SYLLABUS

KURUKSHETRA UNIVERSITY, KURUKSHETRA

INORGANIC CHEMISTRY

B.Sc.–3rd Year (Semester–6)

Time : 3 Hrs. *M. Marks : 32*

Note: *Nine questions will be set. Q.No. 1 based on whole syllabus, is compulsory. There will be four questions from each section A and four from section B. Candidates will be required to attempt five questions in all, selecting at least two questions from each section. Questions no. 1 carry 8 marks and all questions in section A & B (not more than 2-3 parts) carry 6 marks each.*

SECTION-A

I. Acids and Bases

Arrhenius, Bronsted-lowry, Lux-Flood, solvent system and Lewis concept of acids and bases, relative strength of acids and bases, levelling solvents, hard and soft acids and bases (HSAB), Applications of HSAB principle.

II. Organometallic Chemistry

Definition, nomenclature and classification of organometallic compounds. Preparation, properties, and bonding of alkyls of Li, Al, Hg and Sn, a brief account of metal-ethylenic complexes, mononuclear carbonyls and the nature of bonding in metal carbonyls.

SECTION-B

I. Bioinorganic Chemistry

Metal ions present in biological system, classification on the basis of action (essential, non essential, trace, toxic), metalloporphyrins with special reference to haemoglobin and myoglobin, Biological role of Na^+, K^+, Mg^{2+}, Fe^{2+} ions, Cooperative effect, Bohr effect.

II. Silicones and Phosphazenes

Nomenclature, classification, preparation and uses of silicones, elastomers, polysiloxane copolymers, poly phosphazenes and bonding in triphosphazene.

CONTENTS

1

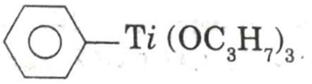
Organometallic Chemistry

Introduction

Organometallic chemistry is the study of chemical compounds containing at least one chemical bond between a carbon atom of an organic compound and a metal, including alkaline, alkaline earth, transition metal and other cases.

Metal carbides are not considered as the organometallic because the corresponding carbon moiety belongs to the inorganic family. If the metal centre is linked through the bridging atoms like N, O, S etc. then such compounds like [Ti (OR)$_4$], |Ca(en)$_3$|$^{3+}$, [Co (acac)$_3$] etc. are not regarded as the organometallic compounds.

On the other hand, the compound C_6H_5 Ti (O $C_3H_7)_3$ is an organometallic compound because it contains a Ti—C bond in the compound.

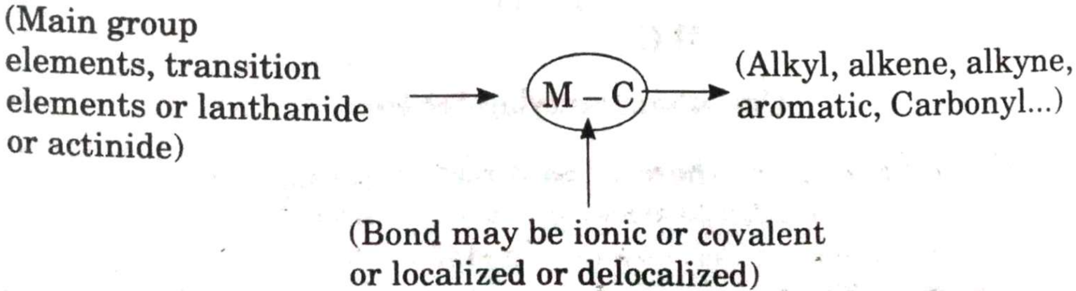


Organometallic compound
with Ti—C bond

Organometallic chemistry is a rapidly growing field of chemistry. It is an important branch of chemistry which connects the fields of organic and inorganic chemistry together. The field of the organometallic chemistry has had a phenomenal development after 1950, and various types of reactions, and unusual structures, and the practical importance in the field of organic synthesis, industrial catalytic processes has grown into a thriving area, during last few decades.

Definition of Organometallic Compounds

Organometallic compounds are those compounds contain one or more metal carbon bonds.



Types of Organometallic Compounds

Organometallic compounds can be classified into four types on the basis of nature of the metal.

1. Ionic organometallic compounds : These organometallic compounds are formed by the most electropositive metals of the group 1 and group 2 i.e., alkali and alkaline earth metals. In these compounds the hydrocarbon residue $(C_5H_5)^-$ exists as a carbanion. The carbanion being negatively charged, is attracted to the metal cation by non-directional electrostatic (or ionic) forces. The negative charge of the carbanion can either be localized at a particular carbon atom (e.g. in ethyl sodium) or can be delocalized over several carbon atoms (e.g. in cyclopentadienide)

$CH_3\overset{-}{C}H_2\overset{+}{Na}$

Ethyl sodium

Cyclopentadienide
sodium

Other examples of ionic organometallic compounds are :

Methyl sodium	$Na^+ CH_3^-$
Butyl sodium	$Na^+ C_4H_9^-$
Phenyl sodium	$Na^+ C_6H_5^-$
Trityl sodium	$Na^+ (C_6H_5)_3C^-$

Characteristics :

(a) These are colourless solids which are soluble in polar solvents and are insoluble in non-polar solvents.

(b) These ionic solids behave like electrolytes in the fused or molten state.

(c) These compounds acquire extra stability when the carbanion in them either acetylenic triple bond e.g. $R - C \equiv C^-$ or a conjugated system e.g. $CH_2 = CH - C\overline{H}_2$

(d) These compounds are readily hydrolysed in water

$$\underset{\text{Butyl sodium}}{C_4H_9Na} + H_2O \longrightarrow \underset{\text{Butane}}{C_4H_{10}} + NaOH$$

The reactivity of these compounds depends upon the stability of anion. Compounds containing unstable anions are found to be reactive. T[illegible] compounds are sensitive to oxygen.

Organometallic compounds of alkaline earth metals (e.g., Ca, Sr and Ba) are ionic in nature and reactive. These compounds have little advantages over the organometallic compounds of Li and Mg.

(e) These compounds show a gradual transition from ionic to σ-bonded covalent forms. Usually, the covalent character increases with increase in size of the alkyl group.

Classification of Ligands

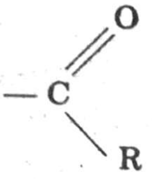
We have learnt that any atom, ion or molecule which is capable of donating a pair of electrons to the metal atom is called a ligand. Representative metals have the ability to form organometallic compounds with simple ligands such as alkyl or aryl groups. The transition metals have the ability to form organometallic compounds by forming bond with more than one carbon atoms of the organic ligand. Certain ligands get bonded to central metal atom using many of its atoms simultaneously e.g. in ferrocene, five carbon atoms of C_5H_5 ligands are within bonding distance of ions. Similarly in organometallic compounds formed through ethylene ligand, the two carbon atoms of ethylene are within the same bonding distance.

The number of atoms of the ligand which are within bonding distance of the metal atom is called its hapticity (η). It is represented by the term η (ita). Ligands with hapticity 1–8 are well known. Let us discuss these ligands one by one.

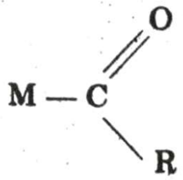
1. One carbon bonded ligands – These are the molecules in which one carbon atom of the ligand is bonded directly to the metal. Such ligands are named as monohapto ligands and are represented as η^1. The simplest example of monohapto ligand is — CH_3 group which binds the metal with a single M–C bond. These ligands are further subdivided into three groups as :

(i) **Hydrocarbon groups** : Hydrocarbon ligands include alkyl ($-CH_3$), aryl ($-C_6H_5$), alkenyl — CR = CR), alkynyl ($-C \equiv CR$), σ–cyclopentadienyl ($-C_5H_5$) etc. groups. All these groups are well known to form organometallic compounds with both the

(ii) **Acyl ligands** : Acyl ligands include acyl group whose carbon atom is directly bonded to only a transition metal atom as shown

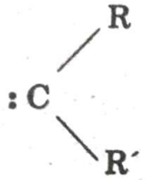


Acyl group

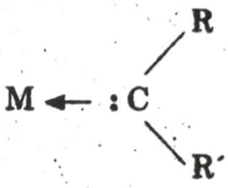


σ-bonded organometallic compound

(iii) **Carbene ligands** : Carbene ligands include carbene or alkylidene whose carbon atom is directly bonded to a metal atom as shown



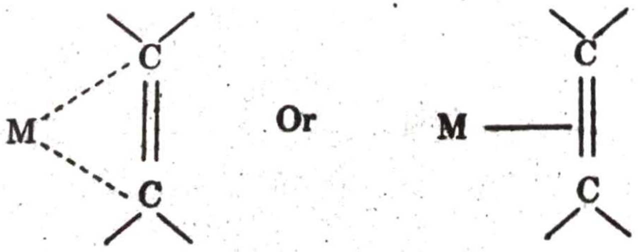
Carbene ligand



Organometallic compound

The substituents R and R´ on the carbon atom may be alkyl, aryl, —OR, —NR_3 etc. group. These compounds are generally formed by transition metals.

2. Two carbon bonded ligands – These are the molecules in which two carbon atoms of the ligand are bonded to the metal atom. These ligands are named as **dihapto ligands** and are represented as η^2. These ligands include alkenes ($>C=C<$) and alkynes ($-C\equiv C-$) in which both the carbon atoms present at the end of the multiple bond are involved in bonding to the metal atom. The bonding of ligand to metal is indicating either by two dotted lines to the participating carbon atoms of by a single solid line from the centre of the participating carbon atoms of the ligand to the metal atom as shown.



The two atoms bonded to transition metal atom need not be at equidistant from the metal atom. Unsymmetrical substituted ligands are like R—CH = CH_2.

3. Three-Carbon bonded ligands : These are the molecules in which three carbon atoms of the ligand are bonded to metal atom. These ligands are named as **trihapto ligands** and are represented as η^3.

Effective Atomic Number

The first attempt to show bonding in coordination compounds was made by Sidgwick in 1927. He extended the octet theory of G.N. Lewis to the coordination complexes by giving a new term called coordinate bond in which metal atom or ion accepts a pair of electron from the ligand molecule.

In other words, the metal atom or ion acts as **lewis acid**, if it accepts a pair of electron from the molecule of ligand while ligands act as **Lewis bases**, that donate pairs of electrons to the central metal atom or ion.

He suggested that the transition metal atom or ion accepts pair of electron and acquires stable noble gas configuration i.e., 36 (Kr), 54 (Xe) and 86 (Rn). This is called **effective atomic number rule (EAN).** Thus,

Effective atomic number (EAN) represents the total number of electrons possessed by the central metal ion in the complex and the electrons donated by the ligands.

In other words

Effective atomic number = Number of electrons on central metal atom or ion + Number of electrons donated by the molecule of ligands.

To illustrate this

Consider the complex ion, $[Fe(CN)_6]^{4-}$. The atomic number of Fe is 26 and therefore, number of electrons in, Fe^{2+} ion is 24. Each of six CN^- ions donates a pair of electrons so that total of 12 electrons are donated by six CN^- ions.

Thus,

Number of electrons in Fe^{2+} = 24

electrons from six NH_3 molecules 2 × 6 = 12

Total number of electrons in the complex = 36

Thus, EAN, is same as the atomic number of Krypton (36).

Similarly, the concept of EAN can be discussed by taking suitable examples of coordination complexes.

PROBLEMS : EAN

1. In which of the compound EAN rule is not obeyed?

(i) $Cr(C_6H_6)(CO)_4$ (ii) $Co(\pi - C_5H_5)_2$

(iii) $Fe(\pi - C_5H_5)(CO)_3$ (iv) $Co(\pi - C_5H_5)(CH_3)_2$

(v) $Mn(CO)_5Cl$ (vi) $|V(CO)_6|^-$

Ans. (i), (ii), (iii) and (iv).

2. In Which of the following complexes EAN rule is obeyed?

(i) $Co_2(CO)_8$ (ii) $|Mn(CO)_5|^-$

(iii) $Cr(CO)_6$ (iv) $W(CO)_6$

(v) $Ni(CO)_4$ (vi) $[Ag(NH_3)_2|^+$

(vii) $|PdCl_4|^{2-}$.

