray and electron diffraction studies of metal carbonyl is linked to the metal atom. The metal-carbon distance in nickel carbonyl is 1.82 A° . It is 0.18 A° shorter than the expected single bond distance. Also it is near to the Ni-C double bond distance of 1.79A°. But the nature of bonding in CO groups appears to remain without much alteration from that in carbon monoxide molecule. The Co-bond distance in carbonyls is about 1.14A° to 1.16A° as compared with 1.13A° in carbon monoxide. Perhaps a resonance hybrid involving Ni: :C: :O: and Ni:C: : :O: describes the situation in nickel carbonyl. Similar bonding may be assumed to be present in other metal carbonyls as well..

Further the -M::C::O structure removes the unlikely accumulation of negative charge on the metal atom. By acceptance of a pair of electrons from a CO group the metal acquires partial negtive charge. Pauling has suggested the back donation of a pair of electrons from a d-orbital into the vacant p-orbital of carbon ($2s^2 2p_x^1\ 2p_y^1\ 2p_z^0$) in the CO group. This back donation results in the formation of an additional bond between the metal and carbon. Thus by backdonation, the metal atom gets rid of the negative charge.

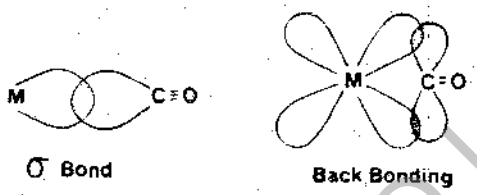


Fig. 6.2 Back donation in metal carbonyls

The number of carbon monoxide molecules coordinated to the metal atom determines the structure of the metal carbonyl. $M(CO)_4$ type of metal carbonyls like Ni $(CO)_4$ are tetrahedral. $M(CO)_5$ type of carbonyls like $Fe(CO)_5$ are trigonal bipyramidal. And $M(CO)_6$ type of carbonyls such as $Cr(CO)_6$ are octahedral. In as much as these contain only one metal atom they are called *mononuclear metal carbonyls*. They are formed by transition metals with even atomic number.

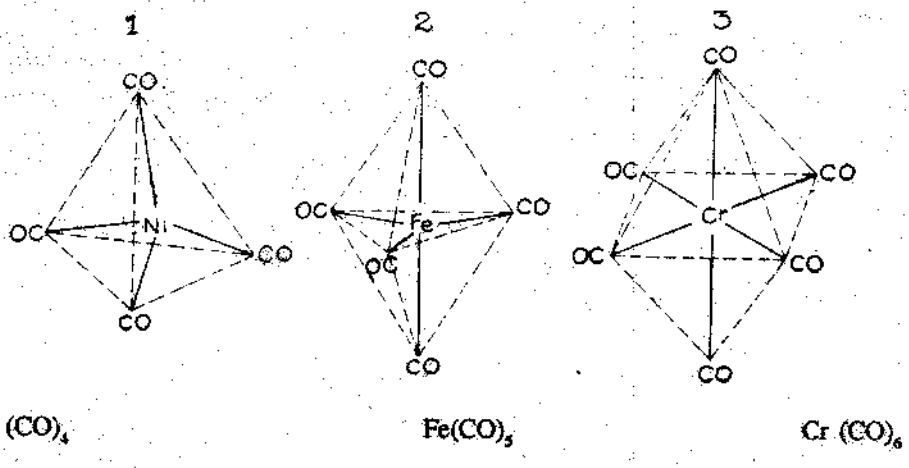
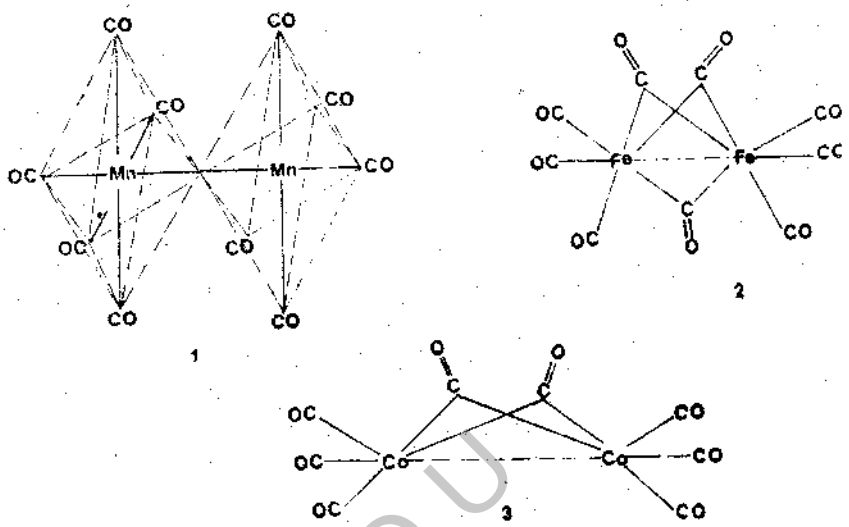


Fig. 6.3 mono nuclear carbonyls.

They are quite stable compounds. Transition metals with odd atomic number are not known to form mononuclear carbonyls. They however form polynuclear metal carbonyls, e.g., $C_2(CO)_8$, $Mn_2(CO)_{10}$. The structures of the polynuclear carbonyls are somewhat complicated. Polynuclear carbonyls are also formed by even atomic numbered transition metals, eg. $Fe_2(CO)_9$.

The stability and diamagnetic character of the metal carbonyls is explained by Sidgwick in his *effective atomic number* concept. The term effective atomic number refers to the total number of electrons a central atom attains in its outer shell after bond formation equal to that of the next bnoble gas element. An atom is said to attain effective atomic number when the central atom attains a total of elcctrons equal to the atomic number of the next noble gas element. Each CO group donates a pair of electrons to the metal atom.



1) Mn_2 (CO) 2) $Fe_2(CO)_9$ 3) $Co_2(CO)_8$

Fig. 6.4 - Binuclear metal carbonyls

Such groups donating electrons to metal atoms are called ligands. Transition metal elements with even atomic number can thus attain the effective atomic number readily. Sidgwick's EAN formula is G=m+2y, where M is the atomic number of the noble gas element next to the metal atom. A transition metal with even atgomic number gaining two electrons from each ligand will necessarily attain an even number (hence, diamagnetic) of electrons. If that number is equal to the atomic number of the noble gas element the metal is said to attain EAN. This explains why even atomic numbered transition metals form metal carbonyls. In the case of odd atomic numbered transition metals the total of electrons after bond formation is only odd and the metal will not attain EAN. As such the carbonyl cannnot be stable. However they form polynuclear carbonyls and gain stability. Blanchard's formula applies to metals forming polynuclear carbonylsi is

$$G\text{----------} = x - 1$$

where x is the number of metal atoms in a molecule of the polynuclear carbonyl while the other letters have the same significance as in Sidgwick's formula.

Examples: (a) Ni $(CO)_4$

Atomic number of Ni = 28
No. of CO groups = 4
Next noble gas element is kryption, its at.\no. 36
36 = 28 + (2x4) = 36
(b) no. of CO = 27

$$36 - \frac{(2 \times 27) + (2 \times 8)}{2} = 2 - 1$$

In the polynuclear carbonyls one or more CO groups serve to bridge metal atoms by bonds in a ketone like fashion. Some of the polynuclear metal carbonyls have metal - metal distances which permit metal-metal bonding. Without the metal-metal bond the diamagnetic character can not be explained.

6.9 GASEOUS FUELS OF CARBON

A fuel is a combustible substance which on burning liberates much heat energy without forming highly objectionable products. A fuel can be a solid, liquid or gas. A gaseous fuel is most convenient to handle but has the disadvantage of storage problem (inflammable character). They require containers which withstand high pressure.

Among the gaseousfuels used in industry and in the homes the most important are producer gas, water gas, coal gas, natural gas and waste gases from oil refineries. Natural gas and the gases from petroleum refineries are gaining importance not only as kitchen gas fuel but also as raw materials for many petrochemical industries.

6.9.1 Producer gas

This is essentially a mixture of carbon monoxide and nitrogen. It is prepared by burning coal in a limited supply of air. It is produced by passing a current of air through a red-hot bed of coal in a vertical cylindrical vessel called the producer through a hopper. Air is sent in from the bottom. The producer gas formed leaves the producer through a side tube at the top.

As air enters the hot bed of coal, carbon burns to form carbon dioxide.

$$C + O_2 \rightarrow CO_2 + \text{Energy}$$

The carbon dioxide then interacts with carbon of coal forming carbon monoxide.

$$CO_2 + C \rightarrow 2CO + \text{Energy}$$

The fuel value of producer gas is low as it contains large proportion of the uncombustible gas namely nitrogen of air. The producer gas is produced at the spot where it is needed as a fuel and used even as it emerges hot out of the producer.

It contains about 40% carbon monoxide and 60% nitrogen and a little of carbon dioxide.

6.9.2 Water gas

This is a mixture of carbon monoxide and hydrogen, twqo combustible gases. it is produced by passing a current of steam through a white hot bed of coal.

$$C + H_2O \rightarrow CO + H_2 - \text{Energy}$$

This reaction is endothermic. As concequence the coal bed gets cooled and the reaction comes to a stop. To revive the coal bed a current of air is passed through. The energy released in the burning of coal heats up the coal bed so that it is ready for use again. The production of water gas however efficient is as fuel it is only an intermittent process. It can be made a continuous process by simultaneous blowing of air and steam through the white hot bed of coal. The products of the two

reactions mix up as they emerge out. It is therefore called *semi-water gas*. This is lower in its calorific (or heating) value as compared with water gas due to the presence of considerable nitrogen.

The calorific value of the gas is however improved by mixing it with hydrocarbon gases. These hydrocarbon gases are obtained by a process of cracking or breaking up large molecules of less useful oils in a carburettor. Accordingly the mixed gaseous fuel is called *carburetted water gas* or enriched water gas.

Water gas contains about 50% each of carbon monoxide and hydrogen with little carbon dioxide. The carburetted water gas contains about 25-30% carbon monoxide, 20-25% hydrogen, 25-30% hydrocarbons, 20-25% nitrogen and 5-10% carbon dioxide.

6.9.3 Oil gas

This fuel gas is obtained by cracking a cheap oil. Generally kerosene is cracked for production of oil gas. The large molecules of liquid hydrocarbons making up kerosene are cracked at red heat into much smaller molecules. Hydrocarbons with small molecules are gaseous even at room temperatures by virtue of their low molecular weight. The cracking process is carried out by allowing the oil to drop on the red hot bottom of an iron retort in a thin steam. The retort is heated externally. The gases formed leave the retort through a bonnet and a hydraulic syphon. Tarry matter is separated. The gses pass on into a gas holder for collection over water.

The oil gas contains about 90-95% hydrocarbons, about 5% hydrogen with little carbon monoxide and carbondioxide and nitrogen.

6.9.4 Coal gas

The coal gas is obtained by destructive distillation of coal (distillation of coal in the absence of air) in iron retorts. The volatile matter in coal leaves the retort through a hydraulic main. Tarry matter and soluble ammonical matter separate and collect in a tank. The volatile products then pass through a series of pipes cooled in air for removal of condensible vapours. The uncondensed gases further pass over shelves containing moist ferric oxide and lime. Here the poisonous gases (HCl, H_2S) are removed from the coal gas.

$$2\,Fe(OH)_3 + 3\,H_2S \rightarrow Fe_2S_3 + 6H_2O$$

$$Fe(OH)_3 + 3\,HCN \rightarrow Fe(CN)_3 + 3H_2O$$

$$Ca(OH)_2 + H_2S \rightarrow CaS + 2H_2O$$

The purified gas is then collected in a gas holder over water.

Coal gas contains about 45-55% hydrogen, 35-40% hydrocarbons, 5-10% carbon monoxide and small quantity of carbon dioxide.

6.9.5 Natural gas

Now-a-days the term natural gas has become very common after the digging of oil wells in our country by the ONGC. It consists of gaseous hydro carbons collected deep down in the bowels of the earth along with the liquid hydrocarbons comprising the crude petroleum. When a hole is drilled into the oil bearing strata the natural gas pushes out under high pressures. It is chiefly a mixture of saturated and unsaturated hydrocarbons with 1-4 carbons in a chain. The Indian Government is arranging to utilize the natural gas for its petrochemical industries and to meet the growing demands of kitchen gas in the country.

The kitchen gas or cooking gas that is in wide use in our urban homes is the waste gas mixtures from petroleum refinries. Like the natural gas it is also a mixture of saturated and unsaturated hydrocarbons of low molecular weight.

The *gober gas* or biogas is another fuel gas gaining importance in rural areas of our country. It is originally produced by fermentation of dung (exereta of cattle). But now any waste organic matter like weeds growing in mostly methane with small quantities of other low molecular weight hydrocarbons, saturated and unsaturated.

6.10 GLASS

The term glass refers to any matter which solidifies without crystallization from the liquid state. In common usage it applies to silica and silicate materials. Glass is essentially a solution of silica in metal silicates which escaped crystallization on cooling. Though it looks like a solid it is a liquid with very high viscosity. It is an amorphous solid. Glass is best described as super cooled liquid.

Being a mixture of many silicates and silica it has no difinite melting point. It melts over a range of temperature. It first softens on heating at a temperature and then its fluidity increases as temperature increases. Ultimately it flows freely like a liquid. This property of glass allows it to be blown into any desired shape when it is in the solid state. Very slow cooling of the semisolid mass of glass favours crystallization spoiling its quality.

It is not attacked by water or acids. However hydrofluoric acid dissolves it forming silicon tetrafluoride.

$$SiO_2 + 4\ HF \rightarrow SiF_4 + 2H_2O$$

The chief raw materials used for the preparation of glass are silica (quartz or sand), lime or limestone, sodium carbonate or potassium carbonate, litharge (lead monoxide), boron, cerium oxide, and barium carbonate. Ordinary glass is prepared from sodium carbonate, limestone and sand together with broken glass. For special quality glass the sodium carbonate and calcium carbonate are replaced by potassium carbonate, borax, litharage etc. To produce coloured glass certain metal oxides are added to the molten glass.

The raw mateials are mixed in the requisite proportion and heated in special pots in a furnace to about 1400°C. The whole mass melts to a liquid mixture of silicates and silica. The escaping gases help to stir the mixture. When the melt is free from gas bubbles it is allowed to cool. Any scum formed on the surface is removed. The clear molten mass is then shaped into glass articles of desired shape and size. A glass blower collects a semisolid mass of glass at the end of a long iron blow-pipe and blows it into the desired shape with or without the help of a mould. Laboratory glassware and a few special grade table ware are mouth blown. For other articles machines are used in place of men.

The keeping quality of glassware is improved by subjecting the glass articles to a process of *annealing*. The prepared glass articles are cooled very slowly by passing them over a moving conveyer belt through a long narrow chamber called lehr. One end of the lehr is kept hot and the other is almost at the room temperature. The articles move very slowly from the hot end to the cool and over several hours or even days. This slow process of cooling is called annealing.

6.10.1 Varieties of glasses

Soft Glass is soda-lime glass. It is used for cheap glass ware, sheet and bottle glass.

Hard Glass is potash-lime glass. It has a higher fusion temperature and more resistant to water and acids than soft glass.

Jenaglass and *pyrex glass* are essentially borosilicates with low coefficient of expansion. They resist the action of common chemicals, shock and sudden change in temperature.

Crookes glass is a special variety of optical glass used for lenses for spectacles. It contains cerium oxide which cuts off ultraviolet rays harmful to the eyes.

Quartg glass is made of pure silica. It has a low coefficient of expansion. It does not break even when a red hot article is dropped in water.

Safety glass is a sandwhich type of glass. Between two layers of sheet glass a transparent sheet of vinyl plastic is suitably cemented. It does not splinter when struck. It is used for automobile wind-sheets and showcase windows for display.

6.10.2 Coloured glass

Coloured glass is obtained by adding an appropriate metal oxide so that oloured metal silicate (glass) is formed imparting colour to it. Certain elements in the colloidal state are also responsible for colour in some glasses. Blue cobalt glass is obtained by adding cobalt oxide. Ruby red glass, used for red lights as danger signals in railways is formed by adding selenium oxide or colloidal gold. Green glass is made by adding chromium oxide. Cheap blue glass is made by adding cupric oxide and cheap red glass by adding cuprous oxide. Manganese dioxide is added as a corrective for masking the light greem tint of cheap glass due to iron impurity. The cheap glass thereby acquires the look of quality glass.

6.11 SUMMARY

Group IV is an important group from two points of view. One, it presents a clear gradation from non-metallic character and, two it has silicon and germanium, the most important semiconductor materials. And carbon has an extensive chemistry of its own.

All the elements form hydrides of the type MH_4, the stability decreases from carbon to lead. Besides the oxides of the type MO, these form the most characteristic types MO_2. While the dioxides are feebly acidic, SnO and PbO are fairly basic.

They form tetra halides MX_4. And again their stabilities decrease from C to Pb. While that of carbon is resistant to hydrolysis, those of the later elemnts are easily hydrolysed.

With more electropositive elements, carbon forms binary ionic carbides. While non metals yield covalent carbides transition metals form interstitial carbides.

Carbonyls are an important class of compounds that CO molecules form with several transition metals in their zero oxidation states.

Their properties and bonding have been studied in great detail. Carbon forms several gaseous fuels like coal gas, producer gas and water gas etc. Liquid petroleum gas (LPG) is a fuel gas obtained from the waste gases of petroleum refineries.

6.12 MODEL EXAMINATION QUESTIONS

I. **Answer the following in 10 lines**

1. Explain how both positive and negative oxidation states are realised in carbon?
2. Write a note on catenation as observed in hydrocarbons.

3. Account for the ready hydrolysis of $SiCl_4$.
4. What is meant by ligand? Illustrate your answer.
5. Why and how water gas is enriched?

II. Answer the following in 30 lines

1 a) Examine the trends obseved in the physico-chemical properties of IVB group elements.

b) What is inert pair effect? Illustrate this effect with reference to the oxidatio states of IVB elements.

2 Present a comparative account of the oxides and halides of IVB group elements.

3 Discuss the preparation and composition of producer gas and water gas.

4 Describe the preparation of glass. Give the compoisition of (i) hard glass (ii) pyrex glass and (iii) safety glass.

6.13 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. The property to bond its own atoms so that long chains are formed is called catenation. Carbon shows this property to maximum, while it is less in silicon.

2. Carbon dioxide is a gas as it contains discrete molecules. In silicon dioxide a three dimensional network of silicon-oxygen bonds. Each silicon is tetrahedrally bonded to four oxygen atoms and each oxygen is bound to silicon atoms leading to giant molecule. This silicon dioxide is a solid.

6.14 GLOSSARY

Catenation : It is the property of forming bonds between like atoms so that long chains are formed. This is most pronounced in the case of carbon.

Coordination compound : It is a compound formed by atoms or groups of atoms bonded together by coordinate covalent bonds. Metal carbonyls are good examples of coordination compounds.

Interstitial compound : It is a compound like substance formed by the occupation of interstitial sites in transition metal lattices by small sized atoms like hydrogen, boron, carbon or nitrogen. There are no bonds between the metal atoms and the nonmetallic atoms in the interstices.

Non-stoichiometric compound : It is a compound in which the ratio of the constituent atoms of elements does not conform to simple integral numbers. Interstitial compounds are non--stoichiometric compounds.

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UNIT - 7 ELEMENTS OF GROUP VB

Contents

7.1 AIMS AND OBJECTIVES

The purpose of this unit is to explain you the trend in properties from non metallic to metallic nature in respect of elements of group VB i.e. nitrogen to bismuth. And also to enable you to justify these elements in one group.

After a detailed study and understanding the various aspects of VB group elements in this unit, you must be able to:

- Justify that all these elements from N to Bi belong to group V in terms of their electronic configurations.
- Explain how the metallic character progressively increases from nitrogen to bismuth.
- Account for the decreasing stability of their trihydrides of the type MH_3.
- Explain why nitrogen forms only trihalides but rest of the elements form both tri and penta halides.

- Account for both the oxidising and reducing character of nitrous acid.
- Describe the manufacture of nitric acid.
- State the preparation and uses of superphosphate.

7.2 INTRODUCTION

Nitrogen, phosphorous, arsenic, antimony and bismuth constitute group VB of the periodic table. They are characterized by $ns^2\ np^2$ configuration for their outermost shell. Nitrogen with its inner $1s^2$ shell of electrons behaves differenly from the rest of the elements. Nitrogen and phosphorus with the noble gas configuration ($ns^2\ np^6$) in their penultimate shell differ from the rest of the members namely arsenic, antimony and bismuth. The latter elements have $s^2\ p^6\ d^{10}$ configuration for their penultimate shells. Bismuth has 4f- subshell also filled to completion in the prepenultimate shell. These differences in their electronic configuration are responsible for the trend in properties they exhibit. The same outermost electronic configuration governs their general chemical behaviour. As in the earlier groups, an inert pair effect manifests in the chemistry of bismuth.

7.3 THE PHYSICAL PROPERTIES OF THE ELEMENTS OF GROUP VB

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
At. no.	7	15	33	51	83
Outer elec. confign.	$2s^2\ 2p^3$	$3s^2\ 3p^3$	$3d^{10}\ 4s^2\ 4p^3$	$4d^{10}\ 5s^2\ 5p^3$	$4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$
At wt. (amu)	14.007	30.974	74.922	121.75	208.9
Covalent radius (A°)	0.75	1.06	1.20	1.40	1.46
Ionic radius (A°)	1.719-3) 0.1(+5)	2.12(-3) 0.34(+5)	2.22(-3) 0.47(+5)	2.45(-3) 0.62(+5)	1.20(+3) 0.74(+5)
Density (g/cc)	0.81	1.82	5.72	6.62	9.8
Melting pt. (°C)	-210	44.2	814.5 (36 atm)	630.5	271.3
Boiling pt. (°C)	--195.8	280	610 (sub1)	1380	1560
Heat of vapn. (Kcals/mole)	0.666	2.97	7.75	46.6	42.7
Ionization potential (ev)	14.54	11.0	10	8.64	8
Electroniegativity	3.0	2.1	2.0	1.9	1.9
Oxidation states	-3, +3+5	-3+3,+5	-3,+3,+5	+3,+5	+3, +5
*Std. oxidation Potential (V)	-1.44(HNO_2)	+5 ..	+5 -0.25 ($HAsO_2$)	-0.21 (Sbo)	-0.32 (BiO)

*$M+3H_2O \rightarrow H_3\ MO_3 + 3H^+ + 3e$

Atomic number, as expected increases with an increase in atomic weight for reasons stated in earlier units.

Atomic radius increases as the atomic number increases. But this increase in size beyond phosphorus is less because of the less effective shielding, offered by the d^{10} electrons in their prenultimate shells. Further, the increase in size from antimony to bismuth is much less inspite of the increase in atomic number by 32 units. This is due to much less or feeble shielding effect of the f^{14} electrons in the prepenultimate shell of bismuth. Accordingly the atoms of bismuth are smaller than expected because of increased effective nuclear charge. The ionic radii register a similar trend.

Density is another property which increases with the increase in atomic number. Apart from packing of atoms the increase in density reflects the increase in atomic weight and the increase in atomic size. Accordingly bismuth has a high density. This is true in the case of all 6th period elements.

Melting point increases with increase in atomic number from nitrogen to arsenic and thereafter decreases. The very low melting point of nitrogen is due to its discrete triply bonded diatomic molecules. Phosphorus, arsenic and antimony do not form diatomic molecules. They form tetrahedral P_4 As_4 and Sb_4 molecules. Diatomic molecules can be formed only through multiple bonding involving pi bonds. And large atoms like P, As or Sb can not approach closely for pi-bond formation because of repulsion from the electrons of the inner core. Such a repulsion is non-existent in the case of nitrogen atoms with $1s^2$ core.

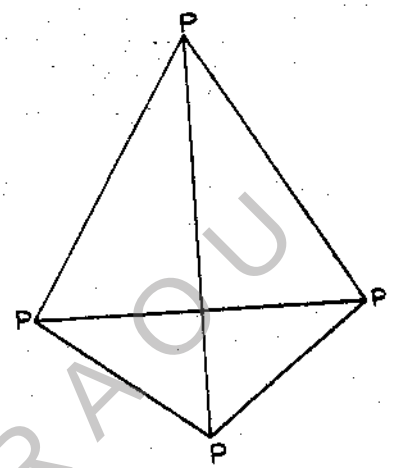


Fig. 7.1 Phosphorus molecule

Further, the melting point of arsenic is high due to a layer-like structure consisting of As_4 tetrahedral. Although this layered structure continues in antimony, the melting point shows a decrease. This is because of its large size atoms and more metallic character (delocalised metallic bonds). It further decreases in bismuth in which metallic bonding forces operate between atoms. As the metallic bonding forces continue to operate even in the liquid state the boiling points are high. The heats of vaporization also increase for the same reasons down the group.

Check your progress - 1

Account for the low melting point of nitrogen.

The Ionization potentials and electronegativities down the group decrease as the atomic

number increases. The high ionization potential of nitrogen together with its high electronegativity and small size atoms allow nitrogen to enter into -3 oxidation state. Nitrogen forms nitride (N^{3-}) anion with highly electropositive metals in forming salt-like or ionic nitrides. The electronegativity of other members are so omuch reduced that even when bonded to most electropositive metals the bonding is predominantly covalent. The tendency to attain -3 oxidation state decreases from nitrogen to bismuth.

The ns^2 np^3 configuration for the valence shell suggests the possibility of +3 and +5 states. This is due to involvement of p-electrons and s and p electrons respectively. In the tripositive state the electron pair donation is well pronounced with nitrogen. The tripositive state becomes more characteristic and more resistant to oxidation from arsenic down to bismuth. This reflects the inert pair effect. In the pentapositive state all these elements are acidic in character. This oxidation state becomes less characteristic and difficult to attain as the atomic number increases (inert pair effect). With the exception of nitrogen the other elements may act as electron pair acceptors in the +5 state. They form (MF_6) ions.

Nitrogen differs from the other elements in that it forms compounds in other oxidation states as well.

The negative oxidation potentials indicate that these elements are not active. They enter into combination only at elevated temperatures. All these elements form compounds with highly electro-positive metals. But this tendency decreases from nitrogen to bismuth. Only nitrogen combines with hydrogen in presence of a catalyst to form the hydride, ammonia. All of them except nitrogen combine with oxygen to form trioxides. However, phosphorus forms pentoxide with excess of oxygen. Nitrogen forms nitric oxide and nitrogen dioxide. All these elements except nitrogen combine with halogens to form their trihalides. But phosphorus, arsenic, antimony and bismuth form pentafluorides with excess fluorine. The chemical behaviour of the elements of this group is summarised in 7.5

7.4 ISOLATION

Nitrogen occurs in the free state in air. It can be recovered by fractional distillation of liquid air. Phosphorous is obtained by the carbon reduction of rock phosphate (calcium phosphate) mixed with sand in an electric furnace.

$$2Ca_3(PO_4)_2 + 10C + 6\,SiO_2 \rightarrow 6\,Ca\,SiO_3 + 10\,CO + P_4$$

7.5 CHEMICAL BEHAVIOUR OF ELEMENTS OF GROUP VB

Reagent	Reaction	Remarks
1. Highly electro positive metals	$xM+yA \rightarrow M_x A_y$	Tendency decreasess from N to Bi.
2. Hydrogen	$3H_2+2A \rightarrow 2AH_3$	With N only
3. Oxygen	$3\,O_2 + 4\,A \rightarrow 2\,(A_2O_3)$	With P, As, Sb & Bi. Also P gives P_4O_{10}, N gives NO & NO_2 only
4. Halogens (X_2)	$3\,X_2 + 2\,A \rightarrow 2\,AX_3$	With P, As, Sb Bi. AX_5 is formed with excess X_2 and P, As, Sb and Bi.

Where A is group VB element except otherwise stated.

Arsenic, antimony and bismuth are obtained by carbon reduction of their oxides.

$$As_4O_6 + 6C \rightarrow As_4 + 6CO$$

$$Bi_2O_3 + 3C \rightarrow 2Bi + 3CO$$

7.6 COMPARATIVE STUDY OF HYDRIDES, HALIDES AND OXIDES

7.6.1 Hydrides

All the elements of the group form hydrides of the type MH_3 in keeping with the characteristic valence. The ease of formation and their stability decreases down the group. They are covalent in nature.

Only nitrogen can directly combine with hydrogen, of course, in the presence of a catalyst like platinum. All give their hydrides by the action of water or dilute acids on their binary metal compounds like Mg_3N_2, Ca_3P_2, Zn_3As_2, Mg_3Sb_2 or magnesiumbismuth alloy.

$$Mg_3N_2 + 6H_2O \rightarrow 3MG(OH)_2 + 2NH_3$$
$$Zn_3As_2 + 6HCl \rightarrow 3ZnCl_2 + 2AsH_3$$

Phosphine (PH_3) is obtained by the action of hot concentrated solution of caustic alkali on white phosphorus.

$$P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$$

All have pyramidal structures with the bond angle approaching 90° as the size of the element increases down the group.

The stability of the hydrides decrease down the group as their decomposition temperatures indicate.

$NH_3 \rightarrow$ 1300 °C; $PH_3 \rightarrow$ 400 °C; $AsH_3 \rightarrow$ 280 °C; $SbH_3 \rightarrow$ 150 °C; $BiH_3 \rightarrow$ room temp

Arsine and stilbine decompose to the corresponding elements and are deposited as a mirror as they are passed through a tube heated at a point. The decrease in stability is a consequence of the weak covalent bond between atoms which are widely different in size. The stability of ammonia is further enhanced by its ability to form hydrogen bonds. The hydrides of phosphorus, arsenic and antimony are strong reducing agents. They are inflammable.

Ammonia is basic because of its strong ability to donate an electron pair. This character of electron pair donation disappears rapidly down the group. This is again a consequence of the inert pair effct observable from arsenic.

Ammonia dissolves freely in water to form a weakly basic solution called ammonium hydroxide.

$$NH_3 + H_2O \rightarrow NH_4OH \rightarrow NH_4^+ + OH^-$$

But phosphine does not so dissolve in water to form basic solution because it is a poor donor. Ammonia forms salts readily with acids. Under anhydrous conditions, phosphine forms salts with hydrogen chloride, hydrogen bromide or hydrogen iodide.

$$PH_3 + HI \rightarrow PH_4 I$$

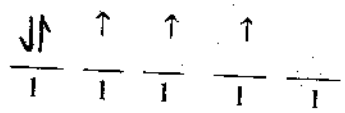
Besides MH_3 type of hydrides, nitrogen, phosphorous and arsenic form dihydrides of the type M_2M_4. In addition, nitrogen forms hydrazoic acid, NH_3, Hydrazine is more acidic (or less basic) than ammonia just as H_2O_2 is more acidic than water.

The dihydrides are less stable and are stronger reducing agents than the trihydrides.

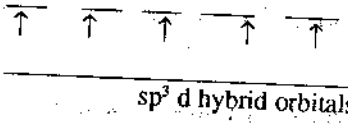
7.6.2 Halides

All the elements form trihalides with all the halogens. The ionic character increases from that of nitrogen to bismuth. Phosphorus, arsenic, antimony and bismuth too form pentahalides with fluorine. Phosphorus forms pentachloride and bromide also while antimony forms pentachloride. The formation of the pentahalides is possible because of the availlability of d-orbitals in the valence shell for hybridization.

Shell with n = 3 or more valence shell configuration (ground state) excited state



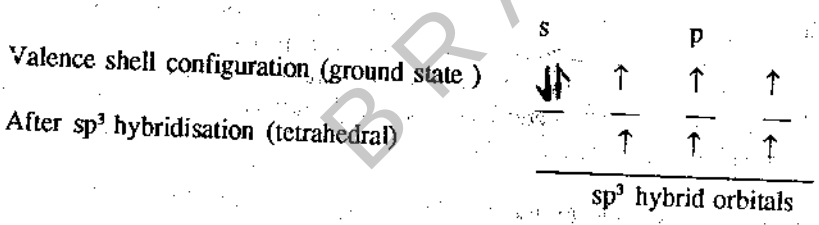
After sp^3d hybridisation (trigonal bipyramidal)



sp^3 d hybrid orbitals.

Nitrogen does not form a pentahalide even with fluorine because of the limitation to four orbitals in its valence shell and absence of d-orbitals therein.

The trihalides except in the case of nitrogen are prepared by direct combination of elements under controlled conditions to prevent the formation of pentahalides. They are pyramidal in structure as the atoms use three of the sp^3 hybrid orbitals for bonding, the fourth being occupied by a lone pair electrons.



They are volatile being covalent. The ionic character of the trihalides increases from that of nitrogen to bismuth, and among the halides the fluorides are more ionic. Thus bismuth trifluoride is ionic. This is reflected in increased melting pioints and decreased hydrolysis.

Nitrogen trihalides except the fluoride are explosive. They are endothermic compounds. They are completely hydrolysed forming ammonia and hypohalous acid.

$$NX_3 + 3\ H_2O \rightarrow NH_3 + 3HOX$$

Trihalides of phosphorus and arsenic are also completely hydrolysed to yield their corresponding-ous acid (in the +3 state).

$$MX_3 + H_2O \rightarrow H_3MO_3 + 3\ HX$$

(where M= P&As)

Trihalides of antimony and bismuth are partially hydrolysed to the oxyhalides or basic salt.

$$MX_3 + H_2O \rightarrow MOX + 2\ HX$$

(Where M=Sb & Bi)

Thus the hydrolytic reactioins of these trihalides show that the non-metallic character in nitrogen and phosphorus (complete and irreversible hydrolysis) changes over to the metallic character (Partial and reversible hydrolysis) in bismuth.

The pentahalides in the vapour state are trigonal bipyramidal in structure. In the solid state phosphorus pentachloride is found to be composed of tetrahedral $(PCl_4)^+$ and octahedral $(PCl_6)^-$ complex anion respectively. But the solid phosphorus pentabromide has the ionic structure. $(PBr_4)^+$ Br^-. The non-existence of pentaiodide is perhaps due to steric factors arising in accommodating large iodine atoms around the small phosphorus atom.

The pentahalides of phosphorus like the trihlides are readily hydrolysed. The hydrolysis takes place in two stages.

$$PX_5 + H_2O \rightarrow POX_3 + 2\ HX$$
$$POX_3 + 3H_2O \rightarrow H_3PO_4 + 3\ HX$$

Phosphorus pentafluoride is thermally stable while the pentachloride decomposes reversibly to the trichloride and chlorine. The pentabromide of phosphorus is partly dissociated even in the liquid state.

The pentafluorides of phosphorus, arsenic and antimony form fluoroanions $(MF_6)^-$ with excess fluoride ions.

7.6.3 Oxides

All the elements form two types of oxides, the trioxides and the pentoxides. The trioxides and pentoxides of phosphorus, arsenic and antimony are dimeric. The oxides of nitrogen are monomeric. Bismuth does not form a pentoxide.

The dimeric pentoxides of arsenic and antimony decompose on heating to form the trioxides by loss of oxygen. This is again a consequence of the inert pair effect noticeable among the heavier members in any periodic group. Nitrogen forms some more oxides like the nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2) and its dimer, the dinitrogen tetroxide (N_2O_4) in which nitrogen is in +1, +2, +4 and +4 states respectively.

Nitrous oxide is obtained by thermal decomposition of ammonium nitrate.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

Nitric oxide is obtained as a colourless gas by the action of 1:1 dilute nitric acid on copper.

$$3Cu + 8\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 2\ NO + 4H_2O$$

Dinitrogen trioxide (N_2O_3) is obtained as a blue liquid when an equimolecular mixture of nitric oxide and nitrogen dioxide is cooled to about -- 20°C.

$$NO + NO_2 \rightarrow N_2O_3$$

Nitrogen dioxide is obtained as a reddish brown gas when concentrated nitric acid is treated with copper metal.

$$Cu + 4\ HNO_3 \rightarrow Cu(NO_3)_2 + 2\ H_2O + 2\ NO_2$$

Dintogen tetroxide (N_2O_4) is obtained as a colourless solid by cooling nitrogen dioxide to about –13°C.

$$2NO_2 \rightarrow N_2O_4$$

At room temperature it changes over to an equilibrium mixture of 28.5% NO_2 and 71.5 N_2O_4.

Dinitrogen pentoxide (N_2O_5) is obtained as a colourless crystalline solid by dehydration of concentrated nitric acid with phosphorus pentoxide and distilling at about 27°C in a glass retort.

$$4HNO_3 + P_4O_{10} \rightarrow 4\ HPO_3 + 2\ N_2O_5$$

The trioxides of all other elements are obtained by burning the elements in air. In a limited supply of air, phosphorus burns to give the trioxide (P_4O_6); but if the oxygen is in excess the pentoxide (P_4O_{10}) is formed. The pentoxides of arsenic and antimony are obtained by indirect means. For example, oxidation of the trioxides with concentrated nitric acid and ignition give their pentoxides.

$$As_4O_6 + 4H^+ + 4\ NO_3^- + 4H_2O \rightarrow 4H_3\ AsO_4 + 2\ N_2O_3$$
$$4\ H_2\ AsO_4 \rightarrow As_4\ O_{10} + 6\ H_2O$$

Bismuth does not form a pentoxide but one approaching the composition of Bi_2O_5 is obtained as a brown powder by evaporating bismuthates with dilute nitric acid. It is unstable and decomposed to the trioxide when heated.

$$KBiO_3 + H\ NO_3 \rightarrow KNO_3 + HBiO_3$$
$$2HBiO_3 \rightarrow H_2O + Bi_2O_5$$
$$Bi_2\ O_5 \rightarrow Bi_2O_2 + O_2$$

The trioxides and pentoxides are colourless crystalline solids. Antimony pentoxide is a yellow powder. The oxides of nitrogen, phosphorus and arsenic are soluble in water to form the corresponding acids. The oxides of antimony are sparingly soluble and bismuth oxide is insoluble.

$$N_2\ O_5 + H_2O \rightarrow 2\ HNO_3$$
$$N_2\ O_4 + H_2\ O \rightarrow HNO_2 + HNO_3$$
$$P_4\ O_6 + 6H_2\ O \rightarrow 4H_3\ PO_3$$
$$P_4\ O_{10} + 6\ H_2\ O \rightarrow 4H_3\ P\ O_4$$

Nitrous oxide and nitric oxide are neutral. The others exhibit a distinct trend from strongly acidic character of the trioxides of nitrogen and phosphorus to weekly basic character of the bismuth trioxide. Arsenic trioxide is weekly acidic while that of antimony is amphoteric. This reflects the increase in size of their atoms in the tripositive state. The elements exhibit strongly acidic character in their higher oxidation states when they are relatively much smaller in size.

In the lower oxidation state (+3) the oxides of nitrogen, phosphorus and arsenic exhibit reducing properties. In the +3 and +5 states the oxides of nitrogen are strong oxidizing agents because of the still lower oxidation states the element can attain. Bismuth in the +5 state is unstable and readily reverts to the stable+3 state. It is therefore a powerful oxidizing agent. Accordingly bismuthates ($KBio_3$, $NaBiO_3$) are used in the laboratory as good oxidizing agents. For example sodium bismuthate is used to oxidize manganese (II) ion in nitric acid solution to the purple coloured manganese (VII) of permanganate ion, a delicate test for qualitative detection of manganese.

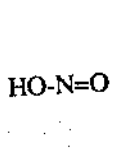
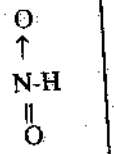
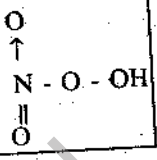
The difficulty in attaining the +5 state in arsenic and antimony and especially in bismuth, and the instability of bismuth pentoxide are a consequence of the inert pair effect.

The oxides of these elements clearly show that (a) the stability of higher oxidation state decreases with increasing atomic number and (b) in a given oxidation state the metallic character (basicity of the oxide) increases with increasing atomic number.

7.7 OXYACIDS OF NITROGEN

Niytrogen forms four important oxyacids. They are given in the following table

Table: Some important oxyacids of nitrogen

Name	Formula	Structure	Oxidn. no.	Property
1. Hyponitrous acid	$H_2N_2O_2$	HO-N=N-OH	+1	very weak
2. Nitrous acid	HNO_2	HO-N=O or 	+3	weak, oxidising and reducing
3. Nitric acid	HNO_3	HNO_3 	+5	strong oxidizing
4. Per(oxy)nitric acid	HNO_4	HNO_4 	+7	oxidising

Of these nitrous and nitric acids are of importance.

7.7.1 Hyponitrous acid

Hypronitrous acid is known chiefly in the form of its salts. The free acid can be obtained by the action of an ethereal solution of hydrogen chloride on the silver salt of the acid.

$$Ag\ N_2\ O_2 + 2HCl \rightarrow 2\ AgCl + H_2\ N_2O_2$$

It decomposes readily to nitrous oxide and water and slowly even in aqueous solutions. It is soluble in water.

$$H_2N_2O_2 \rightarrow H_2O + N_2O$$

It is such a very weak acid that it does not decompose carbonates. It is oxidized by air to nitrous and nitric acids.

$$2H_2\ N_2\ O_2 + 3O_2 \rightarrow 2\ HNO_2 + 2\ HNO_3$$

7.7.2 Nitrous acid

Free nitrous acid has not been isolated. An aqueous solution can be obtained by dissolving dinitrogen trioxide in water,

$$N_2\ O_3 + H_2O \rightarrow 2\ HNO_2$$

or by adding ice-cold dilute sulphuric acid to a well cooled solution of barium nitrite.

$$Ba(NO_2)_2 + H_2SO_4 \rightarrow BaSO_4 + 2\,HNO_2$$

An aqueous solution in slightly bluish in appearance probably due to dinitrogen trioxide. It is a weak acid. It is unstable even in aqueous solution and decomposes readily when heated.

$$3\,HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

It is a good oxidizing agent. It oxidises an iodide ion to iodine,

$$2\,HI + 2HNO_2 \rightarrow 2\,H_2O + 2\,NO + I_2$$

ammonium ion to nitrogen,

$$(NH_4)_2\,SO_4 + 2\,HNO_2 \rightarrow H_2SO_4 + 4\,H_2O + 2\,N_2$$

and urea to nitrogen and carbon dioxide.

$$CO(NH_2)_2 + 2\,HNO_2 \rightarrow CO_2 + 3\,H_2O + 2N_2$$

Strong oxidixzing agents oxidise it to nitric acid

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O$$

Thus it decomposes an acidified solution of potasium permanganate to manganous salt.

$$2KMnO_4 + 3H_2SO_4 + 5\,HNO_2 \rightarrow K_2SO_4 + 2\,MnSO_4 + 5HNO_3 + 3H_2O$$

It also decolorises bromine water to hydrogen bromide.

$$Br_2 + H_2O + HNO_2 \rightarrow 2\,HBr + HNO_2$$

Even weak oxidizing agents like oxygen convert nitrite ion to nitrate ion in alkaline solutions.

$$HNO_2 + O_2 \rightarrow HNO_3$$

7.7.3 Nitric acid

This is the most important of the oxyacids of nitrogen. It is prepared by the distillation of sodium nitrate with concentrated sulphuric acid.

$$NaNO_2 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

It is manufactured by Ostwald's process in which ammonia is catalytically oxidised to nitric oxide. It gives with oxygen nitrogen dioxide which when dissolved in water forms nitric acid.

Ostrwald's process. Nitric acid is manufactured by the oxidation of ammonia prepared by the Haber's process from atmospheric nitrogen. Ammonia prepared by the Haber's process is mixed with purified air 1:8 ratio. The mixture is passed through a catalyst chamber containing plantinum gauze. The Platinum gauze is initially heated to about 700° - 900° C. Ammonia is catalytically oxidised to nittric oxide in presence of heated platinum.

$$4NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O + \text{Energy}$$

The heat of the reaction maintains the temperature of the catalyst for optimum conversion.

About 95% of the ammonia is oxidised to nitric oxide. Part of ammonia is burnt to nitrogen and water also. The mixture of gases issuing out of the converter is passed through a cooling chamber. It is mixed with air in an oxidation chamber. Nitric oxide is converted to nitrogen dioxide.

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

NO_2 is absorbed in an absorption tower in water to give nitric acid.

$$3NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$$

The nitric oxide is recycled to be converted to nitric acid.

Concentration. The nitric acid solution is concentrated by distillation when a constant boiling mixture distils off. This acid contains about 68% HNO_3 boiling at about 120.5° C. When this acid is further distilled with concentrated sulphuric acid, a more concentrated acid (98% HNO_3) distils off at 86° C. It freezes to a colourless solid at — 42° C.

Properties. It is a colourless liquid which fumes in air. It is generally coloured yellow due to its partial decomposition to nitrogen dioxide. It decomposes slowly even on exposure to light at room temperatue. It is freely soluble in water. It forms two hydrates HNO_3. H_2O and HNO_3. $3\ H_2O$.

It is extremely corrosive and causes painful sores when it comes in contact with skin (yellow stain on skin is due to xanthoproteic acid formed).

On heting it decomposes to nitrogen dioxide and oxygen.

$$4HNO_3 \rightarrow 2\ H_2O + 4\ NO_2 + O_2$$

It is one of the strong acids. In aqueous solutio it ionizes virtually completely.

$$HNO_3 + H_2O \rightarrow H_2O^+ + NO_2^-$$

It forms salts with bases. The salts are called nitrates.

It is a powerful oxidixing acid. The reduction products are usually nitric oxide at low concentration and nitrogen dioxide at high concentrations. Other reduction products also form depending upon the conditions employed, such as nature of the reducing agent, concentration of acid and temperature, in certain reactions.

Less active metals like copper, silver and lead react with dilute acid to give nitric oxide.

$$3\ Cu + 8HNO_3 \rightarrow 3\ Cu\ (NO_3)_2 + 4\ H_2O + 2\ NO$$

With very dilute and cold nitric acid more active metals like zinc, iron and tin give ammonium nitrate.

$$4\ Zn + 10\ HNO_3 \rightarrow 4\ Zn(NO_3)_2 + NH_4\ NO_3 + 3H_2O$$

With hot dilute nitric acid the product is however nitrous oxide probably due to decomposition of the ammonium nitrate.

$$4\ Zn + 10\ HNO_3 \rightarrow 4\ Zn\ (NO_3)_2 + N_2O + 5\ H_2O$$

With very dilute nitric acid only magnesium and manganese lilberate hydrogen gas.

$$Mg + 2\ HNO_3 \rightarrow Mg\ (NO_3)_2 + H_2$$

However, with acid of higher concentration the oxides of nitrogen are the products of reduction of the acid.

Metals like aluminium, chromium, iron, and nickel are rendered *passive* by the concentrated acid probably due to surface oxidation forming a tough coat of insoluble metal oxide.

Noble metals like gold and platinum are unaffected by acid of any concentration. They are, however, dissolved by a mixture of concentrated hydrochloric acid and concentraed nitric acid called *aqua regia*.

$$3\ HCl + HNO_3 \rightarrow 2H_2O + NOCl + Cl_2$$

$$2\ Au + 2\ HNO_3 + 8\ HCl \rightarrow 2\ HAuCl_4 + 2\ NO + 4\ H_2O$$

Dilute nitric acid has no action on non-metals like carbon, phosphorus, arsenic, sulphur and iodine. Concentrated nitric acid oxidizes them to their oxyacid namely carbonic acid (carbon dioxide), phosphoric acid, arsenic acid, sulphuric acid and iodic acid respectively.

Nitric acid also oxidizes inorganic reducing agents like hydrogen sulphide, sulphur dioxide and ferrous sulphate to sulphur, sulphuric acid and ferric sulphate respectively.

A mixture of concentrated nitric acid and concentrated sulphuric acid is used as *nitration mixture*. Nitration mixture is used in the preparation of nitro derivatives of organic compounds. Nitroglycerine, nitrocellulose (gun cotton) and trinitrotoluene (TNT) are valuable explosives.

Structure. Nitric acid contains the nitrate anion $(NO_3)^-$ which is planar triangular. The three oxygens and the nitrogen are coplanar as required by resonance, the double bond between N and O resonating among all three positions. It is a monobasic acid, the hydrogen atom bonded to one of the oxygens attached to nitrogen being split off as proton, when the acid is dissolved in water. Spectroscopic evidence and electron diffraction data of the gaseous nitric acid molecule suggests the structure.

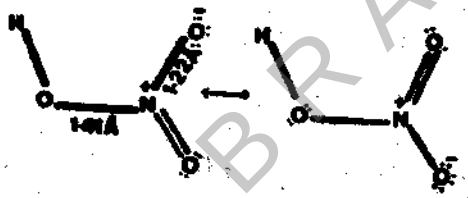


Fig. 7.2 Structure of nitric acid

The attachment of a hydrogen atom to one of the oxygen atoms disturbs the bond angle in nitrate ion. N-O bond (1.22A) is shorter than the N-OH bond (1.41 A). The shortness of N-O bond indicates double bond character. This can be attributed to the resonance of the pi-bond between the two N-O bonds giving a resonance hybrid of the two forms.

Per (oxy) nitric acid (HNO_4). This is obtained by dissolving dinitrogen pentoxide i anhydrous hydrogen peroxide at low temperatures.

$$N_2O_2 + H_2O_2 \rightarrow HNO_3 + HNO_4$$

It is unstable and explosive. Isolation of the free acid has not been achieved. It is soluble in water. But even the solution is unstable.

Check your progress - 2

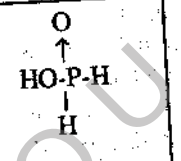
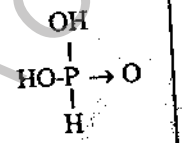
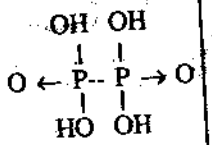
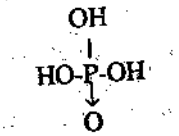
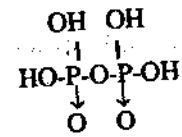
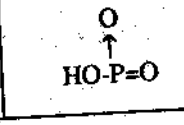
Explain the passivity of metals caused by concentrated nitric acid.

7.8 OXYACIDS OF PHOSPHORUS

The important oxyacids of phosphorus are listed in 7.8.1.

In these acids the phosphorus atom is sp^3 hydridised being tetrahedrally surrounded by atoms. The basicity of the acid is given by the hydrogen atoms bonded to oxygen atoms. The hydrogen atoms attached to the phosphorus confer reducing property. Further the acids in which phosphorus is in a lower state of oxidation (+1, +3, or +4) undergo disproportionation on heating, when part of the phosphorus is oxidized to the +5 and the other part is reduced to +3 state.

7.8.1 Some Important Oxyacids of Phosphorus.

Name	Formula	Structure	Oxidn. state	Property of the acid
Hypo hosphorus acid	H_3PO_3		+1	Monobasic, reducing
Phosphorus acid	H_3PO_3		+3	Dibasic, reducing
Hypophosphoric acid	$H_4P_2O_6$		+4	Tetrabasic
Orthophosphoric acid	H_3PO_4		+5	Tribasic
Pyrophosphoric acid	$H_4P_2O_7$		+5	Tetrabasic
Metaphosphoric acid	HPO_3		+5	Monobasic

7.8.2 Hypophosphorus acid

Hypophosphorus acid is obtained by the action of dilute sulphuric acid on the barium salt of the acid.

$$Ba(H_3PO_2)_2 + H_2SO_4 \rightarrow BaSO_4 + 2\,H_3PO_2$$

The corresponding salt is formed when white phosphorus is heated with a strong solution of caustic alkali.

$$P_4 + 3\,KOH + 3\,H_2O \rightarrow PH_3 + 3\,KH_2PO_3$$

It is a colourless crystalline solid which is soluble in water. It is monobasic acid. It decomposes on heating to phosphine and phosphoric acid.

$$2H_3PO_2 \rightarrow PH_3 + H_3PO_4$$

It is a powerful reducing agent. It reduces silver and mercury salts to the corresponding metals.

$$H_3PO_2 + 4\,AgNO_3 + 2\,H_2O \rightarrow H_3PO_4 + 4\,Ag + 4\,HNO_3$$

7.8.3 Phosphorus acid

Phosphorus acid is obtained by dissolving phophrus trioxide in water.

$$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$$

It is also formed by hydrolysis of the trihalides of phosphorus.

$$PBr_3 + 3\,H_2O \rightarrow H_3PO_3 + 3\,HBr$$

It is white deliquescent solid with garlic odour. It is very soluble in water. It is a dibasic acid and the salts are phosphites. It ionises in two steps in aqueous solution.

$$H_3PO_3 + H_2O \rightarrow (H_3O)^+ + (H_2P_3O)^-$$

$$(H_2PO_3)^- + H_2O \rightarrow (H_3O)^+ + (HPO_3)^{2-}$$

On heating it decomposes to phosphine and phosphoric acid.

$$4\,H_3PO_3 \rightarrow PH_3 + 3\,H_3PO_4$$

It is a strong reducing agent. It reduces copper and silver salts to the metal and mercuric salts to mercurous salts.

$$2\,HgCl_2 + H_3PO_3 + H_2O \rightarrow Hg_2Cl_2 + H_3PO_4 + 2HCl$$

7.8.4 Hypometaphosphoric acid

Hypometaphosphoric acid is, obtained by the action of hydrogen sulphide on a suspension of the lead salt of the acid in water.

$$Pb_2P_2O_6 + 2\,H_2S \rightarrow H_4P_2O_6 + PbS$$

It is a white crystalline solid ($H_4P_2O_6$ 2 H_2O). It is a tetrabasic acid giving two types of salts, Na_4 P_2 O_6 and Na_2 H_2 P_2 O_6.

It hydrolyses in warm water to phosphorus and phosphoric acids.

$$H_4P_2O_6 + H_2O \rightarrow H_3PO_3 + H_3PO_4$$

7.8.5 Orthophosphoric acid

Normally this term should apply to H_3PO_5 or P $(OH)_5$ in which phosphorus exhibits its maximum valence. But in the absence of this its first dehydration product namely H_3PO_4 is called orthophosphoric acid.

It is obtained by dissolving phosphorus pentoxide in water and boiling the solution.

$$P_4O_{10} + 6\ H_2O \rightarrow 4\ H_3\ PO_4$$

It is the hydrolytic product of phosphorus pentahalides.

$$PCl_5 + 5\ H_2O \rightarrow H_3PO_4 + 5\ HCl$$

It is prepared by heating calcium phosphate with concentrated sulphuric acid.

$$Ca_3\ (PO_4) + 3\ H_2\ SO_4 \rightarrow 3\ CaSO_4 + 2\ H_3\ PO_4$$

The mass is extracted with water, filtered and the clear solution evaporated under reduced pressure to a syrupy liquid.

It is a white deliquescent crystalline solid. It is soluble in water. It forms a hemihydrate, ($2H_3$ PO_4 H_2O). It is a tribasic acid ionizing in three steps in aqueous solution. It thus forms three types of salts.

$$H_3PO_4 + H_2O \rightarrow (H_3O)^+ + (H_2\ PO_4)^-$$

$$(H_2PO_4)^- + H_2O \rightarrow (H_3O)^+ + (HPO_4)^{2-}$$

$$(HPO_4)^{2-} + H_2O \rightarrow (H_3O)^+ + (PO_4)^{3-}$$

It is a weak acid. On strong heating it loses water at about 250°C to form pyrophosphoric acid.

$$2\ H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

On further heating to red heat (about 600°C) it loses more water forming metaphosphoic acid.

On heating with excess ammonium molybdate and excess concentrated nitric acid, phosphoric acid and its salts yield a canary yellow precipitate of ammonium phosphomolybdate $(NH_4)_3$ PO_4 12 MoO_3

7.8.6 Pyrophosphoric acid

Pyrophosphoric acid is obtained by heating orthophosphoric acid to 250-260°C.

$$2\ H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

It is a white crystalline solid. It is soluble in water. On boiling its aqueous solution it is converted into orthophosphoric acid.

$$H_4P_2O_7 + H_2O \rightarrow H_3PO_4$$

On strong heating it loses water forming metaphosphoric acid.

$$H_4P_2O_7 \rightarrow 2\ HPO_3 + H_2O$$

It is a tetrabasic acid and forms two types of salts, $Na_2\ H_2P_2O_7$ and $Na_4\ P_2O_7$.

7.8.7 Metaphosphoric acid

It is prepared by igniting orthophosphoric acid at red heat.

$$H_3PO_4 \rightarrow HPO_3 + H_2O$$

It is a transparent glassy solid and is generally known as *glacial* phosphoric acid. It is a deliquescent solid. It is soluble in water. On boiling an aqueous solution it is converted into the orthophosphoric acid.

$$HPO_3 + H_2O \rightarrow H_3PO_4$$

It is a monobasic acid and forms metaphosphates, eg., $NaPO_3$

The so called sodium hexametaphosphate also known as Graham's salt or Calgon does not contain $(PO_3)_6$ units. It contains Na_2O and P_2O_5 in 1 : 1 ratio. It is obtained by rapid cooling of molten sodium metaphosphate. It crystallizes on reheating the glassy mass to 300°C

It has a striking sequestering ability, (ability to remove metal ions as their soluble complex ions). It is therefore used in water softening under the name *calgon* (meaning, calcium gone). It is also used in washing powders for sinks and floors.

7.9 SUPERPHOSPHATE

The chief ingredient is monocalcium phosphate, $Ca_3\ (HPO_4)_2$. The natural or normal calcium phosphate, $Ca_3(PO_4)_2$, is insoluble in water. Phosphorus is an important element for the proper growth of plants and even animals. The animals derive their requirements of phosphorus from plants and plant products. As such the insoluble calcium phosphate is to be converted into a water soluble form. This is effected through its conversion into monocalcium phosphate.

Powdered rock phosphate, $Ca_3\ (PO_4)_2$, is mixed with a calculated amount of concentrated (69-70%) sulphuric acid. The mixture is allowed to mature over several days when the conversion would be complte.

$$Ca_3\ (PO_4)_2 + 2H_2SO_4 \rightarrow Ca\ (H_2PO_4)_2 + 2CaSO_4$$

The resulting mixture of monocalcium phosphate and calcium sulphate is called *super-phosphate*. It invariably contains some phosphoric acid produced in a side reaction.

$$Ca_3\ (PO_4)_2 + 3\ H_2SO_4 \rightarrow 3\ CaSO_4 + 2\ H_3PO_4$$

In this soluble form when it is spread on the soil and watered, the plants absorb the phosphate through their roots along with soil water.

7.10 SUMMARY

The group VB includes nitrogen, phosphorous,arsenic antimony and bismuth and is considered as a typical group in which we can see the steady change over from non metallic to metallic character down the group. Nitrogen being smallest and most electronegative of the VB elements, exhibits certain peculiar properties uncommon to the rest of the elements.

They form hydrides of the type MH_3 and their thermal stability decreases from N to Bi. Their solubility in water and ability to donate the lone pair of electrons also decrease. The oxides are of the type M_2O_3 and M_2O_5. The basic character of the trioxides increases from N to Bi. The oxides in +5 state are quite acidic compared to those of +3 state. The solubilities of those pentoxides in water decreases and so is the acidic character of these oxyacids.

All the elements form trihalides with all the halogens. They are susceptible to hydrolysis. Except nitrogen the rest of the elements form penta halides and this anomoly has been explained in terms of the peculiar electronic configuration of nitrogen.

As the non metallic character is dominant in N,P and to some extent in As, they form a large number of oxyacids. Nitric acid is a powerful oxidant and an important commercial chemical. Super phosphate, an important phosphatic fertilizer contains water soluble monocalcium phosphate.

7.11 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines.

1. Explain why nitrogen is a non-metal while bismuth is a metal?
2. Discuss the trend in the stability of the hydrides of group VB elements.
3. Illustrate the high oxidising power of bismuth with (+5) oxidation state.
4. Write the structure of nitric acid molecule and comment on the same.
5. Write a note on the preparation and use of superphosphate.

II. Answer the following in 30 lines.

1. (a) Justify the inclusion of N,P, As in the same group in the periodic table.
   (b) Discuss the trends in the ion sizes, electronegativity and ionisation potentials of group VB elements.
2. Present a concise account of the oxides and oxyacids of VB elements. How does the strength of oxyacids vary in this group?
3. Discuss the need for the optimum conditions for the manufacture of ammonia by Haber's process.
4. Analyse the chemical reactions of nitric acid with metals.

7.12 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. The low melting point of nitrogen is due to its discrete triply bonded diatomic molecules. Phosphorus, arsenic and antimony form tetrahedral P_4, As_4 and Sb_4 molecules and have high melting poins.

2. Metals like aluminium, chromium, iron and nickel are rendered passive by the concentrated nitric acid, probably due to surface oxidation forming a tough coat of insoluble metal oxide.

Block - 4 STUDY OF ELEMENTS OF GROUPS VI B, VIIB

These elements belonging to 'P' block are known as chalcogens of oxygen family (VI B) and halogens (VII B). They show regularity in their proprities, specially the trend from non-metallic to metallic character is very clear. The last elements of these VI B and VII B groups are polonium (Po) and astatine (At) respectively. They are radioactive elements.

UNIT - 8 ELEMENTS OF GROUP VI B

Contents

8.1 AIMS AND OBJECTIVES

This unit is mainly to make you understand the various aspects of group VIB elements and justify the similarities and differences in their properties in terms of the electronic configuration of the elements.

When you have completed reading and understanding the various items presented in this unit yu must be able to:

- Appreciate how the first element of the group stands above with special properties with little comparison with the rest.
- Justify the progressive increase in metallic character from S to Po in terms of the properties of several types of compounds of these elements.
- Account for the variable oxidation states of elements except oxygen.

- Explain the puckered ring structure of sulphur.
- Account for the decresing thermal stabilities and bond strength of the binary hydrides of oxygen to polonium.
- Describe the structures of tetra and hexahalides of sulphur.
- Present a concise account for the manufacture of sulphuric acid.
- Describe the preparation and properties of permono and perdisulphuric acids.

8.2 INTRODUCTION

Among the representative elements (group B elements in the periodic table) it is clear that the lightest member of any periodic group has chemical properties that differ rather noticeably from those of the heavier members of the group. This behaviour is particularly clear in group VI B. The elements oxygen and sulpur of this group are comparatively common, while the other members, selenium, tellurium and polonium are relatively rare. All these five elements are collectively known as members of the oxygen family.

The first four elements are non-metallic in character and are called collectively **chalcogens** or ore forming elements because many metals occur in nature either as oxides or sulphides. The most important trend in the group is the general increase in electropositivity on descending the group from oxygen to polonium. Non-metallic character is strongest in oxygen and sulphur, weaker in selenium and tellurium, while polonium which is radio-active and short lived is markedly metallic in character. The increase in metallic character from oxygen to polonium is shown in the structure of the elements and in the increased tendencies to form M^{2+} ions and a decreasing stability of the M^{2-} ions. These latter two aspects will be fully explained at the appropriate place in the text of the unit.

8.3 OXYGEN AND OTHER ELEMENTS-A COMPARATIVE STUDY

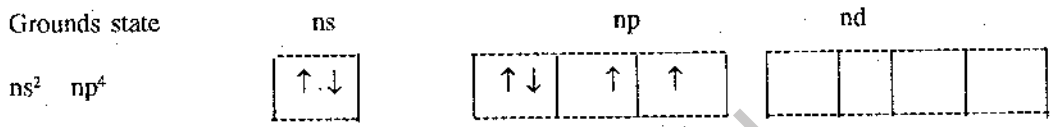
Some of the important physical and chemical properties of group VI B elements are presented in the following table

Property	Oxygen O	Sulphur S	Selenium Se	Tellurium Te	Polonium Po
Atomic no.	8	16	34	52	84
Elec.confgn.	$2s^2\ 2p^4$	$3s^2\ 3p^4$	$3d^{10}\ 4s^2\ 4p^4$	$4d^{10}\ 4s^2\ 5p^4$	$4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$
Atomic weight	15.99	32.06	78.96	127.6	210
At. radius(A°)	0.74	1.04	1.17	1.37	1.64
Ionic radius,M_2 (A°)	1.40	1.84	1.98	2.21	
Melting point (°C)	-219	119	217	450	254
Boiling point (°C)	-183	444	684	1390	962
Density of of solid (cm^3)	1.27	2.06	4.80	6.24	9.4
Ionization potential IP_1 (KJ mol-1)	1314	1000	941	869	--
Electronegativity	3.5	2.5	2.40	2.02	1.75
Enthalpy of vapourisation(KJ mol^{-1})	3.39	10.5	27.7	50	103
Common oxidation numbers	-- 2,2	-2,2,4,6,	-2,2,4,6,	2,2,4,6	2,4

8.4 ELECTRONIC STRUCTURES AND OXIDATION STATES

All the elements have the outer electronic configuration of s^2p^4. This allows the atoms to attain a noble gas configuration by gaining or sharing two electrons. When bonded to more electronegative atoms elements of this group show positive oxidation states such as 2,4, and 6 (eg; S in SCl_2-2: Se in SeO_2 – 4 and Te in TeO_3 –6). The electronegativity value of oxygen (3.5), suggests that most metal oxides will be ionic and contain O^{2-} ions , thus giving an oxidation state of -2. The positive oxidation states in case of oxygen are found only in compounds with fluorine since fluorine is the only element more electronegative than oxygen. eg. F_2O, fluorine monoxide. With most electropositive elements, S, Se and Te form few compounds which are more than 50 percent ionic in character, hence ions of the type S^{2-}, Se^{2-} and Te^{2-}, sulphides, selenides and tellurides respectively are quite probable. In all these cases the latter three elements show-2 oxidation states.

The valence of oxygen is surprisingly limited to 2 because of the fact that the second shell is limited to eight electrons. It requires exceedingly large quantity of energy to excite an electron into a higher orbital i.e. 2p into 3s. Oxygen being a first row element, generally obeys octet rule and cannot involve higher orbit also for bonding purposes. Hence valency is limited to 2. However, the other elements S,Se, Te and Po have 'd' orbitals available for bonding so as to enable them to form four or six bonds. The variable oxidation states of these elements are believed to arise from the following electronic configurations.



without excitation

-2 0r +2 oxidation states

with excitation

Process	*Oxidation state*	*Examples*
P_x electron in to d	+4	SO_2, SeO_2, SF_4
s electron into d	+6	SO_3, SF_6, TcF_6

It is interesting to observe that the most common oxidation states are - 2,2,4 and 6. There is an obvious difference of two units between the various oxidation states in this group. One may recall the same difference of two units in the common oxidation states of group VB elements i.e. 3 and 5. This odd number oxidation states can be attributed to the electronic configuration of VB elements in terms of ns^2 np^3 which may provide 3 or 5 unpaired electrons for bonding. In case of VIB elements, the configuration of ns^2 np^4 permits the availability of 2,4 or 6 electrons for bonding purposes. Hence even number of common oxidation states.

8.5 ALLOTROPY AND MOLECULAR STRUCTURE

All the elements in the oxygen family exist in a variety of modifications. These modifications may be truly allotropic modifications or they may differ from each other in molecular complexity. Oxygen exists as two allotropes, oxygen, O_2 a colourless gas and ozone O_3, a pale blue gas. Oxygen stands alone from the group in being a diatomic gas at room temperature. This is attributed to the ability of oxygen atoms to form double bonds resulting in gaseous state. The bond energy of oxygen-oxygen double bond O=O is more than thrice of that of O-O single bond. This evidently permits the formation of double bonded oxygen molecules rather than 0-0-0 chains. Such a chain structure becomes characteristic and important of sulphur, selenium and to certain extent, tellurium.

Oxygen molecules exhibit very low intermolecular attractions and therefore condense and freeze only at very low temperatures. The liquid oxygen is pale blue in colour and is para-magnetic giving evidence to the presence of two unpaired electrons per molecule. Therefore, the usually written structure as O=O with a double covalent bond is not correct in a stricter sense. The best structure that can be written is that which contains one two electron bond, and two three electron bonds each containing one pair of electrons and one unpaired electron. This structure readily accounts for the bond strength and para-magnetism.

The bond length is intermediate between single and double bonds (1.48 A° and 1.21 A° respectively). Ozone is a bent molecule with a bond angle of 117°.

Sulphur shows a wide variety of different allotropic forms in different physical states. It has two common crystalline forms, α or rhombic form which is stable at room temperature and β or monoclinic form which is stable above 95.5°C. In both of these forms eight sulphur atoms are covalently bonded together in a puckered ring as shown in fig.8.1. It is instructive to realise that while O=O is many times stronger than O-O bond. S==S bond is less than twice stronger than S-S bond. This results in the catenated S-S-S chains being stable relative to the molecule S=S. Thus at normal temperatures O_2 is a gas and S_8 is a solid. The intermolecular forces between the S_8 molecules in the solid state are the weak van der Wall's forces. Hence the melting point of sulphur is low (m. pt. 113°C).

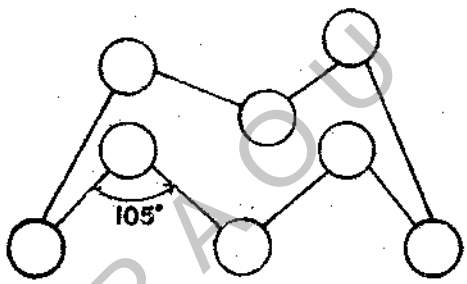


Fig. 8.1 Puckered ring structure of sulphur

In liquid sulphur at temperature about 200°C the ring molecules open up and long chain molecules are formed. When liquid sulphur is poured into water a solid plastic sulphur which contains helical chains of atoms of sulphur results. Sulphur vapour consists of S_8, S_4 and S_2 molecules in relative amounts that depend on the temperature. Thus in its solid, liquid or vapour phase sulphur displays a variety of molecular structures.

Selenium and tellurium both have several allotropes studied, however, less in detail than those of sulphur, the rhombic and monoclinic modifications of selenium exist as Se_8 molecules. Both these forms are obtained as dark red solids by evaporating solutions of the elements in carbondisulphide. A grey metallic form of selenium may be obtained by slow cooling of molten selenium. Several amorphous allotropes of selenium are also known. Tellurium exists both as a metallic allotrope, as well as a semimetallic allotrope, similar to that of grey form of selenium. Polonium has two metallic allotropes, α and β forms.

It is obvious from the above discussion that there is an increase in metallic character within the group. The structures change from simple diatomic molecules to rings, chains and to a simple metallic lattice. Further, the electrical properties show an interesting trend. Oxygen and sulphur are insulators, selenium and tellurium are semiconductors and polonium is decidedly a metal.

8.6 GROUP TRENDS

Table in 8.3 illustrates the trends in physical and atomic properties much in line with the expectations. The trends are very much similar to those in group VB elements. However, there are great differences between the chemistry of oxygen and that of the other group VIB elements and then are more gradual variations through the sequence S, Se, Te and Po.

As usual, the first member of the group is anomolous. This is very much obvious in this group where oxygen differs from sulphur most dramatically and the remaining three elements form a well-graded series. The following are some of the probable reasons for the anomolous nature of oxygen.

1. Oxygen is smaller and more electronegative than sulphur and other elements. This accounts for the ionic nature of many oxygen compounds. And for the same reason, hydrogen bonding is very important for oxygen compounds. This is obvious in the chemical nature of water with large hydrogen bonding which is almost completely absent in hydrogen sulphide and rest of the hydrides. The lower electronegativities of S to Po elements lessen the ionic character of their compounds and the importance of hydrogen bonding is greatly reduced.

2. It has been already mentioned that the valency of oxygen is restricted to two because of the limitation of eight electrons in valency electron shell. This permits a coordination number of four and in practice it rarely exceeds two. However, 2,4 and 6 are the common oxidation numbers in rest of the elements and six is the familiar coordination number. These large numbers of oxidation and coordination in S to Po have been possible because of the possible expansion of valency electron shell and low electronegativities.

3. The bond energy of O=O is many times larger than O-O bond in comparison to that of S=S verses S-S. This has been earlier discussed and interms of these sulphur and other elements show strong tendencies to catenation. Because of restricted valency, oxygen shows very limited tendencies to catenation. One may cite the examples of peroxides and superoxides where three are two consecutive oxygen atoms and three in ozonide ion.

In the S to Po series, gradual changes of properties are evident with increase in size, increasing ionisation potentials and decreasing electronegativities. Most of these trends are very similar to these in group VB and are listed below. The full discussion of these trends will of course be taken at the appropriate place with pertinent examples.

1. Increase in metallic character of the group
2. The stability of the - 2 oxidation state decreases down the group
3. The ability of elements to show larger coordination numbers increases down the group
4. Catenation decreases sharply from S to Se
5. The acidity of the oxides decreases down the group
6. The hydrides, H_2X compounds, show decreasing thermal stability and increasing acidity.

8.7 REACTIVITY OF THE ELEMENTS

The general reactivity of the elements decreases in the order O>S>Se>Te. Oxygen and sulphur are fairly reactive. Indeed oxygen is chemically somewhat more like the halogens than S, Se and Te. However, oxygen is less reactive than halogens but reacts with all elements, usually at elevated temperatures except the noble gases, the halogens and a few noble metals. Selenium and tellurium react with most elements on heating to form selenides and tellurides. The elements S, Se, Te do not react with water or dilute acid but are oxidised by concentrated nitric acid to yield respectively H_2SO_4, H_2SeO_3 and H_2TeO_3. In the three compounds the VIB elements show an oxidation number of +6,

+4 and +4 respectively and the chemical properties clearly bring out the fact of decreasing stability of higher oxidation state of +6 from S to Te. Oxygen does not react with alkali, but the remaining elements react to produce anions like M^{2-} and MO_3^{2-} ions. Polonium dissolves in H_2SO_4, HNO_3, HF etc. revealing its enhanced metallic character.

8.8 HYDRIDES

All the elements of group VIB form volatile binary hydrides of the type H_2X i.e. H_2O, H_2S, H_2Se, H_2Te and H_2Po. The hydrides are prepared in general by the action of acids on metal chalconides i.e. sulphides, selenides and tellurides.

$$Al_2X_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2X \ (X{=}{=}S,Se, Te)$$

H_2Po, hydrogen polonide, has been obtained, by the action of HCl on Mg-Po alloy.

At normal temperatures, except water, rest are all gases with obnoxious odours and are extremely poisonous. Water has an abnormally low volatility because it is associated by means of hydrogen bonds in the solid and liquid state. The thermal stability and bond strengths decrease in the order $H_2O > H_2S > H_2Se > H_2Te > H_2Po$.

H_2Po is unstable even at 0°C. It is pertinent to state that on descending the group, the bonding orbitals become larger and so overlap less favourably with the 1s orbital of the hydrogen. This results in a gradual decrease in the stabilities of the hydrides. This trend is well reflected in the heats of formation of the hydrides which are shown in KJ mol^{-1} for H_2O + 242; H_2S= - 20; H_2Se = 81 and H_2Te=154.0.

It is well known that volatility of a compound decreases as atoms become larger and heavier. This contention is in tune with the boiling points of the hydrides; H_2O=100°C; H_2S= -60°C; H_2Se= -42°C and H_2Te= - 2.3°C. All the hydrides are weak acids in aqueous ssolution and their acid dissociation constants increase with atomic number. This particular trend is well reflected in the K_1 value of these hydrides $H_2S = 1 \times 10^{-7}$; $H_2Se = 1.3 \times 10^{-4}$.

The reducing power of the hydrides increases down the group. This is illustrated by the standard electrode potential E_o for the couples. X/H_2X recorded in acid solutions O/H_2O=1.23 V; S/H_2S=0.14 V; Se/H_2Se = -0.4 V and Te/H_2Te = - 0.72 volts. It may be recalled that a fall in the standard reduction potentials as furnished above is a sign of increasing reducing power of the compound. It is a fact that the oxidation of water to oxygen is being difficult and requires a strong oxidising agent. In other words, water is a poor reductant. The remaining hydrides are increasingly stronger reducing agents. For example, H_2S reduces Fe (III) to Fe (II) and Cl_2 to Cl^-. It has been reported that H_2Se and H_2Te reduce water to hydrogen very slowly. All the hydrides burn in air with a blue flame to produce either the dioxide MO_2 or the metal M (M=S, Se, Te), depending on the amount of oxygen available.

Check your progress - 1

Explain the difference in the physical state of H_2O and H_2S at room temperature.

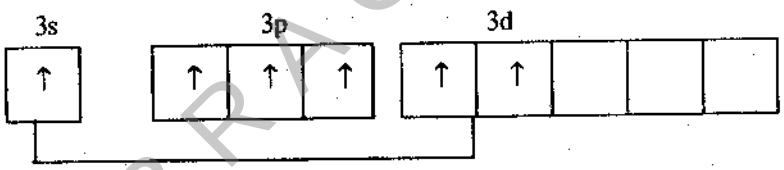
8.9 HALIDES

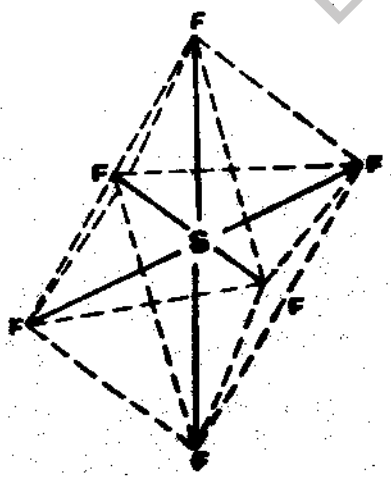
All the elements of this group from many binary compounds with halogens of the type M_2X_2, MX_2, MX_4, and MX_6 (M=S, Se, Te and X = Cl, Br, I and F). It should be remembered that since fluorine is more electronegative than oxygen. the binary compounds of these two are preferably called oxygen fluorides while the rest of the halides may be called as chlorine oxides to iodine oxides. It is obvious from this that oxygen in fluorides shows positive oxidation state and in rest of the halides it is in a negative oxidation state. Gnerally, the order of thermal stability of such compounds decreases in the order F>Cl>Br>I. Some of the typical binary halides are presented in the table 8.9.1.

8.9.1 Binary halides of group VIB elements

Element	M_2X_2	MX_2	MX_4	MX_6
O	O_2F_2	OF_2 ClO_2	-	-
S	S_2F_2 S_2Br_2	SF_2 SCl_2	SF_4 SCl_4	SF_6
Se	Se_2Br_2		SeF_4 $SeBr_4$	SeF_6
Te	-	$TeCl_2$ $TeBr_2$	TeF_4 TeI_4	TeF_6
Po	-	$Po Cl_2$	$Po Cl_4$ $Po I_4$	-

It is interesting to observe that fluorine brings out the maximum valency of six with S, Se and Te. All these compounds. SF_6, SeF_6 and TeF_6 are obtained by direct combination. They are all colourless gases and show an octahedral structure with sp^3d^2 hybridisation.. This geometrical arrangement may be pictured as





Six
six
octa

Six unpaired electrons form bonds with six fluorine atoms-sp^3d^2 hybridisation octahedral structure.

Fig. 8.2 Structure of SF_6

The boiling points of these hexafluorides are obviously very low and certainly indicate a very high degree of covalent character of the bonds SF_6 is an extremely inert gas while the rest slightly

more reactive. This increasing chemical reactivity is best illutrated by hydrolysis. Heat, fused alkalies and many heated metals have no action on SF_6. SeF_6 is more reactive while TeF_6 is readily hydrolysed by water.

$$Te\ F_6 + 6\ H_2O \rightarrow 6H\ F + H_6\ Te\ O_6$$

The case of hydrolysis of TeF_6 can be easily accounted for by the increased size of Te which naturally permits the attainment of larger coordination numbers. Because of this, water molecules are initially brought into the coordination sphere of Te which in later stages facilitate the removal of the fluorides thus causing hydrolysis. This may be represented as

$$Te\ F_6 + 6\ H_2O \rightarrow Te\ (OH)_6 + 6HF$$

The inertness of SF_6 has been attributed to the coordinative saturation of the sulphur and lack of polarity in the molecule because of fairly high electronegative character of sulphur. Thus SF_6 molecule is considered to be highly stable and inert. This accounts for its use as gaseous insulator in high voltage generators and other equipment.

Tetrahalides of the type MX_4 are quite common. Direct action between fluorine and VIB elements, no doubt produces tetrafluorides but they readily change over to hexafluorides. Hence tetrafluorides are prepared by indirect methods.

$$S+4Co\ F_3 \longrightarrow SF_4+4\ Co\ F_2$$

$$Se\ Cl_4+4AgF \longrightarrow Se\ F_4+ 4AgCl$$

$$TeO_2+ 2SeF_4 \longrightarrow Te\ F_4 + 2\ SeOF_2$$

It is of interest to observe that SF_4 is gaseous while SeF_4 and $Te\ F_4$ are respectively liquid and solid. The tetrahalides serve as good, selective fluorinating agents in orgnic reactions.

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!C = O + SF_4 \rightarrow \begin{matrix} R \\ R \end{matrix}\!\!>\!C = F_2$$

As a strange contrast to hexafluorides, the tetrahalides in general and fluorides in particular are easily hydrolysed.

$$S\ F_4 + H_2O \rightarrow SOF_2 + 2\ HF$$

All the elements from S to Po form readily tetrachlorides by direct reaction with chlorine. SCl_4 is believed to be an unstable liquid while others are solids. The last three elements form tetrabromides, $SeBr_4$, $TeBr_4$, and $PoBr_4$. $SeBr_4$ undergo rapid hydrolysis.

$$Se\ Br_4 + 3H_2O \longrightarrow H_2SeO_3 + 4HBr$$

Tetraiodides are known only in case of Te nd Po.

Of all the di and dimeric monohalides, MX_2 and M_2X_2 respectively, SCl_2, S_2Cl_2 and S_2F_2 are well characterised. AgF reacts with sulphur in vacuum to produce S_2F_2. It is unstable compound but exists in two isomeric forms, F_2S = S and F-S-S-F. Chlorination of molten sulphur gives S_2Cl_2 as an orange liquid of objectionable smell. Use of excss chlorine, under the influence of a catalyst like $FeCl_3$ or $SnCl_4$, SCl_2 is believed to have been obtained as a dark red liquid. Sulphur chlorides are readily hydrolysed by water. They find much use as solvents for rubber and in vulcanisation of rubber.

8.10 OXIDES

The principal types of oxides of this group are MO_2 and MO_3, the dioxides and the trioxides. Other oxides include the type M_2O and MO. There is another way of classifying oxides into normal oxides, peroxides, superoxides, ozonides, suboxides, dioxides, trioxides and other higher oxides and neutraloxides.

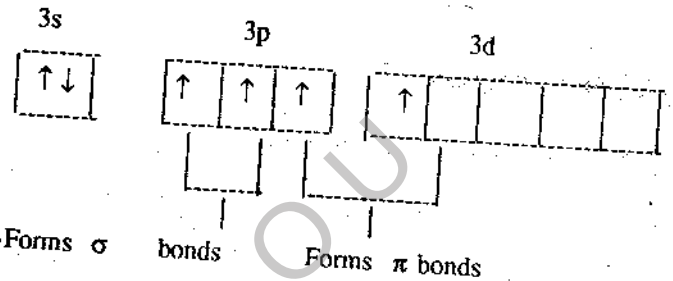
8.10.1 Dioxides : MO_2

All the dioxides of this group, SO_2, SeO_2, TeO_2 and PoO_2 are easily produced by burning the element in air. As metllic character of the elements increases in descending the group, the dioxides become more ionic, weaker reducing agents, stronger oxidising agents and decreasingly acidic. These trends require proper illustrations. Perhaps their structures and physical state will provide sufficient background information to appreciate the trends mentioned above.

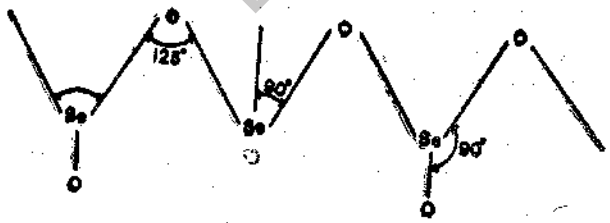
SO_2 is a gas with a covalent molecular structure. Surprisingly SeO_2 has a non-planar chain structure and exists as a solid at room temperature. TeO_2 and PoO_2 are all solids and have ionic structures.

SO_2 molecule is angular, the $\overset{\Lambda}{SO}_o$ being 119.50°. The S-O bond distance of 1.43A° indicates some double bond character.

Electronic config. of sulphur excited state



Each S=O double bond is believed to arise due to the presence of Pπ - Pπ and pπ-dπ bonding between two oxygen atoms and sulphur SO_2 forms discrete molecules even in the solid state. SeO_2 although has similar structure as SO_2 in gaseous state remains as non-planar infinite chains in the solid state. Perhaps the low electronegativity and catenation capacity of selenium are responsible for such chain structures.



8.3 - SeO_2 chains in the solid state

The reactivity of these dioxides shows interesting variations. SO_2 freely dissolves in water but the product H_2SO_3 cannot be isolated. However, it is fairly a strong acid. SeO_2 dissolves in water and forms a weak seleneous acid, H_2SeO_3 is obtained in a crystalline state. TeO_2 is practically insoluble in water but dissolves in alkalies forming tellurites and in acids, basic salts. The latter reactions provide an example of amphoteric character. Thus from S to Se one can observe steady decrease in acidic or an increase in basic character with reference to the action of water on dioxides.

SO_2 acts as a fairly strong reducing agent in both acid and alkaline solutions. The active

species in these solutions is believed to be H_2SO_3. Thus sulphurous acid and solutions of sulphites and bisulphites, act as reducing agents.

$$Cr_2O_7^{-2} + SO_3^{-2} + 8H^+ \rightarrow 2Cr^{+3} + 3SO_4^{-2} + 4H_2O$$

$$2\ Fe^{+3} + SO_3^{-2} + H_2O \rightarrow 2\ Fe^{+2} + SO_4^{-2} + 2H^+$$

Dichromate, $Cr_2O_7^{-2}$ and Fe (III) ions are easily reduced to respective chromium (III) and Fe(II) ions.

SO_2 acts as an oxidising agent too. It oxidises H_2S into elemental sulphur.

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S$$

SeO_2 is a selective oxidising agent converting CH_2 groups of aldehydes and ketones into CO groups. The oxidation of a ketone is a typical case.

$$R.CH_2.CO.R + SeO_2 \rightarrow R\text{-}CO\text{-}CO\text{-}R + Se + H_2O$$

Thus the oxidising ability of SeO_2 is decidedly greater than that of SO_2. TeO_2 is an established oxidant in many reactions. Hence the trend of decreasing reducing character and increasing oxidising ability of the oxides down the group is corroborated.

Check your progress - 2

Why is SO_2 a gas whereas SeO_2 is a solid?

8.10.2 Trioxides

All the three elements, S, Se and Te form trioxides of the type MO_3; however, SO_3 is the most important oxide in this group. It is obtained by the interaction of MO_2 with molecular oxygen in the presence of a catalyst. The optimum conditions established for the preparation of SO_3 in large quantities will be discussed under the manufacture of sulphuric acid.

Sulphur trioxide exists essentially in two allotropic modifications, α and β forms. The α form is an ice-like transparent solid with a melting point of 17° C, while β form exists as asbestos like silky needles. The latter sublimes between 40--50°C. The existence of these two forms has long been recognised, but more recently, a third form has been reported and called γ -sulphur trioxide. It may be stated that these forms have not been clearly distinguished and a given sample may well contain different proportions of the three forms.

The structure of solid sulphur trioxide is polymeric and quite complex. The free molecule, in the gaseous phase, has a planar triangular structure. The molecule has zero dipolemoment and presumably involves sp^2 hybridization. The S-O bond length of 1.43 A may be accounted by the usual bond between S-O strengthened and consequently shortened by π -bonding as has been observed in case of sulphur dioxide.

Selenium exhibits less tendency to exist as SeO_3; in fact the most stable is SeO_2 and not SeO_3. is obtained, however, by the dehydration of selenic acid, H_2SeO_4 by P_2O_5 at 150--160°C. It is a white

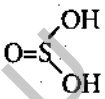
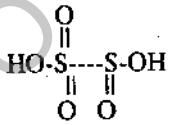
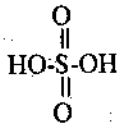
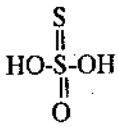
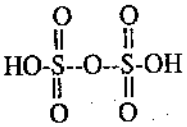
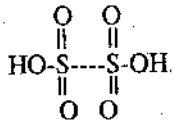
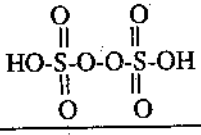
solid existing in two different allotropic forms resembling the two α, β forms of SO_3.

Because of much low electronegativity of tellurium than Se and S, the bonds of Te with oxygen are much polar and Te is not easily oxidised to TeO_3. Again, TeO_2 is much stabler than TeO_3. Tellurium trioxide can, however, be prepared by dehydration of orthotelluric acid, $Te(OH)_6$ about 300°C. It is an orange red non-volatile solid of which again two allotropic forms are clearly known.

Solid sulphur trioxide reacts explosively with liquid water and fumes strongly in moist air, Selenium trioxide reacts vigorously with water producing selenic acid, H_2SeO_4 while tellurium trioxide is notably insoluble in water and chemically unreactive. Selenic acid resembles closely sulphuric acid in general characteristics. However, selenic acid is less stable but a more powerful oxidising agent. The thermal stabilities of these trioxides are in the order of $TeO_3 > SeO_3 > SO_3$.

8.10.3 Oxyacids

The oxyacids of sulphur are more numerous and more important than those of selenium and tellurium. Many of them do not exist as free acids, but are known as anions or salts. The oxyacids of sulphur are listed into five groups based on the structural type. They are (1) Sulphoxylic acid (2) Sulphurous acid (3) Sulphuric acid (4) Thionic acid (5) Peroxo acid series. The classification is rather orbitrary and few typical examples with relevant data are presented in the table.

Type	Name	Formula	Structure	Coordination number
1.	Sulphoxylic	H_2SO_2	HO-S-OH	+2
2.	Sulphurous	H_2SO_3		+4
	Pyrosulphurous	$H_2S_2O_5$		+4
3.	Sulphuric	H_2SO_4		+6
	Thiosulphuric	$H_2S_2O_3$		+6
	Pyrosulphuric	$H_2S_2O_7$		+6
4.	Dithionic	$H_2S_2O_6$		+6
5.	Peroxoacids	$H_2S_2O_3$		+6

The well known oxyacids of Se and Te are H_2SeO_3, H_2TeO_3, and H_2SeO_4 and H_2TeO_4 selenous, tellurous and selenic, telluric acids respectively. Se and Te do not form any oxyacids with bonds analogous to S-S. Another form of telluric acid H_6TeO_6 is quite different from H_2SO_4 or H_2SeO_4. This is known as orthotelluric acid and exists as octahedral $Te(OH)_6$ molecules in the solid state.

In most of the oxyacids, the acidic proton is bound to an oxygen atom which is in turn linked to the central atom eg. M-O-H. Depending upon the oxidation state and electronegativity of the central atom, M, the acidities of oxidation state and electronegativity of the central atom, M, the acidities of oxyacids vary. Some generalisations have been possible in this regard. For instance, if the central atom is in a low oxidation state, eg. S in H_2SO_4, the proton finds an adequate electron density on the oxygen and is held fairly strong. Hence a weak acid. If the central atom has a higher oxidation number, 6 for example S in H_2SO_4, the protons do not find oxygen atoms readily accepting them because of their low electron densities and so are not tightly held up. Consequently, the protons can easily dissociate, hence a strong acid. The acid dissociation constant, Ka values of H_2SO_3 and H_2SO_4 are 1.3×10^{-2} and $> > 1$ respectively. The trend certainly speaks of the larger acidity of the latter acid.

The size effect and the increase in coordination number both contribute to a decrease in acid strength. For example the Ka values of H_2SeO_4 and H_6TeO_6, selenic and orthotelluric acids are $> > 1$ and 10^{-7} respectively. The larger size and the greater coordination number (6) of the Te is admitedly responsible, for the very low acidic character of orthotelluric acid.

8.11 SULPHURIC ACID : MANUFACTURE, STRUCTURE AND PROPERTIES

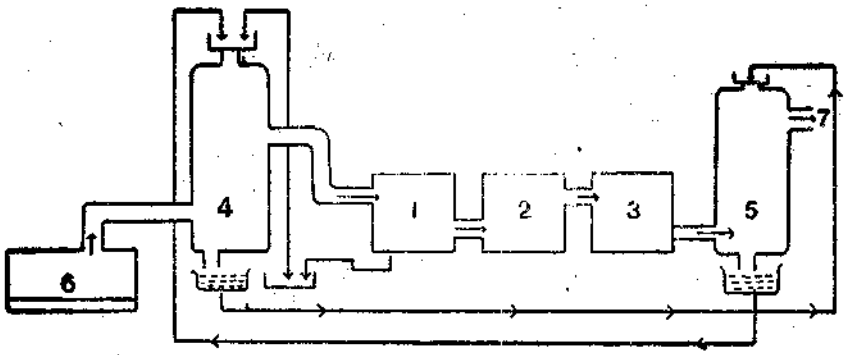
This is the most important chemical in any industrial country. The manufacture is of world wide importance. There are several methods of manufacture, all of which involve essentially three steps : Preparation of sulphur dioxide SO_2, conversion of SO_2 to SO_3 and dissolution of SO_3 to form H_2SO_4. The two important methods of manufacture are (1) Lead chamber's process and (2) Contact process. Both the methods involve the oxidation of SO_2 in to SO_3. This reaction is exothermic.

$$SO_2\,(g) + 1/2\,O_2\,(g) \rightleftharpoons SO_3(g)\ ;\ \Delta H - 98\ Kj\ mol^{-1}$$

It is slow to attain equilibrium. The rate of the reaction can be increased by the presence of a suitable catalyst or in terms of Le Chatelier's principle, by lowering the temperature, or increasing the pressure or by using excess of oxygen. However, for better yields the reaction is carried around 500°C, one atmosphere pressure, with excess of oxygen and a suitable catalyst. These optimum conditions are arrived at balancing the cost, yield and rate considerations.

8.11.1 Lead chambers's process

Fig. 8.4 illustrates the modern plant in plan for the manufacture of H_2SO_4. Pyrites but other sources such as native sulphur or flue gases produced in smelting ores of copper and zinc may also be used. The last named source of zinc ore smelting has recently become much important. The types of burners used vary with the material being burnt. The air supply to the burner is so adjusted that ceexcess of oxygen that is present in the gases enter later the glower tower. A typical reaction that produces SO_2 shown below:



Fig, 8.4 Lead chamber's process.

1,2, 3. Lead chambers; 4. Glower's tower; 5. Gay-lussac's tower; 6.Burners; 7. Exhaust gases

$$4\ FeS_2 + 11O_2 \rightarrow 2\ Fe_2O_3 + 8SO_2$$

The oxides of nitrogen ($NO + NO_2$) acting as catalysts in Lead-chmber's process are made by the oxidation of ammonia and then mixed with SO_2 and excess O_2. This gas mixture is freed from dust and then passed in to the base of the glower tower. This is a tower lined with acid-proof material, packed with flints down which trickles a mixture of weak sulphuric acid drawn from the lead chambers and the strong nitrated acid recovered in the Gaylussac's tower.

The mixture of SO_2, air (O_2) and oxides of nitrogen next passes in to a set of three lead chambers. These are quite big towers made up of lead but based on wooden frames. Cold sulphuric acid has little action on these chambers. Hence the process is popularly known as led-chamber's process. The gases are intimately mixed in these chambers and oxidation of SO_2 into SO_3 mainly occurs in the first two chambers. On the top of these chambers a fine spray of water is blown which dissolves SO_3 and sulphuric acid of 60-70 percent strength is formed. This acid is called chamber acid. The chambers are kept cool enough to condense fumes of sulphuric acid. Family the chamber acid is run off from the floor.

The excess air which leaves the lead chambers is highly charged with oxides of nitrogen. These are recovered by causing the emerging gases from the chambers to pass up a tower called Gay-lussac's tower. This tower is packed with coke down which conc. H_2SO_4 obtained from an alternate source is trickling. This concentrated acid absorbs the oxides of nitrogen to form nitrated acid, which is later mixed with the dilute chamber acid and pumped to the top of the glover's tower. The mixture of acids passes down the tower, meets the upcoming strea of hot gases from burners. The oxides of nitrogen are relieved from the nitrated acid and pushed into the lead chambers. Incidentally the chamber acid gets heated up and concentrated to a strength of about 80 percent.

Thus one may observe some important functions of the glower tower as (1) to recover the oxides of nitrogen, (2) to cool the incoming gases from the burners and (3) to aid the concentration of the weak chamber acid trickling down the tower.

The exhaust gases from the Gay-lussac's tower mainly comprise of nitrogen of the air used for the burning of pyrites. These gases pass on to a chimney and creates a partial vacuum which helps in drawing the gases through the plant.

The reaction mechanism of H_2SO_4 formation in lead chambers is now thought to be:

$$2NO + O_2 \rightarrow 2NO_2$$

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$H_2SO_3 + NO_2 \rightarrow SO_3NH_2 \text{ or Sulphonitronic acid.}$$

This substance can then react in two possible ways.

$$2SO_3.NH_2 + NO_2 \rightarrow 2\ NOHSO_4 + NO + H_2O$$

or $$SO_3.NH_2 \rightarrow H_2SO_4 + NO$$

$$4\ NOHSO_4 + 2H_2O \rightarrow 4\ H_2SO_4 + 4NO + O_2$$

The final products are then sulphuric acid, nitric oxide and oxygen, the latter two react and the cycle is continued. The $NOHSO_4$ has been isolated as an intermediae solid substance called nitrosyl hydrogen sulphate or chamber crystals.

Chamber acid is used nowadays as such, but prior to the advent of the contact process, it was concentrated to form the commercial acid. Among various methods for such concentration, Gaillard tower may be mentioned. This tower consists of frame work made up of acid resisting brick and stone on the top of which a very fine spray of chamber acid is introduced. In the tower the spray meets a current of hot gases from a coke furnace. Progressive concentration of the chamber acid takes place as it passes down the Gaillard tower and a strong acid is run off from the bottom.

In the modern plans, lead chambers have been replaced by towers filled with acid proof tiles. These ensure efficient mixing of the gases. The rest of the operations are more or less the same.

8.11.2 Contact process

This process depends on the ctalytic oxidation of SO_2 to SO_3 by atmospheric oxygen followed by the abosorption of the latter in H_2SO_4. The resultant product called 'oleum' or fuming sulphuric acid is diluted with water to yield almost cent percent sulphuric acid. The reactions are :

$$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3\ ; \qquad \Delta H = -98\ KJ\ mol^{-1}$$

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7 \text{ 'oleum'}$$

$$H_2S_2O_7 + H_2O \rightarrow 2\ H_2SO_4$$

For a successful operation of this process, the following optimum conditions have been arrived at. An excess of air preferably oxygen from a liquid air plant is employed. The use of the latter prevents undue dilution of the reacting gases. The optimum temperature and pressure are 400-500°C and 1.5 to 1.7 atmospheres respectively. Hastening of the slow conversion of SO_2 to SO_3 is achieved by employing catalysts. The two best known catalysts The two best know catalysts are platinum deposited on asbestos or vanadium pentoxide, V_2O_5. Platinum is no doubt more efficient but is rendered inactive or poisoned by the presence of arsenic, which, however, has no inhibiting effect on V_2O_5. For this reason as well as of its cheapness V_2O_5 is increasingly preferred.

The catasysis in Lead-Chmber's process is homogeneous while it is heerogeneous in case of contact process as it provides a solid phase to promote a gas phase reaction. Since the process involves a contact of the promote a gas phase reaction. Since the process involves a contact of the reacting gaseous species with a solid surface, the process is usually referred to as contact process. The details of the process are illustrated in Fig. 8.5

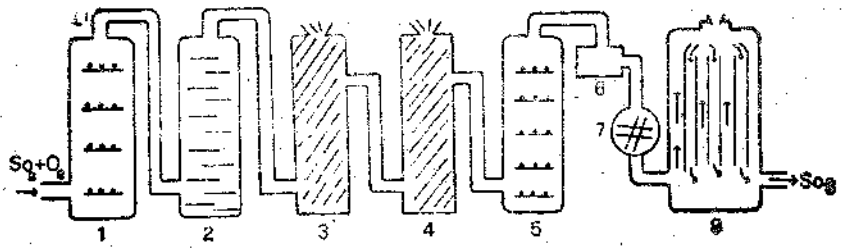


Fig. 8.5 Contact process - plan

1. Dust chamber; 2. Mist precipitator; 3. Scrubber; 4. Drying tower; 5. Arsenic purifier; 6. Test box; 7. Pre- heater; 8. Contact chamber

SO_2 is obtained in a manner similar to the chamber process but requires intense purification with a view to avoid poisoning of the catalyst. It is all the more necessary for the gases to be meticulously free from arsenic. The gases are cleaned by blowing them though dust chambers, a water cooler and a glover tower in each of which the incoming gase a descending spray of water which removes chlorine and other gases or solids.

The last traces of suspended matter are removed by a mist precipitator. The gases are then dried by means of conc. H_2SO_4 and finally passed through water to remove any sulphuric acid. The gases are periodically tested for dust, arsenic etc. Thus purified gases are then passed through a heat interchanger and then into the catalyst chamber. SO_3 is formed and heat evolved. The rate of flow of gases is so adjusted that the temperature in the catalyst chamber is well maintained around 400-500°C.

The exhaust gases consist primarily of SO_3 and N_2. On cooling SO_2 forms a mist of very fine droplet which is absorbed by water or dilute sulphuric acid with great difficulty. On the contrary, it is completely and rapidly absorbed by 98 percent sulphuric acid. Hence the gases that leave the contact chamber pass into cast iron tanks containing 98.5 per cent strong H_2SO_4. A stream of water is run into the condensing tank at such a rate that the strength of the acid is maintained finally at 98.5 percent.

Platinum was formerly used as a catalyst either in the form of platinum deposited on asbestos or on silica gel. For example, Baudisch process for the manufacture of H_2SO_4 employs Pt-asbestos as catalyst. In recent years, V_2O_5 has been preferred for the reasons already stated earlier. In another process called Manheim's process, Fe_2O_3 is used as the catalyst. This is not sensitive to arsenic impurity,. Indeed it totally absorbs arsenic and acts as a purifier. However, this catlyst suffers from the disadvantage that it requires 700°C as the optimum temperature and the yield is limited to 60 - 70 percent.

8.11.3 Properties

Pure anhydrous sulphuric acid is a colourless, viscous, dense oily liquid (density 1.84 gr/ml) without odour. On heating , it decomposes near its boiling mixture (*b.pt.* 330°C) of water and sulphuric acid containing 98 percent of the latter. This one is the commonly used as concentrated sulphuric aid.

Pure conc. H_2SO_4 has a great affinity for water and is used as a dehydrating agent in drying

of the gases like O_2, Cl_2 and SO_3 and in dessicators. The reaction with water is highly exothermic liberating large quantities of heat, hence the acid must be added to water in diluting it. It chars orgnic matter, for instance sucrose, removing water and leaving a black carbon residue.

$$C_{12}H_{22}O_{11} \rightarrow 11\ H_2O + 12\ C$$

Conc. H_2SO_4 is extremely corrosive to the skin and all the body tissues and so causes very serious painful burns. This corrosive action has been attributed to the strong dehydrating power of the acid.

Conc. H_2SO_4 is a powerful oxidant, especially when hot. It oxidises non metals and metals liberating invariably SO_2.

$$C+2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$$

$$S+2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$

$$2P + 5H_2SO_4 \rightarrow 2H_3PO_4 + 5SO_2 + 2H_2O$$

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

It oxidises bromides and iodides to the respective halogens.

$$2KX + H_2SO_4 \rightarrow K_2SO_4 + 2HX\ (X=Br, I)$$

$$2HX + H_2SO_4 \rightarrow X_2 + SO_2 + 2H_2O$$

Anhydrous sulphuric acid sulphonates organic compounds i.e. replaces H atoms by SO_3H groups and assists in nitration i.e. replacing H by NO_2 groups.

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_6SO_3H + H_2O$$

$$C_6H_6 + HNO_3 + H_2SO_4 \rightarrow C_6H_5NO_2 + H_2O$$

Dilute sulphuric acid reacts with electropositive metals to evolve hydrogen and carbonates to liberate carbondioxide.

$$H_2SO_4 + Zn \rightarrow ZnSO_4 + H_2$$

$$H_2SO_4 + MgCO_3 \rightarrow MgSO_4 + CO_2 + H_2O$$

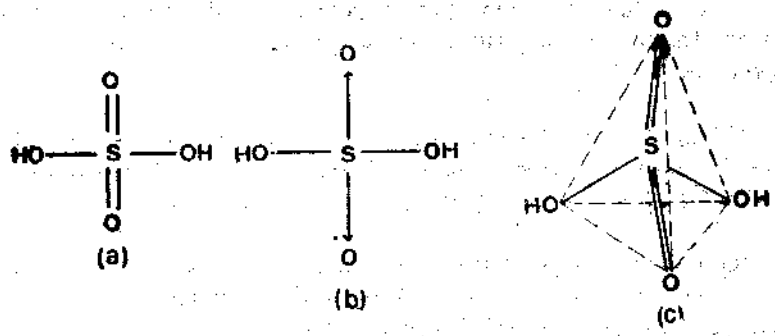
In aqueous solution sulphuric acid is a strong dibasic acid forming two series of salts, sulphates and bisulphates, on neutralisation with bases.

$$H_2SO_4 + NaOH \rightarrow \underset{\text{Sod. bisulphate}}{NaHSO_4} + H_2O$$

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

8.11.4 Structure

The following structures are proposed for sulphuric acid.



8.6 Structures of sulphuric acid

The structure (a) reveals the hexavalent nature of sulphur and two oxygens are linked to sulphur by double bonds. The two OH groups readily account for the dibasic character of the acid as protons can easily be displaced from them. The parachor, values of the acid (experimentally determined on the basis of surface tension and molecular volume measurements) propose a semipolar nature of the linkage between the two oxygens and sulphur and a valency of four to the latter structure-b). The structure (a) seems to be preferable one based on experimental determination of the structure of sulphate and also from the deductions of Gillespie-Nyholm rules regarding the shapes of molecules.

The sulphate ion is tetrahedral as expected since it is shown involve four sp^3 hybrid orbitals to form bonds between sulphur and oxygen. Further, two α bonds involving d-electrons of sulpur and two oxygens strengthen and form double bonds between S and O.

8.12 PEROXOACIDS OF SULPHUR

Two peroxoacids of sulphur are known; peroxo-monosulphuric acid, H_2SO_5 (Caro's acid) and peroxodisulpuric acid, $H_2S_2O_8$. These are believed to have been derived from hydrogen peroxide by substituting of one and two hydrogen atoms respectively by sulphuric groups, SO_3H.

$$H\text{-}O\text{-}O\text{-}SO_3\ H \leftarrow H\text{–}O\text{–}O\text{–}H \rightarrow HO_3S\text{-}O\text{-}O\text{-}SO_3\ H$$

Both the acids can be prepared by the reaction of anhydrous hydrogen peroxide with chlorosulphonic acid. These reactions illustrate their structures also. Peroxomonosulphuric acid, often called, Caro's acid is also obtained by the hydrolysis of peroxodisulphuric acid.

$$\begin{array}{l} \begin{array}{cc} OH & OH \\ | & | \end{array} \\ O=S\text{--}O\text{-}O\text{-}S=O + H_2O \\ \begin{array}{cc} \| & \| \\ O & O \end{array} \end{array} \rightarrow \begin{array}{l} \begin{array}{cc} OH & OH \\ | & | \end{array} \\ O=S\text{-}OH + O=S\text{-}O\text{-}OH \\ \begin{array}{cc} \| & \| \\ O & O \end{array} \\ (H_2SO_4) \quad (H_2SO_5) \end{array}$$

Peroxodisulphuric acid is obtained by the electrolysis of a moderately concentrated sulphuric acid (60 percent) at 0°C using a high current density and a platinum anode and copper spiral as cathode.

$$2HSO_4 \rightarrow 2e^- + H_2S_2O_8$$

This acid is better known in the form of its ammonium or potassium salts, made by the electrolysis of a saturated solutions of ammonium or potassium hydrogen sulphate under the above mentioned conditions. The peroxy disulphate crystallises out at the anode and its formation is assisted by a trace of fluoride ion.

Caro's acid (H_2SO_5) is a crystalline hygroscopic solid melts at 45°C with slight decomposition. It is a monobasic acid. Aqueous solution of this acid decomposes to give mainly oxygen and sulphate ion with small amounts of H_2O_2 and $S_2O_8^{2-}$ persulphate ion. It acts as an oxidising agent.

Peroxodisulphuric acid is a crystalline solid with a melting point of 65°C. In aqueous solution it gradually passes on into Caro's acid. Peroxydisulphates, popularly known as persulphates are one of the most powerful and widely used oxidising agents. Most of these reactions proceed slowly but can be hastened in the presence of catalysts. Ag^+ion being a common one. It oxidises manganous and chromic salts into permanaganate and dichromate respectively. The liberation of idoine from an interaction between potassium persulphate and potassium iodide has been extensively studied from chemical kinetics point of view.

$$K_2S_2O_3 + 2\ KI \rightarrow 2\ K_2\ SO_4 + I_2$$

The constitution of peroxosulphuric acids is based on their synthesis from chlorosulphonic acid and hydrogen peroxide and both are found to contain the -O-O, the so called peroxo linkages. Persulphate ion is known from X-ray studies of its salts to posses the structure, ($-O_2$ S-O-O-SO_3-).

8.13 SUMMARY

Group VIB elements, O, S, Se, Te and Po provide an interesting set of elements for comparative studies. The metallic character progressively increases from S to Po with the consequential changes in the properties of several types of compounds of these elements. Oxygen is most electronegative of all the elements, second to fluorine and being the first element of the group VI, it stands alone with some special properties with no comparison with the rest. It shows a charactristic oxidation state of -2 in most of its compounds. All the elements of this group exist in various allotropic modifications, the most prominent being the non metallic allotropes of sulpur. Sulphur has an interesting molecular structure with eight sulphur atoms covalently bonded together in a puckered ring. While sulphur behaves as an insulator, selenium and tellurium re semiconductors and polonium is a typical metal, of course radio active in nature.

All the elements form typical binary hydrides of the type H_2X and their stabilities and bond strengths decrease from O to Po. The principal oxides of this group are MO_2 and MO_3. The dioxides, MO_2 become more ionic and decreasingly acidic in character from S to Po. Sulphur forms a variety of oxyacids in addition to two peroxo acids with O-O-linkage. These are peroxo-mono and peroxo dissulphuric acids H_2SO_5 and $H_2S_2O_8$ respectively.

8.14 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines

1. How is V_2O_5 preferable to platinum as a catalyst in contact process?
2. What are the favourable conditions for $2SO_3 \rightleftharpoons SO_3$ equilibrium ?
3. Why is SO_3 absorbed in conc. sulphuric acid and not in water?
4. How is the corrosive nature of conc. H_2SO_4 on skin accounted for ?
5. What are the bonds involved in the structure of SO_4^{2-} ion?
6. What structural relation do you observe between H_2O_2 and $H_2S_2O_8$?

7. How do VI B group elements acquire +6 oxidation state?
8. Account for the paramagnetism of oxygen molecule?
9. Explain the structure of rhombic sulphur.
10. Explain the variation in the acidities of binary hydrides in aqueous solution.
11. Account for the inertness and easy hydrolysis of SF_4 and TeF_5 respectively.
12. How do you explain the strong and weak acid character of H_2SO_4 and H_2SO_3 respectively. ?
13. Discuss the structure of sulphuric acid.

II. Answer the following in 30 lines

1. (a) Write the electronic configuration of elements of VI B and justify the similarities in their oxidation states.
   (b) How do you account for the variation in the physical states of VI B elements?
2. (a) Compare the thermal stability and chemical reactivity of VI B hydrides.
   (b) Present a concise account on the properties and structure of VI B halides.
3. (a) Account for the variation in the physical states of dioxides of VI B elements.
   (b) Discuss the comparative chemistry of SO_2 and SeO_2.
4. Outline the manufacture of sulphuric acid by contact process with due emphasis on the optimum conditions involved in the process.
5. Describe the preparation, reactivity and structures of peroxoacids of sulphur.