Ans. Complexes : (i), (ii), (iii), (iv) and (v)

3. Give two examples of π–acid ligands similar to CO.

Ans. (i) NO (ii) RNC

4. What is the EAN of the following complexes?

(i) $V(CO)_6$ (ii) $|Fe(CN)_6|^{3-}$

(iii) $|Ni(NH_3)_6|^{2+}$ (iv) $Cr(CO)_6$

(v) $Fe(CO)_5$ (vi) $[Mn(CO)_6]^+$

(vii) $Mo(CO)_6$ (viii) $V(CO)_6^-$

Ans. (i) 35, (ii) 35, (iii) 38, (iv) 36, (v) 36, (vi) 36, (vii) 54, (viii) 36.

5. Give one example each of a metal carbonyl which

(i) obeys EAN rule (ii) does not obey EAN rule

Ans. (i) $[Ni(CO)_4]$, (ii) $[V(CO)_6]$

6. Calculate the EAN in the following compounds :

(i) $Cr(CO)_3(C_6H_6)$ (ii) $Fe(\pi - C_5H_5)(CO)_3$

Ans. (i) 36, (ii) 37.

Nomenclature of Organometallic Compounds

Most of the organometallic compounds are co-ordination compounds containing one or more ligands attached to the metal through metal-carbon bonds.

IUPAC nomenclature of co-ordination compounds or complexes has already been discussed in earlier classes. All the main rules which were applicable to cordination complexes are more or less applicable for organometallic compounds also but with a light modification. Some important additional rule are :

(i) The names of simple alkyl or aryl organometallic compounds are given by writing the name of the metal after the name of organic group e.g.

CH_3Li	Methyllithium
$(C_2H_5)_2Zn$	Diethylzinc
CH_3MgCl	Methyl magnesium chloride
C_6H_5MgI	Phenyl magnesium iodide.

Nomenclature of Carbonyls

Carbonmonoxide is a neutral ligand ($2e^-$ donor) and its compound with metals are called carbonyls. CO, does not affect the oxidation state of the metal. For a neutral compound, the oxidation state can be omitted. e.g.

$Co_2(CO)_8$	Octacarbonyl dicobalt
$Fe_2(CO)_9$	Nonacarbonyl diiron
$Co_4(CO)_{12}$	Dodecarbonyl tetracobalt
$V(CO)_6|^-$	Hexacarbonyl vanadate (I)
$|Co(CO)_4|^-$	Tetracarbonyl cobaltate (–I)
$|Mn(CO)_5|^-$	Pentacarbonyl manganate (–I)
$|Mn(CO)_6|^+$	Hexacarbonyl manganese (I)
$|Mn(CO)_5C_2H_4)|^+$	Pentacarbonyl (ethylene) manganese (I)

(ii) (a) Ligands which act as a bridge between two metal atoms are named by placing Greek letter μ (mu) before the name of each different type of bridging ligands. Greek letter μ is separated from the rest of the complex by hyphens (–).

(b) Two or more bridging ligands of the same type are indicated by *di* – μ or bis – μ etc.

(c) If the same ligands is present as a bridging as well as a non-bridging ligand, the name of the bridging ligand is written first.

(d) Name of all types of the ligands are listed in alphabetical order unless the symmetry of the molecules permits simpler names by the use of multiplicative prefixes. e.g.

$[(CO)_3Fe(CO)_3Fe(CO)_3]$	Tri – μ-carbonyl bis (tricarbonyliron)
$[(CO)_4Os(CO)Os(CO)_4]$	μ–Carbonyl bis (tetracarbonylosmium)
$[(CO)_3Co(CO)_2Co(CO)_3]$	Di–μ–Carbonyl bis (tricarbonylcobalt)

(iii) Compounds containing M – M bond are classified into symmetrical and unsymmetrical. The symmetrical metal carbonyls are named by the use of multiple prefixes (such as bis, – tris, tetrakis etc). However, in case of unsymmetrical metal carbonyls, one central metal atom and its ligands are treated as a ligand. On the other central metal atom. e.g.

$[(CO)_5Mn-Mn(CO)_5]$	Bis (pentacarbonylmanganese).
$[(CO)_4Co-Co(CO)_4]$	Bis (tetracarbonylcobalt)
$[(CO)_4Co-Re(CO)_5]$	Pentacarbonyl (tetracarbonyl cobaltio) rhenium
$CH_3Hg-Ta(CO)_6$	Hexacarbonyl (methylmercurio) tantalum

Nomenclature of σ and π-bonded ligands

In case of transition metal allyl compounds a system of symbol σ and π – was used to analyze between one carbon bonded ligand and three carbon–bonded ligands. Similarly, cyclopentadiene (C_5H_5) when behaving as one carbon bonded ligand was mentioned as ($\sigma - C_5H_5$) and when behaving as five carbon bonded ligand was mentioned as ($\pi - C_5H_5$).

For more systematic scheme, F.A. Cotton in 1968 introduced a new system of symbols. He classified the ligands by prefix **hapto** and to denote the number of carbon atoms in a ligand that are bonded to the metal. For example, a one carbon bond ligand is designated by prefix **mono hapto,** two carbon bonded ligand as **dihapto**, three carbon bonded of **trihapto**, four carbon bonded ligand as **tetrahapto**, five carbon bonded as **pentahapto** and so on. These symbols can be shortened as η^1, η^2, η^3, η^4, η^5 etc. Thus according to these rules, some of the examples of the η (symbol) are :

$Fe\ (\pi - C_5H_5)_2$	Bis (η^5 – cyclopentadienyl) iron
$Cr\ (\pi - C_6H_6)_2$	Bis (η^6 – benzene) chromium
$K\ [Pt\ Cl_3\ (C_2\ H_4)]$	Potassium trichloro (η^2 – ethylene) platinate (II)
$(\pi - C_5H_5)\ Mn\ (CO)_3$	Tricarbonyl (η^5 – cyclopentadienyl) manganese
$Fe_2\ (CO)_4\ (C_5H_5)_2$	Bis (η^5 – cyclopentadienyl) tetracarbonyl diiron
$Co\ (CO)_3\ (\pi - C_3H_5)$	(η^3 – allyl) tricarbonyl cobalt
$ReH\ (\pi - C_5H_5)_2$	Bis (η^5–cyclopentadienyl) hydridorhenium
$Fe\ (CO)_2\ (\sigma - C_5H_5)\ (\pi - C_5H_5)$	Dicarbonyl (η^1 – cyclopentadienyl) (η^5 – cyclopentadienyl) iron
$Mn\ (CO)_5\ (\sigma\ C_3H_5)$	(η^1 – allyl) pentacarbonyl manganese
$Fe\ (CO)_3\ (C_4H_6)$	(η^4 – butadiene) tetracarbonyl iron
$(Me_3Si)\ W\ (CO)_3\ (\pi - C_5H_5)$	Tricarbonyl (η^5 – cyclopentadienyl) trimethylsilyl tungsten
$(\sigma - C_5H_5)\ Ti\ (\pi - C_5\ H_5)_2$	Bis (η^1 – cyclopentadienyl) bis (η^5 – cyclopentadienyl) titanium

ORGANOLITHIUM COMPOUNDS

Organolithium compounds, R–*Li* are extremely important compounds used generally in preparative organic and inorganic chemistry. These are readily prepared and are broadly used as alkylated and arylated agents for metals as well as non-metals. These are soluble in hydrocarbon and spread extreme chemical reactivities. These compounds are generally polymeric in nature.

Preparation : The organolithium compounds are very sensitive towards oxygen, water and carbon dioxide. The preparation is generally carried out in inert atmospheres of nitrogen and argon. Some of the methods of preparation are given below :

1. **Direct synthesis :** When alkyl halides or aryl halides are heated in hydrocarbon solvent such as ether, cyclohexane, light petroleum or benzene, alkyl or aryl lithium is formed.

2. **Reaction between lithium and organocompounds :** The reaction between organomercury compound and excess of lithium metal gives alkyl or aryl lithium compounds

$$HgR_2 + 2Li \longrightarrow 2LiR + Hg\downarrow$$

e.g. $(CH_3)_2Hg + 2Li \longrightarrow 2CH_3Li + Hg\downarrow$

Dimethyl mercury

$$HgAr_2 + 2Li \longrightarrow 2LiAr + Hg\downarrow$$

e.g. $Hg(C_6H_5)_2 + 2Li \longrightarrow 2C_6H_5Li + Hg\downarrow$

Diphenyl mercury — Phenyl lithium

Alkyl or aryl lithium are crystallized from the hydrocarbon solvents after removing mercury.

3. **Metal-metal exchange (Transmetallation reaction) :** In this method the organolithium derivatives of vinyl compounds are prepared as

$$(CH_2=CH)_4Pb + 4Li \xrightarrow{\text{Ether}} 4CH_2=CHLi + Pb$$

$$(CH_2=CH)_4Sn + 4C_6H_5Li \xrightarrow{\text{Ether}} 4CH_2=CHLi + (C_6H_5)_4Sn$$

4. **Metal-halogen exchange :** Organolithium compounds can be prepared by metal-halogen exchange reaction as,

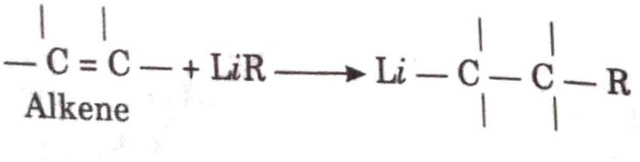
$$n\text{-}C_4H_9Li + C_6H_5Cl \xrightarrow{\text{Ether}} n\text{-}C_4H_9Cl + C_6H_5Li$$

Butyl lithium — Phenyl lithium

$$n\text{-}C_4H_9Li + C_6H_5I \xrightarrow{\text{Ether}} n\text{-}C_4H_9I + C_6H_5Li$$

Phenyl lithium

5. **Lithiated alkenes and alkynes :** Alkenes and alkynes are readily metated (i.e., lithiated)



$$-\overset{|}{C}=\overset{|}{C}- + LiR \longrightarrow Li-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-R$$

Alkene

$$-C\equiv CH + RLi \longrightarrow -C\equiv CLi + R-H$$

Alkyne

In alkyne, the attached hydrogens is more acidic in nature.

Properties :

1. It is colourless crystalline solid. It decomposes above 473 K. It is an insoluble covalent compound.
2. It is non-conductor of electricity in fused state.

Organolithium compounds are more reactive than "Grignard's reagent. Some of the important reactions are :

1. **Reaction with CO and CO_2 :** Organolithium compound react with CO and CO_2 to give ketones and carboxylic acids

$$2LiR + 3CO \longrightarrow \underset{\text{Ketone}}{R_2CO} + 2LiCO$$

e.g. $$2LiCH_3 + 3CO \longrightarrow (CH_3)_2CO + LiCO$$

$$LiR + CO_2 \longrightarrow \underset{\text{Carboxylic acid}}{RCOOH} + LiOH$$

e.g. $$CH_3Li + CO_2 \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + LiOH$$

2. **Reaction with halogens :** Organolithium compounds react with halogens and regenerate the parent alkyl or aryl halide.

$$LiR + X_2 \longrightarrow LiX + RX$$

(R = alkyl or aryl)

e.g. $$\underset{\text{Methyl lithium}}{CH_3Li} + Cl_2 \longrightarrow LiCl + \underset{\text{Methyl chloride}}{CH_3 - Cl}$$

3. **Reaction with main group halides (trans-metallation) :** Organolithium compounds can be used to prepare a variety of organometallic compounds of main group elements as :

$$3LiR + BCl_3 \longrightarrow BR_3 + 3LiCl$$

$$4LiR + SnCl_4 \longrightarrow SnR_4 + 4LiCl$$

$$3LiR + SnCl_3 \longrightarrow SbR_3 + 3LiCl$$

Applications

The important applications of organolithium compounds are :

(1) **Valuable synthetic reagents :** The organo-lithium compounds are valuable synthetic reagents and have been increasingly used in organic research laboratory. Alkyl and aryl lithium organometallic derivative are extensively used in place of Grignard reagents because of their higher speed of the reactions and their easier handling of reaction mixtures. For example, C_6H_5Li is about 100 times more reactive than C_6H_5MgBr.

(2) **Polymerisation catalysts :** Organolithium are being used extensively as polymerisation catalysts. For example, n – Butyllithium catalyses polymerisation of butadienes. Polymerisation of isoprene with alkyllithiums has been shown to produce synthetic rubber with properties resembling to natural rubber.

(3) **Alkylating and arylating agents :** Organolithium compounds are used as alkylating and arylating agents in preparing a series of organometallic compounds. For example,

$$\underset{\text{Diethyl titanium chloride}}{(C_2H_5)TiCl_2} + 2LiR \xrightarrow{\text{Ether}} (C_5H_5)_2TiR_2 + 2LiCl$$

$$3LiR + BCl_3 \longrightarrow BR_3 + 3LiCl$$

$(R = CH_3, C_6H_5)$

(4) **Block copolymerisation :** The alkyl lithium compound add to butadiene and tend to copolymerise with monomers such as styrene to give block copolymers by forming the stable living polymers.

Organoaluminium Compounds

Organoaluminium compounds are known for more than a century. The first organoaluminium compound was synthesized in 1865. These compounds became important after the discovery of their catalytic properties in the stereospecific polymerization of olefins by Zeigler-Natta. Inspite of their extreme sensitivity to air and moisture, organoaluminium compounds are currently manufactured and handled on an industrial scale. These compounds contain 1, 2, 3 or 4 Al – C bonds per atom. Most of these exist as dimers as Al_2R_6 or Al_2Ph_6.

Preparation :

1. Organoaluminium compounds are prepared by the reaction of trihalide of aluminium with Grignard reagent or organolithium reagent.

$$AlX_3 + 3\,RMgX \xrightarrow[\text{ether}]{\text{Diethyl}} R_3Al + 3MgX_2$$

However, this method is not suitable for the synthesis of organoaluminium compound because the reactive organoaluminium compound reacts with solvent diethylether to form ether adduct, $R_3Al \cdot OEt_2$

$$AlX_3 + 3RMgX \xrightarrow{Et_2O} \underset{\text{Ether adduct}}{R_3Al \cdot OEt_2} + 3MgX_2$$

2. Trialkyl aluminium, R_3Al can be prepared on large scale by the direct reaction of aluminium metal powder, olefins and H_2 as

$$Al + \frac{3}{2}H_2 + \underset{\text{Olefins}}{R-CH=CH_2} \xrightarrow[200\text{ atm}]{100^\circ C} \underset{\text{Organoaluminium compound}}{Al(CH_2CH_2R)_3}$$

Properties :

1. Aluminium trialkyls and triaryls are colourless volatile liquids having low melting points and are very reactive.
2. Lower alkyl aluminium compounds react violently with water, alcohols and air.
3. Alkyl aluminium compound are soluble in aromatic and saturated aliphatic hydrocarbons. However, with ethers and *t*-amines these form complexes.
4. Branched chain trialkylaluminium compounds such as tri-isobutyl aluminium decompose around 50°C forming olefins. This property is used for purification of Al metal and Al thin films.

$$R_3Al \xrightarrow{\text{Heat}} \text{Olefin} + R_2AlH$$

$$R_3AlH \xrightarrow{\text{Heat}} Al + \frac{3}{2}H_2 + 2\ \text{Olefins}$$

5. On oxidation and subsequent hydrolysis, the alkylaluminium compounds give alcohols.

$$Al(CH_2CH_2R)_3 \xrightarrow{O_2} (RCH_2CH_2O)Al \xrightarrow[H^+]{H_2O} \underset{\text{Alcohols}}{3RCH_2CH_2-OH}$$

On thermolysis they give terminal alkenes some more important reactions of alkyl aluminium have been summerized as under : Fig.14.

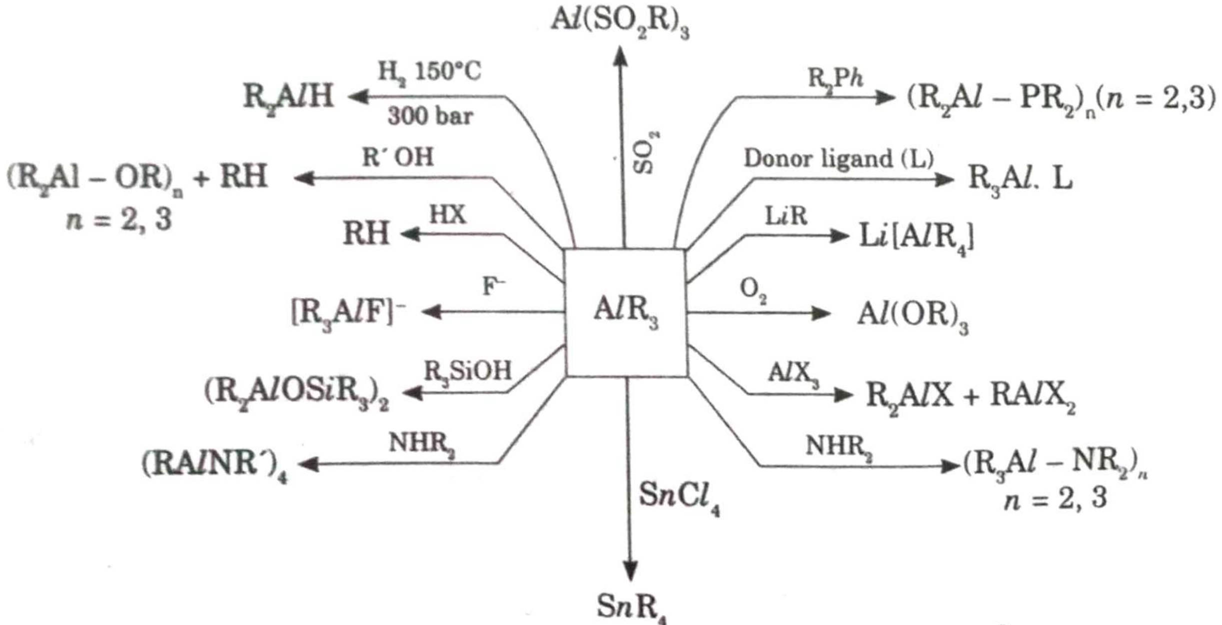


Fig. 14. reactions of organoaluminium compounds.

Organomercury Compounds

Organomercury refers to the group of organometallic compounds that contain mercury. Typically the Hg – C bond is stable toward air and moisture but sensitive to light. The first organomercury compound was obtained by E. Frankland (in 1853) by the action of CH_3I on mercury under sunlight

$$2CH_3I + 2Na/Hg \longrightarrow (CH_3)_2Hg + 2NaI$$

Ever since then, a large number of organomercury compounds of types of R_2Hg and monomeric RHgX have been synthesized.

Preparation

1. Organomercury compounds are prepared by the action Na/Hg on alkyl halide.

$$2RX + Hg/Na \longrightarrow HgR_2 + HgX_2$$

The compound methyl mercury iodide can be prepared by the direct combination of methyliodide and mercury in the presence of sunlight.

$$CH_3I \quad + \quad Hg \xrightarrow{\text{Sunlight}} \underset{\text{methyl mercury iodide}}{CH_3HgI}$$

However, the rate of reaction is slow.

Generally, organomercury compounds can also be prepared as by the reaction of alkyl or arylhalide and sodium amalgam, Na/Hg. The reaction occurs in the presence of methyl acetate or ethyl acetate as catalyst.

$$2RX + 2Na + Hg \xrightarrow{\text{Ethyl acetate}} R_2Hg + 2NaX$$

2. Alkyl or aryl derivatives of organomercury compounds can be prepared from Grignard reagents.

$$HgCl_2 + RMgX \longrightarrow RHgCl + MgXCl$$

$$RHgCl + RMgX \longrightarrow HgR_2 + MgXCl$$

This method has recently been applied to the synthesis of bis (pentafluorophenyl) mercury $(C_6H_5)_2Hg$.

3. Organomercury compounds can be synthesized by using the corresponding diazonium chloride with elemental mercury.

Benzene diazonium chloride

4. Organomercury compounds can be obtained by mercuration reaction which inovlves the direct replacement of hydrogen by mercury.

$$HgX_2 + RH \longrightarrow RHgX + HX$$

$$C_6H_5-H + (CH_3COO)_2Hg \longrightarrow C_6H_5HgOCOCH_3 + CH_3COOH$$

5. Disubstituted derivatives of organomercury compounds can be synthesized from the organolithium and organoaluminium compounds as given :

$$HgCl_2 \xrightarrow{RLi} RHgCl \xrightarrow{RLi} R_2Hg$$

$$3HgCl_2 + 2AlR_3 + 2NaCl \longrightarrow 3HgR_2 + 2NaAlCl_4$$

Addition of NaCl helps in the separation of HgR_2.

Alkene or Olefin Complexes

These are organometallic complexes which contain unsaturated ligands such as alkenes. The first compound of olefin complex of transition metal was isolated in 1827 by a Danish chemist W.C. Zeise having the empirical formula $PtCl_2 \cdot C_2H_4$. Some years later, Zeise discovered the pale yellow crystalline solid having composition $K[PtCl_3 \cdot (C_2H_4)]$ which is also known as **Zeise salt**. This compound was prepared by passing ethylene gas through an aqueous solution of potassium tetrachloroplatinate (II), $K_2|PtCl_4|$.

$$\underset{\text{Potassium tetrachloroplatinate (II)}}{K_2|PtCl_4|} + \underset{\text{Ethylene}}{C_2H_4} \longrightarrow \underset{\text{Zeise salt}}{K[PtCl_3(C_2H_4)]} + KCl$$

Now a days complexes of olefins or alkene with transition metal like Cu(I), Pt(II), Pd(II) Hg(II) and Ag(I) are well known.

It was later observed that the complex with metal ions or halides formed when these metal treated with a variety of olefins.

Structure and bonding in the metal olefins complexes : The structure of anion of the Zeise salt, K[Pt$Cl_3(C_2H_4)$] was established in 1975. The important features of the salt are the followings :

(i) The three chlorine atoms and the middle point of the ethylene double bond form a square plane.

(ii) The C = C double bond is perpendicular (at 90°) to the plane containing platinum and the three chlorine atoms.

(iii) The C_2H_4 group no longer remains planar and show significant distortion from planarity Fig. 22.

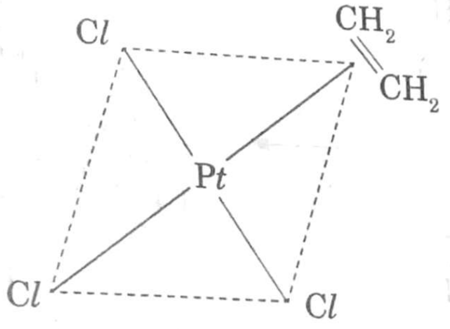


Fig. 22. Structure of Zeise salt anion, $|Pt\,Cl_3C_2H_4|^-$

In order to understand bonding between the metal atom and the ethylene molecule, let us consider the molecular orbitals present in ethylene. Each carbon atom of ethylene is sp^2 hybridised and form three sigma bonds, one with other carbon atom and two with hydrogen atoms. As a result, one *p*-orbitals containing a single electron is left on each carbon atom. These two π-orbital on carbon atoms containing one electron each interact to form two molecular orbitals, one will be bonding molecular orbital (i.e. π B.M.O.) and other will be anti-bonding molecular orbital (i.e. π-A.B.M.O.). The bonding-molecular orbital will have lower energy than antibonding-molecular orbital. Thus, the two electrons in two *p*-orbitals will be present in the lower bonding molecular orbitals of ethylene. Therefore, ethylene molecule has a filled π-bonding molecular orbital (shown shaded) and a empty π-molecular orbital (shown unshaded).

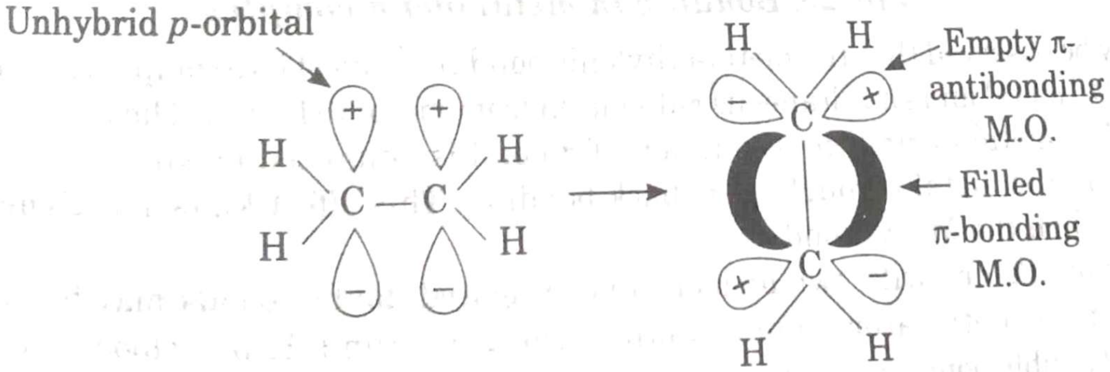


Fig. 23. Molecular orbitals of ethylene molecule.