8.15 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Except water, all other hydrides (H_2S, H_2Se, H_2Te) are gases at room temperature. This is because water is associated by means of hydrogen bonds in the solid and liquid state.

2. $S0_2$ is a gas with a covalent molecular structure. SeO_2 has non-planar chain structure and exists as a solid at room remperature.

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UNIT - 9 ELEMENTS OF GROUP VII B - HALOGENS

Contents

9.1 AIMS AND OBJECTIVES

The purpose of this unit is to make you understand the various aspects of group VII B elements and justify the similarities and differences in their properties in terms of the electronic configuration of the elements.

When you have finished reading and understanding the various items presented in this unit you should be able to:

- Account for the variable oxidation states of elements except fluorine in terms of electronic configuration.
- Explain the different colours exhibited by halogen molecules and also their physical states.
- Explain the extensive hydrogen bonding in HF molecules.
- Rationalize the decreasing oxidising power of halogens from fluorine to iodine.
- Account for the decreasing reactivity of hydrogen halides on descending the group.
- Appreciate the difficulties encountered in the isolation of fluorine and finally describe the preparation of fluorine.

- Account for the increasing acid strength of hydrogen halides from HF to HI in aqueous solutions.
- Describe the different types of interhalogens and their methods of preparation.
- Explain the chemical behaviour of pseudohalogens.

9.2 INTRODUCTION

The group VII B comprising halogens is often considered as one of the best groups for a comparative study because the trends in their properties from the first element to the last halogen are very clearly brought out. And the rationalization of the properties of the elements and their compounds can be convincingly spelt out on the basis of the electronic configuration of the elements.

The electronic configuration of all the elements is .... $ns^2 np^5$, one electron short of the noble gas configuration. Consequently, the chemistry of halogens is dominated by their tendency to complete the octet and to form (i) ionic compounds with metals, containing the negative halide, $\overline{X}$ ion and (ii) covalent compounds with non-metals. Further, halogens form bridged compounds in which they are two coordinate, such as Al_2Br_6 and KHF_2.

The most important physico-chemical features of halogens are presented in the table 9.3.

9.3 PROPERTIES OF HALOGENS

Property	Fluorine F	Chlorine Cl	Bromine Br	Iodine I
Atomic number	9	17	35	53
Electronic confign.(outer)	$2s^22p^5$	$3s^23p^5$	3d $4s^24p^5$	4d $5s^25p^5$
Atomic weight	18.99	35.45	79.91	126.91
Atomic radius(A)	0.72	0.99	1.14	1.33
Ionic radius, X^-(A)	1.36	1.81	1.95	2.16
Van der Waals radius (A)	1.35	1.85	1.95	2.16
Melting Point (°C)	–220	–101	–7.3	113
Boiling point (°C)	–188	–34.5	59	183
Enthalpy of vapourisation (KJ mol^{-1})	3.27	10.2	15.0	30
Enthalpy of hydration X (g) (KJ mol^{-1})	460	385	351	301
Bond energies (KJ mol^{-1})	159	243	193	151
Electronegativity	4.0	2.85	2.75	2.20
Ionisation energy (KJ mol^{-1})	1681	1255	1142	1007
Electron affinity(KJ mol^{-1})	333	348	340	297
Electrode potential $1/2\ X_2+e= (aqx^-)$ (V)	+2.87	+1.36	+1.07	+0.54
Oxidation states	–1	–1,1,2,5,7	–1,1,3,5,7,	–1,1,3,5,7,
Colour and physical state at 20°C	Pale yellow gas	greenish yellow gas	reddish brown liquid	black solid

9.4 COMPARATIVE STUDY OF ELEMENTS

All the halogens are highly reactive nonmetals that are always found in the combined state in nature. Because the outer electronic configuration remaining more or less same except for the change in the principal quantum number, the halogens resemble each other chemically. However, they present a noticeable gradation in their properties. Fluorine is the most electronegative of the elements and displays an oxidation state of - 1. The other halogens are no doubt electronegative but form compounds in which both positive and negative oxidation states are assigned to them (vide table 9.3). The tendency for exhibiting positive oxidation state becomes much more pronounced in case of iodine. This is clear indication for the gradual change over of elecfronegative to electropositive character from fluorine to iodine.

As a typical feature of p-block elements the oxidation numbers of halogens differ in steps of two. This may be explained on the basis of electronic configuration shown below with particular reference to chlorine.

	3s	3p			3d				
Electronic structure of chlorine (ground state.)	↑↓	↑↓	↑↓	↑↓					

State	Transition	Oxidation States	Examples
Ground State	nil.	-1 + 1	HCI, HClO
Excited state	$3p_y$ into 3 d	+3	Cl_2O_3
Excited state	$3p_x$ into 3 d	+5	Cl_2O_5
Excited state	3s into 3 d	+7	Cl_2O_7

These higher oxidation states are presumed to arise by unpairing the s or p filled orbitals and promoting the unpaired electrons into the adjacent empty d-orbitals. Thus the oxidation states ranging from +1 to +7 can be realised. Suitable examples are found in the halogen oxides and interhalogen compounds. These variable oxidation states are also exhibited by bromine and iodine but their relative stabilities depend on several factors.

The ionization energies of the halogens are very high which clearly indicates that halogens have extremely low tendencies to form cations by losing electrons. No cation F^+ is possible under all possible conditions. However, the possibility of the existence of X^+ ion increases down the group and iodine cation possibly exists. Compounds such as iodine monochloride, ICl, are believed to contain I ion. This fact also corroborates the natural trend that in any vertical group the electropositive character increases with increase in atomic number.

Halogens possess enoromous oxidising power. Oxidation may be regarded as the removal of electrons such that an oxidising agent gains electrons. The electron affinities of halogens (vide table 9.3) amply prove their high oxidising power. It is surprising to note that the electron affinity reaches a maximum at chlorine and not at fluorine although it is an undisputed fact that fluorine is the strongest oxidising agent amongst the halogens. It should be pointed that the strength of an oxidising [illegible]

greatest oxidising power of fluorine. This trend is easily reflected in the ability of any halogen of low atomic number to oxidise halide ions and liberate halogens of higher atomic number. For instance fluorine displaces chlorine and other halogens from their respective halides while chlorine can displace bromine and iodine from bromide and iodides respectively.

9.5 COVALENT CHARACTER OF HALOGENS

All the halogens form non-polar diatomic molecules, X_2. The melting and boiling points of the elements increase with increased atomic number. While fluorine and chlorine are gases, bromine is a liquid and iodine is a solid. This trend in increasing molecularity can be easily accounted for in terms of Van der Walls radii and forces. From fluorine to iodine, the Van der Walls radii steadily increase 1.35A to 2.15A and there appears an increasing intermolecular attraction resulting in liquid and solid states to bromine and iodine respectively at normal temperature.

The halogen are coloured, the depth of colour increasing down the group. Colour of the molecular species can be explained on the basis of the absorption of visible light. When light falls on the species, part of it is abosrbed by the species to excite outer electrons into higher energy levels. Depending on the electronic configurtion, the amount of energy abosrbed varies. For instance, in case of fluorine, since its ionisation potential is relatively high, large quantity of energy is required for excitation compared to small quantity in case of iodine with comparatively low ionization potential. Accordingly gaseous fluorine molecules absorb violet light corresponding to high energy and therefore appear yellow. Iodine molecules, on the contrany, absorb yellow light, corresponding to low energy, and appear violet. The intermediate colours of green and red of chlorine and bromine respectively fall in line with the arguement based on energy considerations.

The halogen molecules are highly covalent in character as evidenced by their low melting and boiling points and high volatility. All the halogens dissolve slightly in water but largely in organic solvents, another evidence for ltheir covalent nature. The solutions in organic solvents, are coloured depending uupon the halogen and solvent. In non-polar organic solvents such as carbon disulphide and carbon tetrachloride, iodine is violet, bromine is red and chlorine, yellow. It is presumed that these halogens exist as free molecules in these solvents, hence their typical colours.

As atomic size increases from fluorine to iodine, one can expect a gradual decrease in the bond energies of halogen molecules. This is true in case of chlorine to iodine but the bond energy of fluorine is exceptionally low compared to that of chlorine. This abnormally low bond energy of fluorine has been attributed to the great repulsion between the non-bonding electrons which facilitates the easy dissociation of fluorine molecule. This extreme weakness of the F-F bond makes fluorine one of the strongest oxidising agents known.

It has been stated earlier that the oxidising power of halogens steadily decrease from fluorine to iodine. This is well illustrated in the reactions of halogens with water. Fluorine is so powerful as oxidising agent that it oxidises water readily to ozone.

$$3F_2 + 3H_2O \rightarrow 6HF + O_3$$

[illegible] oxidising agent in a similar way but the reaction seems to be energetically [illegible]

fluorides with the largest number of fluorine atoms but the corresponding chlorides or other halides are not observed. For instance AsF_5, SiF_6, IF_7 and XeF_6 have neither chloride nor other halide analogues. Such exceptional behaviour of fluorine has been attributed to its smallest size, highest electronegativity, low bond dissociation energy and many other factors.

Check your Progress - 1

How does fluorine compare with bromine in oxidising abilities?

9.6 HALOGEN HYDRIDES OF HYDROGEN HALIDES.

The products of hydrogen and halogen combination may be called halogen hydrides or better hydrogen halides, HX. The reactivity of the elements decrease on descending the group. Fluorine is undoubtedly the most reactive of all elements. Whilst the reaction of hydrogen with fluorine is quite violent even in darkness, that of hydrogen with chlorine is slow in darkness, but proceeds with explosive violence in sun light. The reaction with iodine is extremely slow at room temperatures. Thus the decreasing reactivity of halogens with increased atomic number is well substantiated.

HF and HCl are usually prepared by the action of conc. sulphuric acid on fluorides and chlorides respectively.

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

It is interesting to note that a similar reaction does not produce HBr or HI since sulphuric acid oxidises HBr to Br_2 and HI to I_2. The usual laboratory method of producing HBr and HI involves the action of bromine or iodine on a mixture of red phosphorous and water.

$$2P+3Br_2 \longrightarrow 2PBr_3$$

$$PBr_3+3H_2O \longrightarrow H_3PO_3 + 3HBr.$$

These hydrogen halides are colurless pungent gases at 20°C, but HF is a fuming liquid at 15°C. This unexpected high boiling point of HF is due to extensive hydrogen bonding between the molecules. Even in the gas phase of HF, association of HF molecules is fairly large. The hydrogen bonding capacity of HCl, HBr and HI is much less than that of HF. It is doubtless that the very high electronegativity of fluorine is responsible for the extensive hydrogen bonding in HF.

All the hydrogen halides are essentially covalent in the gaseous state, but in aqueous solution, they ionise and behave as acids.

$$HX(g)+H_2O(l) \rightarrow H_3O^+ X^-$$

Such a behaviour has been accounted for by the fact that the hydration energies of halogens are greater than the bond strengths of the corresponding halides, hence their easy dissociaion in aqueous medium. Their aqueous solutions are good conductors of electrocity and all undergo typical reactions of acids with metals, metal oxides and metal carbonates.

The apparent degree of dissociation values of these hydrogen halides in dilute aqueous solutions (HF=0.085; HCl=0.92; HBr=0.93 and HI=0.95) reveal that HF is slightly ionised while others are more or less completely ionised. the degree of dissociation broadly reveals that HI is the strongest acid followed by HBr and HCl and HF is the weakest. One may wonder here that how HF being more ionic in character than HI by virtue of largest electronegativity difference, is the weakest acid in aqueous medium. It should be remembered in this context that the acid strength may be an outcome of the tendency of the acid shown as:

$$HX \rightarrow H^+ + X^-$$

Detailed calculations of the above energy terms have revealed the order of acid strengths of HI> HBr> HCl> HF. It is believed that the highest bond srength of HF compared to the other halides (The bond energies (KJ mol^{-1}); HF=565.3; HCl=433.4; HBr=367.50 and HI=299.8) and the great hydrogen bonding in HF is responsible for the above anomolous but weakest acid character of HF in the series. Their acid dissociation constants are bound to be in the order; K values for HF=10^{-3}; HCl=10^{8}; HBr=10^{10} and HI=10^{11}.

Hydrogen halides act as reducing agents in certain situations. The reducing power generally decreases in the order HF(not at all) <HCl <HBr<HI. Hydrogen chloride reacts only with strongest oxidising agents such as metal peroxides, permanganates and dichromates etc, while hydrogen bromide reacts with moderately strong oxidants such as concentrated sulphuric acid, chlorine and hydrogen peroxide, hydrogen iodide reacts even with mild oxidants such as oxygen, Fe(III) salts and dilute nitric acid. It is worth remembering that HBr and HI are slowly oxidised even by air to the respective halogens. Thus it may be summarised that while HI is the strongest reductant, HF is the weakest.

9.7 HALOGEN OXIDES

The known halogen oxides are listed in 9.7.1. While the oxides of fluorine are called oxygen fluorides because of the greater electronegativity of fluorine than oxygen, those of the remaining halogens are conventionally and properly called halogen oxides, since oxygen is more electronegative than the rest three halogens.

Many of the oxides are characteristically unstable with respect to dissociation into the elements but are reactive. Except for those of iodine, all the oxides tend to be explosive. At room temperature they exist as gaseous or volatile liquids with the exception of I_2O_5, a solid. The bonds in all these compounds are largely covalent because of the narrow differences in their electronegativities. The stabilities of the oxides generally lie in the order I> Cl>Br (least stable oxides). Further, the higher oxides tend to be more stable than the lower. The important characteristic feature of all the oxides is that they are powerful oxidants.

9.7.1 Known halogen oxides

Oxidation state	Fluorine	Chlorine	Bromine	Iodine
+1	OF_2; O_2F_2	Cl_2O	Br_2O	-
+3	-	-	-	-
+4	-	-	-	-
+5	-	ClO_2	BrO_2	I_2O_4
+6	-	Cl_2O_6	BrO_3	I_2O_5
+7	-	Cl_2O_7	-	I_2O_7

Various oxides of fluorine exist but only OF_2, oxygen difluoride, is thermally stable at 25°C. It is a non-explosive, colourless gas formed by bubbling fluorine through an aqueous 2 percent

solution of sodium hydroxide.

$$2F_2+2NaOH \rightarrow 2NaF+OF_2+H_2O$$

It reacts vigorously with metals and nonmetals and gives fluorides and oxides. It is slowly hydrolysed by alkalies to oxygen. OF_2 dissolves in water and gives a neutral solution, thus it is not an acid anhydride. It is a powerful oxidising agent and liberates iodine from KI solution.

$$OF_2+4KI+H_2O \rightarrow 2KF + 2KOH + 2I_2$$

O_2F_2 is obtained when an electrical discharge is passed through a mixture of fluorine and oxygen at low temperature . It is highly unstable and decomposes readily above - 100°C.

Cl_2O is a yellowish–red gas at room temperature, Br_2O is a dark brown liquid (m.pt - 17°C) decomposing appreciably at ordinary temperature. They are prepared by heating freshly precipitated mercuric oxide with the halogen gas.

$$2Cl_2+2HgO \rightarrow HgCl_2\ HgO+Cl_2O$$

Both these compounds explode on heating yielding halogen and oxygen.

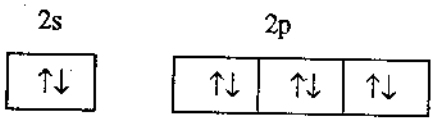
$$2Cl_2O \rightarrow 2\ Cl_2+O_2$$

These oxides dissolve in NaOH solution and form hypochlorites and hypobromites, thus showing their acidic character.

$$Br_2O+2NaOH \rightarrow 2NaOBr + H_2O$$

A the three oxides have tetrahedral structures with two positions occupied by lone pairs of electrons.

Electron structure of oxygen atom, (ground state.)



Two unpaired 2p electrons form, bonds to two halogen atoms-sp^3 hybridisation-tetrahedral structure with two lone pairs.

The bond angles are either smaller or larger than the typical tetrahedral angle, 109° 28'. Obviously the bond angles are distorted. Probably this is a consequence of differing electronagativities and mutual influence of lone pair electrons and bond pair electrons. In OF_2, the bonding electrons are nearer to more electronagative fluorine hence repulsion between lone pair electrons exceeds that between bond pairs and consequently the bond angle is reduced. The situation is different in Cl_2O. Because of greater electronegativity of O than Cl, the repulsion between bond pair exceeds that between lone pairs, hence the bond angle is greater than the tetrahedral angle. Based on the same arguement, still a larger bond angle 111° is predicted for Br_2O.

Chlorine dioxide,, ClO_2 is colourless liquid, (b.pt 11°C) and forms a yellowish gas at room temperature. It easily explodes unless diluted with another gas such as CO_2. It is best prepared by the action of conc.sulphuric acid on a chlorate in presence of oxalic acid that produces CO_2 to act as a diluent for ClO_2.

$$2KClO_3+H_2SO_4+H_2C_2O_4 \rightarrow K_2SO_4 + 2ClO_2 + 2CO_2 + 2H_2O$$

ClO_2 is a powerful oxidising and chlorinating agent. It reacts with alkalies to produce a mixture of

chlorite and chlorate ions.

$$2ClO_2 + 2OH^- \rightarrow ClO_2 + ClO_3 + H_2O$$

Thus it is a mixed acid anhydride i.e. produces a mixture of chlorous, $HClO_2$ and chloric acid $HClO_3$. ClO_2 is an odd electron molecule and is, therefore, paramagnetic. The bond lengths are appreciably shorter than a single bond.

Bromine dioxide; BrO_2 is a yellow solid unstable above 40°C. It is prepared by the action of an electric discharge on a mixture of bromine and oxygen gas at low temperature and pressure. It is a powerful oxidant and reacts with water to yield a mixture of acids.

Chlorine hexoxide Cl_2O_6, is a red oily liquid prepared by treating ozone with chlorine dioxide.

$$2O_3 + 2ClO_2 \rightarrow Cl_2O_6 + 2O_2$$

The molecular weight determination of this compound in carbon tetrachloride indicates its dimeric nature. It is unstable decomposing readily into ClO_2 and O_2. It reacts explosively with organic matter. It disproportionates readily in water or alkali to chlorate and perchlorate.

$$Cl_2O_6 + 2OH^- \rightarrow ClO^-_3 + ClO^-_4 + H_2O$$

BrO_3 is a white solid and is produced from ozone and bromine or oxygen and bromine under the influence of a silent electric discharge. It is unstable above 70°C. It is an oxidising agent and gives acidic solution with water.

Chlorine heptoxide, Cl_2O_7 is the most stable of the chlorine oxides. It is prepared by dehydrating perchloric acid with P_2O_5 at - 10° C followed by vacuum distillation. It is a colourless oily liquid and explodes on shock. It is acidic and is a strong oxidant. It reacts with water and alkalies to generate perchlorate ion.

$$Cl_2O_7 + 2OH^- \rightarrow 2ClO^-_4 + H_2O$$

The iodine oxides are insoluble solids which decompose on heating. Iodine pentoxide, I_2O_5 is the most important of all the oxides. It is a white solid prepared by heating iodic acid, HIO_3 at 200°C.

$$2HIO_3 \rightarrow I_2O_5 + H_2O$$

It is stable at 25°C and is used as an oxidant. The most important reaction is the estimation of carbon monoxide employing the iodometry.

$$I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$$

The other oxides of iodine are less stable and are uncertain in nature.

9.8 PREPARATION AND PROPERTIES OF FLUORINE

It may be reiterated that fluorine is the most chemically reactive of all the elements and this fact has hindered for a long time its isolation. Rapid progress in the knowledge of fluorine has been made only in the recent past. In view of its great reactivity, it has been appropriately called a "Super halogen". It occurs principally as the minerals fluorspar CaF_2, cryolite ($Na\ AlF_6$) and fluorapatite ($3Ca_3\ (PO_4)_3.\ CaF_2$). Sea water contains on the averge about 0.3 p.p.m. of fluorine. The presence of fluorine in potable water is objectionable and if the amount reaches 1 ppm level it is inimical to health.

The isolation of elemental fluorine was a chemical challenge in yester years and engaged the attention of many chemists. The element was first prepared by **Moissan** in 1886. None of the ordinary chemical oxidising agents is capable of extracting electrons from fluoride ion and furthermore electrolysis of aqueous fluoride solutions yielded oxygen rather than fluorine since fluorine reacts at once with water. Hence fluorine has to be prepared only by the electrolysis of scrupulously anhydrous molten fluorides. Anhydrous hydrogen fluoride may be used but it is a non-conductor and therefore potassium fluoride is added to HF to make the solution conducting.

Moissan electrolysed a solution of one mole of potassium fluoride in 12 moles of anhydrous HF at -23°C using platinum-iridium apparatus immersed in a bath of methylchloride, CH_3Cl using platinum-iridium electrodes. Substantial amounts of fluorine were obtained at the anode. The hydrogen liberated at the cathode was prevented from mixing with fluorine by a diaphragm. This method of isolation, although of great historical value, remains uneconomical and also obsolete.

A typical modern electrolytic cell employs an electrolyte containing KF and HF in approximately 1:2.5 ratio with a small amount of lithium fluoride, LiF. It operates at 1500 amperes in the temperture range of 70°-100°C. The cell is made of copper or copper-nickel alloy. The electrolysis is conducted with carbon anode impregnated with copper to render it inert and steel cathode. During electrolysis, fluorine is liberated at the anode, collected in a metal bell and withdrawn. The fluorine obtained is almost pure, containing only a trace of HF which is removed by the passage of fluorine gas over anhydrous NaF.

Fluorine is exceedingly reactive and reacts with almost all elements. The union of hydrogen of large quantities of heat. This reaction seems to be the underlying principle of fluorine-hydrogen torch used for welding purposes. Fluorine does not react directly with oxygen and nitrogen. However, at low temperatures and pressures and under the influence of electrical discharge the reactions are possible.

Most metals, for instance, Na, K, and Mg catch fire in fluorine. Others react with incandescence on heating and form fluorides.

$$Mg + F_2 \rightarrow MgF_2$$

$$2Ta + 5F_2 \rightarrow 2TaF_5$$

Fluorine oxidises chlorates to perchlorates, chromic salts into dichromates and a warm solution of $KHSO_4$ to potassium peroxydi-sulphate.

$$2HSO_4^- + F_2 \rightarrow S_2O_8^{-2} + 2HF$$

9.9 INTERHALOGEN COMPOUNDS

The compounds that result from the mutual interaction of halogens are known as interhalogen compounds. The well known amongst them are listed in the table 9.9.1. The compounds are binary and are of the type ABn where A and B are halogens, A being heavier than B and n=1,3,5 and 7. The element B is always more electronegative than A.

Table 9.9.1 Interhalogen compounds

Type	AB	AB_3	AB_5	AB_7
Compound	ClF	ClF_3	-	-
	BrF	-	-	-
	BrCl	BrF_3	BrF_5	-
	ICl	ICl_3	IF_5	IF_7
	IBr	-	-	-

More than two halogens are never observed in a molecule. It means that ternary interhalogens eg. AB_nX do not exist. This is understandable because any ternary molecule once formed can readily redistribute to form a mixture of the more stable binary compound and/or elemental halogens. Another significant observation in this regard is that the stability of these interhalogen compounds with higher 'n' values increases as A becomes larger and B becomes smaller. Evidently the higher fluorides of iodine, eg. IF_5 and IF_7 must be highly stable.

$$Cl_2 + F_2 \xrightarrow{200°C} 2ClF\ (g)$$

Equal vols.

$Cl_2 + F_2$ (excess)	300°C	$2ClF_3$ (g)
$Br_2 + F_2$ (excess)	→	$2BrF_5$ (l)
$I_2 + Cl_2$ (excess)	→	$2ICl_3$ (l)
$I_2 + Br_2$	→	2IBr (s)
$I_2 + F_2$ (excess)	250° – 270°C →	$2IF_7$ (s)

The various physical states (g,l and s) in which the above mentioned interhalogen compounds exist at room temperatures are noted in the brackets. Obviously they exist in all the three physical states.

They are all covalent molecules which exist as diamagnetic solids or liuqid except ClF which is a gas at 25°C. It is significant to note that since n of the general formula AB_n happens to be an odd number, it becomes clear that all the interhalogen molecules should be diamagnetic having valence electrons either as shared (bonded) or unshared pairs. The bonds in these molecules are essentially covalent because of little electronegtivity difference. However, in case of higher fluorides of bromine and iodine eg.BrF_5 and IF_7, the bonds may develop polarity because of considerable difference in their electronegativities.

The interhalogens are more active than halogens. Their physical properties (for example, colour) are intermediate between those of constituent halogens. It is of interest to observe that their reactions are similar to those of halogens. The interhalogens are hydrolysed by water or alkali to the halide ion of the lighter halogen, B and the hypohalite ion, OA^- or the halate ion AO_3^- of the heavier one.

$$ClF + 2NaOH \rightarrow NaF + NaOCl + H_2O$$

$$BrF_5 + 6NaOH \rightarrow 5NaF + NaBrO_3 + 3H_2O$$

The diatomic interhalogens easily add to ethylenic double bonds.

$$CH_2 == CH_2 + ICl \rightarrow CH_2\,I - CH_2Cl$$

They are strong oxidnts and also function as halogenating agents. Many metals and metal oxides (MO) are easily fluorinated.

$$3MO + 2BrF_3 \rightarrow 3MF_2 + Br_2 + 3/2\ O_2$$

$$MO + 2Cl\,F_3 \rightarrow MOF_6 + 3Cl_2$$

All the interhalogen compounds serve as useful non-aqueous solvents, showing similar solvent properties to water. Their self-ionisation may be shown as

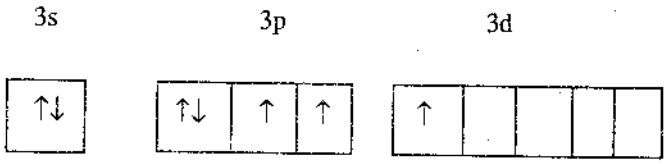
$$2ICl_3\ (l) \rightarrow ICl_2^+ + ICl_4^-$$

$$2BrF_3\ (l) \rightleftharpoons BrF_2^+ + BrF_4^-$$

In view of these ionisations, many typical acid-base reactions can be conducted in these non-aqueous solvents.

It should be pointed out that the main interests in the study of these interhalogens lie in (1) the knowledge of their structures (2) their halogenating abilities. Some account of the geometry of a few typical interhalogens such as ClF_3 and IF_5 will be presented here.

Electronic structure of chlorine (excited state)



Three unpaired electrons form bonds with three fluorine atoms (ClF_3) -sp^3d hybridisation trigonal bipyramid with two positions of chlorine occupied by lone pairs.

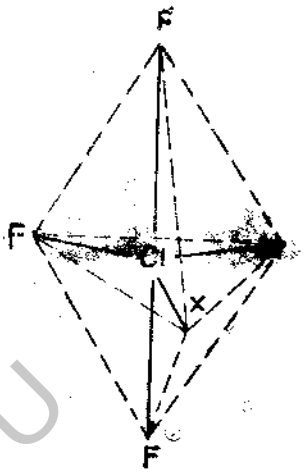


Fig.9.1 Structure of ClF_3

Structural studies have indicated T-shapes for this ClF_3 molecule. By anology BrF_3 and ICl_3 are also expected to be T-shaped. Experiments on structural aspects prove this beyond doubt.

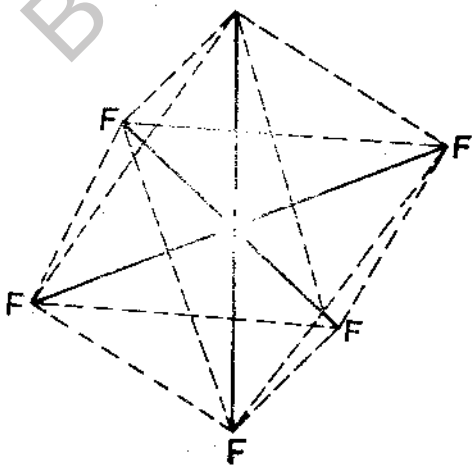


Fig. 9.2 Structure of IF_5

The structures of BrF_5 and IF_5 have been found to be octahedral involving sp^3d^2 hybridisation with the central bromine or iodine as the case may be surrounded by five fluorines and the sixth position being occupied by a lone pair of electrons.

The structures of many of these interhalogen compounds are known from spectroscopic and electron diffraction studies on their vapours. Bonding in these compounds may be satisfactorily explained in terms of electron-pair bonds and non-bonding pairs occupying the vacant stereochemical sites (vide above structures of ClF_3 and IF_5). The rules in deducing the various types of stereochemical arrangements have been well brought out by gillepse-Nyholm.

9.10 PSEUDOHALOGENS

It was noted earlier that certain univalent electronegative inorganic radicals showed great resemblance to the halides in their chemical properties. The principal radicals in this catagory are cyanide $(CN)^-$, cyanate $(OCN)^-$ thiocyanate $(SCN)^-$, Selenocyanate $(SeCN)^-$, Tellurocyanate $(TeCN)^-$ and azide (N_3^-). It is surprising that most of these radicals incude the element nitrogen. Several of these have been isolated in their dimeric forms. Because of the fact of their great resemblance to halogens in several aspects, they have been aptly called as 'pseudohalogens'.

The chemistry of these pseudohalogens is revealing. They are obtained like halogens in dimeric forms. They are oxidising in nature and form many stable salts resembling halides. These pseudohalides are capable of forming coordinate bonds with many metals and so their complexes. The compounds from which the above radicals are obtained correspond to ocyanogen $(CN)_2$, oxycyanogen $(OCN)_2$, thiocyanogen $(SCN)_2$ Selenocyanogen $(SeCN)_2$, Tellurocyanogen $(Te\ CN)_2$ and hydrazoic acid (HN_3) respectively.

It is interesting to note that there are a number of other electronegative radials which satisfy some of the typical criteria for their classification as pseudohalogens. The examples include NF_2, OSO_2F and ScF_3. However, the discussion in the subsequent paragraphs will concern mainly with the first mentioned group known as classical pseudohalogens.

9.11 CYANOGEN

The well known amongst pseudohalogens is cyanogen $(CN)_2$. It is easily prepared in the laboratory by heating mercuric cyanide or by the action of Cu^{2+} ions with cyanide in aqueous solution.

$$2Cu^{2+}+4CN^- \rightarrow 2CuCN+(CN)_2$$

Cyanogen is a very poisonous gas (m. pt -27.8°C b.pt-21.1°C). The cyanogen and cyanides are extremely stable to heat. Polymetisation of cyanogen about 600°C produces the so called paracyanogen.

Hydrolysis of cyanogen in basic solutions produces a mixture of cyanide and cyanate resembling that of chlorine to form chloride and hypochlorite.

$$(CN)_2 + 2NaOH \rightarrow NaCN + NaOCN + H_2O$$

The cyanide $(CN)^-$ ion is an excellent electron donor and forms tetracyanocomplexes with metal ions such as Ni^{2+}, Pt^{2+} and Pd^{2+} (e.g. $[Ni\ (CN)_4]^{2}$) and octacyano complexes with Mo^{5+} and was W^{5+} etc. In organic reactions hydrogen cyanide, HCN, gives both normal and isocompounds. Hydrogen cyanide is a weak acid in aqueous solution and resembles much HCl in many reactions. The most common salts of cyanides, are sodium and potassium cyanides, NaCN and KCN. Cyanides of metals as well as of non-metals are well known and show general resemblance to the corresponding halides. The ready hydrolysis of $Si\ (CN)_4$ and $B\ (CN)_3$ is comparable to that of corresponding chlorides.

$$(Si(CN)_4 + 4H_2O \rightarrow Si\ (OH)_4 + 4HCN$$

The cyanides of Ag (I), Cu(I), Hg(I) and Pb(II) are all insoluble as the chlorides, and find extensive application in inorganic analysis. Silver and gold form stable complex cyanides Na [Ag $(CN)_2$] and K [$Au(CN)_2$] which forms the basis of the successful extraction of the above metals from their ores.

Check your progress - 2

Give two examples where cyanide resembles chloride.

9.11.1 Oxycyanogen

Although metal cyanates are very familiar, the isolation of free oxycyanogen $(OCN)_2$ has been considered extremely difficult. The anhydrous acid of oxycyanogen, HOCN has been found to produce two series of salts, like KOCN and KNCO.

9.11.2 Thiocyanogen

Action of bromine on ethereal suspension of silver or lead thiocyanate produces thiocyanogen

$$2Ag\ CNS + Br_2 \rightarrow 2AgBr + (CNS)_2$$

It is also prepared by electrolysing an alcoholic solution of ammonium or potassium thiocyanate.

Thiocyanogen $(CNS)_2$ is a poisonous substance melting at –30°C. Water hydrolyses it rapidly to a mixture of thiocyanic and hydrocyanic acids. Free hydrothiocyanic acid, HCNS, can be prepared by heating potassium thiocyanate with potassium bisulphate.

$$KCNS+KHSO_4 \rightarrow K_2SO_4 + HCNS$$

The thiocyanate ion, SCN^-, is highly useful in many reactions as it possesses two donor atoms S and N. It acts as a birdging group in certain metal complexes of platinum, molybdenum etc. The important chemical reactions that suggest the similarity of thiocyanogen with halogens are several addition reactions to olefines.

$$C_2H_4+(SCN)_2 \rightarrow C_2H_4\ (SCN)_2$$

9.11.3 Selenocyanogen and tellurocyanogen

Selenocyanogen is obtained by treating an excess of an ether suspension of silver selenocyanate with iodine.

$$2AgSeCN + I_2 \rightarrow 2AgI + (Se\ CN)_2$$

It can also be prepared by electrolysing a solution of potassium selenocyanate in methanol.

It is a yellow crystalline powder fairly stable in dry conditions. It is soluble in many organic solvents such as benzene, chloroform etc.

Tellurocyanogen has been produced in the electrolysis of a solution of potassium tellurocyanate KTe CN in methanol. The chemistry of this pseudohalogen is still unclear.

9.12 AZIDES

The azide radical is unknown in the free state. However, many derivatives of it which resemble those of halogens are clearly known. Azides are salts of hydrazoic acid N_3H of HN_3. Sodium azide NaN_3 is prepared by heating sodamide, $NaNH_2$ with nitrous oxide at 190°C.

$$NaNH_2+N_2O \rightarrow NaN_3+H_2O$$

The free acid, HN_3, is obtained by distilling the sodium salt with 1:1 sulphuric acid and dehydrating the distillate with anhydrous $CaCl_2$.

Hydrazoic acid is a poisonous and highly explosive liquid (m. Pt, -80°C. b.Pt. -37°C). It is slightly stronger than acetic acid, and is easily decomposed by light or catalyst such as platinum black. It undergoes hydrolysis to produce hydroxylamine and free nitrogen..

$$HN_3+H_2O \xrightarrow[\text{Pt catalyst.}]{\text{light}} NH_2OH+N_2$$

Many metal azides resemble corresponding halides in respect of their solubilities and chemical reactions. For instance, azides of silver, lead, mercury (I) etc. are insoluble in water. The azide radical is a good coordinating ligand as shown by the complex $K_2[Cu(N_3)_4]$.

The ion is linear and symmetrical with N-N bond distance of 1.15A.

9.13 SUMMARY

Group VII B elements, popularly known as halogens provide an interesting set of elements for comparative studies. Their electronic configurations suggest the existence of both ionic and covalent compounds. Halogens display variable oxidation states from -1 to +1, +3, +5, and +7 which are easily explained on the basis of their electronic structures.

Halogens are simple diatomic species and powerful oxidising agents and their oxidising power decreases from fluorine to iodine. Further, they are coloured and show different physical states at room temperature. All the halogens react with hydrogen to form compounds of the type HX which are colourless pungent gases and their ease of formation and reactivity decreases from F to I. Hydrogen bonding is extensive in case of HF. These hydrides behave as acids in aqueous medium and the order of acid strengths is HF < HCl< HBr< HI.

Halogens form several oxides exhibiting oxidation states from -1 to +7. Most of these are powerful oxidants. The halogens combine with ease among themselves to form binary interhalogen compounds. These are more active than halogens although chemically they are similar. Certain nitrogen containing univalent electronegative radicals show similar chemical behaviour to halogens and so are popularly known as pseudohalogens.

9.14 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines

1. Explain the variable oxidation states of chlorine.

2. Account for the extensive hydrogen bonding in hydrogen fluoride.
3. Give reasons for the greater acid srength of HI in the series of hydrogen halides.
4. Explain why fluorine spans any central element in large coordination numbr.
5. Why are not tertiary interhalogen compounds isolated?
6. Compare the chemical reactivity of azide with chloride.
7. Justify the grouping of halogens in VIIB group.
8. Explain the various colours of halogen molecules.

II. Answer the following in 30 lines

1. (a) Discuss the trends in (i) reducing action (ii) thermal stability and (iii) acid strength of hydrogen halides.
   (b) Give the methods of preparation of Cl_2O and Br_2O compare the structure of these two oxides with OF_2.
2. (a) Describe the modern method of preparing fluorine.
   (b) Discuss he important reactions of fluorine.
3. (a) Give the general methods of preparation of interhalogen compounds.
   (b) Justify the statement that interhalogens are more reactive than halogens.
4. (a) Explain the term pseudohalogens. Give suitable examples
   (b) Describe the preparation (i) cyanogen and (ii) thiocyanogen (iii) sodium azide Give typical reactions where the above compounds resemble halogens.

9.15 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Oxidising ability of halogens steadily decreases from fluorine to iodine. Fluorine is a powerful oxidising agent that it oxidises water readily to ozone.

$$3F_2 + 3H_2O \rightarrow 6HF + H_2O$$

Bromine is capable of oxidising water but the reaction is energetically unfavourable and different products are formed.

$$Br_2 + H_2O \rightarrow HBr + HOBr$$

2. Cyanides of sodium or potassium silicon and other metals show general resemblance to the corresponding halides.

(a) Hydrolysis: $Si(CN)_4 + 4H_2O \rightarrow Si(OH)_4 + 4\ HCN$

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4\ HCl$$

(b) With Ag^+, Hg^+, Cu^+, Pb^{+2}, form insoluble salts.

$$NaCN + AgNO_3 \rightarrow AgCN \downarrow + NaNO_3$$

$$NaCl + AgNO_3 \rightarrow AgCl \downarrow + NaNO_3$$

Author : Prof. U.V. Seshaiah

BOOKS CONSULTED AND SUGGESTED FOR FURTHER READING

1.	New Concise Inorganic Chemistry	-	J.D. Lee
2.	Inorganic Chemistry	-	Chiswell and James
3.	Chemistry - Facts, Patterns and Principles	-	Kneen, Rogers and Simpson
4.	Chemical periodicity	-	R.T. Sanderson
5.	College/University Chemistry	-	E. Bruce H. Mahan
6.	Inorganic Chemistry	-	T. Moeller
7.	Inorganic Chemistry	-	R.T Sanderson
8.	Advanced Inorganic Chemistry	-	Cotton and Wilkinson
9.	Advanced Inorganic Chemistry	-	Emeleus and Anderson
10.	Inorganic Chemistry	-	Heslop and Robinson
11.	Inorganic Chemistry Vols. I and II	-	Telugu Akademi

Dr. B.R.AMBEDKAR OPEN UNIVERSITY

Faculty of Science

(Under graduate programme)

II - Year

CHEMISTRY COURSE - II

ASSIGNMENT - 1

Section –A

N.B.: 1. Do not copy the answer directly from any of the books.
2. As far as possible try to anser the questions independently in your own words.
3. If it is necessary to quote from any source give the correct reference.
4. Use your own foolscap pages for writing the assignment.
5. Leave sufficient margins for the comments of the evaluator.
6. Completion of this assignment normally should not take more than two hours time.

Answer the following in 30 lines.

1. What are transition elements ? discuss the trend in the ionic radii, ionization potential of 3d and 4d elements.

2. What are interhalogen compounds? How are they prepared?

3. Discuss the properties of oxides, Hydrides and halides of the elements of V(B) group.

Section - B

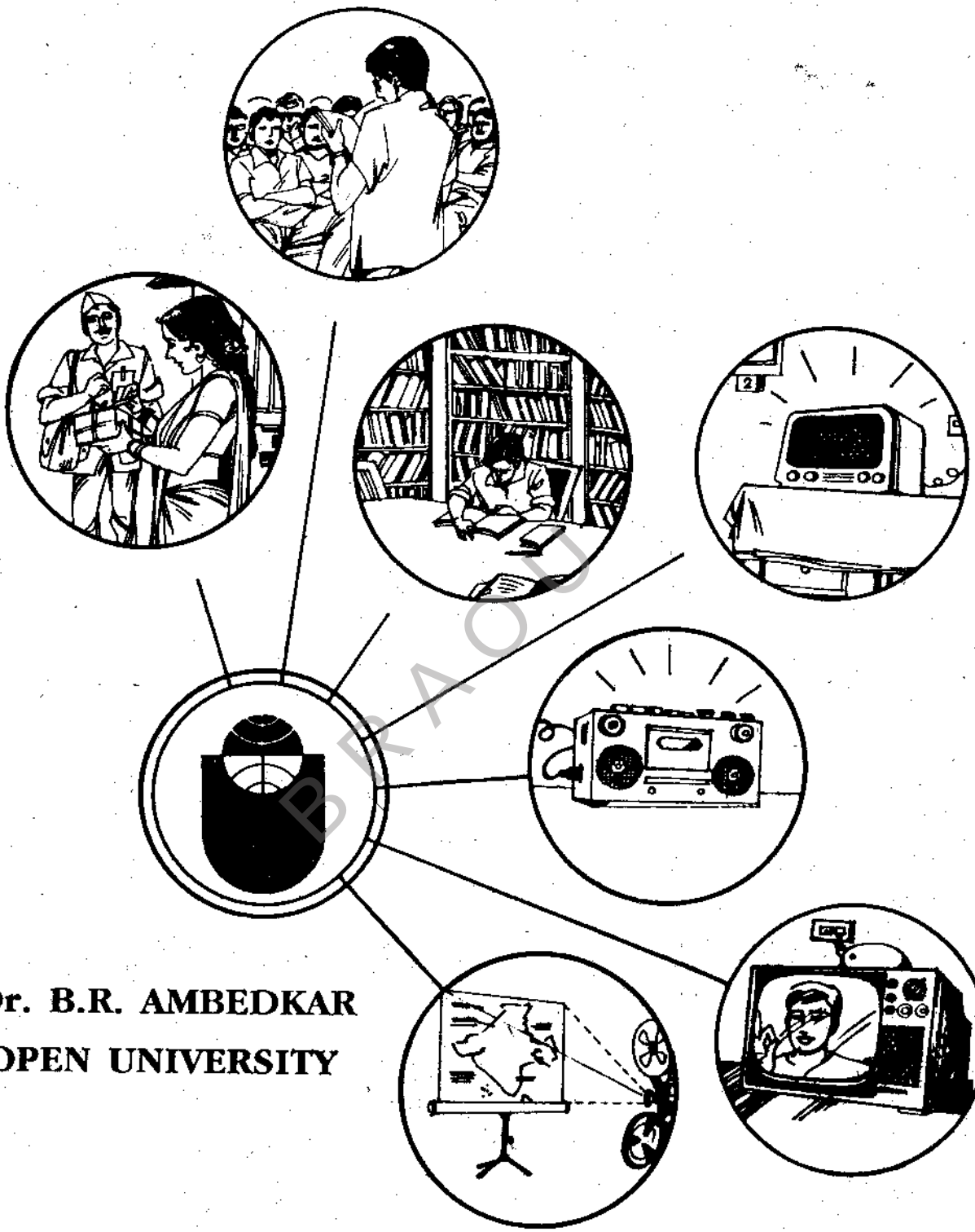
Answer the following in 10 lines.

1. Discuss the oxidation states of VI B Group elements.

2. Discuss the stability of IV B group hydrides.

3. How do you account for the high ionisation potential of zero group elements?

UNIVERSITY AT YOUR DOOR STEP



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CHEMISTRY

INORGANIC CHEMISTRY
ORGANIC CHEMISTRY

Blocks 5 - 10

Dr. B.R. AMBEDKAR OPEN UNIVERSITY

HYDERABAD

1993

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PREFACE

This book deals with the topics in Inorganic Chemistry and Organic Chemistry included in the syllabus for the Second year of the B.Sc. course offered by the Andhra Pradesh Open University. These topics cover the *core area* of the subject to be sudied to be studied in the Second Year of the Three Year Degree Course in Science. The syllabus is for the sake of convenience divided into blocks, each of which comprises a number of *units*. Each block generally covers a specific area of the subject. The units are prepared by specialists in accordance with a format so designed as to enable the student read and understand them without much difficulty. Each unit begins with a statement of its aims and objectives. fEach unit has two short answer questions (as check your progress) and has at its end examination questions intended to test the student's comprehension of its subject matter. Generally technical terms with which the student may not be familiar are given at the end of each block under the head, Glossary.

First book (section A), of this course - II delaing with *Inorganic Chemistry*, it is attempted to explain the properties of chemical elements and their compounds in terms of the electronic configuration of the atoms of the elements. This section seeks to compare in groups the properties of those elements which have similar electronic arrangements. It is hoped that this will help the student to use known facts about one element to deduce probable facts about an unfamiliar element.

The second book (section B), dealing with *Organic Chemistry*. Efforts are made to describe the preparation, properties adn structure of carbon compounds. Attempts are made to explain the reaction mechanisms in terms of modern electronic theories. The University hopes that this course material will help the student to get acquainted with the concepts and princples of *Chemistry* in general and of *Inorganic chemistry* and *Organic chemistry* in particualr.

SECTION - B

ORGANIC CHEMISTRY

CONTENTS

Block - 5 GENERAL CONCEPTS OF ORGANIC CHEMISTRY

UNIT - 10 INTRODUCTION TO ORGANIC CHEMISTRY

Contents

10.1 AIMS AND OBJECTIVES

In this unit we introduce you the classification of carbon compounds, tetravelency of carbon and the formation of single double and triple bounds by carbonations. When you have finished reading and understanding this unit you must be able to know :

- Classification of organic compounds based on carbon skeleton
- Classification of organic compounds based on functional groups
- Types of covalent bonds
- Types of hybridization
- General properties of organic compounds

10.2 INTRODUCTION

Chemical compounds can be divided into two classes namely inorganic and organic compounds. This classification of compounds is based on their origin. Inorganic compounds are obtained from minerals, while organic compounds are obtained from vegetable or animal sources, i.e., living organisms. Oils and fats, starch, sugars, gums, resins, vinegar, spirit, indigo, purfumes, flavours and textiles are some of the organic substances known to ancient people. All these are obtained from animal and vegetable matter. Such substances which are formed from living organisms are termed as **organic compounds.** It was believed that organic substances are produced only by living organisms and it is not possible to synthesise them in the laboratory from simpler compounds. Inorganic substances such as sodium chloride could be prepared from their elements whereas organic compounds such as methyl alcohol and ethyl alcohol are obtained from wood and molasses respectively. It was suggested by **Berzelius** that a mysterious or vital force is responsible for the formation of organic compounds in living organisms. He also thought all living organisms inherently contain "vital force" or 'life force". This theory is known as vital force theory. The "vital force" theory was discarded after the synthesis of urea, a substance present in the urine. In 1828, **Friedrich Wohler,** a German pupil of Berzelius, accidentally obtained urea by the reaction of potassium cyanate with ammonium sulphate and evoparating to dryness an aqueous solution of the resulting ammonium cyanate.

$2\ KCNO$	+	$(NH_4)_2\ SO_4$	$\rightarrow$	$2\ NH_4\ CNO$	+	K_2SO_4
Potassium cyanate		Ammonium culphate		Ammonium cyanate		Potassium sulphate

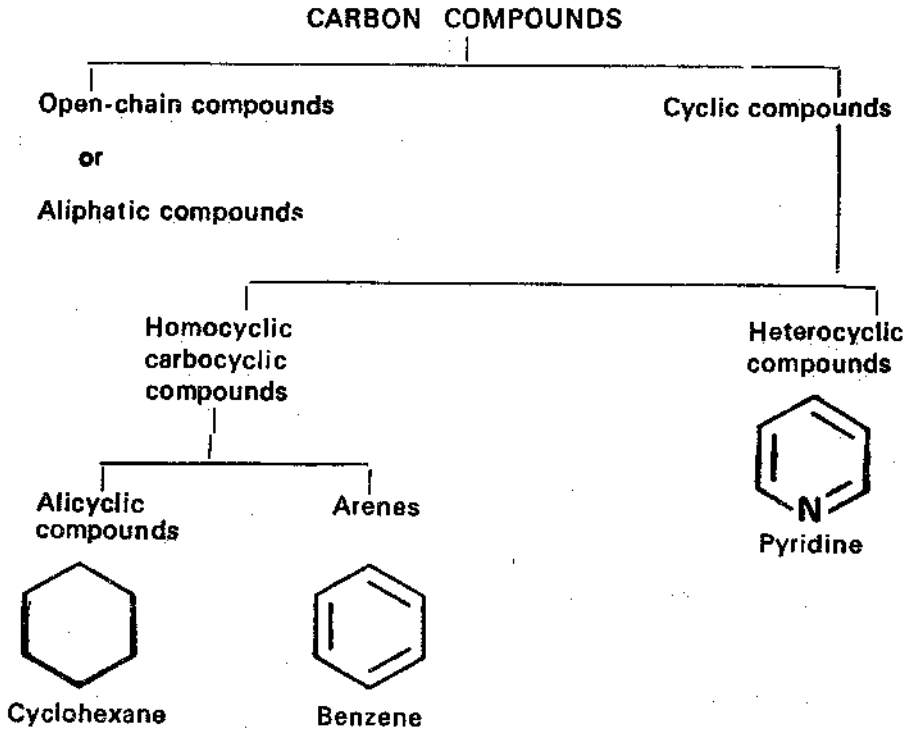
$\downarrow$

$$2\ H_2N\text{ -- }\underset{\underset{\text{urea}}{\|}}{\overset{\overset{O}{\|}}{C}}\text{ -- }NH_2$$

After this, ethyl alcohol was synthesised in the same year by **Hennel,** and acetic acid by **Kolbe** in 1844. Afterwards a number of other organic compounds are synthesised and it was generally recognised that similar chemical principles govern the formation of both inorganic and organic compounds. All the organic compounds have one common feature. They all contain the element carbon. Now organic chemistry is defined as the **chemistry of carbon compounds.** Though organic compounds need not necessarily be obtained from living organisms, the term organic is still retained for convenience.

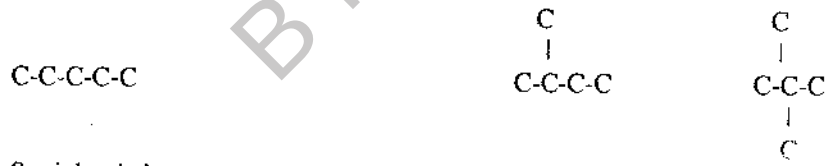
Thus "organic chemistry is defined as the chemistry of carbon compounds", carbon is present in all organic compounds, whether isolated from plant and animal sources or synthesised. In organic compounds carbon atom is tetravelent. Cabon can form single or double or triple bonds. The element carbon has unique property to form chains and rings containing carbon atoms-a phenomenon called **catenation.** Carbon compounds are generally covalent. Many organic compounds exihbit isomerism. For example H_2SO_4 stands for only one compound namely sulphuric acid whereas C_2H_6O represents two organic compounds namely ethyl alcohol and dimethyl ether. Thus the number of compounds with the same molecular formula can be more than one, in the case of organic compounds.

All these factors are responsible for the existance of comparatively large number of organic compounds. Although organic chemistry is a recent branch of chemistry, organic compounds now known number more than millon.



10.3.1 Openchain or aliphatic compounds

The word aliphatic comes from the greek word "aleip-har" which means fat. These compounds are so named because fats are some of the typical members belonging to othis type. In these compounds the carbon atoms are arranged in open chains. Therefore aliphatic compounds are also called open chain compounds. The carbon atoms in open-chain compounds may be arranged in a straight chain or in branched chains. In a straight chain of carbon atoms, no carbon atom is directly linked to more than two other carbons. In branched chains, a carbon atom may be linked to three or four carbon atoms.



Straight chain

Branched chains

10.3.2 Cyclic compounds

Cyclic compounds are those in which the atoms are linked to one another, in such a way that closed rings are formed. Cyclic compounds are classified into "homocyclic" compounds and "hetro-cyclic compounds" depending upon the nature of atoms present in the ring.

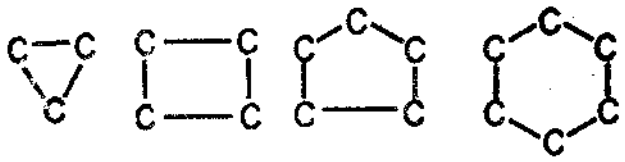
10.3.3 Homocyclic compounds

These compounds are sometimes known as isocyclic or carbocyclic compounds. In these

compounds rings are formed from carbon atoms only. Homocyclic compounds are again classified into two types (a) Alicyclic or cycloaliphatic compounds (b) Arenes or aromatic compounds.

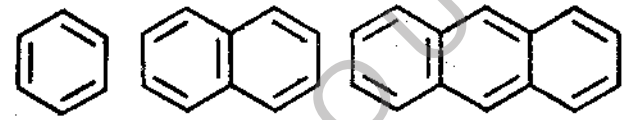
10.3.4 Alicyclic or cycloaliphatic compounds

These compounds contain carbon atoms in the form of closed rings. These compounds may be saturated or unsaturated. They resemble the aliphatic compounds in properties. In alicyclic compounds, rings may contain three, four, five, six or more carbon atoms.



10.3.5 Aromatic compounds or arenes

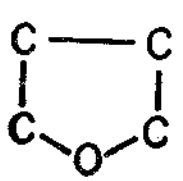
Aromatic compounds contain cyclic structure with alternate arrangement of double and single bonds. Benzene is the parent atomatic compound. These compounds are unsaturated as per the formula but do not readily undergo addition reactions like typical unsaturated compounds. Other examples of aromatic compounds are naphthalene and anthracene.



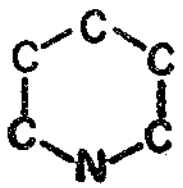
Benzene Naphthalene Anthracene

10.3.6 Heterocyclic compounds

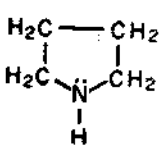
In heterocyclic compounds the rings contain, in addition to carbon atoms, one or more atoms of other elements such as nitrogen, oxygen, sulphur etc. Atoms of elements other than carbon and hydrogen are known as heteroatoms. Heterocyclic compounds may be aromatic or non aromatic



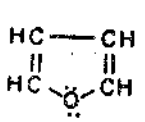
FIVE MEMBERED HETEREOCYCLIC RING



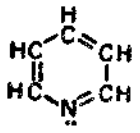
SIX MEMBERED HETEROCYCLIC RING



PYRROLIDINE



FURAN



PYRIDINE

10.4 CLASSIFICATION OF ORGANIC COMPOUNDS BASED ON FUNCTIONAL GROUPS

According to this type of classification, all organic compounds containing a particular functional group are considered as belonging to one class or family. The properties of an organic compound depend upon the functional group or groups present in it.

Classification according to functional groups rationalises the behaviour of vast number of known organic compounds. It is logical and convenient to divide organic compounds into families with similar properties in the same way that the periodic classification of the elements divides the elements into groups or families having related properties. For instance compounds such as methyl alcohl (CH_3 OH), ethyl alcohol (CH_3CH_2OH), and n-propylalcohol ($CH_3CH_2CH_2OH$) behave more or less similarly. They all contain the same functional group alcoholic group i.e hydroxyl group (-OH), attached to a saturated carbon atom. So all the compounds containing the alcoholic group form a family of compounds known as alcohols. The atom or a group of atoms determining the properties of a family of organic compounds is called the "functionl group". Various functional groups are possible in organic compounds. Following table gives functional groups derived from different elements and the classes of organic compounds in which these functional groups are present. (See page -6)

10.5 TYPES OF COVALENT BONDS

Most of the organic compounds contain covalent bonds only. Carbon atom exhibit tetracovalency, it can form four covalent bonds. Covalent bonds are classified as single bonds, double bonds and triple bonds respectively depending on one. Two or three pairs of electrons are shared between two atoms.

The atomic number of carbon is six, in other words six electrons are present in a carbon atom. The electronic configuration of carbon in the ground state is $1s^2$, $2s^2$,$2px^1$, $2py^1$, $2pz^o$

1s and 2s orbitals have their full compliment of two electrons, 2px and 2py orbitals are half-filled and 2pz orbital is vacant. Because of two unpaired electrons (in 2px & 2py orbitals) a carbon atom might be expected to be only bicovalent. But with a very few exceptions carbon exhibits tetravalency in carbon compounds. This should be possible only when four orbitals with unpaired electrons are available in a carbon atom. Four orbitals with unpaired electrons can result by promotion of one of the electrons from the 2s orbital to the vacant $2P_z$ orbital.

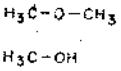
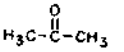
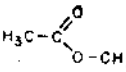
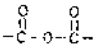
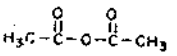
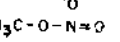
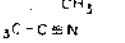
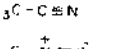
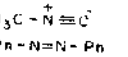
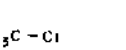
The four unpaired electrons present in these orbitals can form four covalent bonds. Thus carbon atom in order to exhibit characteristic quadrivalency, assumes the electron distribution $1s^2$, $2s^1$, $2px^1$, $2py^1$, $2pz^1$. Bond formation results in the release of energy. The energy needed, for the promotion of an electron from 2s to 2p level is more than compensated in the formation of four covalent bonds, as against two bonds normally possible from a carbon atom in the ground state.

From the electronic configuration of carbon one may expect carbon atom to form three bonds of one type using orbitals and one bond of different type using s-orbital. This is contrary to the observation. For instance the four C-H bonds in methane (CH_4) molecule are identical in all respects. The formation of four identical bonds can be explained by a concept called sp^3 hybridization.

10.6 sp^3 HYBRIDIZATION: FORMATION OF SINGLE BONDS

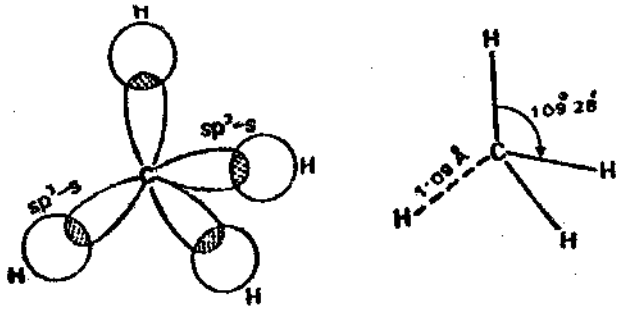
In this one s-orbital (2s orbital) and three p orbitals (2p orbitals) are mixed (hybridized) so as to form four new identical orbitals. These four orbitals are neither and nor p in character but are of mixed type ie, sp^3 type. These four new orbitals of carbon are oriented in space towards the four

CLASSIFICATION BASED ON FUNCTIONAL GROUP

FUNCTIONAL GROUP	CLASS OF COMPOUNDS	EXAMPLE	FORMULA
(A) COMPOUNDS CONTAINING CARBON & HYDROGEN ONLY:			
	ALKANES	METHANE	
	ALKENES	ETHYLENE	
	ALKYNES	ACETYLENE	
(B) COMPOUNDS CONTAINING CARBON, HYDROGEN & OXYGEN:			
	ETHERS	DIMETHYL ETHER	
	ALCOHOLS	METHYL ALCOHOL	
	ALDEHYDES	ACETALDEHYDE	
	KETONES	ACETONE	
	CARBOXYLIC ACIDS	ACETIC ACID	
	ESTERS	METHYL ACETATE	
	ANHYDRIDES	ACETIC ANHYDRIDE	
(C) COMPOUNDS CONTAINING CARBON, HYDROGEN, OXYGEN & NITROGEN:			
	NITRO COMPOUNDS	NITROMETHANE	
	NITRITES	METHYL NITRITE	
	AMIDES	ACETAMIDE	
(D) COMPOUNDS CONTAINING CARBON, HYDROGEN & NITROGEN:			
	PRIMARY AMINES	METHYL AMINE	
	SECONDARY AMINES	DIMETHYL AMINE	
	TERTIARY AMINES	TRIMETHYL AMINE	
	CYANIDES OR NITRILES	METHYL CYANIDE	
	ISO CYANIDES OR ISONITRILES	METHYL ISO CYANIDE	
	AZO COMPOUNDS	AZO BENZENE	
(E) COMPOUNDS CONTAINING CARBON, HYDROGEN AND HALOGEN:			
	HALIDES	METHYL CHLORIDE	
(F) COMPOUNDS CONTAINING CARBON, HYDROGEN, OXYGEN AND HALOGEN:			
	ACID HALIDES	ACETYL CHLORIDE	
(G) COMPOUNDS CONTAINING CARBON, HYDROGEN & SULPHUR.			
	THIOLS OR MERCAPTANS	METHANE THIOL	

corners of a regular tetrahedron. The angle between any two sp^3 orbitals is 109° . 28′ (tetrahedral angle) sp^3 . Hybridized carbon is also known as tetrahedral carbon.

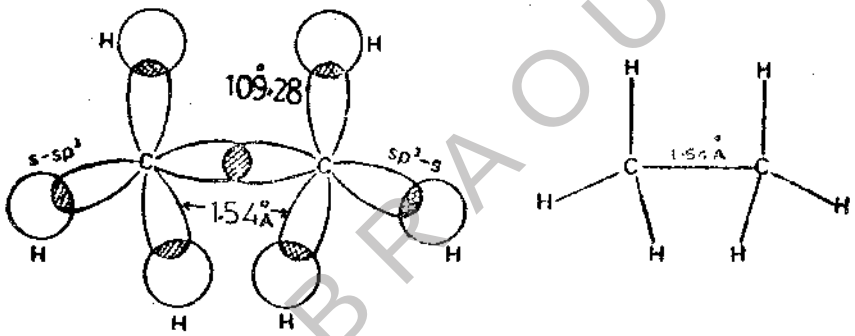
In the formation of methane (CH_4) four sp^3 hybrid orbitals of a carbon (each containing one electron) overlap with 1s orbitals of four hydrogen atoms. This leads to the formation of four C-H bonds of methane. These bonds are called sigma bonds.



Methane

10.6.1 Structure of Ethane

The molecular formula of ethane is C_2H_6. In this molecule each carbon is in sp^3 hybridised state. Each of these carbons forms three C-H bonds by overlap of three sp^3 orbitals of carbon with 1s orbitals of three hydrogen atoms. In addition a C-C sigma bond is formed by the overlap of sp^3 orbitals of the two carbons.



Ethane

10.6.2 Sigma bonds (σ - bonds)

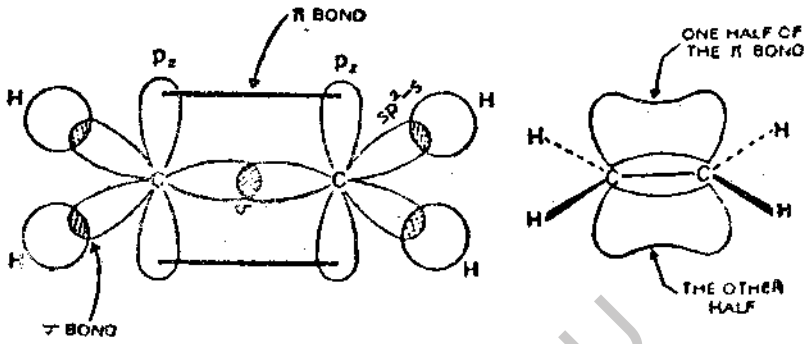
The line that joins the nuclei of two atoms which are bonded is known as bond axis. In a single bond there is highest electron density about the bond axis. Such bonds are called **sigma bonds.**

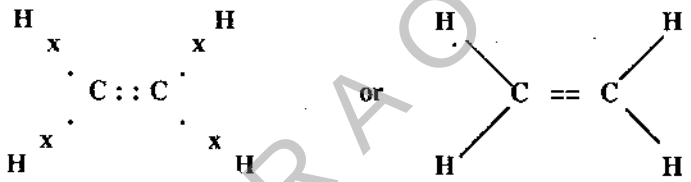
For example we have four sigma bonds in methane. In the case of ethane we have seven sigma bonds. Sigma bonds are formed by linear overlap of orbitals. Further all the H-C-H and C-C-H bonds in ethane form tetrahedral angles. The C-C bond length is 1.54A°

10.7 sp^2– HYBRIDIZATION: FORMATION OF CARBON-CARBON DOUBLE BOND

Hybridization of s-orbital and two p-orbitals is called sp^2– Hybridization. By sp^2– hybridization in a carbon atom, three identical orbitals known as sp^2– hybrid orbitals result.

These three sp^2– hybrid orbitals including the carbon atoms lie in one plane and are directed towards the corners of an equilateral triangle. The angle between any pair of sp^2 hybrid orbitals is 120°. sp^2 Hybridization is therefore known as trigonal hybridization and sp^2 hybrid orbitals as trigonal orbitals. There is one unhybridized p-orbital in a plane perpendicular to that of sp^2 hybridized carbon. In the formation of ethylene, two sp^2 hybridized carbons are involved. Each carbon utilizes three sp^2 orbitals in the formation of a C-C bond and two C-H bonds. C-H Bonds are formed by the overlap of s-orbital of hydrogen with a sp^2 hybrid orbital of carbon, while a C-C bond is formed by overlap of sp^2 orbitals of two carbons. The sigma framework of ethylene molecule is planar i.e. the two carbons and four hydrogen atoms linked to them are co-planar the same (lie in plane). In addition, each carbon has an unhybridized p-orbital perpendicular to the plane of molecular framework. Overlap of unhybridized p-orbital of one carbon atom with that of the carbon atom, leads to a bond calledπ -bond (pi-bond). π- Bond is formed by the lateral overlap of p-orbitals present on two carbons that are already bonded by a σ- bond. Lateral overlap of p-orbials is less effective. Therefore π-bond is weaker than a sigma bond, which is formed by linear overlap of orbitals. The H-C-C bond angle in ethylene is 120°.





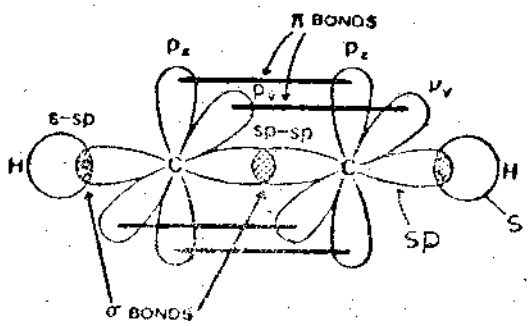
Ethylene

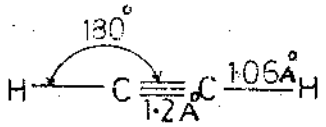
The carbon -carbon double bond is thus made up of a strong sigma bond (60K.cal) and a weak pi-bond (40.K. cal). The C-C bond energy in ethane on the otherhand is about 80 K. cal / mole.

Due to lateral overlap of p orbitals the distance between two carbon atoms (C-C bond length) in ethylene is less (1.34 A°) than the C-C bond distance in ethane (1.54 A°). Due to π - bond formation there is π - electron cloud above and below the C-C bond axis in ethylene. A double bond may be formed between a carbon and other heteroatoms such as oxygen and nitrogen. Such bonds (> C = O and > C = C = N-) are present in carbonyl compounds (aldehydes and ketones, and oximes respectively).

10.8 sp-HYBRIDIZATION: FORMATION OF CARBON - CARBON TRIPLE BOND

Hybridization of a s-orbital and a p-orbital is called sp-hybridization. sp-Hybridization of a erbon atom leads to formation of two equivalent orbitals called sp-hybrid orbitals. These two sp-hybrid orbitals are co-linear i.e., the angle between the wo sp-orbitals is 180°. At a sp-hybridised carbon there are two additional unhybridized p-orbitals in mutually perpendicular planes.





sp-Hybridization : Acetylene

Check your Progress - 1

What is hybridization? Describe briefly the different types of hybridizations in carbon compounds.

One sp orbital of carbon overlaps with the sp-orbital of the other carbon to form a carbon-carbon sigma bond. Each carbon utilizes its second sp-orbital to form a C-H bond by overlap with s-orbital of hydrogen atom. This gives rise to molecular frame work of acetylene which is linear. The H-C-C bond angle in acetylene is 180°. Overlap between two unhybrized p-orbitals of two sp hybridized carbon atoms results in the formation of two π - bonds.

Acetylene is thus a linear molecule with π - electron cloud on all four sides of the C-C bond axis. In fact H-C-C-H axis is surrounded by a sheath of π - electron cloud. The triple bond in acetylene consists of a sigma bond and two π - bonds. The C $\equiv$ C bond distance in acetylene is 1.21A°. A carbon atom can also form a triple bond with nitrogen (C $\equiv$ N bond). Such bond is present in organic compounds called nitriles or cyanides.

Check your progress - 2

What are the differences between σ and π bonds?

10.9 GENERAL PROPERTIES OF ORGANIC COMPOUNDS

1) Carbon compounds being covalent have low boiling and melting points, In these compounds the intermolecular forces are very weak. Therefore it requires relatively little energy to separate the molecules. Accordingly the boiling and melting poins of carbon compounds are much lower than that of inorganic compounds of comparable molecular weights.

	M . P	B. P
Sodiumchloride	804°	1413°
Carbontetrachloride	-23°	76.8°

Most organic compounds melt below 350° C.

2. "like dissolves like" is an extremely useful thumb rule. Non-polar or weakly polar compounds dissolve in non polar or weakly polar solvents. Highly polar compounds dissolve in polar solvents. Organic compounds are nonpolar and therefore are soluble in nonpolar solvents like ligroin, (petroleum ether) benzene, carbon tetrachloride, chloroform etc., but are insoluble in water which is a polar solvent.

3. Carbon compounds do not conduct electricity either in solution or in molten state.

4. Carbon compounds burn readily.

10.10 SUMMARY

In this unit you should have learnt the chemical compounds both inorganic and organic with examples, classification of organic compounds as alipatic, carbocyclic and heterocyclic based on carbon framework and also as hydrocarbons (alkanes, alkenes, alkynes), ethers, alcohols, aldehydes, ketones, carboxylic acids, esters, anhydrides containing oxygen besides C and H; amines, cyanides, isocyanides containing nitrogen, based on their functional groups. The type of bonding-tetravelency - and bonds - formation of single bonds - sp^3 hybridization double bonds - sp^2 hybridization - triple bond - sp hybridization - with methane, ethane, ethylene and acetylene as examples along with their structures, shapes, bond angles and bond energies should be clear.

10.11 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines

1. If a carbon atom loses four electrons it acquires the electronic configuration of helium and forms C^{+4}, Why?
2. Explain how carbon forms four covalent bonds.

II. Answer the following in 30 lilnes

1. Discuss briefly the classification of organic compounds based on carbon skeleton.
2. What do you understand by the term 'functional group'? what are the functional groups present in each of the following classes of compounds?

(a)	Ketones	(b)	Aldehydes	(c)	Alcohols
(d)	Ethers	(e)	Esters	(f)	Carboxylic acids
(g)	Alkenes	(h)	Alkynes	(i)	Alkanes.

3. What are multiple bonds and how are they formed in carbon compounds?
4. Discuss the typical properties of carbon compounds.

10.12 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Mixing up of unequal orbitals into equal orbitals in the same number is called hybridisation. There are three different types of hybridisations occuring in carbon compounds viz; Sp^3 - the saturated compounds; sp^2 - the compounds containing double bond and Sp - in compounds containing triple bond.

2. Sigma bonds are formed by axis overlapping (head on) of orbitals while Pi bonds are formed by parallel (side wise) overlapping of orbitals. The overlapping is more effective in sigma bonds and hence they are stronger than Pi - bonds.

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UNIT - 11 ISOMERISM

Contents

11.1 AIMS AND OBJECTIVES

In this unit we introduce you the concept of isomerism in organic compounds and how to classify isomers as chain, poisition, functional, geometric and optical isomers. At the end of this unit you will be able to know :

- Types of isomers
- Structural isomers
- Chain isomers
- Position isomers
- Functional isomers
- Stereo isomers
- Geometric isomers
- Optical isomers

11.2 INTRODUCTION

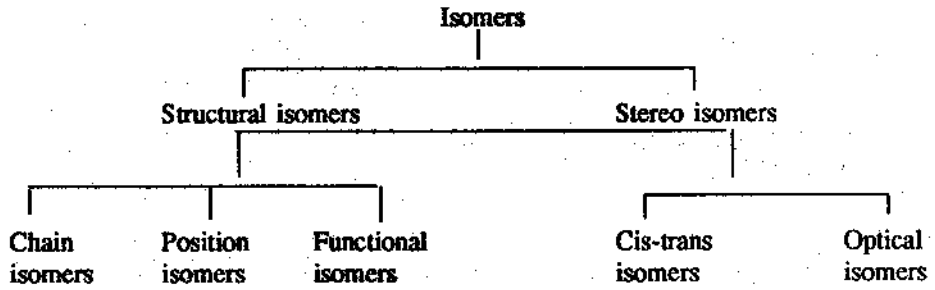
Compounds with same molecular formula but different molecular structures are called isomers (greek : isos=equal, meros=parts). This phenomenon is called isomerism, Isomers contain the same number of the same kind of atoms but the atoms are attached to one another in different ways. Therefore isomers are compounds having different molecular structures. For example, ethyl alcohol and dimethyl ether have the same molecular formula C_2H_6O. But they show different properties. The difference in the properties of isomers is due to the difference in their molecular structures. Therefore ethyl alcohol and dimethyl ether are examples of isomers.

$CH_3 - CH_2 - OH$
Ethyl alcohol

$CH_3 - O - CH_3$
Dimethyl ether

11.3 TYPES OF ISOMERS

Several types of isomers are possible. Following is the classification of isomers.



11.3.1 Structural isomers

Structural isomers contain the same type and number of atoms but the combination of bonded pairs of atoms will be different in each isomer. This type of isomerism which deals with the isomers differing in their molecular structure is known as **structural isomerism.**

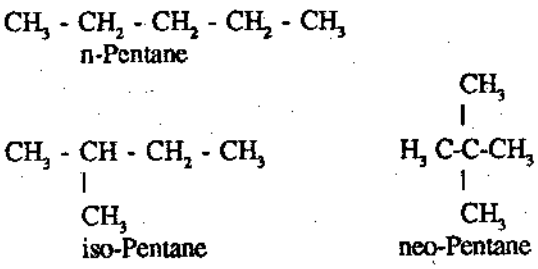
11.3.1.1 Structural isomers are of three types.

Chain Isomers

These isomers differ in the nature of the carbon skeleton. The phenomenon is known as *chain isomerism.* n-Butane and iso-butane have same molecular formula C_4H_{10}. But the arrangement of carbon atoms in these two compounds is different. In one isomer the four carbons are arranged in a straight chain, and in the other the carbon chain is branched. These isomers are known as n-butane and isobutane respectively.

n-Butane iso-Butane

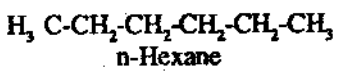
Chain isomers with molecular formula C_5H_{12} :



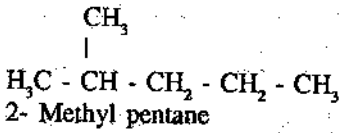
n-Pentane

iso-Pentane neo-Pentane

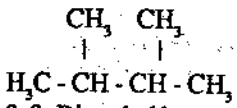
chain isomers with molecular formula C_6H_{14}



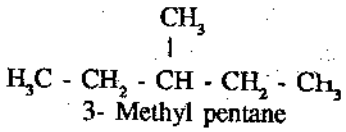
n-Hexane



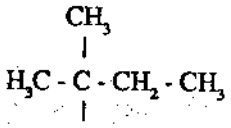
2- Methyl pentane



2,3- Dimethyl butane



3- Methyl pentane



2, 2 - Dimethyl butane

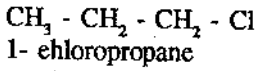
As the number of carbon atoms increases, the number of chain isomers also increases. The number of chain isomers that are possible for different alkanes is given in the following table. No chain isomerism is possible in the first three members of alkanes, i.e. methane, ethane and propane.

No. of carbon atoms in the alkane	Name of the Alkane	Calculated number of chain isomers
4	Butane	2
5	pentane	3
6	Hexane	5
7	Heptane	9
8	Octane	18
9	Nonane	35
10	Decane	75
20	Eicosane	3,66,319
30	Triacontane	4,11,1, 8,46,763

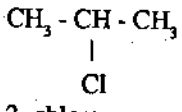
11.3.1.2 Position Isomers

Structural isomers which differ in the position of some reference atom or group (functional group) are known as *position isomers*, and the phenomenon is called *position isomerism*.

A monochloropropane (C_3H_7Cl) exists as two isomers. Both isomers have a chain of three carbon atoms in their structures. In one, the chlorine atom is attached to the terminal carbon atom (first carbon), and in the other chlorine is present on the middle carbon atom (second carbon atom). These isomers differ in the position occupied by chlorine atom. These are known as 1- chloro and 2- chloro propanes respectively.

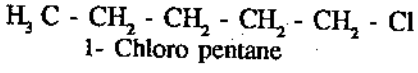


1- ehloropropane

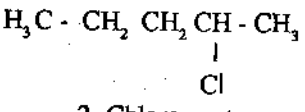


2- chloropropane

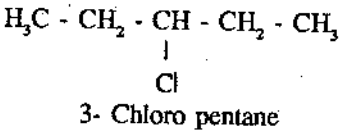
Other examples of position isomers:



1- Chloro pentane



2- Chloro pentane



3- Chloro pentane

11.3.1.3 Functional Isomers

Isomers having different functional groups are called *functional isomers*. The Phenomenon is known as *functional isomerism*.

For example ethyl alcohol and dimethyl ether have same molecular formula (C_2H_6O). In ethyl alcohol the functional group is *hydroxyl* (OH), and in dimethyl ether the functional group is ether linkage (C-O-C). Since these two isomers have different functional grops, they are called functional isomers.

Functional isomers with molecular formula C_2H_6O :

$H_3C - CH_2 - OH$	$H_3C - O - CH_3$
Ethyl alcohol	Dimethyl ether

Functional isomers with molecular formula C_3H_6O :

O ‖ $CH_3 - CH_2C - H$	O ‖ $H_3C - C - CH_3$
Propionaldehyde	Acetone

In acetone the functional group is ketonic (> C=O) group and in propionaldehyde the functional group is aldehyde (- CHO) group. Notice that the same specific atoms are not joined to one another in any particular set of isomers given above. Hence the two compounds given in each of the above are differing in their structure though they have same molecular formula. Hence such sets of isomers are called as structural isomers. It is also to be noticed that two or more compounds may exhibit more than one type of isomerism. For example porpionaldehyde and acetone are functional isomers. In these compounds the position of carbonyl group (> C=O) is different. Therefore acetone and propionaldehyde are also position isomers.

Check your progress - 1

Explain the types of isomerism exhibited by C_2H_6O.

11.3.2 Stereo Isomers

Stereoisomers have the same structure but differ in the orientation of atoms of groups. In otherwords in stereo isomers the same respective atoms are bonded to one another, but their relative spatial positions are different. These descriptions will be clear when examples are considered. Following is the further classification of structural and stereo isomers.

11.3.2.1 Stereo isomers are of two types

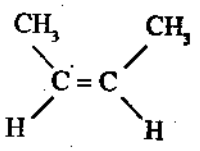
Cis-trns isomers or Geometric isomers

This type of isomerism is shown by alkenes i.e. compounds containing carbon-carbon double bond. Cis-trans isomerism arises when each of the carbon atoms linked by double bond carries two different groups.

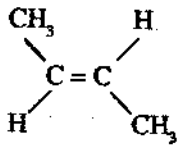
For example, in 2-butene each unsaturated carbon carries two different groups H and a CH_3.

$H_3C - CH = CH - CH_3$

With reference to carbon-carbon double bond, the two hydrogens (or the two CH_3 groups) can be on the same side or opposite sides. As a result two compounds (isomers) are possible.

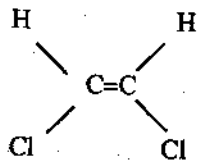


cis- 2- Butene

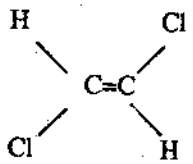


trans - 2- Butene

These two compounds differ only if the spatial arrangements of hydrogens and methyl groups. The isomer having two identical groups on the same side of the carbon-carbon double bond is known as cis- isomer, and the other isomer which contains similar groups on opposite sides of the double bond is known as trans- isomer. This type of stereoisomerism is therefore known as cis-trans isomerism or geometric isomerism. The following are other examples of cis-trans isomers.

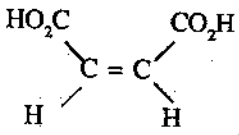


cis- 1,2- Dichloro ethylene

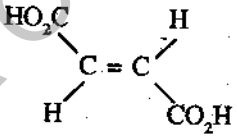


trans 1,2 - Dichloro ethylene

Molecular formula $C_2 H_2 Cl_2$; Structural formula ClHC = CHCl



Maleic acid
(cis-isomer)



Fumaric acid
(trans-isomer)

Molecular formula $C_4H_4O_4$; Structural formula HOOC - HC = CH - COOH

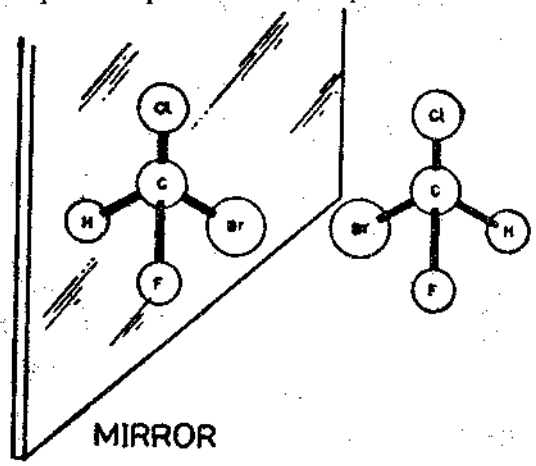
Under normal conditions a cis-isomer can not be transformed into trans- isomer or vice-versa. This is due to prevention of rotation about the carbon-carbon double bond. Cis-trans isomerism is shown also by compounds containing C=N and N=N groups and suitably substituted cycloalkanes

Check your progress - 2

Write possible different structures for the molecular formula $C_2H_2Cl_2$ and name the type of isomerism exhibited by them.

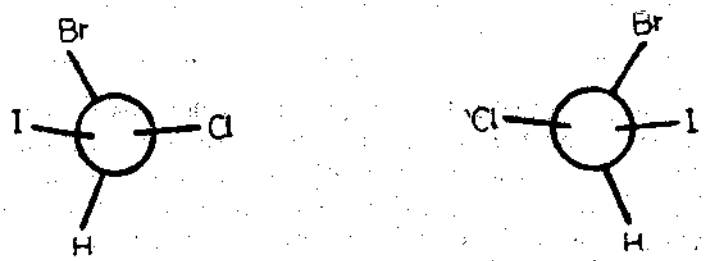
11.3.2.2 Optical isomers

A carbon atom to which four different groups are attached is called an assymmetric carbon atom. Organic compounds containing one or omore asymmetric carbon atoms have the ability to rotate the plane of the polarized light either to the right or to the left. Such substances are called optically active compounds. The phenomenon is called optical activity. If the plane of polarized light is rotated to the right, the substance is called dextro rotatory (dexter = right), if the rotation is to the left, the substance is called laevoratatory (laevus = left). Molecules which contain an asymmetric carbon atom can exist as two optical isomers. The two optical isomers are non-superimposable mirror images of each other. That is when either molecule is placed before a mirror its reflection is identical to the other isomer. For example two optical isomers are possible for fluoro chlorobromo methane

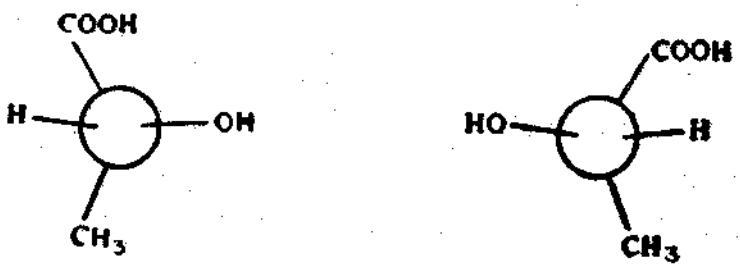


Neither molecule is identical to the other i.e. non-superimposble. The molecules will not fit into the same mould, just as two hands of a person cannot wear the same glove. Optical isomers bear non-superimposable mirror image relationship to one another. One of the above isomers rotates the plane polarized light to left and the other to right. Such non-superimposable mirror image isomers are called enantiomers, since they differ from one another only in the way the atoms are oriented in space. Enantiomers belong to general class of isomers called sterco isomers. Most of the properties are same for two enantiomers. They differ in their effect on the beam of plane polarized light. One isomer rotates a beam of plane polarised light to the left and the other isomer rotates the beam by an equal angle to the right. Whether an isomer is dextro or levo is known, by its action on plane polarised light but not just from its structure.

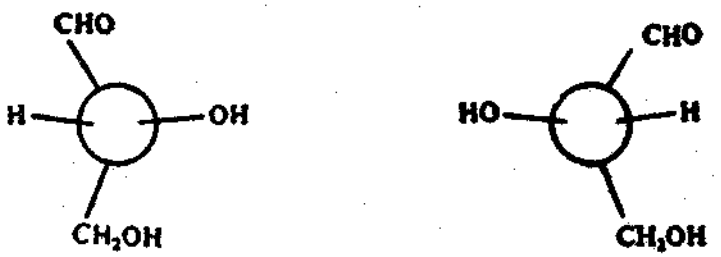
The following are some of the examples of compounds exhibiting optical isomerism.



Enantiomers of Bromo, chloro, iodomethane



Enantiomers of lactic acid



Enantiomers of glyceraldehyde

Entiomers of 2-chlorobutane

11.4 SUMMARY

After finishing this unit you should understand compounds with same molecular formula about differing in their physical and chemical properties called isomers and their classification as structural and stereo isomers. Structural isomers differ in their molecular structure either in the carbon chain (chain isomerism) such as n-butane and isobutane; in the position of some atom or group (position isomers) as in 1-chloroporopane and 2-chloropropane or have different functional groups (functional isomers). ex: ethyl alcohl and dimethyl ether. In stereo isomers the spatial arrangements are different. When carbon-carbon double bond with different groups show isomerism, it is cis-trans or geometric isomerism (ex: 2-butene) and involvement of an asymmetric carbon atom shows optical isomerism (lactic acid).

11.5 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines

1. Write the structural formula and possible types of isomers for the compound with molecular formula, $C_6H_{13}Cl$.
2. Write four possible structures for the compound with the molecular formula $C_6H_6O_2$.
3. Which of the following compounds can exhibit cis-trans isomerism ? Write the structures of isomers,

(a) $H_2C=C(CH_3)_2$ (b) $HC_3\text{-}CH = CH\text{-}CH_3$

(c) $H_2C=C(Cl)\text{-}CH_3$ (d) $H_3C\text{-}(Cl)C = C(Cl)CH_3$

(e) Cl-C=CH-Cl
|
H

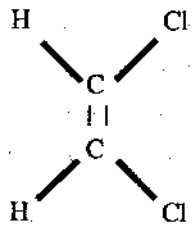
II. Answer the following in 30 lines

1. Explain different types of isomerism exhibited by organic compounds. Illustrate with suitable examples.
2. There are nine possible isomers for a compound with molecular formula C_7H_{16}. Write their structural formulae and name them according to IUPAC system of nomenclature.

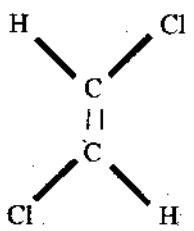
11.6 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. The two possible structures for the molecular formula C_2H_6O are CH_3CH_2OH and CH_3OCH_3. They are functional isomers.

2. The possible structures for the molecular formula $C_2H_2Cl_2$ are $CCl_2 = CH_2$; $CHCl = CHCl$
They are positional isomers.
It can also show cis-trans isomerism.



cis



trans

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UNIT - 12 ORGANIC REACTIONS AND POLARITY OF ORGANIC MOLECULES

Contents

12.1 AIMS AND OBJECTIVES

In this unit we have presented salient features of homolytic and heterolytic cleavages and also the classification of organic reagents and organic reactions. After going through this unit you must be able to know:

- Bond cleavages - homolytic and heterolytic cleavages of covalent bonds.
- Reagents and reactants - electrophiles, nucleophiles and free radicals.
- Classification of reactions - polar and free radical reactions, electrophilic, nucleophilic and free radical reactions, and addition, substitution and elimination reactions.

12.2 INTRODUCTION

Chemical reactions may be ionic or molecular. Most inorganic reactions involve ions as the reacting species, and therefore take place in aqueous media. This allows the reactions to occur rapidly.

Sodium chloride is present as Na^+ and Cl^- ions. Similarly, silver nitrate is present as Ag^+ and NO^-_3 ions. When aqueous solutions of sodium chloride and silver nitrate are mixed, silver chloride (AgCl) is precipitated immediately.

$$NaCl \rightarrow Na^{+} + C\bar{l}$$

$$AgNo_3 \rightarrow Ag^{+} + N\bar{O}_3$$

$$NaCl + AgNO_3 \rightarrow AgCl + Na^{+} + N\bar{O}_3$$

Organic reactions are molecular i.e. organic reactions involve lmolecules. For instance, chlorination of methane involves reaction of chlorine methane molecules.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \text{ etc}$$

However, there are some organic reactions in which the reagent is ionic in nature. The reaction of methylbromide with alkali ($\bar{O}H$ ions) to give methyl alcohol may be taken as an example.

$$CH_3Br + \bar{O}H \rightarrow CH_3OH + B\bar{r}$$

But in most organic reactions, the organic reactant (substrate) (in the above example methyl bromide) is always in the molecular form.

12.3 BOND CLEAVAGES

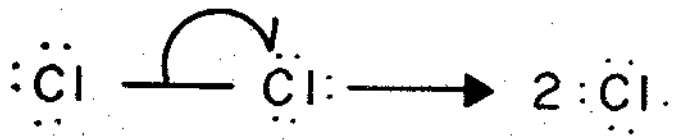
Thus in all organic reactions molecules of an organic compound (reactant) react with molecules or ions of the reagent. In molecular reactions covalent bonds are made and broken. A covalent bond between two atoms consists of a shared pair of electrons. There are two distinct ways in which a covalent bond is broken.

12.3.1 Homolytic cleavage

If the covalent bond between two atoms or groups, X and Y, is symmetrically broken, the resulting fragments retain one electron each. This is called homolysis of covalent bond or homolytic cleavage of a covalent bond.

$$X\text{-}Y \rightarrow X + Y$$

X and Y are odd electron containing species or free radicals. For example, in the presence of sun light or at higher temperatures homolysis of chlorine molecule can occur,



Chlorine atoms or free radicals

Fish-hook arrow indicates one electron transfer and homolytic cleavage of a covalent bond.

Monoatomic free radicals are actually atoms of an element. Free radicls are neutral species i.e. they are not associated with any formal charge (see appendix-I), free radicals are transient species in some organic reactions. There reactions involve homolytic cleavage of covalent bond.

$$X - Y \rightarrow X^{+} + Y^{-}$$

The atom which gains both the electrons as a result of heterolysis is negatively charged and is

called on anion. While the atom which does not receive any electron is positively charged and is called a cation.

Heterolytic cleavage of the covalent bond in hydrogen chloride is represented in the following way.

The formal charge on the chlorine containing fragment is one minus and on the hydrogen conbtaining fragment is one plus (see appendix-2). In all heterolytic cleavages ions are produced. The reactions of organic compounds in which ions are formed are called ionic organic reactions. All ionic organic reactions involve heterolytic cleavage of covalent bonds.

12.4 REAGENTS AND REACTANTS

A chemical reaction is best represented by a chemical equation. The chemical equation precisely indicates the number of moles of substances (starting materials or reactants and products) involved in the reaction. Consider the reaction of methane with bromine. CH_4 and Br_2 are reactants while CH_3 Br are products. The reactants may be further differentiated as substrate and reagent. The organic substance from which product is obtained is called a substrate. The other reactant, sometimes an inorganic substance used to bring about the chemical change is called a reagent. Hydrogen bromide which accompanies methyl bromide (product) in the reaction is called by-product.

$$\underset{\text{Substrate}}{CH_4} + \underset{\text{reagent}}{Br_2} \xrightarrow{h\nu} \underset{\text{product}}{CH_3\,Br} + \underset{\text{by-product}}{HBr}$$

The reaction between methane and bromine takes place under the influence of light and such reactions are called photochemical reactions. In thermal reactions heat energy is used. In some reactions an organic substance may also be used as the reagent.

$$C_6H_5 - \overset{\overset{O}{\|}}{C} - OH + CH_3OH \xrightarrow{H^+} C_6H_5 - \overset{\overset{O}{\|}}{C} - O - CH_3 + H_2O$$

benzoic acid methanol methyl benzoate

In this reaction benzoic acid and methanol are substrate and reagent respectively. The reaction is catalysed by an acid. Formation of acetophenone from benzene and acetylchloride in the presence of aluminium chloride, provides another example of a reaction in which an organic substance is used as reagent.

$$\underset{\substack{\text{benzene}\\\text{(substrate)}}}{C_6H_6} + \underset{\substack{\text{Acetylchloride}\\\text{(reagent)}}}{H_3C\text{-}CO\text{-}Cl} \xrightarrow{AlCl_3} \underset{\substack{\text{Acetophenone}\\\text{(product)}}}{C_6H_5\text{-}CO\text{-}CH_3} + HCl$$

12.5 CLASSIFICATION OF REAGENTS AND REACTANTS

Reagents, and also substrates may further be classified as electrophiles and nucleophiles.

12.5.1 Electrophiles

Some reagents (molecules or ions) are associated with less electron density. These are called electron deficient species. These electron deficient species search for sites of higher electron density or electron surplus centres in the substrates. These electron seeking or electron loving reagents are called electrophiles. For instance, hydrochloric acid is a proton donor. The active species in HCl is therefore proton (H^+). Electron deficiency of proton is clearly indicated by its formal charge. Protons tend to seek electron rich centres in substrate molecules. Therefore proton is called an electrophiles may be neutral species also. Consider the case of boron trifluoride (BF_3). In BF_3 (a Lewis acid) the central atom (boron) has not completed its octet of electrons. It has only a set of six electrons (sextet) from three covalent bonds from it. B in BF_3 is thus electron deficient, and therefore in chemical reactions seeks to complete octet around it. Thus, boron trifluoride as a whole is considered as an electrophile. $AlCl_3$, on similar grounds, is classified as an electrophile. All Arrhenius acids (proton donors) and all Lewis acids (electron pair acceptors) are electrophiles. Neutral species, such as carbene ($:CH_2$) are generated as intermediates in some organic reactions. These species also function as reagents. Carbene ($:CH_2$) intermediate, like BF_3, may be considered as an electrophile.

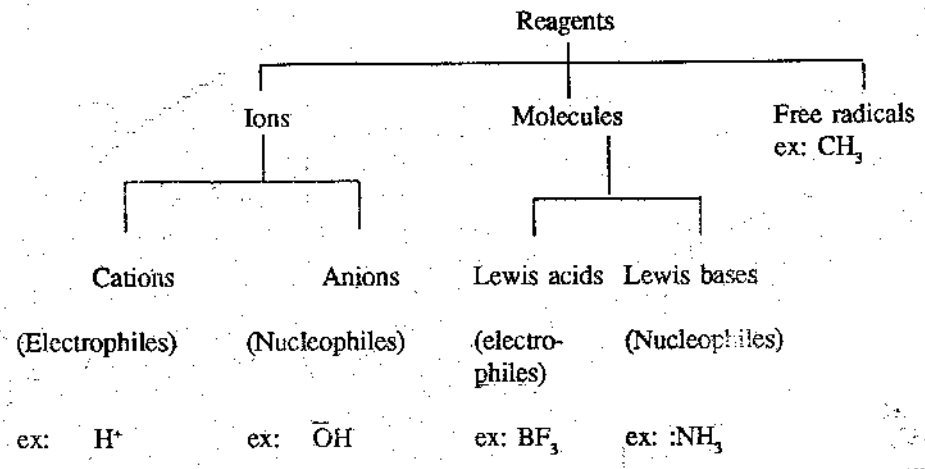
12.5.2 Nucleophiles

Molecules or ions, on the other hand, with electron rich centres are attracted by electron deficient species (nuclei). The word nucleus, by convention, denotes electron-poor centre of an atom. Electron rich reagents which seek nucleus viz. electron poor centre in a reaction are called nucleophiles. The active species available from an alkali such as sodium hydroxide (an Arrhenius base) are hydroxide ($\bar{O}H$) ions. The formal charge on this ion indicates it as an electron surplus species. Therefore, $\bar{O}H$ ions are nucleophiles.

A molecule of ammonia ($: NH_3$) may be considered as a nucleophile. In ammonia, the nitrogen atom (linked to three hydrogen atoms by covalent bonds and carrying a lone pair of electrons) has completed the octet. Further, ammonia due to the presence of a pair of non-bonding electrons on nitrogen atom. functions as electron donor i.e. Lewis base. These electrons are available for any electron deficient species. Thus, ammonia is a nucleophile. All bases (Arrhenius, Bronstted and Lewis bases) are nucleophiles. Molecules with π - bonds may also be considered as nucleophiles. Ethylene and benzene, due to the π - electron cloud associated with them, function as Lewis bases or nucleophiles.

There are some organic compounds which function both as electrophiles and nucleophiles. In aldehydes and ketones the functional group is the carbonyl group. Due to resonance the carbonyl group is polarised resulting in fractional positive and negative charges on carbon and oxygen respectively.

Therefore carbon atom of he carbonyl group in aldehydes and ketones functions as an electrophile, whereas oxygen atom serves as a nucleophile. A classification of reagents, based on the above discussion, is given below.



12.6 CLASSIFICATION OF REACTIONS

It may also be remembered that an electrophile reacts with a nucleophile, and vice versa. All ionic reactions involve electrophiles and nucleophiles. Ionic reactions are also called polar reactions. In some reactions the reagent may be a free radical or a source of free radicals. As already mentioned free radicals are odd-electron containing species. Free radical reactions are also called non-polar reactions.

Follow : are the characteristics of polar and non-polar reactions :

12.6.1 Polar reactions

i) Proceed readily in polar solvents.
ii) Often catalyed by acids and bases.
iii) These are seldom chain reactions.

12.6.2 Non-polar reaetions

i) Proceed readily in the gas phase.
ii) Initiated by radiation, peroxides and other sources of free radicals and by high temperatures.
iii) These are chain reactions.

12.7 CLASSIFICATION OF ORGANIC REACTIONS

Organic reactions may be classified as:
a) Electrophilic reactions
b) Nucleophilic reactions and
c) Free radical reactions.

Electrophilic reactions are initiated by electrophiles or under the catalytic influence of acids. Nucleophilic reactions take place by the attack of nucleophiles on the substrate or under the catalytic influence of bases. On the other hand free radical reactions occur in the presence of light. High temperatures or the preence of substances such as oxygen and peroxides that are capable of generating free radicals also facilitate free radical reactions. Each of the above mentioned reaction types viz. electrophilic, nucleophilic and free radical reactions may be further classified as addition, elimination and substitution reactions. When two or more substances react to give a single product the reaction is called an addition reaction. In the addition of chlorine to ethylene, ethylene chloride is formed. This is an exmple of addition reaction.

$$\underset{\text{ethylene}}{CH_2 = CH_2} + Cl_2 \longrightarrow \underset{\text{ethylene chloride}}{ClCH_2 - CH_2 Cl}$$

Elimination reaction is the reverse of additin reaction. Here a molecule of subsance eliminates or loses a smaler molecule to give a product. Ethyl alcohol on heating with conc. H_2SO_4 at 170°C forms ethylene. In this reaction, a molecule of water is eliminated from ethyl alcohol. This serves as an example of elimination reaction.

$$\underset{-H_2O}{CH_3 - CH_2 OH} \xrightarrow[\text{ethyl alcohol}]{\text{con. } H_2SO_4} \underset{\text{ethylene}}{CH_2 = CH_2}$$

In substitution reaction an atom (or group) of the substrate is displaced or replaced or substituted by an atom (or group) of the reagent. The reaction of methane with chlorine giving methyl chloride and hydrochloric acid is an exmple of substitution reaction.

$$\underset{\text{methane}}{CH_4} + Cl_2 \longrightarrow \underset{\text{methyl chloride}}{CH_3Cl} + HCl$$

In this reaction a hydrogen atom of methane is displaced by a chlorine atom. Thus organic reactions may be classified as follows.

1. Electrophilic addition
2. Electrophilic substitution
3. Electrophilic elimination
4. Nucleophilic addition
5. Nucleophilic substitution
6. Nucleophilic elimination
7. Free radical addition
8. Free radical substitution
9. Free radical elimination

12.8 POLARITY OF MOLECULES

Electron availability in various bonds of a molecule determines its polarity. There are three principal types of electronic effects that determine the availability of electrons in molecules.

12.8.1 Inductive effect

This is due to polarisation of single or sigma bond. A single covalent bond consists of a shared pair or electrons. When the two atoms or groups linked by a single bond are of equal electron attracting capacity (electronegativity), the bond is said to be a homopolar or non-polar bond. In such covalent bonds the pair of electrons is located in an ideal position i.e. midway between the two atoms. In chlorine molecule the Cl-Cl single bond is homopolar. The electron pair constituting the single bond is attracted equally by the two chlorine atoms. Therefore the dipolement of chlorine molecule is zero.

When the two atoms or groups linked by a single bond differ in electronegativity, the electron pair constituting the sigma bond is disturbed from the ideal position. They are shifted (displaced) closer to the more electronegative atom. Chlorine is more electronegative than hydrogen. Therefore in hydrogen chloride (H-Cl) the bond pair of electrons moves closer to chlorine. The electrons still remain in the internuclear region but are slightly disturbed from the ideal position. As a result of this, the more electronegative atom becomes slighty negtively charged and the less electronagative atom becomes slightly positively charged ($\overset{\delta+}{H} - \overset{\delta-}{Cl}$). The electrial disymmetry, caused in a single bond due

to the difference in the electronegativics of the atoms or groups joined by a single bond, is called inductive effect (I effect). The inductive effect is indicated by an arrow head in the single bond ($\rightarrow$—) pointing towards the more electronegative atom. In hydrogenchloride it is shown as H $\rightarrow$– Cl. Here the chlorine atom is said to exert releasing inductive effect (+I effect). H in HCl exerts electron releasing inductive effect (+I effect).

Carbon is more electronegative than hydrogen. Therefore the electrons constituting the H-C single bond are closer to C (H $\rightarrow$-- C). In methyl (-CH_3) group there are three H-C bonds. The electron displacement in three H-C bonds of methyl groups is as shown below in otherwords, the carbon end of the -CH_3 group (linked to other group say X) is electron surplus, and CH_3 group can function as electron releasing group.

This explains the + I effect exerted by methyl group and other alkyl groups. The +I effect exerted by alkyl groups is in the following order.

t-butyl > i-propyl > ethyl > methyl > H

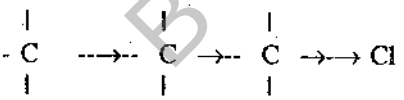
+ I effect decreases

-- I effect of few groups is as follows:

$-F > -OH > -Cl > -NH_2 > -Br > -SH > -I > -H$

- I effect decreases

Inductive effect is transmitted along a chain of carbon atoms. This is called chain induction. It decreases with distance, and may be ignored after three or four bonds. Inductive effect is a permanent efectronic effect. It is reflected in the physical properties (such a dipole moment, boiling points, melting points, acid strengths and basic strength) and the chemical properties of organic compounds.



Inductive effect causes polarisation of a single bond. This in turn is responsible for the bond moment. Dipole moement of a compound is the net result of the bond moments in a molecule. There are four C-H bonds in methane. In a symmetric molecule, such as methane, mutual cancellation of four C-H bond moments leads to zero dipolemoment. Zero dipolemoments of carbon tetrachloride (CCl_4), benzene (C_6H_6), acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6) etc., can be similarly explained.

Check your progress - 1

C-C- Single bond in propyne is shorter than C-C bond in ethane explain.

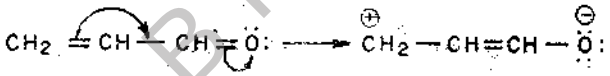
12.8.2 Resonance or mesomeric effect

Delocalisation of π electrons and nonbonding electrons in unsaturated organic molecules is called mesomeric effect (M- effect) or resonance. Consider the carbonyl group, the functional group present in aldehydes and ketones. The carbon -oxygen double bond can be considered as combination of a σ and a π bond. Shift of π electrons (from π bond between carbon and oxygen) to the oxygen atom leads to a positive charge on the carbon and a negative charge on the oxygen.

Resonance structures of carbonyl group.

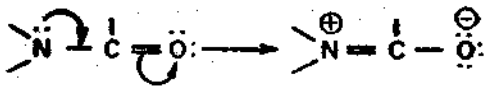
The arrow indicates movement of an electron pair (non bonding electron pair or π electron pair). The origin and terminus of the electron pair shift is clearly shown by the tail and head of the arrow respectively.

Here carbonyl oxygen is said to exert electron-attracting resonance or mesomeric effect (- M effect). The resulting structures are also known as resonance structures or canonical forms. They are convenient for explaining the properties of compounds exhibiting resonance. The compound exhibiting resonance is called resonance hybrid. A double-headed arrow is used as resonance symbol. While writing resonance structures, possible for a compound, are interconvertible by shift of π and non-bonding electrons. Various resonance structures of a compound have same sigma molecule frame work. Only π and nonbonding electrons shift from one octet to another octet. In carbonyl compounds a π electron pair from the combined octet of carbon and oxygen moves in to the octet of oxygen. Resonance is also possible in α, β - unsaturated carbonyl compounds, amides and vinyl chloride. Acrolein is an example of α, β - unsaturated carbonyl compound. In this compound the carbon-oxygen double bond is conjugated with a carbon-carbon double bond.



Resonance structures of acrolein

Due to this conjugation there is extensive delocalisation of electrons of two double bonds. In amides and vinyl chloride double bond is in conjugation with a pair of non-bonding electrons on the hetero atom. Two resonances structures are possible in each case.



(a)

(b)

(a) Resoonance structures of an amide
(b) Resonance structures of vinyl chloride

Resonance explains non-basic character of the amide nitrogen and shorter C-Cl bond in vinyl chloride. While writing resonance structures care should be taken to see that there are not more than eight electrons around atoms of elements belonging to 2nd period. In the case of atoms of elements belonging to higher periods (such as P and S) there can be more than eight electrons around them due to the presence of d-orbitals. Delocalisation of π electrons is quite effective in conjugated system and is not governed by distance factor. Larger the number of resonance structures possible for a compound greater would be its stability.

12.8.3 Resonance energy

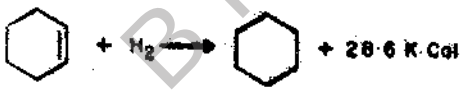
Resonance hybrid is more stable than the most stable single resonance structure. The stability of a compound is determined by the heats of combustion data. The heat of combustion of resonance hybrid i.e. compound exhibiting resonance can be experimentally determined. From the heat of combustion the chemical stability of the resonance hybrid can be found whereas the chemical stability of the most stable resonance structure may be calculated on the basis of covalent bond energies. The chemical stability of resonance hybrid is always higher than that of the most stable single resonance structure. The difference in the chemical stabilities of resonance hybrid and the most stable resonance structure is called resonance energy. Benzene, a colourless liquid, B.P 80°, is a resonance hybrid. The most stable resonance structure of benzene is cyclohexa - 1,3,5 -triene.

Resonance energy of benzene =chemical stability of benzene = Chemical stability of cyclochexa - 1,3,5 - triene.

= (1300 K. cal - 1264 K. cal) = 36. K. cal / mole

The heats of hydrogenation of unsaturated compounds are also useful in computing their resonance energy.

The heat of hydrogenation of cyclohexene is 28.6 K. cal / mole



In hydrogenation of one double bond, 28.6 K. cal. of heat energy is liberated. For cyclohexa - 1,3,5 -triene (most stable resonance structure of benzene, containing three double bonds) the heat of hydrogenation should be 28.6X3 = 85.8 K. cal / mol. The heat of hydrogenation of benzene was actually found to be 49.8 K. cal / mole. The resonance energy of benxzene = 85.8 - 39.8 = 36 K. cal / mole.

12.8.4 Hyperconjugation

This concept was first proposed by Baker and Nathan. Therefore it is called Baker-Nathan effect. The + I effect of alkyl groups is in the following order.

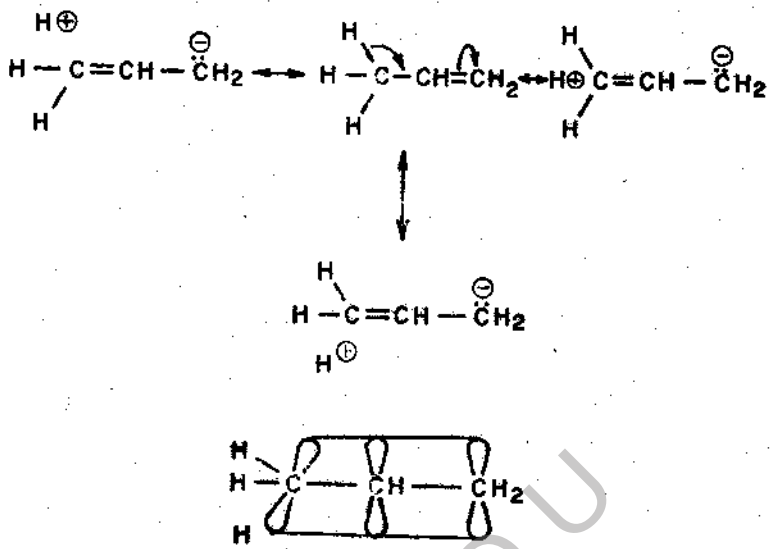
t-butyl > i-propyl > ethyl > methyl

When the alkyl groups are attached to an unsaturated atom, the order of their electron releasing

capacity is exactly reversed.

methyl — ethyl > i-propyl > t-butyl

This has been explained on the basis of a concept called hyperconjugation or no-bond resonance. Delocalisation of electrons of C-H bond in α - position of an unsaturated carbon atom is called hyperconjugation. In propene molecule, for instance, there are three hydrogens on carbon atom α– to the double bond ie, there are three α - C-H bonds. When part of electron density belonging to an α- C-H is shifted between α– carbon and unsaturated carbon, further delocalistion of π electrons becomes necessary. This leaves the hydrogen with partial no-bond character. Involving three α - hydrogens, three separate resonance structures may be written. Hyperconjugation is a special type of resonance.



Hyper conjugation in propene

Delocalisation of electron density of a C-H sigma bond does not mean that the hydrogen becomes completely free from the rest of molecule. Only part of the electron cloud belonging to bond overlaps with the p-orbital of the adjacent unsaturated carbon. This overlap, however, is not very effective. Hyperconjugation is thus a special type of resonance and is weaker compared to even inductive effect. Though not accepted universally, hyperconjugation is a valuable concept in explaining a number of phenomena such as stability of olefins, carbonium ions, free radicals, and bond lengths and dipolemoments of organic molecules.