These molecular orbitals of ethylene molecule will overlap with the suitable orbitals of the metal atom. The metal atom has also filled and empty orbitals. The bonding between ethylene to transition metal occurs in two ways :

(i) The filled π-MOs of the ethylene molecule are donated to the suitably directed vacant orbitals of the metal to from alkene-metal sigma bond Fig. 23.

(ii) A back bonding occurs by the overlap of the filled metal hybrid orbitals with the vacant π-molecular orbital of the olefin. This leads to the formation of π-bond. The back bonding will strengthen the metal-olefin bond but weakens the C – C bond in alkenes Fig. 24.

Alkyne Complexes

It has been observed that, like alkenes, alkynes can form π-complexes with a variety of transition metals. It is very well known that there are two π-bonds at right angles to each other. The transition metal can bind to the one or both the π-bonds. Some of the important difference in the bonding to metals compared to alkenes are :

(i) Alkynes are stronger π-acceptors than alkenes.
(ii) Alkynes undergo insertion reactions and cyclotrimerized to give arenes.
(iii) Alkynes have two orthogonal π-systems which are perpendicular to each other. These π-systems can act as 2 and 4 -electron donor ligands.
(iv) Alkynes frequently form integral parts of metal clusters with the loss of high energy C ≡ C triple bond.

Synthesis of alkyne complexes : Some of the important methods of preparation of alkyne complexes are given below :

(i) The alkyne may coordinate to only one metal atom and function like alkenes. Alkyne molecules in these complexes occupy one of the position like that of ethylene in Zeise salt. The C ≡ C triple bond of the alkyne is perpendicular to the plane of coordination. These complexes can be prepared by the following methods :

$$PtCl_2 + {}^tBuC \equiv CBu^t + p - CH_3C_6H_4NH_2 \longrightarrow pCH_3C_6H_4NH_2({}^tBu_2C_2)PtCl_2$$

$$Pt\,Cl_4^{2-} + {}^tBuC \equiv CBu^t \longrightarrow [PtCl_2({}^tBu_2C_2)]_2$$

$$(\eta^5 - C_5H_5)Mn(CO)_3 + Ph\ C \equiv C\ CPh \xrightarrow{h\nu} (\eta^5 - C_5H_5)Mn(CO_2)(PhC \equiv CPh) + CO$$

The structure of these complexes are given below : Fig. 27.

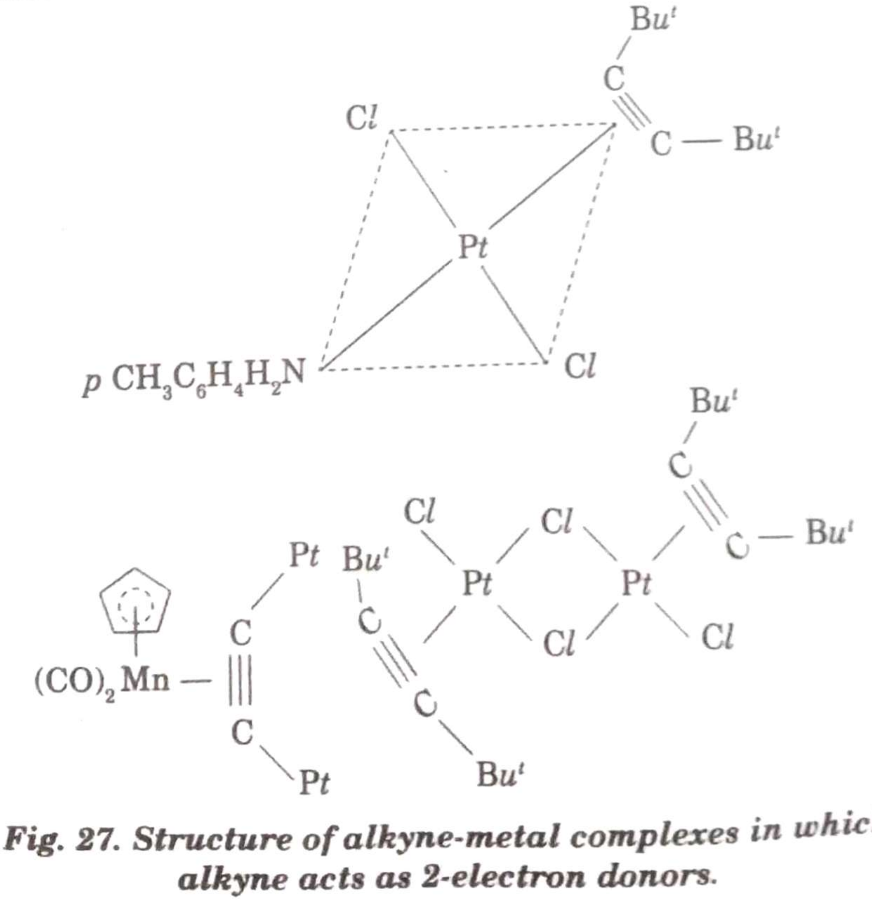


Fig. 27. Structure of alkyne-metal complexes in which alkyne acts as 2-electron donors.

Preparation of metal carbonyl

(1) **Direct synthesis :** Simple metal carbonyls can some times be made by the direct combination of carbon monoxide with the finally powdered metal, especially if the surface is very clean and free from the oxide.

$$Ni + 4CO \xrightarrow[1\ \text{atm}]{298\ \text{K}} Ni(CO)_4$$

$$Fe + 5CO \xrightarrow[100\ \text{atm}]{423\ \text{K}} Fe(CO)_5$$

$$Mo + 6CO \xrightarrow[250\ \text{atm}]{473\ \text{K}} Mo(CO)_6$$

$$2Co + 8CO \xrightarrow[\text{Pressure}]{\text{Heat}} Co_2(CO)_8$$

(2) **Reductive carbonylation :** Many metal carbonyls can be prepared from carbon-monoxide and a compound of metal such as oxide, sulphide or halide in the presence of a reducing agent. The reducing agent may be hydrogen, sodium, Mg, Al, $LiAlH_4$ or sometimes even excess of carbon monoxide. E.g.

$$OsO_4 + CO \xrightarrow[350\ \text{atm}]{523\ \text{K}} Os(CO)_5 + Os_3(CO)_{12} + CO_2$$

$$RuI_3 + CO + Ag \xrightarrow[250\ \text{atm}]{450\ \text{K}} Ru(CO)_5 + AgI$$

$$CoS + CO + Cu \xrightarrow[200\ \text{atm}]{473\ \text{K}} Co_2(CO)_8 + Cu_2S$$

$$CrCl_3 + CO + LiAlH_4 \xrightarrow[70\ \text{atm (ether)}]{388\ \text{K}} Cr(CO)_6 + LiCl + AlCl_3$$

$$CoCO_3 + CO + H_2 \xrightarrow[\text{Petroleum ether}]{423\ \text{K, 300 atm.}} Co_2(CO)_8$$

Properties of metal Carbonyls

Physical Properties : The metal carbonyls are all crystalline solids, except for $Fe(CO)_5$, $Ru(CO)_5$, $Os(CO)_5$ and $Ni(CO)_4$ which are liquids. On heating, they decompose at low temperatures, or sometimes change into polynuclear carbonyls. In any case, they finally decompose into the metal and carbon monoxide at higher temperatures. They are insoluble in water and are often decomposed by it. Except for $Fe_2(CO)_9$, all are soluble in organic solvents.

Chemical properties : Metal carbonyls undergo a variety of chemical reactions. Some of the important reactions are discussed below :

1. **Displacement reactions :** Metal carbonyls give displacement reactions in which one or more carbonyl ligands is displaced by electron donors such as phosphine (R_3P), pyridine (*py*) or isocyanides (RNC) etc.

   An electron pair donor molecule replace a molecule of CO, therefore, a six electron donor such as benzene could displace three molecules of CO. Some of the important displacement reactions are.

$$Fe(CO)_5 + Ph_3P \rightarrow Fe(CO)_4(PPh_3) + CO$$

$$Fe(CO)_5 + 2Ph_3P \rightarrow Fe(CO)_3(PPh_3)_2 + 2CO$$

$$Mo(CO)_6 + Py \rightarrow Mo(CO)_5(Py) + CO$$

$$Mo(CO)_5(Py) + Py \rightarrow Mo(CO)_4(Py)_2 + CO$$

$$Ni(CO)_4 + 2PPh_3 \rightarrow Ni(CO)_2(PPh_3)_2 + 2CO$$

$$Cr(CO)_6 + C_6H_6 \rightarrow (C_6H_6)Cr\,(CO_3)_2$$

$$Cr(CO)_6 + 2\,C_5H_5N \rightarrow Cr(CO)_4(C_5H_5N)_2 + 2CO$$

$$Fe(CO)_5 + 2C_5H_6 \rightarrow 2[(\eta^5 - C_5H_5)Fe(CO)_2]_2 + 2CO$$

$$Co_2(CO)_8 + RC \equiv CR \rightarrow Co_2(CO)_6(RC \equiv CR) + 2CO$$

$$Mo(CO)_6 + C_5H_5Na \rightarrow Na[\,(\eta^5 - C_5H_5)Mo(CO)_3] + 3CO$$

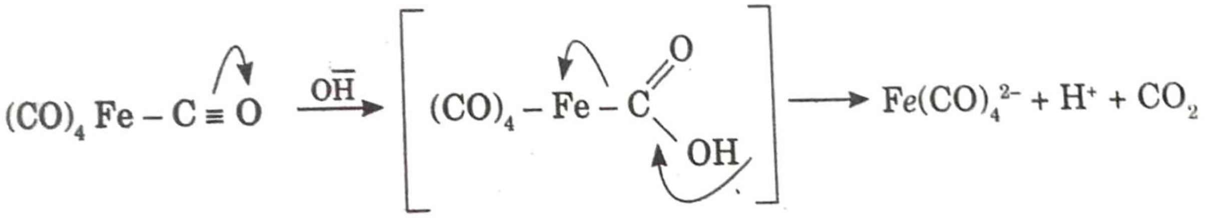
2. **Formation of carbonyl anionic complexes :** There are three important methods for the conversion of metal carbonyls into the corresponding anions :

(i) All neutral metal carbonyls can be converted into anions by the action of sodium hydroxide solution, with the loss of one CO group. E.g.

$$Fe(CO)_5 + 2\,\bar{O}H \rightarrow |Fe(CO)_4|^{2-} + H_2O + CO_2$$

$$Fe_2(CO)_9 + \bar{O}H \xrightarrow[Et_4NI]{CH_3OH} (Et_4N)_2\,[Fe_2(CO)_8] + CO$$

The anion may pick up protons to yield $|HFe(CO)_4|^-$ and then $H_2Fe(CO)_4$. The reaction is supposed to proceed by nucleophilic attack of $\bar{O}H$ on the carbon atom of the carbonyl group followed by the electron transfer of the metal atom of carbon dioxide which gets converted into carbonate as.



(ii) The carbonylate anions can also be obtained by the reduction of metal carbonyls with alkali metal amalgams or borohydrides produce carbonylate ions. E.g.

$$Cr(CO)_6 \xrightarrow{Na/NH_3} Na_2[Cr(CO)_5]$$

$$Cr(CO)_6 \xrightarrow[THF]{NaBH_4} Na[HCr_2(CO)_{10}]$$

$$Cr(CO)_6 \xrightarrow[NH_3]{NaBH_4} Na_2[Cr_2(CO)_{10}]$$

$$Co_2(CO)_8 \xrightarrow[THF]{Na/Hg} 2Na[Co(CO)_4]$$

$$Mn_2(CO)_{10} \xrightarrow[THF]{Na/Hg} 2Na[Mn(CO)_5]$$

$$Re_2(CO)_{10} \xrightarrow[THF]{NaBH_4} Na_2[Re_4(CO)_{10}]$$

$$V(CO)_6 + Na \xrightarrow{NH_3(l)} Na^+[V(CO)_6]^-$$

(iii) Many substituted carbonyl anions can be obtained by displacement of CO from a metal carbonyl E.g.

$$Mo(CO)_6 + NaB_3H_8 \rightarrow Na[Mo(CO)_5B_3H_8] + CO$$

$$(CH_3)_4NI + Mo(CO)_6 \rightarrow (CH_3)_4\,N[Mo(CO)_5I] + CO$$

$$Fe(CO)_5 + |Mn(CO)_5|^- \xrightarrow{hv} [Fe(Mn)(CO)_9]^- + CO$$

*Ferrocene

Ferrocene is an organometallic compound with the general formula $Fe(C_5H_5)_2$. It is the prototypical metallocene, a type of organometallic chemical compound consisting of two cyclopentadienyl rings bound on opposite sides of a central metal atom. Such organometallic compounds are also known as **sandwich compounds** (It is a chemical compound featuring a metal bound by haptic covalent bonds to two arene ligands. The arenes have formula C_nH_n, substituted derivatives and heterocylic derivatives.) The rapid growth of organometallic chemistry is often attributed to the excitement arising from the discovery of ferrocene and its many analogous.

Its IUPAC name is bis(η^5-cyclopentadienyl) iron.

Preparation of ferrocene

Different methods to prepare ferrocene are :

(i) **Reaction of iron halide with cyclopentadienide in the presence of strong base :** When iron (II) chloride is treated with cyclopentadiene in an amine, ferrocene is formed.

$$FeCl_2 + \underset{\text{Cyclopenta-diene}}{2C_5H_6} \xrightarrow{2(C_2H_5)_2NH} \underset{\text{Ferrocene}}{Fe(C_5H_5)_2} + 2(C_2H_5)_2NH_2Cl$$

(ii) **By the reaction of iron halide with sodium cyclopentadienide :** When sodium cyclopentadiene is refluxed with $FeCl_2$ in the presence of tetrahydrofuran (THF) ferrocene is obtained.

$$FeCl_2 + 2C_5H_5Na \xrightarrow[\text{THF}]{\text{Reflux}} (C_5H_5)_2Fe + 2NaCl$$

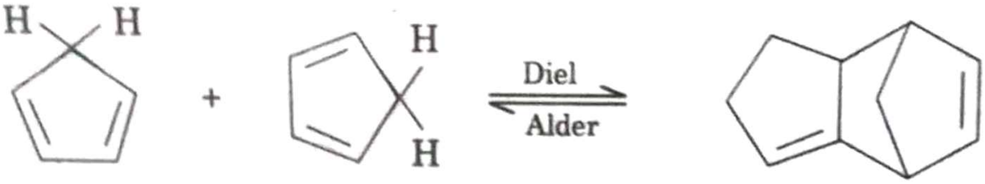
(iii) **By the reaction of iron halide with Grignard reagent :** Ferrocene can be prepared by heating Grignard reagent with $Fe(II)Cl_2$.

$$FeCl_2 + 2(C_5H_5)MgBr \longrightarrow \underset{\text{Ferrocene}}{(C_5H_5)Fe} + MgCl_2 + MgBr_2$$

(iv) **By the reaction of iron oxide with cyclopentadiene :** When cyclopentadiene is heated with iron oxide, ferrocene is formed.

$$\mathrm{FeO} \quad + \quad 2C_5H_6 \xrightarrow{523\ \mathrm{K}} \underset{\text{Ferrocene}}{(C_5H_5)_2Fe} \quad + \quad H_2O$$

(v) **Laboratory preparation :** Ferrocene is prepared in the laboratory by the use of cyclopentadiene. But at the room temperature cyclopentadiene exists as a dimer i.e., dicyclopentadiene ($C_{10}H_{10}$). In order to get monomer (C_5H_6), the dimer is cracked at 453 K slowly in a flask placed in an oil bath.



After initial frothing, the monomer starts distilling off at 315.44 K and collected in a receiver which is placed in an ice bath to prevent dimerisation of monomer fig. 36.

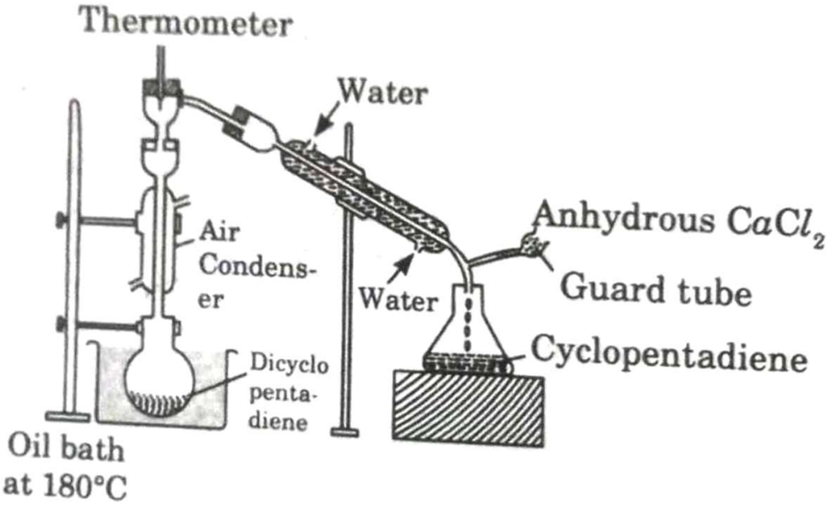


Fig. 36 Cracking of dicyclopentadiene.

Cyclopentadiene so obtained is firstly converted to potassium cyclopentadienide which on treatement with fresh $FeCl_2$ gives ferrocene.

$$C_5H_6 + KOH \rightarrow C_5H_5K + H_2O$$

$$2C_5H_5K + FeCl_2 \rightarrow (C_5H_5)_2\,Fe + 2KCl$$

The fresh sample of $FeCl_2$ is recommended because older sample are contaminated with oxidised product, $FeCl_3$. The water formed in the reaction is removed by using excess of KOH. C_5H_5K being air sensitive, therefore, the reaction is carried out in the atmosphere of N_2.

In actual Practice, potassium hydroxide (50 g) and diethyl ether (120 mL) are taken in a conical flask and stirred for about 10 minutes. Then 11 mL of cyclopentadiene is added and the mixture is stirred for another 10 minutes. Then a solution of powdered $FeCl_2 \cdot 4H_2O$ (13 g) is 50 mL of dimethyl sulphoxide (DMSO) is added dropwise with stirring into the above mixture with the help of dropping funnel fig. 37.

Physical Properties : The important physical properties of ferrocene are :

(i) It is an orange yellow solid.

(ii) It is soluble in organic solvent and insoluble in water.

(iii) Its melting point is 446 K

(iv) It has high thermal stability and is stable upto 773 K.

(v) It has the property of sublimation.

2

Acids and Bases : HSAB Concept

Acid and **base** are very frequent terms, but it is difficult to define term accurately. However, they show typical behaviour in chemical actions. Such behaviour may lead to their definitions which may be called operational definitions.

The operational definitions of acids and bases were closely experimental. An acid is a substance whose aqueous solution :

(i) tastes sours (ii) turns blue litmus red (iii) neutralises bases (iv) reacts with active metals to liberate hydrogen. On the other hand base is defined as a substance whose aqueous solution :

(i) tastes bitter (ii) turns red litmus to blue (iii) neutralises acids and (iv) gives a soapy touch

Some important theories of acids and bases are described below :

Arrhenius concept of acids and bases

S. Arrhenius in 1887 put forward his famous theory of electrolytic dissociation. According to this theory acids are those substances which dissociate in water to give hydrogen (H^+) ions. For example, substances such as HCl, HNO_3, H_2SO_4, CH_3COOH and HCN are acids because they liberate H^+ ions when dissolved in water.

$$HCl\,(g) \xrightarrow{\text{Water}} H^+\,(aq) + Cl^-\,(aq)$$

$$HNO_3\,(l) \xrightarrow{\text{Water}} H^+\,(aq) + NO_3^-(aq)$$

$$HCN\,(g) \xrightleftharpoons{\text{Water}} H^+\,(aq) + CN^-\,(aq)$$

$$CH_3COOH \xrightleftharpoons{\text{Water}} CH_3COO^-\,(aq) + H^+\,(aq)$$

$$H_2SO_4(l) \xrightleftharpoons{\text{Water}} 2H^+\,(aq) + SO_4^{2-}\,(aq)$$

In general

$$\underset{\text{Acid}}{HA} \xrightleftharpoons{\text{Water}} H^+\,(aq) + A^-(aq)$$

Lewis Concept of Acids and Bases

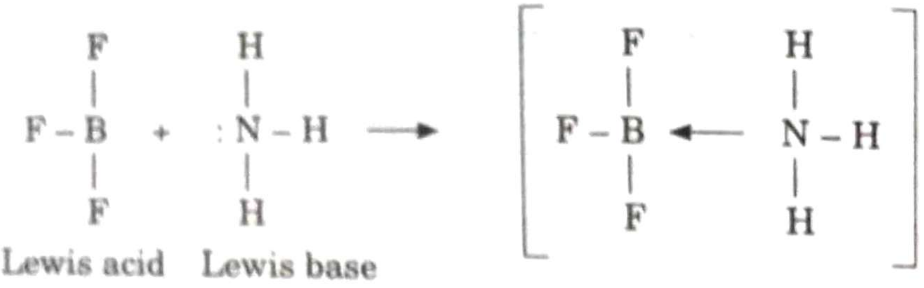
In 1923, G.N. Lewis proposed a broader concept of acids and bases. This concept eliminated the necessity of the presence of hydrogen in the acid and this included many more substances as acids and bases. According to Lewis concept.

An **acid** is a substance which can accept a pair of electrons whereas a base is a substance which can donate a pair of electrons. In other words, an acid is an electron pair acceptor while base is an electron pair donor.

According to this concept, the reaction between an acid and a base is the formation of a coordinate bond or dative bond between them.

E.g.

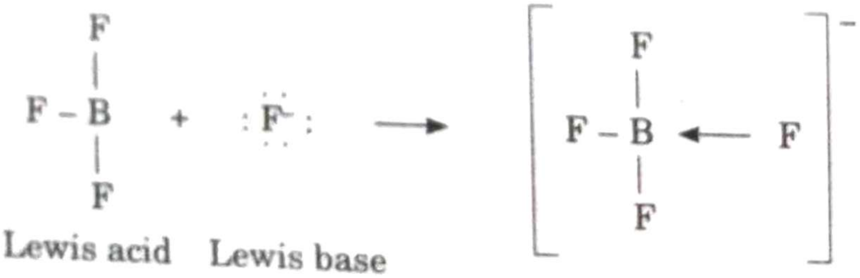
(i) **Reaction between BF_3 and NH_3**



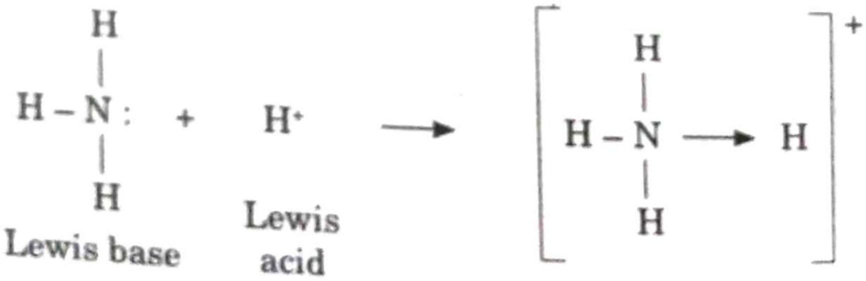
Since NH_3 can donate *a* pair of electrons while BF_3 can accept a pair of electrons, NH_3 is a Lewis base and BF_3 is a Lewis acid.