Check your progress - 2

Why hyperconjugation is called no-bond resonance?

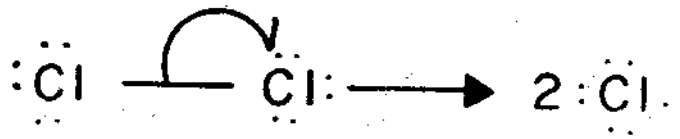
APPENDIX - 1.

Formal charge : In a structure, an atom may be neutral or may carry a charge (positive or negative). By applying a simple rule we can locate the formal charge on an atom in any structure.

For this one must remember the group number of the atom of the element, the number of bonds it has formed and the number of non-bonding electrons associated with it. The group number of the atoms of an element corresponds to the group in the periodic table to which the element belongs. Following are the group numbers of elements commonly encountered in organic compounds.

Elements	Group Number
H	1
Mg and Zn	2
B and Al	3
C and Si	4
N and P	5
O and S	6
F,Cl, Br and I (Halogens)	7

The nonbonding electrons are the electrons not involved in bonding. These electrons belong exclusively to one atom. Consider the homolysis of chlorine molecule.



In chlorine molecule each chlorine atom has six non-bonding electrons. In chlorine atom there are seven non bonding electrons. The formal charge on an atom in a structure is determined by substracting the sum of the number of bonds the atom has formed and number of non bonding electrons associated with that atom, from the group number of the atom.

Formal charge on an atom = Group number of the atom- (number of bonds the atom formed + number of non bonding electrone on it). Two fragments, each containing a chlorine atom are obtained by homolytic cleavage of the chlorine molecule, the group number of chlorine is seven. In these fragments there are no bonds from the chlorine atom and there are seven non-bonding electrons on the chlorine.

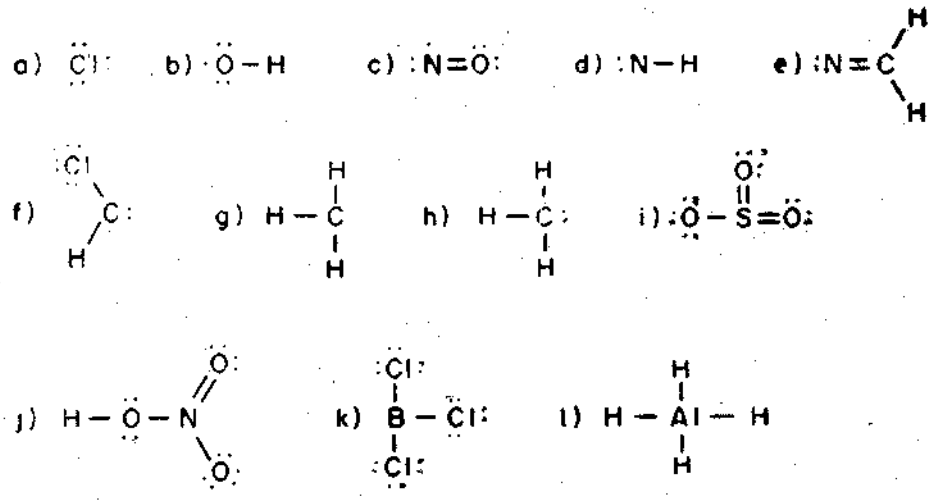
Therefore formal charge on chlorine = 7 - (0+7) = 7 -7 = Zero. In other words the chlorine-containing fragments obtained by homolytic cleavage of chlorine molecule are neutral. The utility of these simple rules will be appreciated when applied to complicated structures (see under assignment).

APPENDIX - 2

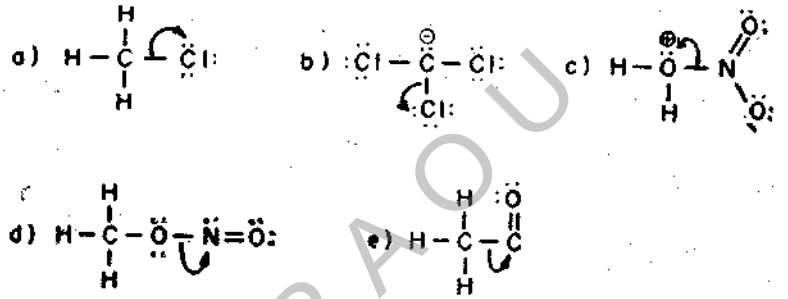
The formal charge on hydrogen containing fragment = 1 - (0+0) = (1-0) = 1 or +1

The formal charge on chlorine - containing fragment = 7 -(0+8) = (7-8) = - 1

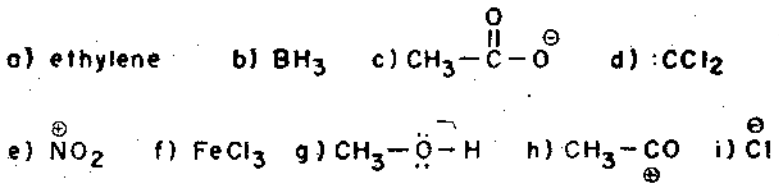
→ **PROBLEM** - 1: Indicate the formal chrge, if any, associated with the appropriate atom (s) in the following structures.



PROBLEM - 2 : Classify the following bond cleavages. Give the complete structures (including formal charge and non bonding electrons associated) of the fragments resulting due to the indicated bond fissions.



PROBLEM - 3: Classify the following as electrophiles and nucleophiles.



PROBLEM - 4: Classify fully the following reactions : (such as free radical substitution reaction).

a) $C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$

b) $CH_2 = CH_2 + H_2O \xrightarrow{\text{conc. } H_2SO_4} CH_3 - CH_2 - OH$

c) $CH_3 - CH = O + CH_3 - CH = O \xrightarrow{\overline{O}H} CH_3 - CH(OH) - CH_2 - CH = O$

d) $CH_4 + Cl_2 \xrightarrow{h\upsilon} CH_3Cl + HCl$

e) $CH_3 - CH = CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3 - CH_2 - CH_2 - Br$

f) $CH_3 - \overset{O}{\overset{\|}{C}} - O - O - \overset{O}{\overset{\|}{C}} - CH_3 \xrightarrow{h\upsilon} CH_3 - CH_3 + 2\,CO_2$

g) $CH_3Cl + O\bar{H} \longrightarrow CH_3OH + \bar{Cl}$

h) $CH_3 - CH_2 - Cl \xrightarrow{\bar{O}H} CH_2 = CH_2 + HCl$

i) $CH_3 - CH_2 - OH \xrightarrow{\text{conc. } H_2SO_4} CH_2 = CH_2 + H_2O$

PROBLEM - 5: Write the resonance structures, due to hyperconjugation, in the following compounds, and arrange them in order of increasing stability.

$CH_3 - CH = CH_2$ $CH_3 - CH = CH - CH_3$ $(CH_3)_2C = C(CH_3)_2$
$(CH_3)_2 = CH(CH_3)$

PROBLEM - 6: Explain why the, C-C single bond in $CH_3 - C \equiv CH$ is shorter than C-C bond in ethane (Hint: hyperconjugation)

12.9 SUMMARY

In this unit the concept of chemical reactions as ionic (mostly inorganic) or molecular which proceed slowly as in organic compounds is given. The molecular reactions involve covalent bonds breakage and their formation. The bond breaks in two ways a) Homolytic-the covalent bond breaks symmetricallly resulting in odd electron containing species called free radicals. b) Heterolytic cleavage involves unsymmetrical breakage of covalent bond giving negtivcly charged and positively charged species called nucleophiles and electrophiles respectively. Thus reagents re classified as:

i) Free-radicals (odd electron species)
ii) Electrophiles (cations or electron deficient molecules)
iii) Nucleophiles (anions or electron rich molecules) based on the reagent the organic reactions are classified as:

I. Ionic or polar reactions and

II. Free - radical or non-polar reactions.

Ionic reactions are electrophilic reactions when initiated by electrophiles or under catalytic influence of acids and are called nucleophilic reactions when occur by the attack of nucleophiles or under catalytic influence of base. Thus the major organic reactions addition, substitution or elimination reactions are classified as:

a) Electrophilic
b) Nucleophilic and
c) Free- radical reactions.

When the two atoms involved in a bond have similar electronegativities they are non-polar and they differ they are polar-due to unequal sharing of electron pair. When sigma bond is polarised inductive effect results which is transmitted along a carbon chain. This is a permanent effect and reflects in their physical and chemical properties .

Polarisation of electrons or non bonded electrons leads to delocalisation called mesomeric effect or resonance. The resonance is effective in conjugative system and increases the stability of a compound.

Another type of delocalisation of electrons of C-H bond in position of an unsaturated cabon atom is called hyperconjugation. This is a special type of resonance and is weak.

12.10 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines

1. How are organic reactions classified ?
2. How are reagents in an organic reaction clasified ?
3. Explain the difference between an inductive effect and resonance ?

II. Answer the following in 30 lines

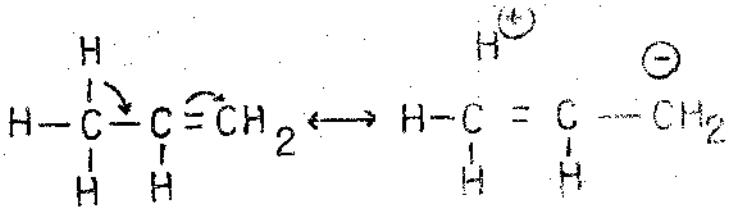
1. How are organic reactions classified ? Discuss the classification of reagents in organic reaction. What are the main differences between organic and inorganic reactions ?
2. What are the electronic effects that affect the polarity of organic molecules ?

12.11 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. The C-C single bond in propyne is formed by overlapping of sp^3 - sp^3 hybrid orbitals which are smaller than sp sp hybrid orbitals that overlap in C-C bond of ethane due to reduced p-character. Hence the bond formed by sp-sp overlap is shorter.

2. Delocalisation of electrons of C-H bond in -position of an unsaturated carbon atom is called hyperconjugation. This heaves the hydrogen in the partial no-bond character. Hence is also known as no-bond resonance.

eg :



Block - 6 ORGANIC CHEMICALS FROM COAL

UNIT - 13 COAL - A SOURCE OF ORGANIC COMPOUNDS

Contents

13.1 AIMS AND OBJECTIVES

This unit aims to make you aware of the use of coal as a source of organic compounds. At the end of this unit you will be able to know:

- Source of organic compounds
- Different form of coal high and low temperature carbonisation of coal
- Coal-tar distillation and chemicals obtained there from

13.2 INTRODUCTION

For the synthesis of organic compounds, we need not start with carbon and hydrogen. Nature provides valuable organic chemicals from a number of sources. Following are the principal natural sources of organic compounds.

Natural Source	Percentage of organic compounds obtained from the source
Natural gas & Petroleum	30%
Plants	2%
Coal	24%
Wood	1%

Only 2% of these materials are used for the production of organic chemicals and the rest of materials are used as fuels in one form or the other. Some of the organic compounds isolated from the above sources are used as ready made starting materials for the synthesis of many hundreds of organic compounds. Therefore a brief survey of the sources of organic compounds is very appropriate.

As a result of slow decomposition beginning some 300 millions years ago. and under the effects of moisture, high temperature and pressure and little air, buried plants and animal matter were changed into various carbonaceous residues.

Buried plant & animal matter —Decomposition under high temp. pressure→ Carbonaceous residues

These carbonaceous residues may be in any of the three physical states viz., gas, liquid and solid.

1. Gaseous carbon compounds: Naatural gas
2. Liquid carbon compounds : Petroleum
3. Solid Carbon : Coal

13.3 COAL

This is a black coloured mineral present in the earth's crust. Coal cotains principally carbon mixed with some organic compounds. There are different forms of coal. The carbon content of coal varies from one form to othe other. These different forms of coal are named as peat, lignite, bituminous coal, anthracite coal and diamond. The carbon contents of different forms of coal are given below:

Forms of Coal	Percent Carbon
Peat	11%
Lignite (brown coal)	35%
Bituminous coal (soft coal)	65%
Anthracite coal (hard coal)	85%
Diamond	100%

13.4 PYROLYSIS OF COAL

For many years coal was used only for the production of coke, a form of carbon. Coal is converted to coke by heating in big ovens in the absence of air at 1000°C. This process is called Pyrolysis. The coke thus obtained was mainly used as a fuel and as reducing agent in metallurgical industries. Recently chemists have discovered that valuable organic compounds can be isolated from coal for - a liquefiable by product (accounting for about 25%) in the pyrolysis of coal.

13.4.1 High temperature carbonisation

If the pyrolysis of coal is carried out at 1000°C to 11300°C, it is known as high temperature carbonisation. Generally in this process more of aromatic compounds will be obtained.

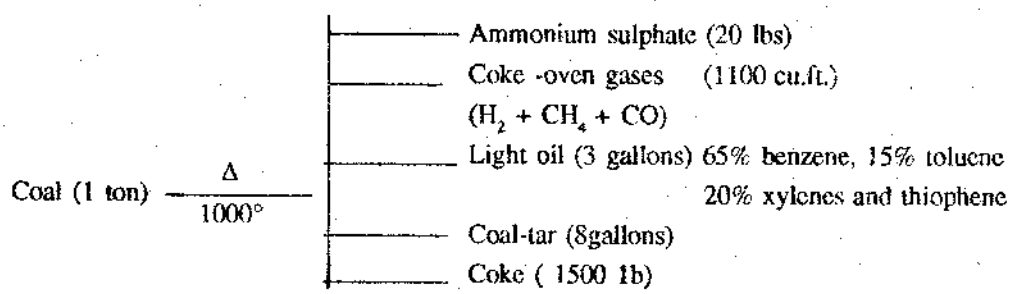
13.4.2 Low temperature carbonisation

If the pyrolysis of coal is carried out at 500-600°C it is known as low temperature carbonisation. Here we get more of aliphatic compounds.

When the coal is heated to 1000°C in the absence of air, volatile substances such as ammonia, hydrogen sulphide and illuminating gas are evolved. These are passed through a condensor into sulpjuric acid (scrubbing solution). Sulphuric acid dissolves out ammonia and hydrogen sulphide, while the illuminating gas, also called coke-oven gas, passes on. Illuminating gas is used as a source of heat. The organic compounds present in the distillate form separate layers - one such layer which floats on sulphuric acid is called light oil. A block, foul smelling lid which settles to the bottom is

called coal-tar.

Some of the initial products of pyrolysis of coal are given below.

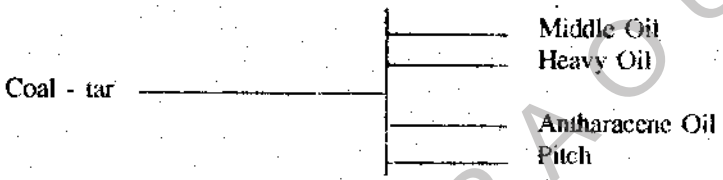


Check your progress - 1

What are the products obtained during the pyrolisis of the ton of coal?

13.5 COAL-TAR DISTILLATION

When coal-tar is subjected to fractional distillation it yields different fractions at different temperatures. These are called Middle Oil Hevy Oil, Antharacene oil and pitch.



The fraction may be either acidic or basic in nature depending upon the compounds present in it.

Each of the fractions obtained from coal-tar distillation is washed with acids and bases to separate basic constituents (nitrogenous compounds) and acidic constituents (phenols) respectively. The neutral compounds left out are separated by franctional distillation.

From middle oil fraction, naphthalene, phenol, pyridine are obtained. These are useful in the preparation of phthalic acid and also find use in dyes, drugs, antioxidants and plastics.

Cresols are obtained from heavy oil fraction. They are useful as antiseptics, and in synthesis of organic compounds.

From Anthracene oil, anthracene and creasotes (cresols) are obtained. They are useful dye intermediates.

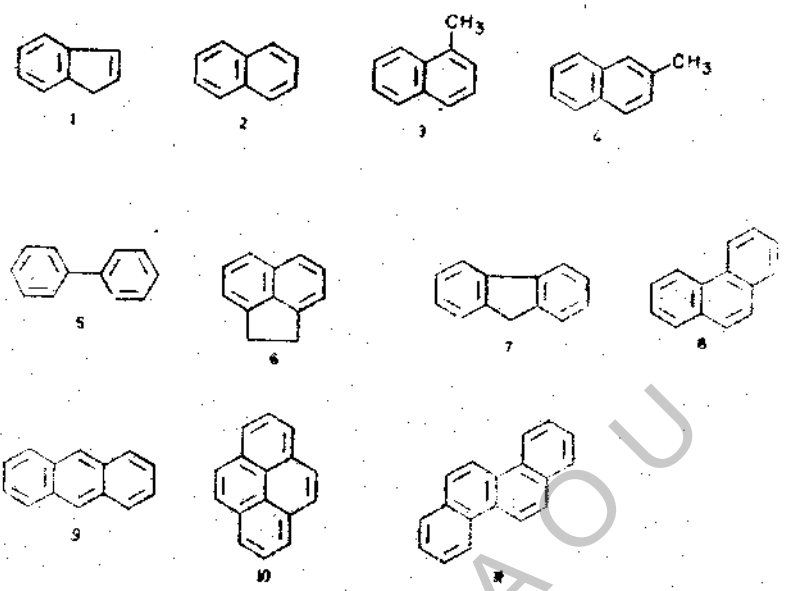
Pitch is residual matter which is useful in roofing and paving roads.

Following are some of the important compounds obtained from coal-tar.

Check your progress - 2

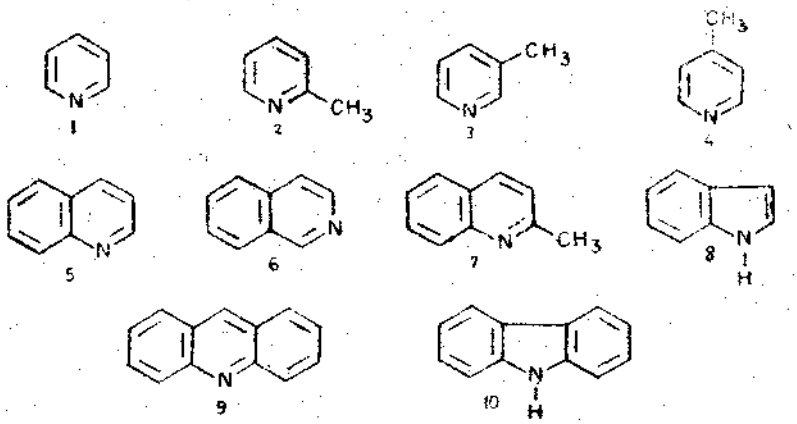
What are the products obtained by fractional distillation of coal-tar.

13.5.1 Aromatic hydrocarbons



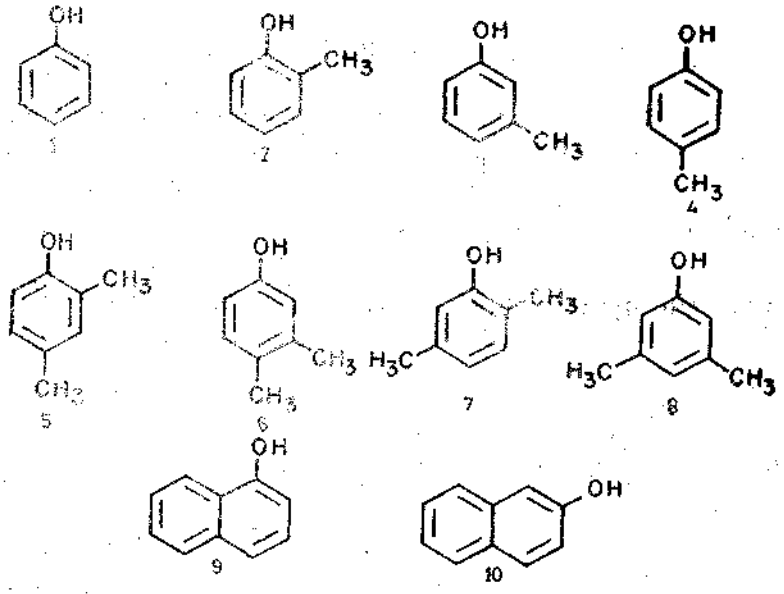
1. Indene 2. Napthalene 3. α - Methyl naphthalene 4. β - Methyl naphthalene 5. Diphenyl 6. Acenaphthene 7. Fluorene 8. Phenanthrene 9. Anthracene 10. Pyrene 11. Chrysene

13.5.2 Nitrogen heterocyclic compounds



1. Pyridine 2. α - Picoline 3. β - Picoline 4. γ -Picoline
5. Quinoline 6. Isoquinoline 7. Quinaldine 8. Indole
9. Acridine 10 .Carbazole

13.5.3 Phenolic Compounds



1. Phenol 2. o-Cresol 3. m- Cresol 4. . p-Cresol
5 to 8 Dimethyl phenols (Xylenols) 9. α - Naphthol 10. β - Naphthol

13.6 SUMMARY

This unit presented the principal sources of organic compounds natural gas (50%), Plants (25%), Coal (24%), and Wood (1%). Coal is of different types with varying carbon percentges. They are peat (.. %), lignite (35%), bituminous (65%), anthracite (85%), and diamond (100%). Strong heating in absence of air (pyrolysis) of Hon coal yields 2016. $(NH_4)_2SO_4$, 1100 cm. ft coal-gas, 3g. light oil, 8g. coal-tar & 1500 lb coke. Different fractions of coal-tar are middle oil (phenols, naphthalene etc.) heavy oiil (cresols), anthracene oil (anturacene, cresotoes) and pitch.

13.7 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines

1. Write notes on
   (a) High-temperture carbonisation
   (b) Low-temperature carbonisation

II. Answer the following in 30 lines

1. Coal is a source of organic compounds. Justify.

13.8 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. The products obtained on pyrolysis of one ton of coal are ammonium sulfate (20lb); Coal-gas (1100 Sq.ft.), Light oil (3 gallons) coal tar (8 gallons) and coke (1500 lb).

2. Coal tar on fractional distillation gives middle oil (phenols, naphthalene etc.) heavy oil (cresols) Anthracene oil (anturacene, creosotes) and pitch with several aromatic hydrocarbons, heterocyclics and phenolic compounds.

Author : Dr. P.N. Sarma

BLOCK - 7 CHEMISTRY OF CARBON COMPOUNDS

UNIT - 14 ALKANES

Contents

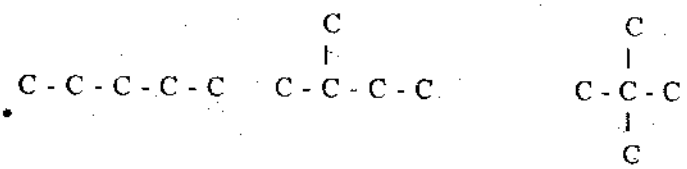
14.1 AIMS AND OBJECTIVES

In this unit we would like to introduce you the nomenclature of alkanes, concept of homology, preparation, physical and chemical properties of alkanes. By the end of this unit you should be able to know:

- The nomenclature of alkanes
- Meaning of homology, chain isomerism, primary, secondary, tertiary and neo carbons
- Methods of preparation of alkanes
  - a) Catalytic reduction of unsaturated hydrocarbons.
  - b) Reduction of alkyl halides,
  - c) Hydrolysis of Grignards reagents,
  - d) Wurtz reaction
  - e) Decarboxylation of fatty acids,
  - f) Kolbe's electrolysis of fatty acids.
- Physical properties of alkanes
  - a) Gradation in melting and boiling points of alkanes.
  - b) Conformational isomerism - conformers of ethane, propane and n-butane.
- Chemical properties of alkanes:
  - Chemical inertness, tendency to undergo substitution reactions.
  - b Halogenation - free radical mechanism, reactivity of halogens and reactivity of different types of hydrogen atoms in alkanes.
  - c) Nitration - vapour phase nitration.
  - d) Sulphonation with fuming sulphuric acid and by sulphonyl chloride.
  - e) Oxidation - incomplete combustion, combustion in excess of oxygen and catalytic oxidation.
- Industrial sources of alkanes - natural gas and petroleum - fractionation of petroleum, cracking of petroleum.

14.2 INTRODUCTION

Organic compounds containing only carbon and hydrogen are called hydrocarbons. The carbon atom in the hydrocarbons may be arranged in an open chain or a cyclic structure.



Open chain structures

Cyclic Structures

Hydrocarbons containing open chain carbon frame work are called aliphatic hydrocarbons. Aliphatic hydrogarbons in which the atoms are linked by only single bonds (C - H and C - C bonds) are called saturated hydrocarbons or alkanes. Saturated hydrocarbons do not react with usual laboratory reagents under ordinary conditions. That is why they are also known as paraffins. (In Latin param means little, affinis means affinity). Petroleum and natural gas are the main sources of alkanes.

The general or empirical formula of alkanes is C_nH_{2n+2} where n is the number of carbon atoms. Alkanes are open chain saturated hydrocarbons. They contain only single covalent bonds. The C-C and C-H bonds in alkanes are formed by the overlap of sp^3 hybridised orbital of one carbon atom with that of another carbon atom or with a s-orbital of hydrogen atom respectively. Due to this all the bonds in alkanes are sigma (σ) bonds. These bonds are very strong when compared to Pi- (π) bonds. In alkanes the four bonding orbitals of each carbon are directed towards the four corners of tetrahedron. So the H-C-H, C-C-H or C-C-C bond angles are 109° 28' The carbon-carbon single bond length in alkanes is 1.54A.

14.3 NOMENCLATURE

The class suffix for this group of compounds is 'ane'. The molecular formula of any alkane corresponds to the general formula C_nH_{2n+2} where n is number of carbon atoms present in the alkane. The common or trivial names of the first four members, of alkanes containing one, two, three and four carbon atoms are respectively methane, ethane, propane and butane. These names are derived from the natural source of these hydrocarbons.

Name of alkane (CnH_{2n+2})	Formula of alkane	Name of the alkyl group	Formula of alkyl group(CnH_{2n+1})
Methane	CH_4	Methyl	CH_3
Ethane	C_2H_6	Ethyl	C_2H_5
Propane	C_3H_8	Propyl	C_3H_7
Butane	C_4H_{10}	Butyl	C_4H_9
Pentane	C_5H_{12}	Pentyl or Amyl	C_5H_{11}
Hexane	C_6H_{14}	Hexyl	C_6H_{13}
Heptane	C_7H_{16}	Heptyl	C_7H_{15}
Octane	C_8H_{18}	Octyl	C_8H_{17}
Nonane	C_9H_{20}	Nonyl	C_9H_{19}
Decane	$C_{10}H_{22}$	Decyl	$C_{10}H_{21}$

The higher members of alkanes are named according to Latin or Greek numericals indicating the number of carbon atoms in the molecules. Thus penta (for 5), hexa (for 6), hepto (for 7), octa (for 8) nona (for 9) and deca (for 10) prefixes are used while naming the alkanes containing 5 to 10 carbon atoms.

The groups obtained by removal of a hydrogen atom from an alkane are called alkyl groups. These groups are named by replacing the suffix 'ane' with ('yl') in the name of the corresponding alkane. For instance from methane (CH_4), methyl group (CH_3) is derived. Thus alkane is combination of an alkyl group and a hydrogen atom. Alkane and alkyl groups are indicated by R-H and R respectively. The names of alkyl group derived from alkanes containing one to ten carbons are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl respectively.

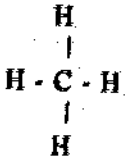
14.4 HOMOLOGY

The molecular formulae of the first four members of alkanes are CH_4, C_2H_6, C_3H_8 and C_4H_{10} respectively. From the molecular formulae it is evident that any two successive members differ by

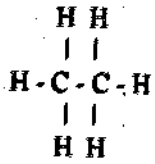
one carbon and two hydrogen atoms (CH_2). Such a closely related group of organic compounds where any two successive members differ by a methylene unit ($-CH_2$) constitute a homologous series. The members of homologous series are called homlogues. Propane and butane belong to the homologous series of alkanes, and butne is the higher homologue of propane.

14.5 ISOMERISM

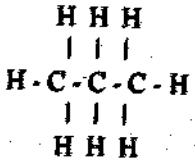
Compounds with same molecular formula but different structures are called isomers. Considering the tetravalency of carbon and univalency of hydrogen the structural formulae of first three alkanes may be written as follows:



Methane

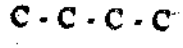


Ethane

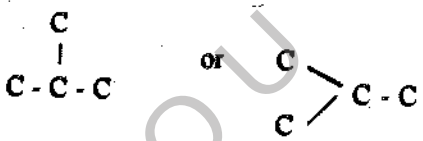


Propane

Higher alkanes exhibit chain isomerism. Chain isomers have same molecular formula but differ only in the arrangement of carbon atoms in the molecule. The carbon atoms in higher alkanes may be arranged in different ways. In butane (C_4H_{10}) for instance, two different arrangements of carbon atoms are possible.



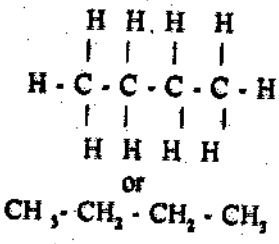
Straight chain containing four carbons



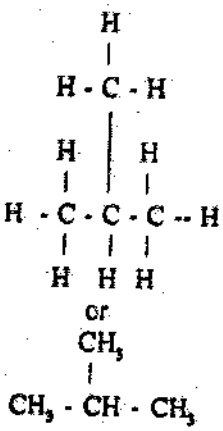
Brnched chain containing four carbons

In straight chain arrangement no carbon atom is directly linked to more than two other carbons, whereas in branched chains a carbon atom is directly linked to three, and sometimes to four other carbon atoms.

The two butanes with straight chain and branched chain carbon frame work are n-butane and i-butane respectively.

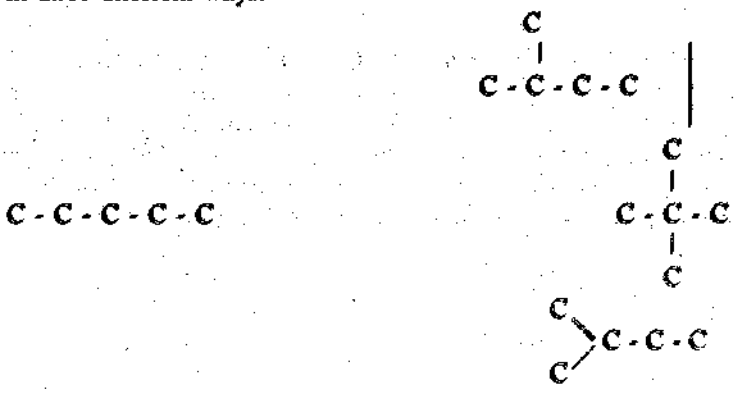


n - Butane

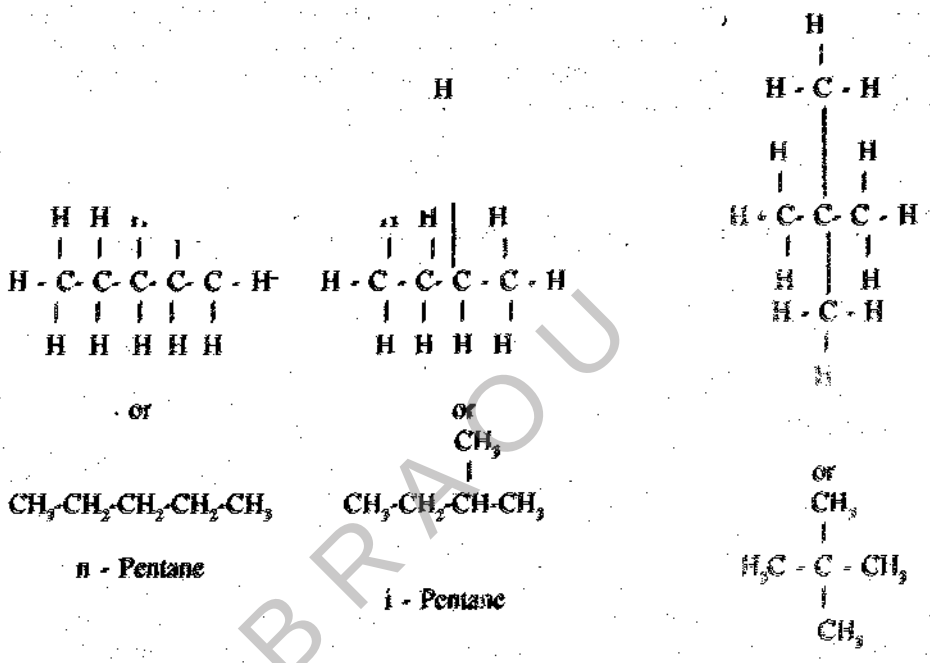


i - Butane

The two butanes are differentiated by prefixes n- (normal) and i- (iso) respectively. n - Butane and i - butane are chain isomers. Similarly the five carbon atoms in a pentane (C_5H_{12}) may be arranged in three different ways.



pentanes, are n-pentane, isopentane and neopentane,

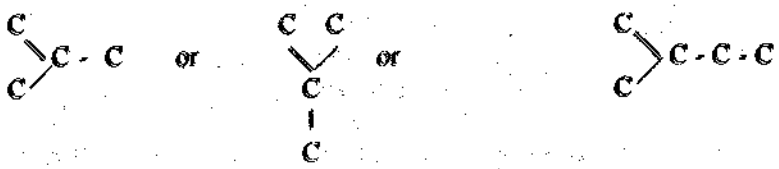


n - Pentane

i - Pentane

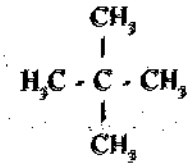
neo pentane

Note that in all isoalkanes the carbon chain is in the form of a fork.



IUPAC system of nomenclature restricts the use of the prefix 'iso' to compounds containing six or fewer carbon atoms.

It may be noted that in neo - pentane a carbon is directly attached to four other carbons.

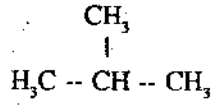


Neopentane

Thus the chain isomers differ only in the arrangement of carbon atoms.

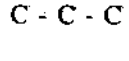
14.6 IUPAC NOMENCLATURE

Alkanes with straight and as well as branched carbon chains are systematically named according to IUPAC nomenclature. In this system of nomenclature, longest straight chain of carbon atom is picked up in the structure, and the compound is named as a derivative of that alkane. The prefix of the name indicates the nature, number and position of alkyl group(s) attached to the longest straight chain of carbon atom. In the case of isobutane, there are three carbon atoms in the straight chain. It is named as a derivative of propane. Thus isobutane may be considered to be obtained by

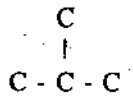


isobutane or 2 - methyl propane

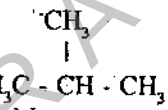
substituting a hydrogen present on the central or second carbon of propane by a methyl group. The IUPAC name of isobutane is therefore 2-methyl propane. Alternatively one may be able to write the structure if the name is given. For writing the structure of 2-methyl propane which is a derivative of propane, first write three carbon atoms in a stright chain.



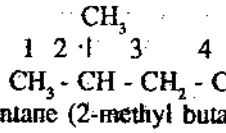
Then to the second carbon attach a carbon representing the methyl group.



Complete the structure by adding required number of hydrogens at each carbon maintaining tetravalency of carbon.

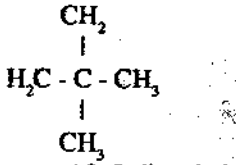


The systematic names of pentanes and hexanes containing branched chains of cabons are given below. The longest straight chain in isopentane contains four carbons. Therefore it is a derivative of butane. A hydrogen on the second carbon is substituted by a methyl group. Therefore the systematic name of isopentane is 2-methylbutane.

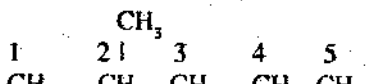


isopentane (2-methyl butane)

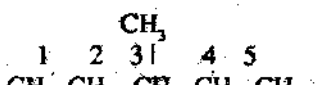
Neopentane is similarly named as 2, 2-dimethyl propane



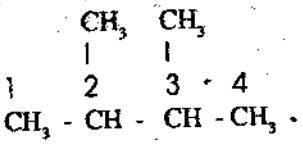
Neopentane (2, 2-dimethyl propane)



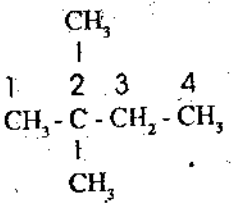
2- Methyl pentane (isohexane)



3- Methyl pentane

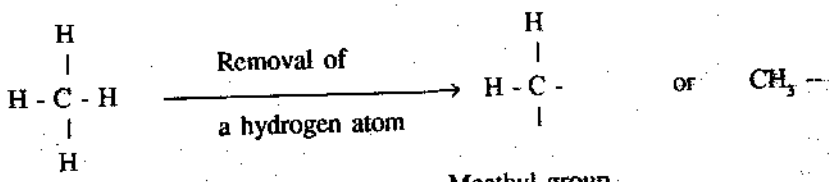


2, 3- Dimethylbutne



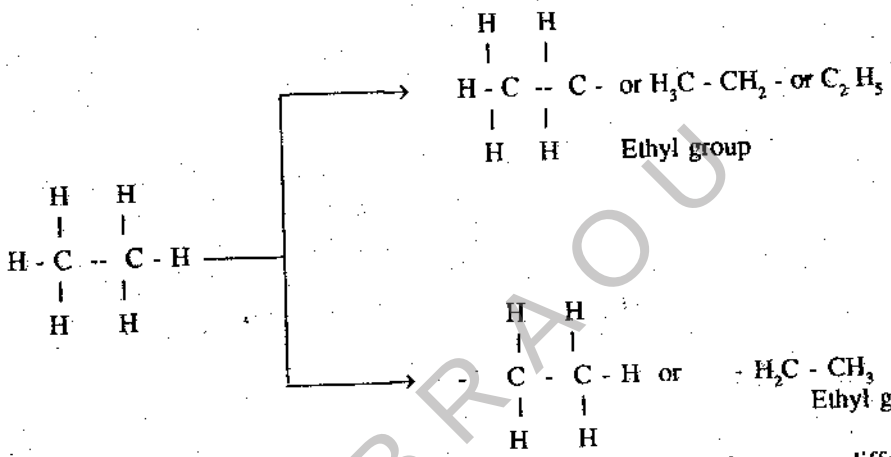
2,2 - Dimethylbutane (neohexane)

From each isomer of an alkane, by removing a hydrogen atom from different carbons, the corresponding alkyl groups are obtained. In methane all the hydrogens are equivalent. Therefore, only one alkyl group viz. methyl group is obtained by removal of any of the four hydrogens in methane.

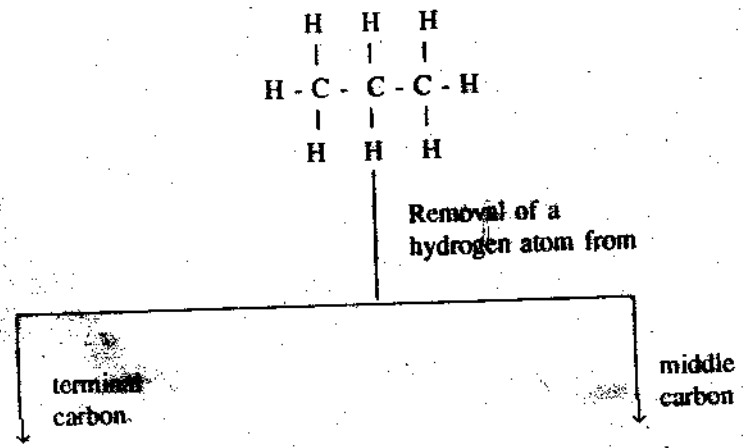


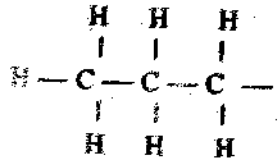
Meethyl group

Similarly from ethane only one ethyl group is possible.



In propane there are two types of carbon atoms. The middle carbon atom differs from the two terminal carbons in having only two hydrogens attached to it. Accordingly two propyl groups (n-propyl and isopropyl groups) are obtainable from propane by removal of different hydrogen atoms.





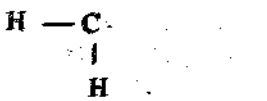
or

$CH_3 - CH_2 - CH_2 -$

or

$n - C_3H_7 -$

n - Propyl group



or

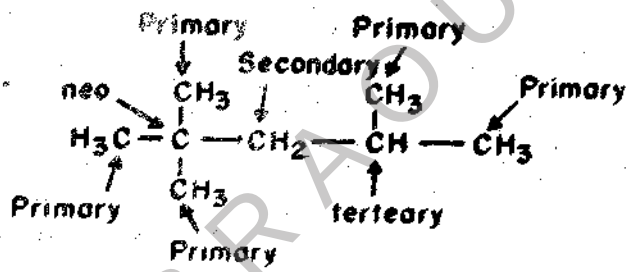
$CH_3 - CH -$

or

$i - C_3H_7 -$

i - Propyl group

The Carbon atoms in alkanes are differentiated as, primary, secondary, tertiary or neocarbons depending upon the number of carbon atoms attached to it. If the carbon atom is directly linked to not more than one carbon it is called primary carbon. Thus the carbon atoms in methane and ethane are all primary. If a carbon is linked to only two other carbons it is called secondary carbon atom. In propane there are two primary carbons and one secondary carbon. $CH_3 - CH_2 - CH_3$. If a carbon is linked to only three other carbon atoms it is called a tertiary carbon. A neo carbon is one which is linked directly to four other carbons. The different types of carbon atoms present in 2,2,4 trimethyl pentane are indicated below.



2.2.4 - Trimethyl pentane (iso octane)

Depending upon the type of the carbon atom of an alkane, from which a hydrogen is removed, the corresponding alkyl group results.

n-Butyl and sec-butyl groups respectively are obtained by removal of a hydrogen from primary carbon and secondary carbon of n-butane.

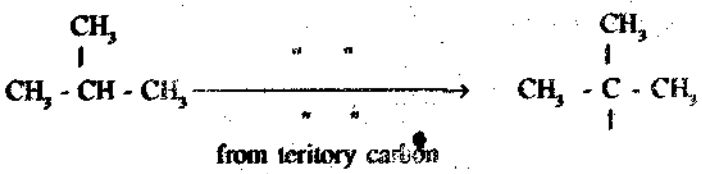
$CH_3 - CH_2 - CH_2 - CH_3$ —(Removal of a hydrogen from primary carbon)→ $CH_3 - CH_2 - CH_2 - CH_2 -$

n - butane

n- Butyl group

$CH_3 - CH_2 - CH_2 - CH_3$ —(Removal of a hydrogen from secondary carbon)→ $CH_3 - CH - CH_2 - CH_3$

sec. butyl group



Whereas by removal of a hydrogen from tertiary carbon of i-butane, tert. butyl group results.

Due to chain isomerism a large number of alkanes and still larger number of alkyl groups are possible. This again is responsible for enormous number of organic compounds.

Check your progress - 1

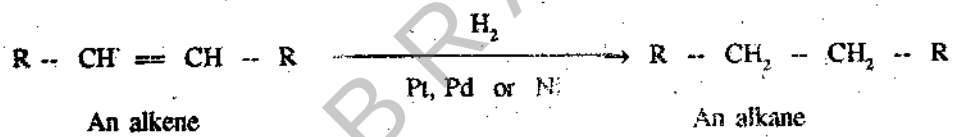
What are primary, secondary, tertiary and neocarbon ?

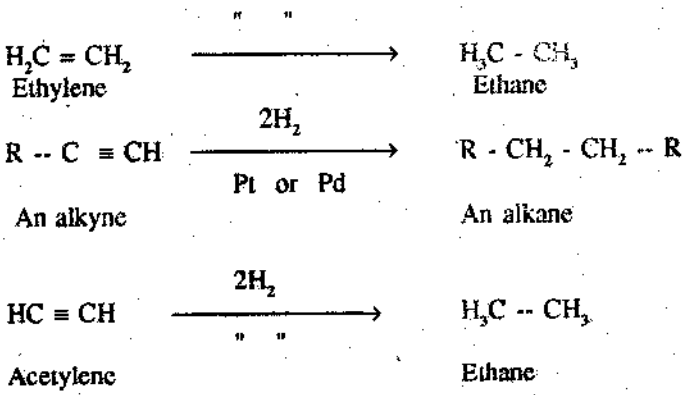
14.7 METHODS OF PREPARATION OF ALKANES

Some of the general methods which can be employed for the preparation of alkanes in the laboratory are given below:

14.7.1 Hydrogenation of unsaturated hydrocarbons

Unsaturated hydrocarbons like alkenes and alkynes on hydrogenration yield alkanes. Hydrogenation is carried out in the presence of finely divided metals. The metals used as catalysts are Pt, Pd, or Ni, Ethane is obtained by hydrogenation of ethylene and acetylene.





Hydrogenation takes place at room temperature when Pt or Pd is used as catalyst. If Ni used as catalyst the hydrogenation is carried out at 250-300°. Methane cannot be prepared by this method.

14.7.2 Reduction of alkyl halides

On reduction, alkal halides (R-X) are converted to alkanes. The reducing agents that can be used are

1. Zn + HCl (2) Li Al H_4 (3) H_2 + catalyst (catalytic hydrogenation)
4. HI + P

$$\underset{\text{An alkyl halide}}{R\text{-}X} \xrightarrow{\text{reducing agent}} \underset{\text{An alkane}}{RH}$$

1. $$R\text{-}X \xrightarrow{Zn+HCl} RH + HX$$

$$\underset{\text{Methyl chloride}}{CH_3\text{-}Cl} \longrightarrow \underset{\text{Methane}}{CH_4\text{-}HCl}$$

$$\underset{\text{Ethyl bromide}}{CH_3\text{-}CH_2\text{-}Br} \longrightarrow \underset{\text{Ethane}}{H_3C\text{-}CH_3} + HBr$$

2. $$4R\text{-}X + Li\,AlH_4 \longrightarrow 4\,R\text{-}H + LiX + AlX_3$$

$$\underset{\text{Methyl chloride}}{4\,CH_3\text{-}Cl} + Li\,Al\,H_4 \longrightarrow \underset{\text{Methane}}{4\,CH_4} + Li\,Cl + Al\,Cl_3$$

3. $$R\text{--}X \xrightarrow{H_2 / Pt} R\text{--}H + HX$$

$$\underset{\text{Methyl chloride}}{CH_3\text{-}Cl} \longrightarrow \underset{\text{Methane}}{CH_3\text{-}H} + H\,Cl$$

$$RI - HI \xrightarrow{P} RH + I_2$$

$$\underset{\text{Ethyl Iodide}}{CH_3\text{-}CH_2\text{-}I} + HI \longrightarrow \underset{\text{Ethane}}{CH_3\text{-}CH_3} + I_2$$

Phosphorous is added to the reaction mixture to remove the iodine as it is formed.

14.7.3 Grignard reaction

Reduction of alkyl halides can also be carried out by an indirect method. First alkyl halide is converted, by treatment with magnesium metal in dry solvent such as ether, to alkyl magnesium halide (Grignard reagent). The Grignard reagent is then hydrolysed by a dilute mineral acid to corresponding alkane. Ethane is obained from ethyl magnesium halides.

$$\underset{\text{dry ether}}{R\text{--}X} \xrightarrow{Mg} \underset{\text{Alkyl magnesium halide (Grignard reagent)}}{R\text{--}Mg\text{--}X}$$

$$R - Mg - X \xrightarrow[H_3O^+]{HOH} R - H + Mg$$

$$C_2H_5Br \xrightarrow[\text{Dry ether}]{Mg} C_2H_5MgBr \xrightarrow{H_3O^+} CH + Mg(Br)OH$$

Ethyl bromide — Ethyl magnesium bromide — Ethane

14.7.4 Wurtz reaction

In this reaction an alkyl halide is refluxed with sodium metal in dry ether. The reaction involves two molecules of alkyl halide, and coupling of two alkyl radicals to give an alkane. The alkane obtained contains double the number of carbon atoms originally present in the alkyl halide.

$$2RX + 2Na \xrightarrow{\text{dry ether}} R - R + 2NaX$$

$$H_3C - I + 2Na + I - CH_3 \longrightarrow H_3C - CH_3 + 2NaI$$

Methyl iodide — Ethane

Wurtz reaction is a good method for the preparation of alkanes containing even number of carbon atoms. However, it cannot be satisfactorily used for the preparation of alkanes containing odd number of carbon atoms. If we are to prepare an alkane with odd number of carbons say propane (C_3H_8) a mixture of two alkyl halides, ethyl bromide (C_2H_5Br) and methyl bromide (CH_3Br) should be used in Wurtz reaction.

$$CH_3 - Br + 2Na + Br - CH_2 - CH_3 \longrightarrow CH_3 - CH_2 - CH_3 + 2NaBr.$$

Propane

In this reaction, in addition to propane, ethane and butane are also formed.

$$2CH_3 - Br + 2Na \longrightarrow C_2H_6 + 2NaBr$$

$$2C_2H_5 - Br + 2Na \longrightarrow C_4H_{10} + 2NaBr$$

In otherwords, a mixture of three alknes (C_3H_8, C_2H_6 and C_4H_{10}) is formed. The separation of these alkanes is difficult. Therefore Wurtz reaction is normally not employed for the preparation of alkanes containing odd number of carbon atoms.

14.7.5 Decarboxylation of carboxylic acids

When the sodium salts of mono carboxylic acids are strongly heated with sodalime, alkanes are obtained. Sodalime is a mixture of NaOH and CaO. Methane is obtained from sodiumacetate.

$$R - COONa + NaOH \xrightarrow{\Delta} R - H + Na_2CO_3$$

Sodium salt of a carboxylic acid

$$H_3C - COONa + NaOH \xrightarrow{\Delta} CH_4 + Na_2CO_3$$

Sodium acetate — Methane

$$H_3C - CH_2 - COONa + NaOH \xrightarrow{\Delta} C_2H_6 + Na_2CO_3$$

Sodium propionate — Ethane

This reaction involves decarboxylation of the carboxylic acid.

14.7.6 Kolbe's electrolysis

Electrolysis of an aqueous solution of alkali salts of a monocarboxylic acid results in the formation of alkane. The resulting alkane contains double the number of carbons originally present in the alkyl group of carboxylic acid salt. Again, Kolbe's method is useful for the preparation of alkanes containing even numbers of carbon atoms.

$$2RCOONa + 2H_2O \xrightarrow{\text{electrolysis}} R\text{ -- }R + 2CO_2 + 2NaOH + H_2$$

$$2CH_3COONa + 2H_2O \longrightarrow H_3C\text{ - }CH_3 + 2CO_2 + 2NaOH + H_2O$$

Sodium acetate — Ethane

In aqueous solution, sodium acetate is present as acetate anion and sodium cation.

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

Sodium acetate — acetate anion

At anode, acetate anion looses an electron to form acetae radical. The acetate radical eliminates CO_2 to form a methyl radical. Combination of two methyl radicals results in the formation of ethane.

$$CH_3COO^- \longrightarrow CH_3COO + e^-$$

$$H_3C\text{ -- }COO \longrightarrow CH_3 + CO_2$$

$$H_3C + CH_3 \longrightarrow CH_3\text{ -- }CH_3 \text{ or } C_2H_6$$

At cathode sodium ion picks up an electron to form sodium atom (sodium metal) . Sodum reacts with water to form NaOH and hydrogen.

$$Na^+ + e \longrightarrow Na$$

Sodium ion — Sodium atom

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

Check your progress - 2

Formulate any three methods of preparation of n-butane.

14.8 PHYSICAL PROPERTIES OF ALKANES

Alkanes are non-polar molecules. Therefore, the intermolecular attractions in alkanes are limited to weak van der Waals forces. These weak attractive forces can be readily overcome by thermal energy, hence their melting and boiling points are very low. The melting and boiling poins and densities of alkanes, however, increase with increase in the number of carbon atoms. The lower

members C_1 - C_4 are colourless gases. C_5 - C_{17} are colourless liquids. Higher alkanes are solids. The boiling points of the branched chain isomers, as seen in the table below, are lower than these of the corresponding straight chain isomers. This is probably because of the greater surface area presented by the straight chain alkanes for better operation of intermolecular attraction forces.

Being non-polar, alkanes are insoluble in water but soluble in organic solvents.

14.8.1 Physical constants of some alkanes

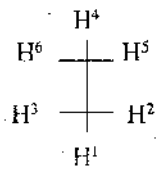
S.No.	Name	Formula	M.P.	B.P.
1.	Methane	CH_4	-183	- 162
2.	Ethane	C_2H_6	-172	- 88.5
3.	Propane	C_3H_8	-187	- 42.0
4.	n-Butane	C_4H_{10}	-138	0
5.	Iso Butane	C_4H_{10}	-159	- 12
6.	n - Pentane	C_5H_{12}	-130	- 36
7.	Iso-Pentane	C_5H_{12}	-160	- 28
8.	Neopentane	C_5H_{12}	-17	9.5

14.9 CONFORMATIONAL ISOMERISM

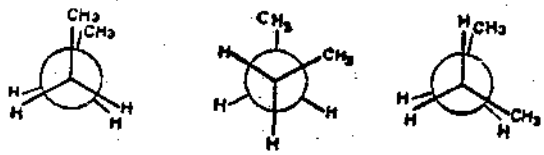
The carbon atoms in alkanes are linked by single or sigma bonds, formed by overlap of sp^3 orbitals. The electron distribution is symmetrical about the internuclear axis in a sigma bond. Due to this, free rotation about the single bond is allowed to a certain extent. As a result of free rotation about single bonds in a molecule it becomes possible to have different spatial arrangements of atoms or groups. These arrangements are readily inter-convertible, by rotations about the carbon-carbon single bond. Different spatial arrangements of atoms or groups resulting by rotation about single bonds in a molecule are called conformers. Alkanes exhibit the phenomenon of conformational isomerism.

14.9.1 Conformers of ethane

In ethane molecule the two carbon atoms are linked by a single bond, and each carbon is linked to three hydrogen atoms by single bonds. If one of the carbon atoms with the three hydrogens attached to it i.e. CH_3 group. in ethane, is rotated about the cabon-carbon bond. Without disturbing the other carbon, a large number of conformers result. These conformers have identical bond lengths and bond angles. Of the infinite number of conformations possible in ethane, two are quite distinct. These are called eclipsed and staggered conformers. In these conformations the relative position of the six hydrogens of ethane in space is different. The hydrogen atoms present on two carbon atoms of ethane may be labelled, for convenience, as H^1, H^2, H^3, H^4 , H^5 and H^6.



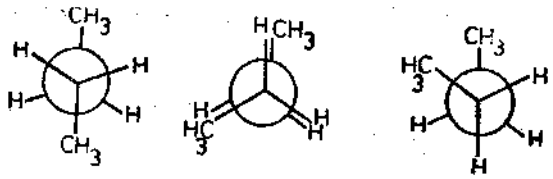
It is difficult to visualise the spatial relationships of groups in a molecule from their projections on a plane. Newman and sawhorse projector formulae are quite useful for demonstrating conformers.



I. Fully eclipsed conformation (syn form)

II. Gauche conformation (after 60° rotation)

III. Eclipsed conformation (CH_3 eclipses H) (after 120° rotation)



IV. Anti conformation (after 180° rotation)

V. Eclipsed conformation (after 240° rotation)

VI. Gauche conformation (after 300° rotation)

Conformers of n- butane

Gauche and anti conformations II and IV are staggered confortmations and are free from torisonal or eclipsing strain. Anti conformation (IV) has the added advantage of being free from van der Vaals stain too (as the methyl groups are maximum apart). Eclipsed conformationss I and III s ffer from torsional strain. Conformation I also suffers from van der Waals strain as the two bulky groups (methyl groups) are thrown very close to each other. Conformation VI and V, are identical with II and III respectively.

The decreasing order of stability of conformations in butane is there for IV> II> III> I.

14.10 CHEMICAL PROPERTIES OF ALKANES

Being saturated molcules alkanes are quite inert towards common reagents at norma reaction conditions. Alkanes are non polar covalent molecules with no centre of either high or low electron density. They are therefore inert towards electrophlic and nucleophilic reagents. Under vigorous conditions however, they can be made to undergo substitution reactions. In these reactions one or more hydrogen atoms are replaced by other groups. The important chemical reactions of alkanes are halogenation, nitration, sulphonation, and oxidation. All these substitution reactions proceed through free radical mechanism.

14.10.1 Halogenation of alkanes

Alkanes react with chlorine and bromine in presence of sunlight or ultraviolet light or at high temperature to yield halogen derivatives. One, two or more hydrogen atoms may be replaced fby halogen atoms, depending upon the amount of halogen used in the reaction. Thus, methane reacts in the presence of sun light with chlorine to yield a mixture of methyl chloride, methylene chloride, chloroform, and carbon tetrachloride.

$$CH_4 + Cl_2 \xrightarrow{h\upsilon \text{ or } \Delta} CH_3Cl + HCl$$
Methane — methyl chloride

$$CH_3Cl + Cl_2 \xrightarrow{"} CH_2Cl_2 + HCl$$
methylene chloride

$$CH_2Cl_2 + Cl_2 \xrightarrow{"} CHCl_3 + HCl$$
chloroform

$$CHCl_3 + Cl_2 \xrightarrow{"} CCl_4 + HCl$$
carbon tetrachloride

Bromine reacts similarly but less vigorously. Fluorinations are highly exothermic and therefore not attempted. Iodinations are too slow and reversible to be of much use. The order of reactivity of halogens with alkanes is, thus $F_2 > Cl_2 > Br_2 > I_2$. A hydrogen atom attached to a tertiary carbon is more readily replaced than a hydrogen atom attached to a secondary or primary carbon atom. Order of reactivity of hydrogens is tertiary hydrogen> secondary hydrogen> primary hydrogen.

14.10.1.1 Mechanism of halogenation

The halogenation of alkanes is a free radical substitution reaction. This is a chain reaction proceeding by the following steps.

1. $Cl - Cl \longrightarrow 2\,Cl$ chain intiation

2. $Cl\cdot + H_3C - H \longrightarrow CH_3 + HCl$
3. $H_3C + Cl - Cl \longrightarrow CH_3Cl + Cl$

} chain propagation

Step 1 is called chain initiation step. The Cl-Cl bond is broken homolytically to yield two chlorine atoms. Each atom retains one electron of the pair that originally formed the covalent bond. Such odd electron containing or unpaired electron containing species are highly reactive and are termed free radicals.

Step 2 and 3 are called chain propagation steps, Generally free radicals prefer to abstract a hydrogen atom from other molecules. In step 2 the chlorine free radical attacks the methane molecule and abstracts a hydrogen atom forming hydrogen chloride and a methyl free radical. In this step the C-H bond is broken homlytically. The resulting methyl free radical, in step 3 attacks a chlorine molecule causing a homolytic cleavage of Cl-Cl bond. In this step methyl chloride is formed and chlorine free radical is set free. Repetition of steps 2 and 3 leads to a chain reaction. Therefore they are called chain propagation steps. Finally the termination of the chain reaction may be brought by any of the following steps, in which the concentration of free radicals decreases.

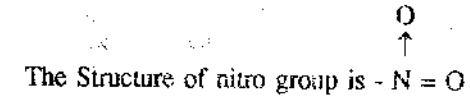
$$Cl\cdot + Cl\cdot \longrightarrow Cl_2$$

$$CH_3 + CH_3 \longrightarrow H_3C - CH_3$$

$$CH_3 + Cl \longrightarrow CH_3 - Cl$$

14.10.2 Nitration of alkanes

Replacement of hydrogen atom by a nitro group in a molecule is called nitration.



The nitration of alkanes is difficult and can be carried out only at elevated temperatures. Only mononitro alkanes are produced.

$$\underset{\text{Alkane}}{R\text{–}H} + HONO_2 \xrightarrow{400^\circ} \underset{\text{Nitroalkane}}{R\text{–}NO_2} + H_2O$$

$$\underset{\text{Methane}}{CH_4} + HO\text{–}NO_2 \xrightarrow{400^\circ} \underset{\text{Nitromethane}}{CH_3\text{–}NO_2} + H_2O$$

A mixture of methane and nitric acid at 400° gives nitromethane. This reaction is also known as vapour - phase nitration.

The order of replacement of a hydrogen atom in nitration is tertiary> secondary> primary. In higher alkanes, during nitration, C - C bonds are also broken. Because of this, a mixture of different products will be formed.. Thus the nitration of propane results in the formation of four nitro compounds.

$$CH_3 - CH_2 - CH_3 + HNO_3 \longrightarrow$$
$$H_3C - CH_2 - CH_2NO_2 + CH_3 - CHNO_2 - CH_3 + H_3C - CH_2 - NO_2 + CH_3NO_2$$

14.10.3 Sulphonation of alkanes

Substitution of the sulphonic acid group (- SO_3H) in place of a hydrogen in an organic compound is called sulphonation. Sulphonation of alkanes yield alkane sulphonic acids.

$$\underset{\text{An alkane}}{R - H} \xrightarrow{\text{Fuming } H_2SO_4} \underset{\text{An alkane sulphonic acid}}{R\,SO_3\,H}$$

Sulphonation can be caried out in the presence of fuming sulphuryl acid. Sulphuric chloride may also be used in the place of fuming sulphuric acid.

$$R - H + SO_2Cl_2 \longrightarrow R - SO_2Cl + HCl$$

$$R - SO_2\,Cl + H_2O \longrightarrow \underset{\text{Alkyl sulphonic acid}}{R\,SO_3\,H} + HCl$$

The higher alkane sulphonic acids are valuable as detergents.

14.10.4 Oxidation

14.10.4.1 Incomplete combustion

When alkanes are burnt in insufficient supply of air or oxygen, soot or carbon black is formed. This is used in the manufacture of Indian ink, black, varnish, printers ink etc.

14.10.4.2 Combustion in excess of air or oxygen

When alkanes are burnt in the presence of excess of air or oxygen, then undergo complete with the formation of carbon dioxide and water.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{Heat}$$

Large amount of heat is liberated in a combustion reaction. That is why this reaction has tremendous importance. Most of the alkanes obtained from petroleum are used as fuels.

14.10.4.3 Catalytic oxidation

Lower alkanes are oxidised to alcohols and aldehydes, where as higher alkanes form long chain fatty acids during catalytic oxidation. The catalytic oxidation is carried out at higher pressure and temperature in the presence of metallic catalysts.

$$C_4H_{10} \xrightarrow[\text{catalyst}]{O_2} CH_3OH + HCHO + CH_3CHO + CH_3COOH \text{ etc}$$

Alkanes genrally do not react with potassium permanganate

14.11 INDUSTRIAL SOURCE OF ALKANES

The principal natural source of alkanes is petroleum and accompanying natural gas. Animal and plant remains, buried in the earth and subjected to high temperature and pressure over millions of years, are changed to carbon containing residue. Most of the carbon is transformed into carbonaceous gases (natural gas), liquid (petroleum) and solid (coal, diamond etc.,). The liquid petroleum is mined out of the bowels of the earth along with natural gas.

Natural gas is chiefly a mixture of lower alkanes (CH_4, C_2H_6, C_3H_8 and C_4H_{10}). The propane-butne fraction is separated from the more volatile members, methane and ethane, by liquifaction, compressed and bottled into cylinders and served as LPG cylinders (liquid propane gas cylinders) for use as fuel. Petroleum mined from the earth is separated by distillation into several fractions as shown below:

S.No.	Fraction	Boiling range	Composition
1.	Gas	below 20°	C_1 - C_4
2.	Petroleum ether	20° - 60°	C_5 - C_6
3.	Ligroin	60 - 100°	C_6 - C_7
4.	Natural gasoline	40 - 205°	C_7 - C_{12} + Cycloalkanes
5.	Kerosene	200 - 275	C_{12}- C_{15}+Aromatic hydrocarbons
6.	Gas Oil	Above 275°	C_{15} - C_{18}
7.	Lubricating oil and waxes	Non-volatile liquid not distilled	
8.	Asphalt or petroleum coke	Non-volatile solid (Residue)	

The gaseous fraction is mainly used as fuel. Gasoline is used as fuel in internal combustion engines. Kerosene is used as fuel in tractors and engines, and gas oil is used in diesel engines. The lubricating oils are chilled to a wax, purified and sold as paraffin wax. Asphalt is used in roofing

and road building. Coke is used as fuel.

Petroleum fractions containing higher alkanes are subjected to the process of cracking, cracking of petroleum is the pyrolysis of higher alkanes in the absence of air to give lower homologues of alkanes, alkenes, hydrogen etc. The gasoline content is there by increased. Different, techniques of cracking used are:

14.11.1 Thermal cracking

Alkanes are passed into a preheated chamber where they break down into smaller units.

14.11.2 Steam cracking

Alkanes are diluted with steam, heated to 700-900° for a fraction of a second and cooled. Alkanes are broken down into ethylene, propylene, butadiene, isoprene, cyclopentadiene and other useful chemicals.

14.11.3 Hydrocracking

Alkanes are mixed with hydrogen and heated under pressure to about 250° - 400° .

14.11.4 Catalytic cracking

Higher boiling alkane fraction are heated under pressure to about 450° - 550° C in the presence of finely divided alumina-silica catalyst. In this process dehydrogenation and cyclisation of alkanes takes place yielding a variety of aromatic compounds.

14.12 SUMMARY

In this unit alkanes which are aliphatic hydrocarbons with single bonds only are discussed. The gen. for is C_nH_{2n+2} and shows chain and conformational isomerism.

The carbon atoms are classified as primary, secondary, tertiary or neocarbons depending upon the number of carbons attached to it. Several alkyl groups result depending upon the type of carbon atom from which hydrogen is removed.

Alkanes are prepared from:

a) alkenes & alkynes by hydrogenation
b) alkyl halides by reduction or on treatment with metallic sodium
c) carboxylic acids either by decarboxylation or kolbe's electrolysis.

These are non-polar with low melting and boiling points which increase with increase in the number of carbon atoms. Insoluble in water but are soluble in organic solvents.

The important reaction in alkanes is free-radical substitution which is a chain reaction. eg. halogenation, where the order of reactivity is F_2, Cl_2, Br_2, I_2.

14.13 MODEL EXAMINTION QUESTIONS

I. Answer the following in 10 lines

1. How is n- hexane obtained from (a) n-propyl bromide (b) 2-bromohexane (c) sodium heptanoate and (d) potassium butyrate? What happens when n- hexane reacts separately with Cl_2 and HNO_3?

2. What is petroleum? what are the products obtained on fractionation of petroleum.

3. Halogenation of alkanes is a chain reaction. Explain

II. Answer the following in 30 lines

1. Discuss the general methods of preparation of alkanes.

2. (a) 'Petroleum' is considered as a source of organic compounds. Explain.
   (b) Comment on the reactivity of alkanes.

14.14 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. The carbon atoms in alkanes are differentiated as primary, secondary, tertiary or neocarbons depending upon the number of carbon atoms attached to it. When carbon atom is directly linked to one carbon atom it is called primary, two carbon atoms is called secondary and three carbon atoms is called tertiary carbon. A neo carbon is one which is linked directly to four other carbons.

2. n-Butane can be prepared by

   a) Hydrogenation of 1 or 2 - butene or 1 or 2-butyne
   b) Reduction of n-butyl chloride
   c) Wurtz reaction of ethyl bromide

a) Hydrogenation of 1 - or 2 -butene or 1 or 2-butyne with one or two moles of hydrogen respectively in presence of catalyst Pt, Pd or Ni yields n-butane.

$$CH_3\,CH = CH\text{-}CH_3 + H_2 \xrightarrow{\text{Pt, Pd or Ni}} CH_3\,CH_2\,CH_2\,CH_3$$

or

$$CH_3\,CH_2 - CH = CH_2 + H_2 \xrightarrow{\text{Pt, Pd or Ni}} CH_3\,CH_2\,CH_2\,CH_3$$

$$CH_3\,CH_2\,C \equiv CH + 2H_2 \xrightarrow{\quad"\quad} "$$

$$CH_3\,C \equiv CCH_3 + 2H_2 \xrightarrow{\quad"\quad} "$$

b) Reduction n-butylchloride with any reducing agent (Zn - HCl ; H_2/Pt; $LiAlH_4$, HI/P, Mg/H_2O) gives n-butane

$$CH_3\,CH_2\,CH_2\,CH_2\,Cl + H_2 \xrightarrow{\text{Pt}} CH_3\,CH_2\,CH_2\,CH_3 + HCl$$

c) Wurtz reaction of ethylbromide also results in the formation of n-butane.

$$2C_2\,H_5\,Br + 2Na \longrightarrow C_4\,H_{10} + 2NC\,Br.$$

UNIT - 15 ALKENES AND ALKADIENES

Contents

15.1 AIMS AND OBJCTIVES

In this unit we introduce you the preparation and properties of compounds containing carbon-carbon double bond and to outline the general methods of preparation and properties of dienes and the special properties of conjugated dienes. When you have finished this unit, you will be able to understand :

- Nomenclature of alkenes.
- Position and cis-trans isomerism in alkenes.
- General methods of preparation of alkenes.
  a) Dehydrohalogenation of alkyl halides.
  b) Dehydration of alcohols.
  c) Dehalogenation of vic-dihalo alkanes.
- Physical and chemical properties
  a) Reaction with hydrogen
  b) Reaction with halogens
  c) Addition of unsymmetrical reagents to unsymmetrical olefines - Markownikoff's rule and peroxide effect.
  d) Catalytic hydration
  e) Hydroxylation
  f) Ozonolysis
  g) Polymerization
- Nomenclature and classification of dienes
- General methods of preparation of conjugated dienes.
- Chemical properties of dienes including, 1-4-addition, Diels-Alder reaction and polymerization.

15.2 INTRODUCTION

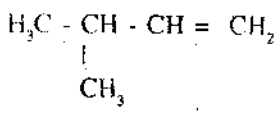
Alkenes are unsaturated aliphatic hydrocarbons. Their molecular formulae correspond to the general formula C_nH_{2n} (n = number of carbon atoms). An alkene contains two hydrogens less than the alkane containing same number of carbon atoms. These compounds are also called the olefins. The first member of this family, ethylene (C_2H_4), is a gas. Dutch chemists obtained an oily liquid ($C_2H_4Cl_2$) on treatment of ethylene with chlorine. Therefore ethylene was called as olefiant gas (meaning oil making gas). Therefore the name olefin was given for the whole family, though other members of this family do not form oily liquids on treatment with chlorine.

15.3 NOMENCLATURE

These compounds are characterised by the presence of a carbon-carbon double bond. The suffix in the names of this class of compounds is 'ene' (ene=double bond). Thus, carbon-carbon double bond is the functional group in alkenes. The double bond in alkenes consists of a sigma (σ) and pi (π) bond.

Formula	Alkylene	IUPAC name
$H_2C = CH_2$	Ethylene	Ethene
$H_3C - CH = CH_2$	Propylene	Propene
$H_3C - CH_2 - CH = CH_2$	α – Butylene	1 - Butene
$H_3C - CH = CH - CH_3$	ß - Butylene	2 - Butene
$H_3C - C(CH_3) = CH_2$	Iso - Butylene	2 - Methyl propene

The IUPAC names of alkenes are derived by replacing the suffix 'ane' of alkene with 'ene'. The position of the double bond is indicated by a number which may precede or follow the name. The numbering of carbon atoms normally starts at the end nearest the double bond. Other basic points of nomenclature, illustrated for alkanes, are followed in the case of alkenes. Thus ethylene and propylene are named as ethene and propene respectively. α, β and isobutylenes are named as 1-butene, 2-butene and 2-methylpropene respectively. The name 3 - methly 1-butene, for instance, indicates that the compound is a derivative of a butene, the double bond is between first and second carbons and a methyl group is present on third carbon atom.

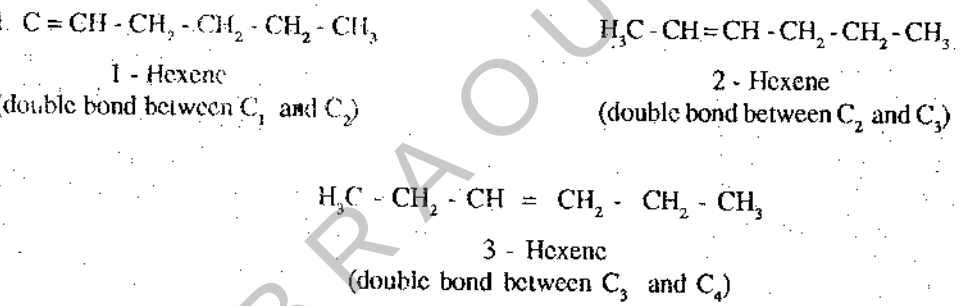


15.4 ISOMERISM

Apart from chain isomerism alkenes also exhibit position isomerism and cis-trans isomerism.

15.4.1 Position isomerism

Position isomers of an alkene have the same molecular formula and carbon skeleton but differ in the position of double bond. For an alkene containing six carbon atoms in a straight chain and one double bond, three position isomers viz., 1-hexene, 2-hexene and 3-hexene are possible.



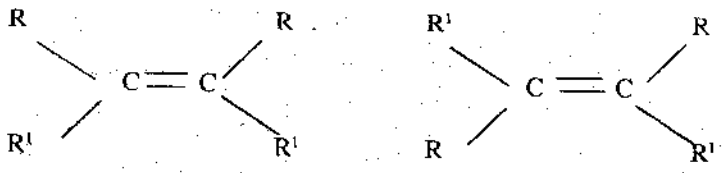
1 - Hexene
(double bond between C_1 and C_2)

2 - Hexene
(double bond between C_2 and C_3)

3 - Hexene
(double bond between C_3 and C_4)

15.4.2 Cis-trans isomerism

In alkenes, rotation about carbon-carbon double bond is totally prevented. This is responsible for geometric isomerism or cis-trans isomerism in appropriately substituted olefins. Alkenes, R (R') C=C(R')R, carrying two different substituents on each olefinic carbon atom exhibit cis-trans isomerism. The two isomers possible are:

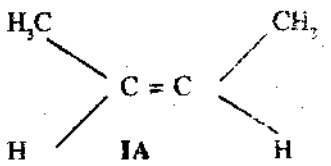


cis-alkene

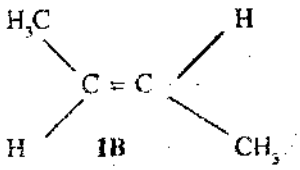
trans-alkene

These two isomers have same structure but differ in the spatial arrangement of the groups about the double bond, and are called geometric or cis-trans isomers. This isomerism comes under

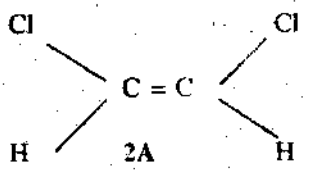
the broad title of stereoisomerism. The arrangement of the groups that characterises a particular stereo isomer is called its configuration. The configuration of geometric isomers is indicated in their name by the prefixes 'cis' or 'trans'. In latin 'cis' means on the same side, trans means across. In a cis compound same (or similar) groups present on the two carbons lie on the same side of the double bond, whereas in trans compound they are present on the opposite sides. Configuration of geometric isomers of 2-butene, 1, 2-dichloro ethylene and 3-hexene are given below:



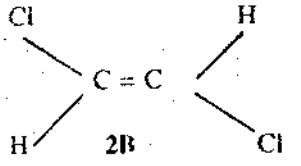
1A



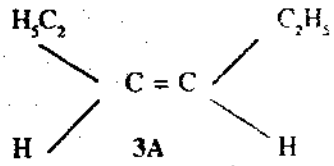
1B



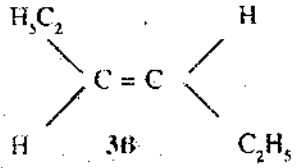
2A



2B



3A



3B

1A: cis-2-Butene

1B: trans-2-Butene

2A: cis-1.2-Dichloro ethylene

2B: trans-1.2-Dichloro ethylene

3A: cis-3-Hexene

3B: trans-3-Hexene

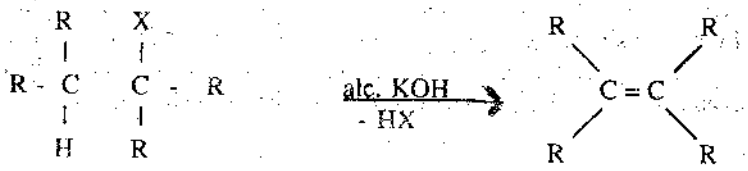
Cis and trans isomers have different physical properties such as boiling points, solubilities, diplole moments etc. A mixture of cis-trans isomers can be separated, and the individual isomers collected in separate containers, in contrast to conformers. It may be recalled that one conformer is spontaneously converted itno another by easy rotation about the C-C single bond.

15.5 GENERAL METHODS OF PREPARATION OF ALKENES

Alkenes are generally prepared by elimination reactions. These include dehydrohalogenation of alkylhalides, dehydration of alcohols and dehalogenation of dihaloalkanes. In addition to these methods, controlled reduction of alkynes also serves as a convenient route for the preparation of alkenes.

15.5.1 Dehydrohalogenation of alkyl halides

Alkyl halides undergo dehydrohalogenation on treatment with alcoholic potassium hydroxide (KOH) giving alkenes. On dehydrohalogenation of alkyl halides, the halogen atom and a hydrogen atom from the adjacent carbon atom are eliminated as HX propene, for instance, is obtained by dehydrochlorination of n-propyl chloride under the influence of alcoholic solution of potassium hydroxide.



An alkyl halide

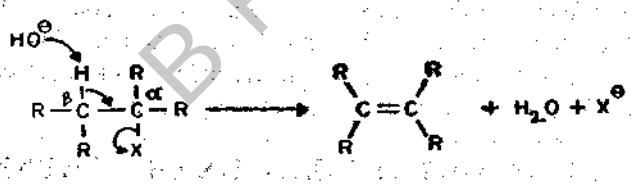
An alkene

n-Propyl chloride

15.5.1.1 Mechanism of dehydrohalogenation

Dehydrohalogenation of alkyl halides may proceed by several routes. Under the influence of a base simple alkyl halides undergo dehydrohalogenation by the converted mechanism i.e., by simultaneous loss of halogen atom (from α - carbon) and a hydrogen from the ß - carbon.

Concerted attack by base (OH) on the hydrogen present on ß - carbon, shift of the electron pair (constituting the bond between hydrogen and ß - carbon atom) between α – and ß - carbons and elimination of halogen as halide ion leads to the formation of olefin.



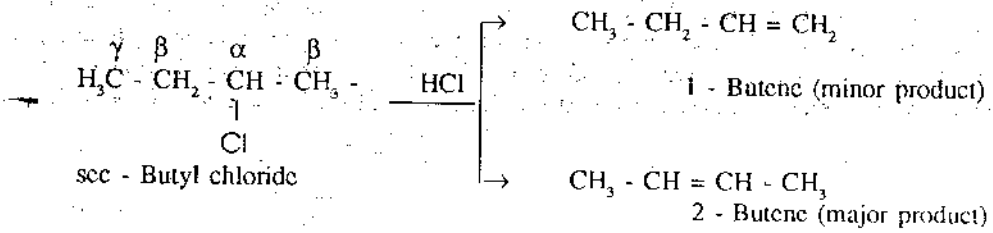
In other words cleavage of bond between ß - carbon and H formation of carbon-carbon double bond and cleavage of bond between α - carbon and halogen occur simultaneously.

The reactivity of alkyl halides in dehydrohalogenation reaction is in the following order.

Alkyl iodide > alkyl bromide > alkyl chloride > alkyl fluoride.

15.5.1.2 Saytzeff's rule

In an alkyl halide if two alternative hydrogen atoms are available, dehydrohalogenation, theoretically, can give two isomeric alkenes. For instance, dehydrochlorination of sec-butyl chloride should result in the formation of both 1-butene and 2-butene



Elimination of a hydrogen from ß - carbon along with chlorine (from α - carbon atom) as HCl gives 1-butene, whereas 2-butene is formed if a hydrogen from ß' carbon along with chlorine (from α-carbon) is eliminated as HCl. A rule of thumb-Saytzeff's rule is useful in deciding which of the two isomers is the major product in the above case. Saytzeff's rule states that during the dehydrohalogenation of alkyl halides hydrogen is preferentially eliminated from a ß carbon carrying the fewer number of hydrogen atoms. Stated differently, the alkene with larger number of hydrogen atoms. Stated differently, the alkene with larger number of alkyl groups attached to the doubly bonded carbons is produced. In the example above, therefore, the hydrogen is eliminated preferentially from a ß carbon. 2-Butene is the major product. Saytzeff's rule is also applicable in the formation of alkenes by dehydration of alcohols.

15.5.2 Dehydration of alcohols

Alcohols on heating with a dehydrating agent eliminate a molecule of water to give alkenes. Concentrated sulphuric acid is commonly used as dehydrating agent. In some instances dehydration has been effected in the presence of dry HCl, aluminia, boron trifluoride or thionyl chloride in pyridine.

$$\underset{\text{alcohol}}{-\overset{|}{\underset{|}{C}}-\overset{OH}{\overset{|}{C}}-} \xrightarrow[-H_2O]{\text{Conc } H_2SO_4} > C = C < \quad \text{alkene}$$

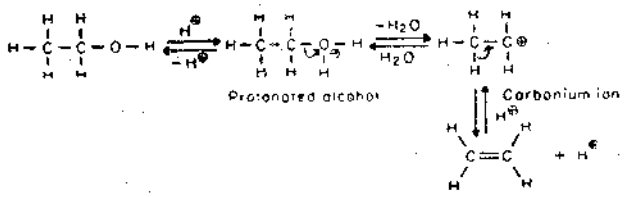
Formation of alkenes from alcohols under the catalytic influence of concentrated sulphuric acid is an example of intramolecular dehydration. A side reaction that generally accompanies this intramolecular dehydration is formation of ehters by inter-molecular dehydration. Ethyl alcohol, on heating with concentrated H_2SO_4 at 170°, gives ethylene as the major product. At lower temperature (135°) and by using excess of ethyl alcohol ethyl ether is obtained as the major product.

$$\underset{\text{Ethyl alcohol}}{CH_3 - CH_2 - OH} \xrightarrow[HSO_4,\ 170°]{-H_2O} \underset{\text{Ethylene}}{CH_2 = CH_2} \quad \text{(Intramolecular dehydration)}$$

$$2CH_3 - CH_2 - OH \xrightarrow[H_2SO_4,\ 135°]{-H_2O} \underset{\text{Ethyl ether}}{CH_3 - CH_2\ O - CH_2 - CH_3} \quad \text{(Intermolecular dehydration)}$$

Mechanism of dehydration: In the first step ethyl alcohol combines with a proton (from concentrated sulphuric acid) to form protonated alcohol-the conjugate acid of alcohol. This is also known as oxonium ion.

In this reaction the oxygen atom of alcohol functions as a Lewis base. In the oxonium ion, the oxygen atom is positively charged i.e., electron deficient. The electron deficient oxygen atom of the oxonium ion exerts effect on oxygen - carbon bond. Heterolytic cleavage of the C - O bond results in a carbonium ion (an ion with a positive charge on the carbon atom) and water. The carbonium ion, in the final step, looses a proton from the adjacent carbon to give ethylene.



All the three steps viz., formation of oxonium ion, carbonium ion and ethylene are reversible. By heating the reaction mixture, ethylene is driven off and the reaction is favoured in the direction of formation of ethylene. Carbonium ion formation is the key step in the acid catalysed dehydration of alcohols. The relative stability of carbonium ions is:

tertiary Carbonium ion > secondary Carbonium ion > primary Carbonium ion

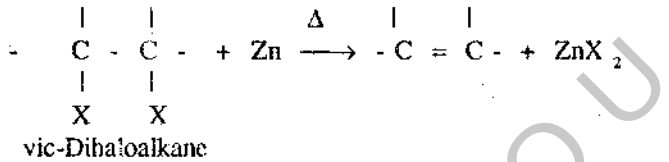
Therefore in the ease of acid-catalysed dehydration of alcohols follows the order

tertiary Carbonium ion > secondary alcohol > primary alcohol

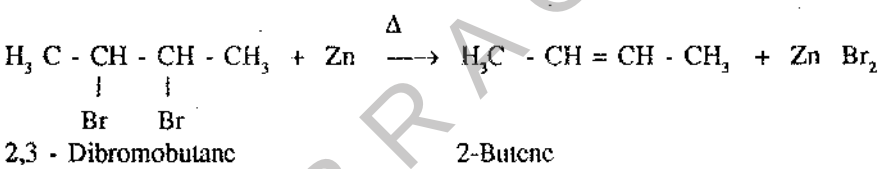
15.5.3 By dehalogenation of vic-dihalo alkanes

Dehalogenation of vic-dihaloalkanes give alkenes. Dehalogenation takes place by heating a vic-dihaloalkane with zinc in alcoholic solution.

In the preparation of alkenes by dehalogenation of vic-dihaloalkanes there is no scope for the formation of a mixture of position isomers. Heating 2,3 - dibromobutane with zinc, for example, gives 2-butene



vic-Dihaloalkane

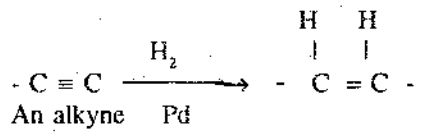


2,3 - Dibromobutane 2-Butene

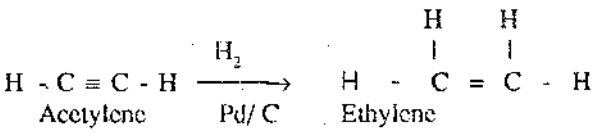
However, this method of preparaton of alkenes is not very important since vicinal dihaloalkanes themselves are obtained from alkenes by the addition of halogens.

15.5.4 Controlled reduction of alkynes

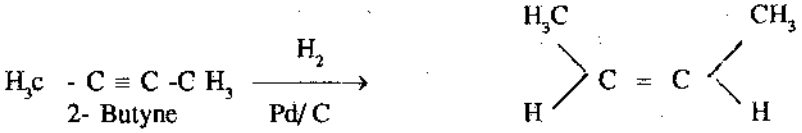
Alkynes are obtained on controlled reduction of alkenes. Controlled and catalytic hydrogenation of alkynes generally gives cis-alkenes. Ethylene is obtained by catalytic hydrogenaion of acetylene in the presence of Pd-C. 2-Butene under similar conditions gives cis-2-butene.



An alkyne Pd An alkene



Acetylene Pd/ C Ethylene



cis - 2-Butene

15.6 PHYSICAL PROPERTIES OF ALKENES

Alkenes resemble alkanes in most of their physical properties. The first three members are gases, the next fourteen are liquids while the higher members are solids. Unsubstituted alkenes are colourless. Branched chain alkenes have lower boiling points than the corresponding straight-chain alkenes. Alkenes are lighter than water. They are non-polar substances and therefore are practically insoluble in polar solvents like water, but soluble in organic solvents such as benzene, chloroform and ether. As is found in other homologous series, the melting and boiling points, specific gravities and densities of alkenes increase with increasing molecular weight.

Physical constants of some alkenes

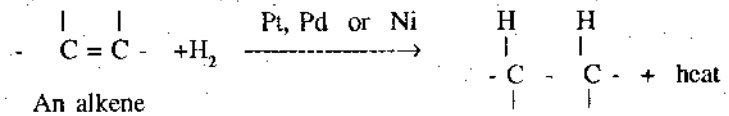
Name of the alkene	Molecular formula	Boiling Point	Specific gravity (liq)
Ethene	C_2H_4	- 102°	0.610
Propene	C_3H_6	- 48°	0.610
1-Butene	C_4H_8	- 6.5°	0.626
1-Hexene	C_6H_{12}	64°	0.675
1-Heptene	C_7H_{14}	93°	0.698
1-Octene	C_8H_{16}	123°	0.716

15.7 CHEMICAL PROPERTIES OF ALKENES

Due to the presence of carbon-carbon double bond, alkenes are unsaturated compounds. Therefore, they readily undergo addition reactions. Alkenes are associated with π electron cloud. For instance, in ethylene, there is a π electron cloud above and below the C-C bond axis. Due to the presence of loosely bonded π electrons, alkenes function as Lewis bases (nucleophiles). Hence alkenes predominantly react with electro-philes leading to addition products. Thercofre, most of the reactions of alkenes are electrophilic addition reactions. During these addition reactions the weak π bond breaks and two additonal bonds, one on each olefinic carbon are formed. Only under special conditions alkenes undergo free radical addition and free radical substitution reactions. The reagents that add on to the double bond include hydrogen (H_2), halogens (X_2) hydrogen halides (HX) and water. Alkenes also react with a variety of oxidising agents and undergo polymerisation reactions.

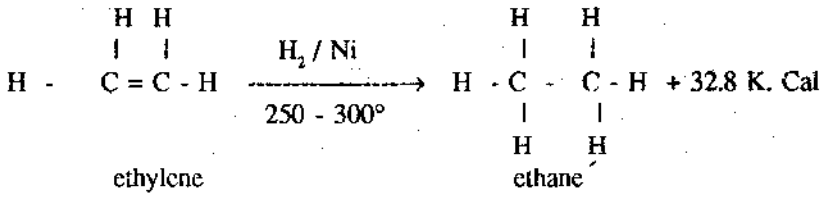
15.7.1 Reaction with hydrogen

Alkenes react with hydrogen in the presence of catalysts like finely divided platinun, palladium or nickel. The temperature and pressure required for hydrogenation vary with the nature of the catalyst.

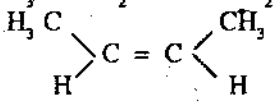
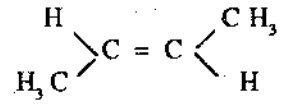


An alkene

An alkane



Hydrogenation of alkenes is an exothermic reaction. Heat of hydrogenation of an alkene is the amount of the heat liberated when one mole of hydrogen is being absorbed by one mole of alkene. It is measured in K.cal/mole. The heats of hydrogenation values of a few alkenes are as follows:

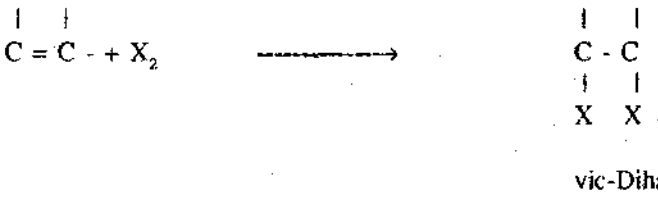
Name of the alkene	Structure	Heat of hydrogenation (K. Cal/mole)
Ethene	$H_2C = CH_2$	- 32.8
Propene	$H_3C - CH = CH_2$	- 30.1
1 - Butene	$H_3C - CH_2 - CH = CH_2$	- 30.3
cis-2-Butene		- 28.6
tras-2-Butene		- 27.6

It can be seen from the heats of hydrogenation that a more substituted olefine is more stable. Trans isomer of 2-butene is more stable than the cis-isomer.

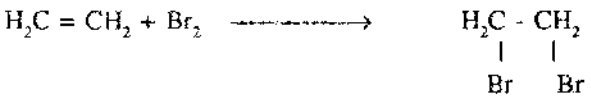
Catalytic hydrogenation is industrially important. Oils (unsaturated glycerides) are reduced with hydrogen in the presence of finely divided Ni to give fats (saturated glycerides). This is called hydrogenation of oils. Catalytic hydrogenation is a valuable method for the estimation of carbon-carbon double bonds (unsaturation)in organic compounds).

15.7.2 Addition of halogens

Hologens (X_2) add to alkenes forming vic-dihaloalkanes



vic-Dihalo alkanes



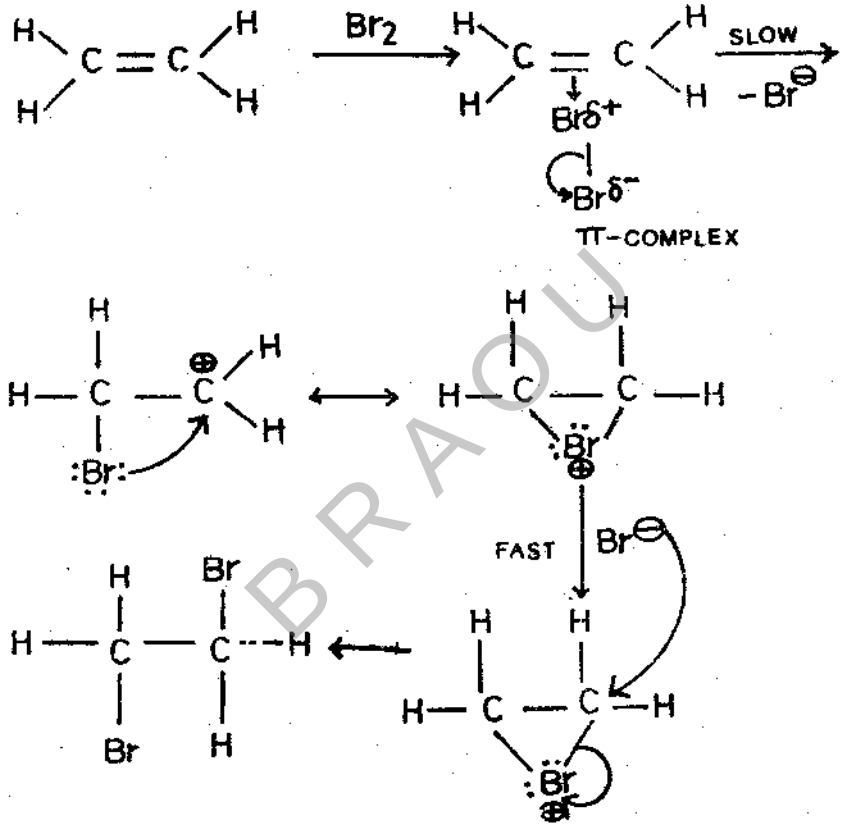
This addition reaction is carried out in solvents like chloroform, carbontetrachloride and acetic acid. The order of reactivity of halogens is $F_2 > Cl_2 > Br_2 > I_2$. Addition of F_2 to alkenes proceeds with explosive violence, whereas addition of I_2 is very slow and reversible. Fluorination of alkenes is not normally carried due to the explosive violence of the reaction. In the addition of bromine to an alkene, no HBr is evolved and the red colour of bromine solution is discharged. Decolorisation

of bromine solution without evolution of HBr serves as a test for unsaturation in organic compounds.

15.7.2.1 Mechanism of addition of halogens

This reaction takes place by an ionic mechanism. consider the addition of bromine to ethylene.

Bromine molecule is polarised by the approach of the π - electron cloud of ethylene. The end of bromine molecule nearer to olefin is associated with a positive charge and the farther end of bromine with a fractional negative charge. The weak association between π - electron cloud of olefin and the positive end of bromine molecule is called a π - complex. Heterolytic cleavage of Br-Br bond in the π - complex results in the formation of a bromide ion and a cation which may be considered as a carbonium ion or cyclic brominium ion. There is considerable evidence in favour of brominium ion. Even if carbonium ion intermediate is formed, it is quickly transformed into cyclic bromonium ion. The bromonium ion is attacked by bromide ion from the rearside, in the fast step, to give the product. The overall addition of bromine to a double bond is trans. Formation of carbonium ion or brominium ion from the complex is the slow step (rate determining step) in the addition of bromine to an alkene.



When bromine is reacted with an alkene in a solution containing anions, some of the addition product will be found to contain the anion. For example, bromination of ethylene in aqueous sodium chloride yields bromochloro ethane and dibromo ethane. This is an evidence in favour of positively charged intermediate in the reaction.

$$H_2C = CH_2 + Br_2 \xrightarrow{\text{Na Cl soln.}} BrCH_2 - CH_2\ Br + Br\ CH_2 - CH_2 - Cl$$

15.7.3 Addition of hydrogen halides

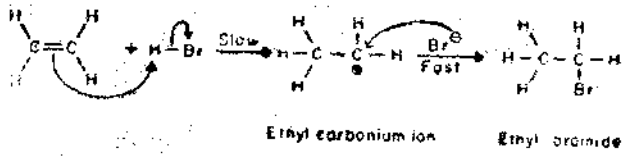
Addition of hydrrogen halides (HX) to an alkene results in the formation of an alkyl halide. The order of reactivity of hydrogen halides is HI > HBr> HCl> HF exactly the order of acidic strength of hydrogen halides.

$$>C + C< + HX \rightarrow -\overset{H}{\underset{|}{C}}-\overset{|}{\underset{X}{C}}-$$

Alkyl halide

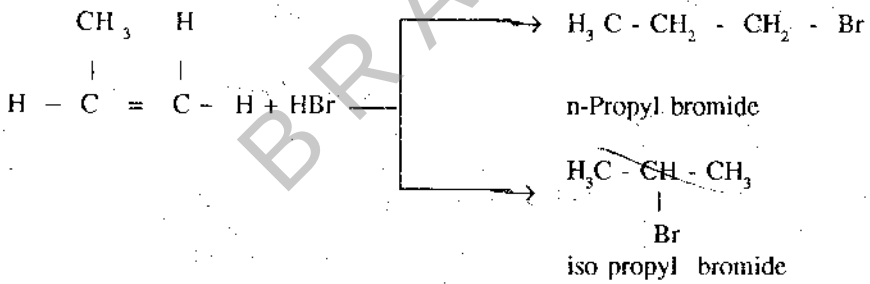
$$H_2C = CH_2 + HBr \rightarrow \underset{\text{Ethyl bromide}}{H_3C - CH_2Br}$$

In the reaction of ethylne with HBr to form ethylbromide, ethylene molecule function as nucleophile and is attached in the rate determining step by a proton (from HBr). This interaction leads to the formation of ethyl carbonium ion. The carbonium ion then quickly reacts with the bromide ion to give ethyl bromide.



15.7.3.1 Normal addition: Markowinkoff rule

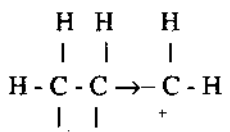
The addition of hydrogen halide to an unsymmetrical olefin can take place in two ways. For instance, in the addition of HBr to propene, both n-propyl bromide and isopropyl bromide may be expected,



Such problems arise in all the addition reactions involving an unsymmetrical reagentand unsymmetrical alkene. Markowinikoff, a Russian chemist, studied the course of addition of several unsymmetrical reagents of various unsymmetrical olefins. He found that, in all these additions, the negative part of the adding reagent usually becomes attached to that olefinic carbon which carriees lesser number of hydrogens, This empirical generalisation is known as Markownikoff rule. If the addition proceds, according to marknownikoff rule, it is called normal addition (Markownikoff addition). Formation of i-propyl bromide by the attachment of $\bar{B}r$ (negatiive part of the reagent. HBr) to the middle carbon of prrpene (the olefinic carbon carrying only one hydrogen) is called Markownikoff's addition. On the other hand formation of n-propyl bromide from propene and HBr is called anti Markownikoff or abnormal addition. In practice, the addition of HBr to propene gives isopropyl bromide as the major product.

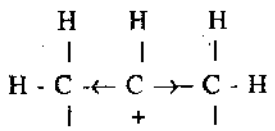
Now we are in a position to give an electronic interpretation for Markownikoff rule. In the addition of HBr to propene, the initial step is the attack by H^+ on he π- bond of propane. In this

process the proton may be attached to either middle or terminal olefinic carbon of propene giving n-propyl carbonium ion, being a secondary carbonium ion, is more stable than n-propyl carbonium ion which is a primary carbonium ion. This is due to the presence of two methyl groups in i-propyl carbonium ion. Which exert electron releasing inductive (+ I effect). The higher stability of i-propyl carbonium ion is also due to hyperconjugation.



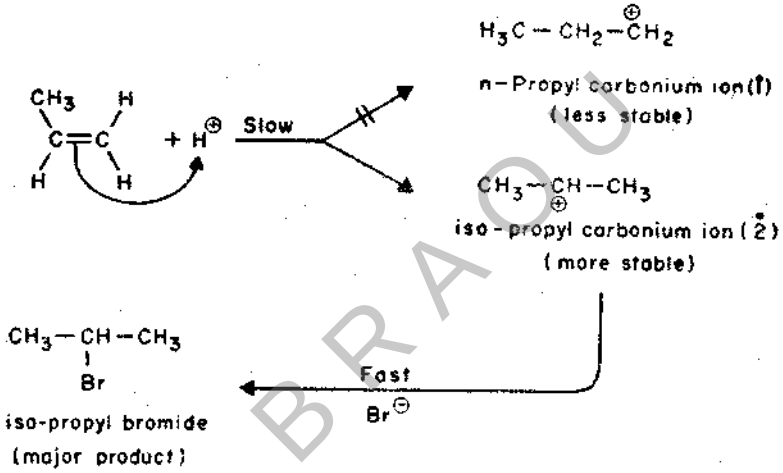
n- propyl carbonium ion
(Primary carbonium ion)

One methyl group exerting + I effect and two -CH bonds (two resonance structures due to hyperconjugation)



n- propyl carbonium ion
(Secondary carbonium ion)

Two methyl groups exerting + I effect and six -H bonds (six resonance structures due to hyperconjugation)



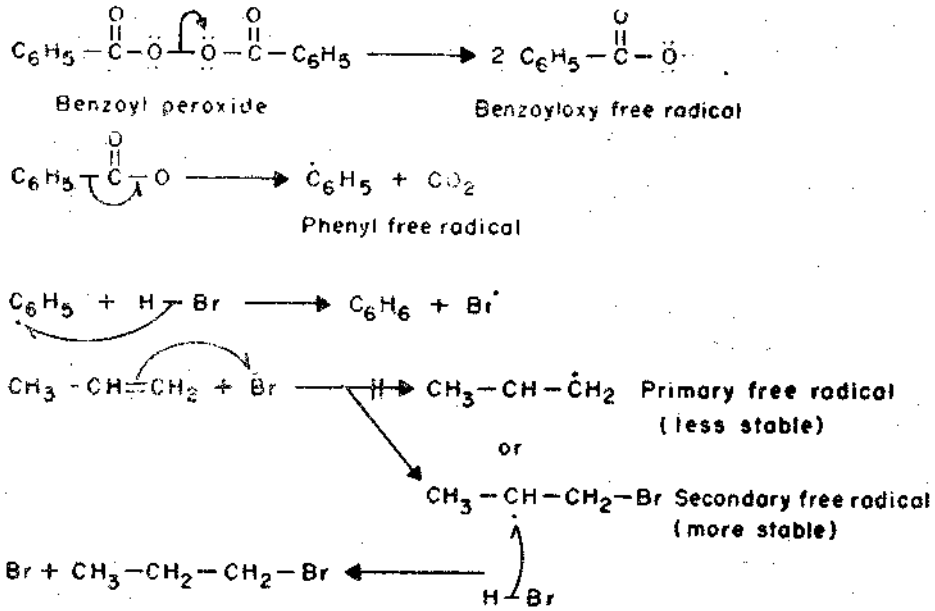
Therefore of the two carbonium ions, formation of i-propyl carbonium ion (more stable ion) is energetically more favourable. i-Propyl carbonium ion then combines readily with the bromide ion to give i-propyl bromide as the major product.

15.7.3.2 Anti-Markownikoff addition: Peroxide effect

In 1933 Kharasch discovered that the normal mode of hydrogen bromide addition to propene is reversed in the presence of a perioxide. Thus, propylene when treated with HBr, in the presence of a trace of benzoyl peroxide, yields n-propylbromide as the major product.

$$H_3C - CH = CH_2 + HBr \xrightarrow[\text{Peroxide}]{\text{benzoyl}} H_3C - CH_2 - CH_2Br$$

This abnormal addition has been shown to proceed through a free radical mechanism.



ie first step is homolytic cleavage of the weak bond in benzoylperoxide to yield benzoyloxy free ra. als. Benzoyloxy free radicals. Benzolyloxy free radical eliminates a molecule of CO_2 to form pi nyl free radical. A free radical has a strong tendency to hydrogen atom from other compou 's. Therefore phenyl free radical reacts with HBr to form benzene, releasing a bromine atom (bromine ree radical). In the next step bromine free radical adds to propene forming, a secondary free radi '. This on reaction with HBr by radical mechanism to form n-propyl bromide. The bromine e ect is also observed in the photochemical addition of HBr to unsymmetrical olefins.

Check your progress - 1

What is Markownikoff rule?

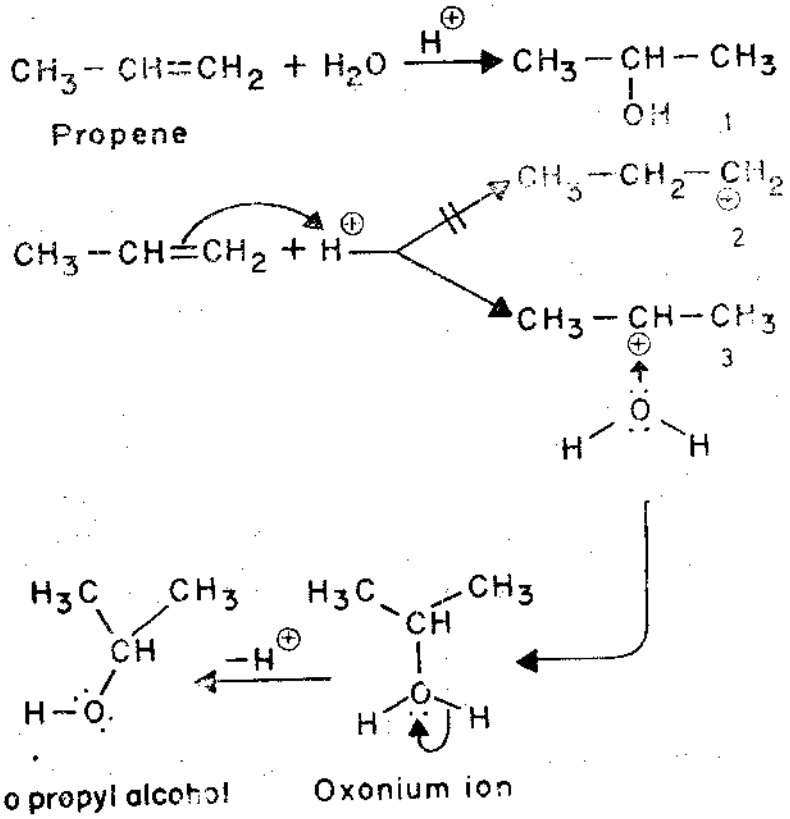
15.7.4 Catalytic hydration

Addition of a water molecule to alkenes takes place in the presence of concentrated sulphuric acid. The products of catalytic hydration of olefins are alcohols.

$$> C = C < + H_2O \xrightarrow{H\,SO_4} > \underset{\displaystyle H}{\overset{|}{C}} - \underset{\displaystyle OH}{\overset{|}{C}} <$$

An alcohol

The hydration of an unsymmetrical alkene such as propene takes place according to Markownikoff's rule.



Addition of a proton to propene yields more stable i-propyl carbonium ion. The carbonium ion is an electrophile, and, therefore, reacts with a water molecule (a nucleophile) giving an oxonium ion. The oxonium ion, in this case, is protonated i-propyl alcohol. Elimination of a proton from the oxonoium ion yields i-propyl alcohol.

15.7.5 Hydroboration

Anti-Markownikoff addition of water molecule to oan unsymmetrical olefin is brought about under the catalytic influence of diborane. In this process an alkene is treated with diborane and the resulting trialkylborane is oxidised with alkaline hydrogen peroxide solution. The addition of boron hydrides at carbob-carbon double bond is known as hydroboration.

$$B_2H_6 \dashrightarrow 2BH_3$$

$$3CH_3 - CH = CH_2 + BH_3 \dashrightarrow (CH_3 - CH_2 - CH_2)_3\ B$$

Tripropyl borane

$$(CH_3\text{-}CH_2\text{-}CH_2)_3\ B + 3H_2O_2 + 3\ NaOH \rightarrow 3\ CH_3\text{-}\ CH_2\text{-}\ CH_2\text{-}\ OH + Na_3\ BO_3 + 3H_2O$$

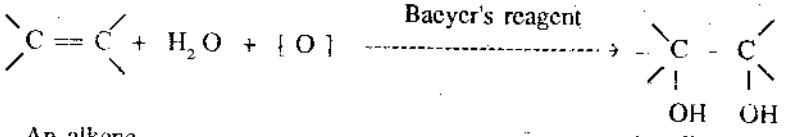
15.7.6 Oxidation

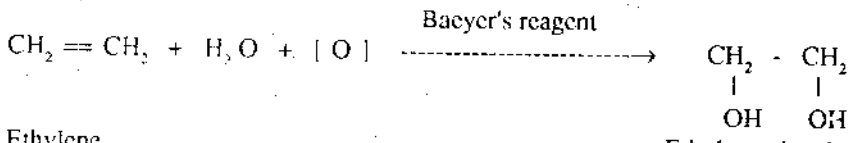
Alkenes are oxidised by a variety of oxidising agents.

15.7.6.1 Hydroxylation

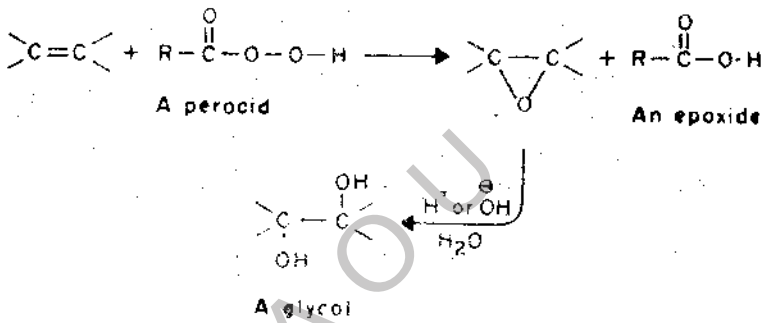
A solution of cold dilute alkaline $KMnO_4$ (Baeyer's reagent) or osmium tetroxide converts an alkene into corresponding glycol. Ethylene is thus converted into 1,2-dihydroxy ethane or ethylene

glycol.



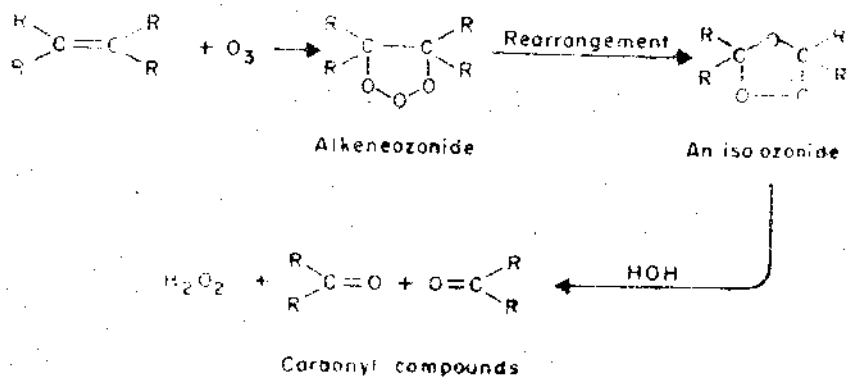


conversion of alkenes into glycols is known as hydroxylation of alkenes. Baeyer's reagent and osmium tetroxide cause cis hydroxylation of alkenes. Glycols are also obtained by conversion of alkenes into eposides, followed by the reaction of an alkene with a peracid such as peracetic acid, pertrifluroacetic acid and perbenzoic and. Hydrolysis of epoxides leads o the formation of trans-glycols.



15.7.6.2 Ozonolysis

In ozonolysis, alkenes are treated with ozone. The resulting unstable (and sometimes explosive) ozonides are hydolysed to give carbonyl compounds (aldehydes and ketones). The hydrolysis is carried out in an inert atmosphere to prevent further oxidation of the carbonyl, compounds.