Similarly, reactions between the followings :

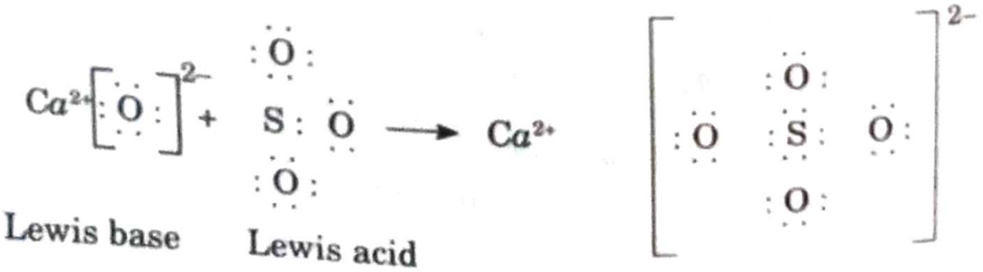
(ii) **Reaction between BF_3 and F^-**



(iii) **Reaction between NH_3 and H^+**



(iv) **Reaction between SO_3 and CaO**



Types of Lewis bases : Lewis bases can be of three types : These are,

(i) **Neutral molecules having at least one lone pair of electrons :** For example : $:NH_3$, $R-\ddot{N}H_2$, $R-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}H$ and $H-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H$ act as Lewis bases because they contain pair of electrons

$:NH_3$	$R-\ddot{N}H_2$	$R-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H$	$H-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H$
(Ammonia)	(1°-amine)	(Alcohol)	Water

(ii) **Negatively charged ions :** For example, F^-, Cl^- Br^-, I^-, $\bar{C}N$, $\bar{O}H$ and O^{2-}. The greater the charge density, the greater is the base strength.

(iii) **Unsaturated hydrocarbons :** For example alkenes ($\rangle C = C\langle$), alkynes ($-C \equiv C-$), butadiene ($\rangle C = CH - CH = C\langle$) and benzene ($C_6H_6$) are treated as Lewis bases because they can form π-complexes with metals in low oxidation states. CO is also act as Lewis base because of the presence of a lone pair on : CO. In these cases both the metal as well as the Lewis base show dual character of donors and acceptors. The reactions may be written as

$$Ni + 4CO \rightarrow Ni(CO)_4$$

$$Fe + 5CO \rightarrow Fe(CO)_5$$

$$Cr + 6CO \rightarrow Cr(CO)_6$$

$$Cr + 2C_6H_6 \rightarrow Cr(C_6H_6)_2$$

Limitations of Lewis Concept : No doubt, the Lewis concept of acids and bases is the most general and has broader applications than Arrhenius and Bronsted concepts. However, it suffered from some serious drawbacks as follows :

(i) It fails to compare the relative strengths of acids and bases because the combination of acids and bases result in the formation of Co-ordinate bond and there is not complete transference of electrons.

(ii) The necessary requirement in Lewis concept is the formation of a coordinate bond between the acid and base, However, acids like HCl and H_2SO_4 are well known protonic acids but they do not form co-ordinate bond with the bases.

(iii) Acid-base reaction are quite fast but formation of coordinate compound is slow, therefore, it does not fit in the normal acid-base concept.

(iv) The catalytic activity of an acid due to H^+ (*aq*) ion. Since the presence of hydrogen is not an essential requirement for a Lewis acid. Many Lewis acids will not have this property.

(v) Lewis concept is so general that it consider every reactions forming a co-ordinate bond to be acid-base reaction. This however, may not be always true. E.g. in $Ni(CO)_4$, nickel is acid because it forms the coordinate bond with CO.

Solvent System Concept (Cady Elsey's Concept)

The solvent system concept of acids and bases was put forward by Cady and Elsey and extended by Franklin. This concept covers aqueous as well as non-aqueous solvents. Non-aqueous solvent like HF, NH_3, H_2SO_4 and CH_3COOH are called protonic solvents and non-aqueous solvents like CCl_4, SO_2 and $COCl_2$ are called non-protonic solvents. This concept depends upon the mode of self ionization of the solvent. It explains the behaviour of solutes in different solvents in terms of various species they form in solutions. According to this concept :

An acid is a substance (solute) which either by direct dissociation or dissolution increases the concentration of cations characteristic of the solvent. Similarly, base is a substance (solute) which either by direct dissociation or dissolution increases the concentration of anions characteristic of the solvent.

For example, consider the dissociation of water, It dissociates as

$$H_2O \quad + \quad H_2O \quad \rightleftharpoons \quad \underset{\substack{\text{Cation}\\ \text{characteristic}\\ \text{(Acid ion)}}}{H_3O^+} \quad + \quad \underset{\substack{\text{Anion}\\ \text{characteristic}\\ \text{(Base ion)}}}{\bar{O}H}$$

When a substance is dissolved in water, if it increases the concentration of H_3O^+ ions in water is an acid while the one that increases the concentration of $O\bar{H}$ ions in water is a base.

E.g : HCl is an acid in water as it produces H_3O^+ ions.

$$\underset{\text{(Acid)}}{HCl} \quad + \quad \underset{\text{(Base)}}{H_2O} \quad \rightleftharpoons \quad \underset{\text{(Acid)}}{H_3O^+} \quad + \quad \underset{\text{(Base)}}{Cl^-}$$

NH_3 is a base in water as it produces $\bar{O}H$ ions.

$$\underset{\text{(base)}}{NH_3} \quad + \quad \underset{\text{(Acid)}}{H_2O} \quad \rightleftharpoons \quad \underset{\text{(Acid)}}{NH_4^+} \quad + \quad \underset{\text{(Base)}}{O\bar{H}}$$

The cations and anions produced by the self-ionization of some protonic and non-protonic acids are :

$$\underset{\textbf{Solvent}}{H_2SO} \quad + \quad H_2SO_4 \quad \rightleftharpoons \quad \underset{\substack{\textbf{Acid ion}\\ \textbf{(Cation)}}}{H_3SO_4^+} \quad + \quad \underset{\substack{\textbf{Base ion}\\ \textbf{(Anion)}}}{HSO_4^-}$$

Classification of Acids and Bases as hard and soft

Based upon the assumption that hard acids prefer hard bases and soft acids prefer soft bases. It is possible to classify any acid or base as hard or soft by its preference for hard or soft associate. For example, given base, B can be classified as hard or soft by its behaviour in the following equilibrium

$$CH_3Hg^+ + BH^+ \rightleftharpoons CH_3HgB^+ + H^+$$

Here monovalent cation of methyl mercury, CH_3Hg^+ is typical soft acid. It will prefer to bind itself to a soft base. If B is soft base then the equilibrium will shift to the right hand side to form CH_3HgB^+. If B is hard base then the equilibrium shifts to left hand side.

A general classification of some common hard and soft acids alongwith some borderline cases is listed in Table : 4.

Table 4. Classification of Acids

Hard Acids	Borderline Acids	Soft Acids
H^+, Li^+, Na^+, K^+, (Rb^+, Cs^+)	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	$Co(CN)_5^{3-}$, Pd^{2+}, Pt^2, Pt^{4+}
Be^{2+}, $Be(CH_3)_2$, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	Rh^{3+}, Ir^{3+}, Ru^{3+}, $B(CH_3)_3$, GaH_3	Cu^+, Ag^+, Au^+, Cd^{2+}, Hg_2^{2+} Hg^{2+}, CH_3Hg^+ BH_3, $Ga(CH_3)_3$, $GaCl_3$
Sc^{3+}, La^{3+}, Ce^{4+}, Gd^{3+}, Lu^{3+} Th^{4+}, U^{4+}, UO_2^{2+}, Pu^{4+}	R_3C^+, $C_6H_5^+$, Sn^{2+}, Pb^{2+}	$GaBr_3$, $GaTl^+$, $Tl(CH_3)_3$,

PEARSON'S HSAB PRINCIPLE

Pearson proposed a simple rule for predicting the stability of coordination compounds formed between acids and bases and often termed as Pearson's HSAB principle. "It states that hard acid prefer to bond to hard bases and soft acids prefer to associate with soft bases."

Particularly, hard acids will exhibit the following order of preference of binding the donor atoms or ions within a group.

$$F^- >> Cl^- > Br^- > I^-$$

$$R_2O >> R_2S$$

$$R_3N >> R_3P$$

Applications of HSAB principle : HSAB principle is extremely useful in explaining the following :

1. Stability of Complexes : Pearson in 1963, used the concept of HSAB principle to explain the relative stability of the complexes. Consider the complex AB which is formed as follows :

$$\underset{\text{Lewis acid}}{A} \quad + \quad \underset{\text{Lewis base}}{:B} \longrightarrow \underset{\text{Complex}}{A:B}$$

(a) The complex AB would be most stable if either A and B both are hard or A and B both are soft.

(b) The complex AB would be least stable if A is hard and B is soft and A is soft and B is hard. E.g.

(i) AgI_2^- is stable while AgF_2^- does not exist. Ag^+ ion is soft acid. I^- is a soft base. According to the principle of HSAB, soft acid, Ag^+ must interact with soft base, I^- to form stable complex, AgI_2^-. This is soft-soft interaction $(s-s)$

$$\underset{\text{Soft acid}}{Ag^+} \quad + \quad \underset{\text{Soft base}}{2I^-} \longrightarrow \underset{\text{Stable complex}}{|AgI_2|^-}$$

(ii) Ag^+ is a soft acid, F^- ion is a hard base. So interaction between soft acid, Ag^+ and hard base, F^- gives unstable product, AgF_2^- so according to the principle of HSAB, soft-soft $(s-s)$ or hard – hard $(h-h)$ interaction give only the stable complex.

$$\underset{\text{Soft acid}}{Ag^+} \quad + \quad \underset{\text{Hard base}}{2F^-} \longrightarrow \underset{\text{Unstable complex}}{|AgF_2|^-}$$

(iii) $|CoF_6|^{3-}$ is more stable than $|CoI_6|^{3-}$. It can be explained as follows. Co^{3+} ion is hard acid while F^- is a hard base. So, the interaction between hard acid, Co^{3+} and hard base, F^- gives a stable complex, $|CoF_6|^{3-}$

$$\underset{\text{Hard acid}}{Co^{3+}} \quad + \quad \underset{\text{Hard base}}{6F^-} \longrightarrow \underset{\text{Stable complex}}{|CoF_6|^{3-}}$$

while the interaction between hard acid, Co^{3+} and soft base, I^- gives unstable complex, $|CoI_6|^{3-}$.

$$\underset{\text{Hard acid}}{Co^{3+}} \quad + \quad \underset{\text{Hard base}}{6I^-} \longrightarrow \underset{\text{Unstable complex}}{|CoI_6|^{3-}}$$

2. Prediction of feasibility of a reaction : According to the principle of HSAB, only those complexes would be more stable which involve soft-soft $(s-s)$ or hard-hard $(h-h)$ interactions. Complexes formed because of hard-soft $(h-s)$ or soft-hard $(s-h)$ interactions are unstable.

The feasibility of a reaction can be predicted by considering the example

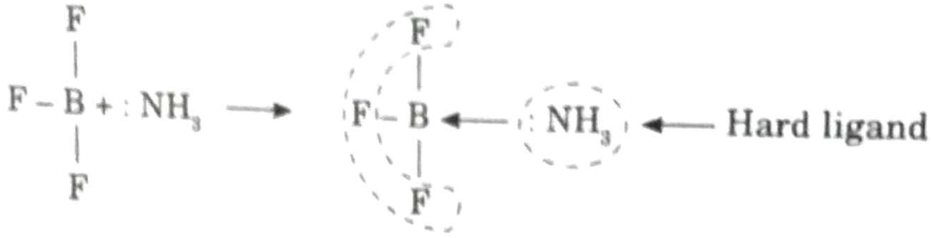
$$LiI + CsF \longrightarrow LiF + CsI \qquad \Delta H = -138 \text{ kJ}$$

Here I^- is a soft base while F^- is a hard base. Li^+ is a hard acid while Cs^+ ion is a soft acid. According to the principle of HSAB, soft-soft $(s-s)$ or hard-hard $(h-h)$ interactions give stable complex.

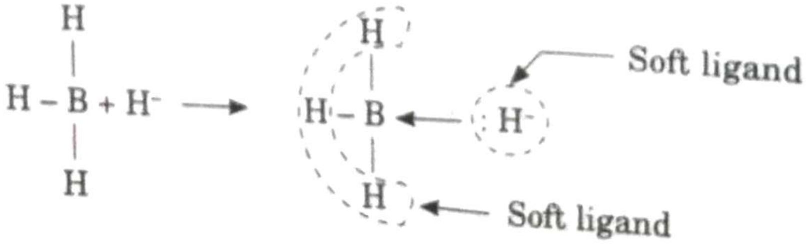
SYMBIOSIS

Soft ligands prefer to get attached with a centre which is already linked with the soft ligands. Similarly hard ligands prefer to get attached with a centre which is already linked with hard ligands. This tendency of ligands is called **symbiosis.** This term was proposed by Jorgenson in 1868. For example, formation of, $F_3B \leftarrow :NH_3$ adduct and BH_4^- ion. Hard ligand like NH_3 co-ordinates with B–atom of BF_3 molecule are also hard ligands.

Thus,



Similarly, the formation of BH_4^- ion by the combination of BH_3, in which H–atoms are soft ligands and H^- ions which is soft ligands can also be explained.



The formation of $F_3B \leftarrow :NH_3$ adduct can also explained on the basis of the fact that since BF_3 and NH_3 are hard acid and hard base respectively, they combine together to form a stable $F_3B \leftarrow :NH_3$ adduct.

BF_3 (Hard acid) + $:NH_3$ (Hard base) → $F_3B \leftarrow :NH_3$ (Stable adduct)

Similarly, since BH_3 is soft acid and H^- ion is a soft base, there combination gives a stable BH_4^- ion

BH_3 (Soft acid) + H^- (Soft base) → BH_4^- (Stable ion)

IMPORTANT QUESTIONS

1. What is Bronsted–Lowry concept of acids and bases? How does this concept differ from Arrhenius concept of acids and bases?
2. Explain the following effects determining the relative strengths of Lawis acids and bases:
   (i) Inductive effect
   (ii) Resonance
   (iii) Steric effect.
3. What is the effect of substituents and solvents on the strengths of acids and bases?
4. (a) Methyl pyridine is weaker base than pyridine. Explain.

(b) Define acids and bases in term of Lux Flood concept.

(c) Justify by Lewis concept that CO_2 is an acid.

5. Which of the following are Hard acids and Hard bases? H^+, Li^+, NH_3, N_2H_4.

6. Classify the following into hard, soft and boarder line acids and bases.
I^-, CO, CO_2, Ag^+, NH_4^+, Ni^{2+}, SO_3^{2-}, H_2O.

7. Which one is the stronger acid out of H_2S and H_2Se and why?

8. Why $(CH_3)_3$ N is a stronger base than NH_3.

9. Write the conjugate acid of the following :
(i) NH_3 (ii) H_2O (iii) S^{2-} (iv) CN^- (v) CH_3COO^-.

10. What is Lux-Flood concept of acids and bases? Explain with examples.

11. Explain hardness and softness of acid and bases by electronegativity.

12. Justify the following reactions on the basis of HSAB principle :
(i) $Ag^+ + 2F^- \rightarrow AgF_2^-$
(ii) $HgF_2 + BeI_2 \rightarrow BeF_2 + HgI_2$

13. Classify the following as hard, soft and boarderline acids : (i) I^{7+} (ii) Pt^{2+}, (iii) Ag^+ (iv) Bi^{3+}.

14. Explain symbiosis with example.

15. (a) Discuss the effect of solvents on the strength of acids and bases.
(b) Explain why H_2S is stronger acid than H_2O?
(c) 2–Methyl pyridine is a weaker base than pyridine. Explain.

16. Explain the following : $HClO_4$ is a stronger acid than HClO.

17. Arrange the following in order of the increasing *pka* value and also give reasons :
$HClO_2$, $HClO_3$, HClO and $HClO_4$.

18. What do you understand by levelling effect of solvent?

19. How will you determine the relative strength of hard and soft acids and bases?

20. Explain in detail symbiosis.

21. Classify the following bases as hard and soft : PO_4^{3-}, ClO_4^-, N_2H_4, C_2H_4, NO_3^-, CH_3COO^-, CO_3^{2-}, I^-.

22. AgI_2^- is stable but AgF_2^- is unstable. Explain why?

23. What are hard acids and bases? Give their important characteristics.

24. What are hard-soft acids and bases. Give two examples of each class.

25. Explain how electronegativity can be used to explain hardness and softness of acids and bases.

26. Why hard-hard interactions are generally ionic, soft-soft interactions are generally covalent. Why is it so?

27. (a) Define symbiosis [K.U.K. 2018]
(b) How is electronegativity related with hardness and softness?
(c) Explain the acidic strength of following compounds : NH_3, CH_4, HF and H_2O.
(d) What is the Lux-Flood concept of acids and bases?

28. Which of the following are hard acids and hard bases?
H^+. Li^+, NH_3, N_2H_4 [GNDU 2006]

29. Classify the following into hard, soft and border line acids and bases : [Pbi. Uni. 2006]
I^-, Co, Ni^{2+}, CO_2, Ag^+, NH^+_4, SO_3^{2-}, BH_3, H_2O, NO_3^-

3

BIOINORGANIC CHEMISTRY

Bio-inorganic chemistry is an interdisciplinary area composed of mainly biochemistry and inorganic chemistry. Bioinorganic chemistry is the understanding of the influence of role of inorganic material (mainly metal ions) to the biological processes e.g. electron transport, ion transport, mineralisation of inorganic materials, mutation, inorganic species in medical therapy and diagnosis etc. In short, bioinorganic chemistry deals with the chemical reactions accompanying life processes of plants and animals. In a very simple way, bioinorganic chemistry deals with the study of the roles of metal ions in biology.

This branch is fast developing branch of chemistry because of its importance in the biological systems. Bioinorganic chemistry have led to the understanding of biological systems and insight into its structure. This has also improved us to synthesize and characterise new inorganic compounds which resemble those rooted in living systems.

Essential and trace Elements in Biological systems :

Bioinorganic chemistry means that the inorganic elements in the chemistry of life. The studies of biochemical relations occurring with the body of living organisms have shown that certain metal ions play an important role in normal growth and functioning of the biological processes.

The inorganic elements have many roles such as skeletal parts of bones and teeth, as prosthetic groups of many enzymes and as electrolytes in sustaining water balance in vascular system and tissues. The abundance of elements in human body, earth's crust and sea water is listed in table–1.

Table–1. Chemical abundance of elements in human body, earth's crust and sea water

Composition of human body		Composition of earth's crust		Composition of sea water	
H	62%	O	46.6%	H	65%
O	26.6%	Si	27.7%	O	33.5%
C	9.5%	Al	8.1%	Cl	0.33%
N	1.42%	Fe	5.0%	Na	0.28%

Essential Elements

The essential elements are those which are absolutely necessary for maintenance of life of plants and animals.

Criteria for an essential elements : Important criteria for an essential elements are :

(i) The elements must be present in tissues in comparable amount.

(ii) The deficiency can be prevented by the addition of that elements.

(iii) The deficiencies are associated by specific biochemical changes which can be prevented when the deficiency is checked.

(iv) A specific bio-chemical function is associated with a particular elements. Depending upon the absolute amounts are divided into two sub-groups.

(a) Bulk elements : These elements are found in higher concentration in biological systems.

(b) Traces elements : These elements are present in very low concentration in biological systems.

There are about 30 elements which are identified as essential to life. These are classified as bulk or structural elements, macrominerals and trace elements. These different types of elements are listed in the Table – 2.

Table–2. Classification of essential elements

Bulk Structural elements	Macro-minerals elements	Trace elements	Ultra-trace elements	
H	Na	Fe	Mo	F
C	K	Cu	Mn	B
N	Mg	Zn	Co	I
O	Ca	V	Cr	

Essential bulk elements

The main essential bulk elements in biological systems are :

(a) **Sodium and Potassium :**

(i) **Sodium** : It is the major cation of the extra cellular fluid and is usually associated with chloride and bicarbonate. It is essential in the regulation of acid-base equilibrium. The sodium ions are also important in maintenance of osmotic pressure of the body fluids and therefore, protect excessive fluid loss. It is widely distributed in food stuffs in the form of common salt. Na^+ ions also help in transportation of CO_2, in neuromuscular irritability and excitability, maintenance of proper viscosity of blood and in the secretion of digestive fluids.

(ii) **Potassium** : It is the principal cation of the intra-cellular fluid. Accordingly, the major sources of dietary K^+ are the cellular materials. K^+ gets very rapidly absorbed by the small intestine in proportion to the requirement and circulates in the plasma. Just like Na^+ ion, K^+ ion also help in maintaning osmotic pressure, in the regulation of acid-base equilibrium, transportation of CO_2, in neuromuscular irritability and excitability, maintenance of proper viscosity of blood and in the secretion of digestive fluids.

(b) **Calcium and Magnesium :** Mg^{2+} and Ca^{2+} ion are essential elements needed for a human body. Mg^{2+} ion is an important constituent of **chlorophyll**. Ca^{2+} present in the body in the form of phosphate. This phosphate gets readily converted into $CaHPO_4$ and $Ca(H_2PO_4)_2$ in acidic medium. These phosphates are absorbed in the intestine and penetrate in the blood plasma. There are many important minerals in biological systems containing Ca^{2+} are listed in Table – 3.

Metalloporphyrins

Porphyrins constitutes an important class of bioinorganic compounds, in which a metal ion is surrounded by four nitrogens of a porphine ring. Porphines are tetradentate ligands made up of four macrocyclic/pyrrole rings linked to each other through methene bridges. Fig. 1 The porphin ligand acts as a conjugated double bonded system with four nitrogen donor sites. Two of the four nitrogen are tertiary (3°) nitrogen while the remaining two nitrogens are secondary (2°) nitrogen. The tertiary (3°) nitrogen atoms form co-ordinate bonds by donating a pair of electrons each to the metal ion by the formation of a co-ordinates bond. It is shown by the arrow head (→). The other two secondary nitrogens (2°) lose a proton each and form a covalent bond with a metal ion as shown in Fig. 2. Therefore, a porphin ring behave as a tetradentate dinegative ligand. As a result, the dipositive cations such as Mg^{2+}, Fe^{2+} or Ni^{2+} will form a neutral complex with porphin.

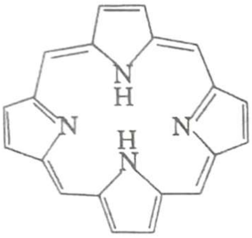


Fig 1. Prophin ligand

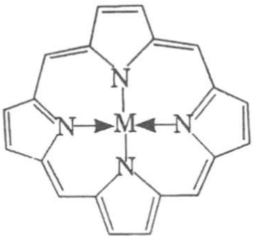


Fig 2. Metal complex with Porphin ligand

When the four pyrrole rings of a porphin are substituted by organic groups other than hydrogen, these are called as **porphyrins.** Therefore, porphyrins are macrocyclic tetrapyrrole systems with conjugated double bonds along with various groups (other than hydrogen) substituted at the periphery of the rings. The substituent attached to the ring are usually organic groups. These groups have electron releasing or electron withdrawing tendencies.

The complexes in which a metal ion, usually a dipositive ion is present in the porphyrin ring are called **metalloporphyrins.** There are biologically important compounds and play a very important role in the plant and animals kingdom. The nature of metalloporphyrins vary with the nature of metal ion and the type of substituents on the porphyrin structures. Porphyrin ring system is fairly rigid because of delocalisation of π-electrons in the molecule. The size of central hole to accommodate metal ion is almost fixed (having a radius of 2A°) and ideal for holding first row transition metal ions or lighter alkaline earth metals. A metal ion of suitable size will form a square planar complex. i.e. the metal ion and four nitrogens lie in the same plane as shown in Fig. 3.

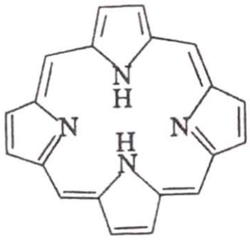


Fig. : 3 Porphin Ligand

Nitrogen Fixation

Nitrogen is an important micronutrient for all forms of life. There is large amount of nitrogen gas (about 78%) in the atmosphere. However, plants are not able to utilize this N_2 because of its unreactive nature. In order to use it as useful compounds it must be changed into some other forms such as ammonium (NH_4^+), nitrates (NO_3^-), nitrites (NO_2^-) or urea (NH_2CONH_2). All these forms are absorbed from the soil water through the root of the plants. In order to fix the nitrogen, the nitrogen cycle occurring in atmosphere involves a cyclic process in which elemental nitrogen is circulated continuously in the living and non-living components of the biosphere.

The process of conversion of atmospheric nitrogen into useful compounds such as ammonia is called nitrogen fixation. The nitrogen cycle involves the transformation of inorganic nitrogen to organic nitrogen and then the reverse degradation process. N_2 is present as nitrate, NO_3^- in the soils and oceans. In this cycle, N_2 take up by biological systems is associated by its reduction to ammonium ion, NH_4^+ and fusion of NH_4^+ into organic linkages such as amino group or amido group. The reduction of nitrate, NO_3^- to ammonium, NH_4^+ occurs in green plants by various fungi and certain bacteria in a metabolic process.