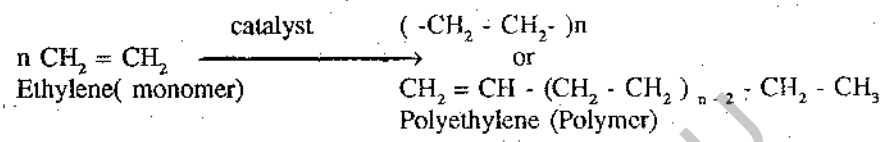
In the first step an addition product known as mol ozonide is formed. This rearranges to give an iso-ozonide. By identification of carbonyl compounds, formed in the ozonolysis reaction, the structure of an alkene can be established. By removing the carbonyl oxygens from the structures of the two carbonyl compounds (formed in ozonolysis), and joining their carbonyl carbons through a double bond, we can write the structure of the starting alkene (subject to ozonolysis).

Carbonyl compounds resulting from ozonolysis of alkenes

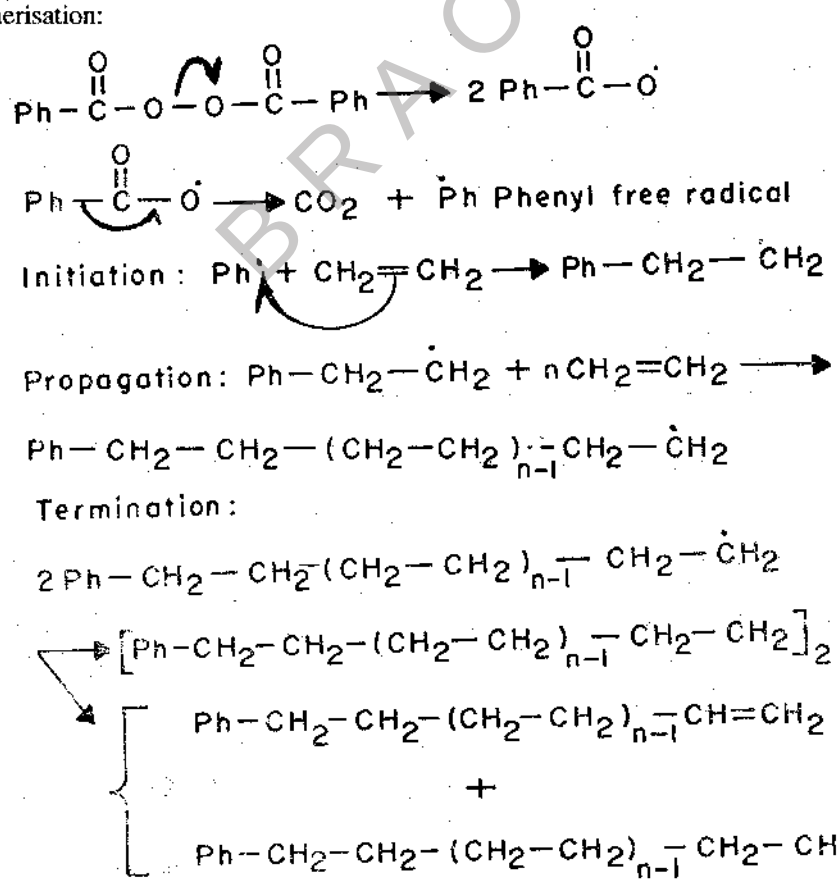
Structure of the alkene subjeted to ozonolysis

15.7.7 Polymerisation

Alkenes undergo polymerisation. Polymerisation is the formation of a large molecule by the repeated addition of small molecules. The small molecule is called monomer and the large molecule a polymer. For example, ethylene (a gas) polymerises in the presence of a catalyst to produce a high-molecular-weight polymer (polyethylene). Polyethylene is a tough, solid substance melting near 118° , and is used for making, among other things, containers for hydrofluoric acid.



Polymerisation may be catalysed by acids, bases or free radicals. Following is the mechanism of free radical polymerisation:



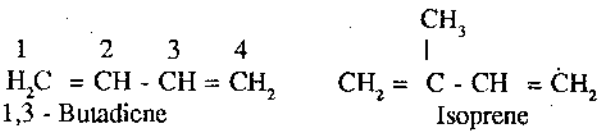
Like any other chain reaction, free radical polymerisation consists of three steps viz., initiation, propagation and termination. Termination is brought about, either by pairing up of radicals of by a free radical taking up a hydrogen from an other free radical. The latter step is known as disproportionation.

15.8 ALKADIENES

Alkadienes are unsaturated open chain hydrocarons carrying two carbon-carbon double bonds. Alkadienes are also known as diolefins. The suffix 'diene' in the name of an orgaic compound indicates the presence of two carbob-carbon double bonds. The empirical formula of alkadiene is C_nH_{2n-2}. 1,3- Butadiene is an important member of alkadiencs family.

15.8.1 Nomenclature

The IUPAC name for an alkadiene is given by replacing the 'ne' of the alkane by 'diene' and indicating the position of the double bonds and other subsituents by the numericals. For instance. , the name 1,3- butadiene suggests that there are four carbons in the compound, and two double bonds- one between C_1 and C_2 and the other between C_3 and C_4. Similarly isoprene is named as 2-methyl 1,3 -butadiene.



Dienes are classsified into three types depending on the position of the doublebonds. Dienes with double bonds separated by a single bond are called conjugated dienes. In an isolated diene the double bonds are separated by more than one single bond. If the two double bonds originate from the same carbon, the diene is called a cumulated diene or an allene. The carbonlinked to two double bonds (allenic carbon) is in SP hybidirised state.

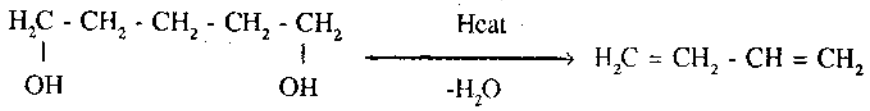
Formula	Name	Type of diene
$H_2C = C = CH_2$	1,2 - Propadiene (allene)	Cumulated
$H_2C = CH - CH = CH_2$	1,3-Butadiene	Conjugated
$H_3C - CH = CH = CH_2$	1,2 - Butadiene	Conjugated
$H_2C = CH - CH_2 - CH = CH_2$	1,4-Pentadiene	Isolated

15.8.2 General methods of preparation

The methods that are generally employed for the preparation of alkenes can also be used for alkadienes.

15.8.2.1 Dehydration of a dihydric alcohol

Dehydration of a dihydric alcohol in the presence of acids leads to the formation of alkadienes. Heating a mixture of pentane 1,5-diol and concentrated H_2SO_4 results in the formation of 1,4 - pentadiene.



1,5 - Pentanediol 1, 4 Pentadiene

15.8.2.2 Dehydrogenation of alkanes

Alkadienes are also obtained by dehydrogenation of an alkane, by passing the vappours over heated Cr_2O_3 catalyst. For example, 1,3 - butadiene is obtained by dehydrogenation of butane.

$$\underset{\text{N- Butane}}{H_3C - CH_2 - CH_2 - CH} \xrightarrow[Cr_2O_3]{\text{Heat}} \underset{\text{1,3 Butadiene}}{H_2C = CH - CH = CH_2} + 2H_2$$

15.8.3 Properties

Among the dienes, cumulated dienes are least stable. Frequently cumulated dienes undergo isomerisation to form an alkyne or a conjugated diene. The conjugated dienes are more stable than isolated dienes. This is reflected in their heats of hydrogenation.

Compound	Heat of hydrogenation
$H_2C = CH - CH = CH - CH_3$ 1,3 Pentadiene (Conjugated)	- 54.1 KCal./mole
$H_2C = CH - CH_2 - CH = CH_2$ 1,3 Pentadiene (isolated)	- 60 K. Cal/mole

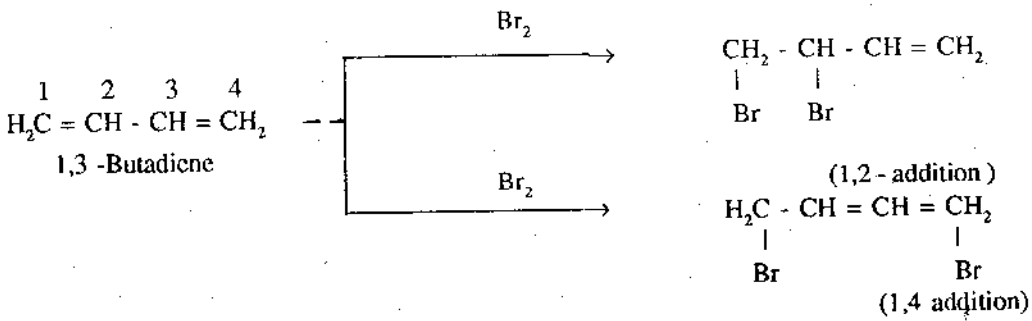
15.8.4 Chemical properties

Like alkenes, alkadienes undergo electrophilic addition reactions. But due to the presence of two double bonds,two molecules of reagent are required to complete the addition reaction. Conjugated dienes show a strong tendency to undergo 1,4-addition reactions.

15.8.4.1 1, 4-Addition reactions

When dienes are treated with one mole of halogen, a dihalide is formed. Formation of a dihalide may involve either 1,2 - or 1,4 - addition. In 1,2 - addition the reagent adds on to one double bond i.e two carbons joined by a double bond in the diene remains uneffected. In 1,4 - addition, on the other hand, the reagent adds on to the two terminal carbons of diene system, and a new double bond appears between the central carbons of the diene. 1,4 - Addition is the preferred mode of reaction of conjugated dienes with one mole of of reagent.

1,2 - and 1,4 - Additions o bromine to 1,3 butadiene is represented as follows:



15.8.4.2 Thiele's partial valence theory

According to Thiele's partial valence theory, atoms forming multiple bonds do not fully utilise all their combining power, but leave a partial valence reaching out in space. In conjugated dienes the partial valencies of unsaturated carbons separated by a single bond are neutralised, leaving partial valences at the two terminal carbons of the diene system. Therefore the terminal carbons react readily by 1,4 - addition.

$H_2C = CH - CH = CH_2$ $\qquad$ $H_2C = CH - CH = CH_2$

1, 3 - Butadiene $\qquad$ Butadiene with partial valences (according to Thiele)

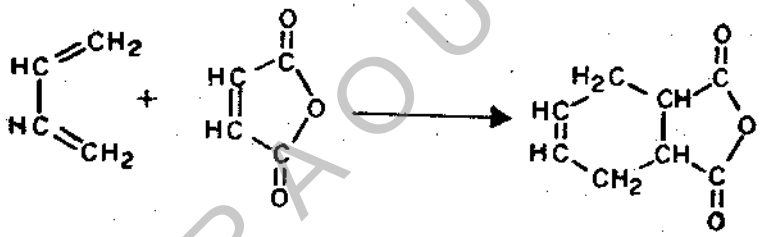
$$H_2C = CH - CH = CH_2 \xrightarrow{Br_2} \underset{\text{Br}}{H_2C} - CH = CH - \underset{\text{Br}}{CH_2}$$

Neutralisation of partial valences of cartons linked by single bond

1,4 - ddition

15.8.4.3 Diels - Alder reaction

This is 1,4 - addition reaction of conjugated dienes with unsaturated compounds like maleic anhydride (called a denophile). For example, 1,3 - butadiene reacts with maleic anhydride to give an adduct (addition product). This reaction is called Diels-Alder reaction. Diels - Alder reaction is valuab in th synthesis of six membered carboxylic compounds. Diels Alder reaction is the characteristic action of conjugated dienes.



1,3−butadiene Maleic anhydride adduct

Check your progress - 2

What is diels-Alder reaction ?

15.8.4.4 Polymerisation

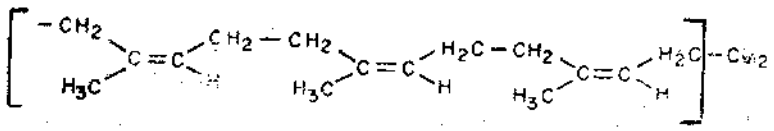
Alkadienes readily undergo polymerisation. For example, 1,3 - Butadiene forms polybutadiene in presence of peroxides.

$$n\ (CH_2 = CH - CH_2) \longrightarrow (-CH_2 - CH - CH - CH_2)_n$$

Polybutadiene

CH_3
|

Synthetic rubber is a polymer of isoprene, ($H_2C = C - CH = CH_2$) or 2 methyl - 1, 3 - butadiene



a polymer of isoprene rubber

15.9 SUMMARY

Alkanes or olefins which contain a carbon-carbon double bond has general formula C_nH_{2n} and exhibits position and geometrical isomerism. They are prepared from

(a) Alkylhalides by dehydrohalogenation
(b) Alcohols by dehydrohalogenation
(c) Vic. dihalo alkanes on dehalogenation

These are non-polar with low melting points and boiling points. They are insoluble in polar solvents but soluble in polar solvents but soluble in organic solvents.

The main type of reaction is electophilic addition with X_2, HX, HCN, H_2O etc. Addition of HX to unsymmetrical olefins gives products, with negative part being added to carbon atom with lesser number of hydrogens (Makownikoff's rule). In presence of peroxide HBr adds contrary to this known as peroxide effect. Ozonolysis is an important reaction which facilitates identification of the position of the double bond in olefins.

Conjugated dienes show 1,4 - addition products due to delocalization of electrons.

15.10 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines

1. An alkene (A) with molecular formula C_4H_8 reacts with HCl to from an addition product (B). (A) On ozonolysis gives acetone and formaldehyde. Write the structures of (A) and (B).
(2) How are the following conversions effected? Write equations.
a) Propene to n-propyl chloride
b) 1,2 Dibromo propane to i-propyl alcohol

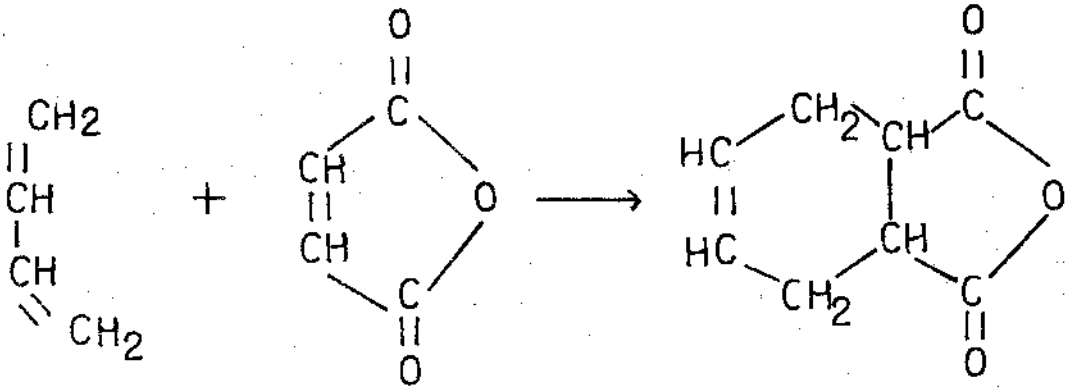
II. Answer the following in 30 lines

1. Outline the mechanism of addition of bromine to an alkene.
2. Write the structures of (i) an isolated diene (ii) conjugated diene (iii) a cumulated diene. Discuss the characteristic reactions of conjugated dienes.
3. Give an account of general methods of preparatin of alkenes and alkadienes.
4. Discuss the mechanism of polymerization of ethylene. What is hydroboration? explain with a suitable example in each case.

15.11 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. In addition of polar molecules to unsymmetrical olefines the negative part of the adding reagent usually becomes attached to that carbon which carries lesser number of hydrogens. This empirical generalisation is known as Karkownikoff rule.

2. The 1, 4 - addition of conjugated dienes with unsaturated compounds like maleic anhydride is called diels-Alder reaction. ex: Addition of 1,3 - butadiene with maleic anhydride.



Author : Mrs. C. Sesharatnam

UNIT - 16 ALKYNES

Contents

16.1 AIMS AND OBJECTIVES

In this unit we wish to introduce you the methods of preparation, properties and uses of alkenes. After completing this unit you should be able to know :

- Nomenclature of alkynes
- General methods of preparation of Alkynes
  1) Dehydohalogenation of dihalo alkanes
  2) Dehalogenation of tetra haloalkanes
  3) Conversion lower alkynes to higher alkynes
- Properties
  A Physical properties of alkynes
  B Chemical properties of alkynes
    1) Reduction
    2) Additon of hydrogen
    3) Addition of hydrogen halides
    4) Caalytic hydration and tautomerism
    5) Reaction with metals
    6) Oxidation
    7) Acdity
    8) Isomerisation

16.2 INTRODUCTION

Alkynes are unsaturated aliphatic hydro carbons. The functional group in alkynes is carbon - carbon triple bond. The suffix for the compounds of this family is 'yne', and the general formula is C_nH_{2n-2}. Acetylene, H-C≡C-H is the simplest alkyne. The carbon triple bond length in alkynes is 1.20 A° which is less than carbon-carbon double and single bonds. The carbon atoms l inked by a triple bond, and the atoms directly linked to them form a linear structure. Thus in acetylene, H - $\hat{C}$ - C bond angle is 180° Alkanes exhibit position isomerism but do not exhibit cis-trans isomerism.

16.3 NOMENCLATURE

The common, and I U P A C names of some alkynes are given below:

Formula of alkyne	Common name	I U P A C name
H - C ≡ C - H	Acetylene	Ethyne
H - C ≡ C - CH_3	Methylacetylene	Propyne
H - C ≡ C - C_2H_5	Ethylacetylene	But - 1 yne or 1 - Butyne
H_3 - C - C ≡ C - CH_3	Dimethylacetylene	But - 2 yne or 2 - Butyne

Alkynes may be named as derivatives of acetylene. In the IUPAC names of alkynes, the suffix is 'yne'. The nature, number and position of substituents and the position of the triple bond in the longest straight chain of carbon atoms are also indicated. The following structure contains five carbon atoms and a

$$\overset{1}{Cl} - \overset{2}{CH_2} - \overset{3}{C} \equiv \overset{4}{C} - \overset{5}{CH}(\overset{CH_3}{\text{ }}) - CH_3$$

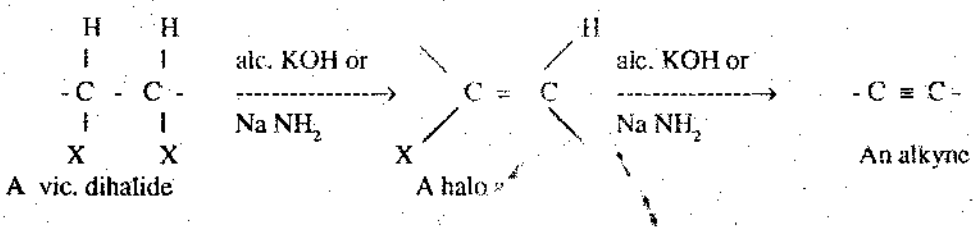
triple bond in the longest straight chain of carbon atoms. The triple bond is between C_2, and C_4 respectively. Therefore the IUPAC name of the compound is 1-chloro - 4 - methyl - 2-pentyne.

16.4 GENERAL METHODS OF PREPARATION

Several methods are available for the preparation of alkynes. All these methods involve elimination reactions.

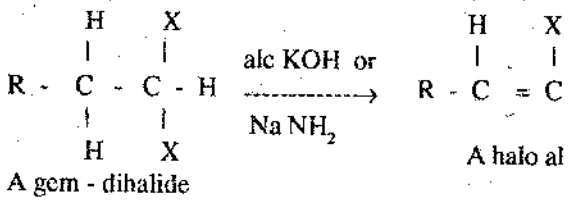
16.4.1 Dehydrohalogenation of vicinal and geminal dihalides

Dehydrohalogenation of vicinal or geminal dihalides or dihaloalkanes leads to the formation of alkynes. When two halogen atoms are present on the same carbon in a dihalide, it is called a geminal (gem) dihalide. If the two halogen atoms are attached to two adjacent carbon atoms, the dihalide is called a vicinal (vic) dihalide. On treatment of dihalide with sodium amide or alcoholic alkali a haloalkene is first formed. This reacts with a second molecule of dehydrohalogenating agent to give alkyne.



A vic. dihalide

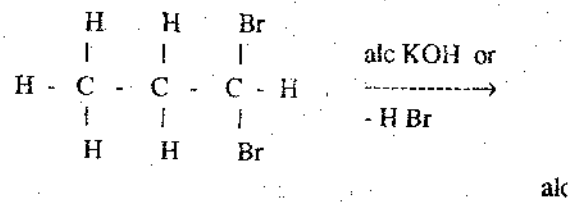
A halo



A gem - dihalide

A halo al

Preparation of propyne from 1,1 -dibromo propane serves

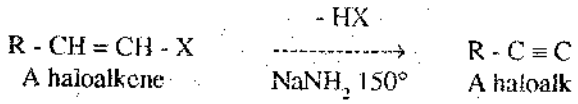


alc

-

A haloalkene may be dehydrohalogenated by NaNH

50° to give alkynes.

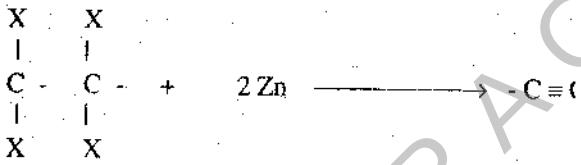


R - CH = CH - X
A haloalkene

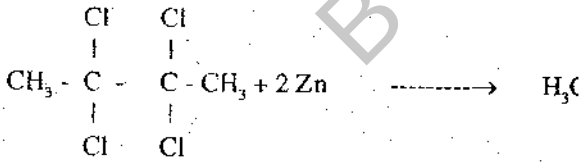
R - C ≡ C
A haloalk

16.4.2 Dehalogenation of tetrahaloalkanes

Dehalogenation of tetrahaloalkanes by treatment with metal leads to the formation of alkynes. Reaction of alcoholic solution of 2,2,3,3 - tetrachlorobutane zinc metal gives 2-butyne.



A tetrahaloalkene



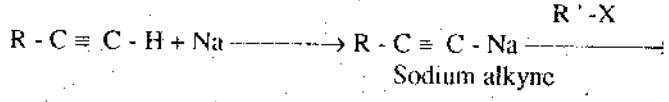
2,2,3,3 - Tetrachlorobutane

- Butyne

16.4.3 Conversion of lower alkynes to higher

nes

Lower alkynes can be converted into higher alkynes. ynes react with sodium metal to form sodio derivatives which on treatment with alkyl halides from er alkynes.



gher alkyne

Preparation of 1-butyne from acetylene may be cited example

$$H-C\equiv C-H + Na \longrightarrow H-C\equiv C-Na + CH_3CH_2I \longrightarrow \underset{\text{1- Butyne}}{H-C\equiv C-CH_2-CH_3} + NaI$$

Check your progress - 1

Explain an important method of preparation of acetylene.

16.5 PHYSICAL PROPERTIES OF ALKYNES

Alkynes resemble alkanes and alkenes in their physical properties. They are insoluble in water but quite soluble in organic solvents of low polarity like benzene, carbon tetrachloride and ether. Their boiling points increase in the numbers of carbon atoms.

The boiling points of some simpler members of alkyne family are given below.

Alkyne	Formula	Boiling point O° C
Acetylene	$H-C\equiv C-H$	- 83
Propyne	$H-C\equiv C-CH_3$	-23
1- Butyne	$H-C\equiv C-CH_2-CH_3$	9
2- Butyne	$H_3C-C\equiv C-CH_3$	27
1- Pentyne	$H-C\equiv C-CH_2-CH_2-CH_3$	40
2- Pentyne	$H_3C-C\equiv C-CH_2-CH_3$	55

16.6 CHEMICAL PROPERTIES OF ALKYNES

The chemistry of alkynes is the chemistry of carbon-carbon triple bond. Alkyne undergo electrophilic addition reactions due to the availability of loosely bonded π electrons. Due to the presence of the two π bonds, alkynes undergo addition of two molecules of the reagent.

16.6.1 Reduction

Alkynes on hydrogenation in the presence of a catalyst like nickel are converted to alkenes in the first step. These alkenes add on the second mole of hydrogen to form the corresponding alkanes.

$$-C\equiv C- \xrightarrow{H_2/Ni} \underset{\begin{array}{cc}|&|\\H&H\end{array}}{-C=C-} \xrightarrow{H_2/Ni} \underset{\begin{array}{cc}|&|\\H&H\end{array}}{-C-C-}$$

An alkyne — An alkene — An alkane

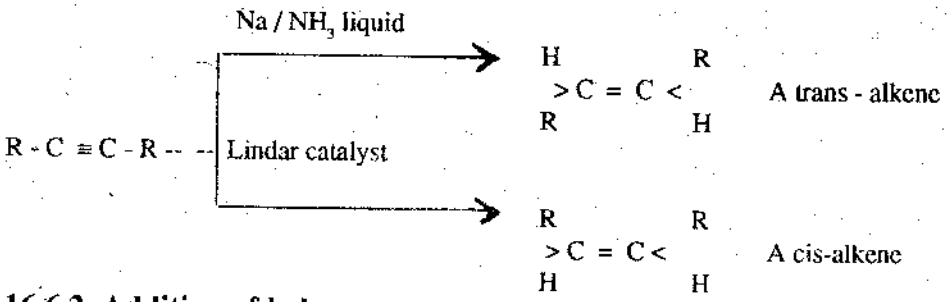
Propyne is converted into propane through propene

16.6.1 Partial reduction

Alkynes are partially reduced by sodium or lithium in liquid ammonia to give corresponding alkenes. Partial reduction of an appropriately substituted alkyne may be expected to yield either a cis-

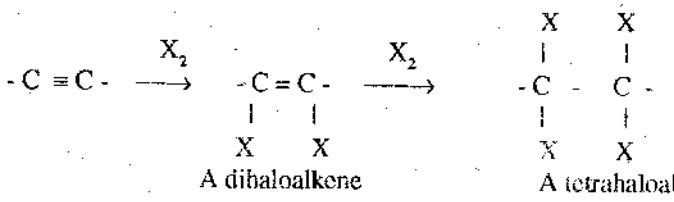
or a trans-alkene. Generally trans-alkenes are obtained, when alkynes are reduced by sodium or lithium in liquid ammonia, where as cis-alkenes result by catalytic hydrogenation.

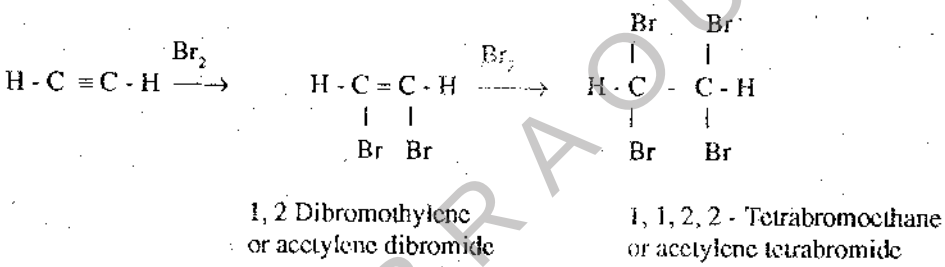
Alkynes are reduced to cis alkenes by hydrogenation in the presence of a specially prepared catalyst called Lindlar catalyst.



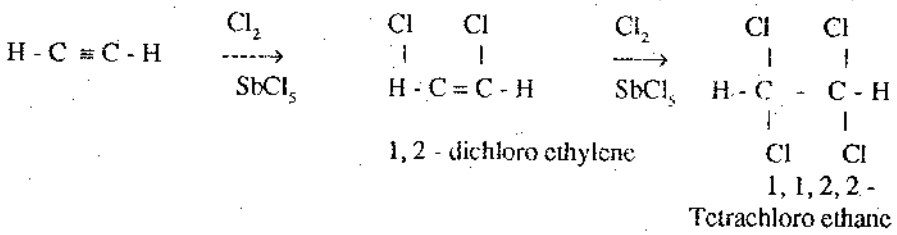
16.6.2 Addition of halogens

Alkanes react with two moles of halogen forming first vic - dihalo alkene and finally tetrahaloalkane.





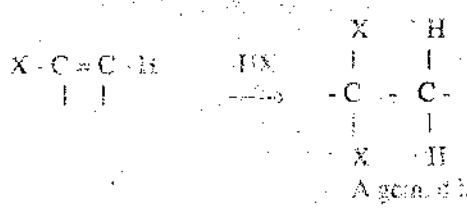
Addition of chlorine to acetylene generally requires the presence of antimony pentachloride or ferric chloride. The product is 1, 1, 2, 2 - tetrachloroethane.



16.6.3 Addition of hydrogen halide

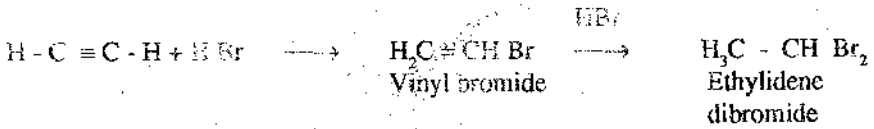
Alkynes add on two molecules of hydrogen halide in stages.

The addition of second molecule of hydrogen halide takes place according to **Markownikoff rule.**



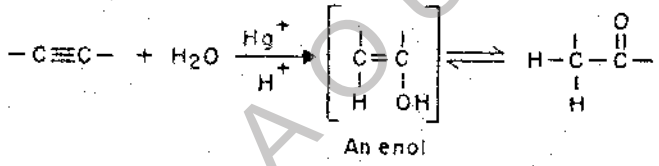
A gem. dihaloalkane

Acetylene reacts readily with one mole of hydrogen chloride to form vinyl chloride. Further addition of hydrogen chloride to vinyl chloride is difficult and takes place very slowly. On the other hand, the addition of HBr or HI to vinyl bromide and vinyl iodide respectively occurs readily.



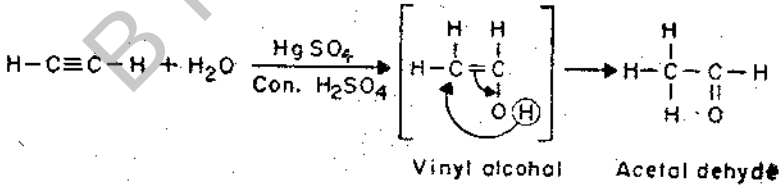
16.6.4 Catalytic hydration

Alkynes can be hydrated in the presence of concentrated sulphuric acid containing mercuric sulphate ($HgSO_4$). A molecule of water adds to the triple bond giving a carbonyl compound as the product. The product of the initial addition is an unsaturated alcohol (enol) which undergoes tautomerism to give the carbonyl compound. The product of catalytic hydration of acetylene is acetaldehyde. Conversion of vinylalcohol to acetaldehyde is called keto-enol tautomerisation. In this process migration of a proton and a double bond may be assumed to proceed in opposite directions. Tautomerisation represents 1, 3-proton shift. The keto and enol forms of carbonyl compounds represent dynamic structural isomers, commonly called tautomers.



An enol

Example

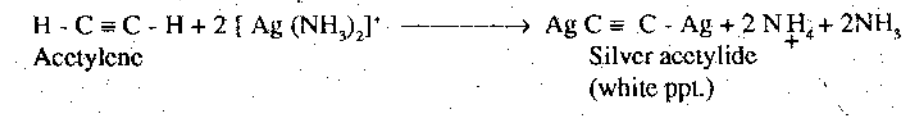


Vinyl alcohol Acetal dehyde

16.6.5 Reactions with metals

1-Alkynes react with ammonial solutions of silver and cuprous salts precipitating corresponding metal alkynides. This test is used to distinguish 1-alkynides. This test is used to distinguish 1-alkynes (eg. 1-butyne) from other alkynes (eg. 2-butyne), in which the triply bonded carbons are not directly attached to a hydrogen atom. Acetylene forms a white precipitate of silver acetylide and a red precipitate of cuprous acetylide.

Free alkynes are regenerated from cuprous salts by treatment with a dilute mineral acid. This reaction provides a qualitative evidence for the presence of 1-alkyne. This reaction may also be used to remove impurities of 1-alkyne from other hydrocarbons.



Acetylene Silver acetylide (white ppt.)

$$H - C \equiv C - H + 2[Cu(NH_3)_2]^+ \longrightarrow \underset{\text{Cuprous acetylide (red ppt.)}}{Cu\,C \equiv C - Ag} + 2NH_4^+ + 2NH_3$$

Alkynes also form salts with alkali metals. For instance acetylene reacts with sodium metal in liquid ammonia to form sodium acetylide. The sodium and other alkali metal salts of acetylenes hydrolyses readily in water.

$$H - C \equiv C - H + Na\,NH_2 \xrightarrow[\text{liquid ammonia}]{} H - C \equiv C - Na + NH_3$$

$$H - C \equiv C - Na + H_2O \longrightarrow H - C \equiv C - H + Na\,OH$$

16.6.6 Oxidation

Acetylene on oxidation in presence of potassium permangartate forms CO_2 and water as ultimate products. The reaction occurs through the intermediacy of an enediol, glyoxal and oxalic acid.

$$H - C \equiv C - H \xrightarrow[KMnO_4]{[O]} \underset{\text{An enediol}}{H - \overset{OH}{C} = \overset{OH}{C} - H} \xrightarrow{[O]} \underset{\text{Gyloxal}}{H - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - H} \xrightarrow{[O]}$$

$$\underset{\text{Oxalic acid}}{HO - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - OH} \xrightarrow{[O]} CO_2 + H_2O$$

16.6.7 Acidity of 1 - alkynes

According to Lowry and Bronsted theory of acids and bases. Acidity is the tendency of a compound to lose hydrogen as proton. In organic chemistry, we come across weaker acids which do not turn blue litmus to red and which do not have sour taste. Acetylene is more acidic than ethylene and ethane. In ethane the carbon atom, linked to hydrogen, is in sp^3 hybridised state i.e. with 25% s-character, in ethylene and acetylene the carbon atoms are in sp^2 and sp hybridisation states respectively. Thus the percentage of s-character of carbon atoms in ethylene and acetylene are 33 % and 50% respectively.

$H_3C - CH_3$	$H_2C = CH_2$	$H - C \equiv C - H$
Ethane	Ethylene	Acetylene
(carbon with 25% s- character)	(carbon with 33% s- character)	(carbon with 50% s - character)

Due to 50% s-character of acetylenic carbon, the electrons of a C-H bond are comparatively closer to the carbon atom. Therefore, the hydrogen atom attached to an acetylenic carbon (sp hybridised carbon) is mobile and can be lost as a proton i.e. acetylene is an acidic hydrocarbon. The ionisation constants of ethane, ethylene and acetylene support this view.

Check your progress - 2

How do you differentiate between propane, propene and propyne?

Name of the compound	Molecular formula	K_a value
Ethane	C_2H_6	$< 10^{-40}$
Ethyl ene	C_2H_4	10^{-40}
Acetylene	C_2H_2	10^{-33}

16.6.8 Isomerisation

Under the catalytic influence of sodium amide, 2 - alkynes isomerise to 1-alkynes. 2 - Butyne is converted to 1-butyne. If 1- alkynes are heated with alcoholic potassium hydroxide, isomerisation takes place in the reverse direction and 2 - alkynes are obtained.

$$H_3C - C \equiv C - CH_3 \underset{\text{alc. KOH}}{\overset{\text{Na NH}_2}{\rightleftharpoons}} H_3C - CH_2 - C \equiv C - H$$

2- Butyne 1- Butyne

16.7 PREPARATION OF ACETYLENE

The alkyne of utmost industrial importance is acetylene. It is prepared by the action of water (hydrolysis) on calcium carbide.

$$Ca\,C_2 + 2H_2O \rightarrow H - C \equiv C - H + Ca(OH)_2$$

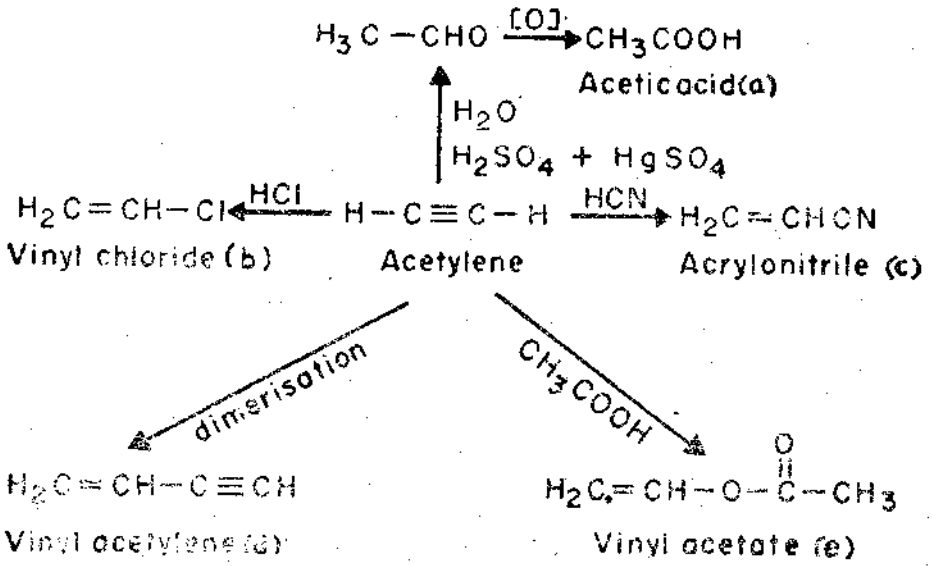
The carbides of other metals also, on hydrolysis, give alkynes. Magnesium carbide gives a mixture of alkene and propyne.

$$2\,Mg_2C_3 + 8H_2O \longrightarrow H_2C = C = CH_2 + H - C = C - CH_3 + Mg(OH)_2$$

16.8 USES OF ACETYLENE

The flame of acetylene burning in oxygen is extremely hot (4000°). Oxy-acetylene torches are used for cutting and welding steel. Most of the acetylene produced is used in the manufacture of other chemicals. Vinyl chloride vinyl acetate, acetaldehyde, acetic cid, acrylonitrile and neoprene are some of the industrially important chemicals commercially obtained from acetylene.

Major routes from acetylene to important chemicals



a) Acetic acid : used in the production of dyes, perfumes, esters, Pharmaceuticals etc.
b) Vinyl chloride : used in plastic industry.
c) Acrylonitrile : used for the preparation of Buna-N-rubber.
d) Vinyl acetylene: used in the production of synthetic rubber.
e) vinyl acetate : used in plastic industry.

16.9 SUMMARY

This unit discussed the aliphatic hydrocarbons with C ≡ C called alkyne or acetylenes. The general formula is C_nH_{2n-2} and exhibits position isomerism.

Alkynes are prepared from
a) dihaloalkanes by dehydrohalogenation
b) tetrahaloalkanes by dehalogenation
c) calcium carbide by hydrolysis
They are insoluble in water but are soluble in C_6H_6, CCl_4, ether etc.
They are conveted to
a) alkanes upon hydrogenation
b) tetrahaloalkanes on halogenation
c) gem. dihaloalkanes on treatment with HX.
d) Carbonyl compounds on treatment with H_2O in presence of catalyst, which involves 1,3-proton shift called tautomerism. I-Alkynes are distinguished by their ability to form metal salts with ammoniacal solutions of copper or silver.

16.10 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines

1. The molecular formula of a hydrocarbon (X) is C_6H_{10}. On hydrogenation X gives 2- methyl pentane. On the treatment with water in the presence of mercuric sulphate and dilute sulphuric acid gives ammoniacal cuprous chloride solution. Write the structures of X Y, and formulate the above reactions.

2. Write briefly about the following:
   (a) Tautomerism (b) Acidity of 1- alkynes
   (c) Vic - dihalides (e) Gem. alkyl dihalides.

II. Answer the following in 30 lines

1. How is a acetylene is prepared industrially? What are the industrially important compounds, obtained from acetylene?
2. Give two methods of preparation of 1-propane, What happens when propyne reacts with the following reagents? Write equations giving names of the products.

   (a) Br_2 (b) HBr (c) 1 mole of HCN (d) Ammonial silver nitrate solution
   (e) $HgSO_4$ dissolved in sulphuric acid (f) $NaNH_2$ and later with ethyl Iodide

16.11 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Acetylene is prepared on large scale by hydrolysis of calcium carbide.

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + HC \equiv CH$$

2. Propyne reacts with ammoniacal soluttions of silver and cuprous salts precipitating corresponding metal alkynides. This test is used to differentiate propyne from propene and propane. Propene is distinguished from propane as it decolourises alkaline $KMnO_4$ solutions (Bayer's test).

Author : Mrs. C. Sesharatnam

UNIT - 17 ARENES

Contents

17.1 AIMS AND OBJECTIVES

In this unit we discuss the structure of benzene, aromatic character and characteristic reactions of benzene. And also we explain you the orientation in electrophilic reactions of monosubstituted benzenes. Finally we discuss the chemistry of alkyl benzenes. By the end of this unit you will be able to understand.

- Structure of benzene
- Resonance energy of benzene
- Aromatic character
- Characteristic reactions of benzene
- Alkyl benzenes - nomenclature
- Preparation of alkyl benzenes
- Physical properties of alkyl benzenes
- Chemical properties of alkyl benzenes

17.2 INTRODUCTION

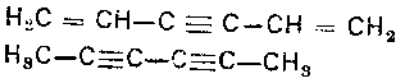
Aromatic hydrocarbons are also called arenes. Benzene is parent aromatic hydrocarbon. Other examples of arenes are naphthalene, anthracene and phenanthrene. Benzene was discovered by Faraday in 1825 from the ocondensates in pipes used for conducting coke-oven gases. Its molecular formula (C_6H_6), was determined by Mitscherlich in 1834. The degree of unsaturation of hydrocarbons is indicated by the C /H ratio. The general formula for alkanes is $C_n H_{2n+2}$, for the alkenes $C_n H_{2n}$ and for the alkynes $C_n H_{2n-2}$. The molecular formula of benzene C_6H_6 - corresponding to general formula $C_n H_{2n-6}$, suggest a high degree of unsaturation. But surprisingly benzene does not undergo addition reactions which are characteristic of aliphatic unsaturated compounds. Benzene under normal enditions undergoes substitution reactions. The following table compares the chemical reactins of benzene with those of alkenes.

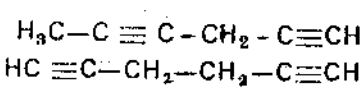
Alkenes	Benzene
1. oxidised rapidly by cold $KMnO_4$ or conc. HNO_3	1. Stable to $KMnO_4$ or conc. HNO_3 at moderate temperatures.
2. Add on halogens, hydrogen, hydrogen halides and H_2SO_4 at O°C.	2. Does not undergo addition of hydrogen halides and H_2SO_4 at O°C
3. Easily polymerized	3. Does not polymerize
4. Undergo addition reactions	4. Undergoes substitution reactions.

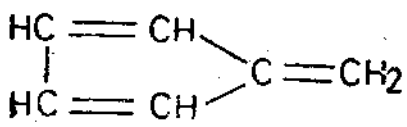
Benzene and its derivatives possessing characteristic aroma were called aromatic compounds. But now-a-days aromatic character or aromoaticity character or aromaticity is linked with the reactivity of a compound. Compounds whose molecular formulas reveal unsaturation but do not undergo addition reactions, and instead undergo substitution reactions are called aromatic compounds. The tendency of unsaturated compounds to undergo preferentially substitution reactions is called aromatic character or aromaticity.

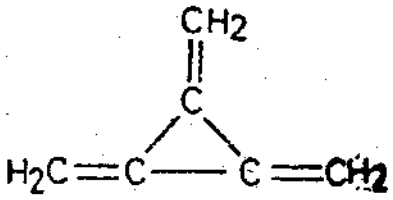
17.3 STRUCTURE OF BENZENE

One of the most perplexing problems facing organic chemists has been the structure of benzene. Several acyclic and cyclic structures indicating unsaturation, with the formula C_6H_6, were suggested for benzene. Following are some such structures:



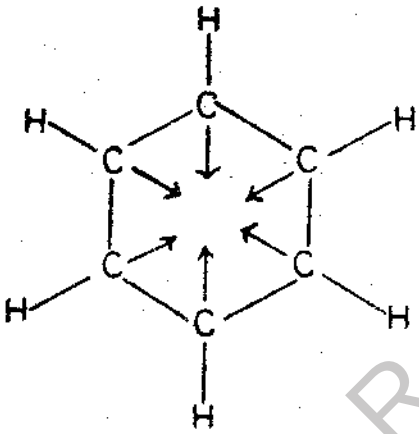




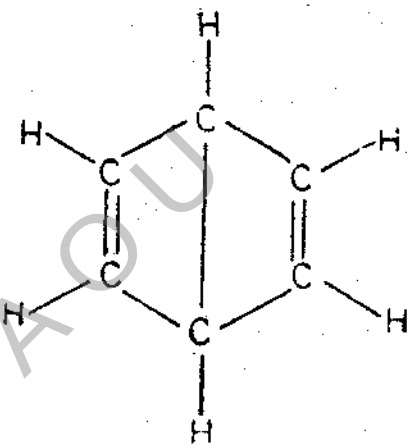


Since benxzene does not undergo addition reactions typical of unsaturated compounds these structures were discarded. Several six membered cyclic structures were proposed for benzene. Following are some of the structures, which were rejected on one ground or the other.

17.3.1 Dewar's structure



Armstrong-Baeyer's structure (1867)

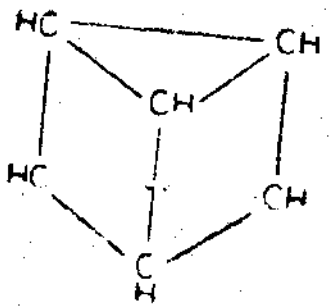


Dewar's structure (1867)

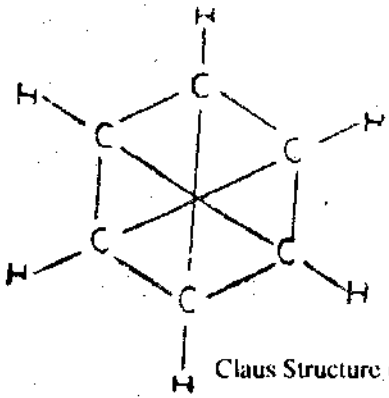
Dewar's of structure would produce only two types of di-substituted products. But in practice benzene produces three types of disubstituted compounds. Hence it was rejected.

17.3.2 Armstrong-Baeyer's structure

In Armstrong-Baeyer's structure the fourth bond of each carbon is directed towards the centre of the ring - a situation quite unacceptable.

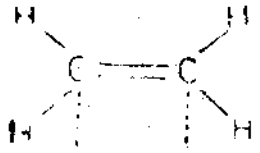


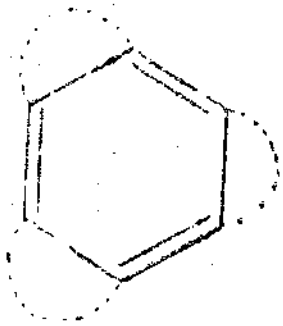
Ladenburg's Prism Structure (1869)



Claus Structure (1867)

The objections to the above sructures are essentially the same as those against the Dewar's structure. These structures suggest that substituted benzenes should exhibit optical activity. This infact has not obeen observed.





Residual Valency

Thiele's Structure (1889)

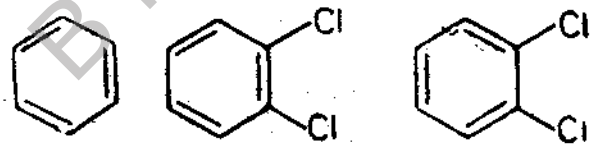
17.3.3 Thiele's structure

According to thiele an unsaturated carbon does not fully utilize its combining capacity, and therefore a residual valency exists at an unsaturated carbon. Therefore, an alkene such as ethylene undergoes addition reactions.

However, in a six membered cyclic structure for benzene the residual valencies on adjacent carbon atoms are neutralized. This accounts for the reluctance of benzene to undergo addition reactions. This structure was also rejected because of the lack of experimental evidence for such a hypothesis. A reasonable structure for benzene was proposed by Kekule in 1865. He suggested a six membered cyclic structure for benzene with alternate single and double bonds.

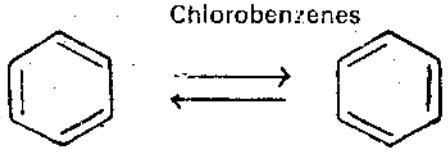
17.3.4 Kekule's structure

On the basis of the structure proposed by Kekule for benzene two o-disubstituted benzenes such as o-dichlorobenzenes are possible. In (I) the two chlorine atoms are attached to two adjacent carons which are joined by a double bond. In (II) the two chlorine atoms are linked to two carbons which are joined by single bond. However all attempts to prepare two-o-dichlorobenzenes have been unsuccessful i.e. only one o-dichloro benzene exists. To account for this discrepancy Kekule proposed that in benzene the double bonds flipped back and forth, giving rise to two types of molecules at any instant.



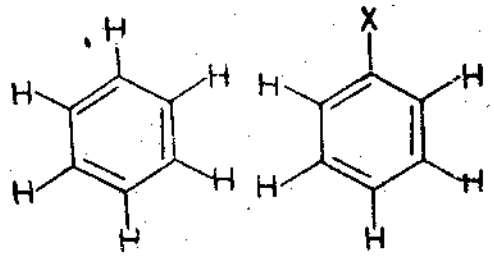
II

Chlorobenzenes

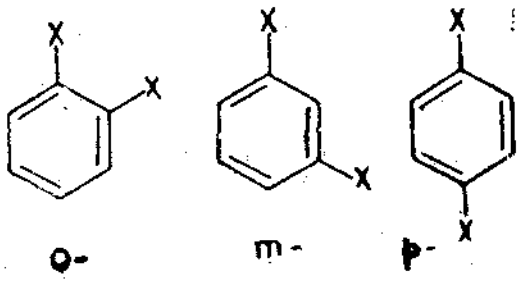


III IV

Kekule proposed that the two equivalent structures for benzene (III & IV) are interconvertible quite rapidly. As a result the structures III & IV become indistinguishable and the double bonds are not localized, explaining the reluctance of benzene to undergo addition reactions. Benzene does not normally undergo addition reactions.

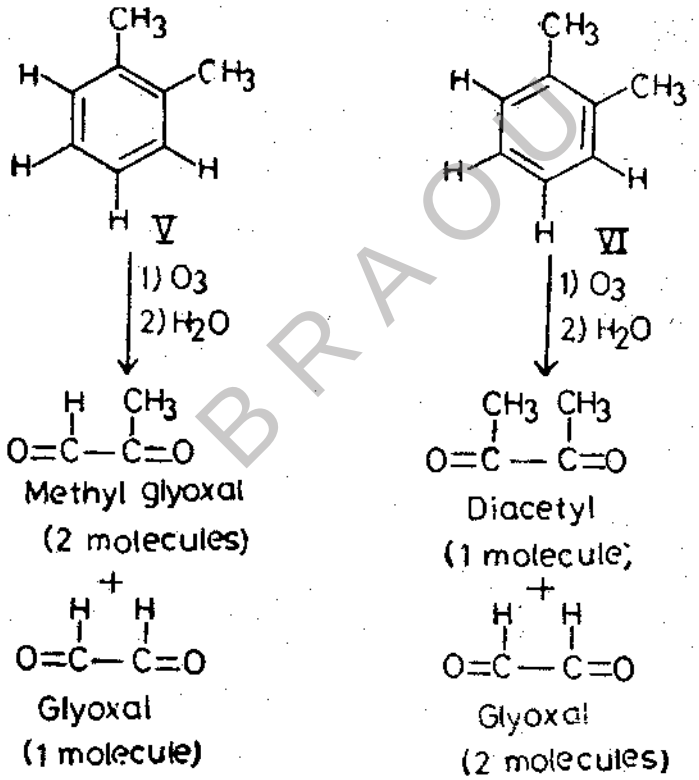


Mono Substituted Benzene



Isomeric disubstituted benzenes

It can form only one mono substitution derivative and three di-substitution products. Not long after this, ozonolysis experiments with aromatic hydrocarbons provided strong evidence for Kekule structure. Levine and Cole proved experimentally the correctness of the dyanamic structure proposed for obenzene by ozonolysis of o-xylene. They obtained glyoxal, methyl glyoxal and diacetyl in 3:2:1 ratio. This can be explained by the two inter convertible Kekule structures, V & VI, for o-oxylene.



Structure	Glyoxal	Methyl glyoxal	Diacetyl
Structure - V	1	2	0
Structure - VI	2	0	1
From a mixture of V & VI	3	2	1

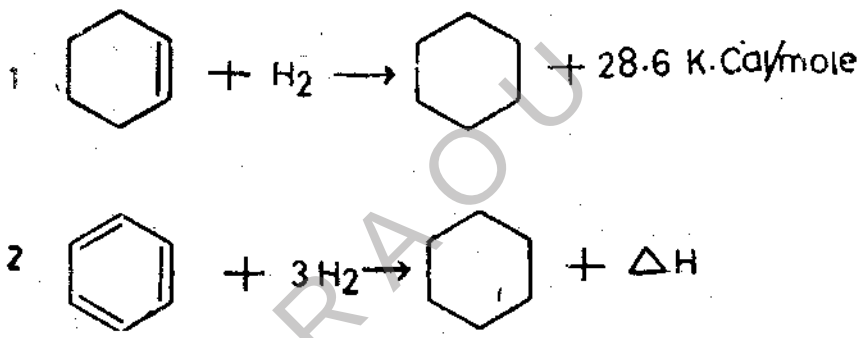
If o-oxylene had structure V, one molecule of glyoxal and two molecules of methyl glyoxal would be formed and diacetyl is not formed. On the other hand, from structure VI, one may expect two molecules of glyoxal and one molecule of diacetyl and no methyl glyoxal. Formation of glyoxal, methyl glyoxal and diacetyl in 3:2:1 ratio only be explained, if at any moment , o-xylene is assumed to be present as a mixture of V & VI.

According to modern structural theory of organic compounds benzene is not regarded as a mixture of III and IV. The structure of benzene is neither III nor IV but has some resemblances to both III and IV. In other words, benzene is regarded as a resonance hybrid of two Kekule structures, When the properties of compound cannot be explained by a single structure, and two or more structures are necessary to account for it's properties, the compound is said to exhibit resonance phenomenon. The compound is called resonance hybrid and the structures are called resonance structures.

17.4 RESONANCE ENERGY

A resonance hybrid is more stable than any of the most stable resonance structures. This difference in energy is called resonance energy. The resonance energy of benzene is 36 K. Cal/mole. This has been determined by measuring the heats of hydrogenatin and combustion of benzene.

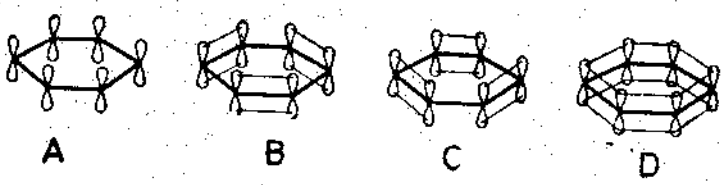
The amount of heat that is liberated when one mole of unsaturated compound undergoes hydrogenation is known as heat of hydrogenation.



1. cyclohexene
2. cyclohexatriene or benzene

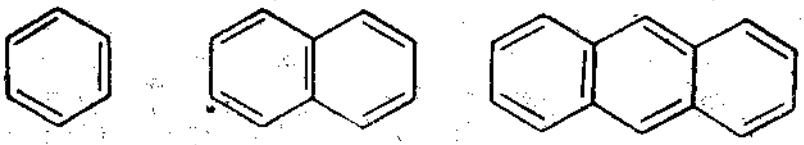
The experimentally determined value for the heat of hydrogenation of a compound containing one double bond such as cyclohexxene is 28.6 K. Cal/mole. If benzene is considered as 1,3,5 cyclohexatriene, as per the above data, the heat of hydrogenation of benzene may be calculated as 3x28.6 = 85.8 K. Cal/mol. But the experimentally determined heat of hydrogenation of benzene is 49.8 K. Cal/mole. This means that benzene is more stable than 1,3,5 cyclohexatriene by (85. 8-49.8) 36 K. Cal/mole. This value of 36.0 K.Cal/mole of benzene is known as resonance energy or stabilization energy of benzene.

The carbon-carbon bonds in benzene are neither double nor single bonds. All the C-C bonds in benzene were found to be 1.39 A° in length i.e. intermediate between a C-C single bond (1.54 A°) and a C-C double bond (1.34A°). Benzene is formed from six sp^2 hybridised carbons and six hydrogens. Each carbon utilizes two sp^2 hybridised carbons and six hydrogens. Each carbon utilizes two sp^2 hybridised orbitals to form two C-C bonds and the third sp^2 hybridised orbital to form a C-H bond. All the six carbons and the hydrogens attached to them are co-planar. Each carbon is then left with one unhybridised p-orbital. These six p-orbitals lie in a plane perpendicular to the plane of the ring (A). When two adjacent p-orbitals laterally overlap a π - bond is formed. Six p-orbitals ovreap in two ways giving rise to two Kekule structures (B & C).



17.5 AROMATIC CHARACTER

Extensive overlap of six π -electrons in benxzene gives rise to a π -electron cloud above and below the plane of the benzene ring. The electron cloud due to six p-electrons is spread over the six carbons. In other words the π -bonds in benzene are not localized. Delocaization of π -bonds is known as resonance. According to Huckel, cyclic conjugated unsaturated structures with $4n + 2\pi$ electrons (where 'n' is an integer) are aromatic. This is known as Huckel's $4n + 2$ π electron rule. Benzene, naphthalene and anthracene are all aromatic compounds according to Huckel's rule.



Benzene Napthalene Anthracene

Although cyclooctatetraene is a cyclic conjugated molecule, it contains $4n$ π electrons and is therefore non-aromatic. Its resonance energy was found to be only 4.8 K. Cal/mole.

Cyclooctatetraene

Check your progress - 1

Explain Huckel's rule.

17.6 CHARACTERISTIC REACTIONS OF AROMATIC COMPOUNDS

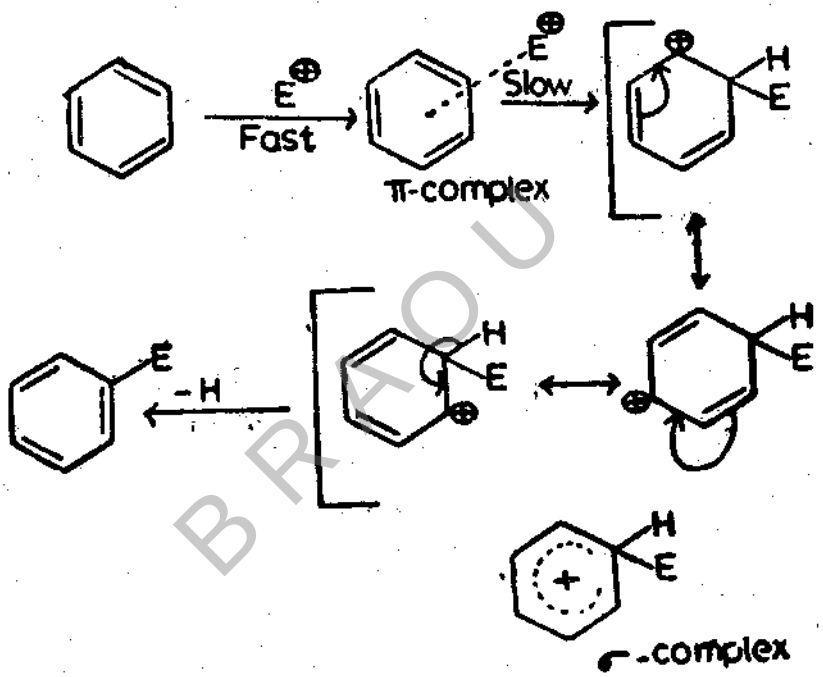
17.6.1 Electrophilic substitution reactions

We have already seen that the characteristic reactions of benzene involves substitution reactions. We have seen that there exists a π -electron cloud above and below the plane of the benzene ring. Any

reagent attacking carbon atoms of the benzene ring has necessarily to come into contact with the π-electron-cloud. Therefore electron deficient species (electrophilic reagents) are attracted by the π-electron cloud, whereas electron surplus species (nucleophilic reagents) are repelled. This precisely is responsible for the electrophilic attack on the benzene molecule. Electrophilic attack may theoretically be expected to result in addition or substitution. Addition leads to loss in aromaticity of benzene, whereas substitution results in the retention, if not enhancement, of aromatic character of benzene molecule. Therefore benzene normally undergoes electrophilic substitution reactions.

17.6.2 General mechanism for electrophilic substitution reactions

In electrophilic substitution reactions benzene serves as a Lewis base. In the first step, the electron seeking i.e. electrophile forms a loose complex with π-electron cloud of the benzene. This complex is kmnown as a π-complex. The π-complex is slowly converted into a σ-complex. In this sigma complex one of the carbon atoms of benzene molecule is bonded to the electrophile by a π bond. The two electrons constituting the σ-bond are derived from the 6 π-electrons of benzene. The formation of the σ-complex, thus, leads to loss of aromatic character. Therefore formation of σ complex is the slow step in the electrophilic substitution reactions of benzene. The σ-complex eliminates a proton to give monosubstituted benzene. It may be noted that elimination of proton results in regaining of aromatic character. Therefore this step is a fast step.

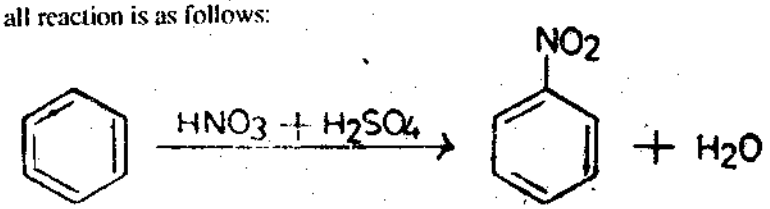


E^+ = Electrophile

The common electrophilic substitution reactions of benzene are nitratiion, halogenation, sulphonation and Frieldel-crafts acylation and alkylation reactions.

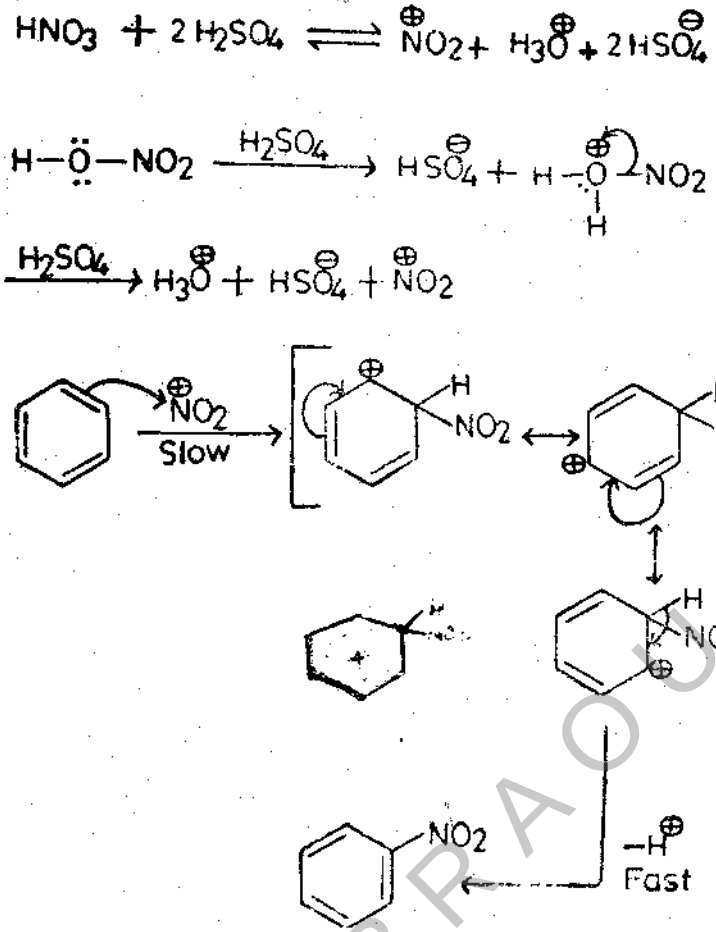
17.6.2.1 Nitration

Benzene on nitration with a mixure of concentrated nitric acid and sulphuric acid produces nitrobenzene. The over all reaction is as follows:



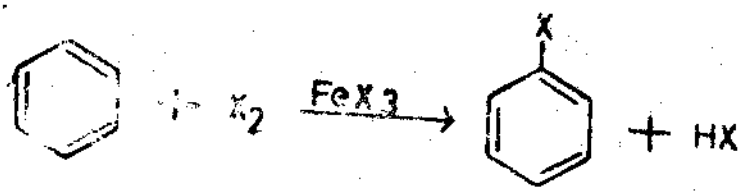
In the nitration of benzene, nitronium ion is the attacking electrophile. The evidence for formation of nitronium ioin has been deduced spectroscopically. A four-fold depression in the freezing point of nitric acid in sulphuric acid supports the formation of nitronium ion. Salts containing nitronium ion such as nitronium perchlorate (No_2^+ ClO_4^-), have actually been isolated.

Mechanism :

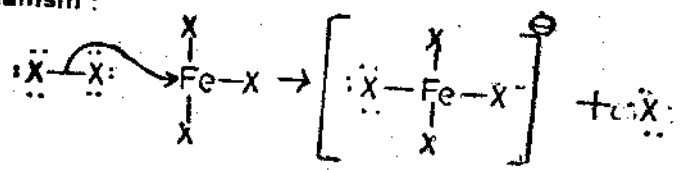


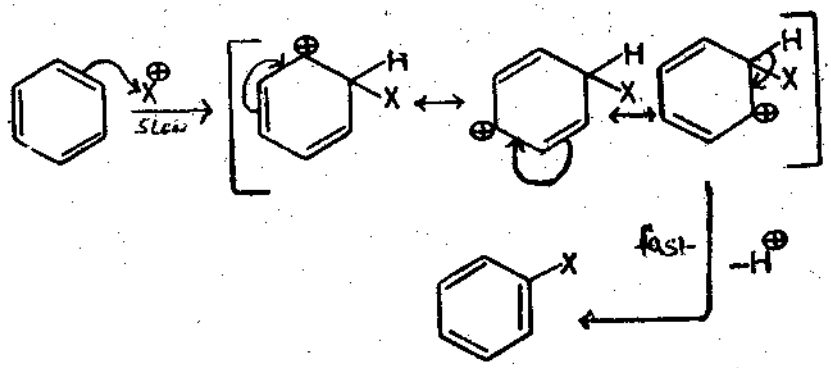
17.6.2.2 Halogenation

When treated with halogens in the preence of Lewis acids such as aluminium, ferric or zinc halides benzene undergoes halogenation. These halides are known as halogen carriers. The reaction with iodine is too slow.



Mechanism :

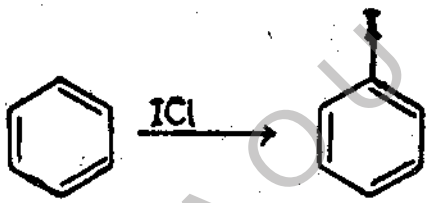




The electrophilic attack, in halogenation of benzene, is supported by the reaction of benzene with

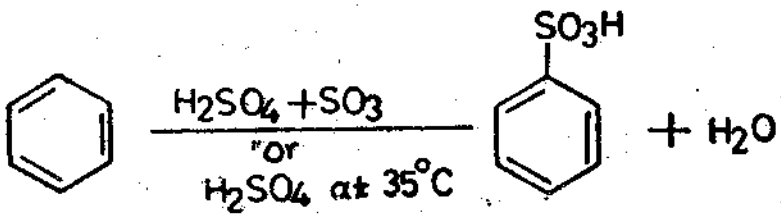
$\overset{\alpha+}{I}-\overset{\alpha-}{Cl}$

interhalogan compounds such as I - Cl. This reaction leads exclusively to iodobenzene. Chlorobenzene is not formed in this reaction.

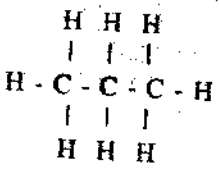


17.6.2.3 Sulphonation

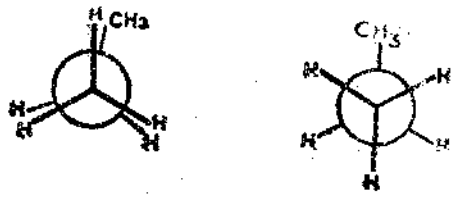
The process of substituting a hydrogen of benzene molecule by a sulphuric acid group (- SO_3H) is called sulphonation. Sulphonation can be carried **out** by oleum i.e. conc. H_2SO_4 containing excess sulphur trioxide, at room temperature or by conc sulphuric acid at higher temperature.



14.9.2 Conformers of propane



Propane is derived by replacement of a hydrogen in ethane by a methyl group. In this molecule there are two C-C bonds around which rotation can occur. The same results are obtained by rotation about any of these C-C bonds. The two extreme spatial arrangements of groups possible in propane due to rotation about C-C bond are called eclipsed and staggered conformations.

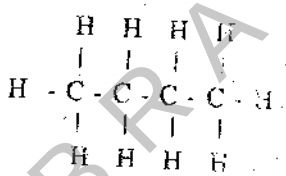


Eclipsed conformation staggered conformation

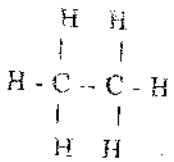
Conformers of propane

The preferred conformer is staggered one. It has been shown to have 3.3 K. cal/mole, less energy than the eclipsed conformation.

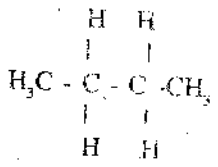
14.9.3 Conformers of n- butane



There are three C-C bonds in butane. The conformations obtained by either C_1 - C_2 or C_3-C_4 bond rotation would be the same as in case of propane except the methyl group is substituted by the ethyl grop. The interest to us, however, would be the various conformations of the molecule obtained by rotatioon around C_2-C_3 bond. When we consider the C_2 - C_3 bond we see an ethane-like molecule but with two methyl groups replaceing one hydrogen on each carbon atom of butane.

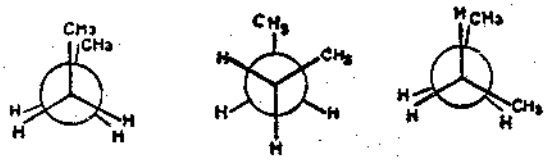


Ethane



n- Butane

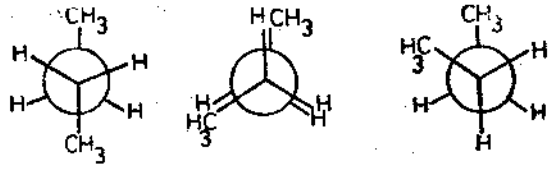
Of the possible conformations for butane six arising due to the rotation around C_2-C_3 bond, are noteworthy.



I. Fully eclipsed conformation (syn form)

II. Gauche conformation (after 60° rotation)

III. Eclipsed conformation (CH_3 eclipses H) (after 120° rotation)



IV. Anti conformation (after 180° rotation)

V. Eclipsed conformation (after 240° rotation)

VI. Gauche conformation (after 300° rotation)

Conformers of n- butane

Gauche and anti conformations II and IV are staggered conformations and are free from torisonal or eclipsing strain. Anti conformation (IV) has the added advantage of being free from van der Vaals stain too (as the methyl groups are maximum apart). Eclipsed conformationss I and III s ffer from torsional strain. Conformation I also suffers from van der Waals strain as the two bulky groups (methyl groups) are thrown very close to each other. Conformation VI and V, are identical with II and III respectively.

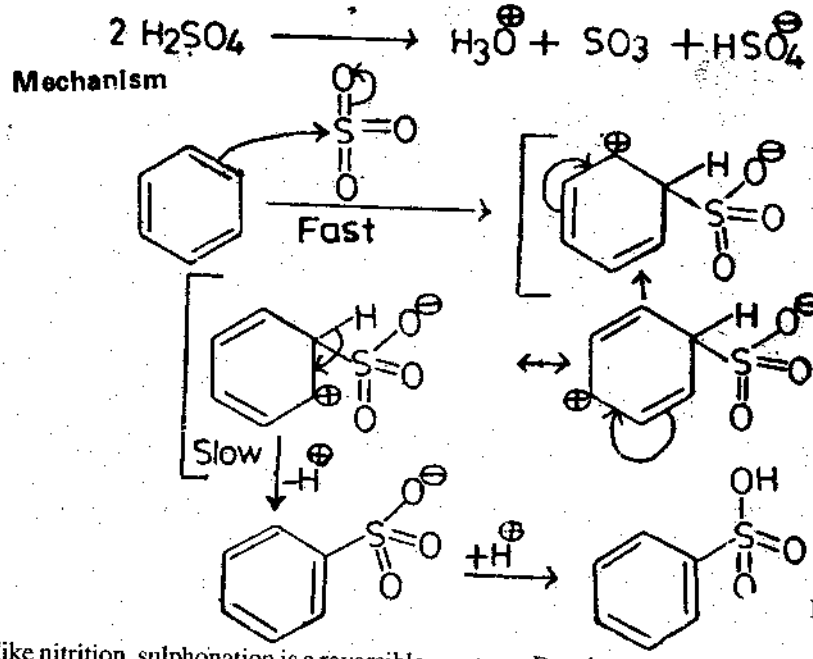
The decreasing order of stability of conformations in butane is there for IV> II> III> I.

14.10 CHEMICAL PROPERTIES OF ALKANES

Being saturated molecules alkanes are quite inert towards common reagents at norma reaction conditions. Alkanes are non polar covalent molecules with no centre of either high or low electron density. They are therefore inert towards electrophlic and nucleophilic reagents. Under vigorous conditions however, they can be made to undergo substitution reactions. In these reactions one or more hydrogen atoms are replaced by other groups. The important chemical reactions of alkanes are halogenation, nitration, sulphonation, and oxidation. All these substitution reactions proceed through free radical mechanism.

14.10.1 Halogenation of alkanes

Alkanes react with chlorine and bromine in presence of sunlight or ultraviolet light or at high temperature to yield halogen derivatives. One, two or more hydrogen atoms may be replaced fby halogen atoms, depending upon the amount of halogen used in the reaction. Thus, methane reacts in the presence of sun light with chlorine to yield a mixture of methyl chloride, methylene chloride, chloroform, and carbon tetrachloride.



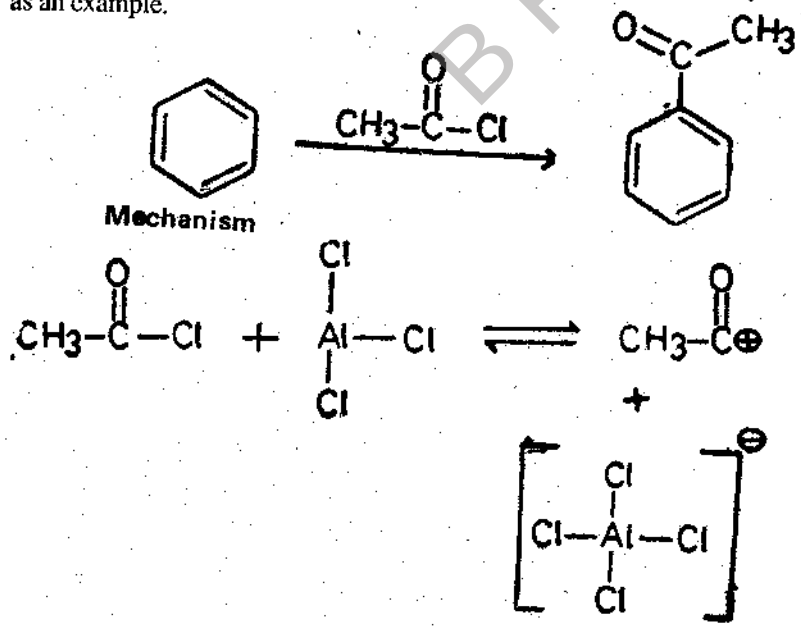
Benzene sulphuric acid

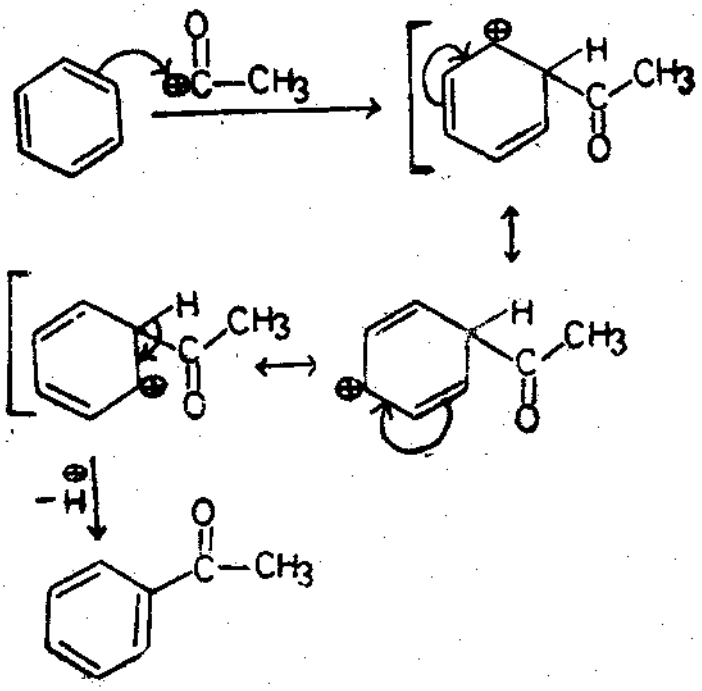
Unlike nitrition, sulphonation is a reversible reaction. Desulphonation is normally carried out by heating benzenesulphonic acid with super heated steam. Further, in sulphonation of benzene the rate determining step is the elimination of proton from the σ - complex.

17.6.2.4 Friedel-Crafts reaction

17.6.2.4.1 C- Acylation

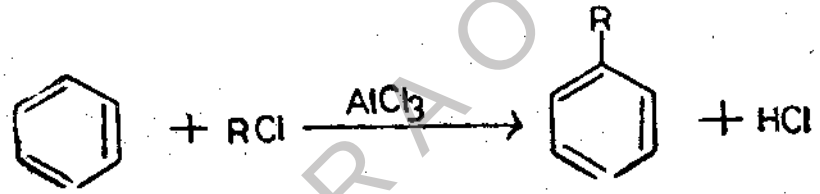
An acyl group (R - CO -) can be introduced on the carbon atom of benzene ring by Fridel -Crafts reaction. Normally benzene is reacted with an acyl chloride in the presence of anhydrous aluminium chloride. The latter is often referred to as Friedel - crafts reagent. $FeCl_3$, BF_3 and other Lewis acids have been used, in other instances. The C-acylation of benzene involves initial formation of σ - complex, by the attack initially formed acyl carbonium ion on the benzene ring. This is then followed by the loss of proton to give an acyl ketone. Both aromatic and aliphatic acyl halides may be used. Formation of acetophenone from benzene and acetyl chloride in the presence of anhydrous aluminium chloride serves as an example.



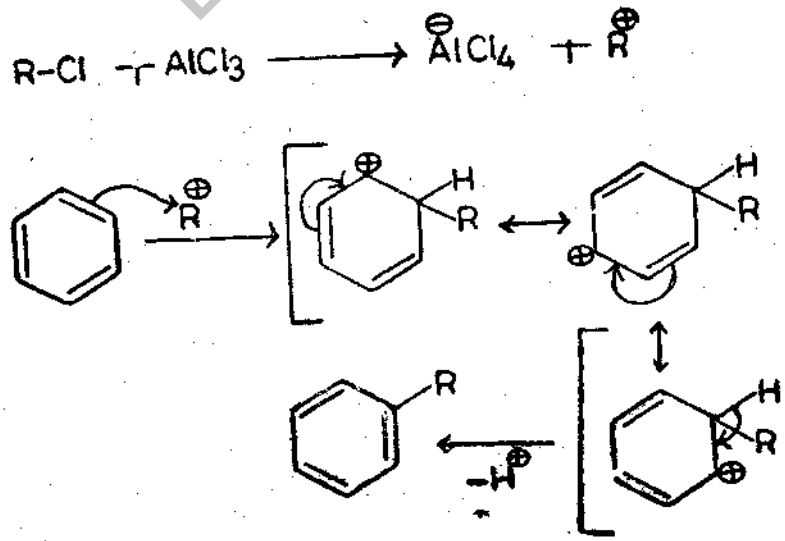


17.6.2.4.2 C- Alkylation

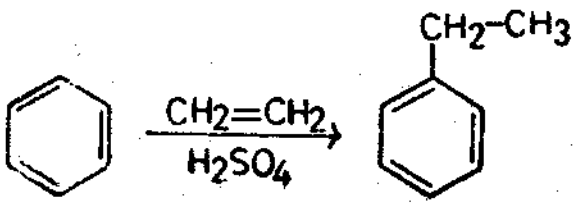
Alkyl benzzenes are also prepared by Friedel - Crafts reaction. When benzene reacts with an alkyl halide . ı the presence of aluminium chloride monoalkyl benzene is formed.



Mechanism

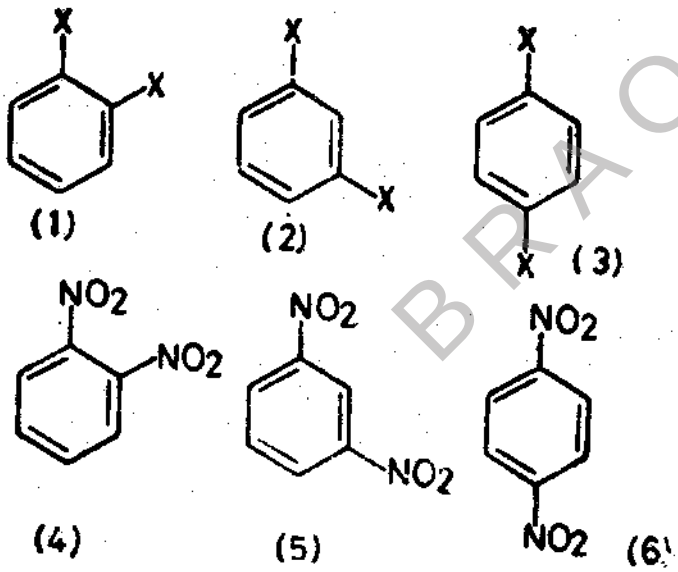


Carbonium ion is the attacking electrophile in C-alkylation of benzene. One important difference between C-alkylation and C-acylation is that the latter stops at monoacylation stage, whereas the former invariably leads to polyalkylation. Alkylation of benzene can also be carried out by using olefin in the presence of sulphuric acid. Benzene reacts with ethylene in the presence of sulphuric acid to give ethyl benzene.



17.6.2.5 Substitution reactions of monosubstituted benzenes

Disubstituted benzenes result due to introduction of another substituent in a monosubstituted benzene. Disubstituted benzenes exhibit position isomerism. Three disubstituted benzene's are possible. 1,2 Disubstituted, 1,3 - disubstituted and 1, 4-disubstituted benzenes are respectively called ortho (o-), meta (m-), and para (p-) disubstituted benzenes.

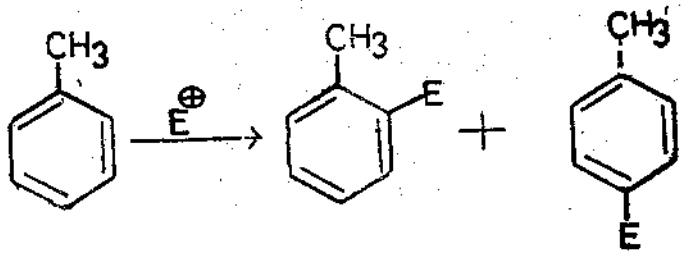


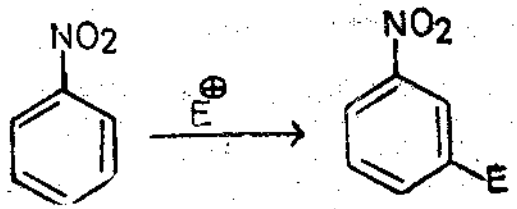
1. 1,2 Disubstituted benzene or ortho isomer
2. i,3 Disubstituted benzene or meta isomer.
3. 1,4 - Disubstituted benzene or para isomer.
4. Ortho dinitro benzene.
5. Meta dinitro benzene.
6. Para dinitro benzene.

17.6.2.5.1 Effect of substituent on electrophilic substitution reactions of monosubstituted benzenes.

All the six carbons in the benzene ring are equivalent. When benzene is subjected to electrophilic substitution reactions, only one mono substituted product is obtained. On the other hand, if a substituent is already present in benzene molecule i.e. in monosubstituted benzenes, introduction of a second substituent may result in the formation of ortho and para isomers or a meta isomer. This depends on the nature of the substituent already present in monosubstituted benzene. This is also known as directive

influence of a substituent in electrophilic substitution reactions. The nature of the substituent, already present in the benzene ring, determines the relative position occupied by the second group introduced, and the ease of electrophilic substitution. For instance, due to the presence of methyl group, toluene undergoes electrophilic substitution reactions more readily than benzene, and the second group introduced in electrophilic substitution irrespective of its nature, is directed to ortho and para positions. Thus methyl group in toluene is ring activating and it also exerts ortho, para directive influence in electrophilic substitution reactions.





Tl nitrogroup in notrobenzzene directs the incoming substituent to meta position, and nitrobenz e is less reactive in electrophilic substitution reactions than benzene. Thus, nitro group is ring deactivati : group and meta directing group.

It ha been observed that group or substituent with electron releasing tendency activates the benzene r ng owards further electrophilic substitution reactions. Such groups are known as ring activating grops. These groups exert o/p directing influence in electrophilic substitution reactions. Following are some examples of ring activating and o/p directing groups.

- OH, - NH_2 - NHR, - NR_2, - NH. CO, CH_3 -OCH_3, alkyl and phenyl groups.

When an electron attracting groups is attached to a carbon atom of the benzene ring, electron density of the ring decreases. Due to this, such a benzene derivative is not readily attacked by an electrophile. Therefore electron attracting groups are ring deactivating groups. They exert meta directing influence.

Following are some examples of meta directing groups.

-NO_2, - COOH, - CHO, - CO. CH_3, - COOR, - S_3O^3H and CN groups.

Halogens, however, are ring deactivating but exert o / p directive influence in electrophilic substitution reactions.

Directive influence of groups and their effect on electrophilic substitution reactions in monosubstituted benzenes.

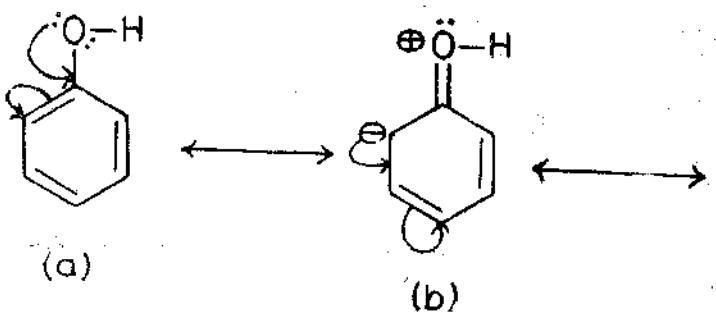
Group	Directive influence	Effect on electrophilic substitution
- OH Hydroxy group	o / p	Activating group
-NH_2 Primary amino group.....	o / p	-do-
- NH - R Secondary amino group ...	o / p	-do-
- NR_2 Tertiary amino group	o / p	-do-
- OCH_3 Methoxy group.....	o / p	-do-
- NH. CO - CH_3 Acetamido group ..	o / p	-do-
- C_6H_5 Phenyl group.....	o / p	-do-
- CH_3 Methyl group	o / p	-do-
- NO_2 Nitro group.....	m	Deactivating group
- SO_3H Sulfonic acid group.....	m	-do-
- COOH Carboxyl group.....	m	-do-
- COOR Ester group	m	-do-
_ $CONH_2$ Amide group	m	-do-
- CHO Aldehyde group	m	-do-
- CO - R Acyl group.....	m	-do-
- C = n Cyanide groups.....	m	-do-
- CF_3 Trifluoro methyl group.....	m	-do-

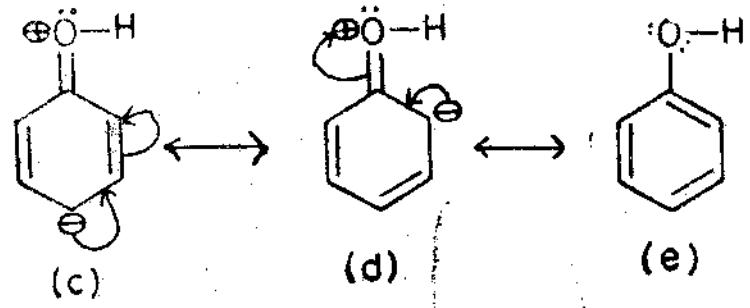
- F, - Cl, - Br, I, - $-CH_2Cl$, - - CH = CH-NO_2 are deactivating groups but exert ortho/para directive influence.

It can be seen that with the exception of halogens all ortho, para directing roups are ring activating and all meta directing groups are ring deactivting. In general, if the central atom of the groups directly attached to benzene ring carried along pair of electrons the groups is ortho, para directing. If the central atom of the group attached to obenzene ring is unsaturated, it exerts meta directive influence.

17.6.2.6 Electronic interpretation of directive influence

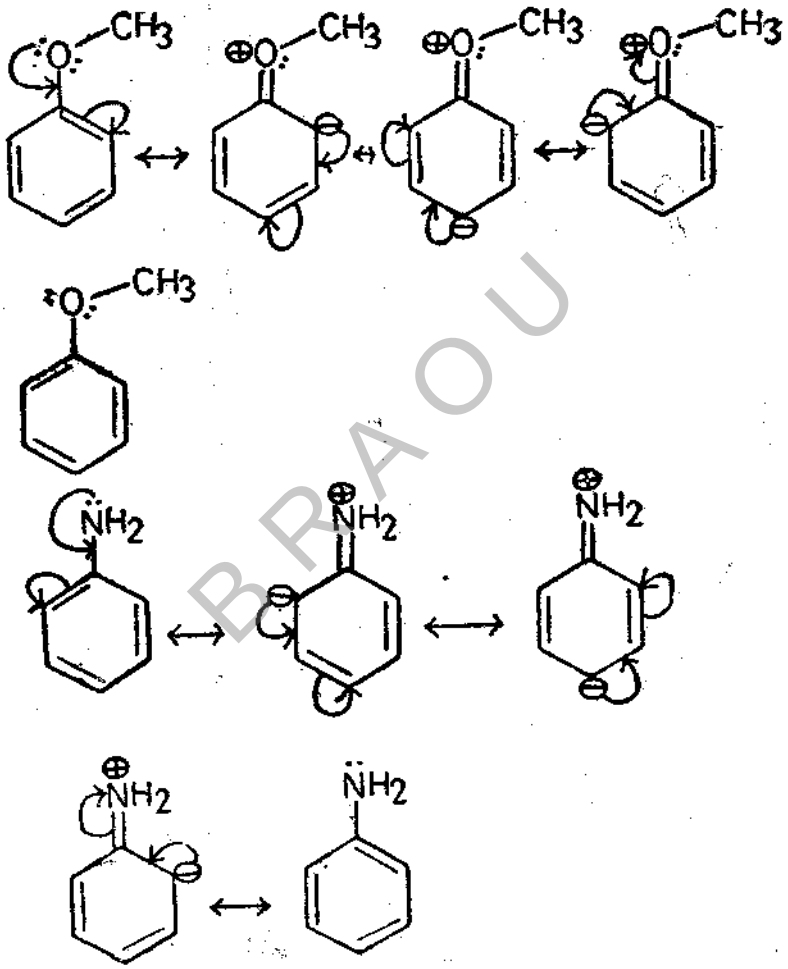
Depending on the naure of the groups attached to the benzene ring the electron density in benzene ring at certain positions increases or decreases. An electron releasing group (by exerting + I or + M effect) increases electron density in o,o' or p-position of benzene ring, leading to activation of ring towards further electrophilic substitution reactions and exerts o / p directive influence. In the case of phenol, due to + M effect of -OH group, following resonance structures are possible.





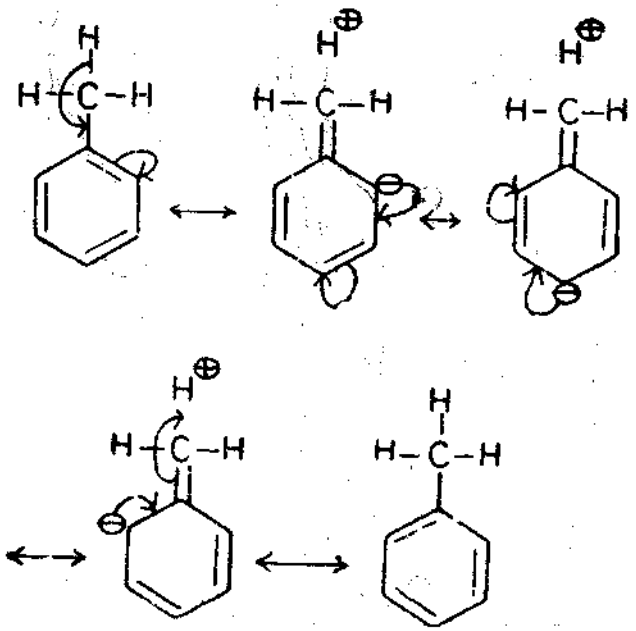
It can be seen that there structures due to charge separation o, o' or para positions carry negative charge. These positions are readily attacked by an electrophile leading to o/p substitution.

Ring activating influence and o/p directing capacity of an alkoxy group and an amino group can be similarly explained on the basis of + M effect exerted by these groups.



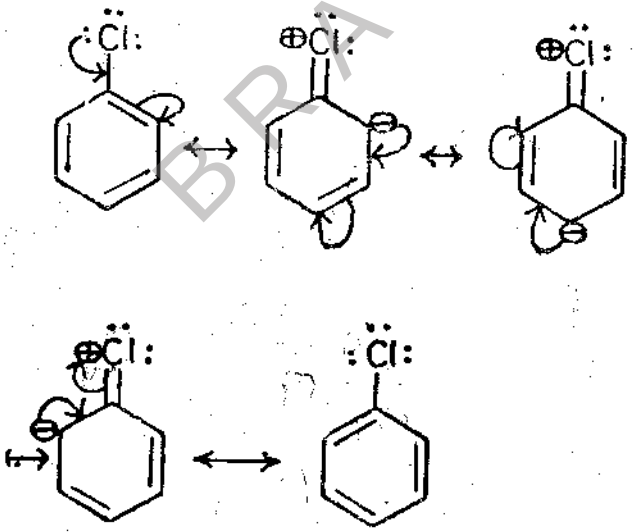
17.6.2.7 Electronic interpretation of the effect of a methyl group on electrophilic substitution reactions.

Alkyl benzenes are more reactive in electrophilic substitution reactions, than benzene. Alkyl groups are electron releasing groups exerting + I effect, and therefore exert o/p directive influence. Part of the o/p directive influence exerted by alkyl groups in alkyl benzenes is attributed to hyperconjugation which explains the electron surplus nature of ortho and para positions in toluene.



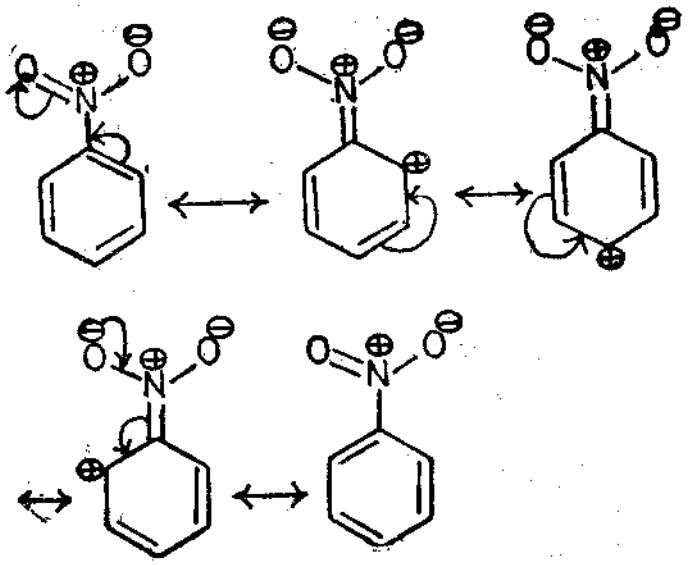
17.6.2.8 Electronic interpretation of the effect of a halogen on electrophilic substitution reactions.

Halogens are unusual in their influence on electrophilic aromatic substitution. They are deactivating groups yet ortho-para directing. The electron withdrawing inductive effect (-I effect) of halogens is responsible in general for electron deficiency of the benzene ring. Therefore, halogens react less readily than benzene in electrophilic subtitution reactions. However, through electron releasing mesomeric effect (+M effect) a halogen attached directly to benzene ring makes ortho and para positions of the benzene ring favourable sites for electrophilic attack. Following resonance structures of chlorobenzene make this point clear.



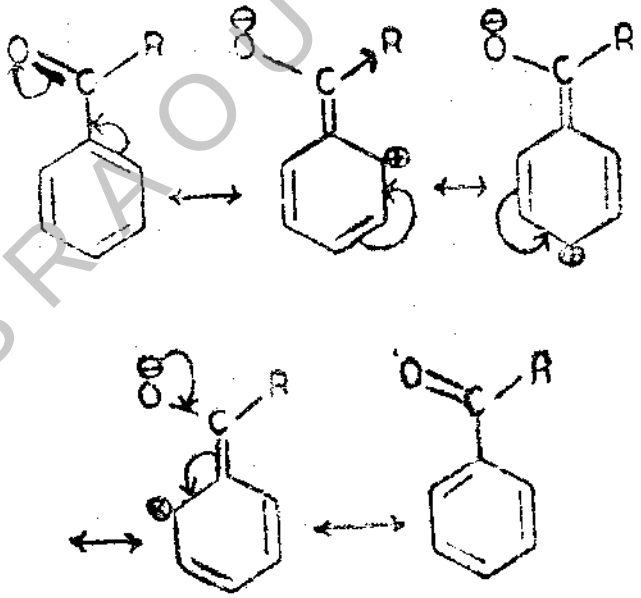
17.6.2.9 Effect of nitro group on electrophilic substitution reactions

The nitro group in nitro benzene exerts a powerful deactivating influence in electrophilic substitution reactions. This is due to - I effect and as well as due to -M effect. The following resonance structures of nitrobenezene indicate that due to -M effect of nitro group, ortho and para positions in benzene ring became electron deficient. Under reaction conditions the other positions in the benzene ring viz. m-positions are attacked by electrophile. Thus, nitrogroup is a meta directing group.



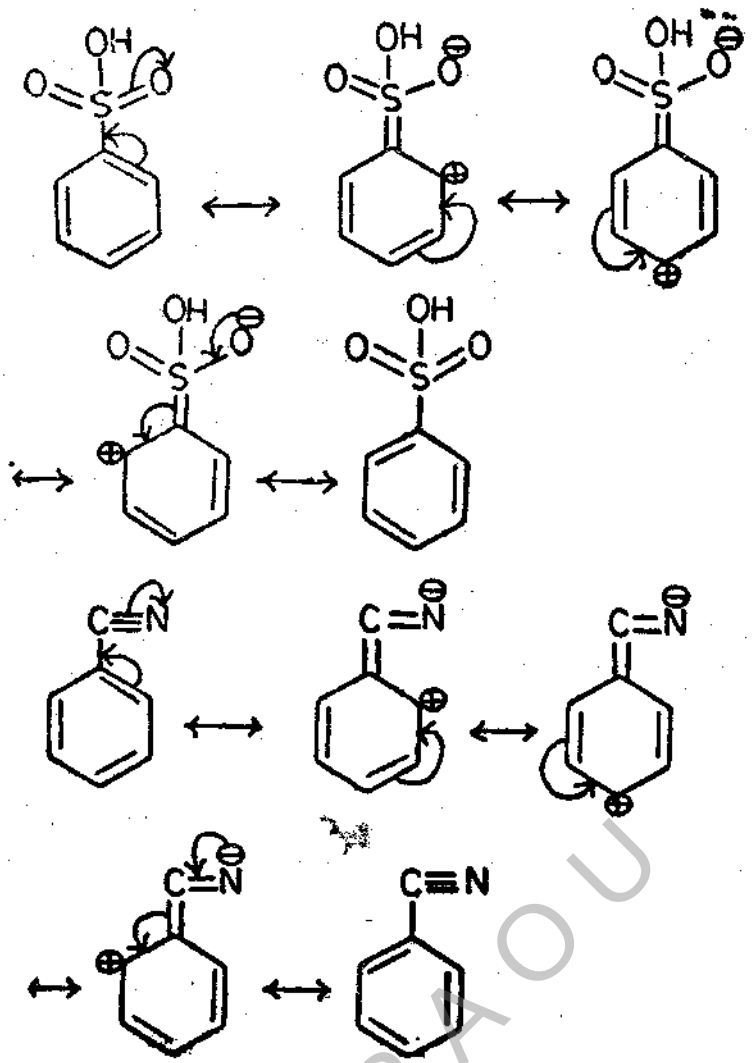
17.6.2.10 Effect of carbonyl group on electrophilic substitution reactions.

Carbonyl group is present in aldehydes, ketones, esters, carboxylic acids etc. If a carbonyl group is attached directly to benzene ring it exerts -M effect. Due to this influence, ortho and para positions of benzene ring become electron deficient and are therefore not attacked by an electrophile. However under favourable reactin conditions, m-positions are attacked by the electrophile, thus leading to the information of a meta disubstituted benzene.



R = H (an aldehyde)
= alkyl or aryl group (-a ketone)
= OH (a carboxylic acid)
= OR (an ester)
= NH_2 (an amide)
= X (an acyl halide)
= O - CO - R (an anhydride)

Following resonance structures of a monosubstituted benzene in which the carbonyl group is directly linked to benzene ring make the point clear. Similarly the m-directing influence exerted by - SO_3H group and C ≡ N group in benzenesulphonic acid and benzonitrile can be explained.

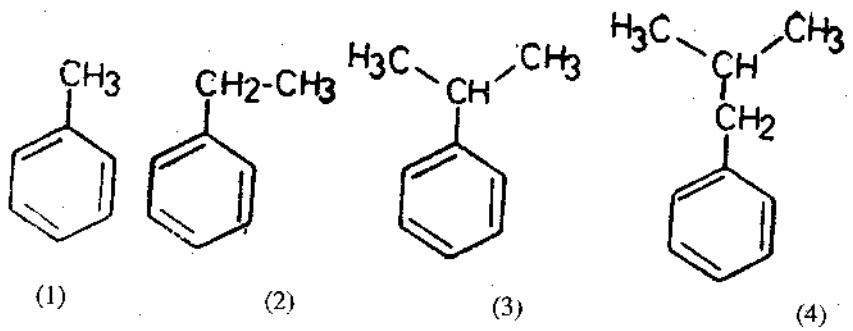


17.7 ALKYL BENZENES

In alkyl benzene the alkyl group is attached to a carbon atom of the benzene ring.

17.7.1 Nomenclature

Following are some alkyl benzenes.

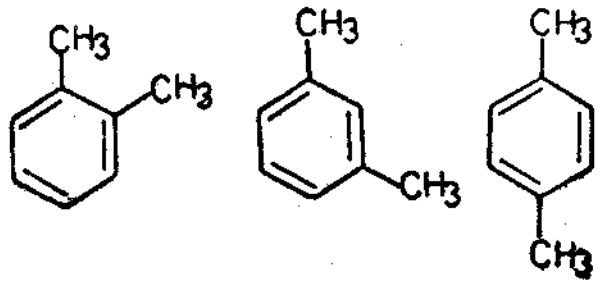


(1) (2) (3) (4)

1. Methyl benzene (tolune)
2. Ethyl benzene
3. Isopropyl benzene (cumene)
4. Isobutyl benzene

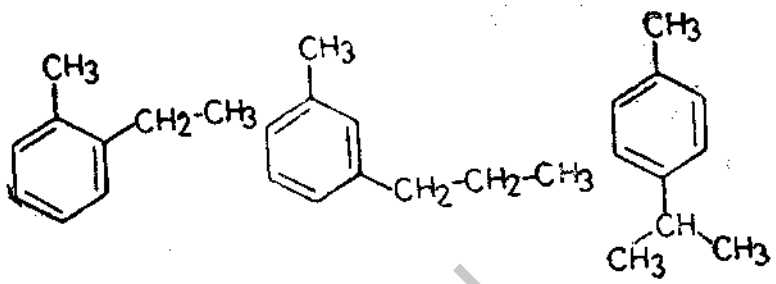
17.7.2 DIALKYL BENZENES

The simplest dialkyl benzenes are dimethyl benzenes. They are also known as xylenes. We have three isomeric xylenes, designated as o,m and p-xylenes.



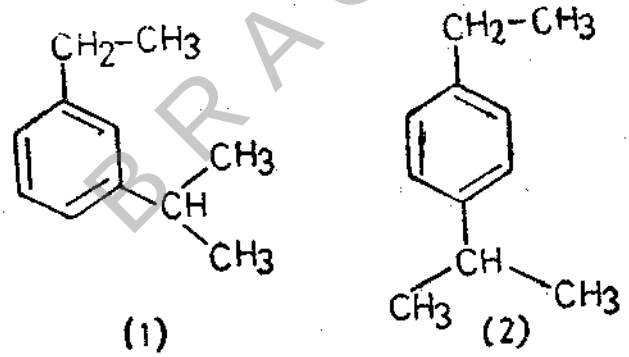
o- xylene m-xylene p-xylene

Other dialkyl benzenes containing a methyl group may be named as derivatives of toluene.

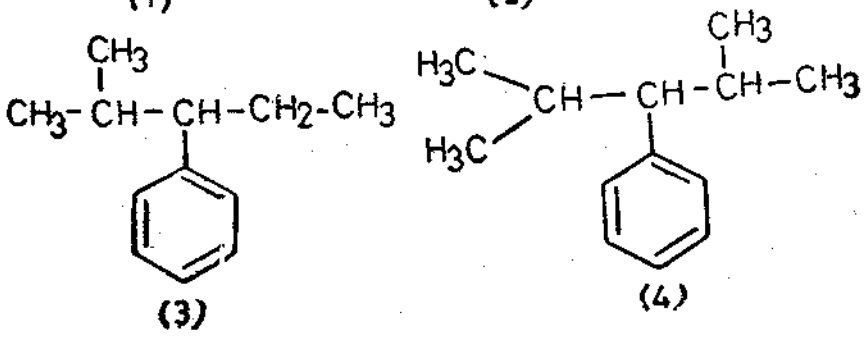


o-ethyl toluene m-propyl toluene p-isopropyl toluene

In the case of other dialkyl benzenes the nature and the relative positions of two akyl groups on the benzenes the nature and the relative positions of two alkyl groups on the benzene ring are indicated in the name.



(1) (2)



(3) (4)

(1) m-ethyl isopropyl benzene (2) 1- ethyl-4-isopropyl benzene or p-ethyl cumene (3) 2 - methyl - 3- phenyl pentane (4) 2-4, dimethyl - 3- phenyl pentane.

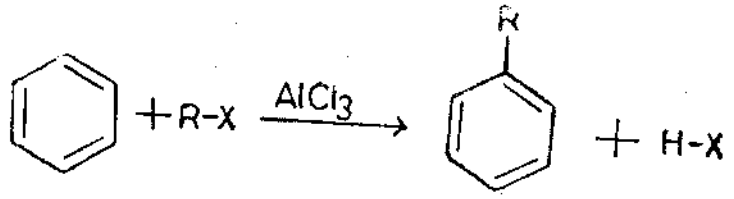
Alkyl benzenes in which a larger alkyl groups are present, may be named as derivatives of alkanes.

17.7.3 Methods of preparation of alkyl benzenes

17.7.3.1 Friedel - Crafts alkylation

This reaction is by far the most important for the preparation of a alkyl benzenes. Benzene and derivatives of benzene carrying electron releasing groups such as alkyl and alkoxyl groups react with alkyl halides in the presence of anhydrous $AlCl_3$ to give C-alkyl derivatives. This reaction is known as Friedel Crats alkylation.

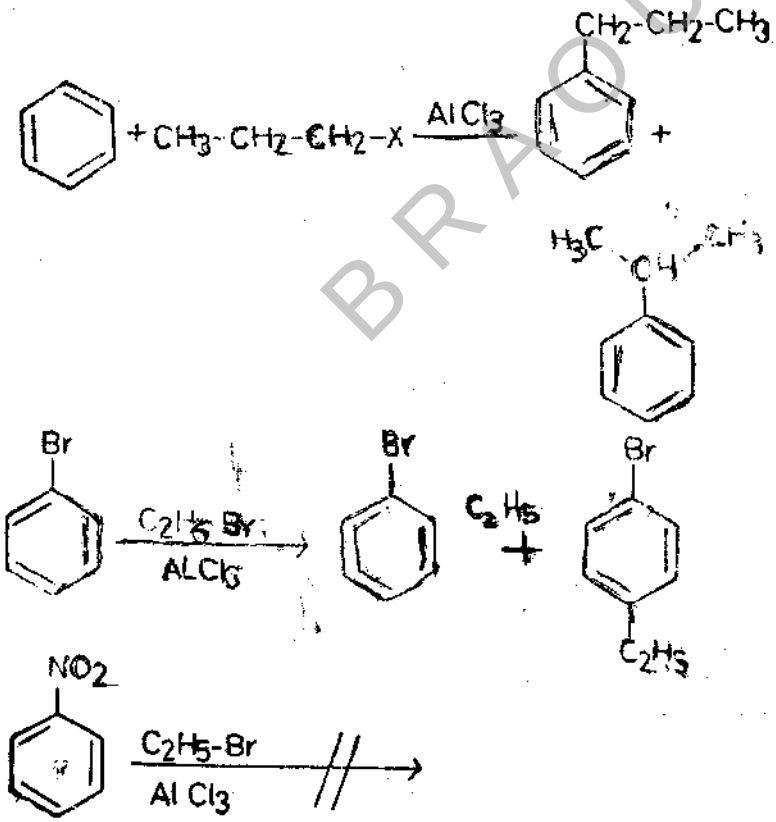
For example:

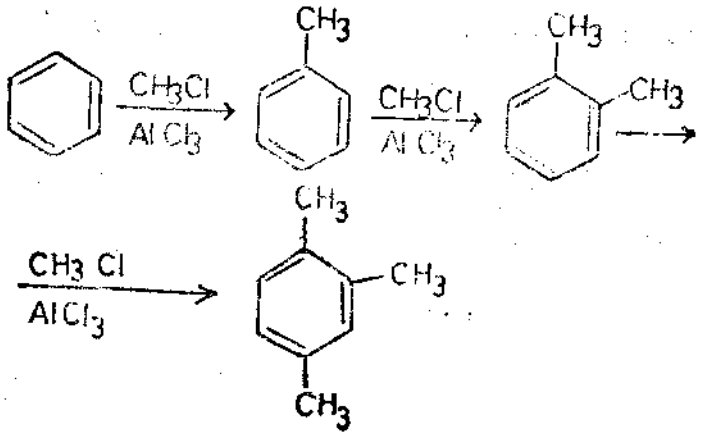


Benzene Alkyl benzene

Where R = may be any alkyl group and X = Cl or Br. In place of $AlCl_3$ other Lewis acids such as BF_3, HF, H_3PO_4, $FeCl_3$ may be used.

Through Friedel - Crafts reaction is used to a great extent for the preparation of alkyl benzenes, it has some limitations - (i) some times alkyl groups of the RX rearranges during the reaction, (ii) benzene derivatives carrying ring deactivating substituents are either less reactive or do not undergo Friedel - Crafts reaction, (iii) C - alkylation of alkyl benzenes generally does not stop at desired stage but proceeds to polyalkylation stage.





17.7.3.2 Reduction of acyl benzenes

A better method of preparation of alkyl benzenes would, therefore, be by the reduction of acyl benzenes with Zn-Hg (zinc amalgam) and dilute HCl. This is known as Clemiensen reduction.

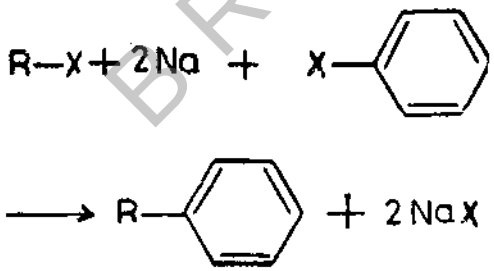
If the same reduction is carried out by using (N_2H_4) hydrazine and a strong base, it is called Wolf-Kishner reduction. The required mono acyl benzenes are obtained by Friedel-Crafts reaction of benzene with suitable acyl halide.

17.7.3.3 Reduction of alkenyl benzenes

Alk nyl benzenes on catalytic hydrogenation produce alkyl benzenes.

17.7.3.4 Wurtz - Fittig reaction

Preparation of alkyl benzenes by the reaction of alkyl halides with aryl halides in the presence of sodium metal is known as Wurtz - Fittig reaction.



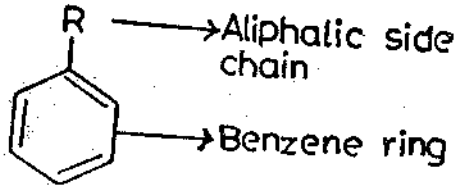
17.7.4 Physical properties of alkyl benzenes

Because of the persence of less polar groups, alkyl benzenes are almost non-polar compounds and resemble hydrocarbons in properties. They are mostly liquids. They are insouble in water, aqueous alkali. But they are soluble in non-polar solvents such as ligroin, petroleum ether, ether, CCl_4, etc. They are lighter than water. The boiling points and melting points of these compounds increase with the increase in the molecular weights.

17.7.5 Chemical Properties of alkyl benzzenes

In alkyl benzenes, the alkyl portion of the molecule exhibits the characteristics of alkanes whereas,

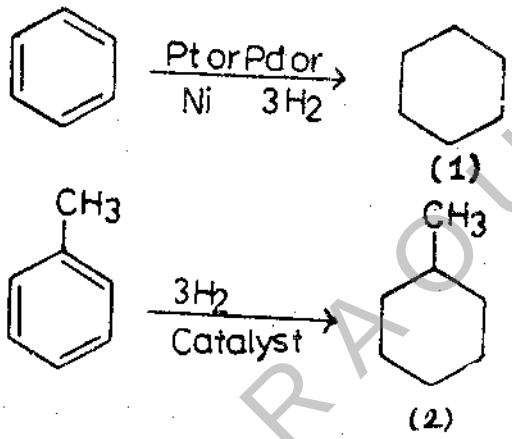
- benzene ring undergoes reactions expected of benzene.



We might expect, these compounds to show two sets of chemical properties. The benzene ring portion should undergo electrophilic substitution reactions which are characteristic of benzene ring. The aliphatic side chain should undergo free radical substitution reactions. These predictions are correct. They are found to undergo electrophilic substitution reactions in the benzene part of the molecule and free - radical substitution reactions in the aliphatic side chain.

17.7.5.1 Hydrogenation

Alkyl benzenes react with hydogen in the presence of catalysts such as Ni, Pd, Pt to yield alkyl cyclohexanes. But the conditions required for catalytic hydrogenation of alkyl benzenes including benzene, are quite drastic compared to that under which catalytic reduction of alkenes are carried out.

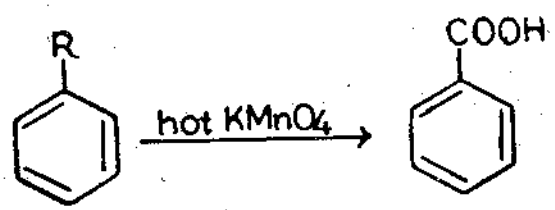


1) cyclohexane 2) Methyl cyclohexane

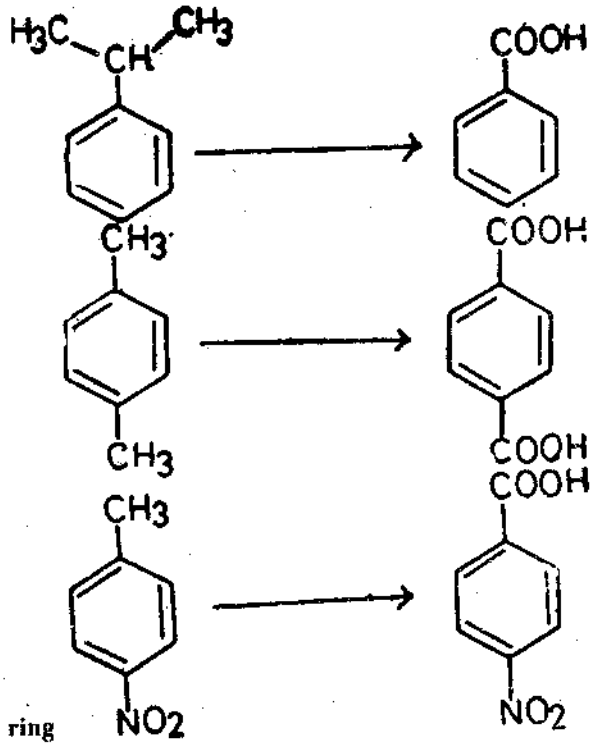
17.7.5.2 Oxidation

Benzene and alkanes do not undergo oxidation. But alkyl benzenes are readily oxidised due to the presence of alkyl side chain. Irrespective of the number of the carbon atoms in alkyl sidechain, all alkyl benzenes are oxidised to benzoic acid. This oxidation is carried out with hot. $KMnO_4$ or $K_2Cr_2O_7$ or dillute HNO_3. This reaction is useful in the preparation of aromatic acids.

In addition, by locatng the position of the cabroxyl group in the resulting aromatic carboxylic acids, one can fix the position of the alkyl side chain in the alkyl benzenes.



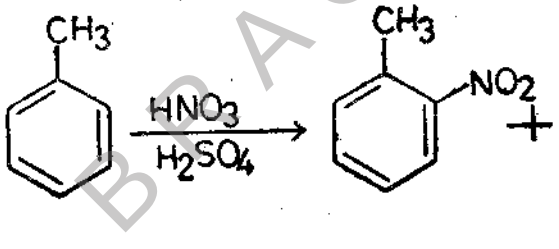
R=Alkyl or Aryl group



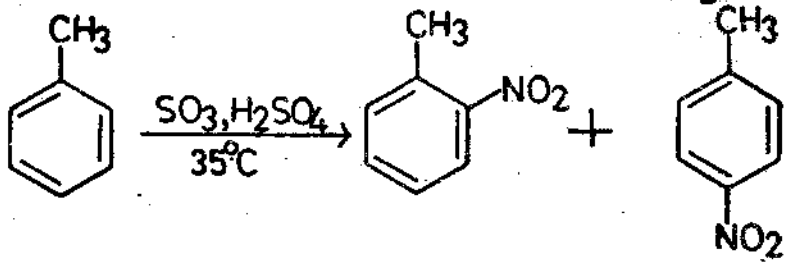
17.7.5.3 Substitution in the ring

Alkyl benzenes are more reactive in electrophilic substitution reactions than benzene. The electron releasing inductive effect (+ I effect) of alkyl groups activate the benzene ring towards electrophilic substitution reactions. Alkyl groups are therefore activating and ortho, para directing groups. Part of the reactivity of alkyl benzenes is explained by the hyperconjugation exerted by alkyl groups. The followng are some of the important electrophilic substitution reactions of alkyl benzenes. Toluene is taken as an example.

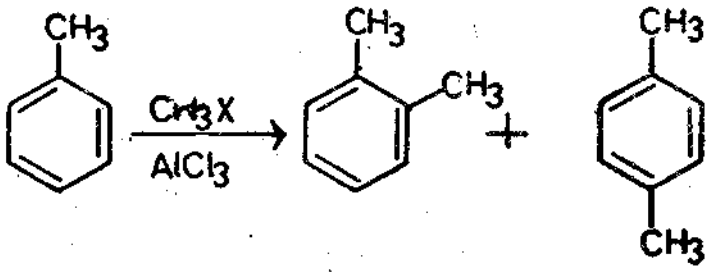
a).



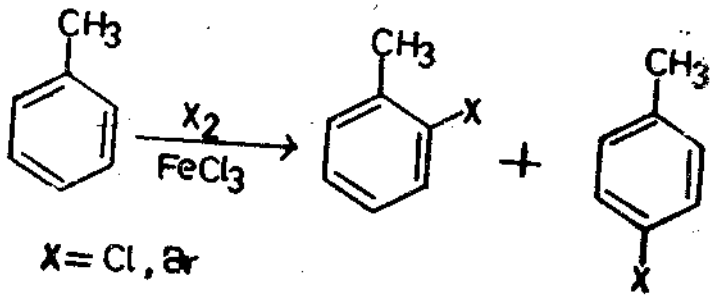
b).



c).



d).

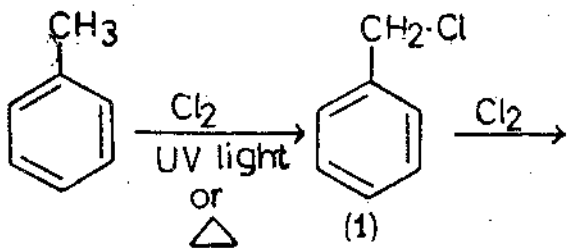


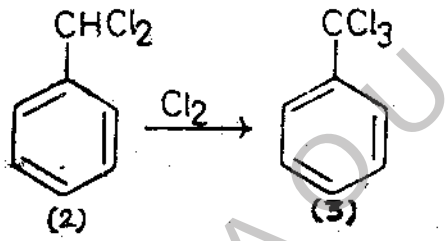
a) Nitration b) Sulfonation c) Friedel- Crafts reaction d) Ring halogention

17.7.5.4 Substitution in the side chain

Halogenation of side chan requires high temperature or U.V. light. This substitution reaction involves free radical mechanism.

For example:

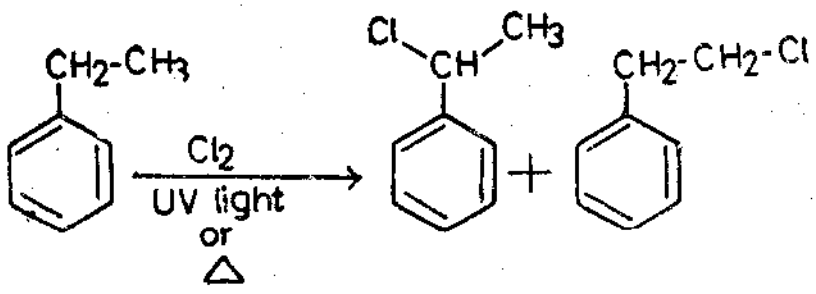




1) Benzyl chloride 2) Benzal chloride 3) Benzotrichloride

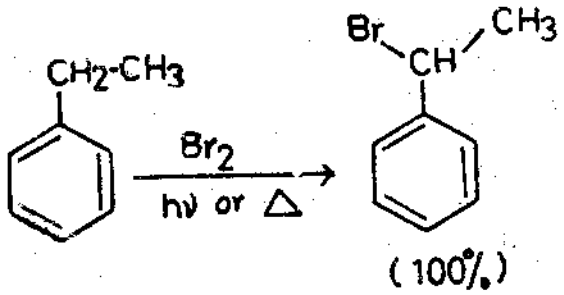
In the same way bromine also reacts with toluene and gives corresponding products.

If the side chain in alkyl benzenes contains two or more than two carbons halogenation is possible at more than one site in the side chain. But the preferred position of halogen atoms is on benzylic position i.e. on carbon α -to benzene ring. Chlorine is more reactive than bromine. Therefore, chlorination is less selective. Chlorination of ethyl benzene leads to a mixture of isomeric chlorophenyl ethanes, but the product of benzyl chlorination is the major compound.



1. 1-chloro - 1 - phenyl ethane (91%) 2. 1-chloro 2-phenyl ethane (9%)

But bromine is less reactive and therefore more selective. Therefore bromination of ethylbenzene leads to exclusive formation of α - brom ethyl benzene or 1 -bromo - 1-phenyl ethane.



Check your progress - 2

Give a brief account of side chain halogenation of tolune.

17.8 SUMMARY

This unit has discussed the various aspects of benzene and alkyl benzenes. The aromatic chracter of benzene and the electrophilic substitution reactions are explained by its structure involving decolization of electrons i.e. resonance. Effect of substituent on electrophilic substitution i.e orientation is given with the electron releasing groups O, P - directors and electron withdrawing groups as m-directors. The notable exception is halogens which are ring deactivating but O, P-directors. Electronic interpretcation involving +I or +M effect; -I, +M effect and -I, -M effect for various substituents is presented. Ring halogenation and side chain halogenation of alkylbenzenes under different conditions is due to the formation of electrophile or free-radical respectively.

17.9 MODEL EXAMINTION QUESTIONS

I. Answer the following in 10 lines

1. How could you obtain benzoic acid from benzene?
2. How could you obtain p-nitri toluene from benzene?
3. Write the ozonolysis products of ortho and para xylenes.
4. Explain the stability of benzene molecule.
5. How can you convert benzene into (a) benzyl chloride (b) o-chloro toluene (c) p-chloro toluene?

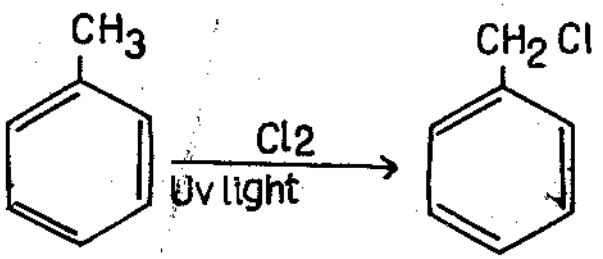
II. Answer the following in 30 lines

1. Discuss the structure of benzene.
2. Give one method for the preparation of alkyl benzenes and discuss the different reactions exhibited by alkyl benzenes.
3. List out o,p - directing and m-directing groups.

17.10 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. According to Huckel, cyclic conjugated unsaturated structures with (4n + 2) electrons (where n is an integer) are aromatic. This is known as Huckel's (4n + 2) electron rule. Benzene, naphthalene and anthracene are all aromatic compounds according to this rule.

2. If the side chain in alkyl benzenes contains two or more than two carbons, halogenation at high temp. or uv light occurs at benzylic carbon i.e. on carbon to benzene ring. Toluene undergoes free radical substitution of side chain similarly and gives benzyl chloride.



UNIT - 18 HALOGEN DERIVATIVES

Contents

18.1 AIMS AND OBJECTIVES

In this unit we describe the preparation and reactivity of alkyl and aryl halides. After finishing this unit you should be able to know:

- Classifcation of halogen derivatives

- Nomenclature
- Preparation of alkyl halides
- Preparation of aryl halides
- Physical properties
- Chemical properties-reduction, formation of Grignards's reagents, dehydrohalogenation, displacement reactions
- Hydrolysis of alkyl halides
- Structure and reactivity of halogen compounds

18.2 INTRODUCTION

Compounds obtained by substitution of hydrogen atoms in a hydrocarbon with halogen atoms are known as halogen derivatives. Usually, chlorine, bromine, and iodine are found in halogen derivatives. A halogen derivative need not necessarily contain only one halogen atom but may contain more than one halogen atom.

18.3 CLASSIFICATION

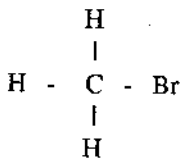
Monohalogen derivatives aliphatic hydrocarbons are broadly classified into two types. They are as follows:

18.3.1 Halo alkanes

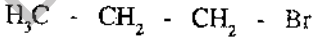
They have the general formula R-X where R is an alkyl group. These are also known as alkyl halides. In alkyl halides the halogen is attached to a sp^3 hybridised or saturated carbon atom. Alkyl halides in turn are classified as primary, secondary and tertiary alkyl halides.

18.3.1.1 Primary alkyl halides

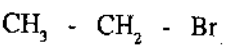
If the halogen atom is linked to a primary alkyl carbon atom, then the resulting halide is known as primary alkyl halide.



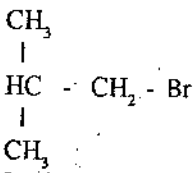
Methyl bromide



n-Propyl bromide



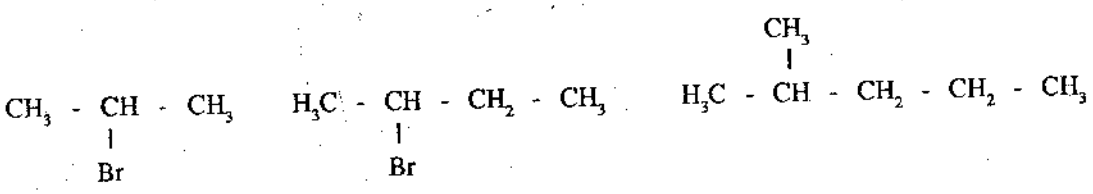
Ethyl bromide



Iso butyl bromide

18.3.1.2 Secondary alkyl halides

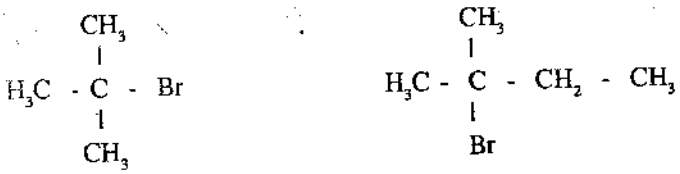
Secondary alkyl halides are those compounds wherein the halogen atom is linked to a secondary carbon atom.



Iso propyl bromide Sec. butyl bromide 2-Chloro pentane

18.3.1.3 Tertiary alkyl halides

In these compounds the halogen is linked to a tertiary carbon atom.



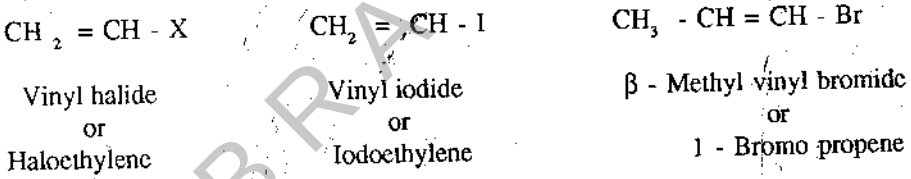
Tertriary butyl bromide 2- Bromo - 2- methyl butane

18.3.2 Haloakenes

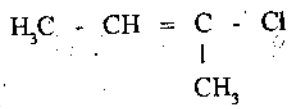
In these compounds in addition to the halogen function, atleast one carbon-carbon double bond is present. Depending on the relative positions of halogen and double bond, they may be further classified as vinyl and allyl halides.

18.3.2.1 Vinyl halides

In these compounds the halogen is linked to an unsaturated (sp^2 hybridised) aliphatic carbon atom. Vinyl halide or halo ethylene is the simplest member of this group.



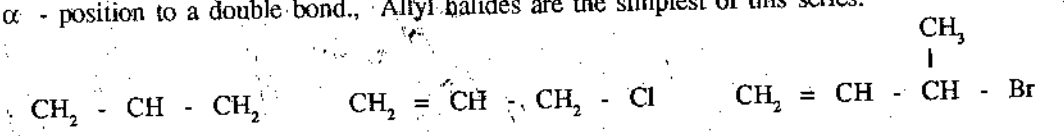
Vinyl halide or Haloethylene Vinyl iodide or Iodoethylene β - Methyl vinyl bromide or 1 - Bromo propene



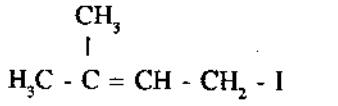
α , β - Dimethyl vinyl chloride
or
2- chloro 2 - butene

18.3.2.2 Allyl halides

In these compounds the halogen atom is bonded to a saturated (sp^3 hybridised) carbon, present in α - position to a double bond., Allyl halides are the simplest of this series.



Allyl halide or 3 - Halo prop - 1 - ene Allyl chloride α - Methy allyl bromide or 3 - Methyl - 3 - bromo propene



γ,γ - Dimethyl allyl iodide

or

2 - Methyl -4- iodo-but-2-ene

Check your progress - 1

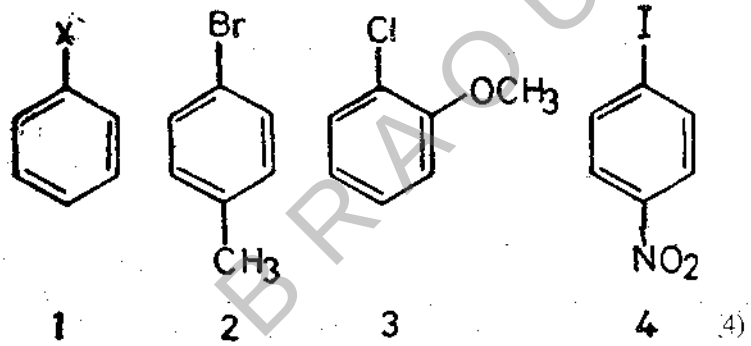
How are the halogen derivatives classified?

18.3.3 Halogen derivatives of aromatic compounds

These are of two types:

18.3.3.1 Aryl halides

In aryl halides a halogen is attached directly to carbon atom of benzene ring. Phenyl halides or halobenzzenes are the parent aryl halides.



(1 **1** **2** **3** **4** 4)

1. Halobenzene
or
Phenyl halide

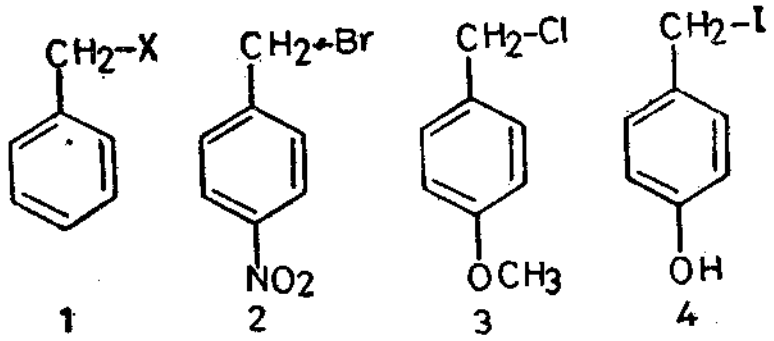
2. p- Tolyl bromide
or
p- Bromo toluene

3. o- anisyl chloride
or
o- Chloro anisole

4. p- Nitro phenyl iodide or p- Iodo nitro benzene

18.3.3.2 Aralkyl halides

In aralkyl halides also a benzene ring is present but the halogen atom is attached to a saturated carbon of the side chain. The important members of this class are benzyl halides. In these compounds the halogen is present on a saturated carbon `α to a benzene ring.



1. Benzyl halide
2. P- Nitro benzyl bromide
3. p- Methoxy benzyl chloride
4. p- Hydroxy benzyl iodide

18.4 NOMENCLATURE

Alkyl halides are represented by the formula R-X and aryl halides by Ar-X where R-is a alkyl group and Ar-is a aryl group.

While naming the halogen compounds the name of the alkyl group is followed by the name of the halogen atom. Alternatively the compound may be named as halogen derivatives of hydrocarbons.

18.5 PREPARATION OF ALKYL HALIDES

18.5.1 Direct halogenation of alkanes

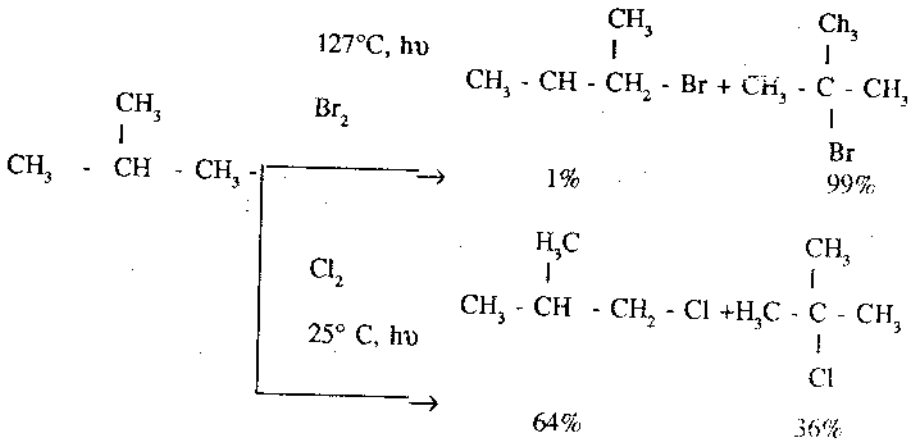
Alkanes undergo halogenation, with Cl_2, or Br_2, in the presence of UV. light or visible, light, or at 250° - 400° C temperature, and yield corresponding alkyl halides.

$$R - H + X_2 \xrightarrow[400^\circ C]{\text{UV.Light or}} R - X + H X.$$

The order of the reactivity of halogen is $Cl_2 > Br_2 > I_2$ with the last halogen the reaction is reversible. The order of reactivity of different carbons in an alkane is tertiary > secondary> primary. This reaction is generally not suitable for the laboratory preparation of alkyl halides. In the halogenation alkanes mixture of alkyl halides are obtained, which are difficult to separate. For example, bromination and chlorination of propane and isobutane yield mixtures of corresponding monohalo alkanes. In bromination, there is a high degree of reactivity as to which hydrogen atoms are to be replaced. Thus, direct bromination of alkanes is, a feasible synthetic route for the preparation of bromoakanes.

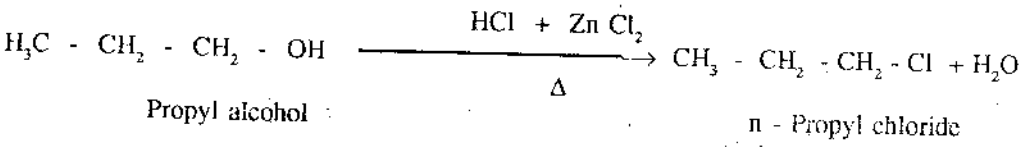
$$CH_3 - CH_2 - CH_3 \xrightarrow[127^\circ C \;\; h\upsilon]{Br_2} \underset{3\%}{CH_3 - CH_2 - CH_2 - Br} + \underset{\underset{Br}{|}\\ 97\%}{CH_3 - CH - CH_3}$$

$$CH_3 - CH_2 - CH_3 \xrightarrow[25^\circ C \;\; h\upsilon]{Cl_2} \underset{45\%}{CH_3 - CH_2 - CH_2 - Cl} + \underset{55\%}{CH_3 - CH - CH_3}$$



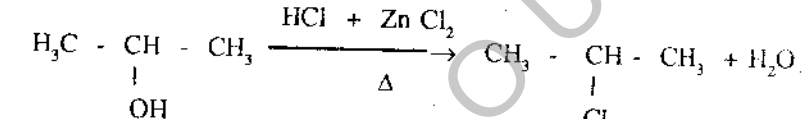
18.5.2 From alchols

Alkyl halides are conveniently obtained by the reaction of alcohols with hydrogen halides. This reaction proceeds quite readily with tertiary alcohols, less readily with secondary alcohols and primayry alcohols are least reactive. For the preparation of alkyl chlorides a solution of anhydrous $ZnCl_2$ in conc. HCl is used as the reagent.



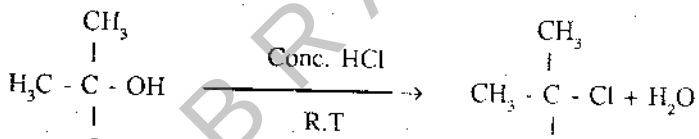
Propyl alcohol

n - Propyl chloride



iso-propyl alcohol

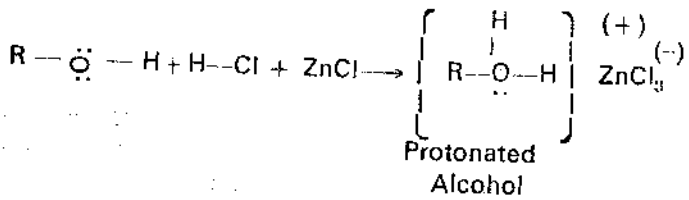
iso-propyl chloride



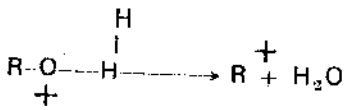
t- butanol

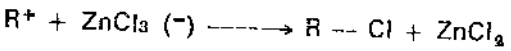
t- butyl chloride

Mechanism



Protonated Alcohol





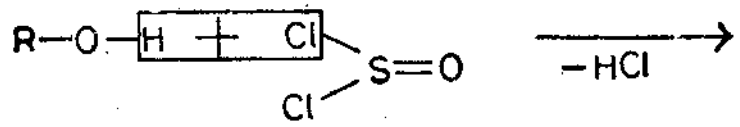
For the preparation of alkyl iodides, alcohols are reacted with iodine in the presence of phosphorus.

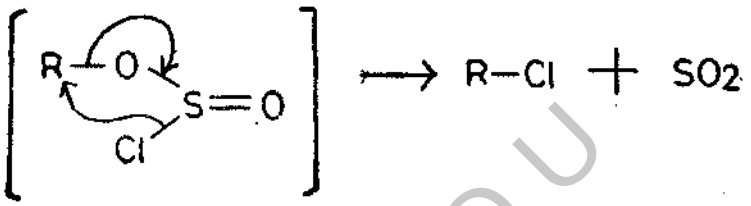
$$\underset{\text{Ethyl alcohol}}{CH_3 - CH_2 - OH} \xrightarrow{P + I_2} \underset{\text{Ethyl iodide}}{CH_3 - CH_2 - I}$$

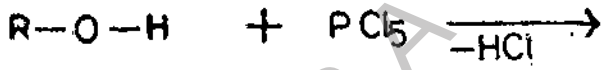
By using a mixture of Na Br and conc. H_2SO_4 alcohols are converted into alkyl bromides.

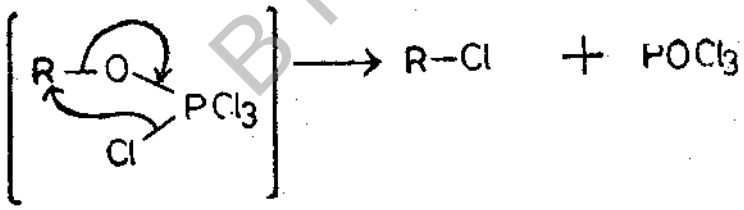
$$\underset{\text{n-propyl alcohol}}{CH_3 - CH_2 - CH_2 - OH} \xrightarrow[H_2SO_4\ \Delta]{Na\ Br} \underset{\text{n-propyl bromide}}{CH_3 - CH_2 - CH_2 - Br}$$

Alkyl halides are also prepared by the action of thionyl halide (SOX_2), PCl_5, PCl_3 or $POCl_3$ on alcohols. By this method, alcohols can be converted very easily into alkyl halides.









18.5.3 Addition of hydrogen halides to alkenes

When hydrogen halides react with alkenes, alkyl halides are produced. For example, ethylene reacts with HCl to give ethyl chloride. With other unsymmetrical alkenes, the addition of hydrogen halides proceeds acording to Markownikoff's rule. For example propene reacts with HCl to give isopropyl chloride.

$$CH_2 = CH_2 + HCl \rightarrow CH_3 - CH_2 - Cl$$

$$\underset{\text{Propene}}{CH_3 - CH = CH_2} + HCl \rightarrow \underset{\text{Isopropyl chloride}}{CH_3 - \underset{\displaystyle Cl}{\underset{|}{CH}} - CH_3}$$

Thus, higher primary alkyl halides cannot be obtained by the addition of HX to alkenes. However, in the presence of peroxides or light, addition of HX to an unsymmetrical alkene takes place giving anti-Markownikoff product as the major compound.

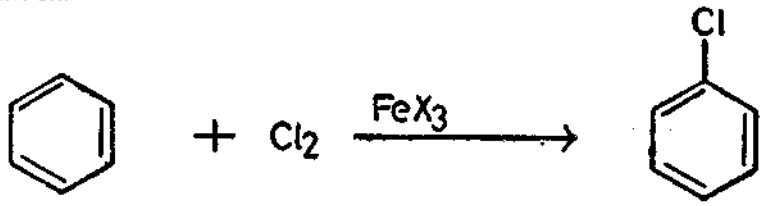
$$CH_3 - CH = CH_2 + HBr \xrightarrow[\text{light}]{\text{Peroxide or}} CH_3 - CH_2 - CH_2 - Br$$

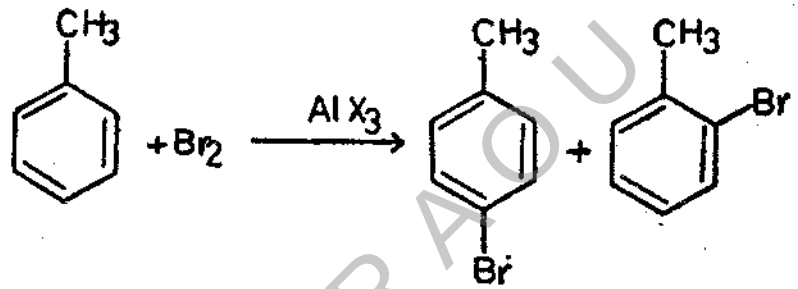
N - Propyl bromide
(Major product)

18.6 PREPARTION OF ARYL HALIDES

By direct halogenation of benzene in the presence of a catalyst

When aromatic hydrocarbons react with halogens in the presence of halogen carriers such as ferric halides, aluminium halides and zinc halides, aryl halides are produced. This is an electrophilic substitution reaction.





p-Bromo toluene

o-Bromo toluene

ıe

18.7 PHYSICAL PROPERTIES OF HALOGEN COMPOUNDS

1. Alkyl halides are sweet smelling liquids. 2. Alkyl halides are insoluble in water but are soluble in organic solvents such as ligroin, benzene, chloroform and ether. 3. Because of increase in molecular weight and polarity, the boiling and melting points of alkyl halides are considerably higher than those of alkanes containing same number of carbon atoms 4. For a given alkyl group, the boiling point of alkyl halides increase with the increasing atomic weight of the halogen, so that a fluoride has the lowest boiling point and the corresponding iodide, the highest boiling. The b. p. and m. p. of alkyl halides are in the following order. With the same halogen the b.p. & m.p.s of

$$RI > RBr > RCl > RF$$

isomeric alkyl halides are in the following order.

Primary alkyl halide > Secondary alkyl halides > Tertiary alkyl halides

Relative densities of the isomeric alkyl halides decreases from primary to secondary to tertiary

and also with the decrease in the size of the alkyl group. Physical properties of halobenzenes are similar to those of benzene. They do not dissolve in water or in alklis or in strong acids. They can be distilled with steam and are inert to permanganate solution.

18.8 CHEMICAL PROPERTIES OF HALOGEN COMPOUNDS

Alkyl halides and aryl halides are polar compounds and are useful as intermediates in the synthesis of different organic compounds. Aryl halides undergo the following reactions. Aryl halides on the other hand, are much less reactive than alkyl halides.

18.8.1 Reduction

Alkyl halides can be reduced either catalytically or chemically. Chemical reduction is brought about by using Zn+HCl, HI+P, $LiAlH_4$, or treatment with Mg followed by hydrolysis.

18.8.1.1 Catalytic reduction

$$R - X + H_2 \xrightarrow[Ni,\ Pd,\ Pt,]{\text{Catalysts}} R - H + H - X$$

$$CH_3 - \underset{\underset{Cl}{|}}{CH} - CH_2 - CH_3 + H_2 \xrightarrow{\text{Catalysts}} CH_3 - CH_2 - CH_2 - CH_3$$

Cl Sec butyl chloride — n - Butane

18.8.1.2 Chemical reduction

$$R - X + Zn + 2HCl \longrightarrow R - H + Zn\,Cl_2 + HX$$

$$3\,R - X + 6\,HI + 2P \longrightarrow 3\,R\text{-}H + 3\,HX + 2\,PI_3$$

$$4\,R - X + Li\,Al\,H_4 \longrightarrow 4\,R\text{-}H + Li\,X + Al\,X_3$$

2. Formation of RMg X (Grignard reagent): When a solution of an alkyl halide in dry ether is allowed to stand over turning of metallc magnesium, a vigorus reaction takes place. The solution turns cloudy, begins to boil, and magnesium metal gradually disappears. The resulting solution is known as Grignard reagnt.

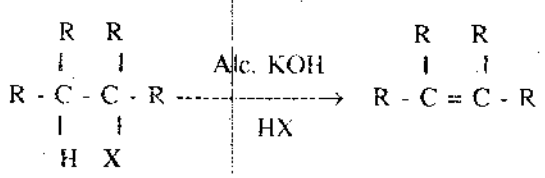
For example:

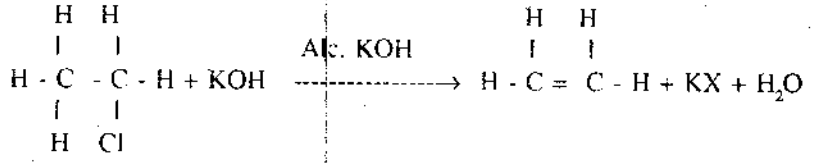
$$CH_3\,I + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Methyl magnesium iodide (a Grignard reagent)}}{CH_3\,Mg\,I} \xrightarrow{H_2O} CH_4 + Mg\,(I)\,OH$$

$$C_6H_5\,Cl + Mg \xrightarrow{THF} \underset{\text{Phenyl magnesium chloride (An aryl magnesium halide)}}{C_6H_5\,Mg\,Cl} \xrightarrow{H_2O} C_6H_6 + Mg\,(Cl)\,OH$$

However, in the preparation of aryl magnesium halides tetrahydrofuran (THF) is used as solvent.

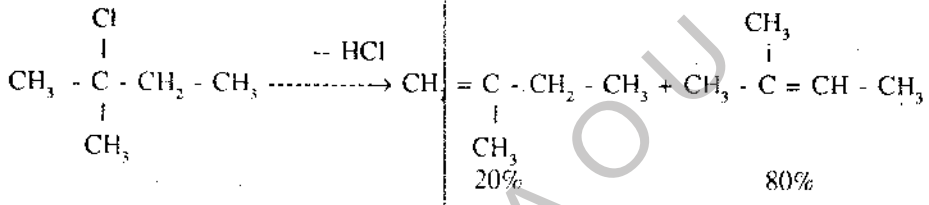
3. Dehydro-halogenation: When alkyl halides react with alcoholic potassium hydroxide alkenes are formed.





For dehydrogenation to occur, presence of a hydrogen on β - carbon is essential. This hydrogen and halogen are eliminated as hydrogen halide in the presence of alcoholic potassium hydroxide. Reactions of this type are known as elimination reactions.

In some cases elimination reactions may lead to two different alkenes. In such cases the major product of elimination can be predicted by applying Saytzeff's rule. According to this rule the major product of elimination reaction of an alkyl halide is the more substituted alkene. Thus dehydrohalogenation of 2-methyl -2-chloro butane gives 2-methyl 2-butene as the major product.



Check your progress - 2

What are the products obtained in the dehydrohalogenation of 2-bromo-2-methyl butane?

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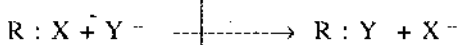
4. Displacement reactions: A displacement reaction involves the replacement of one functional group (X^-) by another (Y^-). In alkyl halides the halogen is displaced, as X^-, by Y^-. In other words, a nucleophile is displaced by a stronger nucleophile. Such reactions are referred to as **nucleophilic substitution (S_N) or nucleophilic displacement reactions.**

The nucleophilic reagents commonly encountered in S_N reactions are listed in the table. The nucleophile may be an anion Y^- or a neutral molecule.

Displacement reactions of alkyl halides



Nucleophile (Y^-)	Product (R : Y)	Product name
Br^-	R -- Br	Alkyl bromide
I^-	R -- I	Alkyl iodide
^-OH	R -- OH	Alcohol
$^-OCH_3$	$R -- OCH_3$	Ether
$^-O - C - R$ (with O)	R - O - C - R (with O)	Ester
^-CN	R -- CN and RNC	Nitrile and Isonitrile
$^-NH_2$	$R -- NH_2$	Amine
$^-C \equiv C$-R	R - C ≡ C - R	Higher alkyne
^-SH	R - SH	Thiol
^-S-R	R-S-R	Thioether (sulphide)
$^-NO_2$	$R-NO_2$ and R-O-N=O	Nitroalkane and alkynitrite
R_3 N:	$(R_4\ N)^+ X^-$	Quarternary salt
$(CH_3)_2S$:	$RS^+(CH_3)_2X^-$	A sulphonium halide
C_6H_5 P:	$C_6H_5\ P^+.\ RX^-$	A phosphonium halide
H_2O	R - OH	Alcohol
$:NH_3$	$R - NH_2$	Amine

A Halogen atom attached to a saturated carbon atom can be readily displaced as halide ion, by other nucleophiles. These nucleophiles attack positively polarised carbon atom to which the halogen atom is attached. Ultimately halide ion which is weaker nucleophile is displaced by strogner nucleophiles. Thus the over all reaction of an alkyl halide is nucleophilic displacement reaction.

18.9 HYDROLYSIS OF ALKYL HALIDES

Alkyl halides undergo hydrolysis in the presence of bases such as Na OH or KOH producing alcohols. The general equation for this reaction is as follows:

$$R - X + \bar{O}H \longrightarrow R - OH + X$$

The hydrolysis of alkyl halide is a typical example of nucleophilic substitution reaction.

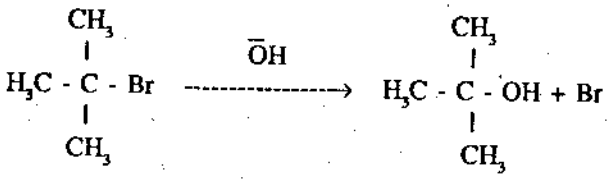
$$CH_3Br + \bar{O}H \longrightarrow CH_3OH + Br$$

$$\begin{array}{l} CH_3 \\ | \\ H_3C - C - CR \\ | \\ CH_3 \end{array} + \bar{O}H \longrightarrow \begin{array}{l} CH_3 \\ | \\ H_3C - C - OH \\ | \\ CH_3 \end{array}$$

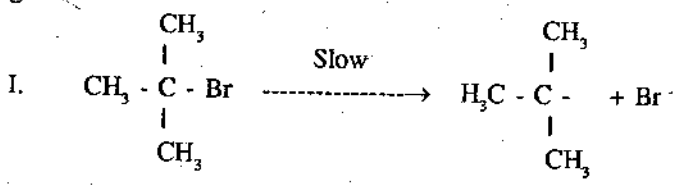
In the examplse given above, the weaker nucleophile (halide ion) is displaced by stronger nucleophile (hydroxide ion). However, the mechanisms of the two reactions given above are quite different.

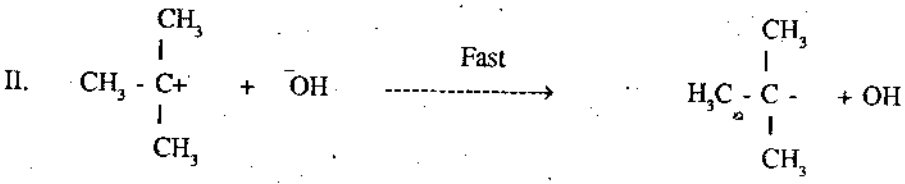
18.9.1 The S_N1 reaction

The rate of the reaction between tertiary butyl bromide and hydroxide ion yielding tertiary butyl alcohol depends upon the active concentration of only one reactant viz. tertiary butyl bromide.



The rate of hydrolysis of tertiary butylbromide [t - butyl bromide] and is independent of the concentration of [$\bar{O}H$]. In otherwords, the reaction follows first order kinetics. To account for this and other observations, a unimolecular nucleophilic substitution (S_N1) mechanism has been suggested.



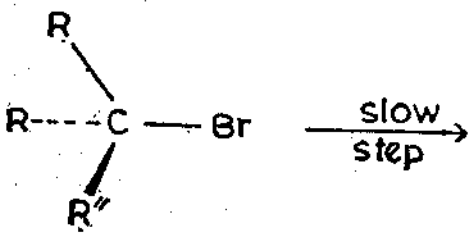


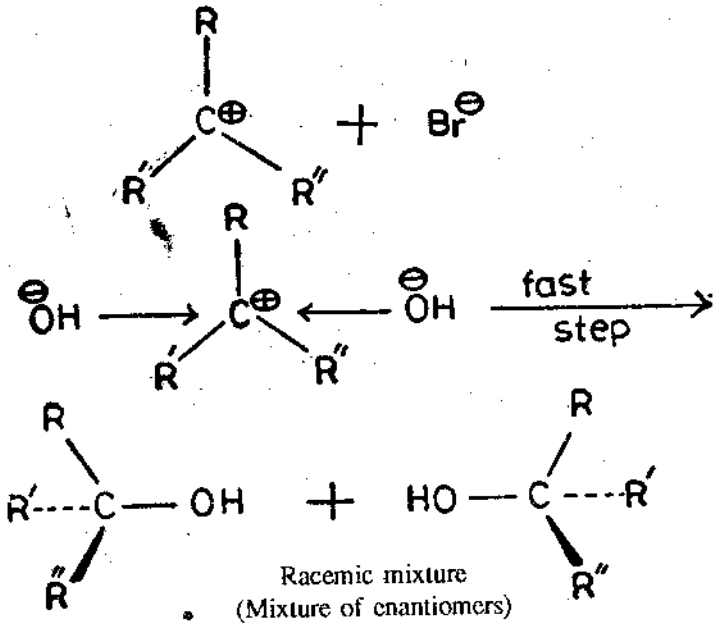
The initial step in this reaction is the ionization of t-butyl bromide by heteroyysis of C-Br bond to form t-butyl carbonium ion and bromide anion. This is then followed by the fast reaction of the carbonium ion with $\bar{O}H$ to yield the product. The first step i.e. formation of carbonium ion is the slow step which determines the over all rate of reaction. The formation of carbonium ion again depends upon the active concentration of t-butyl bromide. Since the hydroxide ion is not involved in the slow or rate determining step of the mechanism, the rate of hydrolysis of t-butyl bromide is not dependent on the active concentration of $\bar{O}H$.

Reactions proceeding by this mechanism are called substitution unimolecular nucleophilic substitution (S_N1) reactions.

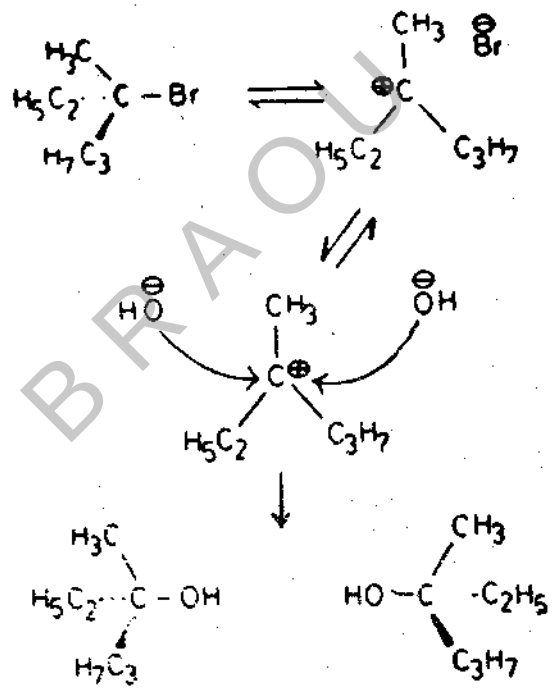
18.9.1.1 Stereochemistry of S_N 1 reactions

It has been already mentioned that the intermediate in a S_N1 reaction is a carbonium ion. In this the carbon of carbonium ion and the three alkyl groups attached to it are coplanar i.e. lie in the same plane. Let us consider a carbonium ion from an appropriate alkyl halide carrying three different substituents. There are equal possibilities for the carbonium ion to be attacked by the $\bar{O}H$ ion from two sides i.e., from above and below the plane in which the carbon and three groups attached to the carbon are present. This should lead to the formation of equal amounts of molecules of alcohols with opposite configuration. These are called enantiomers i.e. molecules whose configuration bear mirror image relationship. One isomer (enantiomer) rotates the plane of polarised light to the right and the other in equal magnitude to the left. When these enantiomers are present in equal quantity, the mixture does not exhibit optical activity, i.e., it is racemic. In other words a racemic mixture is obta obtained





Thus, this effect is not felt in the hydrolysis of t-butyl bromide. But the S_N1 reaction optically active alkyl halides in which the halogen is attached to an assymmetric carbon atom can lead to formation of racemic mixture.



Racemic mixture

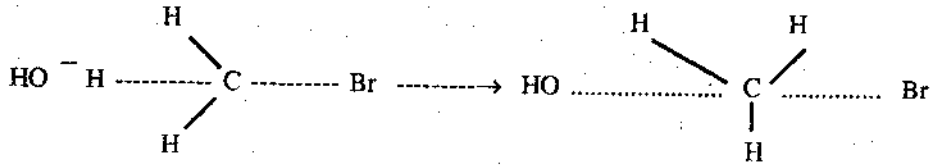
18.9.2 The S_N2 Reaction

The reaction between CH_3 Br and hydroxide ion to yield methanol follows second order kinetics i.e. the rate depends upon the active concentration of both CH_3 Br and ^-OH.

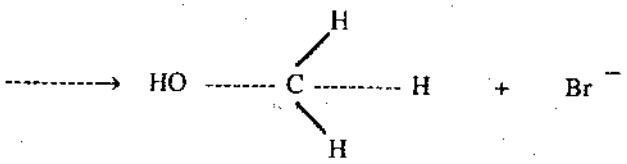
$$CH_3 - Br + {}^-OH \longrightarrow CH_3 - OH + Br^-$$

rate α [CH_3Br] [^-OH]

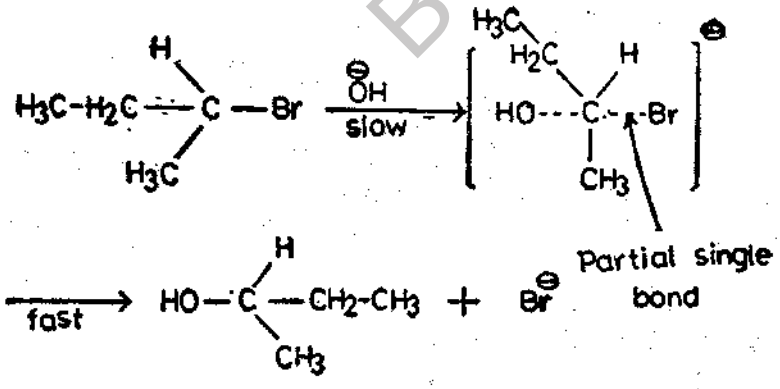
The account for the observed kinetics, a bimolecular nucleophilic substitution reaction (S_N2) mechanism is suggested. According to this mechanism, ^-OH ion approaches the carbon to which the halogen atom is attached, from the back side. This rear side or back side attack by ^-OH on the carbon leads to the formation of a S_N2 transition state.



Partial single bond



The transition state is an imaginary state in which carbon is partially bonded to be the OH and Br groups. The OH and Br groups and the carbon undergoing nucleophilic substitution reaction are all colinear. The three hydrogens and the carbon to which these are attached are all coplanar. The C-H bonds are arranged like the spokes of a wheel and the HO - C - Br form the axle. The negative charge is distributed throughout the transition state. As the C-OH bond begins to form, the C -- Br and begins to break. Ultimately the weaker nucleophile (Br) is displaced by the stronger nucleophile ($\bar{O}H$) to form CH_3OH. The configuration of the three hydrogens in the process undergo inversion. This cannot be experimentally demonstrated in the reaction of methyl bromide. In the case of secondary demonstrated in the reaction of methyl bromide. In the case of secondary butyl chloride, it is possible to show the inversion of configuration.



Here the configuration of the product is quite opposite to that of the starting alkyl halide. In S_N2 reactions, the configuration of the molecule undergoes inversion like an umbrella turning inside out in a wind storm. This is often referred to as Walden inversion.

Usually primary alkyl halides react by S_N2 mechanism, whereas tertiary alkyl halides react either by S_N1 or S_N2 mechanism.

18.10 STRUCTURE AND REACTIVITY OF HALOGEN COMPOUNDS

Alkyl halides undergo nucleophilic substitution reactions quite readily, whereas aryl halides are inert toward nucleophilic reagents.

The order of reactivity of alkyl depends upon the nature of halogens present in them. The order of the reactivity of alkyl halides is:

RI > RBr > RCl

The order of the reactivity of different mono halogen derivatives is:

Allylhalides

or > Alkyl hlides > Vinyl halides or halobenzenes

$$H_2C = CH - CH_2 -- X \xrightarrow[\text{water at R.T}]{\text{Hydrolysis with}} CH_2 = CH - CH_2 -- OH + HX$$

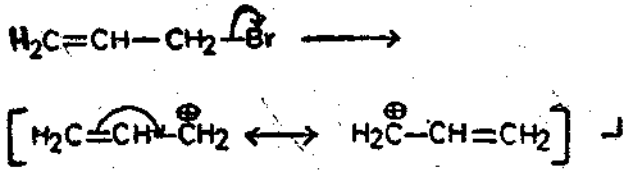
$$R -- X \xrightarrow[\text{at R.T is very slow}]{\text{Hydrolysis with water}} R -- OH + HX$$

$$R -- X \xrightarrow[\text{at boiling point of water is fast}]{\text{Hydrolysis with water}} R -- OH + HX$$

$$CH_2 == CH -- X \xrightarrow[\text{With } H_2O]{\text{At 100° C}} \text{No reaction}$$

$$CH_2 == CH -- X \xrightarrow[\text{water, fast}]{\text{At 200° C with}} CH_2 == CH -- OH + HX$$

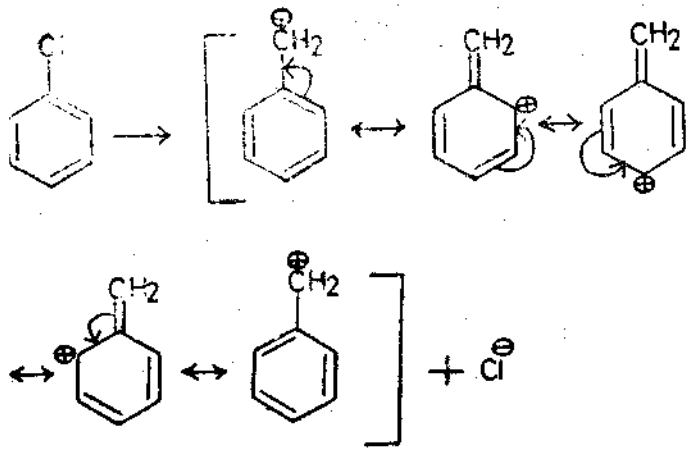
Allyl halides are hydrolysed by water at room temperature, whereas hydrolysis of alkyl halides occurs readily with boiling water. Vinylhalides are not hydrolysed by water at 100°C. Vinyl halides and aryl halides require temperatures above 250°. Allyl halides undergo ionisation to form resonance stabilised allyl carbonium ions.



Resonance stabilised allyl carbonium ion

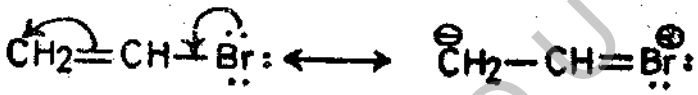
Similarly benzyl halides undergo ionisation to from resonance stablized benzyl corbonium ions.

18.10.1 Resonance stabilized benzylcation



Resonance stabilisation, thus, favours ionisation of allyl and benzyl halides. The resulting carbonium ion readily combines with the nucleophile ($\bar{O}H$) to form the product. This explains the high reactivity of allyl and benzyl halides in nucleophilic substitution reactions. Alkyl halides either react by S_N1 or S_N2 mechanism.

Vinyl halides are not reactive in nucleophilic substitution reactions compared to alkyl halides. Halobenzenes are still less reactive. This is due to resonance in vinyl halides and aryl halides.

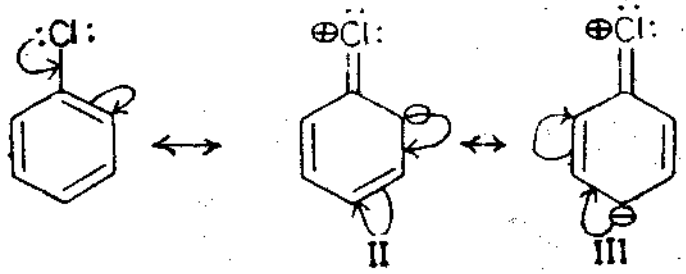


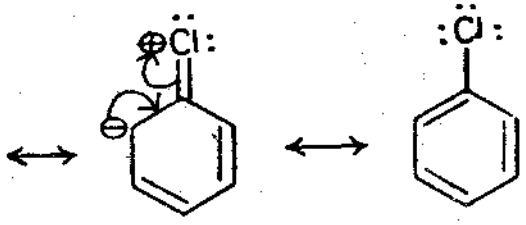
Resonance structures of vinyl bromide

Vinyl bromide may be considered as a resonance hybrid of two structures. In one of the structures the bromine atom is joined to the carbon by a double bond. Also the bromine is positively charged and the carbon bears a negetive charge. In other words the carbon is not electron deficient. Therefore, it cannot be readily attacked by a nucleophile, since the C- Br bond has some double bond character it is difficult to break such a bond.

18.10.2 Resonance structures of chlorobenzene

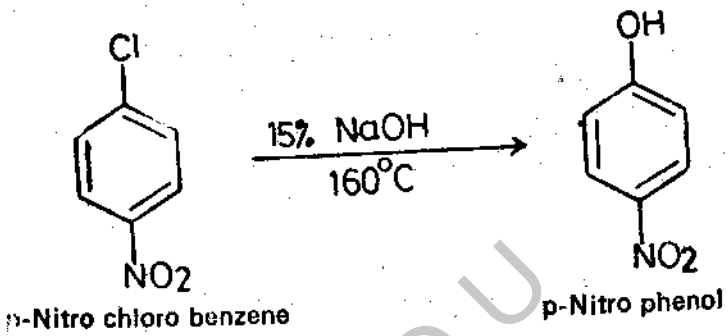
Similarly chlorobenzene is considered as a resonance hybrid of five structures. In structures II, III and IV the carbon - chlorine bond is a double bond. Further the carbon atoms in these structures are not electron deficient. Thus, due to double bond character of carbon - halogen bond, ionisation of chlorobenzene and reaction of resulting cation by S_N1 mechanism is not possible. The reluctance of aryl halides to undergo nucleophilic substitution by S_N2 reaction is explained by the electron surplus nature of the carbons in the benzene ring.



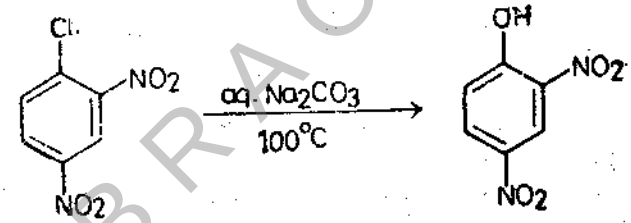


IV V

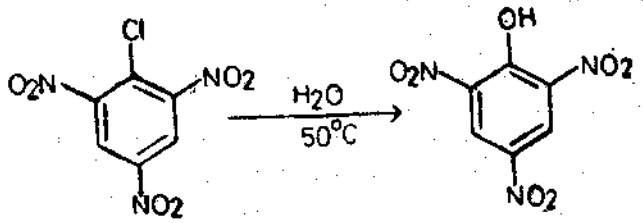
However, aryl halides carrying electron withdrawing groups such as NO_2 and - CN in ortho and para positions, undergo nucleophilic substitution reactions readily. p-Nitrochlorobenzene is readily hydrolysed to p-nitrophenol. 2,4, -Dinitro chlorobenzene and 2,4,6 - trinitro chlorobenzene (Picrylchloride) are more reactive than chlorobenzene in nucleophilic reactions. Infact picryl chloride is more reactive than alkylchlorides.



p-Nitro chloro benzene p-Nitro phenol



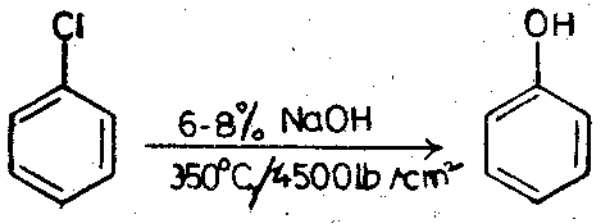
2, 4-Dinitro chloro benzene 2, 4-Dinitro phenol



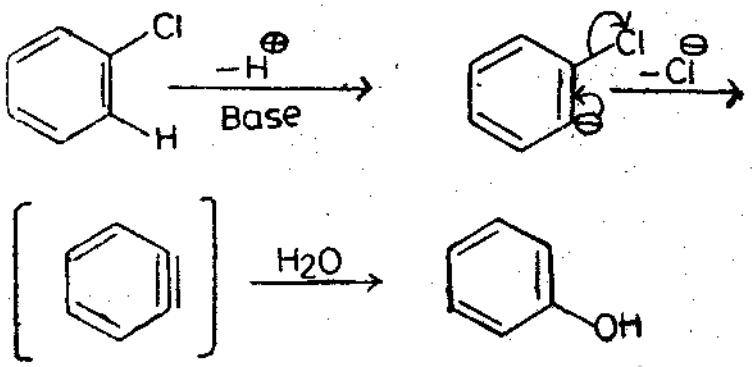
3,4, 6-Trinitro chloro benzene (Picryl chloride)

2,4, 6-Trinitro phenol (Picric Acid)

Chlorobenzene, however, requires drastic conditions for its hydrolysis to phenol.



The reaction is believed to proceed through a different mechanism called benzyne mechanism.



Benzene

18.11 SUMMARY

In this unit we tried to highlight the preparation and properties of Healoalkenes and arylhalides. Direct halogenation is a general method although haloalkanes can also be obtained from alcohols and alkenes more conveniently. Displacement reactions of alkyl halides with nucleophiles involves the formation of carbonium ion in S_N1 and results in a racemic mixture. In S_N2 a transition state with partial single bonds leads to inversion of configuration. Alkylhalides and benzylhalides from resonance stabilised cations and are highly reactive. (S_N1) Alkyl halides react by S_N1 or S_N2 and the o of reactivity is RI, RBr, RCl. Alkylhalides and halobenzenes are least reactive due to some double bond character of C-X bond. However, electron withdrawing groups in ortho and para positions of halobenzenes facilitates nucleophilic substitution.

18.12 MODEL EXAMINATION QUESTIONS

I. Answer each of the following in 10 lines

1. Formulate the mechanism of S_N1 reaction.
2. Discuss the stereochemistry of S_N2 reaction.
3. Vinyl halides undergo hydrolysis less readily than alkyl halides explain.

II. Answer each of the following in 30 lines

1. Discuss the mechanism of hydrolysis of (1) primary alkylchloride (ii) tertiary alkyl chloride
2. The reactivity of halogen compounds depends on their structure. Explain with suitable examples.

18.13 MODEL ANSWERS TO CHECK YOUR PROGRESS

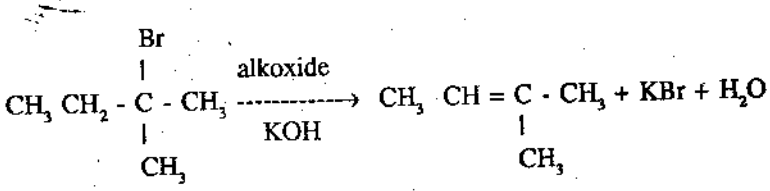
1. Halogen derivatives are two types.

   I. Derivatives of aliphatic hydrocarbons.
   II. Derivatives of aromatic compounds.

   The monohalogen derivatives of aliphatic hydrocarbons includes primary, secondary and tertiary alkyl halides besides vinyl and alkyl halides.

   The halogen derivatives of aromatic compounds are aryl halides and aralkyl halides.

2. When 2-bromo 2-methyl butane reacts with alcoholic potassium hydroxide 2- ethyl 2-butene is formed as the major product.



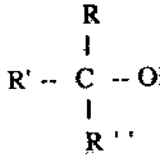
The elimination of hydrogen bromide may lead to two different butenes. But the major product can be predicted by applying Saytzeff's mule, according to which the major product of elimination reaction is the more substituted alkene.

Author : Dr. P.N. Sarma

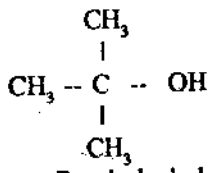
UNIT - 19 HYDROXY DERIVATIVES (ALCOHALS)

Contents

If the hydroxyl group is attached to a tertiary carbon atom (carbon atom not carrying even one hydrogen atom) the alcohol is called a tertiary alcohol. The general formula of a tertiary alcohol is



is an example of a tertiary alcohol.



ter. Butyl alcohol

19.4 NOMENCLATURE

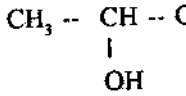
For alcohols three different systems of nomenclature are in use.

The simple alcohols are known by their trivial or common names. The suffix 'alcohol' is used along with the name of the alkyl group to which the hydroxyl group is attached.

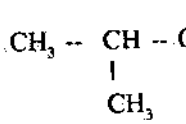
eg. CH_3 OH Methylalcohol (hydroxyl group is attached to methyl group)

CH_3 -- CH_2 -- OH Ethyl alcohol (hydroxyl group is attached to the ethyl group)

CH_3 -- CH_2 -- CH_2 OH n-propyl alcohol (hydroxyl group is attached to the isopropyl group)



iso propyl alcohol (hydroxyl group is attached to isopropyl group)

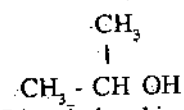


iso Butyl alcohol (hydroxyl group is attached to isopropyl group)

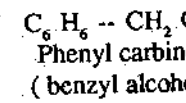
It may be noted that isopropyl alcohol and isobutyl alcohol do not belong to the same class. The former is a secondary alcohol while the latter is a primary alcohol.

In another system of nomenclature, alcohols are considered as derivatives of the simplest alcohol i.e. methyl alcohol (CH_3 OH). Methyl alcohol is also called "carbinol". Thus ethyl alcohol CH_3 -- CH_2 OH (derived by replacing atom of the carbinol by methyl group) is called methyl carbinol.

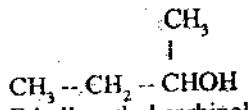
Few more examples are given below:



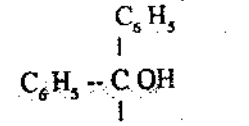
Dimethyl carbinal
(i-propyl alcohol)



Phenyl carbinol
(benzyl alcohol)



Ethyll methyl carbinol
(sec butyl alcohol)



Triephcynyl carbinol

Alcohols are also named according to IUPAC system. This is widely acepted system. The important rules of IUPAC system of nomenclature of alcohls are :

The longest continuous (straight) chain of atoms containing the hydroxyl group is selected. The alcohol is named as derivative of the corresponding alkane i.e. as alkanol.

A numerical prefix indicates the postion of OH group. The lowest number is given to the hydroxyl group.

The nature, number and position of the other groups, if any present on the longest continuous chain of carbon atoms is indicated in the prefix part of the name. For eg. CH_3OH is considered as derivative of alkane containing one carbon atom (methane). Therefore, it is named as methanol.

$CH_3 - CH_2OH$ is named as ethanol, while $CH_3 - CH_2 - CH_2 - OH$ is named as 1-propanol or propan - 1 - ol.

$$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$$

In $CH_3 - CH - CH_3$ there are three carbons in a continuous chain but the hydroxyl group is attached to the second carbon atom. Therefore this compound is named as 2-propanol or propane-2-ol. Few other illustrations of IUPAC system of nomenclature are:

$$CH_3 - \underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - CH$$

(2-Methyl -2-propanol)

$C_6H_5 - CH_2 - CH_2 - OH$

(2 - Phenyl ethanol)

$$CH_3 - \underset{\displaystyle CH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - CH_2OH$$

(2, 2 - Dimethyl propanol)

$$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$$

(4 - Methyl - 2 - Pentanol)

Check your Progress - 1

Write the structures of all possible isomeric alcohols with molecular formula $C_4H_{10}O$. Name them according to IUPAC system.

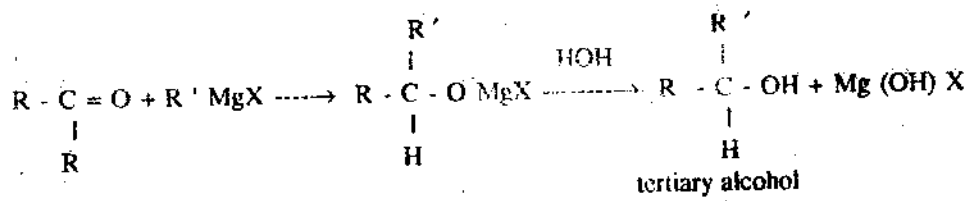
19.5 GENERAL METHODS OF PREPARATION

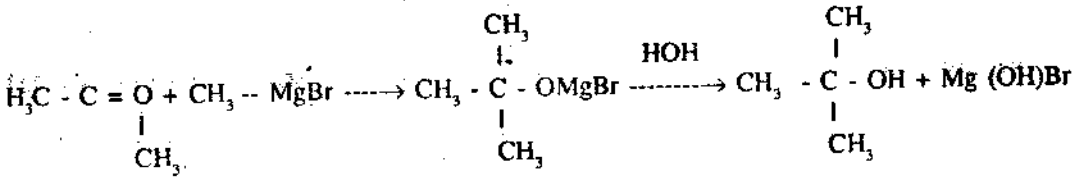
Alkyl halides, carbonyl compounds (aldehydes and ketones) and alkenes serve as convenient starting materials in the preparation of alcohols.

19.5.1 Hydrolysis of alkyl halides

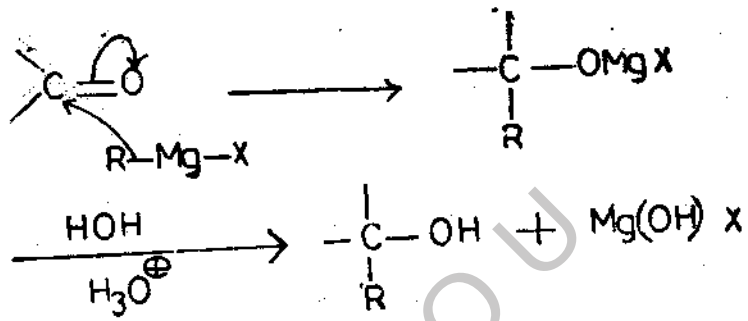
Alkyl halides are hydrolysed by aqueous alkali to give alcohols. In some cases moist silver oxide (AgOH) has also been used. n-propyl alcohol is obtained by the hydrolysis of n-propyl bromide.

A ketone reacts with Grignard reagent to give an addition product which upon hydrolysis gives a tertiary alcohol. Thus acetone and methyl magnesium bromide react to give tert-butyl alcohol.





In all the above reactions, the mode of addition of the Grignard reagent to the carbonyl group is common (Appendix - 2)

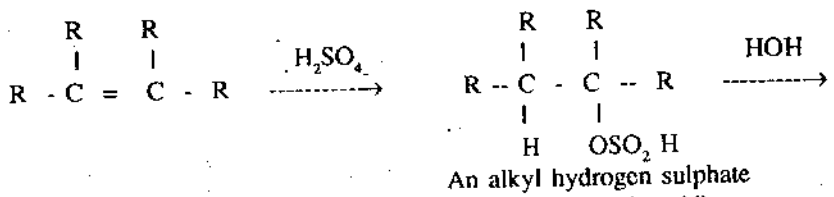


Check your progress - 2

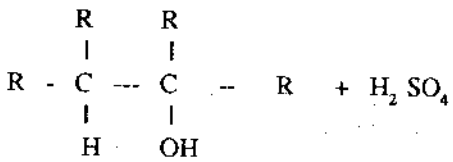
Formulate the synthesis of 2-butanol from Grignard synthesis.

19.5.4 Hydration of alkanes

Hydration of an alkene in the presence of an acid such as conc. H_2SO_4 gives an alcohol. The olefin is absorbed in sulphuric acid to give alkyl hydrogen sulphate which upon hydrolysis gives alcohol.



An alkyl hydrogen sulphate
(alkyl sulphuric acid)



By this method, ethanol and 2-propanol are obtained from ethylene and propylene respectively. This method is quite valuable particulary in countries where alkenes are important by products of petrochemical industry.

$$CH_2 = CH_2 \xrightarrow[(ii)\ HOH]{(i)\ H_2SO_4} CH_3 - CH_2 - OH$$

$$CH - CH = CH_2 \xrightarrow[(ii)\ HOH]{(i)\ H_2SO_4} CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$$

In the second case, the alkene is unsymmetrical and the addition of water takes place according to Markownikoff's rule. Anti-Markownikoff addition of water to an unsymmetrical alkene may be achieved by hydroboration followed by oxidation.

19.6 INDUSTRIAL PREPARATION OF ALCOHOLS

19.6.1 Methanol

19.6.1.1 Wood distillation

Partially dried wood, upon destructive distillation gives an aqueous distillate, called pyroligneous acid. This contains methanol, acetone and acetic acid. The vapours of pyroligneous acid are passed through lime when acetic acid is retained as calcium acetate, and vapoours of acetone (b.p.56°) and methanol (b.p. 64°) pass on. Acetone and methanol are then separated by fractional distillation.

19.6.1.2 From catalytic hydrogenation of carbon monoxide

Now-a-days 90% of methyl alcohol production is from the catalytic hydrogenation of carbon-monoxide. In this synthetic method, a mixture of carbon monoxide and hydrogen (obtained from natural gas, CH_4) is passed over a catalyst (a mixture of chromic oxide zinc oxide) at 35o° under pressure. Alternatively, water gs ($CO + H_2$), obtained by passing steam over red hot coke, may be mixed with hydrogen and converted into methanol in the presence of catalyst.

$$2\ CH_4 + O_2 \xrightarrow[Catalyst]{1000^\circ} 2\ CO + 4H_2$$

$$CO + 2H_2 \xrightarrow[Catalyst]{350^\circ} CH_3 - OH$$

19.6.2 Ethanol

On a large scale, ethanal is obtained by fermentation process either from starchy substances such as rice, maize, oats, potatoes etc. or from molasses.

19.6.2.1 From starch

'Malt' (germinated barley) is added to the starch solution. The enzyme 'diastase' present in the malt converts the starch into maltose. The fermentation of maltose to alcohol is carried out with yeast. The enzyme 'maltase' present in the yeast hydrolyses maltose to glucose. Another enzyme 'zymase' present in yeast converts the glucose into ethyl alcohol. In this process, control of temperature and pH of the solution are essential for a proper functioning of the enzyme. Due to the profuse evolution of carbondioxide the whole solution appears to be boiling but hardly there is any rise in the temperature. This process where bigger molecules like starch are changed into smaller ones like ethanol with evolution of carbondioxide under the agency of enzymes is called fermentation. Ethanol thus obtained industrially from cereals, is commonly called grain alcohol.

$$\underset{\text{Starch}}{2\,(C_6H_{10}O_5)_n} + n\,H_2O \xrightarrow{\text{diastase}} \underset{\text{Maltose}}{n\,C_{12}H_{22}O_{11}}$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2\,C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2\,C_2H_5OH + 2\,CO_2$$

19.6.2.2 From molasses

The syrupy liquid remaining after the crystallisation of cane sugar is called molasses. It contains nearly 40 to 50% of uncrytallisable sugars in the form of sucrose, glucose and fructose. It is diluted to 10%. A little sulphuric acid is added since the enzyme thrives better in a slighily acid conditions. Maintaining the temperature at about 30° C, yeast is added. The enzyme 'invertase' present in the yeast, changes sucrose into a mixture of glucose and fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The enzyme 'zymase' converts glucose and fructose into ethanol

$$\underset{\substack{\text{Glucose}\\ \text{or}\\ \text{Fructose}}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} 2\,C_2H_5OH + 2\,CO_2$$

19.6..2.3 From ethylene

Ethanol is obtained on a large scale by absorbing ethylene in sulphuric acid at 80° under pressure, and by hydrolysing the resulting ethyl hydrogen sulphate.

$$CH_2 = CH_2 + \underset{\text{Sulphuric acid}}{HO - SO_2 - OH} \longrightarrow \underset{\substack{\text{Ethyl hydrogen sulphate}\\ \text{(ethyl sulphuric acid)}}}{CH_3 - CH_2 - O - SO_2 - OH}$$

$$CH_3 - CH_2 - O - SO_2 - OH + HOH \longrightarrow CH_3 - CH_2 - OH + HO - SO_2 - OH$$

19.6.3 Absolute alcohol

Absolute alcohol is pure ethyl alcohol. The yeast ceases to function beyond a certain concentration of ethyl alcohol. Therefore ethyl alcohol obtained by fermentation of starch or molasses is dilute. The fermented liquid, called 'wash' contains about 10 to 15% alcohol. It is distilled in a special type of still known as Cofey's still. By this process, 95% alcohol, known as rectified spirit is obtained. A mixture containing 95% alcohol and 5% water forms a content boiling mixture (azeotrope). Fractional distillation of an azeotropic mixture cannot give pure alcohol.

Small quantities of absolute alcohol may be obtained by drying the rectified spirit over calcium oxide, when water is removed. Then the dry alcohol is distilled. Commercially, absolute alcohol is obtained by adding an appropriate amount of benzene to the rectified spirit followed by distillation. At first a ternary mixture cotaining ethyl alcohol (18.5%), water (7.4%) and benzene (74.1%) distills over at 65°. This removes all the water. Then a binary mixture of benzene (80%) and alcohol (20%) distills over at 68°, leaving only alcohol in the still. Distillation of this affords absolute alcohol.

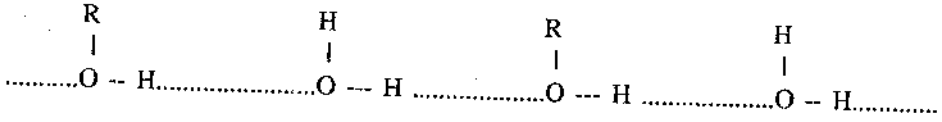
19.7 PHYSICAL PROPERTIS

Alcohols boil at a higher temperature than the alkanes of comparable molecular weight. For e.g. the boiling point of n-pentane (molecular weight 72) is 35-36°, whereas that of n-butyl alcohol (molecular weight 74) is 118°. This abnormality can be explained on the basis of molecular association, through intermolecular hydrogen bonding. In the case of alcohols R- O - H, the O-H bond has considerable ionic character. The hydrogen end carries a partial positive charge and oxygen end

$$\overset{\delta-\ \ \delta+}{R - O - H}$$

a partial negative charge. This may be represented a R - O - H. The hydrogen of one molecular is attracted by the oxygen of the second molecule and so on. The situation may then be represented as

The broken line indicates the hydrogen bond. A hydrogen atom acts as a bridge between two electronegative atoms such as oxygen, nitrogen or fluorine. To one of these electronegative atoms, the hydrogen is covalently bonded, and to the other bonded by an electrostatic attraction. In the case of alcohols, hydrogen acts as a bridge between two oxygen atoms. Thus, several molecules are held together by intermolecular hydrogen bonds. When liquids of this type are boiled, part of thermal energy supplied is used up, to break these hydrogen bonds., This explains the higher boiling points of alcohols. In the case of alkanes there are no attractive forces between their molecules. Intermolecular hydrogen bonding is also responsible for the solubility of alcohols in water. Hydrogen bonds between alcohol and water molecules leads to a solution.



In lower alcohols such as methanol, ethanol etc., the hydroxyl group constitutes bulk of the molecules and the solubilizing effect of the hydroxyl group (by forming hydrogen bonds) predominates. But in higher alcohols, the hydrocarbon part (hydrophobic part) predominates, and this outweighs the solubilizing effect of the hydroxyl group. Therefore the solubility of higher alcohol in water decreases.

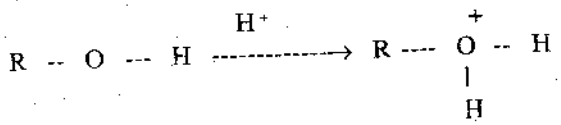
19.8 CHEMICAL PROPERTIES

The properties of alcohols can be studied under two heads: (1) Reactions involving the O-H bond and (2) Reactions involving the C-O bond.

19.8.1 Reactions involving the O - H bond

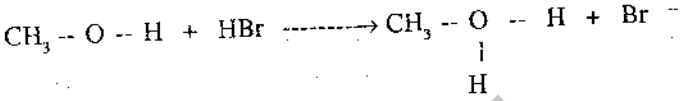
19.8.1.1 Basic and acidic nature

Due to the presence of nonbonding electrons on the oxygen atom, an alcohol can function as a Lewis base. A molecule of an alcohol can accept a proton to form protonated alcohol. The protonated alcohol (conjugate acid of the alcohol) is an oxonium ion.

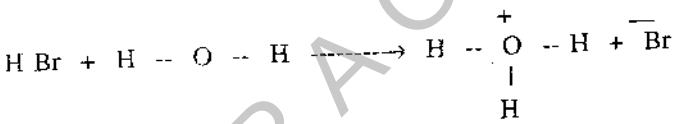


Protonated alcohol
(an oxonium ion)

Methanol for instance, can react with a strong acid such as HBr to give an oxonium ion.

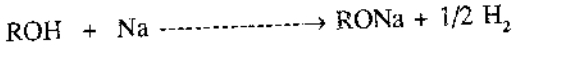


Alcohols and water are comparable as bases. The reaction of water and hydrogen bromide leads to the formation of hydronium ion.

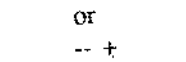


hydronium ion

Water reacts with active metals liberating hydrogen. In these reactions, water behaves as an active hydrogen containing compound i.e., a acid. Just like water, alcohols also react with active metals such as pootassium and sodium. In this reaction hydrogen is liberated, and metal alkoxides or alcoholates are formed.

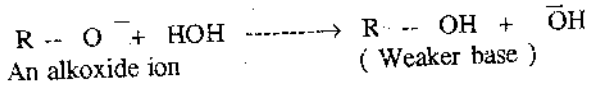


or



Sodium alkoxide

However alcohols are weaker acids than water. Alkoxide ion (the conjugate base of alcohol) is a stronger base than the hydroxide ion (the conjugate base of water). Consequently the alkoxide ion reacts with water to form alcohol and a hydroxide ion.



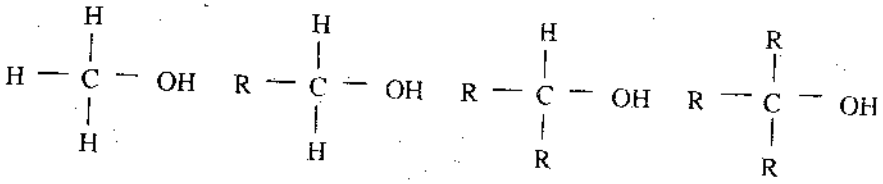
An alkoxide ion
(Stronger base)

(Weaker base)

In the above reaction, a weaker base is displaced by a stronger base. Grignard reagent reacts with alcohols liberating alkanes (alkanes are weaker acids than alcohols).

$$R\text{--}OH + R'\text{--}Mg\text{--}X \longrightarrow R'H + Mg(OR)X$$

The order of acidic strength of alcohols is methanol > primay alcohol > sec. alcohol > ter. alcohol. The + I effect of the alkyl groups is responsible for this order. In these compounds the number of groups exerting the +I effect progressively increases.



In the case of a tertiary alcohol, such as t-butyl alcohol, due to the + I effect of three alkyl groups on the carbon, the electron density between oxygen and hydrogen increases. This makes the hydrogen of the hydroxyl group less labile i.e. proton release becomes difficult.

19.8.1.2 Ether formation

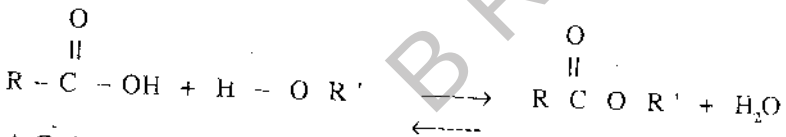
When alkyl halides react with sodium alkoxides ethers are formed. This reaction is called Williamson synthesis of ethers. When sodium ethoxide reacts with methyl iodide methyl ethyl ether is formed.

$$R\text{--}O\text{--}Na + R'X \longrightarrow R\text{--}O\text{--}R' + NaX$$

$$CH_3\text{--}CH_2\text{--}O\,Na + CH_3I \longrightarrow \underset{\text{Methyl / ethyl ether}}{CH_3\text{--}CH_2\text{--}O\,CH_3} + NaI$$

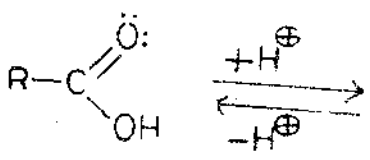
19.8.1.3 Ester formation

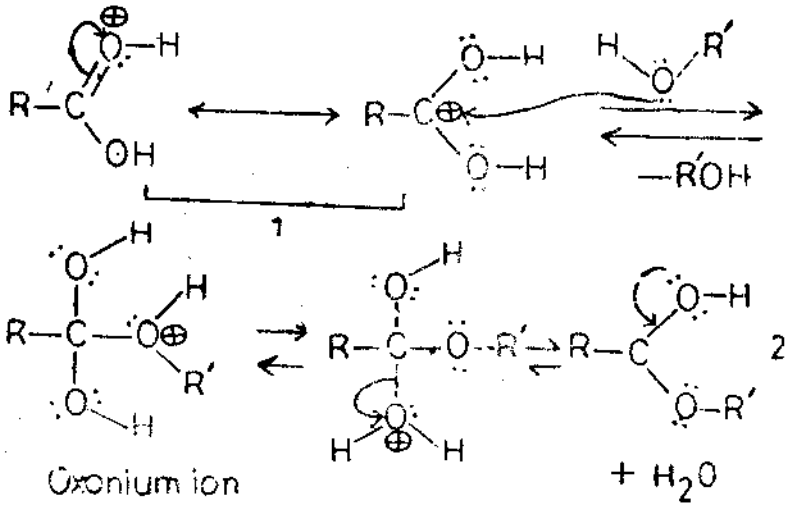
When alcohols react with carboxylic acids, esters are formed. This reaction is called esterification.



A Carboxylicated An alcohol — An ester

In esterification of a given acid the reactivity of alcohols is primary > secondary > tertiary. A acidic catalyst such as sulphuric acid or dry HCl gas is used in this reaction. In this reversible reaction, the equilibrium can be shifted to the right either by increasing the concentration of the reactants or by constantly removing one of the products of the reaction. Thhe mechanism of the acid catalysed esterification is as follows:

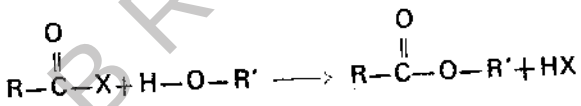




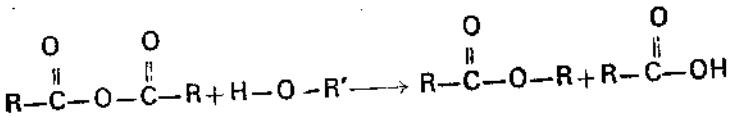
1 – Protonated carboxylic acid

2 – Protonated ester

Esters are also obtained by the reaction of an alcohol with an acid halide or an acid anhydride.



An acid halide



An acid anhydride

19.8.2 Reactions involving the C— O bond

19.8.2.1 Dehydration

Alcohols react with conc. sulphuric acid to give alkyl hydrogen sulphate which upon further heating gives alkenes. The order of reactivity of alcohols in dehydration is tertiary > seconday > primary. In the reaction of ethanol with sulphuric acid ethylhydrogen sulphate is first formed which decomposes at a higher temperature to form ethylene.

$$CH_3-CH_2-OH + H_2SO_4 \longrightarrow CH_3-CH_2-O-SO_3H + H_2O$$
$$\text{or}$$
$$CH_3-CH_2-HSO_4$$

$$CH_3-CH_2-O-SO_3H \xrightarrow{165^\circ} CH_2=CH_2 + H_2SO_4$$

At lower temperature and with excess ethanol, the ethyl hydrogen slphate, first formed, reacts with another molecule of ethanol to give ethyl ether.

$$C_2H_5\ HSO_4 + HO\ --\ C_2\ H_5 \xrightarrow{140^\circ} C_2H_5\ --\ O\ --\ C_2H_5 + H_2\ SO_4$$

(Second molecule) of ethanol — ethyl ether

Dehydration of alcohols may also be effected by passing the vapours of alcohol over heated alumina. Ethylene is obtained by passing ethanol vapours over alumina at 350°.

$$CH_3\ --\ CH_2\ --\ OH \xrightarrow{Al_2O_3,350^\circ} CH_2 = CH_2$$

At a lower temperatures, however, this reaction leads to the formation of ethers.

$$2\ ROH \longrightarrow R\ --\ O\ ---\ R + H_2\ O$$

19.8.2.2 Halide formation

Alcohols react with hydrogen halides to form alkyl halides. This is another example of cleavage of the carbon --- oxygen bond in alcohols.

$$ROH + HX \longrightarrow R\ --\ X + H_2\ O$$

The order of reactivity of alcohols for a given hydrogen halide is tertiary> secondary > primary, and that of hydrogen halides for a given alcohol is HI> HBr > HCl, t-Butyl alcohol reacts readily with HCl to form t-butyl chloride.

$$H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH + HCl \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Cl + H_2O$$

t - Butyl chloride

The rate at which primary, secondary and tertiary alcohols react with HCl in the presence of anhydrous $ZnCl_2$ varies. This is the basis of Lucas test to distinguish the three types of alcohols. To the given alcohol Lucas reagent (a solution of anhydrous $ZnCl_2$ in conc. HCl) is added and kept in a water bath at about 30°C. The time for formation of corresponding alkylhalide (water insoluble) or the time for the appearance of turbidity is noted. With this reagent tertiary alcohols react rapidly and secondary alcohols react slowly to form corresponding alkyl chlorides. Primary alcohols do not react

at this temperature. The alkyl chlorides are insoluble water. Therefore the turbidity appears immediately in the case of ter. alcohol, in one to five minutes. If it is a secondary alcohol, and with primary alcohol no turbidity appears at that temperature.

Alcohols are also converted into alkyl halides by reaction with thionyl halides.

$$R - OH + SOX_2 \longrightarrow R - X + SO_2 + HX$$

$$CH_3 - CH_2 - OH + SO_2Cl \longrightarrow CH_3 - CH_2 - Cl + SO_2 + HCl$$

Alkyl chlorousIphate appears to be the intermediate in this reaction.

$$R - OH + SOCl_2 \xrightarrow{-HCl} \left(R - O - \underset{\displaystyle Cl}{\overset{\displaystyle |}{S}} = O\right) \longrightarrow RCl + SO_2$$

The replacement of the -- OH group of an alcohol by a halogen can also be achieved by using phosphorus pentahalides or trihalides.

$$R - OH + PX_5 \longrightarrow R - X + POX_3 + HX$$

$$C_2H_5OH + PCl_3 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$

Reaction of an organic compound with PCl_5, with the liberation of HCl, is considered as a positive test for the presence of OH group in the compound.

$$3\,R - OH + PX_5 \longrightarrow 3\,R - X + H_3PO_3$$

$$3\,C_2H_5OH + PCl_5 \longrightarrow 3\,C_2H_5Cl + H_3PO_3$$

19.8.2.3 Oxidation of alcohols

Primary alcohols are oxidised first to aldehydes and then to acids by potassium dichromate in acidic medium. There is no loss of carbon atoms during the oxidation of primary alcohols. The alcohol, aldehyde and acid, all contain the same number of carbon atoms.

$$R - CH_2OH \xrightarrow[H^+]{K_2Cr_2O_7} RCHO \xrightarrow[H^+]{K_2Cr_2O_7} RCOOH$$

An alcohol — An aldehyde — An acid

$$CH_3OH \xrightarrow{(O)} H.CHO \xrightarrow{(O)} H.COOH$$

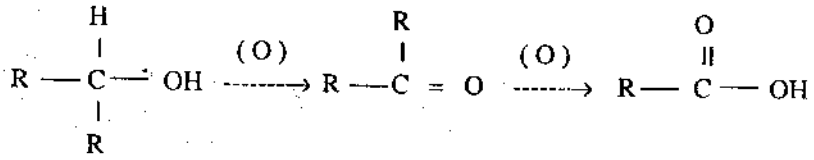
Methanol — Methanal (formaldehyde) — Methanoic acid (formic acid)

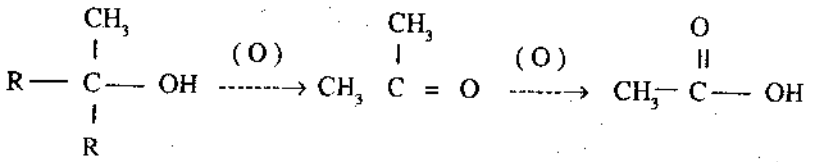
$$CH_3CH_2OH \xrightarrow{(O)} CH_3CHO \xrightarrow{(O)} CH_3COOH$$

Ethanol — Ethanal (acetaldehyde) — Ethanoic acid (acetic acid)

A primary alcohol is directly oxidised to the acid with potassium permanganate.

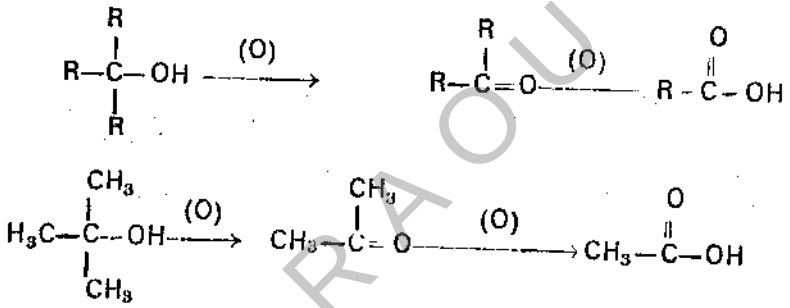
Secondary alcohols upon oxidation, with dichromate and acid, give ketones. Further oxidation of ketones is difficult, and the resulting acids contain lesser number of carbons than the ketone.





2 - Propanol (contains 3 carbon atoms) | Acetone (contains 3 carbon atoms) | Acetic acid (contains 2 carbon atoms)

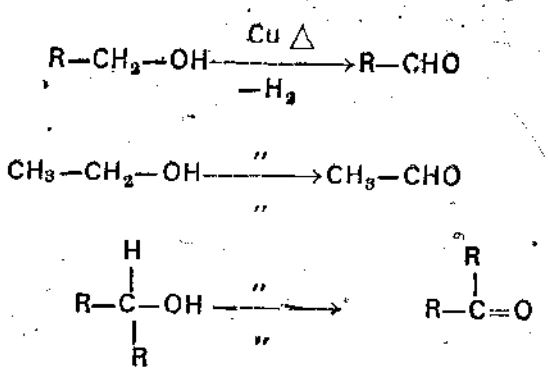
It is difficult to oxzidise the tertiary alcohols. The products of oxidation of tertiary alcohols., obtained under drastic conditions are ketone and carboxylic acid. Oxidation of t-butyl alcohol gives a mixture of acetone and acetic acid.



None of the oxidatio products of tertiary alcohol, contains the same number of carbon atoms as the starting alcohol.

19..8.2.4 Dehydrogenation of alcohols

Dehydrogenation of primary and secondary alcohols results in the formation of carbonyl compounds. The alcohol vapour is passed over heated copper. Primary alcohols give aldehydes, and secondary alcohols give ketones. Tertiary alcohols do not undergo dehydrogenation.

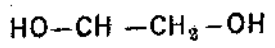


Thus, dehydrogenation of alcohols serves as a test for distinguishng the primay, secondary, and tertiary alcohols.

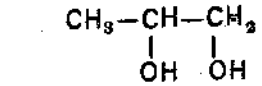
19.9 POLYHYDRIC ALCOHOLS

19.9.1 Dihydric alcohols (Glycols)

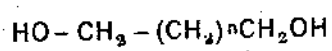
Dihydric alcohols are compounds containing two hydroxyl groups. Depending upon the position of the hydroxyl groups they are called 1,2 glycols; 1,3 - glycols and so on. 1,2 - Glycols are usually named after the alkenes from which they are obtained by hydroxylation.



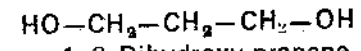
Ethylene glycol
(obtained by hydroxylation of ethylene)



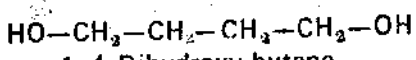
Propylene glycol
(obtained by hydroxylation of propene)



Polymethylene glycol

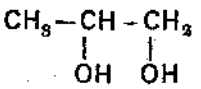


1, 3-Dihydroxy propane
(trimethylene glycol)

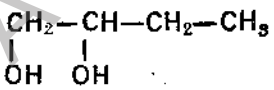


1, 4-Dihydroxy butane
(tetra methylene glycol)

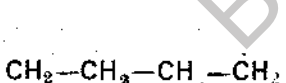
According to IUPAC system, glycols are named as alkane diols. The positions of the hydroxyl groups and the substituents, if any, are indicated in the prefix.



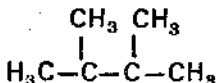
Propan-1,2-diol



Butan-1, 2-diol



Butan-1, 4-diol

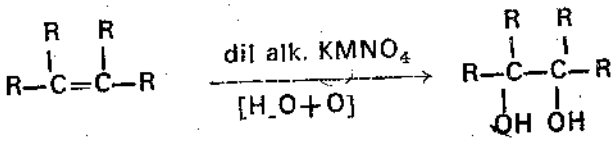


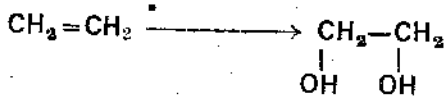
2, 3-Dimethyl butan-2, 3-diol.

19.9.1.1 General methods of preparation of 1,2-glycols

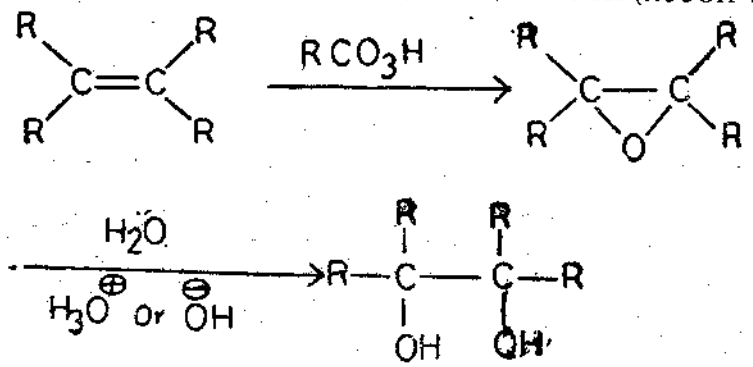
19.9.1.1.1 From alkenes

Oxidising agents, such as cold alkaline $KMnO_4$ convert alkenes into corresponding diols.





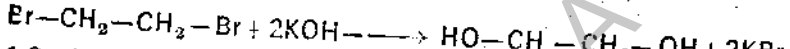
Glycols are obtained by the hydrolysis of epoxides by a dilute acid or alkali. Epoxides, in turn, are obtained by the reaction of alkenes with peracids, RCOOOH (RCOOH $+H_2O_2$)



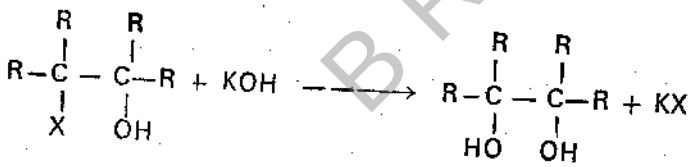
An epoxide

19.9.1.1.2 From Dihaloalkanes and halohydrins

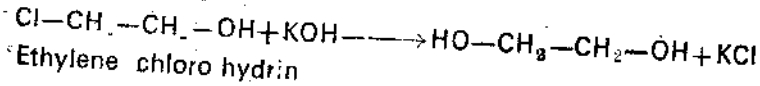
Dihaloalkanes and halohydrins, on hydrolysis with aqueous alkali, form corresponding glycols.



1,2—Dibromoethane



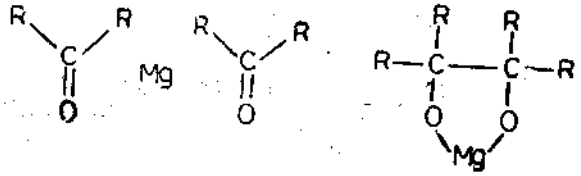
A halohydrin

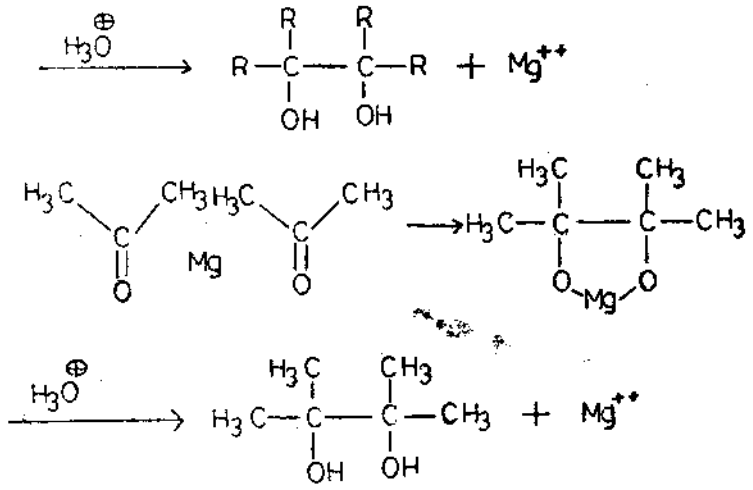


Ethylene chloro hydrin

19.9.1.1.3 Pinacol reduction of ketones

In another method, ketones are reduced with magnesium in acid medium. To increase the reactivity of magnesium it is used as amalgam. This bimolecular reduction is also known as pinacol





Magnesium pinacolate

reduction of ketones, 2, 3 - Dimethyl butan - 1,4-diol (pinacol) is obtained from acetone. The only difference is that glycol consume two moles of reagents that react with monohydric alcohols.

19.9.2 Ethylene glycol

It is an important member of this class of compounds. Various methods are available for the preparation of ethylene glycol.

19.9.2.1 Preparation

Treatment of ethylene with cold, dilute permanganate results in the formation of glycol.

$$CH_2=CH_2 \xrightarrow[(H_2O+O)]{\text{dil alk, } KMnO_4} \underset{OH\ \ OH}{CH_2-CH_2}$$

Ethylne dibromide is converted to ethylene glycol by boiling with aqueous sodium carbonate. Alternatively ethylene dibromide, upon heating with potassium acetate in glacial acetic acid gives ethylene glycol diacetate which is hydrolysed to glycol.

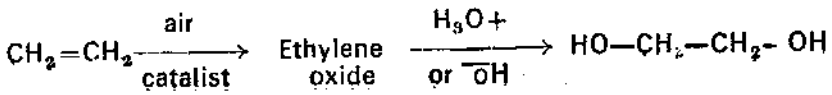
$$Br-CH_2-CH_2-Br + Na_2CO_3 + H_2O \longrightarrow 2\,NaBr + CO_2 + \underset{HO-H\,C-CH_2-OH}{}$$

$$Br-CH_2-CH_2-Br + 2\,CH_3COOK \xrightarrow{\text{acetic acid}} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2 \quad CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3 + 2KBr$$

Ethylene diacetate

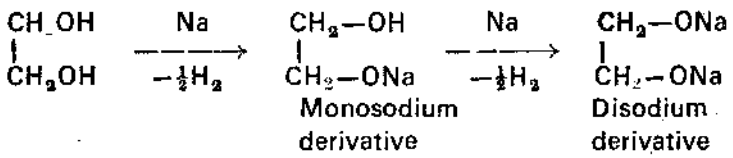
$$H_3C-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{H_3O+} HO-CH_2-CH_2-OH + 2CH_3COOH.$$

Technically glycol is prepared by the hydrolysis of ethylene oxide. Ethylene oxide itself is obtained by passing a mixture of thylene and air under pressure over silver catalyst at 200 - 400°.

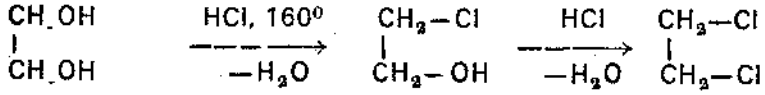


19.9.2.2 Properties of ethylene glycol

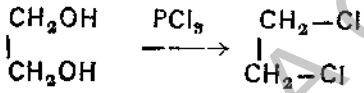
It is a colourless viseous liquid. It is miscible with water. It reacts with metallic sodium to give monosodium and the disodium derivatives.



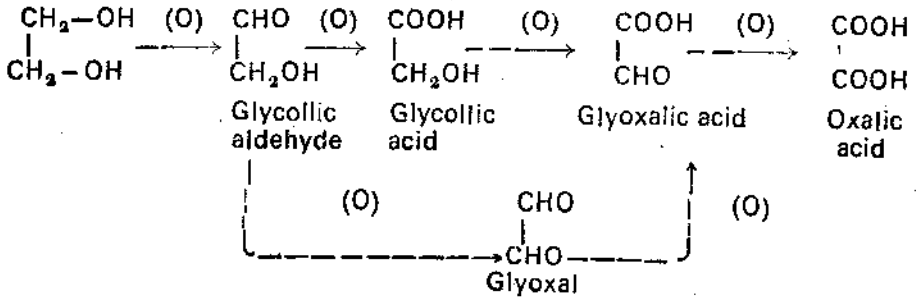
Chlorination: Glycol reacts with hydrogen chloride to give first ethylene chlorohydrin and finally ethylene dichloride.



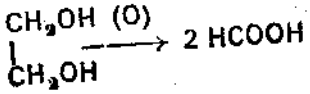
When reacted with phosphorus trichloride the two hydroxyls are replaced by the halogen.



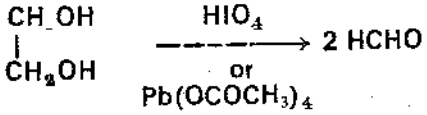
Oxidation: Glycol is oxidised by dilute nitric acid to give a number of products. The final product is oxalic acid.



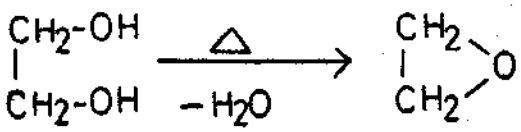
Oxidation of glycol with permanganate or dichromate cleaves the carbon carbon bond. Formic acid is the product in this reaction.



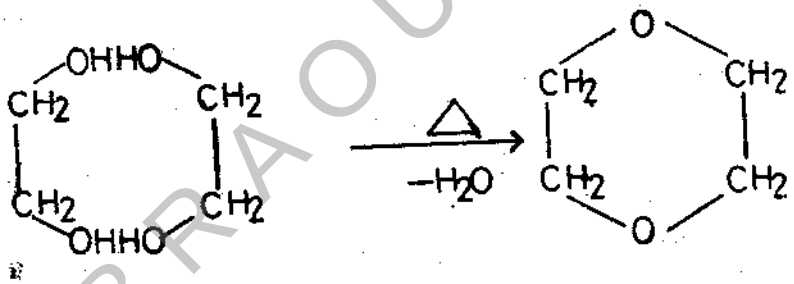
Cleavage of the carbon - carbon bond in ethylene glycol is also effected by periodic acid or lead tetracetate. Formaldehyde is the product.



Dehydration: When heated along, ethylene glycol loses water to give ethylene oxide.



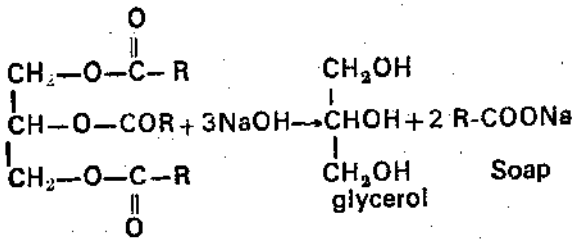
However, dioxane is obtained on heating ethylene glycol with conc. H_2SO_4. Dioxane is used in industry as a solvent.



Pinacol pinacolone rearrangement (Appendix - 3)

19.9.3 Trihydric alcohols

Glycerol: It is the simplest trihydric alcohol. It is a byproduct of soap industry. When an oil or fat is heatedd with 10% NaOH, saponification takes place. Soap (sodium salt of a fatty acid) and glyceorol are obtained.

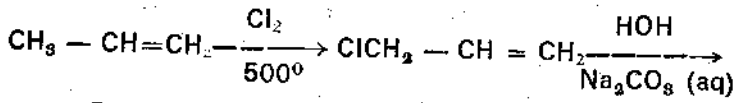


Oil or fat

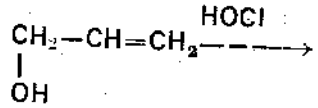
The soltution remaining after the removal of the soap is called spent lye. This contains glycerol. Alum is added to the spent lye to precipitate the impurities and other filtrate is evaporated under reduced pressure to avoid the decomposition of glycerol. The concentrate containing about 70% glycerol is distilled with super heated steam under reduced pressure. Finally glycerol is obtained by evaporating the ditillate in vacuum.

19.9.3.1 Synthesis of glycrol

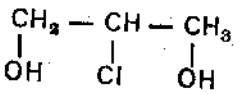
Glycerol is synthesised from propylene. Propylene is treated with chlorine at elevated temperature to give allyl chloride. Allyl chloride is hydrolysed by heating with aq. sodium carbonate solution to give allyl alcohol. This is then treated with HOCl to give glycerol monochloro hydrin which is hydrolysed by alkali to glycerol.



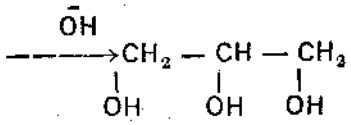
Propylene Allyl chloride



Allyl alcohol



glycerol monochlorohydrism



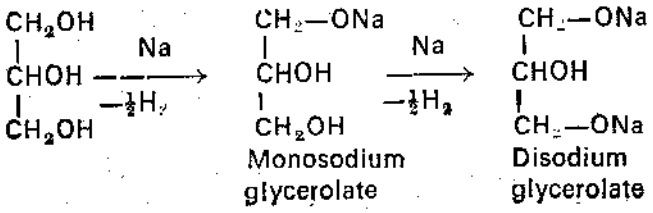
glycerol

Glycerol is s colourless syrupy liquid with sweet taste.

19.9.3.2 Chemical properties

19.9.3.2.1 Reaction with sodium metal

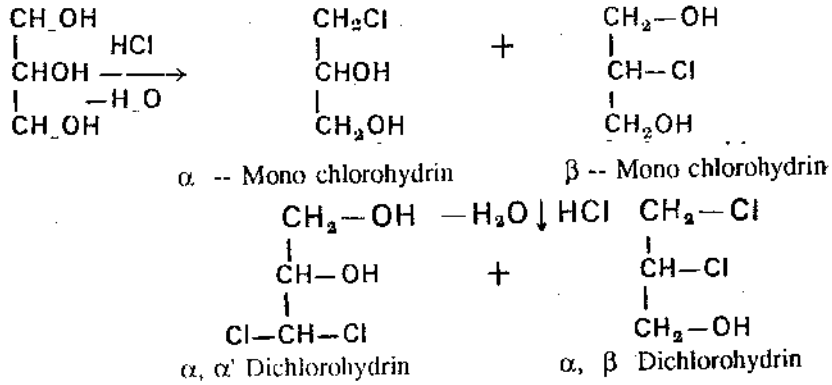
Primary alcoholic groups react readily with sodium metal. Reaction of Glycerol with sodium gives first the monosodium derivative and the disodium derivative. The Secondary alcoholic group is not attacked.



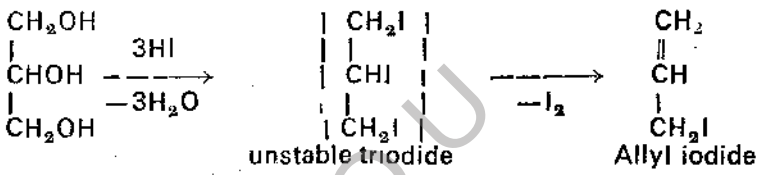
Monosodium glycerolate Disodium glycerolate

19.9.3.2.2 Reaction with hydrogen halides

When hydrogen chloride is passed into glycerol at 110°. a mixture of α and β monochlorohydrins is obtained. When the reaction is continued further a mixture of α, α,' and α, β dichloro hydrins is obtained.

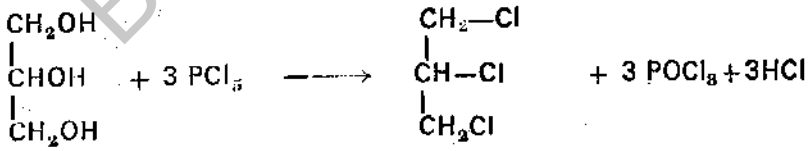


When glycerol is heated with hydrogen iodide, an unstable triiodide is first formed which loses iodine to give allyl iodide.



19.9.3.2.3 Reaction dwith PCl_5

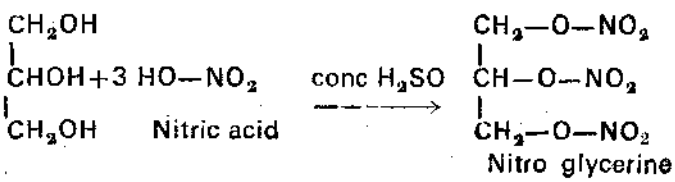
Wgen glycerol reacts with PCl_5, glyceryl trichloride is formed. The three hydroxyl groups replaced by chlorine.



1, 2, 3 Trichloro propane
(glyceryl trichloride)

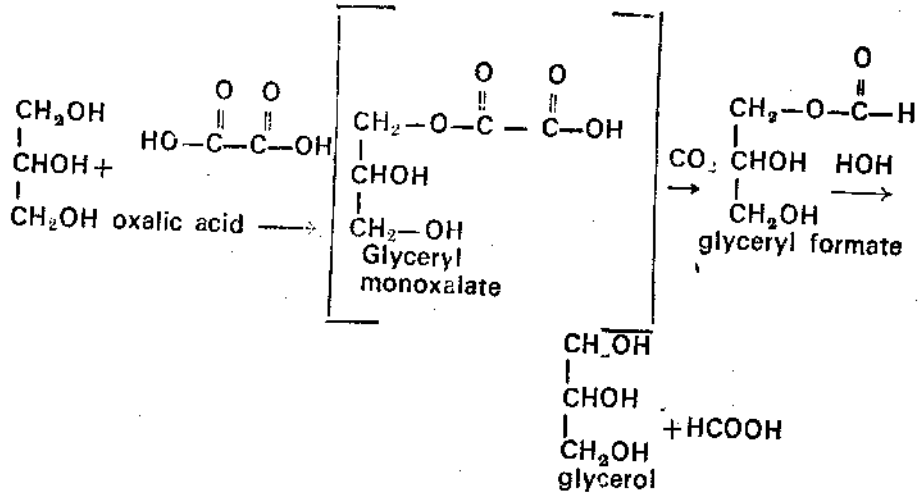
19.9.3.2.4 Nitration

When glycerol is treated wih a well-cooled mixure of conc. H_2So_4 and HNO_3, glyceryl trinitrate or nitroglycerine is formed. This is an explosive substance.



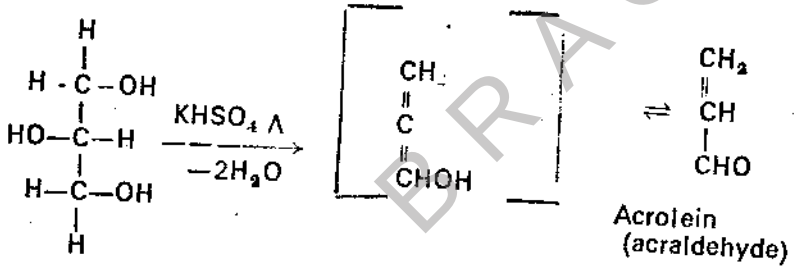
19.9.3.2.5 Reaction with oxalic acid

When glycerol is based with crytalline oxalic acid, $(COOH)_2 2H_2O$, at 110°, formic acid is obtained. Glycerol monoformate, first formed, undergo hydrolysis to give formic aid.



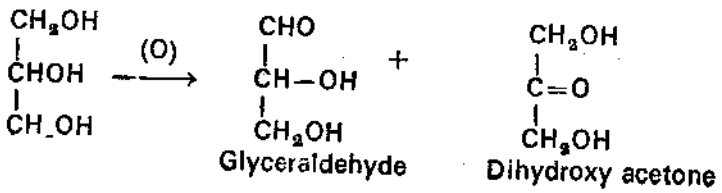
19.9.3.2.6 Dehydrations

When glycerol is heated with potassium hydrogen sulphate, two molecles of water are lost and acrole is fomed.

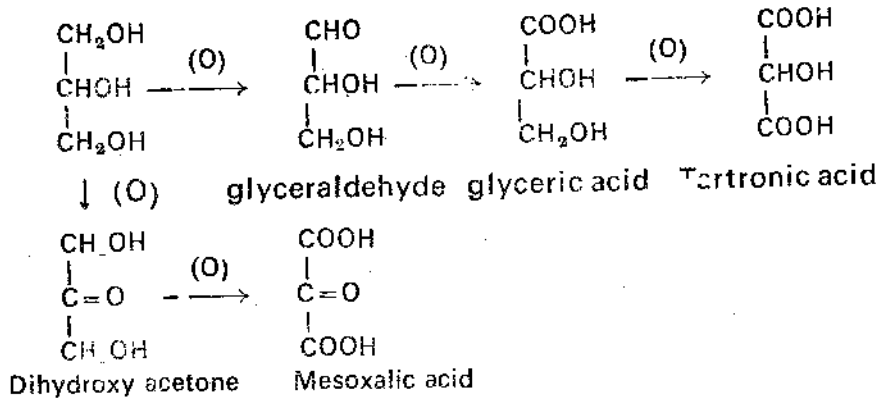


19.9.3.2.7 Oxidation

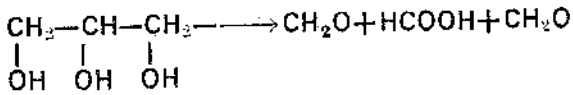
The product of oxidation of glycerol depends upon the nature of the oxidising agent. Oxidation of glycerol with sodium hypobromite, gives a mixture of glyceraldehyde and dihydroxyacetone (This mixture is called glycerose)



Dilute nitric acid oxidise glycerol to glyceric acid and tatronic acids. ConceÿÇÈflÈflrated nitric acid oxidises it to glyceric acid. Bismuth nirate oxidises it to mesoxalic acid.



Periodic acid oxidises glycerol with the cleavage of C-C bonds.



19.10 USES OF ALCOHOLS

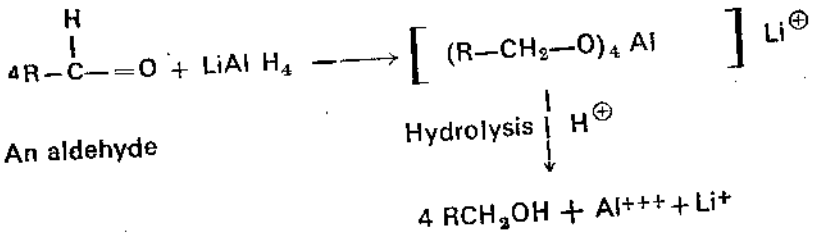
Met anol is used largely as a solvent in the plastic and textile industries (ii) for cleaning metal and glass p..rts (iii) for power boosters in gasoline engines (iv) for antifreezes and for production of formaldeh.yde.

Ethyl alcohol is widely used (1) as a starting material in synthesis (ii) as a solvent (iii) as an ingredient of amny commercial products. It also finds application in lacquers, varnishes, medicinal and flavouring extracts, perfumes, cosmetics, dyes etc.

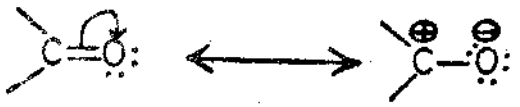
Ethylene glycol is used in the manufacture of plastics. Ethylene glycol dinitrate is used as low freezing dynamite.

Glyceroltrinitrate is a powerul explosive. It is soaked up by sawdust for stabilisation and is commercially known as dynamite.

Appendix-1: A carbonyl compound is reduced by LiAl H_4 to give the corresponding alcohol. Lithium aluminium hydride is a soure of hydride ion (H^-). The hydride ion is a nucleophile and therefore attacks the carbonyl carbon atom.



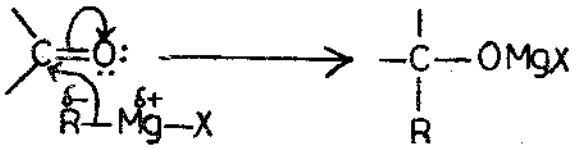
Appendix - 2: both aldehydes and ketones contain the carbonyl (C=O) It is unsaturated function and undergoes addition reactions with Grignard reagent. The double bond between carbon and oxygen is made of sigma (σ) and a Pi (π) bond. Carbonyl group is a resonance hybrid of two structures. In otherwords, in carbonyl groups the carbon end is positive and the oxygen end is negative.



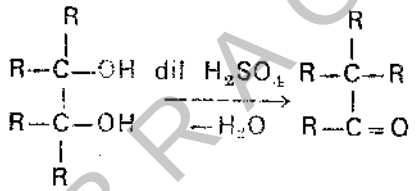
The nucleophilic part of the reagent therefore adds to the carbon of the carbonyl group and the electrophilic part to the oxygen . In R - Mg -- X the carbon magnesium bond is polar

δ— δ =

(R -- Mg -- X) . In the addition reactions of the Grignard reagent at the carbonyl group, the alkyl group, of the reagent becomes attached to the carbonylcarbon and magnesium end to the carbonyl oxygen.

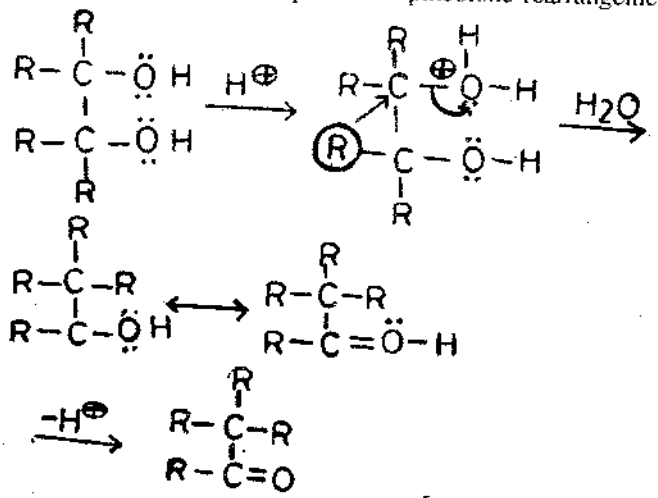


Appendix - 3: Pinacol, upon distilling with dilute sulphuric acid undergoes an elimination reaction. The eli,mination reaction. The elemination reaction is accompanied by a molecular rearrangement to give pinacolone.



A Pinacol A Pinacolone

Following is the mechanism of pinacol -- pincolone rearrangement



19.11SUMMARY

The essential features of monoalkyl derivatives of water i.e. alcohlols are

i. They can redily be prepared from alkyl halides, aldehydes,ketones, alkenes and from natural resources such as wood natural gas, starch and molasses on a large scale.

ii. They are unique in having intermolecular hydrogen bonding which explains the higher boiling points and solubility in water.

iii. Basic and acidic nature.

iv. Conversion to different elders of orgaic compounds such as ethers, alkenes, alkyl halides. monocarboxylic acids, ketones.

v. These alcohols are industrially useful, consmotics, perfumes, lacquers, varnishes etc.

vi. The polyhydric alcohols ethylene glycol and glycerol are used in the manufacture of plastics and explosives.

19.12 MODEL EXAMINATION QUESTIONS

I. Answer the follwoing in each 10 lines

1. Compl te the following

a. Acetaldeyde + isopropylmagnesium bromide $\xrightarrow{H_3O^+}$?

b. Methyl ethyl ktone + methyl magnesium bromide $\xrightarrow{H_2O^+}$?

b. Methyl ethyl ktone + methyl magnesium bromide $\xrightarrow{H_3\ O^+}$?

2. How do you prepare benzyl alcohol starting from benzene?

3. How does n-propyl magnesium chloride react with the following

a) Ethylene oxide (b) formaldehyde (c) acetaldehyde, write equation.

4. How do you dstinguish ?

a) 1- Pentanol from 2 -pentanol
b) Ethanol from methanol.

5, How do you convert 1- propanol to 2- propanol, and vice versa?

6. Complete the following:

a) Ethanol $\xrightarrow{PCl_5}$ $\xrightarrow{\text{alc. KOH}}$ $\xrightarrow[\text{(ic) } H_2O]{\text{(I) } H_2SO_4}$

b) Ethanol $\xrightarrow[160°.C]{\text{conc. } H_2SO_4?}$ $\xrightarrow{HCl}$

c) Isopropyl alcohol $\xrightarrow{P + Br_2}$? $\xrightarrow{C_2 H_2 ONa}$

7) Write equavations for the following reactions.

a) Ethyl alcohol + acetic anhydride ⟶

b) n- butyl alcohol + acetic acid ⟶

II. Answere the following in each 30 lines

1. o.92 gms of a monobydric alcohol reacts quantitatively with excess sodium metal and iberated 224 ml of hydrogen at STP. What can be the molecular weight of the alcohol?

2. Two isomric compounds (A) and (B) with the molecular formula $C_2 H_8 O_2$ are hydrolysed. (A) gave acetic acid and ethanol; (B) gave propionic acid and methanol,. What are (A) and (B).

19.13 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. The possible isomeric structures and their IUPAC names with molecular formula CHO are

a) $CH_3\ CH_2\ CH_2\ CH_2\ OH$ -- 1 Butanol.

b) $CH_3\ CH_2\ \underset{\displaystyle OH}{\underset{|}{C}}H\ CH_3$ -- 2 Butanol.

c) $CH_3\ \underset{\displaystyle CH_3}{\underset{|}{C}}H\ CH_2\ OH$ -- 2 - methyl propanol

d) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - OH$ -- 2 - methyl 2 - propanol

2. Grignard reagent adds on to the carbonyl group of an aldehyde or ketone to from an additio poduct, whch upon hyrolysis gives an alcohol Formaldehyde gives primary alcohols while any other aldehyde yields secondary alcohol. In the synthesis of 2-butanol the carbonyl compound should be acetaldehyde and the appropriate grignard reagent be chyl magnesium bromide.

$$CH_3 - \underset{\displaystyle H}{\underset{|}{C}} = O + CH_3\ CH_2\ MgBr \xrightarrow{H_3O^+} CH_3 - \underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - CH_2\ CH_3$$

UNIT - 20 PHENOLS

Contents

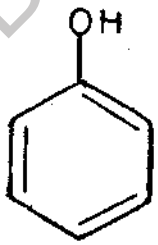
20.1 AIMS AND OBJECTIVES

In this unit we wish to explain you the structural aspects, methods of preparation and properties of phenols. After completion of this unit you must be able to know:

- General methods of preparation
  - i) From sulphonic acids
  - II) From primary amines
- Manufacture
  - i) From chlorobenzene
  - ii) From cumene
  - iii) From Coaltar
- Physical properties
- Chemical proerties
  - i) Aciddic nature
  - ii) For,mation of ethers
  - iii) Formation of esters
  - iv) Fries rearrangement
  - v) Reaction with PCl_5
  - vi) Nitration
  - vii) Sulphonation
  - viii) Halogenation
  - ix) Oxidation
  - x) Reimer - Tiemann reaction
  - xi) Kolbe - Schmidt reaction
  - xii) Coupling with diazonium salts
  - xiii) Hoesch reaction
  - xv) Reaction with formaldehyde
  - xvi) Reaction with phthalic anhydride
  - xvii) Liebermann's nitroso reaction
- Dihydric Phenols
  - i) Catechol
  - ii) Resorcinol
  - iii) Hydroquinone

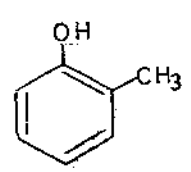
20.2 INTRODUCTION

In phenols, one or more hydroxyl groups are directly attached to the benzzene ring. These are classified as monohydric, dihydric and trihydric phenols depending upon the number of hydroxyl groups present. Monohydric phenols contain only one hydroxyl group.

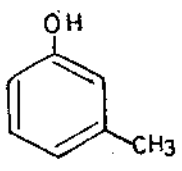


Hydroxybenzene
(phenol)

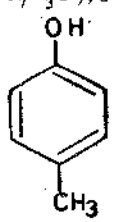
Hydroxy toluenes are known as cresols. Three isomeric cresols (C_7H_8O), o-, m- and p- cresols are known.



o-Cresol

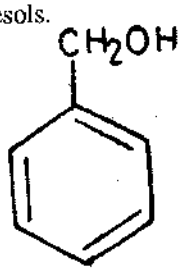


m-Cresol



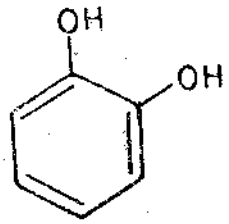
p-Cresol

If the hydroxyl group is not directly attached to the carbon atom of the benzene ring i.e., attached to the carbon atom in the side chain, the compound is not a phenol. Benzyl alcohol $C_6H_5 - CH_2 - OH$ is an aromatic alcohol. It is isomeric with cresols.

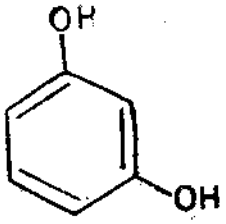


Benzyl alcohol

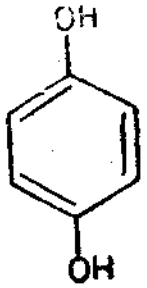
Dihydric phenols have two hydroxyl groups attached to the ring carbons. The three isomeric dihydric phenols are



Catechol

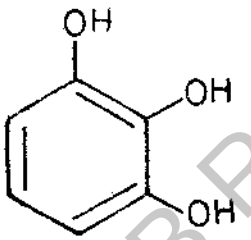


Resorcinol

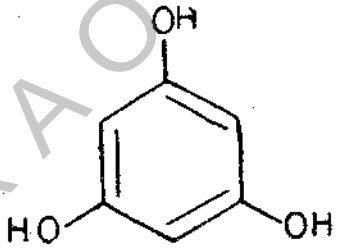


Hydroquinone

Trihydric phenols contain three hydroxyl groups attached to the ring carbons.

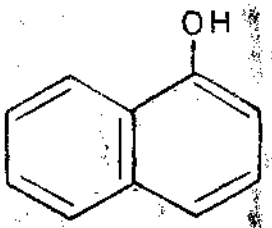


Pyrogallol
(1,2,3-Trihydroxy benzene)

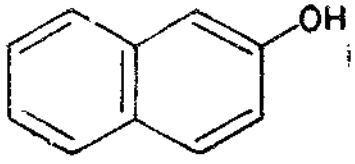


Phloroglucinol
(1,3,5-Trihydroxy benzene)

Hydroxy derivatives of naphthalene are called naphthols. The two naphthols are α – and β - naphthols.



α-Naphthol
(1-Napthol)



β-Naphthol
(2-Naphthol)

20.3 GENERAL METHODS OF PREPARATION OF PHENOLS

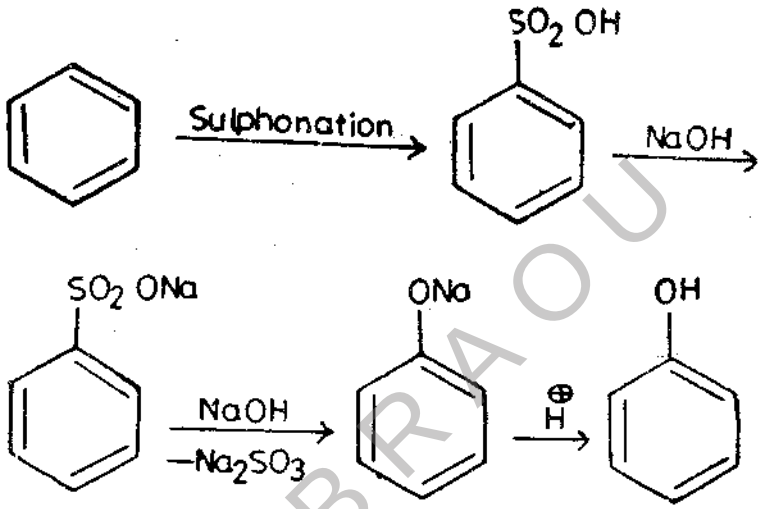
20.3.1 From sulphonic acids

Aromatic hydrocarbons are converted into phenols through sulphonation, followed by fusion of sodium salt of the resulting sulphonic acid with alkali. Phenol is obtained from benzene. Benzene is sulphonated with conc. H_2SO_4 to benzenesulphonic acid. The sodium salt of benzene sulphonic acid upon fashion with sodium hydroxide gives sodium phenoxide, which is acidified to give phenol.

$$\underset{\text{Atomatic hydrocarbon}}{Ar - H} \xrightarrow[H_2O]{H_2SO_4} \underset{\text{Aryl sulphonic acid}}{Ar - SO_2 - OH} \xrightarrow{NaOH}$$

$$Ar - SO2 - ONa \xrightarrow[\text{Fusion}]{NaOH} Na_2SO_3 + Ar - ONa \xrightarrow{H^+} Ar - OH$$

Sodium salt of anyl sylphonic acid

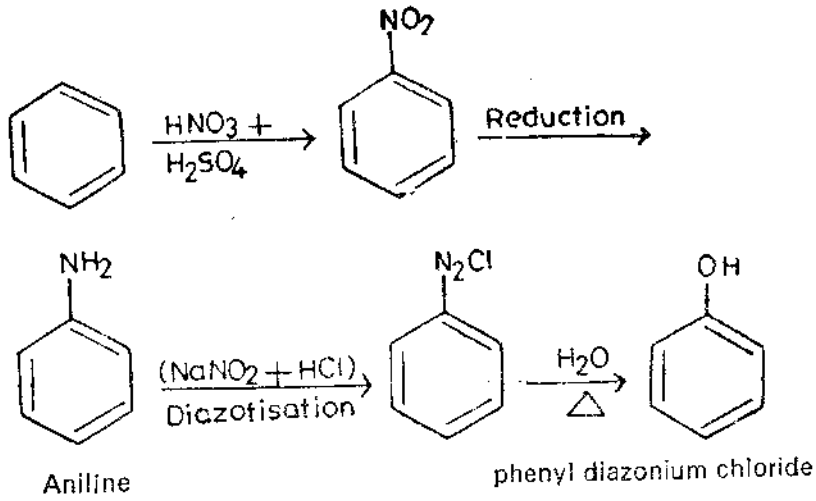


20.3.2 From primary amines

Aromatic nitrohydrocarbons are reduced to amines and then converted into phenols through diazonium salts. Benzene is nitrated to give nitrobenzene. This is reduced to aniline using zinc and HCl. Aniline is treated with sodium nitrite and HCl at O°C when benzene diazonium chloride is formed. Upon heating diazonium salt with water, phenol is formed.

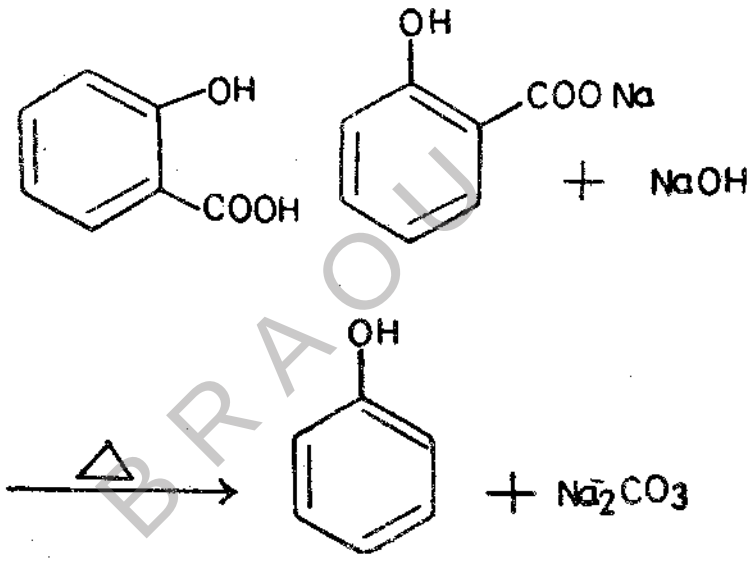
$$\underset{\text{Aromaticnitro hydro carbon}}{Ar - NO_2} \xrightarrow{\text{Reduction}} \underset{\text{Arylamine}}{Ar - NH_2} \xrightarrow[O°C]{HNO_2 \; (NaNO_2 + HCl)}$$

$$\underset{\text{Aryldiazonium ion}}{Ar - N \equiv N - Cl} \xrightarrow[\Delta]{H_2O} \underset{\text{A phenol}}{Ar - OH} + N_2 + HCl$$



20.3.3 From salicylic acid

Another mthod of preparation of phenols is only of theoritical interest. Phenol for instance, is obtained by decarboxylation of sodium salicylate by distilling with sodalime.

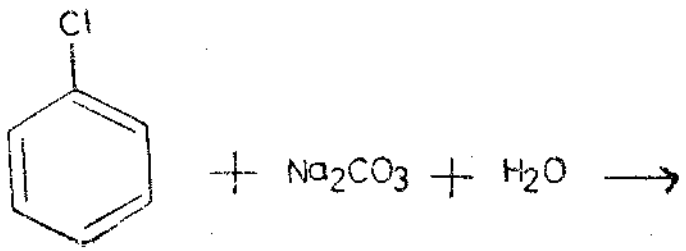


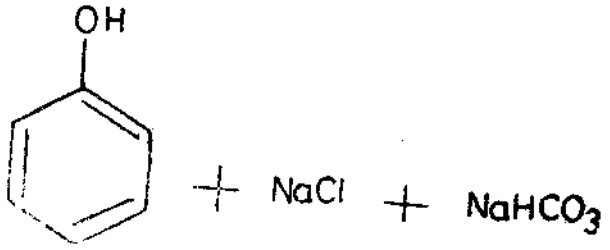
Phenol

20.4 MANUFACTURE OF PHENOL

20.4.1 From chlorobenzene

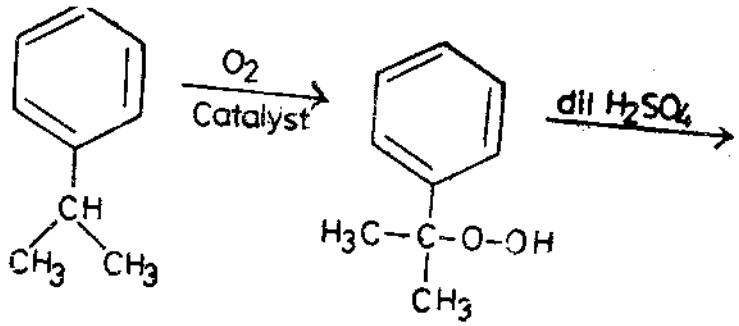
On a large scale phenol is obtained from chlorobenzene. Chlorobenzene is heated with an aqueous solution of sodium carbonate at 325° under pressure.





20.4.2 From cumene

Another method of preparation of phenol is by the oxidation of cumene in the presence of a metal catalyst. In this method acetone is also formed.



Phenol Acetone

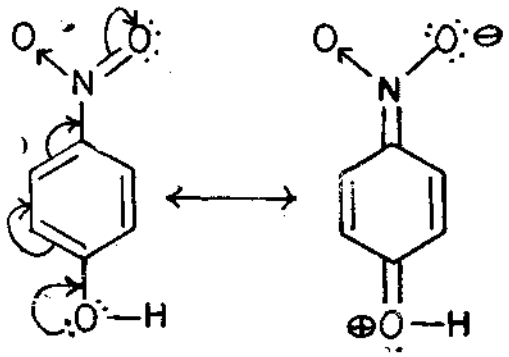
20.4.3 From coal - tar

During coal - tar distillation, the fraction, collected between 170-230° is called middle oil. It consists chiefly of naphthalene, phenols and small quantities of pyridi ne. The middle oil is cooled when naphlene crystallises out. This is seperated by centriguging. The Oil remainning after the removal of naphthalene is treated with warm aqueous sodiuj hydroxide. Phenols deissove in this. By acidification of the resulging aqueous alkaline solution or by passing carbon dioxide through it, phenols are liberated. The crude product is then distilled fractionally. The fraction collected at 180° is pure phenol.

20.5 PHYSICAL PROPERTIES

Phenols are weakly acidic. They dissolve in strong alkalies (NaOH etc) but can not react with weak bases such as $NaHCO_3$. Carboxylic acids being stronger acids liberate carbondioxide when treated with sodium bicarbonate solution but phenols cannot. This property distinguishes phenols from carboxyliic acids.

Phenols differ from alcohols. Alcohols are neutral while the phenols are acidic. Phenols give characteristic colours with feric chloride. Phenol, C_6H_5OH, gives a violet colour with ferric chloride. This characteristic compounds containing; enolic - C = C - OH grouping. The characteristic colours produced by different phenols with ferric chloride are given.



In p-nitrophenol, from one end of the oxygen releases its lone pair to the ring and at the other end the nitrogroup receives the pair of electrons from the ring.

It is obvious that the acidity of the phenol is very much enhanced as more nitro groups are attached to the ring. Hence the order of increased acidity is 2,4,6 trinitro phenol (picric acid) > 2,4 - dinitrophenol > p-ni trophenol > phenol.

Check your progress - 1

How do you distinguish phenol from cyclohexanol ?

20.6.2 Formation of ethers

Sodium phenoxide upon heating with alkyl halide in alcoholic solution forms an ether.

$$C_6H_5ONa + R\ X \longrightarrow C_6H_5 -- OR + NaX$$

$$C_6H_5ONa + C_2H_5I \longrightarrow C_6H_5 -- O - C_2H_5 + NaI$$

Sodium phenoxide Phenetole

When an alkaline solution of a phenol is treated with dimethylsulphate, methyl ethers are obtained. Sodium phenoxide reacts with dimehyl sulphate to give methyl ether of phenol or anisole.

$$C_6H_5 -- ONa + (CH_3)_2SO_4 \longrightarrow C_6H_5 -- O -- CH_3 + CH_3 -- O -- SO -- ONa$$

Dimethyl sulphate Anisole

The phenolic ethers are hydrolysed by heating with conc. HI. When anisole is heated with HI demethylation occurs. Phenol and methyl iodide are obtained (Appendix - I)

$$C_6H_5 -- O -- CH_3 + HI \xrightarrow{\Delta} C_6H_5OH + CH_3I$$

20.6.3 Formation of esters

When phenols are warmed with acid halides or anhydrides, esters are formed. Phenol reacts with acetic anhydride to give phenyl acetate.

$$C_6H_5OH + (CH_3CO)_2O \longrightarrow C_6H_5-O-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3COOH$$

Phenylacetate

When phenol is treated with benzoyl chloride in the presence of alkali, phenyl benzoate is formed. This reaction is known as benzoylation.

$$C_6H_5OH + C_6H_5-COCl + NaOH \longrightarrow C_6H_5-O-\overset{\overset{O}{\|}}{C}-C_6H_5 + NaCl + H_2O$$

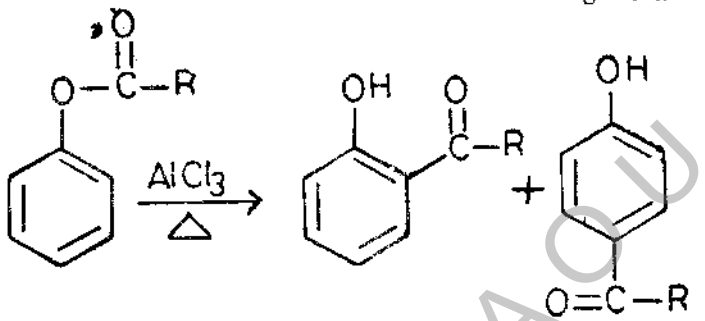
Benzoyl chloride — Phenyl benzoate

This method of benzoylation or aroylation is called **Schotten - Baumann reaction**

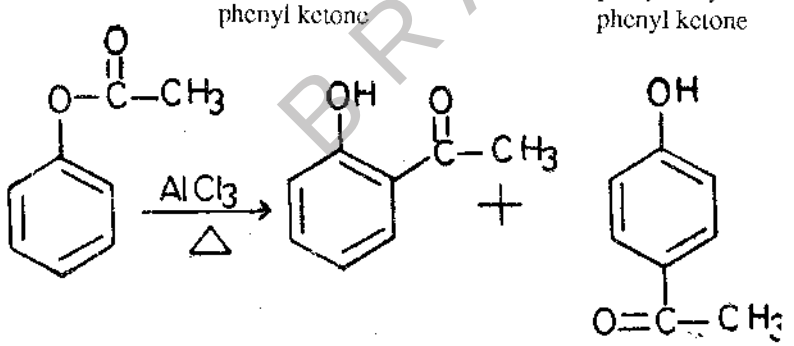
20.6.4 Fries rearrangement

An ester of phenol upon heating with anhydrous aluminium chloride gives a mixture of o-hydroxy and p-hydroxy phenol ketones ie. C-acylphenols.

This transformation is known as Fries reaction or rearrangement.



Phenylester — o- Hydroxy phenyl ketone — p- Hydroxy phenyl ketone



Phenylacetate — 0-Hydroxy acetophenone — p-Hydroxy acetophenone

When phenylacetate is heated with aluminium chloride, a mixture of o-hydroxy acetophenone and p-hydroxyacetophenone is obtained. The ration of the ortho and para isomers brained in Fries rearrangement depends upon the nature of solvent and the temperature of the reaction.

20.6.5 Reaction with PCl_5

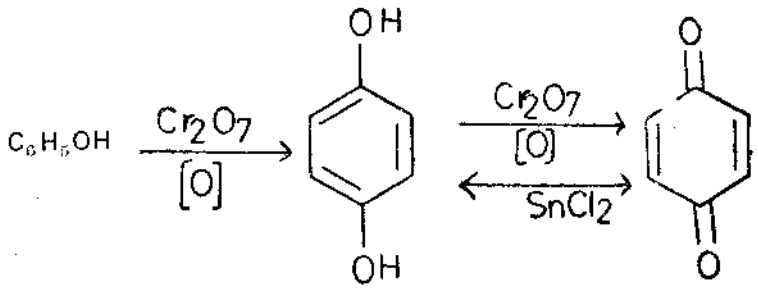
Phenol reacts with phosphorous pentachloride PCl_5 to give very little yield of chlorebenzene. In the case of alcohols this reaction occurs with sufficient ease giving alkyl halides. Thus, a hydroxyl group attached

$$C_6H_5OH \xrightarrow[CS_2]{Br_2} p\text{-}Br.C_6H_4OH$$

p- Bromophenol

20.6.9 Oxidation

Phenol is oxidised to p- benzoquinone or p - quinone

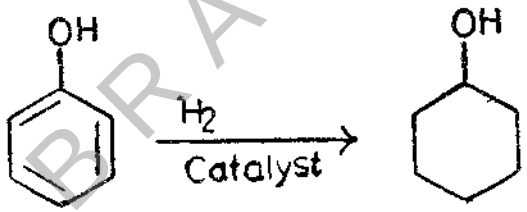


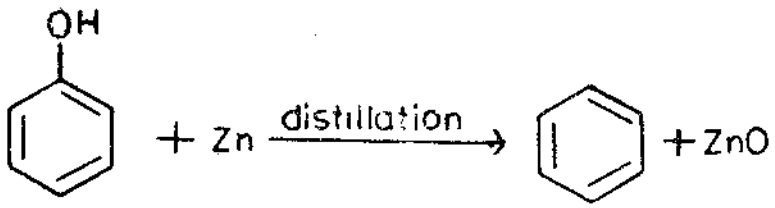
Dihydroquinone (white) p- quinone (yellow)

p- Quinone reversibly forms a molecular addition compound with hydroquinone. This is black and is called quinhydrone.

p-Quinone + Hydroquinone $\rightleftarrows$ Quinhydrone.

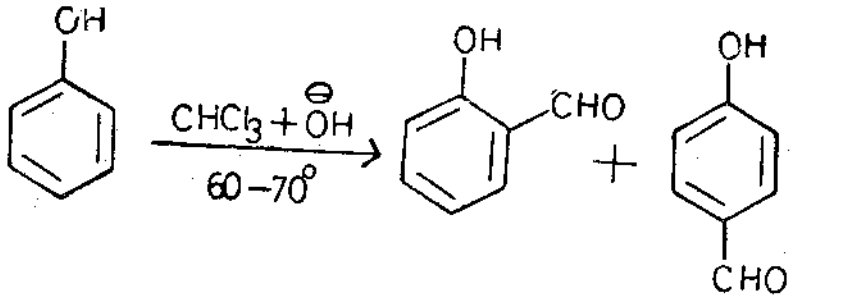
Upon reduction with hydrogen in the presence of a catalyst phenol gives cyclohexanol. On distillation with zincdust phenol gives benzene.





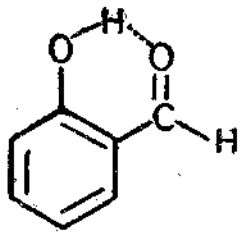
20.6.10 Reimer - Tiemann reaction

Reaction of phenol with cloroform in the presence of alkali at 60-70° gives a mixture of o-hydroxy and p-hydroxy benzaldehydes. This is known as Reimer - Tiemann reaction.



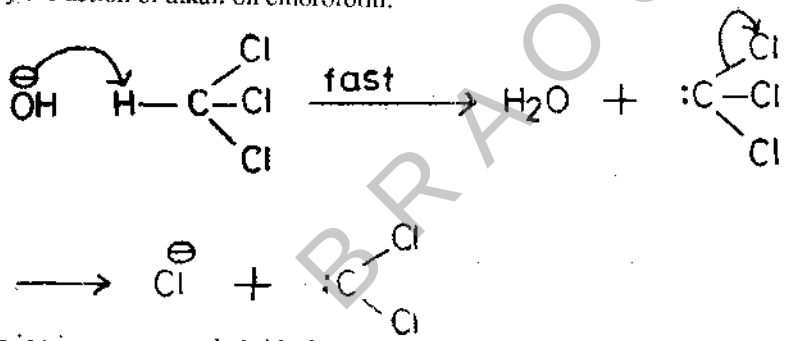
o–Hydroxy benzaldehyde (Salicylaldehyde) p–Hydroxy benzaldehyde

The mixture is separated by steam distillation. Salicylaldehyde is steam volatile. Due to intramolecular hydrogen bonding salicylaldehyde has a lower solubility in water and a lower boiling and melting point than the p-isomer.

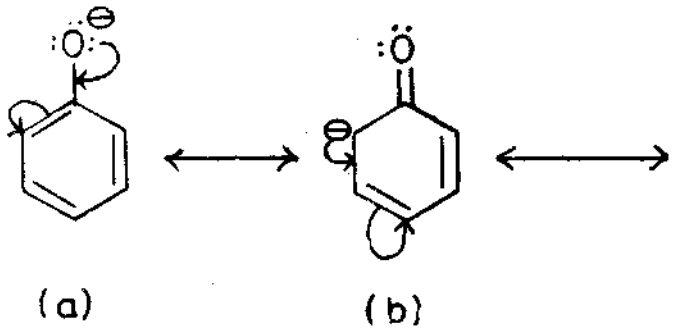


Intramolecular hydrogen bonding in salicylaldehyde

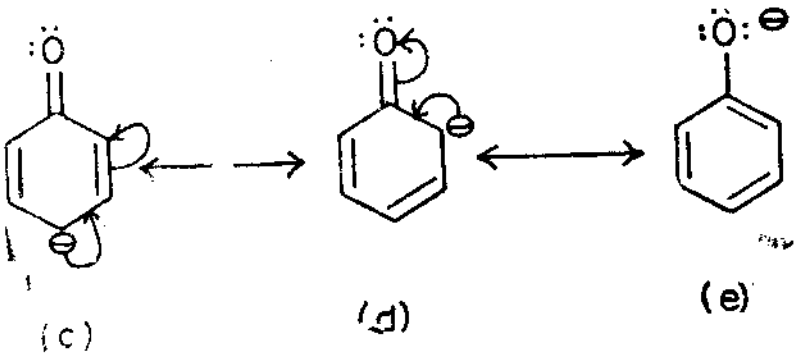
The reactive species in Reimer - Tiemann reaction is dichloromethylene or dichlorocarbene. This is generated by the action of alkali on chloroform.



The phenoxide ion is a resonance hybrid of the following structures.

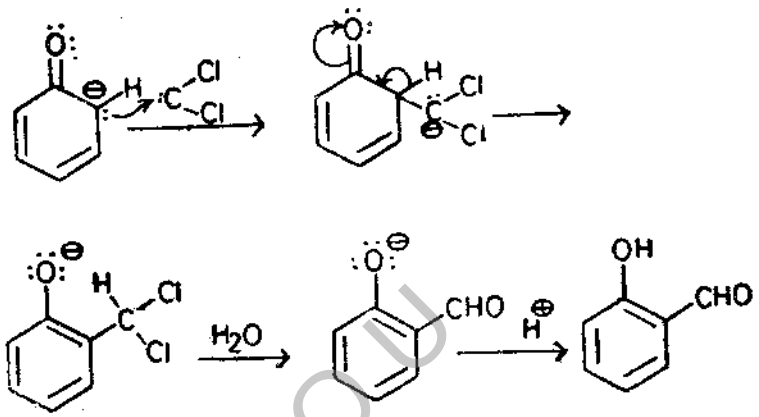


(a) (b)



Carbonion structures

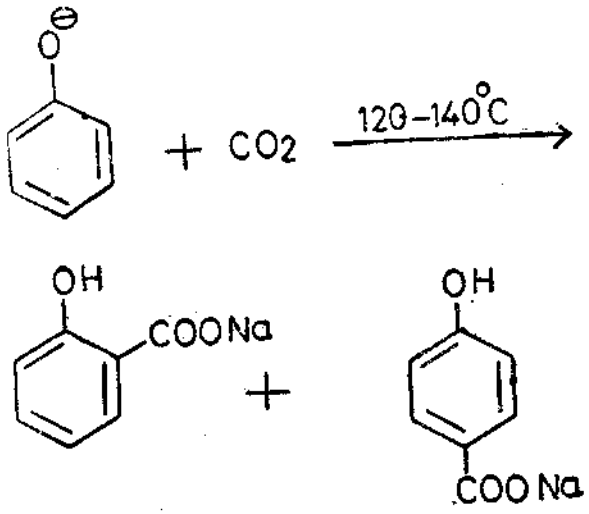
These structures surplus electron density at o-and o' and p-positions. Dichlorocarbene is an electrophile. Therefore, it attacks the ring ortho and para positions of the carbanion structures. (b, c and d)

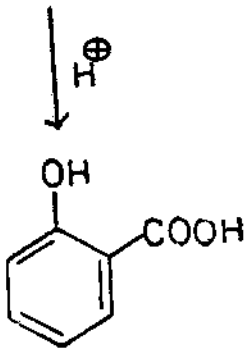


p- Hydroxy benzaldehyde is similarly obtained by the attack of dichlorocarbene at p-position of c.

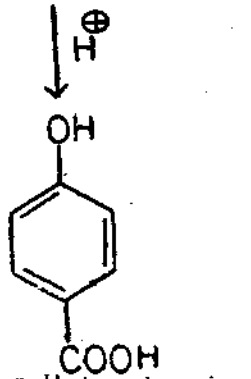
20.6.11 Kolbe - Schmidt reaction

The introduction of a carboxyl on the ring carbon of phenol is carried out by this reaction. Sodium phenoxide and carbon dioxide are allowed to react under pressure at 120-140°, when a mixture of o - and p- hydroxy benzoic acids is obtained.



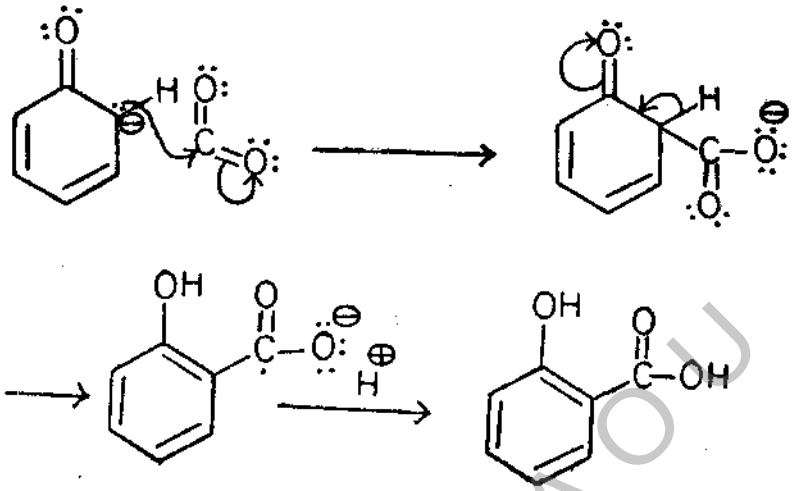


o- Hydroxy benzoic acid
(salicylic acid)



p- Hydroxy benzoic acid

This reaction involves the attack by carbon dioxide at ortho and para positions of phenoxide ion.



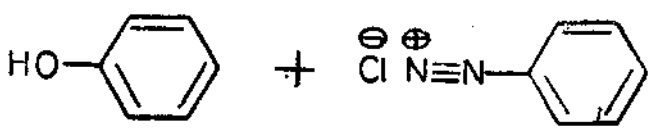
In this reaction carbon dioxide functions as an electrophile.

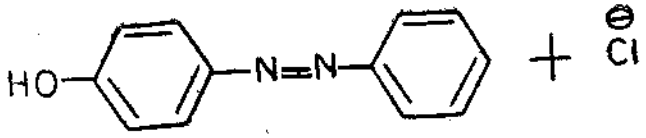
Check your progress - 2

Write all the possible structures of isomeric compounds with the formula C_7H_8O.

20.6.12 Coupling with diazonium salts

Coupling reaction is useful in the introduction of an azo group (- N = N-) in an aromatic compound. Diazonium salts react with some aromatic compounds like phenols, amines to form azo compounds. The characteristic group in an azo compound is- N = N -. Phenol, for instance, couples with benzene diazonium salts to give p-hydroxyazo benzene. Coupling with phenols is usually carried out in a slightly alkaline medium.



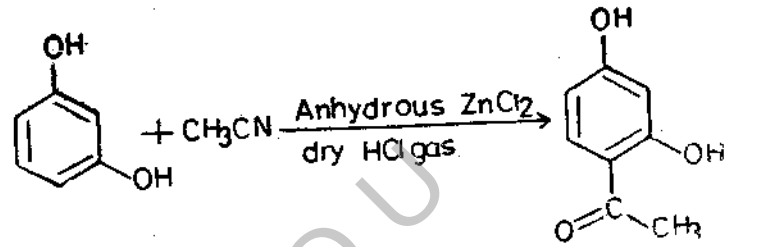


p- Hydroxyazobenzene

The coupling reaction is an electrophilic substitution reaction. The diazonium ion is an electrophile. It attacks ortho and para positions of the phenoxide ion which are activated towards electrophilic attack due to high electron density in these positions. Coupling occurs more readily in the para position partly due to steric factors.

20.6.13 Hoesch reaction

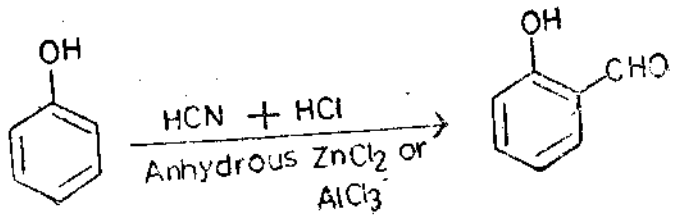
Reactive polyhydric phenols may be condensed with nitriles in the presence of anhydrous zinc chloride and hydrogen chloride to give ketones. Polyhydric phenols, carrying two or more hydroxyl groups in the meta position such as resorcinol and phloroglucinol, undergo this reaction easily. Resorcinol reacts with methyl cyanide, in the presence of anhydrous $ZnCl_2$ and dry HCl gas, to give resacetophenone. Resacetophenone is a phenolic ketene.



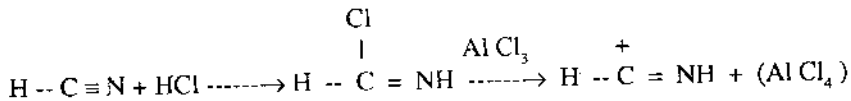
Resorcinol Methylcyanide (acetonitrile) Resacetophenone

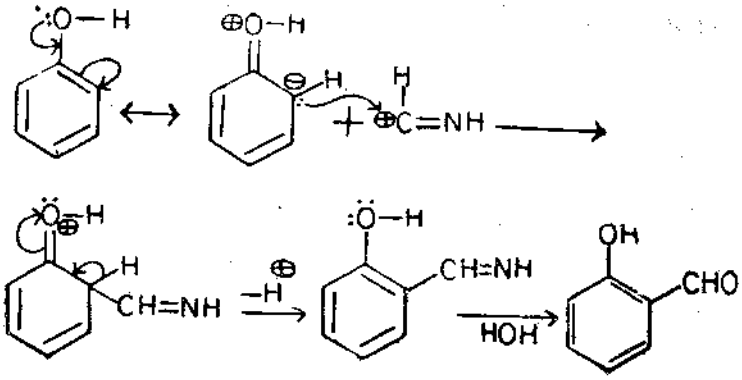
20.6.14 Gattermann reaction

This method is useful for the preparaion of phenolic aldehydes. Phenol is treated with hydrogen cyanide and hydrogen chloride in the presence of anhydrous zinc chloride or aluminium chloride. The resulting complex is hydrolysed to give salicylaldehyde.



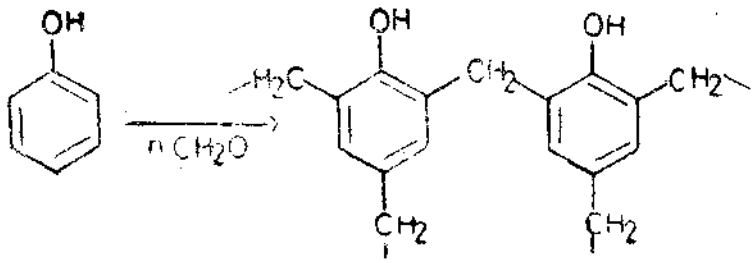
It is believed that formimino chloride is first formed in this reaction. This in turn generates the electrophile, (HC ⊕ = NH)





20.6.15 Reaction with formaldehyde

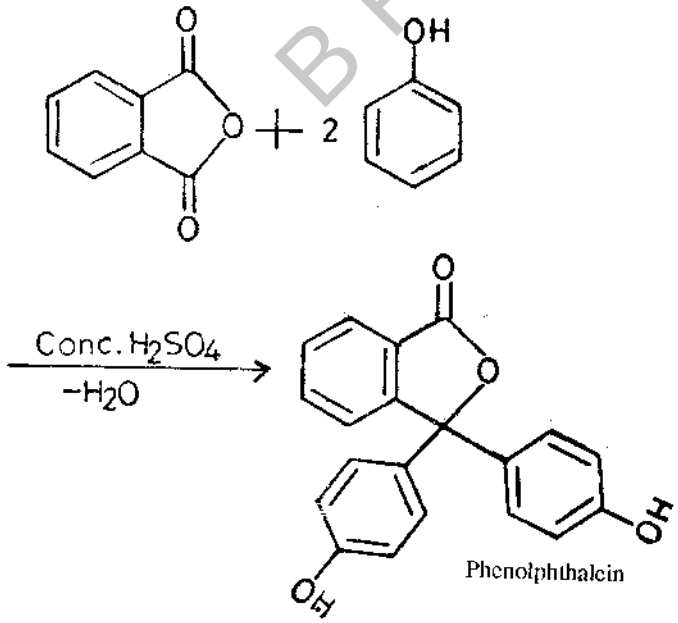
Bakelite is a phenol formaldehyde polymer. Phenol and formaldehyde react in the presence of an acid to give a polymer commercially known as bakelite.



A large fraction of phenol production goes into the manufacture of plastics (bakelite) and resins. Phenols are also used in the preparation of dyes, drugs, photographic developers and wood preservatives.

20.6.16 Reaction with phthalic anhydride

Phenolphthalein is obtained by heating phenol with phthalic anhydride in the presence of conc. H_2SO_4. Phenolphthalein is used as an indicator.



Phenolphthalein

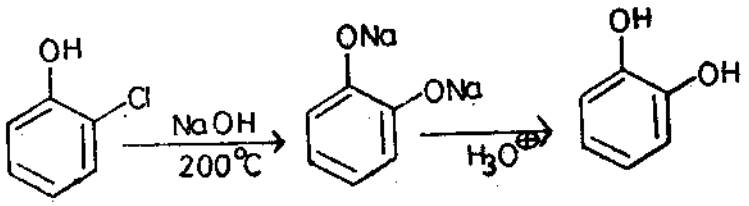
20.6.17 Lieberman's nitroso reaction

When phenol is warmed with sodium nitrite and conc. H_2SO_4, and then diluted a red colour is obtained. The colour changes to green on making the solution alkaline by the addition of aqueous sodium hydroxide. This is used as a test for phenol.

20.7 DIHYDRIC PHENOLS

20.7.1 Catechol (1,2 dihydroxybenzene or o-dihydroxy benzene)

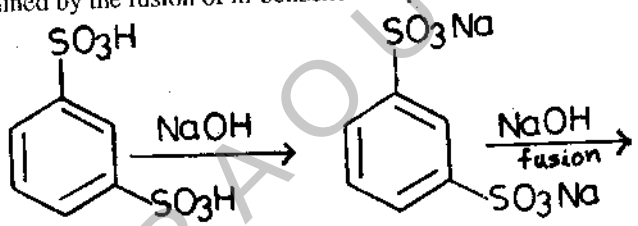
Guaiacol, monomethyl ether of catechol, occur in plants. Demethylation of this compound gives catechol. It is also obtained by heating o-dichlorobenzene or o-chlorophenol with alkali under pressure.

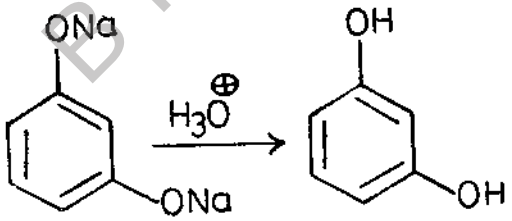


Catechol

20.7.2 Resorcinol (1,3 - dihydroxybenzene or m- dihydroxybenzene)

This is obtained by the fusion of m-benzene disulphonic acid with alkali.

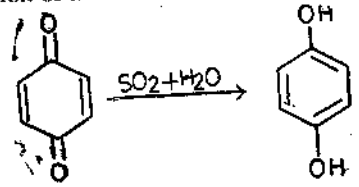




Resorcinol

20.7.3 Hydroquinone (1,4- dihydroxy benzene or p-dihydroxy benzene)

This is obtained by the reduction of p-benzoquinone (quinone) with sulphurous acid. Quinone itself is obtained by the oxidation of aniline.

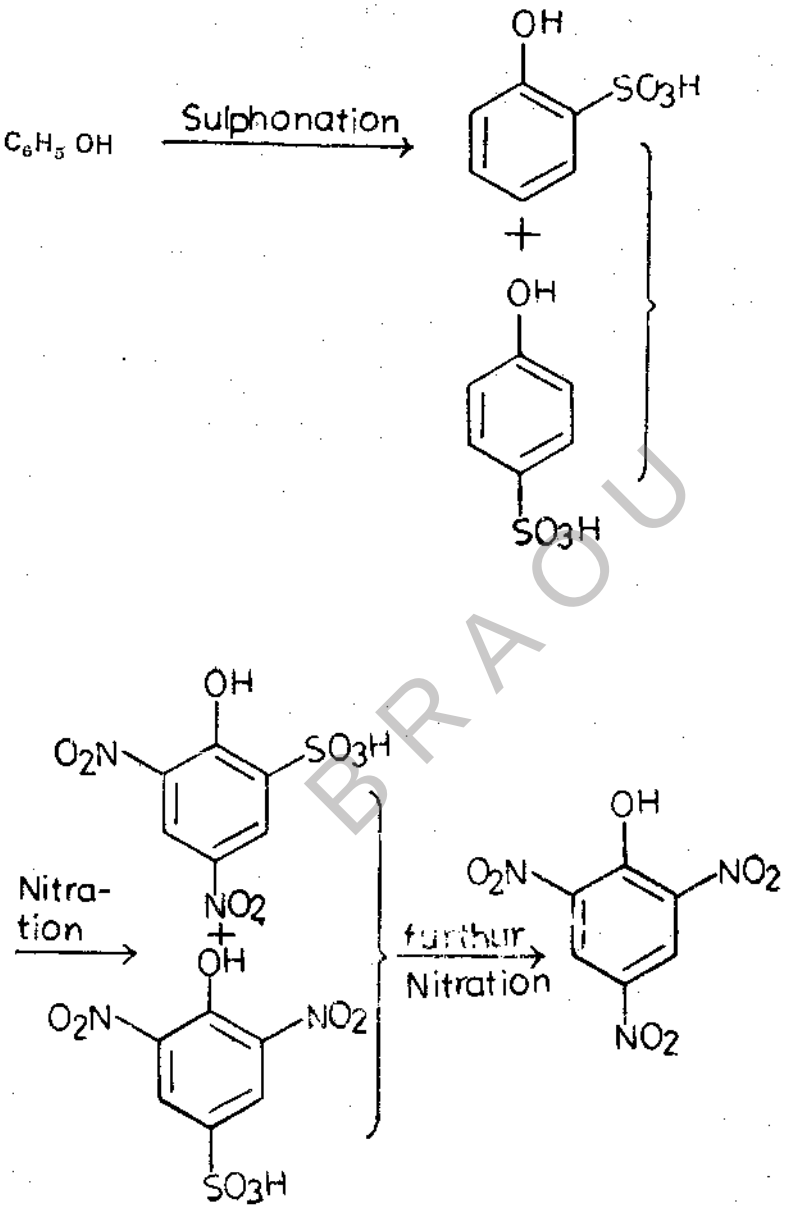


Appendix - I: The estimation of methoxyl group in organic compounds is done by Ziesel method. Suppose it is needed to estimate the methoxyl group in anisole. A known weight of the compound is heated with conc. HI. The vapours of omethyl iodide formed are absorbed in alcoholic silver nitrate solution when silver iodide is precipitated. From the weight of the silver iodide is precipitated. From the weight of the silver iodide obtained the number of methoxyls present in anisole molecule can be calculated.

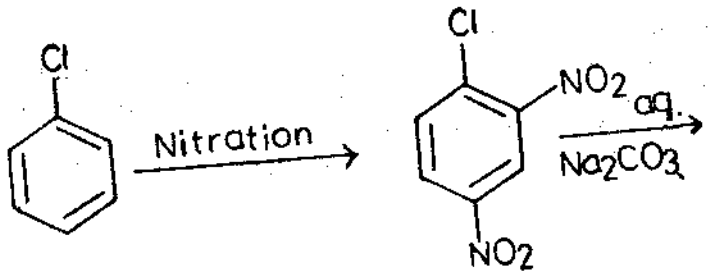
$$C_6H_5 - O - CH_3 + HI \longrightarrow C_6H_5OH + CH_3I$$

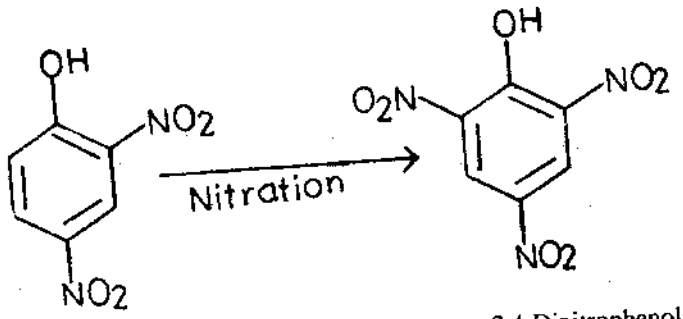
$$CH_3I + AgNO_3 \longrightarrow CH_3NO_3 + AgI \downarrow$$

Appendix - II. Picric acid is obtained by sulphonation of phenol followed by nitration.



Picric acid is also obtained from chlorobenzene by nitration.





2,4 Dinitrochlorobenzene 2,4 Dinitrophenol

20.8 SUMMARY

Phenols with hydroxyl group directly attached to benzene ring can be synthesized from benzene sulphonic acid on alkalifusion; from diazonium salts on warming or by decarboxylation of sodium salt of salicylic acid. On large scale it is convenient to obtain from coal tar cumene and also from chlorobenzene. These are weakly acidic and show o,p-effect. The o,p-mixture are easily separated by steam distillation due to difference in their boiling points and solubility in water depending on intra or intermolecular hydrogen bonding respectively.

Besides the typical electrophilic substitution reactions they also show reaction with CO_2,: CCl_2, CH_3CN, HCN + HCl.

20.9 MODEL EXAMINATIONS QUESTIONS

1. Answer the following in 10 lines each

1. Phenol forms salts with potassium hydroxide while an alcohol do not Explain.
2. Write notes on the following:
   (i) Riemer - Tiemann reaction
   (ii) Fries rearrangement
3. Explain the mechanism of the following reactions.
   (i) Kolbe - Schmidt reaction
   (ii) Gattermann reaction
4. Nitrobenzene $\xrightarrow{\text{Reduction}}$ A $\xrightarrow{NaNO_2 + HCl}$ B $\xrightarrow{H_2O}$ C

   Nitrobenzene $\xrightarrow{\text{Reduction}}$ C

   B $\xrightarrow[\text{Slightly alkaline conditions}]{}$ D

   Give structural formula for each of the compounds A,B,C and D.
5. Explain why phenol is more acidic than water and alcohol.

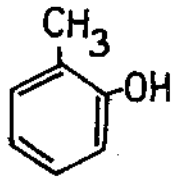
II. Answer the following in 30 lines each

1. Discuss the general methods of preparation of phenols.
2. Outline industrial methods of preparation of phenol. Discuss the diffrences between phenols and alcohols.
3. What are dihydric phenols? give the methods of preparation of each of them. Write note on Kolbe-schmidt reaction.

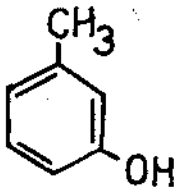
20.10 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Phenols give characteristic violet colour with ferric chloride while alcohols do not give. Phenols are harmful to skin causing burns and are soluble in alkali due to acidic nature. Alcohols are pleasant smelling harmless compounds are neutral.

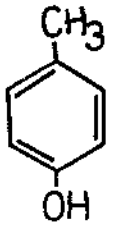
2. The possible structures with the molecular formula $C_7 H_8 O$ are:



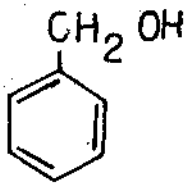
O- Cresol



m- Cresol



p- Cresol



Benzyl alcohol

Author : Y.S.N. Murthy

UNIT - 21 ETHERS

Contents

21.1 AIMS AND OBJECTIVES

In this unit we present you nomenclature, methods of preparation and properties of ethers. When you finish this unit you should be able to understand:

- Nomenclature
- General methods of preparation
  - i) From alkoxides and alkyl halides
  - ii) From alcohols
- General properties
  - i) Formation of oxonium salts
  - ii) Cleavage by acids
  - iii) Reactions with halogens
  - iv) Reaction with Grignard reagent
- Preparation of diethyl ether and anisole
- Uses

21.2 INTRODUCTION

Ethers are organic compounds with the general gormula R-O-R, Ar-O-R or Ar-O-Ar (R=alkyl group and Ar=an aryl group). In these compounds, two hydrocarbon residues are linked through an oxygen atom. They may be regarded as the dialkyl or diaryl derivatives of water. The functional group, present in ethers, is C-O-C. When both the groups attached to the oxygen are the same, the ether is called a simple or symmetrical ether. Ex: CH_3 - O - CH_3 dimethyl ether or methylether C_2H_5 - O - C_2H_5 diethyl ether or ethyl ether

The term ether generally refers to ethyl ether.

When the two alkyl groups are different, the ether is said to be a mixed or unsymmetrical ether. Following are some examples:

$CH_3 - O - C_2H_5$ Methyl ethyl ether

$CH_3 - O - CH_3\,CH_2\,CH_3$ Methyl n-propyl ether

$$CH_3 -- O -- \underset{\displaystyle CH_3}{\underset{|}{CH}} -- CH_3$$ Methyl isopropyl ether

Some examples of aryl alkyl ethers are

$C_6H_5 -- O -- CH_3$ Methyl phenyl ether or anisole

$C_6H_5 -- O -- C_2H_5$ Phenyl ethyl ether or phenetole

$C_6H_5\ O\ C_6H_5$ Diphenyl ether is an example of diaryl ether

21.3 NOMENCLATURE

The two groups attached to the oxygen are named. This is followed by the word ether.

$CH_3 -- CH_2 -- CH_2 -- O -- CH_3$ In this compound, two groups , methyl and n-propyl are attached to the oxygen. Therefore the compound is named as methyl n-propyl ether.

$CH_3 - O - CH = CH_2$ is called methyl vinyl ether ($CH_2 = CH -$ is vinyl group)

According to IUPAC system, ethers are regarded as the alkoxyl derivatives of alkanes. Ether is considered to be obtained by replacement of a hydrogen of alkene by an alkoxyl group (OR). In R--H, H is replaced by an alkoxyl group to give R -- O -- R. The larger of the two alkyl groups in ether represents the alkane. For example, in $CH_3\,CH_2\,O\,CH_3$ (methyl ethyl ether), the larger alkyl group is ethyl group. Therefore the ether is named as derivative of ethane. If the hydrogen of the ethane is replaced by the methoxyl group it becomes methoxy derivative of ethane. Therefore it is named as methoxy ethane.

$CH_3\,CH_2\,CH_2\,.O.\,CH_2.\,CH_3$ n-propyl ethyl ether 1-ethoxy propane

$$CH_3 -- CH_2 -- O -- \underset{\displaystyle CH_3}{\underset{|}{CH}} -- CH_3$$ Ethyl iso propyl ether (2-ethoxy propane)

$$CH_3 -- \underset{\displaystyle CH_3}{\underset{|}{CH}} -- CH_2 -- CH_2 -- OCH_3$$ Methyl isopentyl ether

(1- methoxy 3 - methyl butane)

$HO.\,CH_2.\,CH_2\,OC_2H_5$

Monoethyl ether of ethylene glycol (2 - ethoxy ethanol)

$$CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - OCH_3$$

1- bromoethyl methyl ether (1-methoxy - 1- bromo ethane)

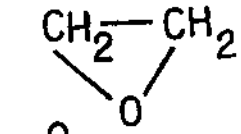
$Cl\ CH_2.\ CH_2.\ CH_2.\ OCH_2.\ CH_2.\ CH_2\ Cl$

Bis (υ - chloro propyl) ether (1 - (3-chloropropoxy) 3-chloropropane)

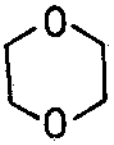
$Br\ --\ C_6H_4\ --\ OCH_2\ --\ CH_3$

p- Bromophenetole (p-bromophenyl ethyl ether or p-ethoxy - bromobenzene).

Besides, there are quite a good number of cyclic ethers, such as



Ethylene oxide



1,4- Dioxan

Tetra hydrofuran

21.4 METHODS OF PREPARATION

21.4.1 Williamson synthesis

One of the methods usually followed for the preparation of ethers is Williamson synthesis. In this, sodium alkoxides are reacted with alkyl halides to give ethers. Sodium ethoxide reacts with methyl bromide or ethyl bromide to give methyl ethyl ether or diethyl ether respectively. This method is useful for the preparation of both symmetrical and unsymmetrical ethers.

$$R - O - Na + X - R' \longrightarrow \underset{\text{Ether}}{R - O - R'} + Na\ X$$
Sodium alkoxide

$$\underset{\text{Sodium ethoxide}}{C_2H_5\ O\ Na} + Br.\ CH_3 \longrightarrow \underset{\text{Ethyl methyl ether}}{C_2H_5 - O - CH_3} + NaBr$$

$$\underset{\text{Sodium ethoxide}}{C_2H_5O\ ---\ Na} + Br\ C_2H_5 \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5\ O\ --\ C_2H_5} + Na\ Br$$

The alkoxide ion is a strong base and acts as a nucleophile. This reaction involve nucleophilic substitution of a halide ion by an alkoxide ion. Here elimination is the competing reaction. Elimination is the major reaction with tertiary alkyl halides. In the reaction of t-butyl bromide with alkoxides, isobutylene is the major product.

$$\begin{array}{l} CH_3 \\ | \\ CH_3 -- C -- Br \\ | \\ CH_3 \end{array} + RO \longrightarrow \underset{\text{isobutylene}}{\begin{array}{l} CH_3 \\ | \\ CH_3 -- C = CH_2 \end{array}}$$

For this reason a t- alkylhalide is not used as a component in williamson synthesis of ethers. Methyl t. butyl ether is therefore obtained by the reaction of sodium t-butoxide and ethyl halide but not by the reaction of t-butyl halide and sodium ethoxide.

$$\begin{array}{l} CH_3 \\ | \\ CH_3 -- C -- O -- Na \\ | \\ CH_3 \end{array} + Br\ C_2H_5 \longrightarrow (CH_3)_3C_3O.C_2H_5 + Na\ Br.$$

In the preparation of aryl alkyl ethers, sodium salt of a phenol and an alkyl halide may be used as the starting materials. Phenetole is obtained from sodium phenoxide and ethyl iodide. For making aryl methyl ethers, methylation of phenols with dimethyl sulphate is a convenient method. Anisole is obtained by the methylation of phenol with dimethyl sulphate in the presence of alkali.

$$Ar - O\,Na + X - R \longrightarrow Ar - O - R + Na\,X$$

Sodium salt of a phenol

$$C_6H_5ONa + C_2H_5I \longrightarrow C_6H_5 - O - C_2H_5 + NaI$$

Sodium phenoxide — Phenetole

$$C_6H_5OH \xrightarrow[OH^-]{(CH_3)_2SO_4} C_6H_5 - O - CH_3$$

Phenol — Anisole

β -- Naphthol is methylated with dimethyl sulphate and alkali.

β -- Naphthyl methyl ether is also known as neroline

$$\beta - C_{10}H_7OH \xrightarrow{(CH_3)_2SO_4} \beta - C_{10}H_7OCH_3$$

21.4.2 From Alcohols

In another method, ethers are obtained by intermolecular dehydration of alcohols. Ethyl ether is obtained from ethanol and sulphuric acid. When excess of ethanol is heated with conc. H_2SO_4 at 140° diethyl ether is the product. The overall reaction is represented by the following equation.

$$2C_2H_5OH \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} C_2H_5OC_2H_5$$

The formation of diethyl ether from ethanol and sulphuric acid proceeds through the intermediary of ethyl hydrogen sulphate.

$$C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5OSO_3H + H_2O$$

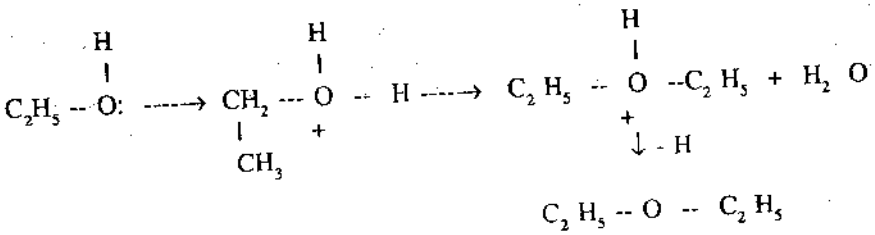
Ethyl hydrogen sulphate

$$C_2H_5O.SO_3H + C_2H_5OH \xrightarrow{140^\circ} C_2H_5 - O - C_2H_5 + H_2SO_4$$

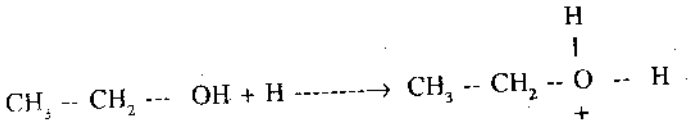
When excess alcohol is present at a lower temperature (140° C), ethyl hydrogen sulphate gives ether. The first step in the formation of ether from ethanol and acid may be the formation of protonated alcohol. The protonated alcohol is attacked by a second molecule of alcohol, functioning as a nucleophile.

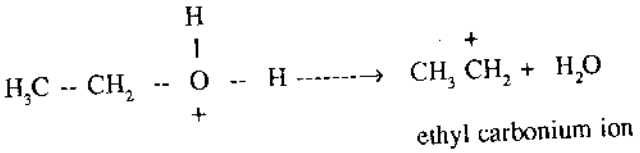
$$C_2H_5 - O - H \xrightarrow{H^+} C_2H_5 - \overset{\overset{H}{|}}{O} - H$$

Protonated alcohol
(conjugate acid of alcohol)

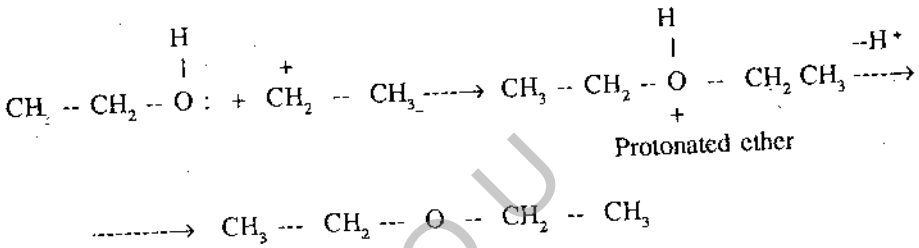


It is also possible that the carbonium ion, formed from the conjugate acid of alcohol, attacks a second molecule of alcohol to give protonted ether. The latter loses a proton to give ether.



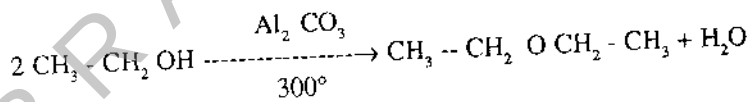


ethyl carbonium ion



Protonated ether

Ethers are also obtained by passing the alcohol vapours over alumina at 300°. However, at higher temperature alkene is the major product. Diethyl ether is obtained from ethanol.



21.4.3 Absolute ether

Ethyl ether contains traces of alcohol and water. These are removed by distilling with conc H_2SO_4. Traces of weter, in ether, can be removed by drying over sodium metal.

21.5 GENERAL PROPERTIES

Ethers are chemically inert. They are not affected at ordinary temparature by reagents like sodium, PCl_5, acids or alkalies. Ethers, being chemically inert, are useful as solvents in a number of reactions. Since there is no possibility for the formation of hydrogen bonds, ether molecules are unassociated. Therefore, ethers boil at lower temperature than alcohols of comparable molecular weight.

Dimethyl ether	[C_2H_6O] B.P. 25° C
Ethanol	[C_2H_6O] B.P. 78° C

Ethers are either gases or volatile liquids. Ethers are highly inflammable. However co-association of ether and water molecules is opossible. This is responsible for the water solubility of lower ethers. Diethyl ether has almost the same solubility as the isomeric n-butyl alcohol. The coassociation of

ether with water molecule may be represented as

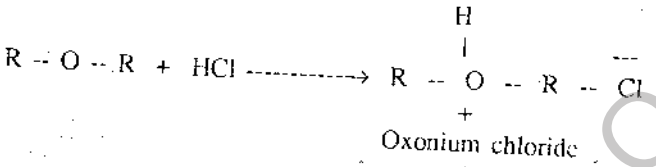
The small net dipolmoment of ethers indicates that they are not linear. For example diethyl ether, with a dipole moment of 1. 12D, is angular and the R -- O -- R bond angle is about 110°

Check your progress - 1

Both diethyl ether and 1 - butanol have the same molecular weight. The former boils at a lower temperature, explain.

21.5.1 Formation of oxonium salts

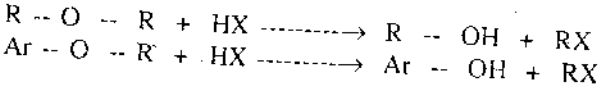
Ethers dissolve in strong acid solutions of mineral acids, like HCl to, form oxonium salts can be isolated at lower temperature. The lone pair of electrons on the oxygen atom is responsible for the formation of the oxonium salts.



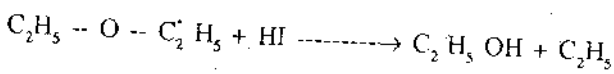
Oxonium salts formed in strongly acidic solutions are polar. Therefore ethers are soluble in strong acids.

21.5.2 Cleavage by acids

Ethers undergo C - O bond cleavage by strong acids. HI and HBr are generally used for this purpose. The order of reactivity of halogen acids is HI> HBr> HCl

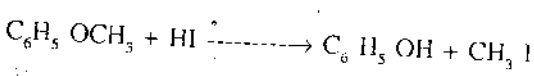


Ethers react with HI in the cold to give ethyl iodide and ethanol



When heated with excess HI. ethyl iodide is the only product

In the case of aralkyl ethers the bond between oxygen and the alkyl group gets cleaved. Anisole, for instance, reacts with HI to give methyl iodide.



The methyl iodide formed in the reaction can be estimated by converting it into AgI on reaction with Ag No_3. This forms the basis of Zeisel's method of estimation of methoxy groups in organic compounds.

In the cleavage of mixed ethers of the type $C_2H_5O\ CH_3$, with one mole at HI at lower temperature, the smaller alkyl group forms the alkyl iodide.

$$C_2H_5OCH_3 + HI \longrightarrow C_2H_5OH - CH_3I$$

21.5.3 Reaction with Halogens

Ethers react with chlorine or bromine under suitable conditions. Substitution occurs at the carbon directly attached to the oxygen atom. Diethyl ether and chlorine react to give mono and dichloro products.

$$CH_3CH_2OCH_2CH_3 \xrightarrow{Cl_2} CH_3 - \underset{\displaystyle Cl}{\underset{|}{CH}} - O - CH_2CH_3 \ \alpha\text{-Monochloro ether}$$

$$+$$

$$CH_3\underset{\displaystyle Cl}{\underset{|}{CH}}O\underset{\displaystyle Cl}{\underset{|}{CH}}CH_3 \ \alpha - \alpha' \text{ dichloro ether}$$

21.5.4 Reaction with Grignard reagent

Pure and dry ether is used as solvent in the preparation of Grignard reagent. It acts as Lewis base towards magnesium atom of Grignard reagent. In ether, Grignard reagent is present as etherate.

$$C_2H_5 - O - C_2H_5$$

$$\downarrow$$

$$R - Mg - X$$

$$\uparrow$$

$$C_2H_5 - O - C_2H_5$$

Grignard reagent etherate

Because of electron donor character associated with them, ethers also dissolve metal salts such as $MgCl_2$ and $FeCl_3$. The cations of these salts accept electron pairs and are thereby brought into solution.

21.6 PREPARATION OF DIETHYL ETHER

i) Ether: This is prepared both in the laboratory and on a large scale by heating ethabol with sulphuric acid 140° alcohol is taken in excess.

$$C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5HSO_4 + H_2O \text{ (at } 100°)$$

$$C_2H_5HSO_4 + HOC_2H_5 \longrightarrow (C_2H_5)_2O + H_2SO_4 \text{ [at } 140°)$$

21.7 ANISOLE

This is obtained by treating sodium phenoxide with methyl idodide.

$$C_6H_5ONa + ICH_3 \longrightarrow C_6H_5OCH_3 + NaI$$

A more convenient method of preparation of anisole is by methylation of phenol by dimethyl sulphate in the presence of alkali.

$$C_6H_5OH \xrightarrow[OH^-]{(CH_3)_2SO_4} C_6H_5-O-CH_3$$

Methyl ethers of phenols are obtained by reaction of phenols with diazomethane. Anisole is obtained by the action of diazomethane on phenol.

$$C_6H_5OH + CH_3N_2 \longrightarrow C_6H_5OCH_3 + N_2$$

Anisole is quite stable towards acids and alkalies. However, conc. HI and HBr demethyl ate anisole.

$$C_6H_5OCH_3 + HI \longrightarrow C_6H_5OH + CH_3I$$

Check your progress - 2

How is anisole obtained starting from benzene ?

21.8 USES

Ether is used as an anesthetic. Anesthetics relieve pain by rendering the person unconscious. Large quantitites of ethylene oxide are consumed in plastic, rubber and synthetic detergent and textile industries. Dioxan is widely used as a solvent.

21.9 SUMMARY

The dialkyl aryl derivatives of water known as ethers are widely used as solvents or anersthetics. They are obtained from alcohols either by intermolecular dehydration or on treatment with alkyl halide. These are chemically inert with low boiling points. They form oxonium salts in strong acids and are cleaved. Substitution on carbon atom attached to oxygen atom occurs. They act as Lewis bases towards $MgCl_2$, $FeCl_3$ and RMgX and hence dissolve them.

21.10 MODEL EXAMINATIONS QUESTIONS

I. Answer each of the following in 10 lines

1. Give the structures of A and B in the following reactions

a) $CH_2 = CH_2 \xrightarrow{HBr} A \xrightarrow{C_2H_5\,ONa} B$

b) Propane $\xrightarrow{HI} A \xrightarrow{CH_5\,ONa} B$

c) Phenol $\xrightarrow{Na\,OH} A \xrightarrow{C_2H_5\,I} B$

2. A neutral organic compound A [Mol.Wt=108] upon heating with HI gave two compounds B and C. reacts with silver nitrate to give silver iodide. Upon zinc dust distillation B gave benzene. Write the structures of A, B and C.

3. The molecular weight of an organic compound is 124. In zeisel method of estimation, 3 g of the compound was heated with HI and the resulting alkyl iodide was then treated with silver nitrate giving 5.8 g of silver iodide. How many methoxyl groups are present in the compound?

II. Answer each of the following in 30 lines

1. Write the structural formulate of the isomeric ethers with the formula $C_4H_{10}O$ and give their IUPAC names.

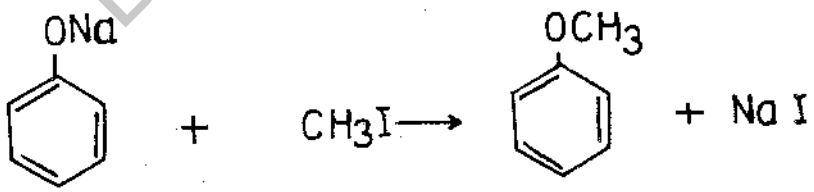
2. Write the structural formulate of [a] allyl ether [b] vinyl ether [c] isopropyl ether [d] phenyl ether. Discuss the preparation of any two.

21.11 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Since there is no possibility for the formation of hydrogen bonds, ether molecules are unassociated. Therefore, ethers boil at lower temperatures than alcohols of comparable molecular weight.

eg: Diethyl ether B.P
1- Butanol B.P.

2. Anisole is obtained by treating sodium phenoxide with methyl iodide.



Author : Y.S.N. Murthy

UNIT - 22: ORGANOMETALLIC COMPOUNDS

Contents

22.1 AIMS AND OBJECTIVES

In this unit we explan you the nature of organometallic compounds and we discuss their preparation, properties and uses.

By the end of this unit you will be able to know:

- Grignard reagent
- Laboratory method of preparation of Grignard reagents
- Synthetic application of Grignard reagents
  - i) Reaction with compounds containing active hydrogens
  - ii) Addition to multiple bonds
- Other organometallic compounds
  - i) N-butyl lithium
  - ii) Tetraethyl lead

22.2 INTRODUCTION

Organometallic compounds contain a metal atom directly linked to a carbon atom. These metals are usually lithium, sodiumn, potassium, magnesium, zinc, cadmium, mercury and aluminium. The carbon end carries a negative charge and the metal end a posiive charge.

$$\begin{array}{l} \delta- \qquad \delta+ \\ C \text{ ----------} M \\ | \end{array}$$

The greater the electropositive character of the metal the greater is the ionic character of the carbon-metal bond. The ionic character of the carbon metal bond is of the order K> Na> Li> Mg> Al> Zn> Hg. With increasing ionic character of the carbon - metal bond the reactivity of the organometallic compounds is that of Grignard reagents with general formula R -- Mg -- X.

22.3 GRIGNARD REAGENTS

These are called Grignard reagents named after the discoverer, Victor Grignard. R is usually an alkyl group and X is a halogen. In other Grignrd reagents, R may be any hydrocarbon group. A convenient method of preparation of an organometallic compound involves the reaction between an organic halide and a reactive metal such as magnesium or lithium. The reaction is carried out in a dry solvent. Generally dry ether is used as the solvent. Solvents such as tretrahydrocarbon group. A convenient method of preparation of an organometallic compound involves the reaction between an organic halide and a reactive metal such as magnesium or lithium. The reaction is carried out in a dry solvent. Generally dry ether is used as the solvent. Solvents such as tetrahydrofuran and tertiary amines may also be used.

22.4 LABORATORY METHOD OF PREPARATION OF GRIGNARD REAGENTS

In the laboratory grignard reagent is prepared by the reaction of an alkyl halide with magnesium turnings in pure dry ether. The reaction is to be carried out in anhydrous ether under perfectly dry conditions.

Ether is washed with water to remove alcohol and then dried over fused calcium chloride. Any trace of moisture is removed by allowing the ether to remain in contact with sodium.

The magnesium ,metal is first washed with ether to remove any greasy matter, then with dil HCl to remove oxide film, and finally dried. The alkyl halide is also dried by distilling over phosphorus pentoxide.

$$R - X + Mg \xrightarrow{\text{dry ether}} R - Mg - X$$

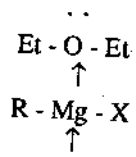
Reaction of dry ethyl bromid with dry magnesium gives ethyl magneisium bromide.

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + Mg \xrightarrow{\text{dry ether}} \underset{\text{ethyl magneisum bromide}}{C_2H_5Mg - Br}$$

The alkyl halides react readily, whereas the aromatic halides react slowly. As the alkyl group in alkylhalide increases in size (becomes bigger I the reactivity decreases. Thus, methyl halides. In cases, where the reaction is slow, a trace of ioidine is added to initiate the reaction. The order of reactivity of the halides is RI> R-Br> R-Cl

As mentioned earlier, ether employed as a solvent should be free from moisture and other impurities, such as alcohols that contain active hydrogen atoms.

The reaction is slow in the beginning. A trace of iodiine helps to initiate the reaction. The reactio once started proceeds vigorously and become exothermic.Grignard reagent is obtained as a solution in ether and may be used directly the reaction without isolation . Evaporation of ether from the solution leaves a white solid with the composition R-Mg-X. $2E_2O$. The two molecules of ether present along with a molecule of R-Mg-x are referred to as ether of crystallisation. Therefore, the Grignard reagent is represented as :



Grignard reagent

22.5 SYNTHETIC APPLICATIONS

Grignard reagnts are valuable in organic synthesis. The reactions of Grignard reagents are valuable in organic synthesis. The reactions of Grignard reagents can be grouped under two heads Viz. The reactions with comounds containing active hydrogen and those multiple bonds.

22.5.1 Reactions witn compoounds containing active hydrogen

Hydrogen atoms linked to electronegative atoms such s oxygen nitrogen and sulfhur are liable. Compounds such as water, alcohol, primary amine, secondary amines, therefore contain the active hydrogen. These comounds react with the grignard reagents to form alkanes. The alkane is derived from the alkyl group of the Grignard reagent and the active hydrogen of the other reactant.

$$R\text{--}MgX + H\text{-}OH \longrightarrow R\text{-}H + Mg(OH)X$$

$$CH_3\text{-}Mg\text{--}Br + H\text{--}OH \longrightarrow CH_4 + Mg(OH)Br$$

$$R\text{--}Mg\ X + R^1\text{-}OH \longrightarrow R\text{-}H + Mg(OR^1)\ X$$

$$CH_3\text{--}MgBr + C_2H_2OH \longrightarrow CH_4 + Mg(OC_2H_5)Br$$

$$R\text{-}MgX + R'\_NH_2 \longrightarrow R\text{-}H + Mg[NH\text{-}R']X$$

$$CH_3\text{--}Mg\ I + C_2H_5NH_2 \longrightarrow CH_4 = Mg[NH\text{-}C_2H^5)I$$

By measuring the volume of the alkane, liberated in their reactions, active hydrogen in alcohols, amines and other organic compounds can be estimated. This is known as Zerevitinoff active hydrogen determination.

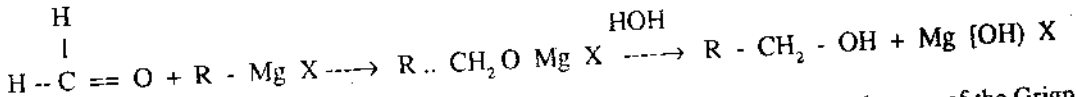
22.5.2 Addition of the reagent to multiple bonds.

Compounds containing multiple bonds readily react with Grignard reagents, These compounds include carbonyl compounds, esters, nitriles etc. In all those addition reactions alkyl group of the Grignard reagent functions as a nucleophiles and attacks the multiply bonded carbon. The addition product is hydroxyl usually by a dilute mineral mineral acid to give the ultimate propoduct.

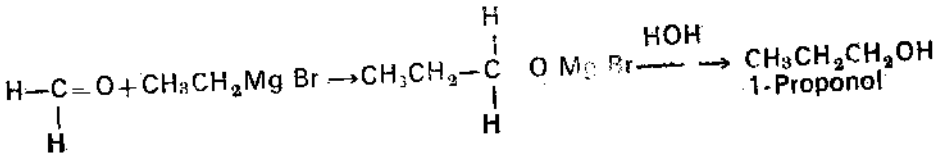
22.5.2.1 Reaction with aldehydes and ketones

Reactions of a Grignard reagent al dehydes and ketones leads to the formation of alcohols.

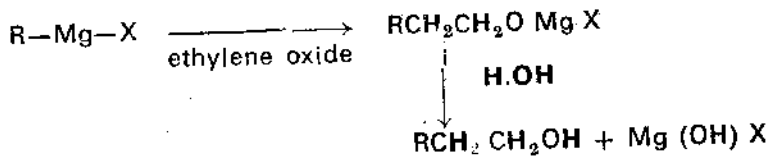
Formaldehyde reacts with a Grignard reagent to give a primary alcohol.



The resulting primary alcohol contains are extra carbon than in the alkyl group of the Grignard reagent. Thus, the reaction of ethyl magnesium iodide with formaldehyde gives n - propyl alcohol..

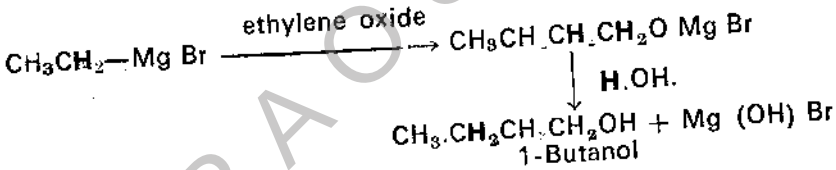


To prepare a primary alcohol containing two extra carbons reaction of the grignard reagent with ethylene oxide is exarried out.

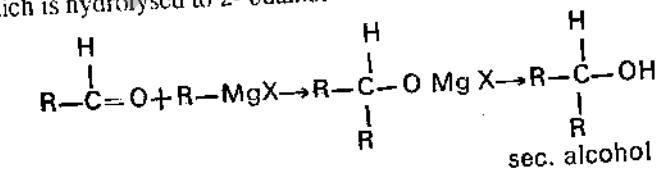


This reaction however, does not involves the addition of the Grignard reagent at the multiple bond.

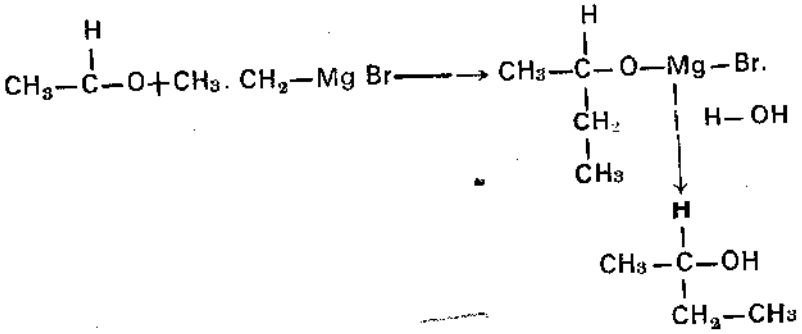
Ethyl magnesium bromide reacts with ethylene oxide, and the product upon hydrolysis, gives n-butyl alcohol.



Aldehydes, other than formaldehyde react with Grignard reagents to give addition products which upon hydrolysis give secondary alcohols. Acetaldehyde and ethyl magnesium bromide give and addition product which is hydrolysed to 2- butanol

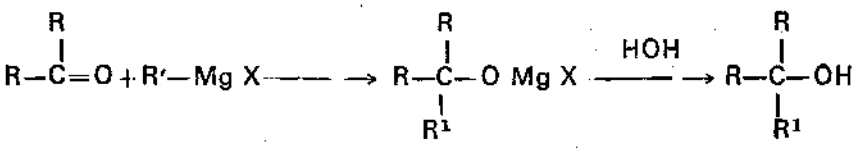


sec. alcohol

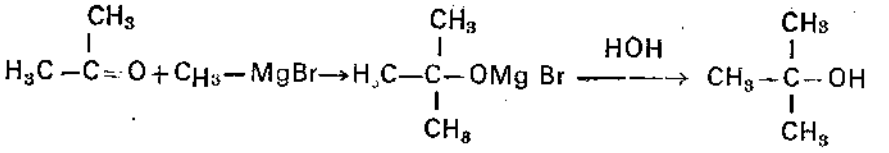


2- Butanol
(Sec. butyl alcohol)

Teriary alcohols arc obtained by the reaction of ketones with Grignard reagents. Thc, acetone and methyl magnesium bromide give butyl alcohol.



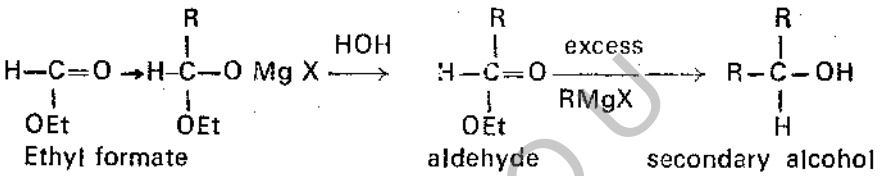
ter. alcohol



tert. Butyl alcohol

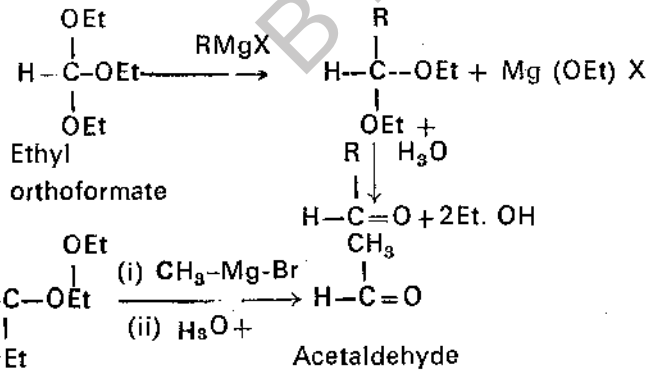
22.5.2.2 Reaction with esters

As aldehyde is obtained by the reaction of ethyl formate with equimolor quantity of a Grignard reagent.



Ethyl formate aldehyde secondary alcohol

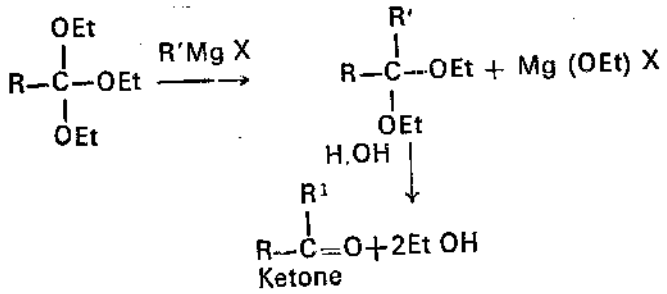
When Grignard reagent is used in excess, the aldehyde firs formed reacts further to give a secondary alcohol. Better yields or aldehydes are obtained by using ethyl orthoformate in the place of ethyl formate.



Ethyl orthoformate

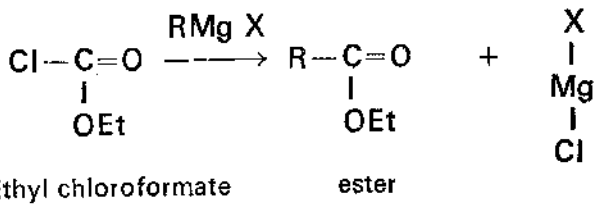
Acetaldehyde

Use ful of ethyl orthoformate also precents the formation of a secondary alcohol. Other ortho esters upon reaction, with Grignard regrent yield ketones.



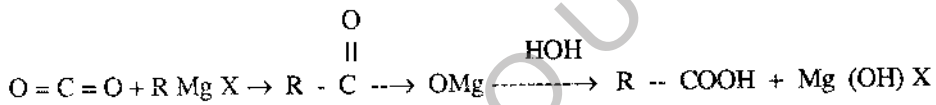
22.5.2.3 Reaction with ethyl chloroformate

Ethers are obtained by the reaction of ethyl choloroformate on Grignard reagents.

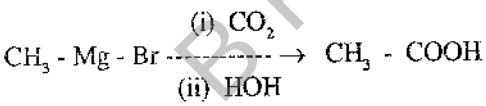


22.5.2.4 Reaction with CO_2

Grignard reagents react with carbonidioxide to give an addition product which is hydrolysed to an acid:



This method of preparation of carboxylic acids is Iso referred to as carbonation of Grignard reagent. Acetic acid results by the carbonation of methyl magnesium bromide.

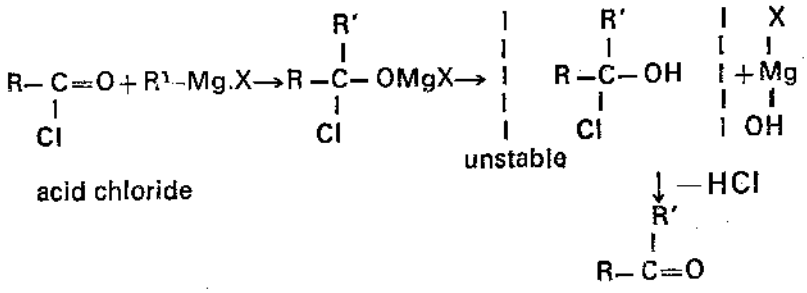


Check your gress - 1

How does grognard reagent react with carbondioxide?

22.5.2.5.1 Reaction with acid Chlorides

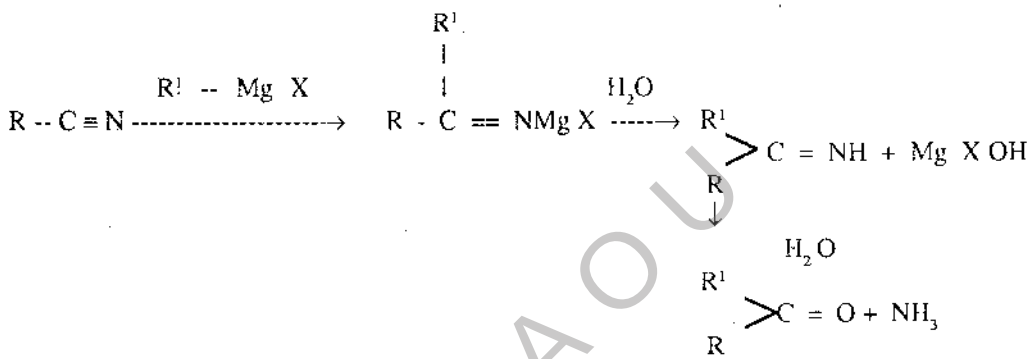
Ketones are obtained by the reaction of a Grignard reagent with an acid chloride.



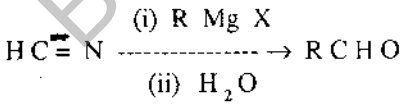
Some tertiary alcohol is also obtained by further reaction of the ketone with grignard reagent.

22.5.2.6 Reaction with nitriles or cyanides

Ketones are formed by the reaction of alkyl cyanides with Grignard reagent. In this reaction the alkyl group of the Grignard reagent function as a 'nucleophile and attacks the triple bonded carbon. Ketimine is formed as unstable intermediate when the addition product of the alkyl cyanide and Grignard reagent is hydrolysed. Further hydrolysis of the ketimine results in the formation of the ketone.

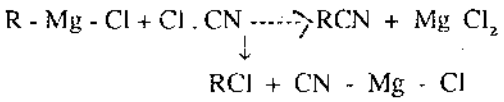


When hydrogen cyanide is used in the place of alkyl cyanide, in reactions with Grignard reagent, aldehydes are produced.



22.5.2.7 Reaction with Cyanogen halide

An alkyl cyanide is formed by the reaction of cyanogen chloride with a Grignard reagent in 1:1 proportion.



Some alkyl chloride is also formed in this reaction.

Excess chanogen chloride is used to avoid further reaction between alkyl cyanide and Grignard reagent.

22.5.2.8 Reaction with sulphur

Sulphur reacts with Grignard reagent to form thioalcohols or mercaptans.

$$R\text{ -- }Mg\text{ -- }X \xrightarrow{S} RSMg\ X \xrightarrow{H_2O} RSH + Mg(X)OH$$

mercaptan

22.6. OTHER ORGANO METALLIC COMPOUNDS

22.6.1 n- Butyl lithium

A solution of n-butyl chloride in benzene or ether reacts directly with lithium to form n-butyl lithium.

$$CH_2 . CH_2 CH_2 CH_2 Cl + 2Li \longrightarrow CH_3 CH_2 . CH_2 . CH_2 . -- Li + LiCl$$

n - Butyl lithium

N- Butyl lithium reacts in the same way as Grignard reagents. It reacts with active methylene group compounds , and reacts with water liberating butane.

$$n - C_4 H_9 Li + H_2 O \longrightarrow n\ C_4 H_{10} + LiOH$$

Other alkyl lithium compounds may be prepared by the reaction of n-butyl lithium with suitabl halides . The reaction involves exchange of alkyl groups.

$$n - C_4 H_9 Li + RX \longrightarrow R Li + n --- C_4 H_9 X$$

22..6.2 Tetraethyl lead

This is obtained by the action of ethyl chloride upon lead sodium alloy.

$$n- C_4 H_9 Cl + 4PB - Na \longrightarrow (C_2H_5)_4 Pb. + 4\ Na\ Cl + 3\ Pb.$$

Tetraethylead

Small quantities of tetraethyllead are obtained by the addition of purveresed lead chloride to ethyl magensium iodide in ether solution.

$$2pb\ Cl_2 + 4Et\ Mg.\ I \longrightarrow Et_4\ Pb + Pb + 4\ Mg\ \begin{matrix} Cl \\ | \\ (I) \\ | \end{matrix}\ d$$

Tetraethyllead is a colourless liquid, soluble in ether but not in water. It is a poisonous substance. It is an anti-knock substance. It controls the ignition of fuels in internal combussion engineers. A mixture of tetraethyllead, ethylene dichloride, ethylenedibromide and a dye is used as antiknock material.

Check your progress - 2

Formulate the products of acetaldehyde with a) methyl magnesium bromoide b) propyl magnesium bromide.

22.7 SUMMARY

Compounds containing a carbon, metal atom bond are called organometallic compounds. Examples are, Grignard reagent + (RM g x) n-butyl lithium (C_4H_9 - Li) and tetraethyl lead (pb $(C_2H_5)_4$). The carbon and carried a negative charge and are turns a good source of carbanions.

You should recollect the use of grignard reagents in preparation alkanes, and alcohols in earlier units. Now you learn that they are also useful in preparatio of esters, Ketones and monocarboxylic acids. N- Butyl lithium reacts in the same way as Grignard regents.

Another organometallic compound tetra ethyl lead is used as proof for formation of free-radicals and is used as anti-knock materials.

22.8 MODEL EXAMINATION QUESTIONS

I. Answer each of the following in 10 lines

1. Formulate the synthesis of the following, using a suitable Grignard reagent.
   a) Methyl ethyl carbinol
   b) Triethyl carbinol
2. What is the structure and quantity of the product resulting by treatment of 12.3 of g of isopropyl bromide with suitable quantity of magnesium and then with CO_2 and a dilute mineral acid?

II. Answer each of the following in 30 lines

1. Involving Grignard reagent as one of the components, how are the following synthesised?
   a) Propionic acid b) 1- Butanol c) Propanal d) 2- Butanol
2. What volume of methane at STP's obtained from 11.9 g of methyl magnesium bromide by treatment with an active hydrogen containing compound?

22.9 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Grignard reagent reacts with carbon dioxide to give an addition product which is hydrolysed to an acid.

$$O = C = O + RMgX \longrightarrow R - \overset{\overset{O}{\|}}{C} - OMgX \xrightarrow{HOH} RCOOH + Mg(OH)X$$

2. a)
$$CH_3 - \underset{\underset{H}{|}}{C}{=}O + CH_3MgBr \longrightarrow CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{OMgBr}{|}}{C}} - H \xrightarrow{\text{dill HCl}}$$

b) $CH_3 - C=O +$ $CH_3\,CH_2\,CH_2\,MgBr$ → $CH_3\,CH_2\,CH_2 - C(OH)H - CH_3$

4 -pentanol

$CH_3 - C(H)(OH) - CH_3$

2-Propanol

Author : Y.S.N. Murthy

UNIT - 23 CARBONYL COMPOUNDS

Contents

23.1 AIMS AND OBJECTIVES

This unit explains you difficult methods of preparation, properties and uses of carbonyl compounds.

After completing this unit you lmust be able to know:

- Nomenclature of carbonyl compounds
  - i) Oxidation of alcohols
  - ii) Dehydrogenation of alcohols
  - iii) Using Grignard reagent
  - iv) From alkanes
  - v) From calcium salts of carboxylic acids
  - vii) Friedel-Craft's acylation
- Chemical properties of aldehydes and ketones
  - i) Reactivity of aldehydes and ketones
  - ii) Addition of sodium bisulphite
  - iii) Addition of hydrogen cyanide

iv) Addition of Grignard reagent
v) Addition of ammonia and amines
vi) Addition of water
vii) Formation of acetal
viii) Polymerisation
ix) Reactions with halogens
x) Reactions with phosphorus pentachloride
xi) Reduction reactions

23.2 INTRODUCTION

The carbonyl group, >C=O, is the characteristic functional group present in aldehydes and ketones. In the case of aldehyde the carbonylcarbon is linked to a hydrogen. So the functional group in an aldehyde is $-\overset{H}{\underset{|}{C}}=O$ or –CHO. This group is also called formyl group. The general formula of an aldehyde is $R-\overset{H}{\underset{|}{C}}=O$ or R–CHO. However, in the simplest aldehyde, formaldehyde, HCHO the carbonyl carbon is lined to two hydrogens. In the case of ketones the carbonyl carbon is attached to two alkyl or aryl groups.

$$\overset{O}{\underset{||}{C}}$$

The general formula of ketones is R–C–R'. If R and R' are same it is a simple ketone and if they are different it is a mixed one or unsymmetrical one. Acetone, $CH_3 CO CH_3$ is a simple ketone and methyl ethyl ketone, $CH_3 COC_2 H_5$, is a mixed ketone. Also the ketone may be purely an aryl ketone (eg. benzophenone, $C_6H_5COC_6H_5$) or an aryl alkyl ketone (eg. $C_6H_5 - CO - CH_3$ acetophenone). Both aldehydes and ketones containing the carbonyl group are referred to as carbonyl compounds. As such, they have many properties in common.

23.3 NOMENCLATURE

The common names of the aldehydes are derived from the names of the acids obtained on oxidation of the aldehydes. The suffix -'ic' in the name ofthe acid is replaced by 'aldehyde'. For example; the acid obtained by oxidation of H–CHO is formic acid (HCOOH). The suffix -'ic acid' in the formic acid is changed to 'aldehyde'.

$$HCHO \xrightarrow{\text{Oxidation}} HCOOH \text{ (formic acid)}$$

Thus the name of the compound, HCHO, is formaldehyde CH_3–CHO, which gives acetic acid upon oxidation is named as acetaldehyde. Other examples are :

$CH_3 CH_2 CHO$	$CH_3CH_2CH_2CHO$	$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHO$
Propionaldehyde	n–Butyraldehyde	iso-Butyraldehyde

Carbonyl carbon atom is part of the functional group. The carbon atoms next to this carbon atom are labelled as α, β and γ carbons. While naming the substituted aldehydes the position of the substituents or side chains on these carbons are indicated by these letter α, β, γ etc.

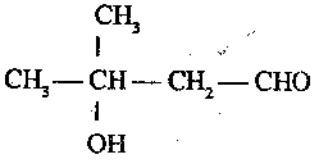
$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CHO$	$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle Cl}{\underset{|}{CH}}-CHO$
β – Hydroxy butyraldehyde	α–Chloro – β – methyl butyraldehyde

In the IUPAC system of nomenclaure, the suffix for aldehydes is 'al'. The longest carbon chain which includes the aldehyde group is chosen and the compound is named as the corresponding alkanal.

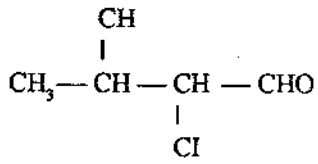
H— CHO is an aldehyde containing one carbon atom. The hydrocarbon containing one carbon is methane (CH_4). Formaldehyde is therefore named as methanal. Other examples of IUPAC nomenclature of aldehydes are given below. In this nomenclature the position of substituent is indicated by numbers. Here carbonyl carbon is considered as first carbon (Appendix - 1).

CH_3 CHO
Ethanal
(Acetaldehyde)

$CH_3—CH_2—CHO$
Propanal
(Propionaldehyde)

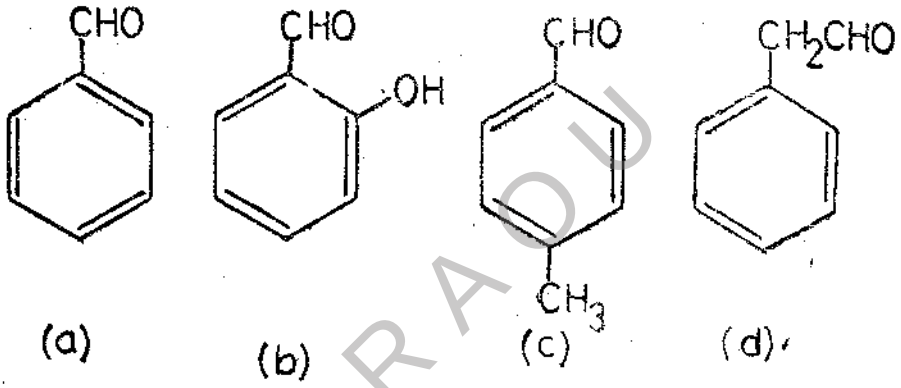


3– methyl – butanal
(iso – Valeraldehyde or
β – methyl butyraldehyde)



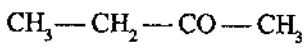
2 – chloro – 3 – hydroxy – butanal
(α–Chloro – β – hydroxy-butyraldehyde)

Following are the names of some aromatic aldehydes:

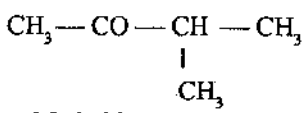


(a) Benzal-dehyde (b) Salicylal-dehyde (c) p-Tolualdehyde (d) Phenyl acetaldehyde

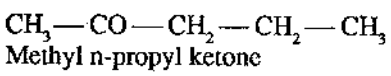
The common names of aliphatic ketones are based on the alkyl groups attached to the carbonyl group i.e., they are named as dialkyl ketones. $CH_3CO.CH_3$ is a ketone with two methyl groups attached to the carbonyl group. This is the simplest aliphatic ketone and is called dimethyl ketone or acetone. Dimethyl ketone is also called methyl ketone. Other examples are:



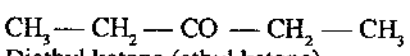
Ethyl methyl ketone



Methyl i-propyl ketone



Methyl n-propyl ketone



Diethyl ketone (ethyl ketone)

It may be noted that, in ketones, the carbonyl carbon (keto carbon) is never a terminal carbon. In contrast, in aldehydes the aldehydic carbon is the terminal carbon. In the IUPAC system of nomenclature 'one' is the suffix in the names of ketones. The longest carbon chain containing the carbonyl group is chosen and the ketone is named as the corresponding alkanone.

The ketone, $CH_3CO CH_3$, contains three carbons and therefore can be considered as the derivative of propane. Its name, propanone is derived by replacing the last letter - 'e' in propane by 'one'. In the prefix part of names of ketones, the position of the carbon atom present as keto group, and nature, position and number of other substituents, if any, are also indicated. The keto carbon is given the lowest possible number (Appendix - 2). Some illustrations of this nomenclature are given below.

$CH_3 — CO — CH_2 — CH_3$
Butan – 2 – one
(Ethyl methyl ketone)

$CH_3 — CH(CH_3) — CO — CH(CH_3) — CH_2 — CH_3$
2, 4 – Dimethyl – 3 – hexanone
(i–proplyl sec. butyl ketone)

$CH_3 — CO — CH(Br) — CH_2 — CH_3$
3 – Bromo – 2 – pentanone
or
(α – Bromo – n – propyl) methyl ketone

$C_6H_5 CO C_6H_5$ is diphenyl ketone or phenyl ketone. This is also called benzophenone. Methyl phenyl ketone is $CH_3 CO C_6H_5$. It is known as acetophenone.

Check your Progress - 1

Write the structures and IUPAC names of the following compounds.

a) γ - Methylvaleraldehyde
b) β - Chloropropionaldehyde
c) Methyl allyl ketone
d) α, β - Dibromo butyraldehyde

23.4 GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

23.4.1 Oxidation of alcohols:

Alcohols are oxidised by acidified potassium dichromate. Oxidation of primary alcohols gives aldehydes whereas secondary alchohols give ketones.

$$R — CH_2OH \xrightarrow[[O]]{K_2Cr_2O_7 + \text{acid}} R — CHO + H_2O$$

primary alcohol — aldehyde

"

$CH_3OH \longrightarrow HCHO + H_2O$
Methanol — Formaldehyde (methanal)

"

$C_6H_5 — CH_2 — OH \longrightarrow C_6H_5 — CHO + H_2O$
Benzyl alcohol — Benzaldehyde

"

$$R — CHOH \longrightarrow R — C(=O) — R$$

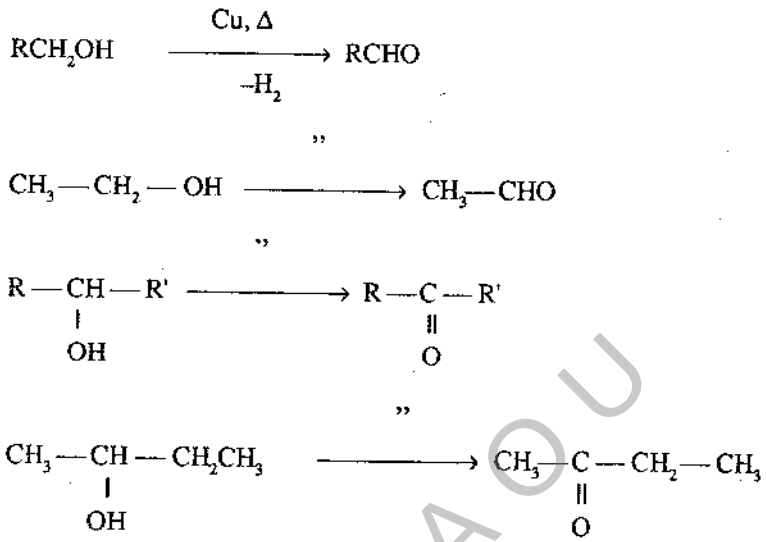
Secondary alcohol — Ketone

2 – propanol Acetone (Propanone)

It is difficult to stop the oxidation of primary alcohols at the aldehyde stage. The aldehyde initially formed is oxidised to the corresponding carboxylic acid.

24.4.2 Dehydrogenation of alcohols

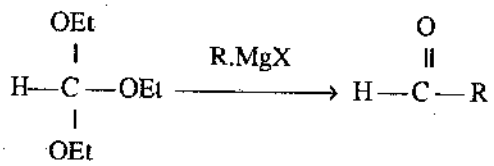
Dehydrogenation of alcohols results in the formation of carbonyl compounds. When the vapours of a primary alcohol are passed over hot copper metal, an aldehyde is obtained. In the case of a secondary alcohol the product of dehydrogenation is a ketone.



Oxidation of alcohols is carried out by Oppenauer method (Appendix - 3)

23.4.3. Using Grignard reagent

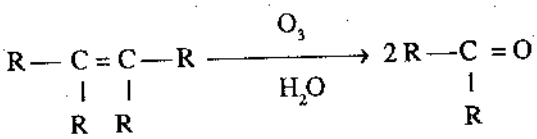
Reaction of Grignard reagents with ortho esters affords aldehydes and ketones. When ethyl orthoformate reacts with Grignard reagent, aldehydes are obtained. If other ortho esters are used the product is a ketone.



(Et = ethyl group)

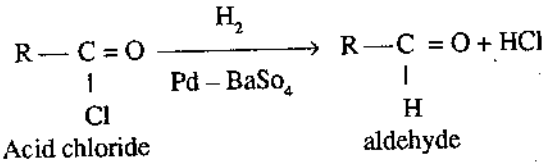
23.4.4 From alkenes

Alkene on ozonolysis from carbonyl compounds. Ozonolysis of symmetrical alkenes serves as a valuable method for the preparation of carbonyl compounds.

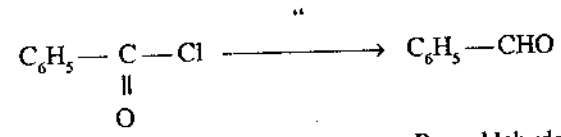


23.4.5. From acid halides

In this, an acid chloride is reduced with hydrogen in the presence of palladium – barium sulphate catalyst to give an aldehyde. This reaction is called **Rosenmund Reduction.**

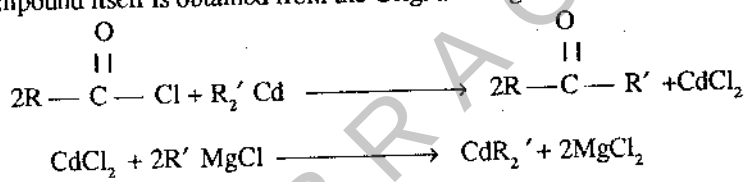


Acid chloride aldehyde



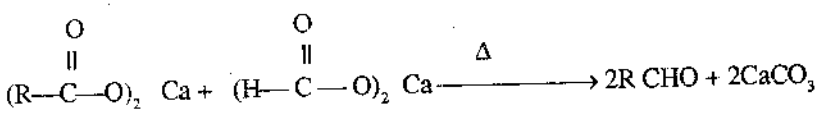
Benzoyl chloride Benzaldehyde

Reaction of acid chloride with organo-cadmium compounds gives ketones. The organo cadmium compound itself is obtained from the Grignard reagent.

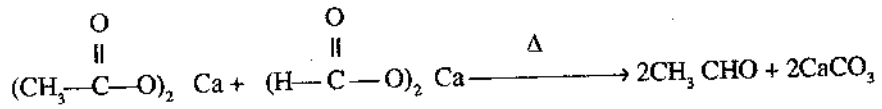


23.4.6. From calcium salts of carboxylic acids

When calcium formate is heated with calcium salts of carboxylic acids, aldehydes are formed. Heating a mixture of calcium acetate an calcium formate gives acetaldehyde.

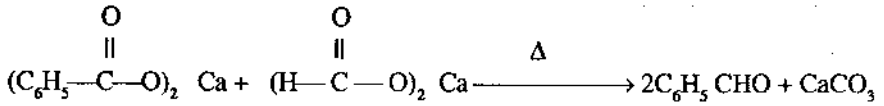


Calcium salt of an acid Calcium formate

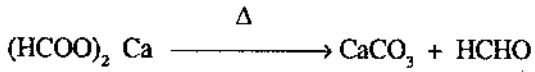


Calcium acetate

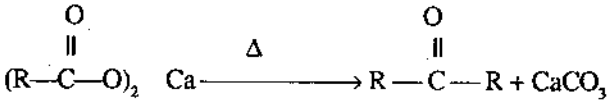
Benzaldehyde is obtained by heating calcium formate with calcium benzoate.

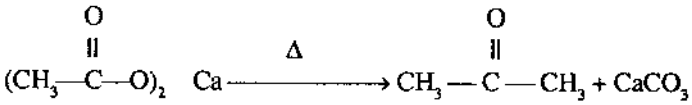


Pyrolysis of calcium formate alone results in the formation of formaldehyde.



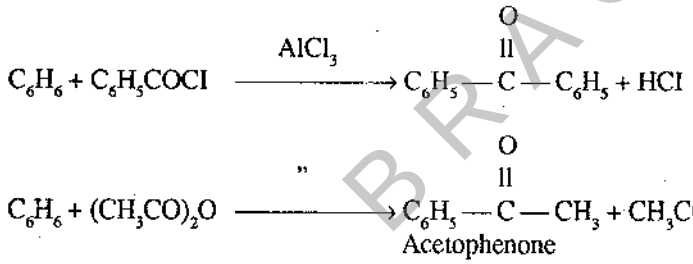
When the calcium salt of an acid is distilled alone a ketone is formed. By the dry distillation of calcium acetate, acetone is obtained.





23.4.7 Friedel - Crafts acylation

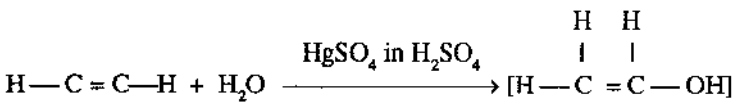
When benzene is treated with benzoyl chloride in the presence of anhydrous aluminium chloride, benzophenone is obtained. Similar reaction between benzene and acetic anhydride yields acetophenone. This reaction is called Friedel-Crafts reaction.

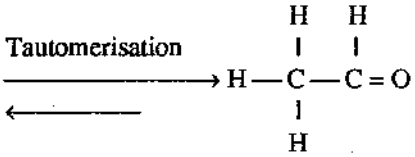


Acetophenone

23.4.7.1 Acetaldehyde

On a large scale, acetaldehyde is obtained by the hydration of acetylene. When acetylene is passed into dil. H_2SO_4 in the presence of mercuric salts, acetaldehyde is obtained. The intermediate in this reaction is the unstable vinyl alcohol which tautomerises to acetaldehyde.



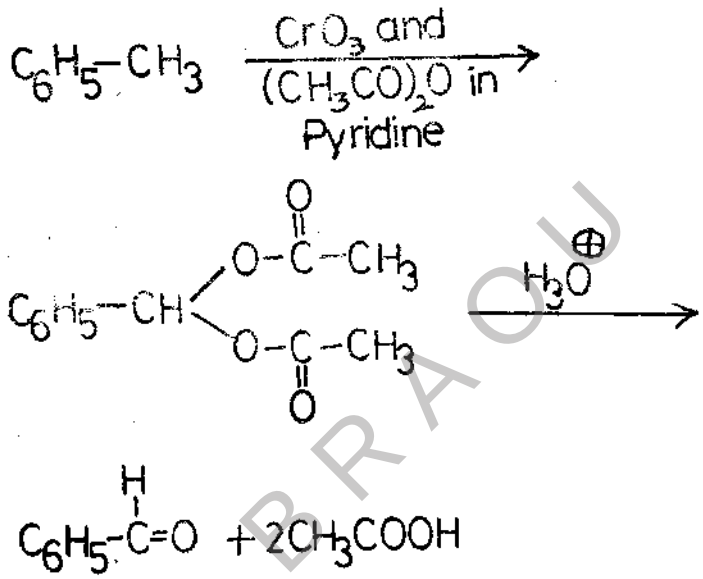


Check your progress - 2

What happens when propyne is passed through dil. H_2SO_4 containing mercuric sulfate?

23.4.7.2 Benzaldehyde

Toluene is oxidised with chromic anhydride in acetic anhydride. In the presence of acetic anhydride, initially formed benzaldehyde is converted into its diacetate by reaction with acetic anhydride. This prevents further oxidation of benzaldehyde to benzoic acid. In the absence of acetic anhydride the product of the reaction is benzoic acid. Hydrolysis of benzaldehyde diacetate gives benzaldehyde.



Benzaldehde

Benzaldehyde is obtained by the hydrolysis of benzylidene chloride which in turn is obtained by the chloride which in turn is obtained by the chlorination of toluene in the presence of light.

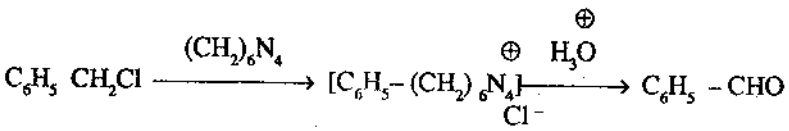
$$C_6H_5-CH_3 \xrightarrow[-HCl]{Cl_2,\ h\upsilon} C_6H_5-CH_2Cl \xrightarrow[-HCl]{Cl_2,\ h\upsilon}$$

Benzyl chloride

$$C_6H_5-CHCl_2 \xrightarrow{H_2O} C_6H_5CHO + 2\ HCl$$

Benzylidene chloride
or benzal chloride

Benzaldehyde is also produced by refluxing benzylchloride with hexamine in alcoholic solution followed by acidification. Thsi reaction is called Sommelet reaction.



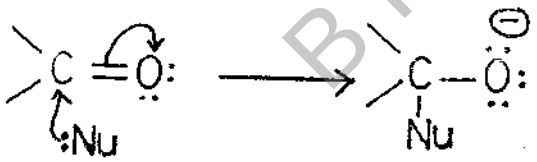
23.5 CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

In the carbonyl group, the carbon and oxygen are linked by a double bond. The carbon makes use of three sp^2 orbitals to form three sigma bonds. The angle between any two bonds is 120°. One unhybridised orbital of the carbon overlaps with that of the oxygen to form a π bond (pi- bond). As in the case of alkenes, the molecule is planar with the electron cloud above and below the C-O bond axis. In alkenes the π bond is between two carbon atoms whereas in aldehydes and ketones the π bond holds atoms of different electronegativity viz. carbon and oxygen. The latter is more electronegative so the shared electrons are not exactly mid way between the carbon and the oxygen atom. The electron cloud is associated more with the oxygen atom than with the carbon. Thus, unlike the carbon-carbon bond in alkenes, the carbon - oxygen bond is polarised, the carbon being slightly positive and the oxygen slightly negative $\overset{\delta+}{>}C=\overset{\delta-}{O}$. Further, the carbonyl group is resonance hybrid of two structures:

In other words, the carbon atom of the carbonyl group is electron deficient (electrophilic) and the oxygen atom is electron rich (nucleophilic). In the reactions of the carbonyl compounds, the electron deficient carbon is attacked by a nucleophile and the carbonyl oxygen reacts with electrophiles. Nucleophilic attack by the reagent at the carbonyl carbon leads to addition. Therefore these reactions are grouped under nucleophilic addition reactions.

23.5.1 Reactivity of aldehydes and ketones

Aldehydes are more reactive than ketones. This may be explained by steric and electronic factors. The nucleophilic addition can be represented as



Nu = Nucleophile

Nucleophilic attack at carbonyl carbon

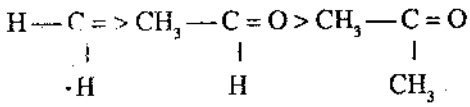
23.5.1.1 Steric factors

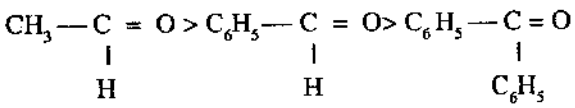
In formaldehyde the carbonyl carbon undergoing nucleophilic attack, is attached to two hydrogen atoms which do not hinder the approach of the nucleophile. In the case of other aldehydes, the presence of a bulkier alkyl group increase crowding around the carbonyl carbon. In the case of ketones due to the presence of two alkyl or aryl groups there is maximum crowding which hinders the nucleophilic attack on the carbonyl carbon. Steric factors thus hinder the appraoch of nucleophile to carbonyl carbon and hence inhibit the reactions of ketones. The observed order of reactivity if HCHO > RCHO>R_2CO. The decrease in the reactivity of aromatic carbonyl compounds is partly due to steric hindrance of the bulky aryl groups.

23.5.1.2 Electronic factors

Electron releasing groups decrease electron deficiency of the carbonyl carbon in aldehydes and ketones. Therefore their reactivity decrease in nucleophilic reactions. These electron releasing groups act through inductive and mesomeric effects. Thus aliphatic ketones (with two + I exerting group) are less reactive than aliphatic aldehydes (with one + I group). The latter are less reactive than formaldehyde in nucleophilic addition reactions.

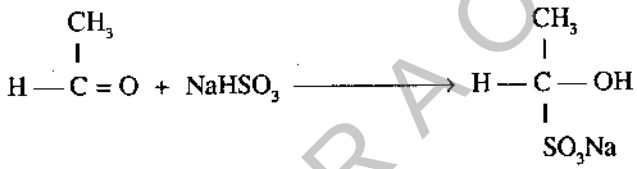
Similiarly + M effect of an aryl group in aromatic aldehydes and ketones is responbsible for their low reactivity. Presence of electron attracting groups on the carbonyl carbon, on the other hand, increases the reactivity of carbonyl compounds is as follows:



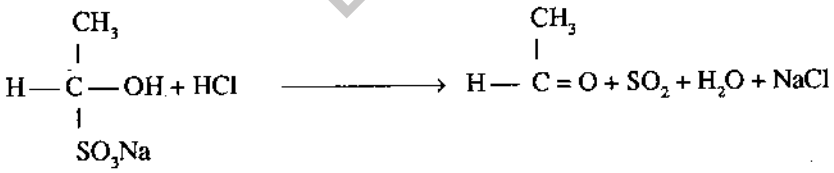


23.5.2 Addition reactions of carbonyl compound

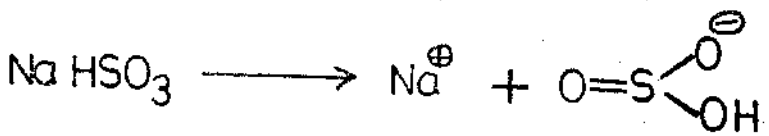
Aldehydes and ketones react with a saturated solution of sodium bisulphite to give crystalline additon products. The addition product, on treatment with a dilute mineral acid or with sodium carbonate solution regenerates the original carbonyl compound.

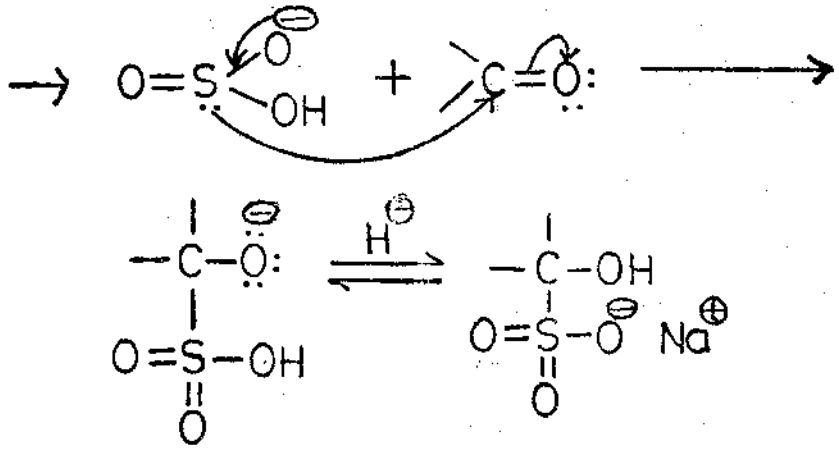


Acetaldehyde - sodium bisulphite addition compound.



This reaction is therefore valuable in the purification of the carbonyl compound and also in the separation of a carbonyl compound and also in the separation of a carbonyl compound from other non-carbonyl compounds. The addition of sodium bisulphite involves the attack of the bisulphite anion (nucleophile) on the carbonyl carbon followed by the transfer of a proton to the oxygen atom. This reaction leads to the formation of a carbonsulphur bond.

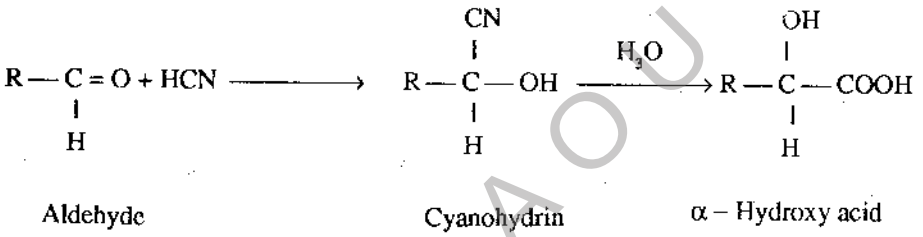




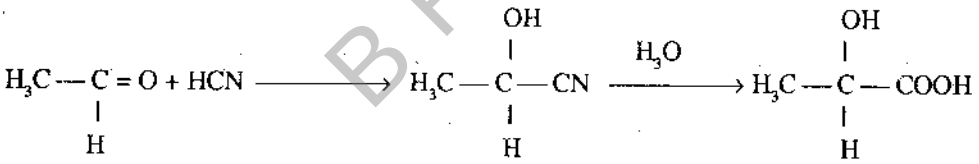
Ketones, with bulky groups attacned to the carbonyl group, due to steric hindrance do not form the addition product (Appendix-4).

23.5.3 Addition of HCN

When a molecule of hydrogen cyanide is added to aldehydes or ketones corresponding cyanohydrins are obtained. The cyanohydrin can be hydrolysed to give an α - hydroxy acid. Acetaldehyde reacts with HCN to form acetaldehyde cyanohydrin which is α - hydrolysed to hydroxy propionic acid (lactic acid).

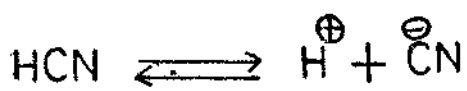


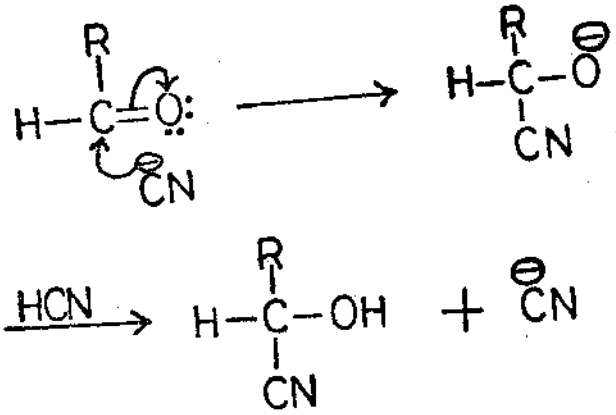
Aldehyde Cyanohydrin α – Hydroxy acid



Acetaldehyde cyanohydrin Lactic acid

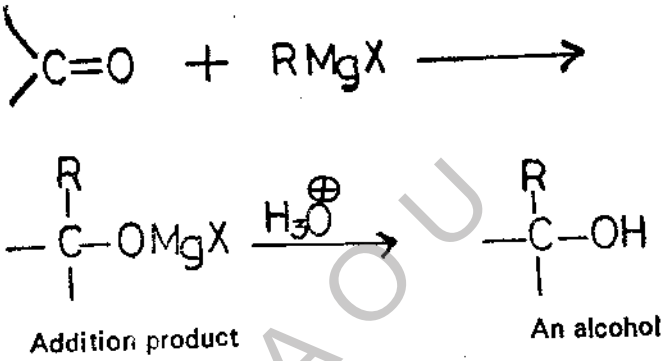
The probable mechanism of the reaction is :





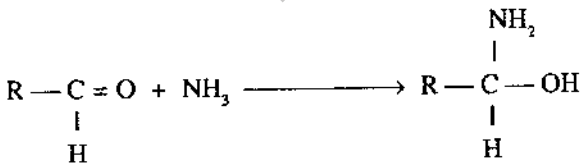
23.5.4 Addition of Grignard reagent

Grignard reagents (R–Mg–X) add on to carbonyl compounds. The resulting addition products on hydrolysis with dilute mineral acid give alcohols. In these reactions, Grignard reagents serve as a source of carbanions. Formaldehyde reacts with Grignard reagents to yield primary alcohols. Other aldehydes give secondary alcohols. Reaction of ketones with Grignard reagents yields tertiary alcohols (see the unit : hydroxy compounds)

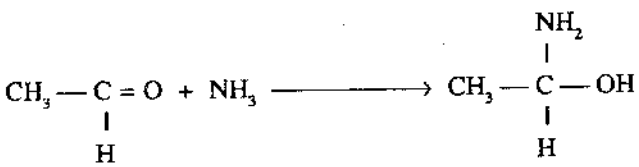


23.5.5 Addition of ammonia and amines

Ammonia and other compounds containing an amino grouop react as nucleophiles. Aldehydes from unstable addition products with ammonia. These are called aldehyde ammonias.



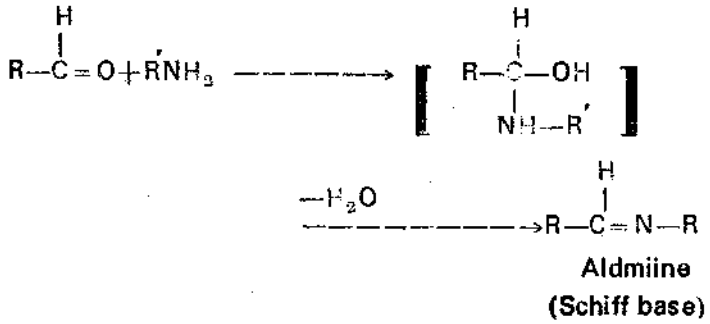
Aldehyde ammonia



Acetaldehyde ammonia

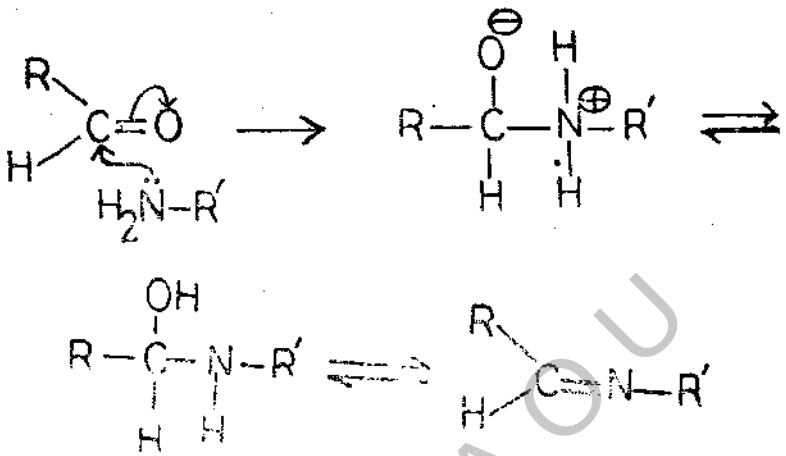
Generally aldehyde ammonias are not isolable. They often undergo further condensation to give polymeric products. Formaldehyde is an exception (Appendix - 5).

Aldehydes and ketones react with primary amines to give addition products. They are usually unstable, sponataneously losing water to give aldimine or ketimines. The aldimines and ketimines are also known as schiff bases.



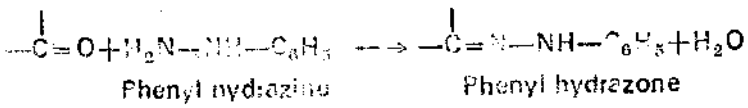
Aldmiine
(Schiff base)

Mechanism:

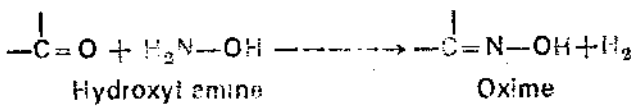


Both aldehydes and ketones react with other compounds containing a primary amino group. Carbonyl compounds thus a react with hydrazine, phebry hydraz, hydroxylamine and semi crbazide to give the coorresponding hydrazewnoes, phenyl hydrazone, oximes, semicarbe zones respectively.

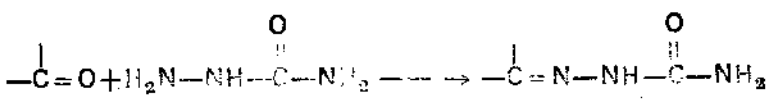
Hydrazine Hydrezone



Phenyl nydrazine Phenyl hydrazone

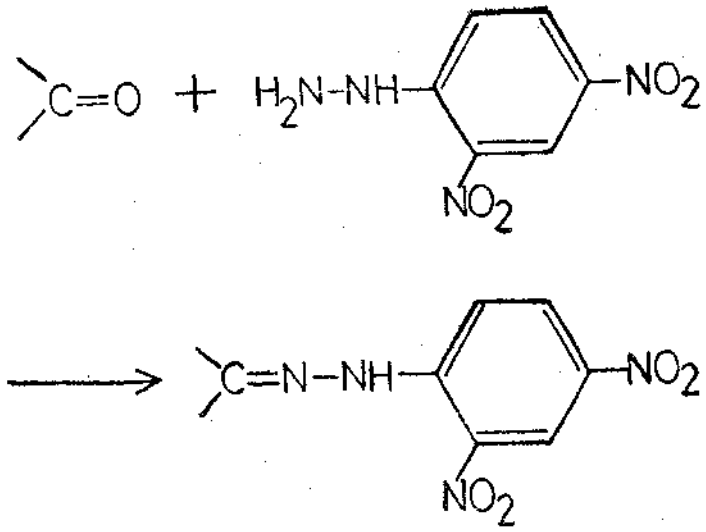


Hydroxyl amine Oxime



Sami Carbazide Semi Carbazone

These derivatives are crystaline and useful or charactrisation of the carbonyl compounds. 2,4-Dinitrophenyl hydrozine is a valuable reagent for the detection of carbonyl function in organic compounds.

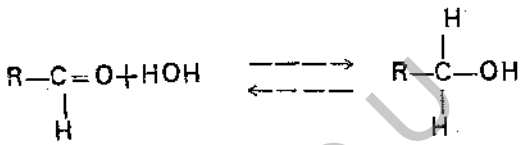


2, 4 - Dinitrophnyl hydrazone

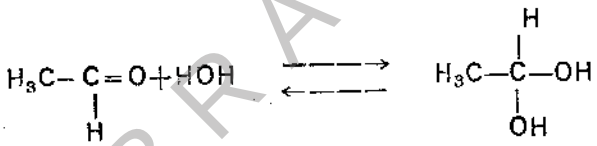
2, 4 - Dinitropnenyl hydrazones are sparingly soluble organge red crystalline prodcuts.

23.5.6 Addition of water

In aqueous solution carbonyl compounds are in equilibrium with their hydrates or gem. diols..

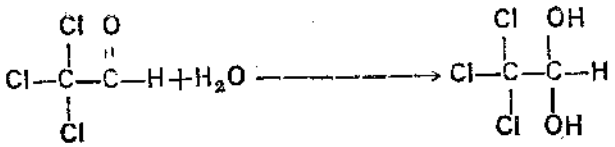


Aldehyde hydrate
(a gem. diol)



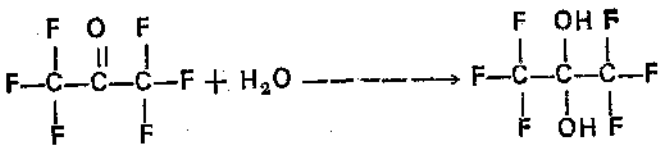
Acetaldehyde hydrate

As a rule these hydates are not stable. A gem diol loses water readily and reverts to the starting material However, carbonyl ompounds, with the carbonyl carbon attached to strongly electron attracting groups, form stable hydrates. Thus chloral, perouoroacetonbe and glyoxal form stable hydrates.



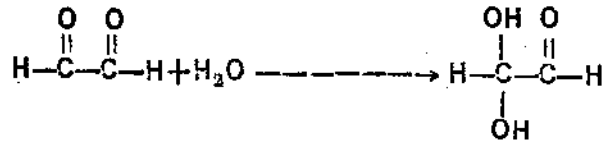
Chloral
(trichloro acetaldehyde)

Chloral hydrate



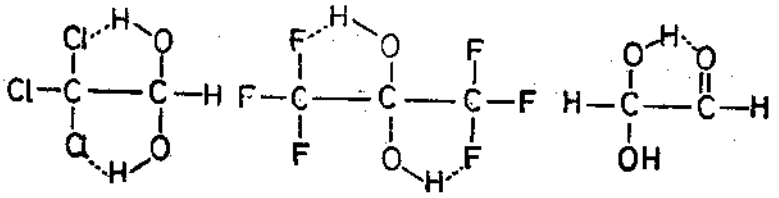
Perfluoro acetone

Perfluoroacetone hydrate



Glyoxal Glyoxal hydrate

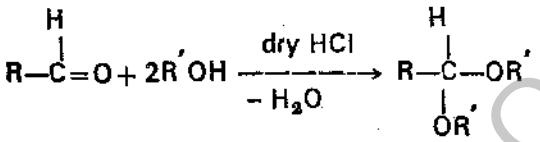
The stability of these hydrates is attributed to the formation of intramolecular hydrogen bonds. In chloral hydrate the hydrogen of the OH group froms a bridge between two electronegative atoms viz. oxygen and chlorine.



Chloral hydrate Perfluoroacetone hydrate Glyoxal hydrate

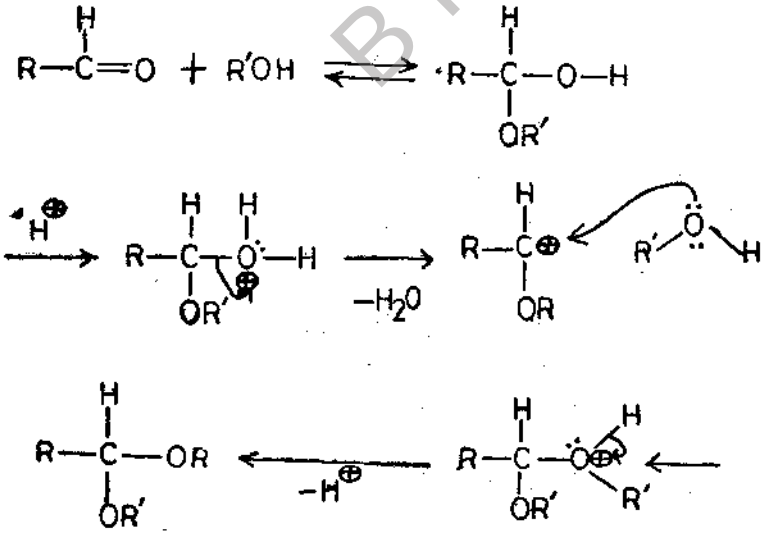
23.5.7 Formation of acetals

Aldehydes combine with alcohols in the presence of dry HCl to form acetals.



An acetal

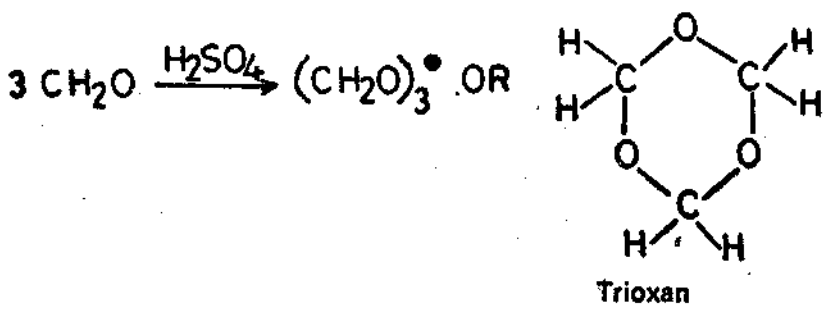
following mechanism has been suggested for acetal formation.



An aldehyde in alcoholic solution is in equilibrium with hemiacetal. Hemiacetals are unstable, but are converted into acetals in the presence of dry HCl. Acetals are hydrolysed by dilute mineral acids, when the aldehyde is recovered. Acetal formation is valuable in the protection of carbonyl group of a aldehyde.

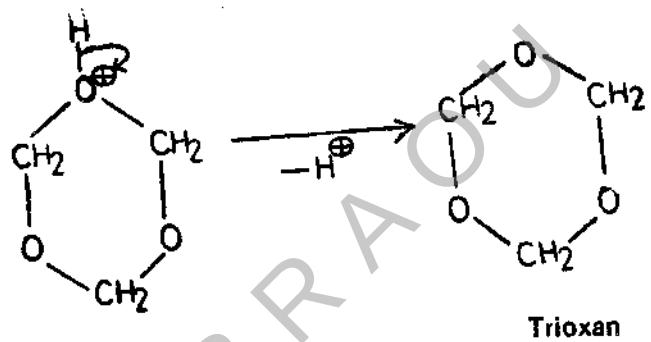
23.5.8 Polymerisation

The lower aldehydes show a tendency to polymerise. Formaldehyde polymerises. The trimer obtained by distillation of formaldehyde solution with a little sulphuric acid is called trioxan.



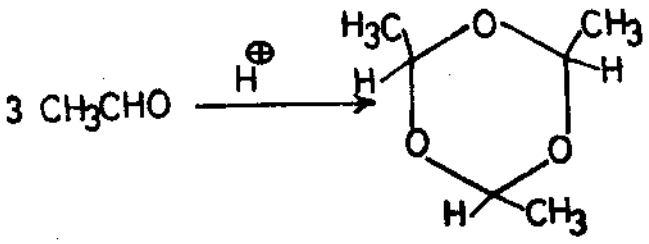
Trioxan

Acid catalysed polymerisation of formaldehyde proceeds as follows;



Trioxan

Acetaldehyde, similarly, trimerises to paraldehyde.



Paraldehyde

Formaldehyde upon evaporation gives a white crystalline solid called paraformaldehyde.

$$n.\ CH_2O \longrightarrow (CH_2O)_n$$

(Paraformaldehyde)

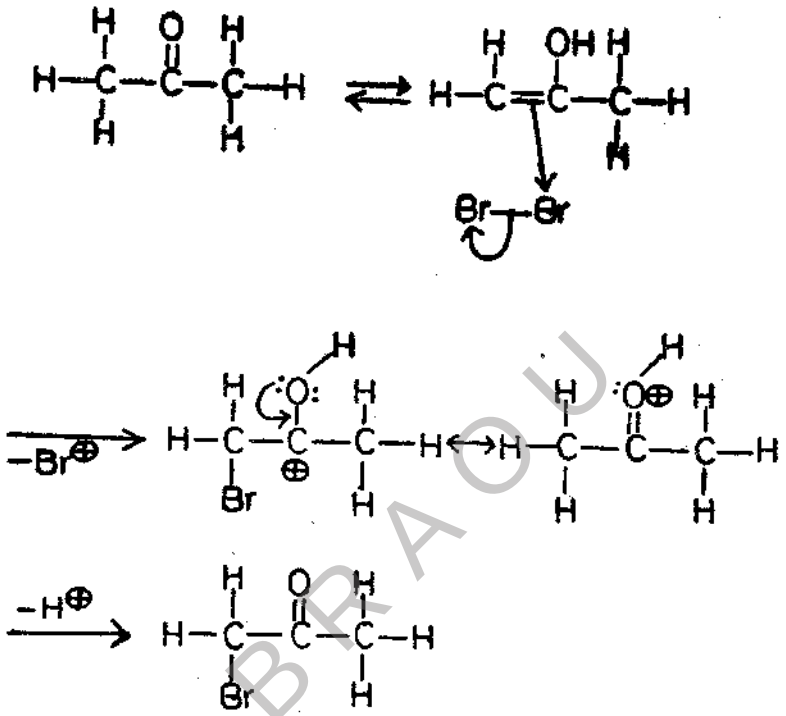
23.5.9 Reactions with halogens

In the case of saturated aldehydes and ketones, halogenation takes place at the α - carbon. i.e. the hydrogen on the carbon adjacnt to the caroonyl carbon is replaced by halogen. Acetone reacts with bromine to from bromoacetone (α - bromoacetone)

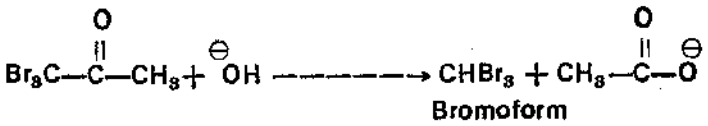
$$CH_3 - CO - CH_3 + Br_2 \longrightarrow CH_3 - CO - CH_2Br + HBr$$

α - Bromoacetone

Acetone reacts readily with chlorine, bromine and iodine. The reaction is catalysed by acids as well as bases. Acetone is a mixture of keto and enolforms. The enol form readily reacts with bromine of keto and enol forms. The enol from readily reacts with bromine. The intermediate cation loses a proton to form the bromocetone.



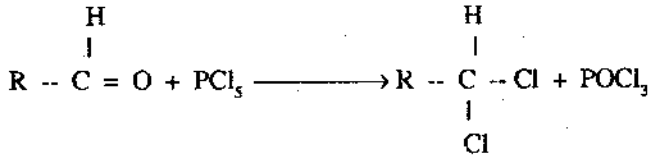
When excess bromine is used trihalogenation occurs. In the presence of a base the triboromo derivative gives bromofrom.

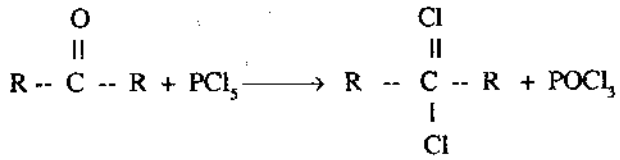


In the laboratory it is convenient to use iodine rather than chlorine or bromine. (Appendix 6).

23.5.1 Reactions with PCl_5

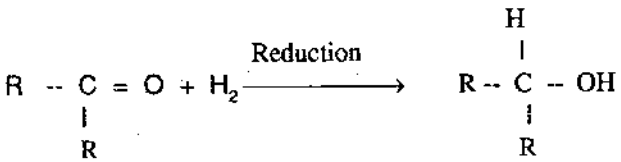
Aldehydes and ketones react with PCl_5 to form gem dihalo alkanes.





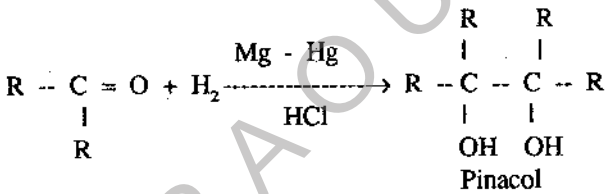
23.5.10.1 Reduction

Carbonyl compounds may be reduced to corresponding alcohols or pinacols. Reduction of a carbonyl compound by H_2 and catalyst, Na-Hg, Iron in acetic acid or $LiAlH_4$ results in the formatio of an alcohol.



Reducing agents (1) H_2 + catalyst (2) Na-Hg_3 Fe + CH_3COOH (4) $LiAlH_4$.

Magnesium amalgam in the presence of HCl converts ketones, but rarely aldehydes, to give pinacols.



Appendix-1: The common names along with the IUPAC names of some aldehydes are given below:

Aldehyde	Common name	IUPAC
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
$CH_3CH(CH_3)CHO$	Iso-butyraldehyde	2- Methyl propanal
CHO-CHO	Glyoxal	Ethanedial
$CH_2=CH.CHO$	Acrolein (acrylaldehyde)	Propenal

Apppendix-2: Common and IUPAC names of Ketones:

$CH_3\,CO.CH_3$	Dimmethyl ketone (acetone)	Propanone
$CH_3\,CH_2.\,CO - CHCH_3$ (with CH_3 branch)	Ethyl isopropyl Ketone	2- Methyl 3- pentanone
$CH_3\,CH_2\,CO - C(CH_3)_2 - CH_3$	Ethyl - butyl Ketone	2, 2 - Dimethyl 3 - pentanone
$CH_3 - CO - CO - CH_3$ $Cl - CH_2 - CH_2\_\,CO\,CH_2\,CH_2Cl$	Di acetyl β , β – Dichloro Diethyl ketone	Butan 2, 3 dione 1, 5 - Dichloro. 3 - pentanone

Appendix-3: In Oppenauer oxidation, the given alcohol, say, a secondary alcohol is mixed with a suitable ketone, such as acetone and refluxed with aluminium t-butoxide or aluminium isopropoxide.

aluminium t- butoxide $\left(CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - O\right)_3 - Al$

Allminuium isopropoxide $\left(CH_3 - \underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - O\right)_3 Al$

The Reaction is represented as

$$R - \underset{\displaystyle R}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - OH + CH_3 - CO - CH_3 \;\rightleftharpoons\; R - \underset{\displaystyle R}{\overset{\displaystyle O}{\overset{||}{C}}} + CH_3 - \underset{\displaystyle H}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}} - CH_3$$

The secondary alcohol gets oxidised to a ketone while acetone is reduced to isopropyl. In this reversible reaction forward reaction is favoured by using excess of acetone (as solvent) and by constant removal of one of the products of the reaction viz. isoropyl alcohol by distillation. The backward reaction which occurs by using excess isopropyl alcohol as solvent and by distilling off the acetone formed is called Meerwein - Ponndorf Verley reduction.

Oppeanauer oxidation is particularly useful in the oxidation of unsaturated alcohols to the corresponding carbonyl compounds. The double bond is not effected in the process.

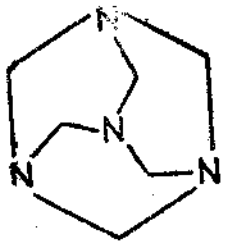
Similarly Meerwein - Ponndorf - Verley reduction is useful in reducing the unsaturated aldehydes and ketones to the corresponding alcohols without affecting the double bond. In fact any reducible functional group is not affected.

Appendix - 4: In the formation of bisulphite addition product the larger $SO_3^{\ominus}Na$ group gets attached to the carbonyl carbon. If the carbonyl carried atleeast, one small group ie. a hydrogen or a methyl group (as in the case of aldehydes and methyl ketones) there is no steric hindrance to the formation of the sodium bisulphite addition product. On the other hand in carbonyl compound with two bulky alkyl and aryl groups attached to the carbonyl carbon (as in the case of diisopropyl ketone and di-tert. butylketone) the formation of bisulphite addition poduct becomes difficult.

Appendix-5: Formaldehyde reacts with ammonia to give hexamethylene tetramine (hexamine)

$$6CH_2O + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6\ H_2O$$

The structure of hexamine is



It is a urinary antiseptic. It is also called urotropin.

Appendix-6: Iodoform test. When a methyl ketone is treated with iodine and alkali, lemon yellow crystals of iodoform seperate.

$$CH_3 - \overset{O}{\overset{\|}{C}} - R + I_2 + \overset{\ominus}{OH} \longrightarrow I_3C - \overset{O}{\overset{\|}{C}} - R + 3HI$$

$$I_3C - \overset{O}{\overset{\|}{C}} - R + \overset{\ominus}{OH} \longrightarrow CHI_3 + R - \overset{\ominus}{COO}$$

All compounds containing the $CH_3 - \underset{\underset{OH}{|}}{CH} -$ group give positive iodo form test. This can be explained as follows. The hypoiodite ion $(\overset{\ominus}{IO})$ (formed from iodine and alkali) oxideses the compound to methyl ketone which further reacts to give iodoform.

$$CH - \underset{\underset{OH}{|}}{CH} - R \xrightarrow[\text{Oxidattion}]{\overset{\ominus}{IO}} CH_3 - \overset{O}{\overset{\|}{C}} - R \xrightarrow[\overset{\ominus}{OH}]{(i)\ I_2} CHI_3 + \overset{\ominus}{RCCOO}$$

Since alkali can hydrolise $CH_3 - \underset{\underset{X}{|}}{CH} -$ group (Where X = halogen) to $CH_3 - \underset{\underset{X}{|}}{CH} -$ group compounds

containing $CH_3 - \underset{\underset{X}{|}}{CH} -$ grouip also give positive iodoform test

23.6 SUMMARY

The carbonyl carbon linked to hydrogen is aldehyde and is called ketone when it is attached to two alkyl or aryl groups. On oxidation of primay alcohols with potassium dichromate or hot copper metal an aldehyde is obained while ketone is formed from secondary alcohol. These are also prepared from ortho esters with grignard reagents; from acid halides by reduction or with organoceadmium compounds and from calcium salts or carboxylic acids on pyrolysis. Acetaldehyde is industrially prepared by hydration of acetylene. Aryl carbonyl compounds are prepared by Friedel-Crafts acylation, oxidtion of alkyl benzene or by somlet reaction.

The main type of reactions are nucleophilic addition with sodium bisulpfite, hydrogen cyanide, Grignard reagents, ammonia and its derivations. Addition of water leads to unstable gem diols while stable acetals are formed with alcohols. Halogens react wi th aldehydes and ketones to give L - halogenated poducts while with phosphorous pentachloride gem dihaloalkanes are obtained. Aldehydes are readily oxidised to carboxylic acids with ammonical silver nitrate (Tollen's test) or Fehling. solution.They also restore the pink colour to shiff's reagent. Ketones do not respond to these testly.

Reduction of aldehydes and ketones result in primary and secondary alcohols respectively with either $LiAlH_4$, NaHg/ HCl, Zn - Hg / HCL, or Aluminium isoprooxide.

23.7 MODEL EXAMINATION QUESTIONS

I. **Answer the following in 10 lines each**

1. How does acetone react with the following?
   a) Chlorine (b) Hydroxylamine (c) Iodine - sodium hydroxide (d) Ethyl magnesium bromide followed by hydrolysis.
2. How many carbonyl compounds are possible with the molecular formula C_5H_{10} ? Write their IUPAC names.
3. How do you distinguish the compounds in each of the following pairs?
   a) Ethanol and methanol
   b) 2- Pentanone and 3 - pentanone
   c) Propanal and propanone
4. An alkene, C_6H_{12}, upon ozonalsis gave a single product. What are the possible structures for the alkene?
5. How do you convert (a) benzene to benzophenone oxime (b) toluene to benzaldehyde ?
6. Write equations for the following reactions.
   a) Trimethyl acetaldehyde + sodium hydroxide ----------→
   b) Propanal + PCl_5 ----------→
   c) Acetophenone + hydroxylamine ----------→
7. Write the structures of A and B in the following reactions

   1. Benzaldehyde $\xrightarrow{KCN}$ (A) $\xrightarrow{\text{Oxidation}}$ (B)

   2. Benzene $\xrightarrow{\text{Benzoyl chloride}}$ (A) $\xrightarrow{H_2NOH}$ (B)

3. Benzene $\xrightarrow[AlCl_3]{CH_3Cl \text{ (one mole)}}$ (A) $\xrightarrow[\text{acetic anhydride}]{CrO_3 \text{ in}}$ (B)

8. Write the structure and name of
   a) An aldehyde having α - hydrogen atom
   b) An α, β unsaturated acid
   c) A phenolic aldehyde
   d) A diketone
   e) An unsaturated aldehyde
   f) An aldehyde without hydrogen atom

II Answer the following in 30 lines each

1. How are the following conversions effected ?
   a) Acetylene to acetone
   b) Propylene to acetone
   c) Acetone to tert-butyl alcohol
   d) Acetylene to lactic acid
2. Explain the following
   a) Aldehydes are more reactive than ketones towards nucleopjhilic addition.
   b) Diisopropyl ketone does not from sodium bisulphite addition product.
   c) Chloral forms a stable hydrate.
3. An alkene (A) Upon catalytic hydration gave an alcohol (B) Oxidtion of B gave a ketone (C) reacts with iodine and sodium hydroxide giving iodoform and CH_3CH_2COONa. What are the structures of A, B and C formulate the chemical changes involved in the reactions mentioned above.
4. An organic compound 'A' with molecular formula, C_6H_6O forms an oxime. A upon heating with sodium acetate and acetic anhydride gives B, B reacts with sodium bicarbonate solution liberating carbondioxide and also decolourises potassium permanganate solution. Suggest structures for A and B and explain the reaction involved.
5. Write equations for the synthesis of
   a) Salicyalldehyde from phenol
   b) Acetophenone oxime from benzene
6. What is the weight of phenyl hydrazone formed from 3.6g of outyraldehyde, if the yield of the product in the reaction is 90%.

23.8 MODEL ANSWERS TO CHECK YOUR PROGRESS

1) a) $CH_3-CH(CH_3)-CH_2-CH_2-CHO$ - 4 - Methyl pentanal

b) $Cl-CH_2-CH_2-CHO$ 3- chloro propanal

c) $CH_3-C(=O)-CH_2-CH=CH_2$ Pent - 4 ene - 2 one

d) $CH_3-CH(Br)-CH(Br)-CHO$ 2,3 -Dibromobutanal

2. When propyne is passed through CH H_2SO_4 containing mercuric sulfare ketone is formedKetone is formed

$$CH_3 - C \equiv CH + H_2O \xrightarrow[Hg\,SO_4]{dil\ H_2SO_4} CH_3 - \overset{\overset{O}{\|}}{C} - CH_3$$

Author : Y.S.N. Murthy

UNIT - 24 BASE CATALYSED REACTIONS OF CARBONYL COMPOUNDS

Contents

24.1 AIMS AND OBJECTIVES

In this unit we introduce you some important base catalysed reactions of Carbonyl compounds and we explain you the mechanism of the reactions.

After going through this unit you should be able to discuss the following reactions.

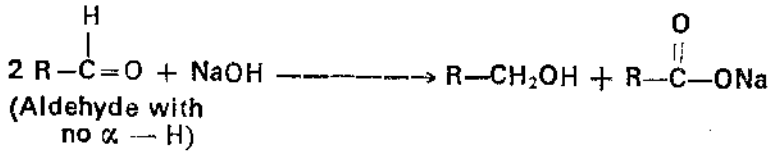
- Cannizzaro reaction
- Aldol condensation
- Perkin reaction
- Benzoin condensation
- Beckmann rearrangement
- Wolff - Kischner reduction
- Clemmensen reduction
- Meerwein-ponndorf - verley reduction
- Tollens' test
- Fehling's test
- Schiff test

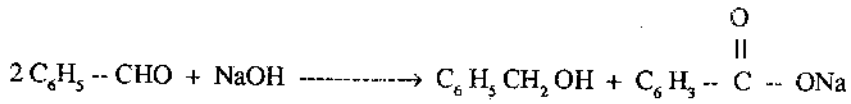
24.2 INTRODUCTION

24.3 CANNIZZARO REACTION

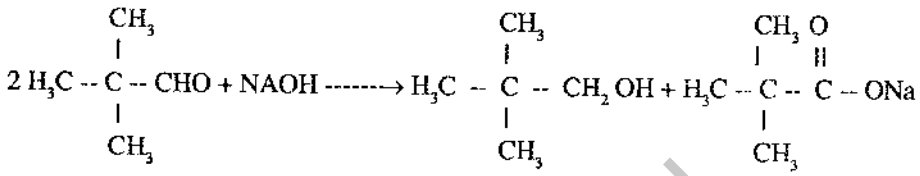
Aldehydes having no α - hydrogen such as formaldehyde (HCHO), benzaldehyde (C_6H_5CHO) and trimethyl acetaldehyde ($(CH_3)_3$ CCHO) undergo this reaction. In this reaction two molecules of the aldehyde are involved. One molecule is reduced to the corresponding primary alcohol and another

molecule is oxidised to the carboxylic acid. Formaldehyde reacts with alkali to form a mixture of methanol and sodium formate. Benzaldehyde gives benzyl alcohol and sodium benzonate, whereas trimethyl acetaldehyde forms neopentyl alcohol and sodium salt of trimethyl acetic acid.





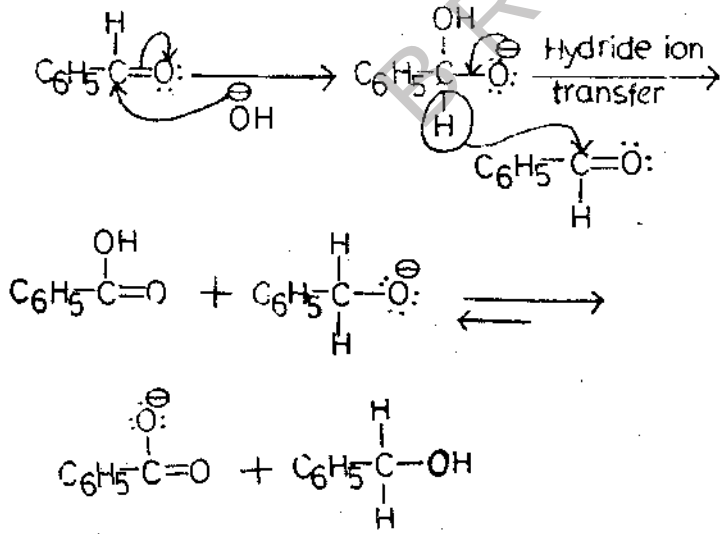
Sodium benzonate



Neopentyl alcohol

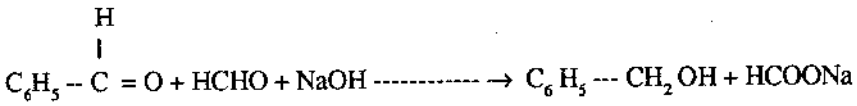
Sodium trimethyl acetate

The reaction involves the transfer of a hydride ion. Following is the mechanism of Cannizzaro reaction of benzaldehyde.



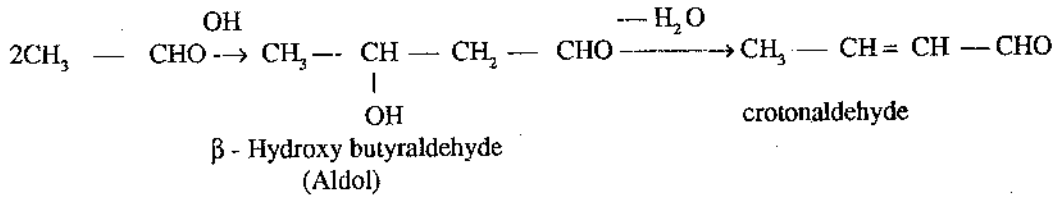
The first step is the nulceophilic attack by OH on the carbonyl carbon of the aldehyde. This is followed by transfer of a hydride ion to a second molecule of the aldehyde. Proton exchange between the benzoic acid and the benyloxy anion is the final step. Cannizzaro reaction taking place between two different

aldehydes is called crossed Cannizzaro reaction. Benzaldehyde, for instance, reacts with formaldehyde in the presence of alkali to give benzyl alcohol and sodium formate.



24.4 ALDOL CONDENSATION

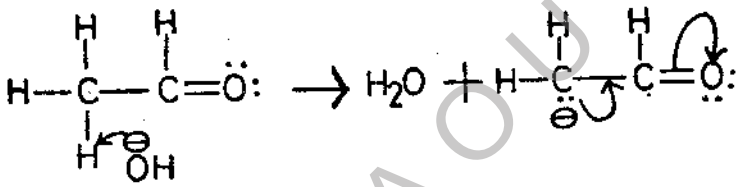
Aldehydes and ketones having α-hydrogens underego this reaction. In the presence of dilute alkyl, acetaldehyde undergoes condensation to give β- hydroxybutyraldehyde or aldol. Aldol upon heating loses water to form crotonaldehyde, an α, β -unsaturated aldehyde.



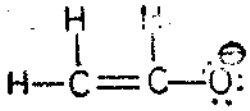
β - Hydroxy butyraldehyde (Aldol)

crotonaldehyde

The first step of the reaction is formation of a carbanion from the aldehyde under the influence of OH,



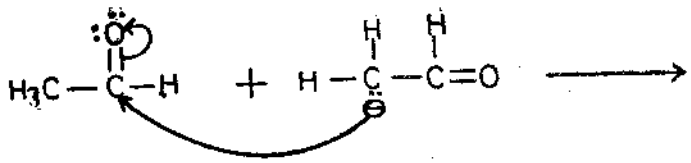
Carbanion

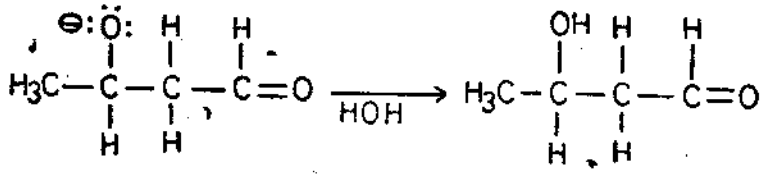


Oxanion

Reasonance of structures of the anion

The carbanion then attacks a second molecule of the aldehyde to form an oxyanion. The oxyanion abstracts a proton from water to form the aldol.





oxyanion Aldol

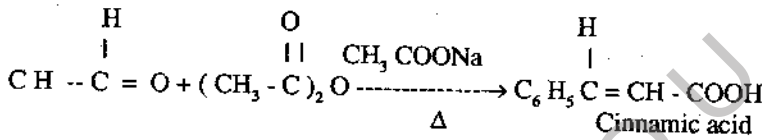
Aldol condensation may involve two molecules of an aldehde, two molecules of a ketone or one molecule each of an aldehyde and a ketone.

Check your progress - 1

Write the equation for aldol condensation

24.5 PERKIN REACTION

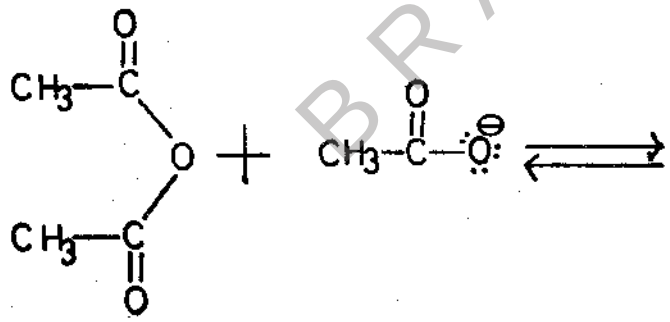
When benzaldehyde is heated with acetic anhydride in the presence of sodium acetate, cinnamic acid is obtained.

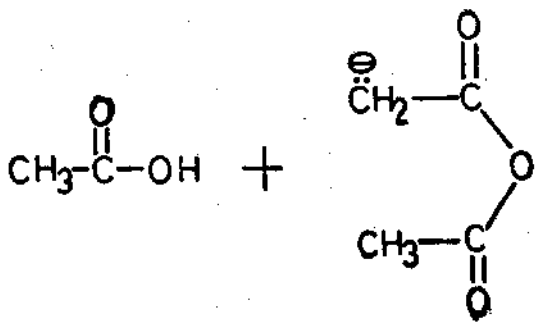


Cinnamic acid

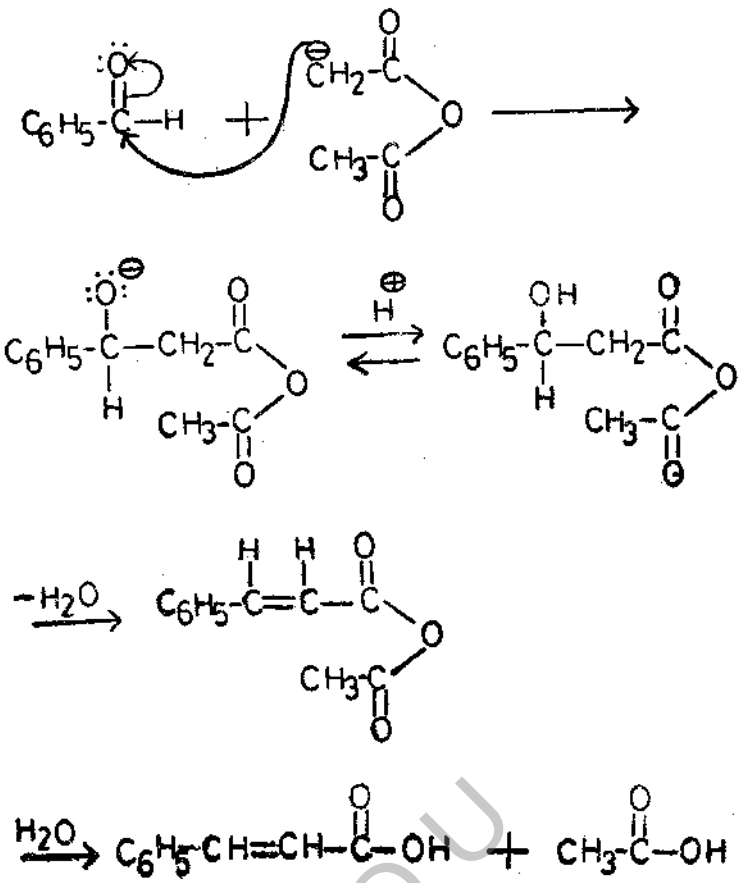
In this reaction acetate anion functions as a base and generates the required carbanion.

Mechanism:





In the next step the carbanion combines with benzaldehyde molecule.



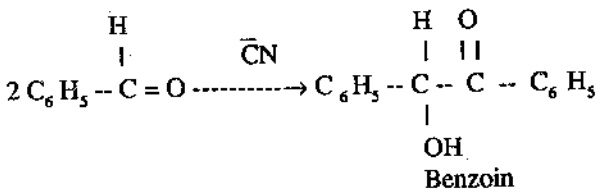
Cinnamic acid

In general, in this reaction an aromatic aldehyde is heated with the anhydride of an aliphatic acid and its sodium salt to get an α, β - unsaturated acid.

Check your progress - 2

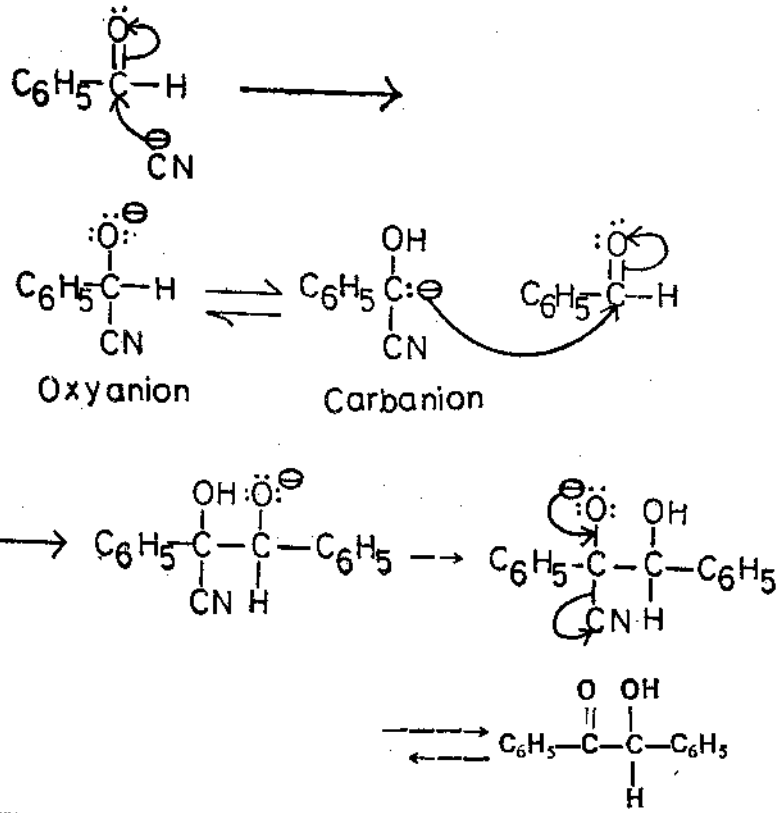
What is Perkin reaction ?

Aromatic aldehydes undergo this reaction. When benzaldehyde is refluxed with aqueous alcoholic potassium cyanide, benzion is formed. The reaction is known as benzoin condensation.



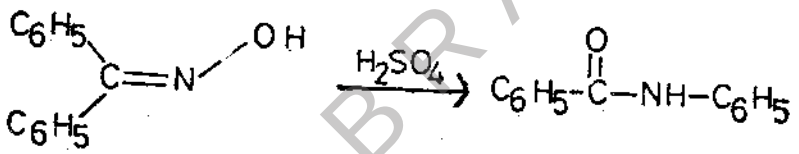
Benzoin

The following mechanism has been suggested for benzoin condensation.



24.7 BECKMANN REARRNGEMENT

This is typical reaction of ketoximes. When treated with reagents such as H_2SO_4 , PCI_5 etc. Ketoximes undergo rearrangement. An amide is obtained in Beckmann rearrangement. Benzophenone oxime yields benzanilide.

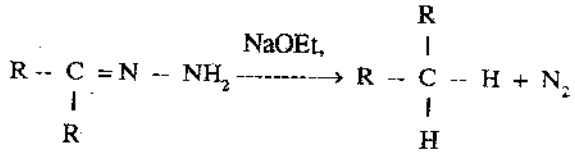


Benzophenone oxime

Benzanilide
(a substituted amide)

24.8 WOLF - KISCHNER REDUCTION

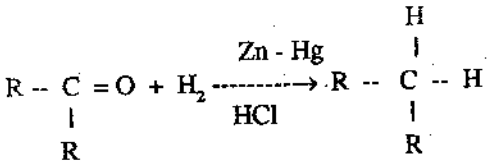
Ketones are usually reduced through their hydrazones. When the hydrazones are heated with sodium ethoxide at 180° usually in ethyleneglycol nitrogen is eliminated. The net reaction is the conversion of the carbonyl group into methylene group.

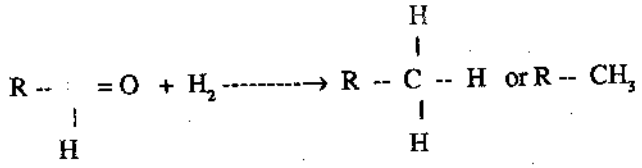


Hydrazone of a ketone

24.9 CLEMENSEN REDUCTION

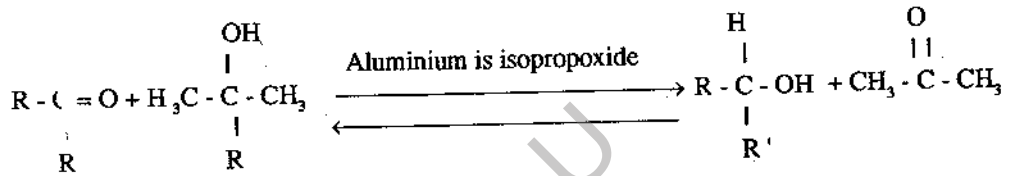
This method is also useful for the reduction of carbonyl group in aldehydes and ketones to methylene (CH_2) function. The reduction is carried out using zinc amalgam and HCl.



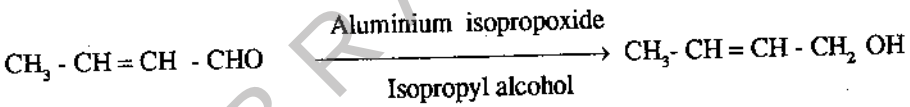


24.10 MEERWEIN - PONNDORF - VERLEY REDUCTION

Aldehydes and ketones are reduced by heating with aluminium isopropoxide in ispropyl alcohol.



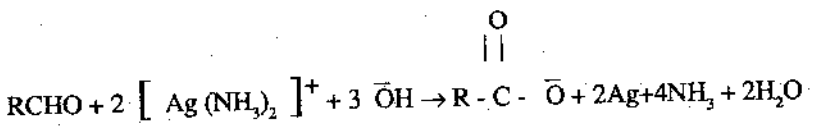
The reaction is specific for the carbonyl function and can be used for the reduction of aldehydes and ketones to give corresponding alcohols. Other reducible functions such as NO_2, C=C, C≡C are not affected under these conditions. Thus crotonaldehyde is reduced to crotyl alchol by this method.



Crotonaldehyde — Crotyl alcohol

24.11 TOLLENS' TEST

Aldehydes are readily oxidised i.e. they are powerful reducing agents. Aldehydes reduce Tollens' reagent to metallic silver. Tollent's reagent is ammonical silver nitrate solution containing the ion $[Ag(NH_3)_2]^+$



When this test is conducted under proper conditions, a fine silver mirror is obtained. Ketones do not give this test, This test is valuable for distinguishing aldehydes from ketones.

24.12 FEHLING'S TEST

This is another test for aldehydes. Ketones do not respond to this test. When an aldehyde is heated with Fehling's solution, a red precipitate of cuprous oxide is obtained.

$$R-\underset{\displaystyle H}{\overset{|}{C}}=O + 2Cu^{++} + 5\ \bar{O}H \longrightarrow R-\overset{\displaystyle O}{\overset{||}{C}}-\bar{O} + Cu_2O + 3H_2O$$

24.13 SCHIFF TEST

Only aldehydes restore the pink colour to Schiff's reagent. Schiff's reagent is prepared by dissolving rosaniline hydrochloride (a dye) in water and passing SO_2 gas until the pink colour is discharged.

24.14 SUMMARY

In this unit the formaton of carbanion when α -hydrogens are present in carbonyl compounds and their reaction with another mole of same compound (Aldol condensation) is presented. Aldehydes having no α - hydrogen undergo Cannizzaro reaction. The carbanions are produced from the reagents as in Perkin reaction. Aromatic aldehydes undergo Benzoin condensation in presence of KCN. The reaction mechanism is also discussed in this unit.

24.15 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each

1. Outline the mechanism of Cannizzaro reaction.
2. Formulate mechanism of aldol condensation
3. Explain the mechanism of Perkin reaction
4. Discuss the mechanism of benzoin condensation
5. Describe the importance of the following tests in the identification of carbonyl compounds.
   a) Tollens' Test b) Fehling's test c) Schiff test

II. Answer the following in 30 lines each

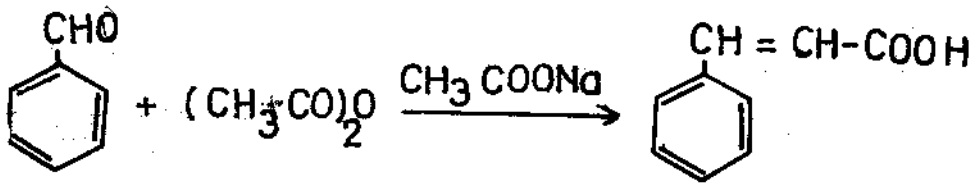
1. Give a critical account of any five base catalysed reactions of carbonyl compounds.
2. Discuss the mechanism of the reduction reaction of carbonyl derivatives of some aromatic aldehydes and ketones.

24.16 MODEL ANSWERS TO CHECK YOUR PROGRESS

1.

$$CH_3CHO + \overset{\ominus}{C}H_2CHO \xrightarrow{\bar{O}H} CH_3-\underset{\displaystyle H}{\overset{\displaystyle OH}{\overset{|}{C}}}-CH_2CHO$$

2. Reaction of bezaldehyde with acetic anhydride in the presence of sodium acetate is called Perkin reaction. Cinnamic acid is produced in this reaction.



Author : Y.S.N. Murthy

UNIT - 25 CARBOXYLIC ACIDS

Contents

25.1 AIMS AND OBJECTIVES

The main aim of this unit is to describe you the methods of preparation and characteristic properties of carboxylic acids.

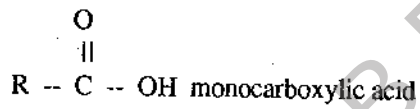
After completing this unit you should be able to know.

Nomenclature of carboxylic acids

- General methods of preparation by
  - (i) Oxidation of alcohols and aldehydes
  - (ii) Hydrolysis of nitriles
  - (iii) Carbonation of Grignard reagents
  - (iv) Oxidation of side chain
  - (v) Hydrolysis of amides, esters and acid chlorides
- Physical properties and acidic strength
- Chemical properties
  - (a) Reaction with metals
  - (b) Reaction with bases
  - (c) Replacement of OH goup by a halogen
  - (d) Ester formation
  - (e) Anhydride formation
  - (f) Formation of alkanes
  - (g) Formation of amides
  - (h) Formation of aldehydes and ketones
  - (i) Hunsdecker reaction
  - (j) Schmidt reaction
  - (k) Halogenation
  - (l) Reformatsky reaction
  - (m) Arndt-Eistert synthesis
  - (n) Reduction of acids
  - (o) Oxidation of acids
- Some individual members
  - (i) Formic acid

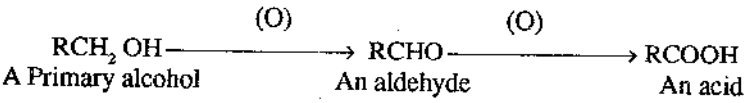
25.2 INTRODUCTION

The functional group present in carboxylic acids is COOH. This group is known as carboxyl group. Carboxylic acids are classified into monocarboxylic acids and dicarboxylic acids depending upon the number of carboxyl groups in the molecule. Monocarboxylic acids contain one carboxyl group.



Formic acid (H-COOH) and acetic (CH_3-COOH) are examples of monocarboxylic acids. Dicarboxylic acids contain two carboxyl groups. Oxalic acid (HOOC - COOH) and malonic acid $CH_2(COOH)_2$ are dicarboxylic acids.

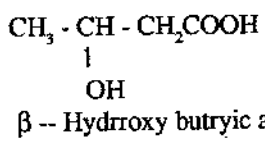
The general gformula of an aliphatic monocarboxylic acid is R-COOH and that of an aromatic monocarboxylic acid is Ar-COOH. Higher members of the aliphatic monocarboxylic acids are present in oils and fats as esters of glycerol viz. glycerides. They are, therefore, named as fatty acids. Upon oxidation, a primary alcohol first gives an aldehyde and then a carboxylic acid. So the carboxylic acid represents the extreme stage in the oxidation series.



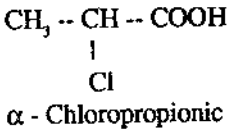
25.3 NOMENCLATURE

The common names of monocarboxylic acids are derived from the source of the acid. The first member of the homologus series of the monocarboxylic acids is H--COOH. HCOOH was originally

obtained from ants. Therefore it is known as formic acid (in latin formica means ant). The next member is acetic acid (CH_3COOH). This is present in vinegar. In Latin 'acetum' means vinegar. Hence the name acetic acid. Similarly butyric acid, C_3H_7COOH is present in butter. In latin butyrum means butter. While giving the common names of substituted acids the position of the side chains and substitutents is indicated by Greek letters α, β, γ, etc.



β -- Hydrroxy butryic acid

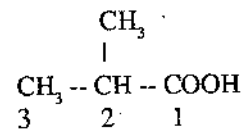


α - Chloropropionic acid

25.3.1 MONO CARBOXYLIC ACID

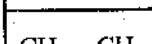
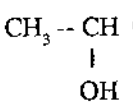
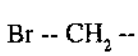
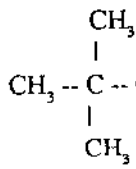
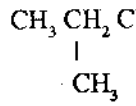
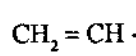
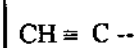
In IUPAC system of nomenclature the longest straight chain of carbon atoms present in the carboxylic acid is chosen. The acid is then named as the corresponding alkanoic acid. Formic acid (HCOOH) contains one carbon. It is, therefore, a derivative of methane and is named as methanoic acid. Acetic acid is similarly named as ethanoic acid.

In IUPAC system of nomenclature of substituted carboxylic acids, the numbering starts with the carbon atom of the carboxyl group. Isobutyric acid is 2-methyl propanoic acid

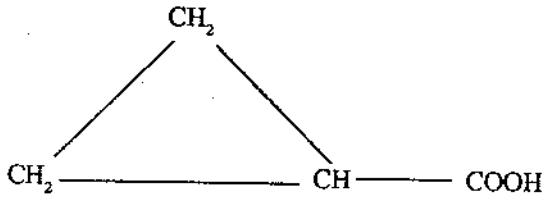


2- methyl propanic acid (isobutyric acid)

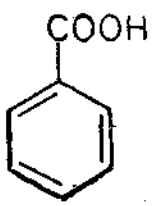
Few other illustrations are given below:

Formula	Common Name	IUPAC name
	Propionic acid	Propanoic acid
	α - Hydroxypropionic acid (lactic acid)	2 -- Hydroxy proponoic acid
	Valeric acid	Pentanoic acid
	α - Bromo acetic acid	2 - Bromo ethanoic acid
	Trimethyl acetic acid (α , α , - dimethyl propionic acid)	2, 2 - Dimethyl Propanoic acid
	α - Methyl butyric acid	2- Methyl butanoic acid
	Acrylic acid	Propenoicacid
	Acetylene carboxylic acid	Propynoic acid

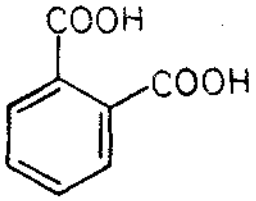
Cyclopropane carboxylic acid



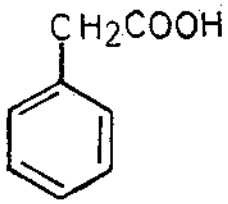
The names of some aromatic acids are given below:



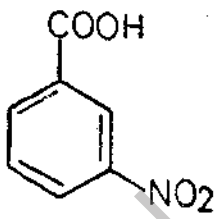
(a)



(b)



(c)



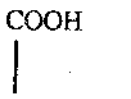
(d)

(a) Benzoic acid (b) Saticyclic acid

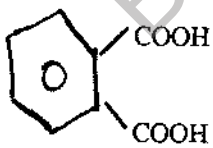
(c) Phynylacetic acid (d) m- Nitro benzoic acid

25.3.2 Dicarboxylic Acids

Compounds contain two carboxylic groups are known as dicarboxylic acids. Following are some examples:



Oxalic acid



Phthalic acid

Terephthalic acid

Following table gives the common and IUPAC names* of some dicarboxylic acids:

Formula	Common name	IUPAC name
COOH | COOH	Oxalic acid	Ethanedioic acid
COOH | CH_2 |	Malonic	Propanediocacid

COOH COOH $(CH_2)_2$ COOH	Succinic	Butanedioic acid
COOH $(CH_2)_3$ COOH	glutaric	Pentanedioic acid
COOH $(CH_2)_4$ COOH	Adipic	Hexanedioic acid

** The nemonic 'Oh My Such Good Apples' is convenient to remember the common names of aliphatic dicarboxylic acids.*

25.4 GENERAL METHODS OF PREPARATION

25.4.1 Oxidation of alcohols and aldehydes

Oxi ation of alcohols and aldehydes with potassium dichromate and sulphuric acid yields monocarbo ylic acids.

$$R.CH_2OH \xrightarrow{(O)} R\text{-}CHO \xrightarrow{(O)} R\text{-}COOH$$

$$CH_3OH \xrightarrow{(O)} H.CHO \xrightarrow{(O)} HCOOH$$

Methanol — Methanal (formaldehyde) — Methanoic acid (formic acid)

$$CH_3CH_2OH \xrightarrow{(O)} CH_3CHO \xrightarrow{(O)} H_3COOH$$

Ethanol — Ethanol (acetaldehyde) — Methanoic acid (formic acid)

$$C_6H_5CH_2OH \xrightarrow{(O)} C_6H_5CHO \xrightarrow{(O)} C_6H_5COOH$$

Benzyl alcohol — Benzaldehyde — Benzoic acid

25.4.2 Hydrolysis of nitriles

When alkyl cyanides (nitriles) are hydrolysed in the presence of an acid or base, carboxylic acids are obtained.

$$R\text{-}C\equiv N + 2H_2O \xrightarrow[H_3^+O \text{ or } \bar{O}H]{HOH} RCOOH + NH_3$$

An alkyl cyanide

$$CH_3\text{-}CN + 2H_2O \longrightarrow CH_3COOH + NH_3$$

Methyl cyanide (acetonitrile) — Acetic acid

$$CH_3CH_2CN + 2H_2O \longrightarrow CH_3CH_2COOH + NH_3$$

Ethyl cyanide (Propionitrile) — Propionic acid

$$C_6H_5CH_2CN \longrightarrow C_6H_5CH_2COOH$$

Benzyl cyanide (Phenylacetonitrile) — Phenylacetic acid

25.4.3 Carbonation of Grignard reagent

When a Grignard reagent reacts with carbondioxide, an addition product is formed. This on hydrolysis gives the carboxylic acid.

$$R\text{-}Mg\text{-}X + CO_2 \longrightarrow R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OMg\text{-}X \xrightarrow{HOH} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH + Mg(OH)X$$

Grignard reagent — An addition Product

$$CH_3\text{-}Mg\text{-}Br \xrightarrow[(ii)\ HOH]{(i)\ CO_2} CH_3\text{-}COOH$$

Methyl magnesium bromide — Acetic acid

$$C_6H_5\text{-}Mg\text{-}Br \longrightarrow C_6H_3\text{-}COOH$$

Phenyl magnesium bromide — Benzoic acid

25.4.4 Oxidation of side chain

Alkyl benzenes are oxidised by alkaline $KMnO_4$ to benzoic acid. Whatever may be length of the side chain the mono alkyl benzene is oxidised down to the ring to form COOH group.

$$C_6H_5\text{-}R \xrightarrow{KMnO_4 + OH^{\ominus}} C_6H_5COOH$$

An alkyl benzene — Benzoic acid

$$C_6H_5\text{-}CH_3 \xrightarrow{KMnO_4 + OH^{\ominus}} C_6H_5\text{-}COOH \xleftarrow{KMnO_4 + OH^{\ominus}} C_6H_5\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

Toluene — Benzoic acid — Propyl benzene

Some times the hydrocarbon is chlorinated and then the chloro derivative is oxidised.

$$C_6H_5\text{--}CH_3 \xrightarrow{Cl_2} C_6H_5\text{--}CH_2\text{--}Cl \xrightarrow{KMnO_4 + OH^{\ominus}} C_6H_5\text{--}COOH$$

Toluene — Benzylchloride — Benzoic acid

25.4.5 Hydrolysis of amides, esters and acid chlorides

Amides, esters and acid chlorides are hydrolysed to give corresponding carboxylic acids.

$$R\text{--}\underset{\underset{O}{\|}}{C}\text{--}NH_2 + 2H_2O \xrightarrow{OH^{\ominus} \text{ or } H_3O^{\oplus}} RCOOH + NH_3$$

An amide

$$R\text{--}\underset{\underset{O}{\|}}{C}\text{--}OR' + H_2O \longrightarrow R\text{--}COOH + R'OH$$

An ester

$$R\text{--}\underset{\underset{O}{\|}}{C}\text{--}Cl + H_2O \longrightarrow R\text{--}\underset{\underset{O}{\|}}{C}\text{--}OH + HCl$$

An acid chloride

This method is of theoretical interest. Amides, esters and acid chlorides are acid derivatives of carboxylic acids, and are themselves obtained from acids.

Benzoic acid is obtained by the hydrolysis of benzoyl chloride. The benzoyl chloride, however may be prepared from benzene and carbonyl chloride (phosgene) by Friedel-Crafts reaction.

$$C_6H_6 + COCl_2 \xrightarrow{Al\,Cl_3} C_6H_5COCl \xrightarrow{H_2O} C_6H_5COOH$$

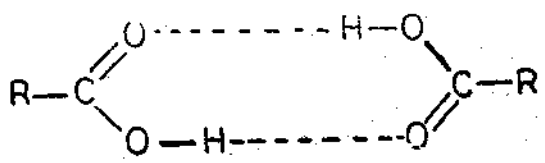
Benzoyl chloride

25.5 PROPERTIES OF CARBOXYLIC ACIDS

25.5.1 Physical Properties

The solubility of the acids is comparable to that of alcohols. The lower acids are soluble in water. The solubility of these compounds in water arises from the intermolecular hydrogen bonding between the molecules of water and the acid. Higher members of the carboxylic acids in which the hydrocarbon group is larger are insoluble in water.

The boiling points of carboxylic acids are higher than those of other substances of comparable molecular weights. This is attributed to molecular association. A pair of carboxylic acid molecules are held together by hydrogen bonds. The cyclic dimer is represented as



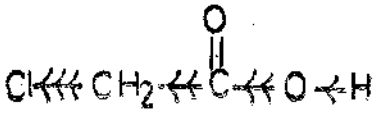
25.5.1.1 Acid strength

The strength of an acid (see Appendix-1) increases considerably by the replacement of the α - hydrogen by a halogen. Thus chloroacetic acid is stronger than acetic acid. The dissociation constants of aceticacid and some of its derivatives are given below.

Acid	Ka
Acetic acid	1.75×10^{-5}
Monochloroacetic acid	1.4×10^{-3}
Dichloroaectic acid	5×10^{-2}
Trichloroacetic acid	13×10^{-2}

Thus the order of acidic strength of these acids is trichloroacetic acid > dichloroacetic acid > mono chloroacetic acid > acetic acid.

The increase in the acidic strength of the chloroacetic acids is due to the strong electron attracting property of (- I effect) of the α - halogen atom (s). Let us consider the case of monochloro acetic acid.



The electron pair of the carbon-chlorine bond is drawn towards more electronegative chlorine whereby the carbon gets a fractional positive charge. This electron deficient carbon, in turn attracts the electron pair present between the α -carbon and the carboxyl carbon. This, ultimatelyweakens the OH bond, facilitating the release of hydrogen as proton. For this reason, monochloro acetic acid is strogner than acetic acid. As the number of chlorine atoms on the α -carbon increases, the effect increases and so the acidic strength increases. The electron withdrawing nature of the halogens in the order F > Cl>Br>I. So the acidic sgrength of the mono halo acetic acids is in the following order.

$F - CH_2 -- COOH > ClCH_2COOH > BrCH_2COOH > I- CH_2COOH,$

Fluoroacetic acid Chloroacetic acid Bromoacetic acid Iodoacetic acid

Thus fluoro acetic acid is strongest monohalo acetic acid. The trifluro acetic acid F_3C- COOH is the strongest carboxylic acid. The electron releasing alkyl groups, like methyl group, decrease the acidic strength of the acid. Hence the order of acidic strength is

$HCOOH > CH_3 COOH > (CH_3)_3 CCOOH$

Formic acid Acetic acid Trimethyl acetic acid

α - Chlorobutyric acid is as strong as chloroacetic acid. The inductive effect decreases with distance. As the distance between the chlorine atom (exerting-I effect) and the carboxylic group increases the acidic strength decreases. Following is the order of acidic strength of isomeric α, β and γ chlorobutyric acids.

$Cl.CH_2.CH_2.CH_2.COOH < CH_3\text{-}CH(Cl)\text{-}CH_2.COOH < CH_3CH_2CH(Cl)COOH$

γ -Chlorobutyric acid β -Chloro butyric acid α - Chlorobutyric acid

25.5.2 Chemical Properties

25.5.2.1 Reaction with metals

Metals react with carboxylic acids liberating hydrogen.

$$2HCOOH + 2Na \longrightarrow \underset{\text{Sodium formate}}{2HCOONa} + H_2$$

$$2CH_3COOH + Zn \longrightarrow \underset{\text{Zinc acetate}}{(CH_3COO)_2Zn} + H_2$$

25.5.2.2 Reaction with bases

Carboxylic acids react with bases to form salts.

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

$$\underset{\text{Sodium acetate}}{CH_3COONa} + H_2O$$

Check your progress - 1

How do you distinguish phenol from a carboxylic acid?

Carboxylic acids react with bicarbonate solution liberating carbondioxide, whereas phenols, being weaker acids, cannot liberate CO_2 from bicarbonate solution. This serves as a test to distinguish a carboxylic acid from a phenol.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa} + CO_2 + H_2O$$

25.5.2.3 Replacement of the OH group by a halogen

When an acid reacts with phosphorus pentahalide (PX_5), phosphorus trihalide (PX_3) or thionyl halide (SOX_2) ,the hydroxyl of the carboxyl group is replaced by a halogen. In all these reactions hydrogen is liberated.

$$R - COOH + PX_5 \longrightarrow \underset{\text{An acid halide}}{R - CO - X} + POX_3 + HX$$

$$R - COOH + SOX_2 \longrightarrow R - CO - X + SO_2 + HX$$

$$C_6H_5COOH + SOCl_2 \longrightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + SO_2 + HCl$$

$$CH_3COOH + SOCl_2 \longrightarrow \underset{\text{An acid halide}}{CH_3 - \overset{\overset{O}{\|}}{C}Cl} + SO_2 + HCl$$

O
||
R -- C -- is known as an acyl group and CH_3- CO as acetyl group.

25.5.2.4 Ester formation

A carboxylic acid reacts with an alcohol in the presence of conc. H_2SO_4 or dry HCl to form an ester. This reaction is known as esterification. Esterification using dry HCl is called Fischer - Speier method of esterification (see appendix-2)

$$R\text{ -- }COOH + HO\text{ - }R' \longrightarrow R\text{ - }CO\text{ - }OR' + H\,OH$$
An acid An alcohol An ester

$$C_6H_5\,COOH + C_2\,H_5\,OH \longrightarrow C_6H_5\,COOC_2\,H_5 + H_2O$$
Ethylbenzoate

$$CH_3\text{ - }COOH + C_2H_5OH \longrightarrow CH_3\,COOC_2\,H_5 + H_2O$$
Aceticacid ethanol Ethyl acetate

25.5.25 Anhydride formation

When the sodium salt of an acid reacts with the acid chloride of the same acid, an acid anhydride is obtained.

$$R\text{ -- }\overset{O}{\overset{\|}{C}}\text{ -- }ONa + Cl\text{ -- }\overset{O}{\overset{\|}{C}}\text{ -- }R \longrightarrow R\text{ -- }CO\text{ -- }O\text{ -- }COR + Na\,Cl$$
An acid anhydride

25.5.2.6 Formation of alkanes

When the sodium salt of an acid is heated with soda lime decarboxylation occurs and an alkane is formed.

$$RCOONa + Na\,OH \longrightarrow RH + Na_2CO_3$$
An alkane

$$CH_3\,COONa + Na\,OH \longrightarrow CH_4 + Na_2\,CO_3$$

$$CH_3\,CH_2\,COONa + NaOH \longrightarrow CH_3\text{ -- }CH_3 + Na_2\,CO_3$$
Sodium propionate Ethane

$$C_6\,H_5\,COONa \longrightarrow C_6\,H_6 + Na_2\,CO_3$$

25.5.2.7 Formation of amides

The ammonium salt of carboxylic acids on strong heating yield the corresponding amides.

$$R\text{ -- }COONH_4 \xrightarrow{\Delta} R\text{ -- }CONH_2 + H_2O$$
Ammonium salt of carboxylic acid An amide

$$CH_3\text{ -- }COONH_4 \xrightarrow{\Delta} CH_3\text{ -- }CONH_2 + H_2O$$
Ammonium acetate Acetamide

Amides are also obtained from carboxylic acids though the acid chlorides by treatment with ammonia.

i) $R\text{ -- }COOH + SOCl_2 \longrightarrow \underset{\text{An acid chloride}}{R\text{ -- }COCl} + SO_2 + HCl$

ii) $R\ COCl + NH_3 \longrightarrow R\ CNH_2 + HCl$

25.5.2.8 Formation of aldehydes and Ketones

Calcium salts of carboxylic acids may be used for the preparation of aldehydes and ketones. When the calcium salt of an acid is heated alone, ketones are obtained.

$$(R\ COO)_3\ Ca \xrightarrow{\Delta} R\text{ -- }CO\text{-- }R + Ca\ CO_3$$

$$\underset{\text{Calcium acetate}}{(CH_3\ COO)_2\ Ca} \xrightarrow{\Delta} CH_3\text{ -- }CO\text{-- }CH_3 + Ca\ CO_3$$
Acetone

When a mixture of the calcium salt of an acid and calcium formate is heated,m an aldehyde is obtained.

$$(R\ COO)_2\ Ca + (HCOO)_2Ca \longrightarrow 2\ RCHO + 2\ Ca\ CO_3$$

$$\underset{\text{Calcium acetate}}{(CH_3\ COO)_2\ Ca} + \underset{\text{Calcium formate}}{(HCOO)_2Ca} \longrightarrow 2\ CH_3CHO + 2\ Ca\ CO_3$$

25.5.2.9 Hunsdiecker reaction

When the silver salt of a carboxylic acid reacts with chlorine or bromine in carbon tetrachloride an alkyl halide is obtained. This reaction is called Hunsdiecker reaction.

$$R\ COO\ Ag + Br_2 \xrightarrow{CCl_4} R\text{ -- }Br\text{ -- }CO_2 + Ag\ Br$$

25.5.2.10 Schmidt Reaction

Carboxylic acids react with hydrazoic acid (Hydrazoic acid is prepared by treatment of sodium azide, NaN_3 with conc. H_2SO_4) to give a primary amine. This reaction is known as Schmidt reaction.

$$\underset{\text{Hydrazoic acid}}{RCOOH + HN_3} \longrightarrow R\ NH_2 + N_2 + CO_2$$

25.5.2.11 Halogenation

Monocarboxylic acids can be halogenated. In the bromination reaction the halogen enters the α – position. In the case of chlorination substitution may occur at β -position also.

$$CH_3\ COOH \xrightarrow{Cl_2} \underset{\text{Monochloro acetic acid}}{Cl\ CH_2\ COOH} \xrightarrow{Cl_2} \underset{\text{Dichloro acetic acid}}{CH\ Cl_2\ COOH} \xrightarrow{Cl_2} \underset{\text{Trichloro acetic acid}}{CCl_3\ COOH}$$

$$CH_3CH_2COOH \xrightarrow{Cl_2} CH_3 - \underset{\underset{Cl}{|}}{CHCOOH} + ClCH_2 - CH_2 - COOH$$

α – Chloro propionic acid

β - Chloro propionic acid

The α - bromination of acids is best carried out in the presence of phosphorus. This reaction is called Hell- Volhard Zelinskly reaction.

$$R - CH_2 - COOH \xrightarrow{Br_2 + P} R - \underset{\underset{Br}{|}}{CHCOOH}$$

An α - bromo carboxylic acid

Probably phosphorus tribromide, formed in the reaction , converts the carboxylic acid into acid halide. The acid halide, being more reactive than the acid, undergoes α - halogenation. The resulting α - haloacid bromide upon hydrolysis yields the α - haloacid.

$$R - CH_2 - COOH \xrightarrow{Br_2} R - CH_2 - COBr \longrightarrow R - \underset{\underset{Br}{|}}{CHCOBr} \longrightarrow R - \underset{\underset{Br}{|}}{CHCOOH}$$

Carboxylic acid — Acidbromide — α - Bromoacid bromide — α - Bromo acid

25.5.2.12 Reformatsky reaction

Aldehydes and ketones react with the zinc and an α - bromo ester. The product obtained is hydrolysed, to yield a β - bydroxy acid. This reaction is known as Reformatsky recaction.

$$R - \underset{\underset{R}{|}}{C} = O + Br.CH_2 - COOEt \xrightarrow{Zn/ether} R - \underset{\underset{OZnBr}{|}}{\overset{\overset{R}{|}}{C}} - CH_2COOEt,$$

ethyl bromo acetate

$$\xrightarrow{\overset{\oplus}{H_3O}} R - \underset{\underset{OH}{|}}{CH_2} - COOH$$

β - hydroxy acid

25.5.2.13 Arndt- Eistert synthesis

This is a method for the conversion of a carboxylic acid, R. COOH, into its higher homologue, RCH_2COOH. The acid is first convered into the acid chloride The acid chloride is then reacted with diazomethane. The diazomethyl ketone thus obtained is treated with moist silver oxide to give the higher carboxylic acid.

$$R - COOH + SOCl_2 \longrightarrow R - COCl + SO_2 + HCl$$

An acid chloride

$$R - COCl + 2CH_2N_2 \longrightarrow R - CO - CHN_2 + CH_3Cl + N_2$$

Diazomethane — A diazomethyl ketone

$$R\text{--}CO\text{--}CHN_2 + H_2O \xrightarrow{\text{moist } Ag_2O} RCH_2COOH + N_2$$

25.5.2.14 Reduction of acids

Carboxylic acids cannot be reduced with the usual reducing agents like H_2/cat, Na/alcohol, Lithium aluminium hydride, a powerful reducing agent, converts the carboxylic acids into primary alcohols.

$$RCOOH \xrightarrow{LiAlH_4} RCH_2OH$$

The overall reaction is written as

$$4R\text{-}COOH + 3\,LiAlH_4 \longrightarrow (RCH_2O)_4AlLi + 4H_2 + 2\,LiAlO_2$$
$$\downarrow 4H_2O$$
$$4\,RCH_2OH$$

Before the introduction of $LiAlH_4$ as a reducing agent, the only course available for the conversion of a carboxylic acid into the corresponding alcohol was preparation of an ester followed by its reduction by sodium and alcohol.

$$\underset{\text{An acid}}{R\text{--}COOH} \longrightarrow \underset{\text{An ester}}{R\text{-}COOR'} \longrightarrow \underset{\text{A primary alcohol}}{RCH_2OH} + R'OH$$

This reduction in known as Bouveult - Blanc reduction

25.5.2.15 Oxidation of acids

With the exception of formic acid the saturated carboxylic acids are inert to oxidation by common oxidising agents such as potassium dichromate and permanganate. However, fatty acids are oxidised by hydrogen peroxide in the presence of ferric salts (Fenton's reagent) to give acids of two fewer carbon atoms,

$$R\text{-}CH_2\text{--}CH_2COOH \xrightarrow{H_2O_2 + Fe^{+++}} RCOOH + 2CO_2 + 2H_2O$$

The biochemical degradation of fatty acids, important as a source of heat and energy in the body, in our diet, also takes place by two carbon-atom cleavages. Formic acid is easily oxidised. It reduces Fehling's reagent and Tollens' reagent. In this reaction formic acid behaves as an aldehyde.

25.6 SOME INDIVIDUAL MEMBERS

25.6.1 Formic acid

It is produced commercially by the reaction of carbon monoxide with sodium hydroxide followed by acidification.

$$CO + NaOH \longrightarrow \underset{\text{Sodium formate}}{HCOONa} \xrightarrow{\overset{\oplus}{H_3O}} HCOOH$$

Formic acid (H- COOH), unlike the rest of carboxylic acids, may be regarded as a hydroxylated aldehyde. Upon heating formic acid decomposes in two ways.

$$H\text{-}COOH \xrightarrow{\Delta} \begin{cases} \longrightarrow H_2O + CO \\ \longrightarrow H_2 + CO_2 \end{cases}$$

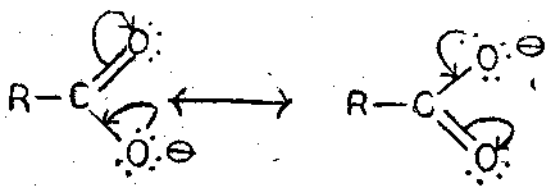
Metals catalyse the decomposition of HCOOH to produce H_2 and CO_2. Action of dehydrating agents leads to the formation of water and cabon monoxide.

Appendix - 1: The carboxylic acid ionises to give carboxylate anion and proton.

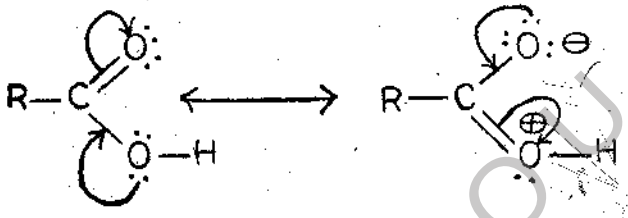
$$R\text{--}CO\text{--}OH \rightleftharpoons R\text{--}CO\text{--}O^{\ominus} + H^{\oplus}$$

Carboxylate anion

The anion is stablished by resonance. The carboxylate anion is a resonance hybrid of the following two structures.



The two structures are equivalent. The resonance in the case of carboxylic acid molecule, involving the two non-equivalent resonance structures, is less important.



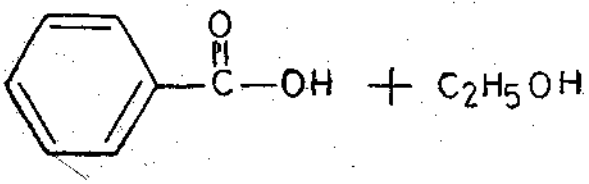
In other words, resonance stabilises the carboxylate anion more than carboxylic acid.

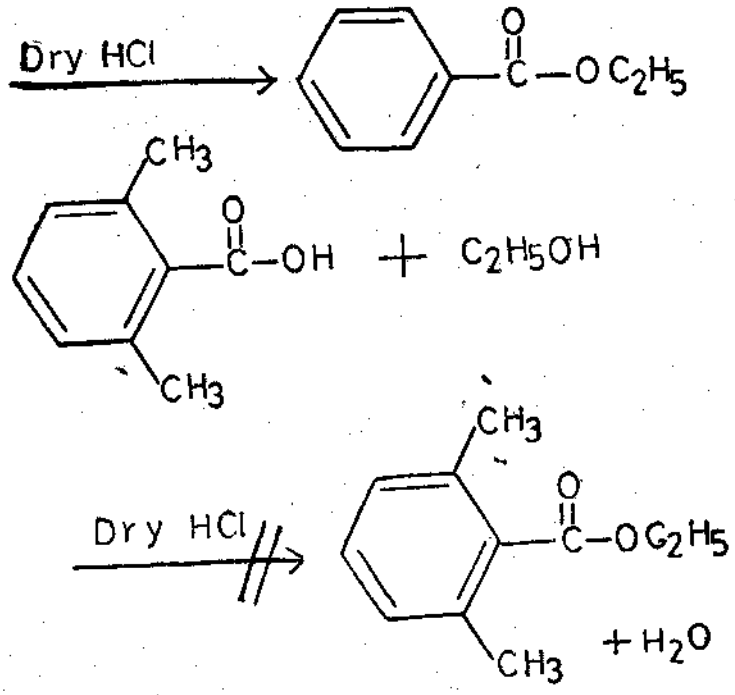
Electron withdrawing groups such as halogens disperse the negative charge of the anion and thereby stabilise the carboxylate anion. Hence acidity increases. On the other hand an electron releasing such as methyl group increases the negative charges in the anion leading to its destabilisation. Consequently the acidic strength of the carboxylic acid decreases. Acetic acid is therefore a weaker acid than formic acid.

Check your progress - 2

Write the reasonance structures of acetate ion.

Appendix - 2 : Benzoic acid reacts with ethanol in the presence of dry HCl, to give ethyl benzoate, whereas 2,6 - disubstituted benzoic acid does not form the ester.





2, 6 Dimethyl benzoid acid

During the terification of 2,6 - dimethyl benzoic acid. The attack by ethanol on the carboxyl carbon is prevented b the two adjacent methyl groups. This is another instance of steric hindrance in organic reactions.

25.7 SUMMARY

In this unit you have learnt the preparation of monocarboxylic acids from alcohols by oxidation, nitriles by hydrolysis, grignard reagents by carbonation, amides, esters and acid carbides by hydrolysis. Besides oxidation of alkylbenzenes also give aromatic carboxylic acids.

The carboxylic acids have high boiling points due to its dimeric nature. They are also soluble in water and show acidity. Alkyl groups decrease the acidity while halogens increases the acidity.

Carboxylic acids react with metals, bases to form salts. The hydroxyl of the carboxyl group is replaced by a halogen when treated with P X_5, PX_3 or $SOCl_2$. Esters are obtained on treatment with alcohols in presence of catalyst. Other derivatives of carboxylic acids such as acid chlorides, anhydrides and amides are also prepared besides their convertion to alkanes, ketones, alkylhalides, amines and alcohols.

25.8 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines

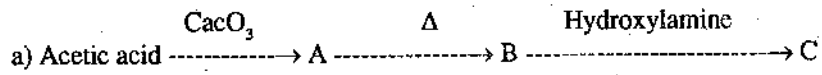
1. Why is fluoroacetic acid stronger than acetic acid?
2. How are the following conversions effected?
   a) Benzene to benzoic acid
   b) Toulene to phenyl acetic acid
3. Suggest two methods for converting n-propyl alcohol to butyric acid
4. Write notes on the following.
   i) Hunsdiecker reaction

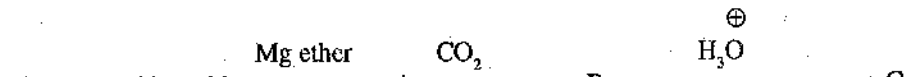
ii) Schmidt reaction

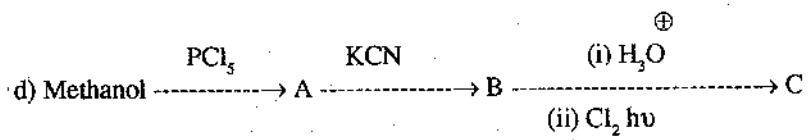
5. Explain the following reactions
   i) Reformatsky reaction
   ii) Arndt - Eistert synthesis

II. Answer he followig in 30 lines

1. Write the structures of A, B and C in the following reaction.







2. Suggest a chemical test to distinguish the compounds in each of the following pairs:
   a) Acetic acid and formic acid
   b) Ethyl acetate and acetic acid
   c) Acetyl bromide and bromoacetic acid
   d) Salicylic acid and benzoic acid

3. Arrange the following carboxylic acids in ascending order of their acidic strength and justify, by giving reasons.
   i) Dichloroacetic acid, monochloroacetic acid, acetic acid, trichloroacetic acid.
   ii) Bromoacetic acid, chloroacetic acid, iodoacetic acid,
   iii) β- chlorobutyric acid, α- chlorobutyric acid, γ- chlorobutyric acid.
   iv) Acetic acid, formic acid, propanoic acid, trimethyl acid.

4. Two compounds (A) and (B) have the same molecular formula $C_4H_8O_2$ (A) liberates carbon dioxide with aqueous bicarbonate solution. (A) is converted by Arndt - Eistert reaction to 3- methyl butanoic acid. (B) is a sweet smelling liquid and upon hydrolysis gave ethanol and acetic acid. What are the structures of (A) and (B) ? Formulate the chemical changes mentioned above.

5. Starting from benzoic acid, how are the following compounds obtained?

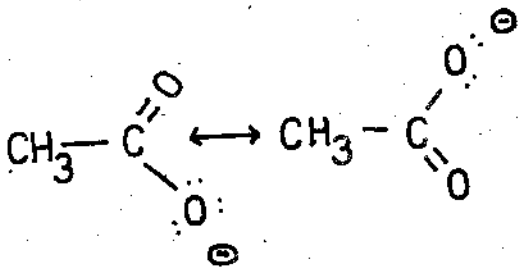
   a) Sodium benzoate
   b) Benzoyl chloride
   c) Benzene
   d) Ethyl benzoate
   e) m- Nitrobenzoic acid
   f) Benzamide

6. 0.74 g. of a monocarboxylic acid required 100 ml of m/10 KCH solution for complete neutralisation. What is the molecular weight of the acid?

25.9 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Carboxylic acids react with bicarbonate liberating carbondioxide, whereas, phenols, being weaker acids cannot liberate carbondioxide from bicarbonate solution. This serves as a test to distinguish a phenol from a carboxylic acid.

2. The resonance structures of acetate ion are



Author : Y.S.N. Murthy

UNIT - 26 ARYLSULPHONIC ACIDS

Contents

26.1 AIMS AND OBJECTIVES

This unit mainly aims to familiarise you with the structure, nomenclature and reactions of arylsulphonic acids.

By the end of this unit you should be able to understand.

- Nomenclature of aryl sulphonic acids
- Preparation " "
- Properties " "
- Reactions " "

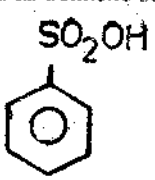
26.2 INTRODUCTION

In the structure of aryl sulphonic acids, a sulphonic acid group SO_2OH is present. The general formula of this group of compounds is $ArSO_2OH$.

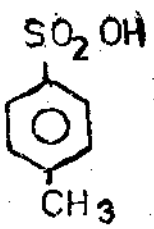
26.3 NOMENCLATURE

The suffix for this class of compounds is - sulphonic acid. The name is derived by adding the suffix sulphonic acid to the name of the compound from which the sulphonic acid is derived.

$C_6H_5SO_2OH$ may be assumed to be obtained by replacement of a hydrogen from benzene. Therefore it is named as benzene sulphonic acid.



Benzene sulphonic acid



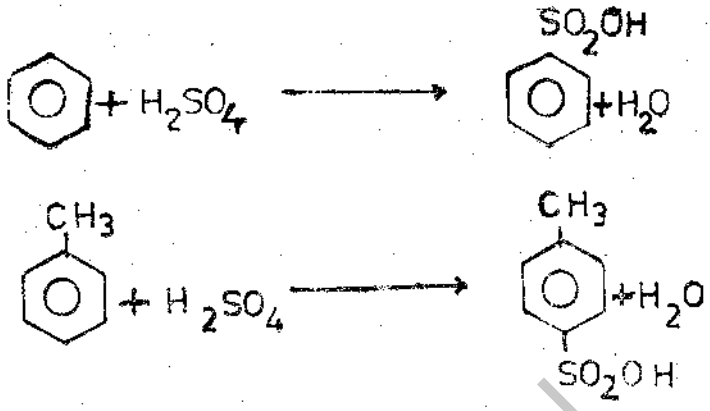
p- toluene sulphonic acid

Check your progress - 1

Write the structures of benzyl sylphonylchloride and p-toluene sulphonic acid.

26.4 PREPARATION

Aryl sulphonic acids are prepared by sulphonation of arenes with conc. sulphuric acid or chlorosulphonic acid of fuming sulphuric acid (Oleum). Benzene on sulphonation gives benzene sulphonic acid.



26.5 PROPERTIES

Sulphonic acids are highly polar substances. These are highly soluble in water but insoluble in nonpolar solvents.

26.6 REACTIONS

26.6.1 Reactions with aalkalis

Aryl sculphonic acids are strong acids and therefore form salts with bases.

$$ArSO_3H + NaOH \longrightarrow \overset{\ominus\ \oplus}{ArSO_2ONa} + H_2O$$

Sodium salt of aryl sulphonic acid

26.6.2 Desulphonation

Sulhonation is a reversible reaction. On strong heating with acids desulphonation occurs.

$$Ar.\ SO_3H \xrightarrow[\Delta]{\overset{\oplus}{H_3O}} Ar -- H_2\ SO_4$$

Check your progress - 2

What happens when p- toulene sulphonic acid is heated with acid?

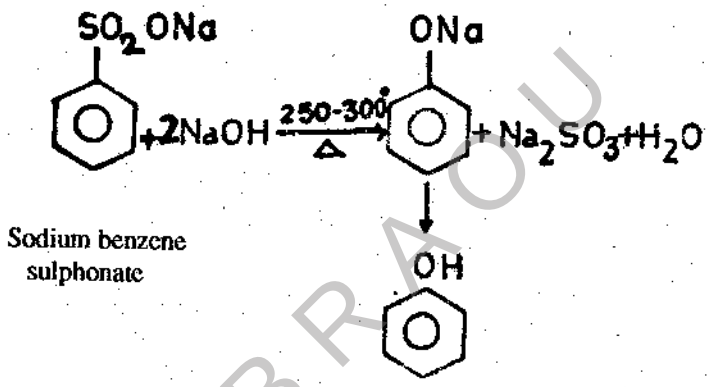
26.6.3 Preparation of Phenols

SO_3H group in arylsulphonic acid may be replaced by OH-group to give corresponding phenols. Fusion of sodium salt of aryl sulphonic acids with NaOH at 250-300° followed by acidification gives phenols.

$$\underset{\Delta}{ArSO_2ONa + 2NaOH} \xrightarrow{250 - 300^\circ} \underset{\downarrow}{Ar\,ONa} + Na_2SO_3 + H_2O$$

ArOH
phenol

Phenol is obtained by fusion of sodium salt of benzene sulphonic acid with alkali.



Sodium benzene sulphonate

Phenol

26.6.4 Preparation of Cyanides

Fusion of sodium or potassium salts of aryl sulphonic acids with sodium or potassium cyanide gives aryl nitrile.

$$ArSONa + NaCN \xrightarrow{250^\circ} Ar\,CN + Na_2SO_3$$

Benzonitrile is obtained from benzene sulphonic acid

$$C_6H_5SO_2OH \longrightarrow C_6H_5SO_2ONa \xrightarrow{NaCN} C_6H_5CN + Na_2SO_3$$

Sodium benzene sulphonate Benzonitrile

26.6.5 Formation of Acid halides

Aryl sulphonyl chlorides are obtained by the action of PCl_5 on sodium salts of aryl sulphonic acids.

$$ArSO_2ONa + PCl_5 \longrightarrow ArSO_2Cl + NaCl + POCl_3$$

Sodium salt of benzene sulphonic acid on treatment with PCl_5 yields benzene sulphonyl chloride.

$$C_6H_5SO_2Na + PCl_5 \longrightarrow C_6H_5SO_2Cl + NaCl + POCl_3$$

Benzene
Sulphonyl chloride

Arylsulphonyl chlorides react with a variety of amines to form arylsulphonides, useful as drugs.

26.7 SUMMARY

This unit deals with the preparation of aryl sulphonic acids from arenes with conc. sulphuric acid or chlorosulphonic acids and their reactions with alkalies to give salts. Their desulphonation to arenes, conversion to phenols, acid halides is also discussed.

26.8 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines

1. Write the equations for the reactions of p-toluene sulphonic acid with the following reagents. Write the names of the products in each case ?

a) Fusion with NaOH followed by acidifiaction
b) Boiled with dil. sulphuric acid
c) Fusion with NaCN

II. Answer the following in 30 lines

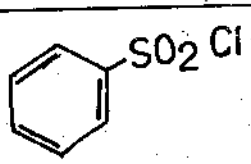
1. How is benzene sulphonic acid prepared? Explain the preparation of the following compounds from it?

a) Benzene b) Phenol c) Benzoic acid
d) Benzene sulphonyl chloride.

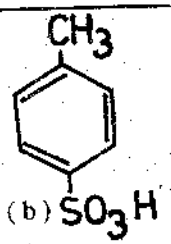
2. Compound A (C_7H_8) on sulphonation with conc. H_2SO_4 yields B and C ($C_7H_8SO_4$). B on fusion with sodium hydroxide followed by treatment with dil. HCL gave cresol. C on fusion with NaCN furnished D (C_8H_7N). Identify the compounds A to D, and explain the reactions involved.

26.9 MODEL ANSWERS TO CHECK YOUR PROGRESS

1.

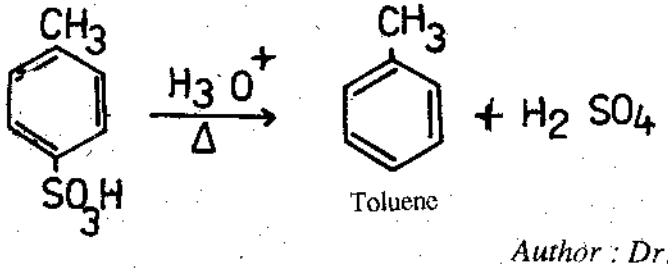


(a)



(b)

2. On strong heating with acids desulfonation occurs.



Toluene

Author : Dr. T. Sundararamaiah

UNIT - 27 CARBOXYLIC ACID DERIVATIVES

Contents

27.1 AIMS AND OBJECTIVE

In this unit we familiaise you with the nomenclature, structure, and reactions of carboxylic acid derivatives, viz. acid halides (acylhalides) and anhydrides and acid amides.

By the end of this unit you should be able to know

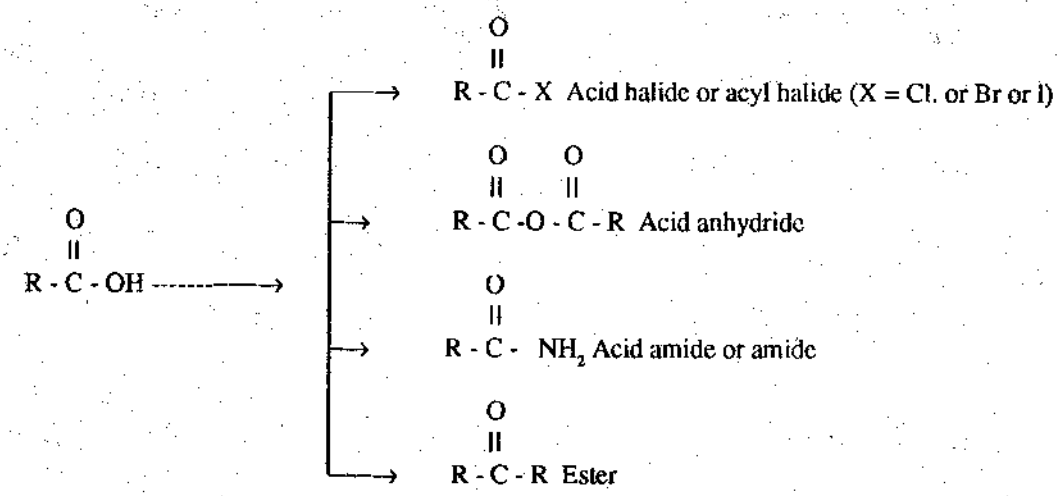
- Acyl halides
  - i) Nomenclature
  - ii) Preparation
  - iii) Physical properties
  - iv) Reactions
- Acid anhydrides
  - i) Nomenclature
  - ii) Preparation
  - iii) Physical properties
  - iv) Chemical reactions
- Amides
  - i) Nomenclature
  - ii) Classification
  - iii) Preparation
  - iv) Physical properties and reactions

27.2 INTRODUCTION

The carboxylic acid derivatives are:

A. Acid halides or a acyl halides
B. Acid anhydrides
C. Amides or acid amides

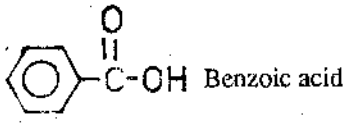
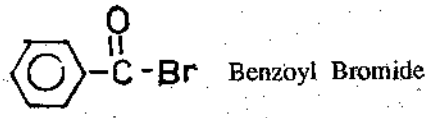
These are derived from carboxylic acid $R-\overset{\overset{O}{\|}}{C}-OH$ by replacement of of - OH group by halogen (X), can Carboxylate ($-\overset{\overset{O}{\|}}{C}-R$),amino ($-NH_2$) and alkoxy ($-OR''$) gruops respectively. $R-\overset{\overset{O}{\|}}{C}$ group is called an acyl group.



R may be an alkyl or an aryl group.

27.3 ACID HALIDES OR ACYL HALIDES

Nomenclature: These compounds are named as halides by changing the ic or oic in the name of the carboxylic acid to - yl or - oyl

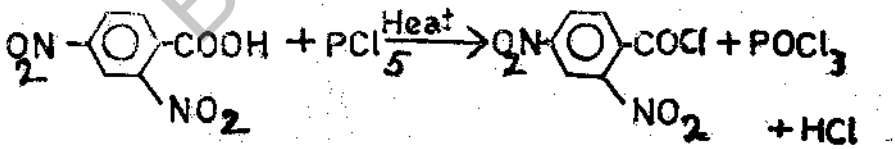
Structure and name of the acid	Structure and name of acyl halide or acid halides
O ‖ H -- C -- OH methanoic acid or Formic acid	O ‖ H -- C -- X Methanoyl halide or Formyl halide O (Unstable)
O ‖ CH_3 -- C -- OH Ethanoic acid oAcetic acid	O ‖ CH_3 -- C -- Cl Ethanoyl chloride or O Acetyl chloride
 Benzoic acid	 Benzoyl Bromide

27.3.1 Preparation of acyl halides

Carbonyl acids are converted into corresponding acid halides by treatment withphosphorus trihalides (PX_3) penta halides (PX_5) or with thionyl halides (SOX_2)

$$R\text{--}\overset{O}{\overset{\|}{C}}\text{--OH} + PCl_5 \xrightarrow{\text{Heat}} R\text{-}\overset{O}{\overset{\|}{C}}\text{--Cl} + POCl_3 + HCl\uparrow$$

$$CH_3\text{--}\overset{O}{\overset{\|}{C}}\text{--OH} + PCl_5 \xrightarrow{\text{Heat}} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{--Cl} + POCl_3 + HCl\uparrow$$



2,4 -- Dinitro benzoic acid

2,4 - Dinitro benzyoyl chloride

$$R\text{--}\overset{O}{\overset{\|}{C}}\text{--OH} + SOCl_2 \xrightarrow{\text{Reflux}} R\text{-}\overset{O}{\overset{\|}{C}}\text{--Cl} + SO_2\uparrow + HCl\uparrow$$

$$C_6H_5\text{--}\overset{O}{\overset{\|}{C}}\text{--OH} + SOCl_2 \xrightarrow{\text{Reflux}} C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-Cl} + SO_2\uparrow + HCl\uparrow$$

Bemzoic acid

Benzoyl chloride

Of these reagents, thionyl chloride is more convenient. In this reaction the byproducts, SO_2, and HCl are gases. Thererore they can be easily separated from the resulting acyl halide. Further any excess of thionyl chloride (B.P. 78 °) eassiy removed by distillation.

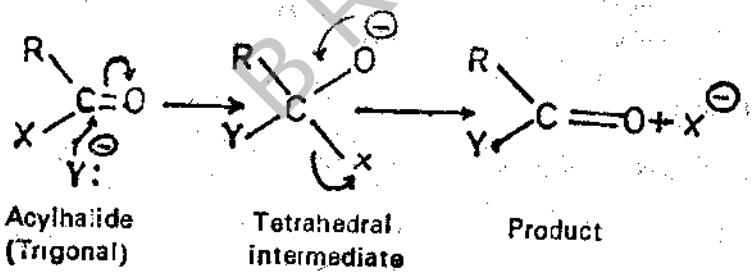
27.3.2 Physical properties

The presence of -- C = O group makes acid halides polar. Due to the absence of inter molecular hydrogen bonding, acid halides are nonassociated substances and possess much lower boiling points than the corresponding carboxylic acids. The lower membes are colourless volatile liquids and the higher members are colourless solids. Acid halides are lachrymators.

Acylchloride	B.P °C	Carboxylic Acid	B.P °C
CH_3 COCl Acetyl chloride	51	CH_3 COOH Acetic acid	118
CH_3CH_2COCl Propionyl chloride	80	CH_3CH_2COCl Propionyic acid	141
CH_3 CH_2 CH_2 COCl Butyryl chloride	100	CH_3 CH_5 CH_2 COC Butyric chloride	163
C_6H_3 COCl Benzoyl chloride	197	C_6H_3 COOH Benzoic acid	250°BP

27.3.3. Reactions of acid halides

Acyl halides undergo nuclcophilic substitution reactions. Due to the presence of carbonyl group, acyl halides undergo nucleophilic substitution reactions more readily than the alkyl halides. Acid halides are the most reactive of the derivatives of crboxylic acids. Thus amides, anhydrides, esters etc. are readily obtainbale from acid halides. In thicse reactions, the halogen is replaced by other nuclcophiles. In these reactions the nuclcophile ($Y^{\ominus}$) attacks the carbonyl carbon of acyl halide, and the resulting tetrhedral intermediate climinates the halide ion ($X^{\ominus}$) to give the product.



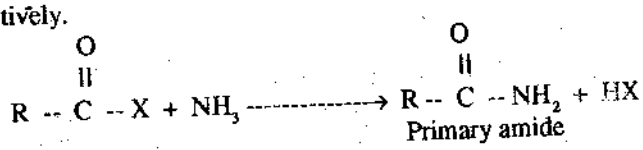
27.3.3.1 HYdrolysis

Acid halides fume in moist air and are readily hydrolysed to give carboxylic acids.

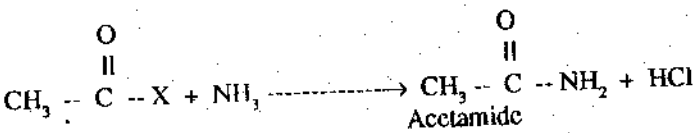
$$R\text{--}\overset{O}{\overset{\|}{C}}\text{--}X + H_2O \longrightarrow R\text{--}\overset{O}{\overset{\|}{C}}\text{--}OH + HX$$

27.3.3.2 Formation of amides

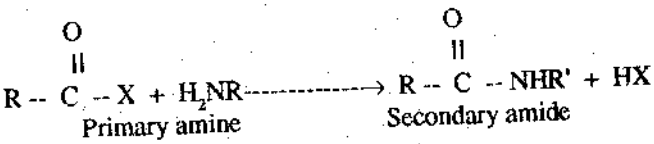
By ammonolysis, acid halides are converted into amides. Reaction of acid halides with ammonia, primary and secondary amines leads to the formation of primary, secondary and tertiary amides respectively.



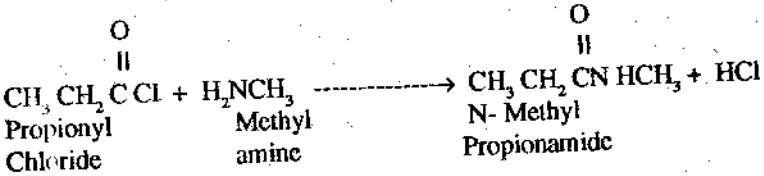
Primary amide



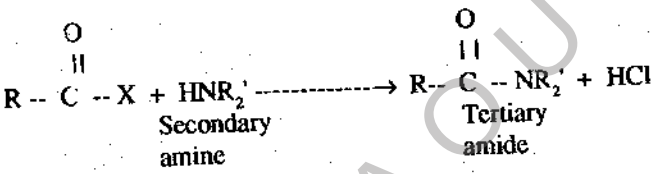
Acetamide



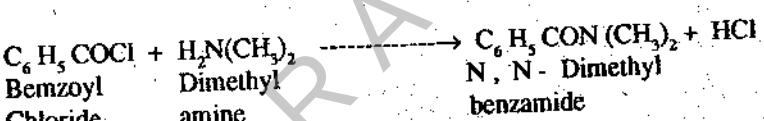
Primary amine — Secondary amide



Propionyl Chloride — Methyl amine — N- Methyl Propionamide



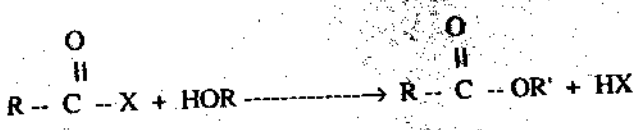
Secondary amine — Tertiary amide

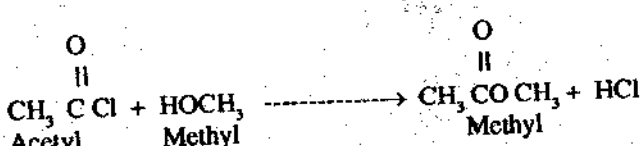


Bemzoyl Chloride — Dimethyl amine — N , N - Dimethyl benzamide

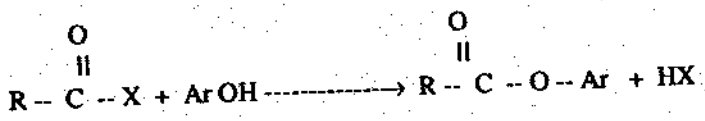
27.3.3.3 Ester formation

Acid halides react with alcohols or phenols to give esters.





Acetyl Chloride — Methyl alcohol — Methyl acetate



$$CH_3COCl + C_6H_5OH \longrightarrow CH_3COC_6H_5 + HCl$$

Phenol — Phenyl acetate

When an alkali or base is used to accept the liberated acid (HX) the reaction is known as Schotton - Baumann reaction.

27.3.3.4 Anhydride formation

Acid halides react with sodium salt of carboxylic acid to give anhydrides.

$$R-CO-X + NaO-CO-R \longrightarrow R-CO-O-CO-R + NaX$$

$$CH_3COCl + NaOCH_3 \longrightarrow CH_3COOCCH_3 + NaCl$$

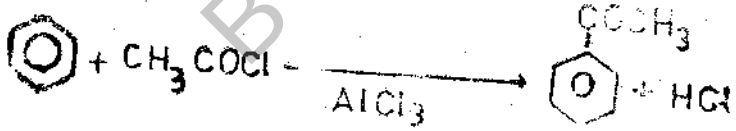
Sodium acetate — Acetic anhydride

27.3.3.5 Formation of Ketones

27.3.3.5.1 Friedel - Crafts acylation

Fridel - Crafts reaction is a method of introducing an acyl group on the carbon of benzene ring. For C- acylation generally an acid chloride is used.

$$Ar-H + RCOCl \xrightarrow{\text{anhydrous } AlCl_3} Ar-CO-R + HCl$$



Acetophenone

Aliphatic ketones can not be prepared by this method.

27.3.3.52 Reaction with cadmium

Reaction of cadmium dialkyls with acid halides leads to the formation of ketones. Both aliphatic and aromatic ketones can be prepared by this method.

$$R_2Cd + 2R\,COCl \longrightarrow 2\,RCOR + CdCl_2$$

$$(CH_3)_2Cd + 2CH_3COCl \longrightarrow 2CH_3COCH_3 + CdCl_2$$

Cadmium dimethyl

$$(CH_3)_2Cd + 2C_6H_5COCl \longrightarrow 2C_6H_5COCH_3 + CdCl_2$$

The alkyl cadmium is obtained by the reaction of cadmium bromide with apropriate Grignard reagent.

$$2RMg\,Br + Cd\,Br_2 \longrightarrow R_2Cd + 2\,Mg\,Br_2$$

27.3.3.6 Formation of aldehydes : Rosenmund Reduction

Both aliphatic and aromatic acid chlorides are reduced by hydrogen in presence of Pd - $BaSO_4$ to give aldehydes.

$$RCOCl + H_2 \xrightarrow{Pd\text{-}Ba\,SO_4} RCHO + HCl \quad (R = \text{alkyl or aryl group})$$

$$C_6H_5COCl + H_2 \xrightarrow{Pd\text{-}Ba\,SO_4} C_6H_5CHO + HCl$$

Benzoyl chloride — Benzaldehyde

27.3.3.7 Arndt - Eistert reaction

Arndt - Eistert reaction is a valuable method for the preparation of higher homologue from a caroxylic acid. In this reaction the acid is first converted into corresponding acid halide. The key intermediate in this reaction is diazomethyl ketone which is obtained by the reaction of acid chloride with diazomethane.

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2\uparrow + HCl\uparrow$$

$$RCOCl + CH_2N_2 \longrightarrow R\text{-}\underset{\displaystyle CHN_2}{\overset{\displaystyle O}{\overset{\|}{C}}}\text{-}$$

Diazomethyl ketone

$$R\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}CHN_2 \xrightarrow{moist\ Ag_2O} RCH_2COOH + N_2\uparrow$$

Thus benzoic and can be converted into phenyl acetic acid in the following manner.

$$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2\uparrow + HCl\uparrow$$

$$C_6H_5COCl + CH_2N_2 \longrightarrow C_6H_5COCHN_2$$

$$C_6H_5COCl + CH_2N_2 \xrightarrow{moist\ Ag_2O} C_6H_5CH_2COOH + N_2\uparrow$$

27.3.3.8 Degradation of acid chlorides

Degradation of acids is carried out by Schmidt and Hunsdiecker reaction. The degradation of acid chloride may also be carried out. This is known as Curtius reaction.

$$RCOCl + NaN_3 \xrightarrow{H_2O} RNH_2 + CO_2\uparrow + N_2\uparrow + NaCl$$

Curtuis Reaction

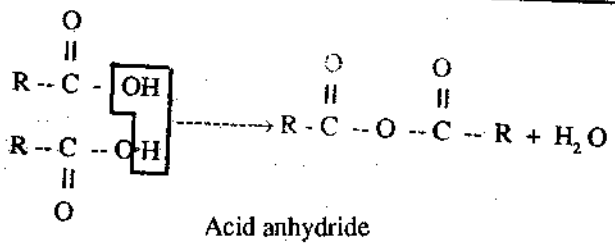
$$CH_3COCl + NaN_3 \xrightarrow{H_2O} CH_3NH_2 + CO_2\uparrow + N_2\uparrow + NaCl$$

$$RCOCl + Ag_2O + Cl_2 \xrightarrow{\Delta} RCl + CO_2\uparrow + NAgCl$$

Hunsdicker reaction

$$C_6H_5COCl + Ag_2O + Cl_2 \xrightarrow{\Delta} C_6H_5Cl + CO_2 + 2AgCl$$

27.4 ACID ANHYDRIDES



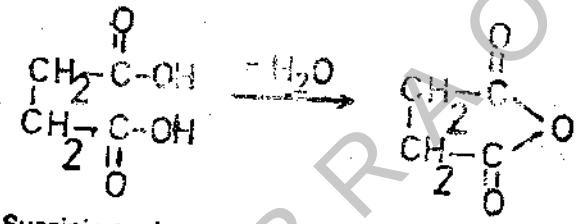
Acid anhydride

Nomenclature: The acid anhydrides can be theorotically looked upon as compounds derived by the elimination of molecule of water from two molecules of a mono carboxylic acid. When both the acyl groups are same, the anhydride is called a simple or symmetrical anhydride. When the acyl groups are different, the anhydride is called a mixed anhydride.

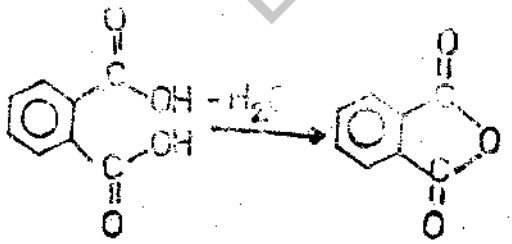
Acetic anhydride $CH_3 - C(=O) - O - C(=O) - CH_3$ is a simple anhydride

Acetic propionic anhydride $CH_3 - C(=O) - O - C(=O) - C_2H_5$ is a mixed anhydride

Cyclic anhydrides are obtained by elimination of a water molecule from a molecule of a dicarboxylic acid.



Succinic acid — Succinic anhydride



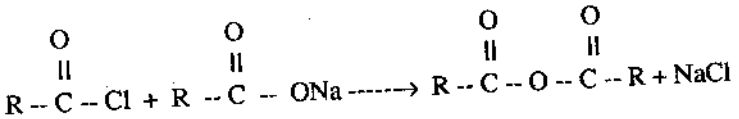
Phthalic acid — Phthalic anhydride

The names of acid anhydrides are obtained by adding the word anhydride to the name of the acid from which it is derived.

27.4.1 Prepartion of acid anhydrides

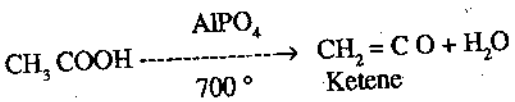
The most common monocarboxylic acid anhydride is acetic anhydride. The acid anhydrides are prepared by the reaction of acyl halides with anhydrous sodium salt of carboxyllic acids. Thus acetyl

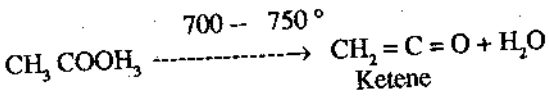
chloride reacts with sodium acetate to give acetic anhydride.

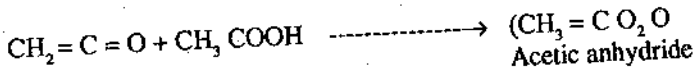


$$CH_3COCl + CH_3COONa \text{ --------- } (CH_3CO)_2O + NaCl$$

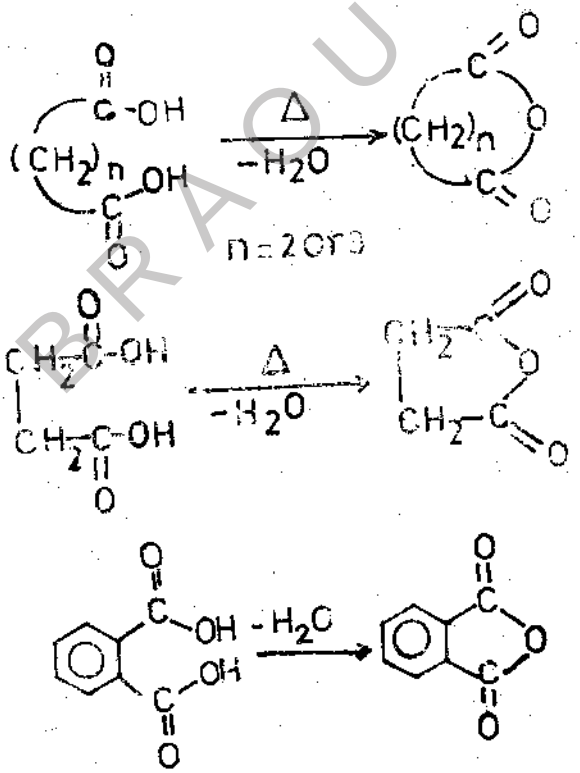
Acetic anhydride is prepared by the action of ketene on acetic acid. Ketene itself is obtained by the dehydration of acetic acid at high temperature in presence of $AlPO_4$ or by the pyrolysis of acetone.



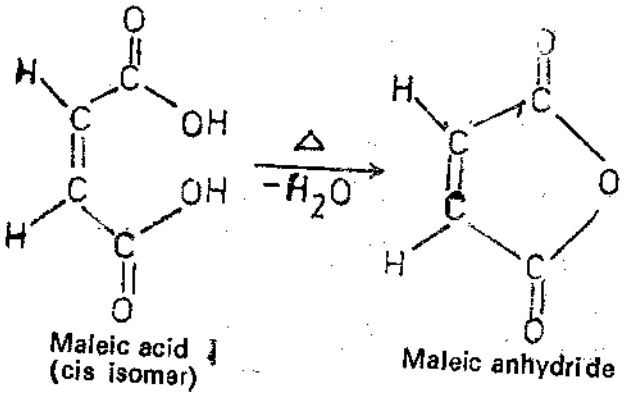


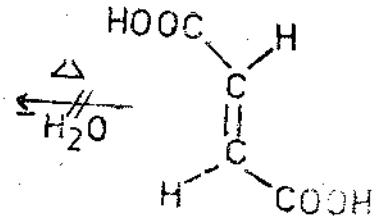


Cyclic anhydrides are prepared by simply heating dibasic acids.



Maleic acid is a cis-dicarboxylic acid. This on heating readily cyclises to maleic anhydride. The geometric isomer of maleic acid, fumaric acid under identical conditions does not cyclise.





27.4.2 Physical Properties

Due to the absence of inter molecular hydrogen bonding anhydrides do not exist as associated molecules. Hence the boiling points and melting points of acid anhydrides are lower than the corresponding acids.

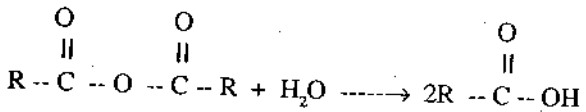
Compound	Mol. Wt.	°C
Acetic acid	60	118 (B.P.)
Acetic anhydride	102	140 (B.P.)
Succinic Acid	118	185 (M.P.)
Succinic Anhydride	100	120 (M.P.)

21.4.3 Chemical Reactions

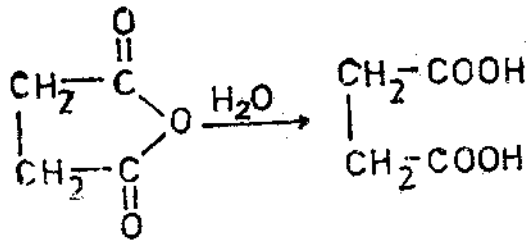
Acid anhydrides resemble acid chlorides in many reactions, but are some what less reactive. Both acid anhydrides and acid chlorides are useful as acylating agents. Acid anhydrides are more stable than acid chlorides. In acylation reactions acid chlorides evolve a molecule of HCl. Acid anhydrides on the other hand expel a molecule of carboxylic acid.

27.4.3.1 Hydrolysis

An acid anhydride is readily hydrolysed. However, cyclic anhydrides undergo addition reaction, to give the corresponding dicarboxylic acid.



$$CH_3COOCOCH_3 + H_2O \longrightarrow 2CH_3COOH$$



Succinic anhydride Succinic acid

27.4.3.2 Reaction with amines

Reaction of an acid anhydride with ammonia or primary and a secondary amines yields primary, secondary and tertiary amides respectively.

$$CH_3CO-O-COCH_3 + 2NH_3 \longrightarrow CH_3CONH_2 + CH_3COONH_4$$

Acetamide
(Primary amide)

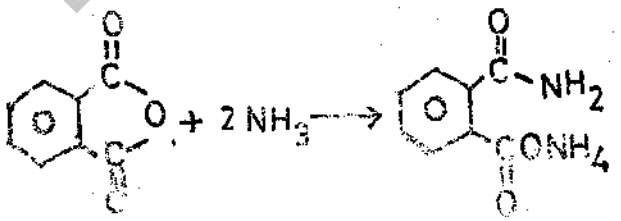
$$CH_3CO-O-COCH_3 + CH_3NH_2 \longrightarrow CH_3CONHCH_3 + CH_3COONH_4$$

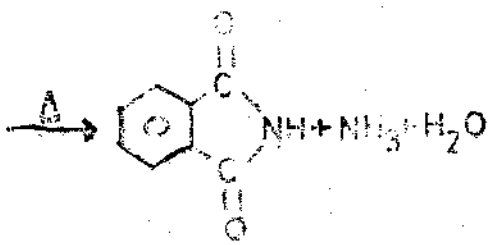
N - Methyl acetamide
(Secondary amide)

$$CH_3CO-O-COCH_3 + (CH_3)_2NH \longrightarrow CH_3CON(CH_3)_2 + CH_3COOH$$

N, N - Dimethyl acetamide
(Tertiary amide)

When phthalic anhydric is heated with ammonia, phthalimide is obtained as the end product.

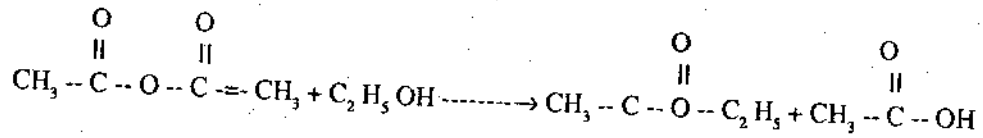




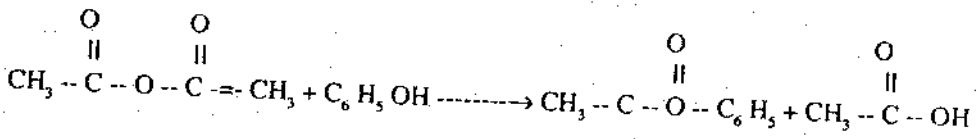
Phathalimide

27.4.3.3 Reaction with alcohols and phenols

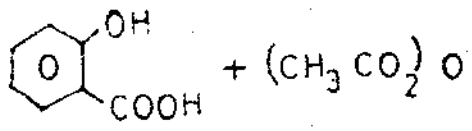
Reaction of acid anhydrides with alcohols and phenols yileds esters.

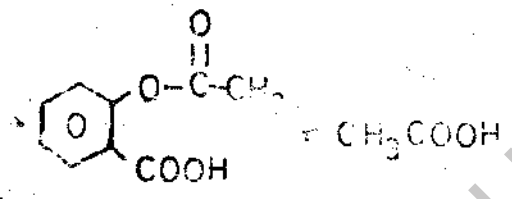


Ethyl acetate

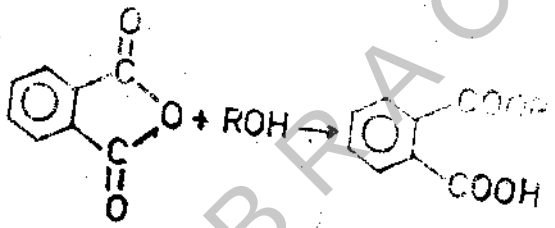


Phenyl acetate



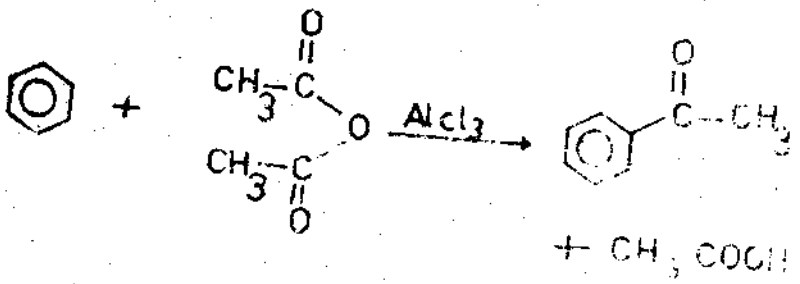


Acetylsalicylic acid
(Asprin)

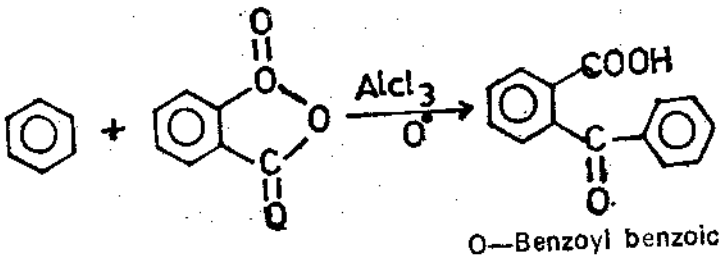


27.4.3.4 Friedel - Crafts reaction

C - Acylation of aromatic compounds is also brought about by reaction with acid anhydride in the presence of $AlCl_3$. Thus, benzene reacts with acetic anhydride in the presence of anhydrous aluminium chloride to give aceptophenone.



Reaction of benzene with phthalic anhydride, on the other hand, yields o-benzoyl benzoic acid.



O—Benzoyl benzoic acid

27.5 AMIDES

Acid amides are obtained by replacement of the hydroxyl group of carboxy lie acids by an amino group. The amide linkage is present in proteins. The carboxylic acids are generally identified by preparing their amide derivatives.

27.5.1 Nomenclature

The names of amides are derived by replacing the suffix - ie of the parent acid by amide. Whereas in the IUPAC system the suffix - oic acid of the parent acid is replaced by amide.

Formula	Nameof the acid	Formula	Nameof the amide
HCOOH	Methanoic acid or Formic acid	$HCONH_2$	Methanamide or Formamide
CH_3COOH	Ethanoic acid or Acetic acid	CH_3CONH_2	Ethanamide or Acetamide
CH_3CH_2COOH	Propanoic acid or Propionic acid	$CH_3CH_2CONH_2$	Propanamide or Propionamide
C_6H_5COOH	Benzoic acid	$C_6H_5CONH_2$	Benzamide
		$C_6H_5C(=O)-NHCH_3$	N-Mecthyl benzamide
		$CH_3CON(CH_3)_2$	N, N- Dimethyl acetamide

Check your progress - 1

Write for structural formula for the following:
a) Benzamide b) Acetamide c) Acetanilige

27.5.2 Classification of amides

Amides are classified into:

i) **Primary amides (unsubstituted amides:** $RCONH_2$ In these, the amide nitrogen carries two hydrogens. Acetamide CH_3CONH_2, Benzamide $C_6H_5CONH_2$ are examples of primary amides.

ii) **Secondary amides:** (N-Substituted amides) RCONHR. In these, the amide nitrogen carries only one hydrogen. N-Methyl benzamide ($C_6H_5C)NHCH_3$) is a secondary amide.

iii) **Tertiary amides:** (N, N - Disubstituted amides): $RCONR_2$ In these, the amide nitrogen is fully substituted and consequently does not carry any hydrogens. N,N - Dimethylacetamide ($CH_3CON(CH_3)_2$ is a tertiary amide.

27.5.3 Prepartion of amides

1. Amides are prepared by acylation of ammonia or amines. For acylation, acylhalide, acid anhydride or esters may be used.

$$CH_3COCl + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + HCl$$

$$(CH_3CO)O + C_6H_5\text{-}NH_2 \longrightarrow \underset{\text{N - Phenylacetamide or Acetanilide}}{CH_3CONH\text{-}C_6H_5} + CH_3COOH$$

$$\underset{\text{Ester}}{RCOOR'} + \underset{\text{a secondary amine}}{HNR_2} \xrightarrow{\Delta} \underset{\text{a tertiary amide}}{RCONR_2} + R'OH$$

2. When a carboxylic acid reacts with ammonia, ammonium salt of the carboxylic acid is obtained. This on strong heating gives amide.

$$CH_3COOH + NH_3 \longrightarrow \underset{\text{Ammonium acetate}}{CH_3COONH_4} \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2}$$

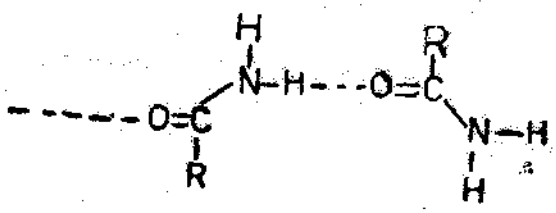
3. Partial hydrolysis of nitriles with dilute acids gives amides.

$$RCN \xrightarrow[HOH]{\overset{\oplus}{H_3O}} R\text{-}\underset{OH}{\underset{|}{C}}=NH \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2$$

(R = alkyl or aryl)

27.5.4 Properties

Physical: Amides have high B.P/M.P. This is due to their polar nature and partly due to their ability to form strong intermolecular hydrogen bonds.



The following table gives the boiling/melting points for some carboxylic acids and of the corresponding acid halides and amides.

Carboxylic acid	Acyl halide	Amide
Acetic acid BP. 118°	Acetyl chloride BP. 51°	Acetamide BP. 221° MP. 82°
Propionic acid BP. 141°	Propionyl chloride BP. 80°	Propionamide MP. 79° BP. 213°
Benzoic acid MP. 121°	Benzoyl chloride BP. 197°	Benzamide MP. 130°

Check your progress - 2

Acetyl Chloride and acetamide are derivatives of acetic acid, which one of them has higher B.P and why?

27.5.5 Reactions

27.5.5.1 Hydrolysis

On hydrolysis acid amides are converted in to corresponding carboxylic acids. The hydrolysis may be catalysed by acids or alkali. In the acid hydrolysis of an amide, a mixture of carboxylic acid and ammonium salt is obtained.

$$RCONH_2 + H_2O \xrightarrow{\overset{\oplus}{H}} RCOOH + \overset{\oplus}{NH_4}$$

In the alkaline hydrolysis of an amide, ammonia is evolved and the carboxylic acid is present as carboxylate anion. From the solution the crboxylic acid is present as carboxylate anion. From the solution the carboxylic acid is generated by acidification with a mineral acid.

$$RCONH_2 \xrightarrow{\overset{\ominus}{OH}} \overset{\ominus}{RCOO} + NH_3$$

$$\overset{\ominus}{RCOO} \xrightarrow{\overset{\oplus}{H_3O}} RCOOH$$

The evolution of ammonia, on heating of an organic compound with alkali, may be taken as a positive test for the presence test for the presence of a primary amide function. In the hydrolysis of secondary and tertiary amides, in addition to the carboxylic acid, primary and secondary amines respectively are obtained.

27.5.5.2 Conversion to amines

Primary amides react with bromine in the presence of aqueous alkali to give primary amines containing one carbon atom less than the amide. This is known as Hofmann bromamide degradation of amides.

$$RCONH_2 \xrightarrow[2\overline{O}H]{O\overline{B}r} RNH_2 + CO_3^{--} + \overline{B}r + H_2O$$

$$C_6H_5CONH_2 \xrightarrow[2\underline{O}H]{OBr} \underset{\text{Anilline}}{C_6H_5NH_2}$$

Following is the mechanism of Hofmann bromamide reaction.

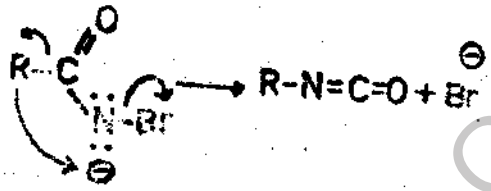
1) N- Bromination of the amide by the hypobromite ion

$$RCONH_2 + \overset{\ominus}{O}Br \longrightarrow RCONHBr + \overset{\ominus}{O}H$$

ii) In N -bromamide the hydrogen present on the nitrogen atom is acidic. This hydrogen is abstracted by a hydroxide ion to give the anion of N-bromamide.

$$RCONH_2Br + \overset{\ominus}{O}H \longrightarrow RCONBr + H_2O$$

iii) Loss of a bromide ion from the anion of N-bromamide with simultaneous rearrangement of alkyl or aryl group gives an isocyanate.



An isocynate

iv) Hydrolysis of the socyanate gives a carbamic acid. The carbamic acids are unstable and therefore instantaneously lose CO_2 to form the amine.

$$RN=C=O \xrightarrow{H_2O} \underset{\text{Carbamic acid}}{(RNHCOH)} \xrightarrow{-CO_2} RNH_2$$

27.5.5.3 Conversion to nitriles

Primary amides undergo dehydration to give cyanides or nitriles. Benzene sulphonyl chloride, thionyl chloride or phosphorus pentoxide are used as dehydrating agents.

$$RCONH_2 \xrightarrow{D.A} RC \equiv N + H_2O \quad (D.A = \text{Dehydrating agent})$$

$$CH_3CONH_2 \longrightarrow \underset{\text{Methyl cyanide or Aceto nitrile}}{CH_3CN} + H_2O$$

27.6 SUMMARY

The derivatives of carboxylic acids, viz., acid halides, acid anhydrides and amides, their preparation and reactions are discussed in this unit. Acid halides are used as reagents in Friedel - Crafts acylation. The ketones, aldehydes, amines are obtained from them by treatment with alkyl cadmium, hydrogen and hydrozoic acid respectively. Acid anhydrides are also used as reagents in Friedel - Crafts acylation. Amides are converted to acids by hydrolysis to amines on treatment with bromine in alkali and nitrites on dehydration.

27.7 MODEL EXAMINTION QUESTIONS

I. Answer the following in 10 lines

1. Formulate the preparation of the following from acetic acid. Give reagents and conditions in each case.

   (a) Acetyl chloride (b) Acetamide (c) Actetic anhydride
   (d) Methyl amine

2. Outline the synthesis of the following from appropriate starting materials.
   (a) Benzoyl chloride (b) Benzamide (c) Benzanilide
   (d) Benzophenone

3. What are the products formed in the reaction of propionyl chloride with the following?
   (a) Water (b) Isopropyl alcohol (c) Methylamine
   (d) Sodium propionate 9c) Toluene + $AlCl_3$
   Write equations.

4. Write equation for the reaction of benzamide with
   (a) dil.NaOH or dil. HCl(b) Br_2 + NaOH at 5° (c) P_2O_5 heat.
   Write the names of products.

5. Write equations, naming the products formed, for the reaction of acetic anhydride with
   (a) Aniline (b) Phenol (c) Benzene + $AlCl_3$
   (d) Amyl alcohol

II. Answer the following in 30 lines

1. (a) Formulate the method of preparation of succinic anhydride starting from acetic acid.

   (b) Write equations for its reaction with
   (i) H_2O (ii) NH_3
   (iii) Benzene in the presence of anhydrous $AlCl_3$ (iv) Alcohol

2. (a) Outline the various methods for the synthesis of acetylchloride and acetic anhydride from acetic acid.

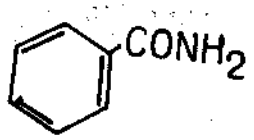
   (b) Give equations for their reaction with
   (i) Isopropyl alcohol (ii) Methylamine (iii) Aniline
   (iv) Toluene and $AlCl_3$

3. A p disubstituted benzene derivative A ($C_8H_9O_2N$) gave B ($C_8H_8O_3$) when boiled with oil. HCl. B. give C ($C_8H_7O_2OCl$) on treatment with PCl_5. C gave D ($C_8H_8O_2$) on reduction with molecular hydrogen in presence of Od-$BaSO_4$. D on oxidation gave B is also obtained by the oxidation of p-tolyl methyl ether. A on treatment with Br_2 and NaOH at 5° C, gave

E (C_7H_9ON). C also gives A on treatment with NH_3. Write the structures of A,B,C,D and E and explain the reactions involved in the above transformations.

27.8 MODEL ANSWERS TO CHECK YOUR PROGRESS

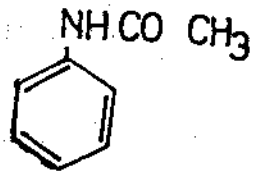
1.



(a)

CH_3CONH_2

(b)



(c)

2. The B.P of acetamide (221°C) is higher than that of acetyl chloride (51°C) although they are the derivatives of the some acid. This is due to polar nature and strong intermolecular hydrogen bonding in acetamide.

27.9 GLOSSARY

1. ***Arndt - Eistert synthesis:*** This is a method for conversion of a carboxylic acid into its next higher homologue. The acid is conveerted to its acyl chloride. The acyl chloride is converted to diazoamethyl ketone by treatment with CH_2N_2 (diamethane). Treatment of diazomethyl ketone with moist Ag_2O gives the higher carboxylic acid.

$$RCOOH \xrightarrow{SOCL_2} RCOCl \xrightarrow{CH_2N_2} V\ RCOCHN_2 \xrightarrow{Ag_2O+\ H_2O} RCH_2\ COOH$$

2. ***Friedel - Crafts reaction:*** This is an electrophilic substitution reaction. Alkylation of aromatic compounds by the action of alkyl halide in the presence of anhydrous $AlCl_3$ is known as Friedel-Crafts alkylation reaction.

$$Ar\text{ -- }H + RCl \xrightarrow{AlCl_3} Ar\text{ -- }R + HCl$$

Acyl halides or acid anhydrides in the presence of anhydrous $AlCl_3$ react with aromatic compounds to give Ketones. This is known as Friedel - Crafts acylation reaction.

$$Ar\text{ -- }H + \begin{matrix}CH_3\ COCl \\ or \\ (CH_3CO)_2O\end{matrix} \xrightarrow{AlCl_3} Ar\ COCH_3$$

3. ***Hunsdicker reaction:*** Silver salts of carboeelic acids can be degraded to alkyl halides, on treatment with halogen. Acyl chlorides also degrade to alkyl halides on treatment with halogen and Ag_2O.

$$RCOOAg + X_2 \xrightarrow{CCl_4} RX + CO_2\uparrow + AgX$$

$$RCOX + X_2 + Ag_2O \longrightarrow RX + CO_2\uparrow + 2AgX$$

4. ***Schmidt reaction:*** Reaction of carboxylic acids with hydrazoic acid to form primary ammines.

$$RCOOH + N_3H \longrightarrow RNH_2\ CO_2\uparrow + N_2\uparrow$$

5. ***Schotten-Baumann Reaction :*** Acylation of hydroxy compounds of amines with acyl halide in the presence of alkali is called schotten - baumann reacrion.

$$ArOH + C_6H_5COCl \xrightarrow[-HCl]{\overset{\ominus}{OH}} Ar\,OCOC_6H_5$$

$$Ar\,NH_2 + C_6H_5\,COCl \xrightarrow[-HCl-]{\overset{\ominus}{OH}} ArNHCOC_6H_5$$

6. ***Rosenmund reduction:*** Acyl chlorides (aliphatic and aromatic) are reduced to aldehydes by molecular hydrogen in the presence of $Pd\text{-}BaSO_4$ catasyst.

$$RCOCl + H_2 \xrightarrow{Pd\ Ba\ So_4} RCHO$$

$$ArCOCl + H_2 \xrightarrow{Pd\text{ - }Ba\ SO_4} ArCHO$$

Author : Dr. T. Sundara Ramaiah

UNIT - 28 ESTERS

Contents

28.1 AIMS AND OBJECTIVES

This unit aims to farmiliarise you with the nomenclature, structure and reactions of esters. And to outline the synthetic applications of malonic and acetoacetic esters and to introduce you the chemistry of oils and fats.

After the finishing this unit you must be able to know:

- Nomenclature
- Preparation
- Physical properties
- Reactions of esters
  - (i) Hydrolysis
  - (ii) Ammonolgis
  - (iii) Transesterification
  - (iv) Reaction with grignard reagents
  - (v) Reduction
  - (vi) Classes condensation
  - (vii) Dickmann condensation
- Malonicester
  1. Preparation
  2. Properties
     - (i) Reaction with bases
     - (ii) C - Alkylation
     - (iii) Synthesis of carboxylic acid
- Acetoacetic ester
  1. Preparation
  2. Keto-enol tautomerism
  3. Reactions
     - (i) reaction with sodium ethoxide
     - (ii) C - Alkylation
     - (iii) C- Acylation
     - (iv) Synthesis of ketones
     - (v) Synthesis of diketones
     - (vi) Synthesis of mono carboxylic acids
     - (vii) Synthesis of dicarboxylic acids
- Oils and fats
  1. Physical properties
  2. Reactions of oils and fats
     - (i) Hydrolysis
     - (ii) Rancidification
     - (iii) Paint dryers
     - (iv) Hydrogenation
  3. Analysis of oils and fats
     - (i) Saponification number
     - (ii) Acid value
     - (iii) Iodine number

28.2 INTRODUCTION

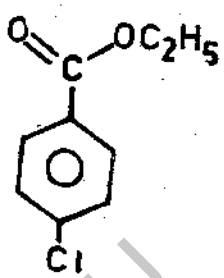
Esters are derivatives of carboxylic acids, in which the OH group of - COOH is replaced OR'. Esters are obtained by the reaction of an acid with an alcohol or a phenol.

$$RCOOH + R'OH \text{ -------- } RCOOR' + H_2O$$

28.3 NOMENCLATURE

An ester is named as derivative of the acid by changing the suffix - ic, in the name acid, to - etc. The nature of the alkyl or aryl group, in the ester, derived from the alcohol or phenol is indicated in the prefix part of the name.

$HCOOC_2H_5$ is considered to be a dederivative of formic acid and ethyl alcohol. Therefore, it is named as ethyl formate. IUPAC name of this compound is ethyl methanoate. Similarly, $CH_3COOC_2H_5$ is named as ethylacetate or ethyl ethanoate. Some othr exapmles are

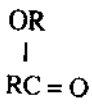


$$CH_3\,CH(Cl)\,OOC_2C_5$$

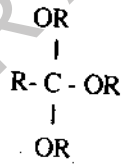
Ethyl - α chloropropionate
(Ethyl 2- chloropropionate)

Ethyl-p-chlorobenzoate

Ortho ester is a compound in which the carbonyl oxygen of an ester is replaced by two alkoxy groups.



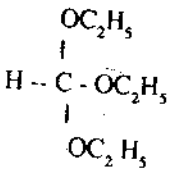
Ester



Ortho ester

$HCOOC_2H_5$

Ethyl formate



Ethyl orthoformate

Check your progress - 1

Write structures and names of any four isomeric esters with the formula $C_5H_{10}O_2$.

28.4 PREPARATION OF ESTERS

1. Esters are prepared by acylation of alcohols or phenols with organic acids, acid halides or anhydrides, reaction btween an acid and alcohol (or a phenol) to give an ester is referred to as esterification reaction.

$$RCOOH + R'OH \underset{\longleftarrow}{\xrightarrow{\text{conc. } H_2SO_4}} RCOOR' + H_2O \qquad (1)$$

$$CH_3COOH + C_2H_5OH \underset{\longleftarrow}{\xrightarrow{\text{conc. } H_2SO_4}} CH_3COOC_2H_5 + H_2O$$

Acetic Acid — Ethyl alcohol — Ethyl acetate

Esterification takes place by elimination of water molecule. The water molecule eliminated in the esterification may be obtained from --OH of the acid and H of the alcohol or vice versa.

By carrying out the esterification of carboxylic acids with alcohols containing labelled oxygen (O^{18}) it was etablished that following is the pathway of esterification or primary alcohols.

$$RCOOH + H^{18}OR \dashrightarrow R\text{--}CO\text{--}{}^{18}O\text{--}R' + H_2O$$

Water is formed from OH of carboxylic aid and H of alcohol.

In the esterification of tertiary alcohols, water is formed from the H of carboxylic acid and OH of Phenol (alcohol).

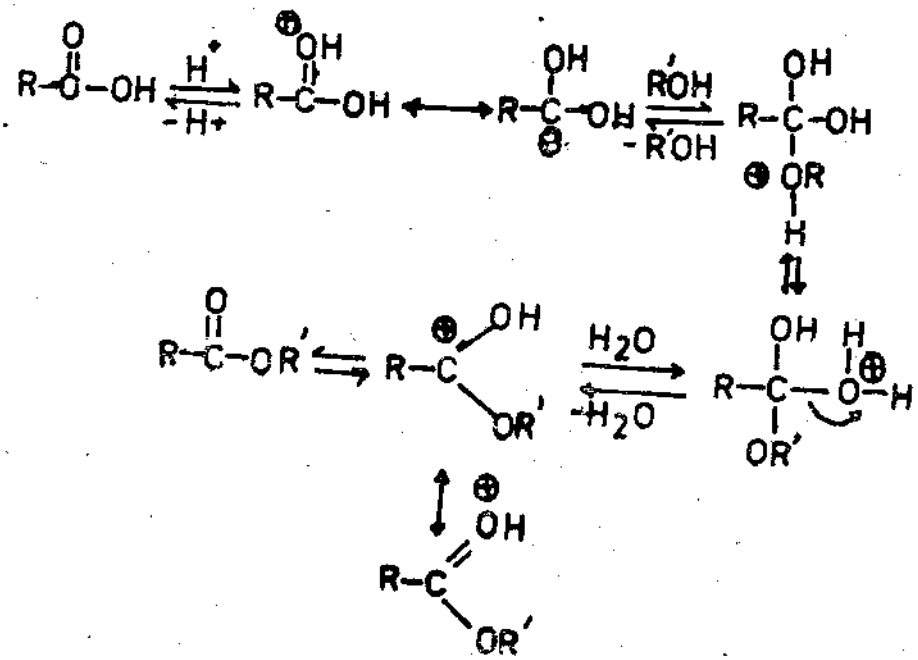
$$RCOOH + H^{18}OR' \dashrightarrow RCOOR' + H_2O^{18}$$

Secondary alcohols may react by their pathway.

With a given acid the rate of esterification of alcohols is primary > secondary > tertiary; and for a given alcohol the reaction rate of esterification by acids is

$$RCH_2COOH > R_2CHCOOH > R_3CCOOH$$

Following is the generally accepted mechanism of acid catalysed esterification:



Acid catalysed esterification is a reversible process. Exactly the reverse steps in the above mechanism therefore constitute the mechanism of acid catalysed hydrolysis of esters.

Esters may also be obtained by the acylation of alcohols or phenols with acid halides or acid anhydrides.

$$RCOX + R'OH \longrightarrow R\,COOR' + HX \qquad (2)$$

Acid halide

Example:

$$C_6H_5\text{--}COCl + C_2H_5OH \longrightarrow C_6H_5\text{---}COOC_2H_5 + HCl$$

Benzoyl chloride — Ethyl benzoate

$$(RCO)_2O + R'OH \longrightarrow RCooR' + RCOOH$$

Acid anhydride

Example:

$$(CH_3CO)_2O + C_6H_5\text{--}OH \longrightarrow CH_3C(=O)\text{--}C_6H_5 + CH_3COOH$$

Acetic anhydride — Phenyl acetate

23.5 PHYSICAL PROPERTIES

Esters are characterised by pleasant odours. They possess lower boiling points than their corresponding acids. Esters are only sparingly soluble in water. However, they dissolve in strong acids like concentrated sulphurric acid.

28.6 REACTIONS OF ESTERS

Esters undergo nucleophilic substitution reactions that are typical of carboxylic acid derivatives. These reactions include hydrolysis and ammonolysis.

28.6.1 Hydrolysis

Hydrolysis of an ester results in the formation of carboxylic acid and an alcohol.

$$RCOOR' + H_2O \xrightarrow{\oplus H \text{ or } \ominus OH} RCOOH + R'OH$$

This is catalysed by both an acid or alkali. Acid catalysed hydrolysis is a reversible reaction whereas base catalysed hydrolysis is irreversible.

$$RCOOR' + H_2O \underset{\oplus H}{\rightleftharpoons} RCOOH + R'OH$$

$$RCOOR' + H_2O \underset{\ominus OH}{\rightleftharpoons} RCOOH + R'OH \rightarrow RCOO^{\ominus}$$

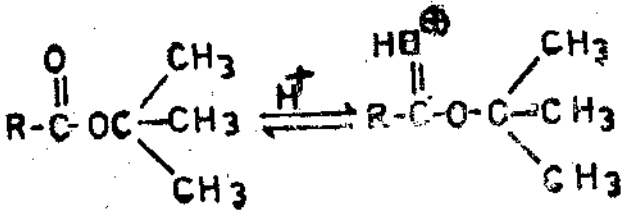
Acid catalysed ester hydrolysis may involve either acyloxy or alkyloxy fission in an ester molecule.

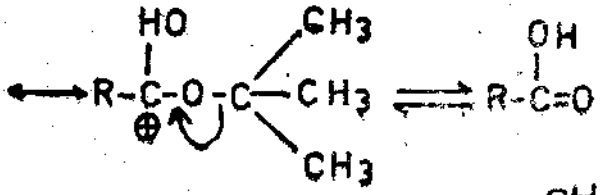
Acyloxyfision $\quad RCO^{18}OR + HOH \longrightarrow RCOOH + R''^{18}OH$

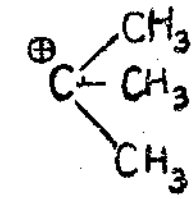
Alkyloxy fission $\quad RCO^{18}OR + HOH \longrightarrow RCO^{18}OH + R'OH$

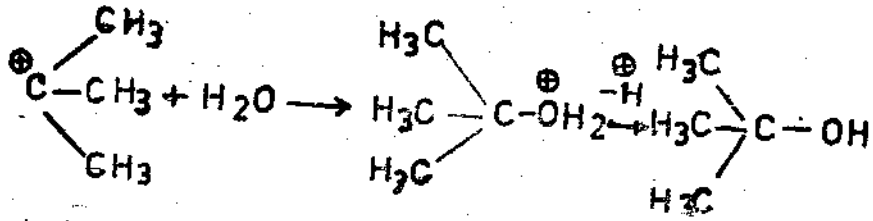
By labelling experiments it has been observed that all esters derived from primary and secondary alcohols, are hydrolysed by acyloxy cleavage of the molecule. Whereas esters of tertiary alcohols are hydrolysed by alkycoxy cleavage. The mechanism of acyloxy fission of esters catalysed by acids is given under esterfiction.

Esters of t-butyl alcohol for instance, undergo acid catalysed hydrolysis by alkyloxy fission mechanism.

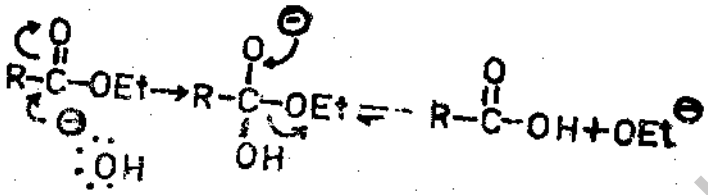








Following is the mechanism of base catlysed hydrolysis of esters, involving acyloxy fission.



28.6.2 Ammonolysis

Esters react with ammonia, primary and secondary amines and to give primary, secondary and tertiary amides respectively.

$$RCOOR' + NH_3 \longrightarrow RCONH_2 + R'OH$$

$$RCOOR' + R''NH_2 \longrightarrow RCONHR'' + R'OH$$

$$RCOOR' + (R'')_2NH \longrightarrow RCON(R'')_2 + R'OH$$

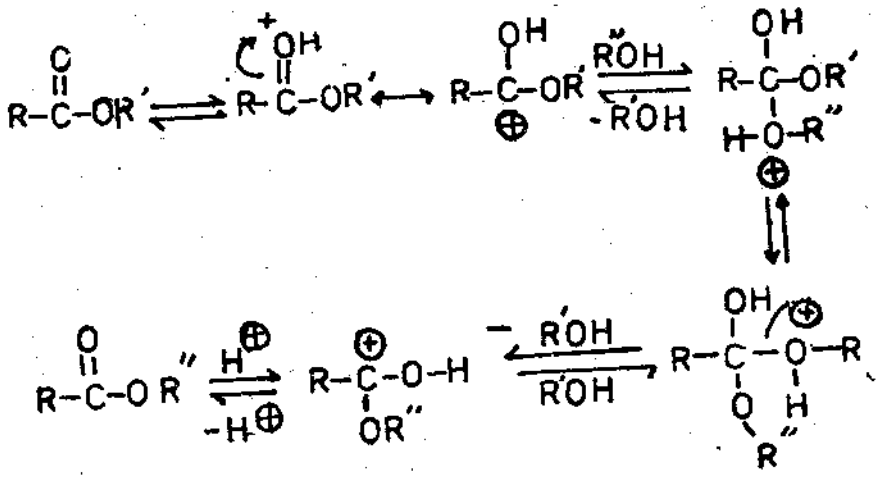
28.6.3 Trans esterification

In this process, an alcohol displace another alcohol by reaction with an ester.

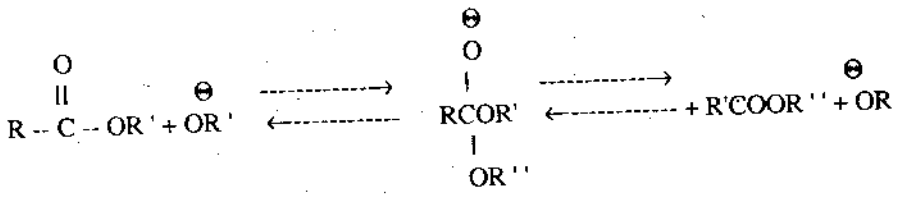
$$RCOOR' + R''OH \rightleftharpoons RCOOR'' + R'OH$$

Trns esterification may be caatlysed by both acids and basis.

Mechanism of acid catalysed trans esterification:



Mechanism of base catalysed trans esterification:



28.6.4 Reaction with Grignard reagents

In the reaction of esters with Grignard reagents the ultimate products are tertiary alcohols.

$$\underset{\text{Ester}}{R'COOR'} + RMgX \longrightarrow \underset{\text{Ketone}}{RCOR} + R'OMgX$$

$$RCOR + RMgX \longrightarrow (R)_3COMgX \xrightarrow{H_2O} \underset{\text{Tertiary alcohol}}{(R)_3COH}$$

28.6.5 Reduction

Esters msay be reduced by $LiAlH_4$ to give primary alcohols.

$$RCOOR' \xrightarrow[Na + C_2H_5OH]{LiAlH_4} RCH_2OH + R''OH$$

Formerly the reduction was carried out by using sodium and ethyl alcohol. This is known as Bouveault-Blanc reduction.

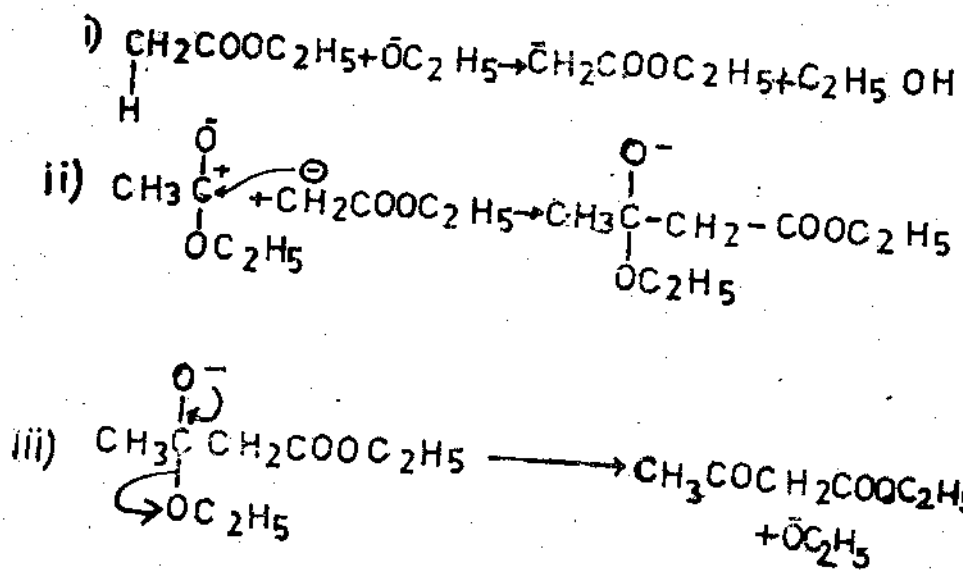
28.6.6 Claisen condensation

In the presence of a strong base like sodium methoxide, esters containing atleast one alpha hydrogen undergo this condensation reaction to furnish β- Ketoesters. For instance, two molecules of ethylacetate condense in the presence of sodium ethoxide to give ethylacetoactate or acetoacetic ester.

$$2CH_3COOC_2H_5 \xrightarrow{NaOC_2H_5} CH_3COCH_2COOC_2H_5 + C_2H_5OH$$

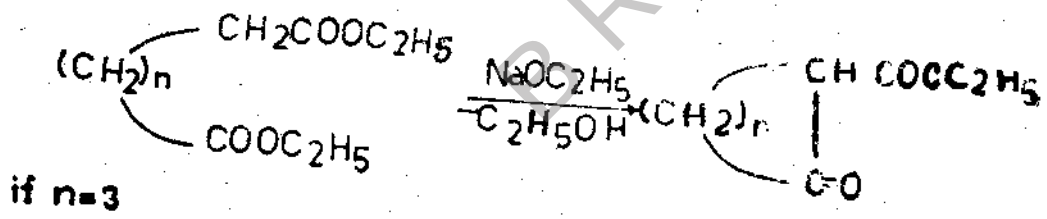
Ethylacetoacetate
(Acetoacetric ester)

Mechanism:

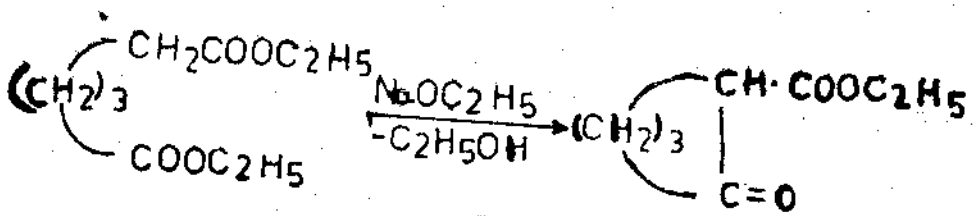


28.6.7 Dickmann condensation

This is an intramolecular Claisen condensation of esters of dicarboxylic acids giving cyclic β - ketoesters.



if n=3



28.7 MALONIC ESTER

Malonic ester or diethylmalonate is an ester of malonic acid. It is prepared starting from acetic acid, by the following procedure.

$$CH_3COOH \xrightarrow{Cl_2P} CH_2(Cl)COOOH \xrightarrow{KCN} CH_2(CN)COOH \xrightarrow{H_3O^+}$$

Chloroacetic acid — Cyano acetic acid

$$CH_2(COOH)_2 \xrightarrow[\text{Conc. } H_2SO_4]{C_2H_5OH} (CH_2(COOC_2H^5)_2$$

Malonic acid — Malonic ester

28.7.1 Properties

28.7.1.1 Reaction with strong bases

The presence of two ester carbonyl groups on methylene carbon in malonic ester makes it an active methylene group containing compound. Therefore, malonic ester on treatment with sodium ethoxide in absolute alcohol is converted into a sodium salt.

$$CH_2(COC_2H_5)_2 + C_2H_5ONa \longrightarrow \overset{\ominus}{CH}(COOC_2H_5)_2\overset{\oplus}{Na} + C_2H_5OH$$

Sodium salt of malonic ester

28.7.1.2 C- Alkylation

The sodium salt of malonic ester reacts with alkyl halides to give monoalkyl derivatives and dialkyl derivatives of malonic ester.

$$\overset{\ominus}{CH}(COOC_2H_5)_2 + RX \longrightarrow CHR(COOC_2H_5)_2\overset{\ominus}{+X}$$

Monoalkyl malonic ester

$$CHR(COOC_2H_5)_2 \xrightarrow{NaOC_2H_5} \overset{\ominus}{C}R(COOC_2H_5)_2\overset{\oplus}{Na}$$

$$\overset{\ominus}{CH}(COOC_2H_5)_2 + RX \longrightarrow CR_2(COOC_2H_5)_2\overset{\ominus}{+X}$$

Dialkylmalonic ester

28.7.1.3 Synthesis of monocarboxylic acids

Malonic ester is hydrolysed by acids to malonic acid. Malonic acid, a dicarboxylic acid, on heating undergoes decarboxylation to give acetic acid.

$$CH_2(COOC_2H_5)_2 \xrightarrow{\text{hydrolysis}} CH_2(COOH)_2 \xrightarrow{140^\circ} CH_3COOH + CO_2$$

Similarly mono and dialkyl derivatives of malonic ester can be hydrolysed and decarboxylated to give higher monocarboxylic acids.

$$RCH(COOC_2H_5)_2 \xrightarrow{\text{hydrolysis}} RCH(COOH)_2 \xrightarrow{140^\circ} RCH_2COOH$$

Monoalkyl malonic ester

$$R_2C(COOC_2H_5)_2 \xrightarrow{\text{hydrolysis}} R_2C(COOH)_2 \xrightarrow{140} R_2CHCOOH$$

Dialkyl malonic ester

Isobutyric acid, for instance, can be obtained from malonic ester by conversion into dimethyl malonic ester and then hydrolysis followed by decarboxylation.

$$CH_2(COOC_2H_5)_2 \longrightarrow (CH_3)_2C(COOC_2H_5)_2 \xrightarrow{\text{hydrolysis}} R_2CHCOOH$$

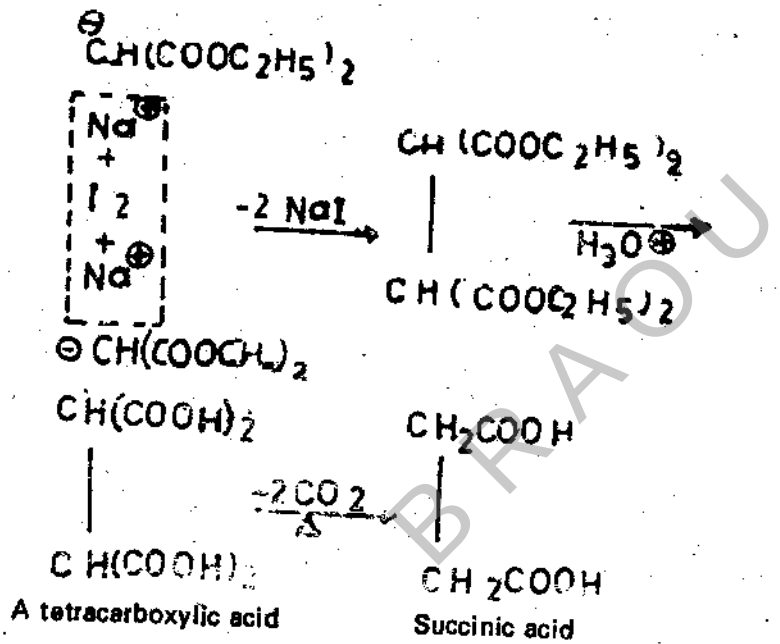
Diethyl malonate — Dimethylmalonic ester

$$(CH_3)_2C(COOH)_2 \xrightarrow{140^\circ} (CH_3)_2CHCOOH$$

Isobutyric acid

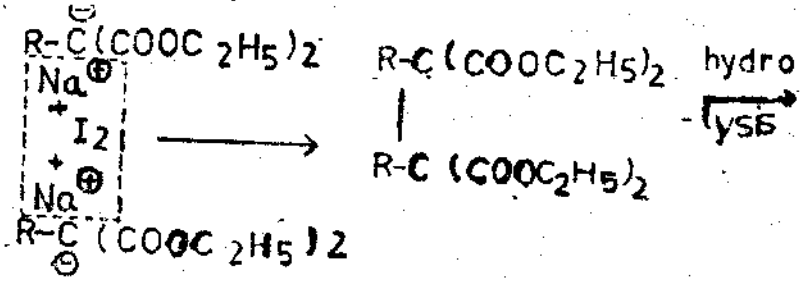
28.7.1.4 Synthesis of dicarboxylic acids

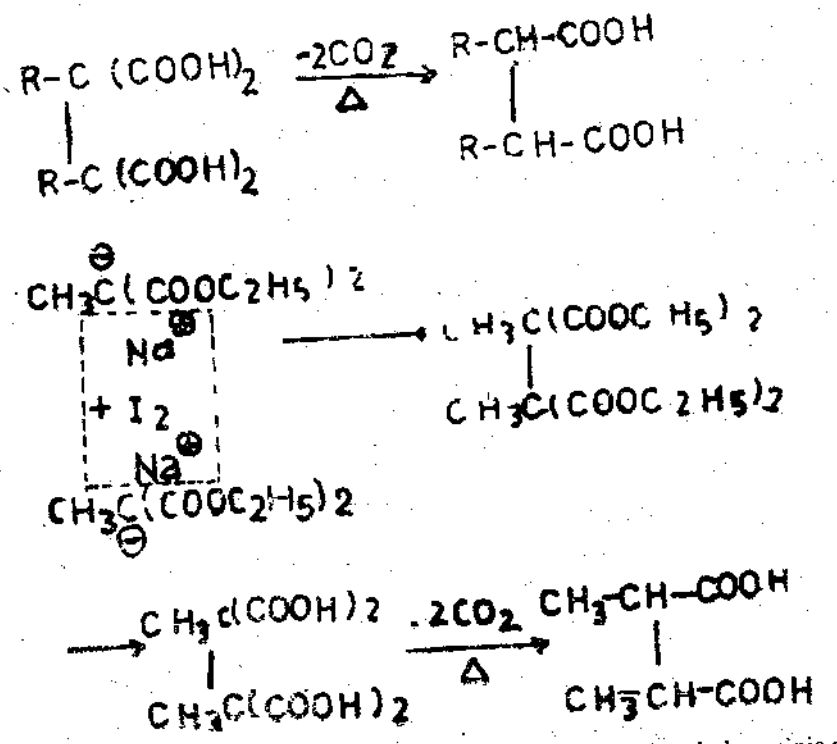
Treatment of sodium salt of malonic ester with iodine, followed by acid hydrolysis gives a tetra carboxylic acid. Decarboxylation of the tetracarboxylic acid gives succinic acid.



A tetracarboxylic acid — Succinic acid

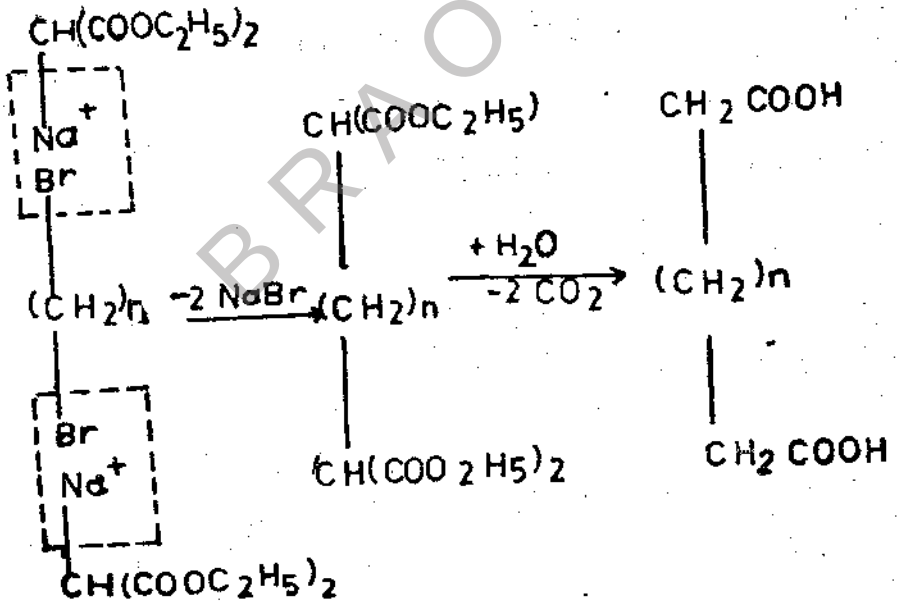
Similar reactons of sodio derivatives of monoalkyl malonic ester give higher dicarboxylic acids. α, β, –Dimethyl succinic acid is obtained from sodium salt of monomethyl malonic ester.



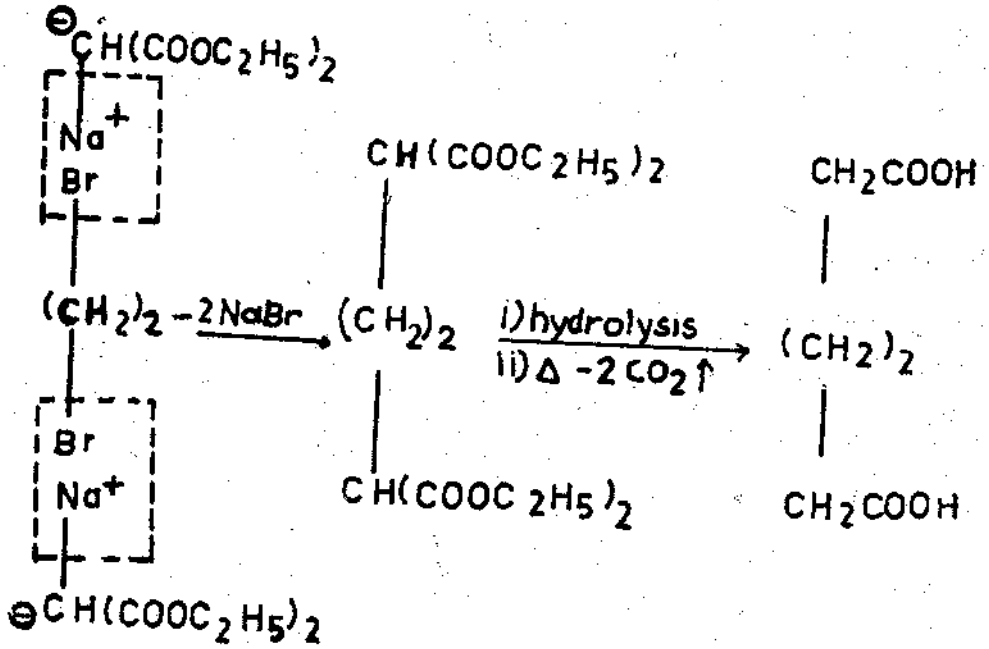


α, β, - Dimethyl succinic acid

Dicarboxylic acids are also obtained by the reaction of sodiomalonic ester with polymethylene halide, followed by hydrolysis and decarboxylation.



Adipic acid is obtained starting from sodium salt of malonic ester and ethylene bromide.



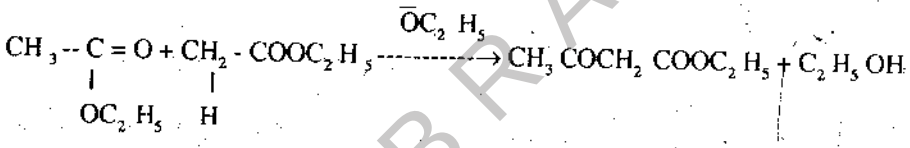
Adipic acid

28.8 ACETOACETIC ESTER

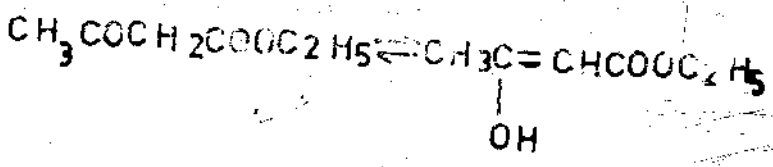
Acetoacetic ester or ethyl acetoacetate is a β -ketoester.

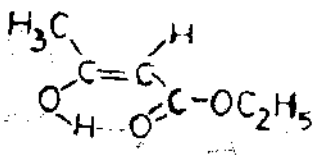
28.8.1 Preparation

It is prepared by claisen condensation of ethyl acetate.



28.8.2 Keto - Enol Tautomerism





Intramolecular H - bonding
Enol form

Acetoactic ester exists as an equilibrium mix e of keto and enol forms. The enol form is stabilised by intramolecular hydrogen bonding. As ketone it forms a bisulfite addition compound. oxime etc and as an enol, it gives deep reddish brown colour with ferric chloride, dissolves in alkali etc. The keto and enol forms of acetoacetic ester were isolated by knorr. By evaporation of an ether solution of ethyl acetate at - 80° under reduced pressure, the keto form was obtained in crystalline form. By decomposition of the sodium salt of acetoacetic ester with dry hydrogen chloride, the enol form was obtained.

28.8.3 Reactions

28.8.3.1 Reaction with sodium ethoxide

In the molecule of acetoacetic ester, a - CH_2 - group is linked on one side to a ketonic group and on the other side to a carbethoxy group. Such a methylene group attached to electron withdrawing groups is called an active methylene group. The hydrogens of an active methylene group are acidic. Therefore acetoacetic ester reacts with bases like sodium ethoxide to form a sodium salt. The anion in this salt is a resonance hybrid of a carbanion and an oxyanion.

$$CH_3COCH_2COOC_2H_5 \xrightarrow[-C_2H_5OH]{NaOC_2H_5} \left\{ \begin{array}{l} CH_3COCHCOOC_2H_5^{\ominus} \\ \text{Carbanion} \\ \longleftrightarrow CH_3C=CHCOOC_2H_5 \\ \quad\quad | \\ \quad\quad O \quad \text{Oxyanion} \end{array} \right\} Na^+$$

28.8.3.2 C- Alkylation

The sodium derivative of acetoacetic ester reacts with alkyl halides to give monoalkyl derivatives of acetoacetic ester.

$$CH_3\bar{C}OCHCOOC_2H_5 + RX \longrightarrow \underset{\quad | \\ \quad R}{CH_3COCHCOOC_2H_5} + X^{\ominus}$$

Monoalkyl acetoacetic ester

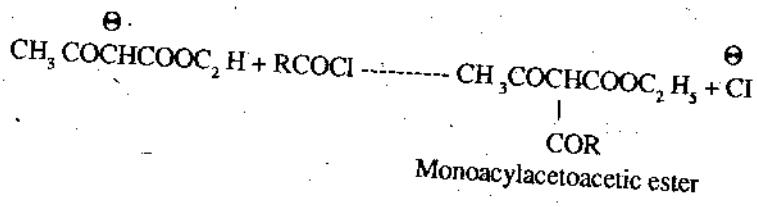
The monoalkyl derivative of acetoacetic ester still contains one more acidic hydrogen. By repeating this reaction the hydrogen can also be substituted by another alkyl group.

$$\underset{\quad | \\ \quad R}{CH_3COCHCOOC_2H_5} \xrightarrow{NaOC_2H_5} \underset{\quad | \\ \quad R}{CH_3CO\bar{C}COOC_2H_5} \xrightarrow{RX} \underset{\quad | \\ \quad R}{\overset{\quad R \\ \quad | \\ CH_3CO-C-COOC_2H_5}{\quad | \\ \quad R}} + X^{\ominus}$$

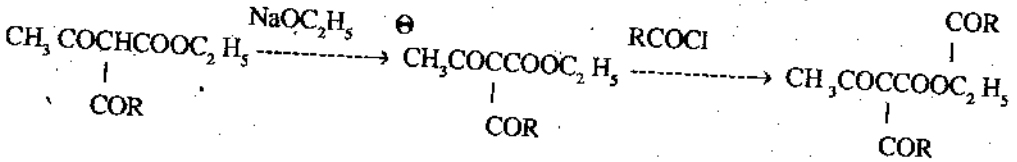
Dialkyl acetoacetic ester

28.8.3.3 C- Acylation

In a similar way monosodium and disodium salts of acetoacetic ester react with acid chloride to form monoacyl and diacyl acetoacetic ester respectively.



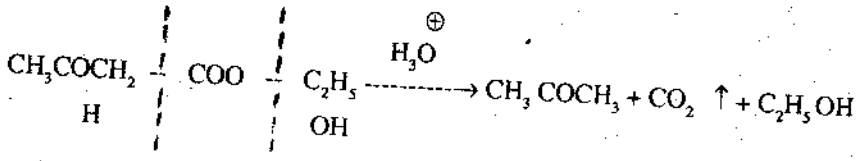
Monoacylacetoacetic ester



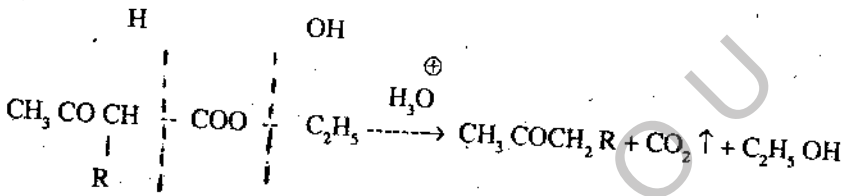
Diacyl acetoacetic ester

28.8.3.4 Synthesis of ketones

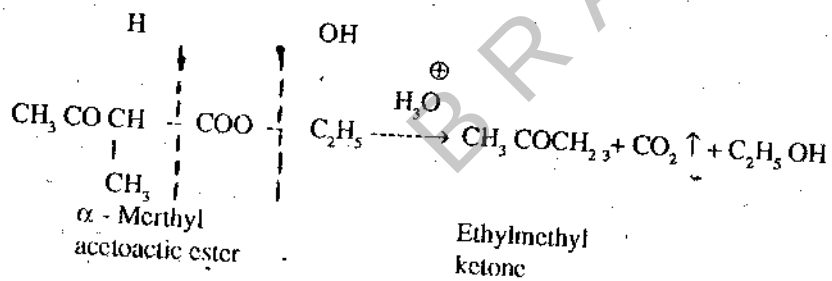
Acetoacetic ester or its derivatives may be hydrolysed by dilute acids or dilute alkalis. When dilute acid is used, acetoacetic ester gives acetone, ethyl alcohol and carbondioxide. This hydrolysis is therefore called ketone hydrolysis.



Higher homologues of acetone are obtained by ketonic hydrolysis of monoalkyl and dialkyl derivatives of acetoacetic ester.

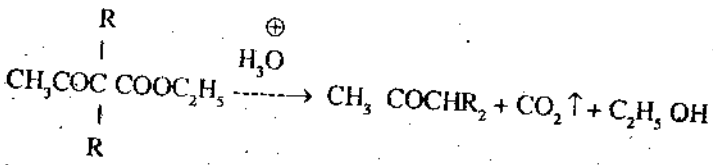


Example:

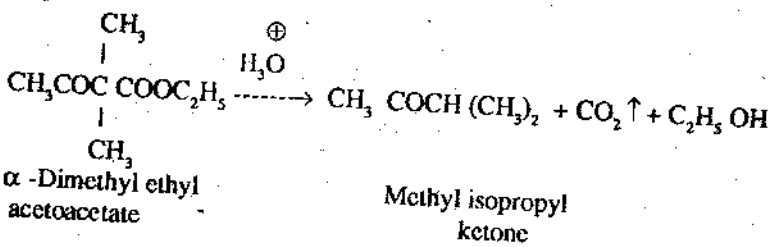


α - Methyl acetoactic ester

Ethylmethyl ketone



Example:

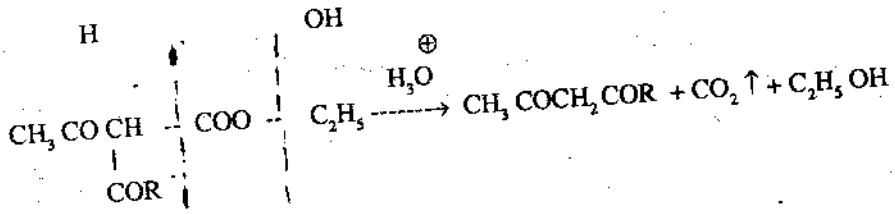


α -Dimethyl ethyl acetoacetate

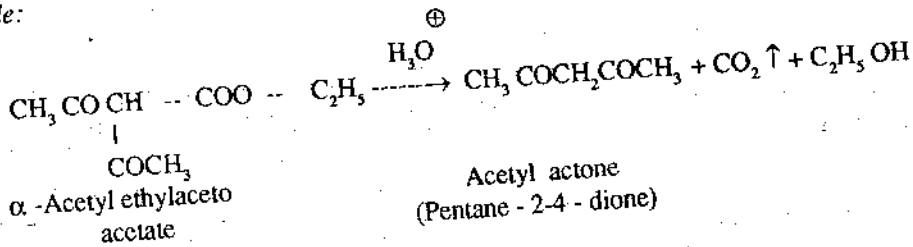
Methyl isopropyl ketone

28.8.3.5 Synthesis of diketones

Ketonic hydrolysis of monoacyl derivatives of acetoacetic ester gives diketones.



Example:

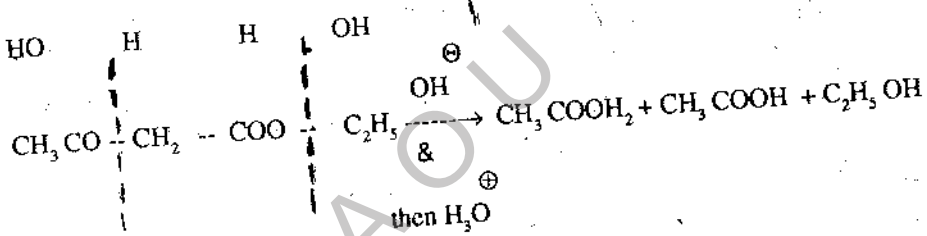


α -Acetyl ethylaceto acetate

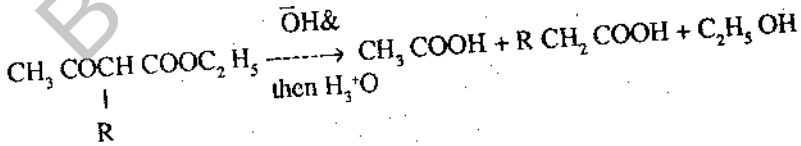
Acetyl actone (Pentane - 2-4 - dione)

28.8.3.6 Synthesis of monocarboxylic acids

When acetoacetic ester and its derivatives are hydrolysed by strong alkali, acids are the products. Acetic acid is obtained from acetoacetic ester.



When monoalkyl and diaklyl derivatives of acetoacetic ester are hydrolysed by strong alkali higher carboxylic acids are obtained.



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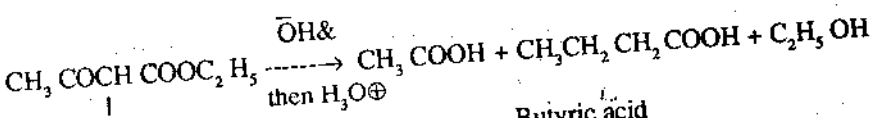
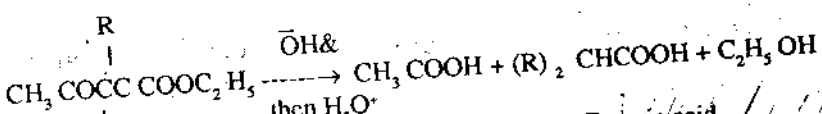
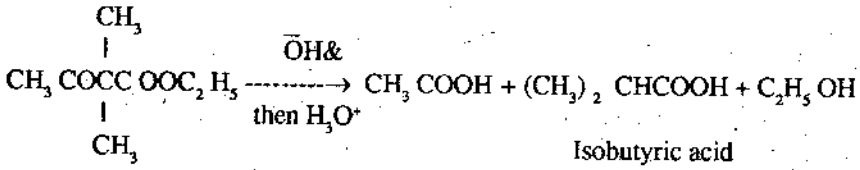


Butyric acid

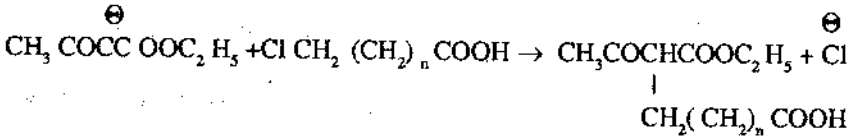


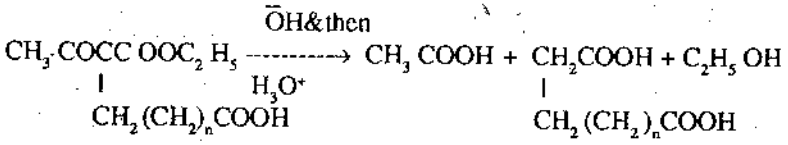
Butyric acid



28.8.37 Synthesis of Dicarboxylic acids

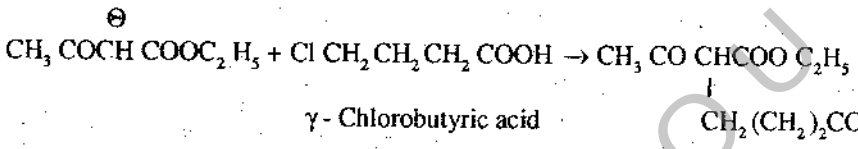
Sodium salt of acetoacetic ester reacts with chloroalkanoic acids. The resulting compound on hydrolysis with strong alkali furnishes a dicarboxylic acid.

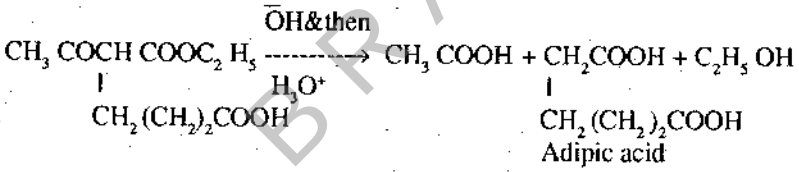




A Dicarboxylic acid

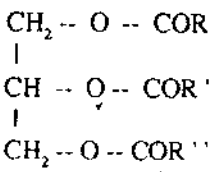
For example, adipic acid is obtained by the following sequence of reactions:





28.9 OILS AND FATS

Oils and fats are the important compounds of animal and vegetable origin. Chemically, oils and fats are glycerides, i.e. esters of glycerol with higher fatty acids. Fats are the main constituents of the fat cells in animals and plants and are one of the important food reserves of the organism. Liquid fats are commonly called oils and are different from mineral oils, which are hydrocarbons. The acyl groups in the glyceride may or may not be alike.



28.9.1 Nomenclature

There are two methods of nomenclature of fats.

28.9.1.1 Method - I

They are named by indicating the nature, number and position of the acyl groups that replace the hydroxyl hydrogens of glycerol.

Examples:

(1) $CH_2OCOCH_2CH_2CH_3$
$CH_2OCOCH_2CH_2CH_3$
$CH_2OCOCH_2CH_2CH_3$

Glycerol tributyrate

(2) $CH_2OCO(CH_2)_3CH_3$
$CHOCOCH_2CH_3$
$CH_2OCO(CH_2)_3CH_3$

Glycerol β- Propio α, υ- divalerate

(3) $CH_2OCOC_{17}H_{35}$
$CH_2OCOC_{17}H_{35}$
$CH_2OCOC_{15}H_{31}$

Glycerol Θα - Paalmito distearate

(4) $CH_2OCOC_{17}H_{33}$
$CHOCOC_{15}H_{31}$
$CH_2OCOC_{17}H_{35}$

Glycerol Θ α, oleo - β, γ- stearate

28.9.1.2 Method - II

They are named by replacing the suffix "ic acid" of the common name of the acid residue present in the fats by "in". Glycerol tributyrate is named as tributyrin.

Structure	Method I	Method 2
$CH_2OCOCH_2CH_2CH_3$ $CHOCOCH_2CH_2CH_3$ $CH_2OCOCH_2CH_2CH_3$	Glycerol tributyrate	Tributyrin
$CH_2OCO(CH_2)_3CH_3$ $CHOCOCH_2CH_3$ $CH_3OCO(CH_2)_3CH_3$	Glycerol- β - Propio α,γ, - divalerate	β- Propio di valerin
$CH_2OCOC_{17}H_{35}$ $CHOCOC_{17}H_{35}$ $CH_2OCOC_{17}H_{33}$	Glycerol - -Palmito-distearate	Palmitodisterin
$CH_2OCOC_{17}H_{33}$ $CHOCOC_{15}H_{31}$ $CH_2OCOC_{17}H_{35}$	Glycerol - α -Oleo-β -palmito-γ stearate	α -Oleo - β - palmito -γ - sterin

28.9.2 Physical properties

The acyl group in oils and fats is derived from long chain carboxylic acids, (highetr fatty acids). The hydrocarbon part in a fat is about 90% and therefore fat behaves like a hydrocarbon. For instance fats are insoluble in water and polar solvents. They are soluble in nonpolar solvens like CCl_4, either, CS_2, etc. The unsaturated glycerides usually have lower melting points than the corresponding saturated glycerides and are frequently oils.

Check your progress - 2

Explain why ethylacetate was lower boiling point than acetic acid.

28.9.3 Reactions of fats and oils

28.9.3.1 Hydrolysis

Hydrolysis of oils and fats by strong base such as KOH or NaOH is called saponification. Hydrolysis of oils and fats by NaOH or KOH furnishes glycerol and salts of fatty acids. The salt of the acid is called soap.

$$\begin{array}{l} CH_2\,OCOR \\ | \\ CHOCOR + 3NaOH \longrightarrow \\ | \\ CH_2\,OCOR \end{array} \qquad \begin{array}{l} CH_2OH \\ | \\ CHOH + 3RCOO^{\ominus}Na^{+} \\ | \\ CH_2OH \qquad \text{Soap} \\ \\ \text{Glycerol} \end{array}$$

Hard soaps are prepared by hydrolysis of cheap oils with NaOH. These are used for washing (laundry) purpose. Soft soaps are prepared from food oils and potassium hydroxide. They are used as toilet soaps, shaving sticks, shampoo etc. Saponification is a method or preparation of soaps and affords glycerol as valuable by - product.

28.9.3.2 Rancidification

Polyunsaturated glycerides (oils) slowly undergo oxidation and hydrolysis by the moisture and oxygen present in the atmosphere to produce products which have unpleasant odour. This process is called rancidification.

28.9.3.3 Paint dryers

Certain unsaturated oils like linseed oil are used as paint dryers because atmosphere oxygen attacks the unsaturated linkages to give products which form a hard protective film on the painted surface.

28.9.3.4 Hydrogenation of oils

Hydrogenation of oils is also known as hardening of oils. Hydrogenation is carried out by molecular hydrogen in the presence of nickel catalyst at 200°. By this process, the unsaturated glycerides in oils are converted into the saturated glycerides (fats). These fats are marketed under different brand names such as DALDA.

28.9.4 Analysis of oils and fats

There are several methods of analysis of oils and fats. The results obtained in these analyses are used to express the quality of the fats in the following ways.

28.9.4.1 Saponification number

Saponification number is the number of milligrams of KOH required to hydrolyse one gram of a fat or oil. Saponification number indicates the molecular weight of an oil or fat.

28.9.4.2 Acid value

This is a measure of the free acid present in a sample of oil or fat. Acid value of an oil or fat is the number of milligrams of KOH required to oneutralise the free acid in 1 gm. of oil or fat.

28.9.4.3. Iodine number

It is a measure of unsaturation of the fat or oil. Iodine number is the number of grams of iodine (or its equivalent of iodinating agent suh as ICI, which will add to 100 gm of fat or oil.

28.10 SUMMARY

After covering this unit the preparation and reactions of esters should be known. Esters which are named as alkyl alkanoates are prepared from alcohols by treatment with either acids, acid chlorides or acid anhydrides. They are easily hydrolysed with acid or base. Claisen condensation of ethylacetate gives ethylacetoacetate. Diethylmalonate is used for its synthetic application of monocarboxylic acids, dicarboxylic acids, Ethylacetoacetate is useful in synthesis of ketones, diketones, monocarboxylic acids and dicarbocylic acids.

28.11 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines

1. Write equations for the reaction of methly butanoate with
   (a) aq. NaOH (b) Ammonia (c) Excess of ethylmagnesium bromide
   (d) $LiAlH_4$. Name the products in each of these reactions.

2. How are the compounds in the following pairs diffrentiated by test tube experiments? Explain briefly the chemistry involved in each test.

   (a) Ethyl α- methyl - acetoacetate and ethyl , α, α - dimethyl acetoacetate.
   (b) Vegetable oil from mineral oil
   (c) Ethylacetoacetate from diethylmalonate
   (d) Diethylmalonate from α, α - dimethyldiethylmalonate

3. Explain the phenomenon of keto-enol tautomerism with a suitable example.

4. Starting with ethyl acetoacetate indicate the sequence of reactions that may be employed to prepare
   (a) Methyl isopropyl ketone
   (b) Methyl ethyl acetic acid
   (c) Acetylacetone

5. Starting from malonic ester how are the following prepared?
   (a) Butyric acid (b) Isobutyric acid (c) Succinic acid

(d) 2,3 - dimethyl butanedioic acid

II. Answer the following in 30 lines

1. Give the mechanism of formation of ethylacetoacetate. Give some of its important properties and synthetic uses.

2. What are acyloxy and alkyloxy fissions in ester hydrolysis? How can these fissions be demonstrated experimentally? Write the mechanism of the two types of fissions undergoing in the presence of acid catalyst?

3. Outline the synthesis of malonic esterf from acetic acid. Starting from diethylmalonate how are the following compounds prepared?

   (a) Pentanoic acid (valeric acid)
   (b) Pentane dioic acid
   (c) 2,3 - Dimethyl butanedioic acid

4. An ester A ($C_{14}H_{12}O_2$) on hydrolysis gave "B" ($C_7H_6O_2$) and C(C_7H_8O). B is soluble in sodium bicarbonate solution. Whereas C is insoluble in alkali. C On oxidation with chromic acid gives B. Reduction of A with $LiAlH_4$ gives C. Write the structure of A, B, C and explain the reactions mentioned above.

28.12 MODEL ANSWERS TO CHECK YOUR PROGRESS

1)

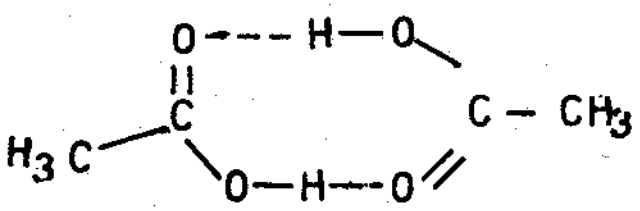
a) $CH_3 - \overset{O}{\overset{\|}{C}} - O\,CH_2\,CH_2CH_3$ n-Propyl ethanoate

b) $CH_3 - \overset{O}{\overset{\|}{C}} - O\,CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}$ i -Propyl ethanoate

c) $CH_3 - CH_2 - O - \overset{O}{\overset{\|}{C}} - OCH_2\,CH_3$ Ethyl proopanate

d) $CH_3 - CH_2\,CH_2 - \overset{O}{\overset{\|}{C}} - OCH_3$ Meethyl butanoate

2) Acetic acid is polar in nature and is dimeric due to strong intermolecular hydrogen bonding while ethyl acetate is not and is monomeric.



Author : Dr. T. Sundararamaiah

RECOMMENDED BOOKS

1. Organic Chemistry - I.L. Finar

2. Organic Chemistry - R.T. Morrison and R.N. Boyd

3. Text Book of Organic Chemistry -Iloyd N.Ferguson

4. Modern Organic Chemistry - Norman and Waddington

5. "కర్బన రసాయన శాస్త్రం" ద్వితీయ భాగం – తెలుగు అకాడమి.

Dr. B. R. AMBEDKAR OPEN UNIVERSITY

(Undergraduate Programme)

SECOND YEAR SYLLABUS

CHEMESTRY - COURSE - 2

Section - A - Inorganic Chemistry

Section - B Organic Chemistry

Dr. B.R.AMBEDKAR OPEN UNIVERSITY

Faculty of Science
(Under Graduate programme)
II - YEAR
CHEMISTRY COURSE - II

ASSIGNMENT - 2

Section - A

N.B.:1. Do not copy the answer directly from any of the books.
2. As far as possible try to answer the questions independently in your own words.
3. If it is necessary to quote from any source give the correct reference.
4. Use your own foolscap pages for writing the assignment.
5. Leave sufficient margins for the comments of the evaluator.
6. Completion of this assignment normally should not take more than two hours time.

Answer the following in 30 lines.

1. Explain the different types of isomerism exhibited by Organic compounds with examples.

2. What are cumulated, conjugated and isolated dienes? Describe two general methods for the preparation of alkadienes.

3. Explain induction effect, resonance effect and hyperconjugation.

Section - B

Answer the following in 10 lines.

1. Explain how carbon forms four covalent bonds.

2. Write a note on pyrlysis of coal.

3. How is ozonolysis useful in the determination of the position of double bonds in alkenes?

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Faculty of Science

(Under Graduate programme)

II - YEAR

CHEMISTRY COURSE - II

ASSIGNMENT - 3

Section - A

N.B.:1. Do not copy the answer directly from any of the books.
2. As far as possible try to answer the questions independently in your own words.
3. If it is necessary to quote from any source give the correct reference.
4. Use your own foolscap pages for writing the assignment.
5. Leave sufficient margins for the comments of the evaluator.
6. Completion of this assignment normally should not take more than two hours time.

Answer the following in 30 lines.

1. Discuss any three for each electrophilic and nucleophilic substitution reactions of benzene giving the mechanism of reactions.

2. Describe any two methods for the preparation of alkyl benzenes. Discuss the chemical reactions of alkyl benzenes.

3. What are SN^1 and SN^2 reactions? Explain in detail the mechanism and stereochemistry of SN^1 SN^2 and reactions for the alkaline hydrolysis of alkyl halides.

Section - B

Answer the following in 10 lines.

1. Phenol is acidic while benzyl alcohol is neutral, Explain.

2. Explain the directive influence of groups of aniline and nitrobenzene.

3. Formulate a method for conversion of benzene into (i) Benzyl chloride and (ii) p-chlorotoluene.

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Faculty of Science

(Under Graduate programme)

II - YEAR

CHEMISTRY COURSE - II

Model Question Paper

Time : 3 hrs. **Max, Marks : 75**

Section - A

Answer any three of the following in 30 lines.

3 x 15 = 45

1. State and discuss the terms Ionisation potential, electron affinity and elctro-negativity.
2. Write an account of the oxides and oxy acids of V-B elements. How does the strength of oxy acids vary in this group?
3. Give a concise account of the preparation properties and structures of inter halogen compounds.
4. Discuss the general methods for the preparation of alkanes with suitable examples.
5. Explain the different types of isomerism exhibited by organic compounds with examples.
6. Write a brief account on Inductive effect, hyper conjugation and Rebonance energy.

Section - B

Answer any five of the following in 10 lines

6 x 5 = 30

7. How do you account for the high ionigation potential of noble gases.
8. What is meant by ligand? Explain with examples.
9. Explain the term allotropy.
10. How ortho hydrogen differs from parahydrogen?
11. Give reasons for the greates acid strengths of HI in the series of hydrogen halides.
12. Explain Markoinkoff's rule.
13. Write a brief account of cis-Trans isomers.
14. Explain the preparation of nitrobengene from benzene.
15. Explain low Carbon forms four covalent bonds.
16. Write the ozonolysis products of ortho and paraxylenes.