This process of conversion of inorganic compounds of nitrogen into organic compounds that become part of living systems is called nitrogen assimilation.

Animal discharge excess of nitrogen in a reduced form either as ammonium, NH_4^+ or as organic nitrogeneous compounds such as urea. The discharge of nitrogen occurs both during life and succeeding death due to microbial decomposition. Certain bacteria return the reduced form of nitrogen back to environment by oxidising them. Nitrifying bacteria oxidise ammonium, NH_4^+ to nitrate, NO_3^- and denitrifying bacteria then reduce nitrates to N_2 by some microorganisms. The whole process is therefore called **denitrification.**

In this process, some nitrogen is lost to the atmosphere but in turn atmospheric nitrogen is fixed i.e. converted to ammonia by various bacteria. Fixation of nitrogen can occur in two ways :

1. Biological nitrogen fixation
2. Abiological nitrogen fixation

1. Biological nitrogen fixation

In biological nitrogen fixation, nitrogen is reduced to ammonia in a biological process using micro-organisms or enzymes. The main reaction occurring in the process is

$$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$$

The reaction for biological fixation of nitrogen may also be presented as :

$$8H^+ + N_2 + 16\ ATP + 8e^- \rightarrow 2NH_3 + 16\ ADP + H_2 + 16\ Pi$$

The ammonia so formed can then further converted into nitrate, NO_3^- or nitrite, NO_2^- or directly used in the synthesis of amino acids or other essential compounds.

There are many bacteria and blue-green algae that involve in nitrogen fixation. These are of two types

(i) Asymbiotic or free living bacteria (ii) Symbiotic bacteria.

Asymbiotic : The common example of asymbiotic bacteria is **azetobacter** which is an aerobic (requring oxygen) microbe. A large number of anaerobic bacteria such as **clostridium pasteurianum** also fix nitrogen in the absence of oxygen. There is another group of asymbiotic bacteria known as **facultative group** which can group aerobically or anaerobically.

Symbiotic bacteria : Symbiotic bacteria are bacteria living in symbiosis with another organism or with each other. These bacteria fix nitrogen in association with plants. The common

4

Silicones and Phosphazenes

Polymers are very long chain macromolecules with high molecular mass compounds, obtained by joining together a large number of simple molecules through covalent bonds in a regular fashion. The simple molecules which combine to form a polymer are called **monomers** and the process of formation of polymers from the simple starting materials is called **polymerisation**.

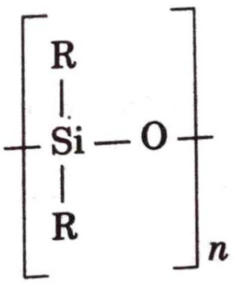
$$x - \text{Monomer} \xrightarrow{\text{polymerisation}} \underset{\text{Polymer}}{(\text{Monomer})_x}$$

The number of monomer molecules which combine to form polymer is called the **degree of polymerisation**. Polymers can be otained from inorganic as well as organic molecules. Silicones and phosphazenes are important examples of inorganic polymers. Inorganic polymers have different properties than organic polymers because of bond formed between inorganic elements are often longer, stronger and more resistant to free radical cleavage reactions in comparison to those formed by carbon atoms. Inorganic elements can have different valencies than carbon and therefore, different number of substituents may be attached to a skeletal atom. Most of the inorganic polymers are based upon relatively few elements of periodic table belonging to group – 13, 14, 15 and 16. The inorganic polymers include elements such as Si, Ge, Sn, P, B, Al, S and a variety of transition elements.

Among these inorganic polymers, silicones and phosphazenes are the two important classes of inorganic polymers. The silicones are a group of organosilicon polymers. They have a wide variety of commercial use in silicone fluids, silicone rubber, silicones grease and silicone resins. Silicones are fairly expensive but have many desirable properties. They are now produced on a large scale than any other group of inorganic polymers.

SILICONES

Silicones are polymeric organo-silicon compounds containing Si – O – Si linkages. These polymer contain alternate silicon and oxygen atoms in which the silicon atoms are joined to organic groups. These are also called as **polysiloxanes.** These polymers having general formula $(R_2SiO)_n$



$$\left[-\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{Si}}}} - O - \right]_n$$

Nomenclature

According to IUPAC system, compounds with the general formula $Si_n H_{2n+2}$ are called **silanes** in relation with alkanes, $C_n H_{2n+2}$. For example, silicon hydride, SiH_4 is called silane like methane, CH_4. A molecule with two silicon atoms, $H_3\,Si - SiH_3$ is called a **disilane** and similarly, $H_3\,Si - SiH_2 - SiH_3$ is called trisilane and so on. The alkyl or aryl halo substituted silanes are named by prefixing 'silane' by the specific group. E.g.

SiH_4	Silane
$H_3\,Si - Si\,H_3$	Disilane
$H_3\,Si - SiH_2 - SiH_3$	Trisilane
$(CH_3)_2\,SiH_2$	Dimethylsilane
$(CH_3)_2\,Si\,Cl_3$	Trichloromethylsilane
$C_2H_5\,SiH_2 - SiH_3$	Ethyldisilane

Hydroxy derivatives of silanes are named by adding the suffixes, – ol, – diol, – triol etc. depending upon the number of hydroxyl groups. These compounds are called as silanols. E.g

$H_3\,Si\,OH$	Silanol
$H_2\,Si\,(OH)_2$	Silandiol
$H\,Si\,(OH)_3$	Silantriol
$(CH_3)_3\,SiOH$	Trimethylsilanol
$(HO)_3\,Si - Si\,(OH)_3$	Disilanehexol

Oxo derivatives are named as **siloxanes :**

$H_3\,Si - O - Si\,H_3$	Disiloxane
$(H_3C)_3 - Si - O - Si\,(CH_3)_3$	Hexamethyldisiloxane

Amino derivatives are named as **silazanes** E.g.

$(CH_3)_3\,Si - NH - Si\,(CH_3)_3$	Hexamethyldisilazane

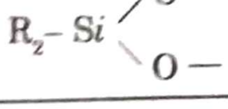
Substituted siloxanes are named after the name of parent compound. E.g.

$Cl_3\,Si - O - SiCl_3$	Hexachlorodisiloxane
$H_3\,Si - O - SiH_2\,(OH)$	Disiloxanol

Polymers are named by specifying the side groups and then the backbone. E.g.

$\{ Si\,(CH_3)_2\,O \}$	Poly (dimethylsiloxane)
$\{ Si\,(CH_3)\,(C_6\,H_5)O \}$	Poly (methylphenylsiloxane)

It may be observed that certain structural segments appear over again in the siloxane backbone and therefore, several abbreviations are commonly used. For example :

Unit	Structure	Designation
Monofunctional group unit	$R_3\,SiO-$	M
Difunctional group unit	 $R_2-Si\begin{matrix}O-\\O-\end{matrix}$	D

Preparation of Silicones

Silicones are prepared by the hydrolysis of alkyl or aryl derivatives of $SiCl_4$ like $R\,SiCl_3$, $R_2\,SiCl_2$ and $R_3\,SiCl$ and polymerisation of alkyl or aryl hydroxy – derivatives obtained by hydrolysis. Therefore, this method consists of the following steps :

(1) **Preparation of alkyl or aryl derivatives of silicon tetrachloride :** Alkyl or aryl derivatives of silicones are prepared by the following methods :

(a) Methyl chlorosilanes such as $(CH_3)\,SiCl_3$, $(CH_3)_2\,SiCl_2$, and $(CH_3)_3\,SiCl$, are prepared by heating methyl chloride, CH_3Cl with Si in the presence of catalyst Cu at 300°C. The reactions gives a mixture of chlorosilanes.

$$2\,CH_3\,Cl + Si \xrightarrow[300^\circ C]{Cu} (CH_3)\,SiCl_3 + (CH_3)_2\,SiCl_2 + (CH_3)_3\,SiCl$$

Methyl Chloride   Mixture of Methyl chlorosilanes + other compounds

The yield of Dimethyldichlorosilane, $(CH_3)_2\,Si\,Cl_2$ is about 50%. These chlorosilanes differ in their boiling points : $CH_3\,SiCl_3$ (66.9°C) $(CH_3)_2\,SiCl_2$ (69.6°C) and $(CH_3)_3\,SiCl$ (87.7°C) are separated by the fractional distillation.

(i) If a mixture of methyl chloride, $CH_3\,Cl$ and HCl is heated with Si in the presence of Cu as catalyst at 300° C, then $(CH_3)SiCl_3$ is obtained as the main product.

$$CH_3\,Cl + 2\,HCl + Si \xrightarrow[300^\circ C]{Cu} (CH_3)\,SiCl_3 + H_2$$

(2) **Hydrolysis of alkyl or aryl derivatives of chlorosilanes :** The hydrolysis of chlorosilanes gives silanols, there polymerises and gives different types of silicones

$$RSiCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} RSi(OH)_3 + 3HCl$$

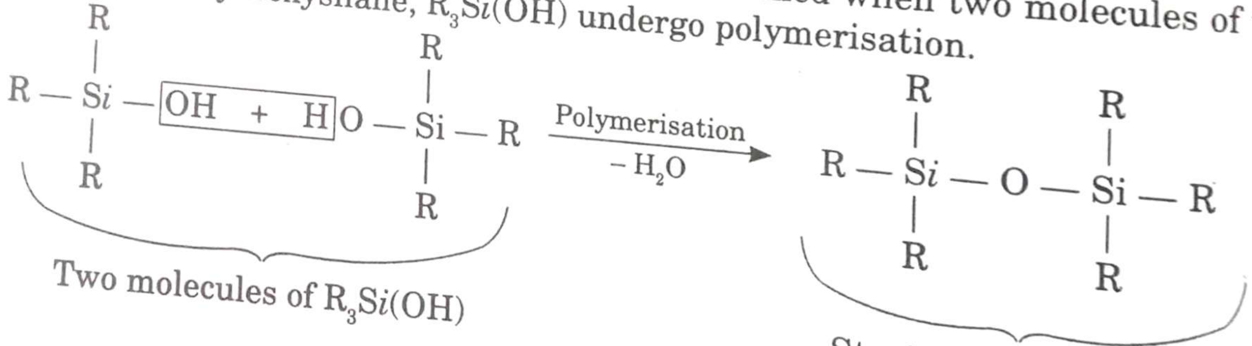
$$R_2SiCl_2 + 2H_2O \xrightarrow{\text{Hydrolysis}} R_2Si(OH)_2 + 2HCl$$

$$R_3SiCl + H_2O \xrightarrow{\text{Hydrolysis}} R_3SiOH + HCl$$

These above reactions generally represented as

$$\text{Chlorosilanes + water} \xrightarrow{\text{Hydrolysis}} \text{Silanols + HCl}$$

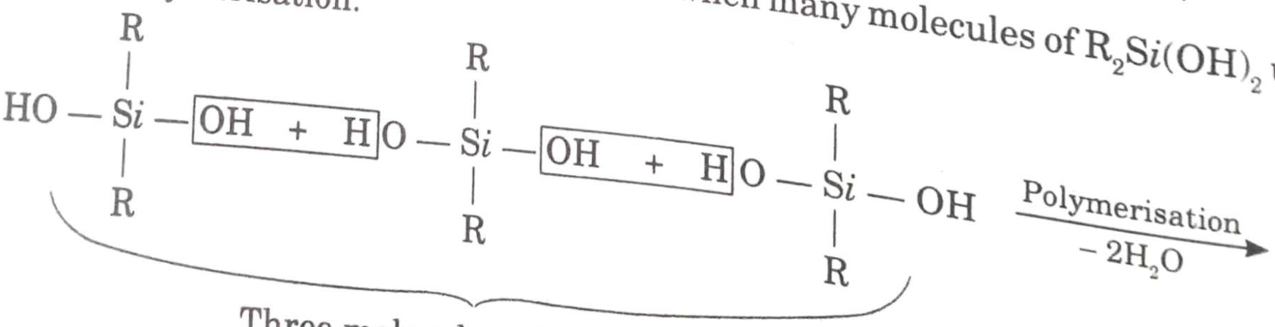
(a) **Straight chain silicones :** These are formed when two molecules of trialkyl monohydroxysilane, $R_3Si(OH)$ undergo polymerisation.



Two molecules of $R_3Si(OH)$

Straight chain silicon
$R_3Si-O-SiR_3$ (dimer)
(It is a siloxane)

(b) **Cyclic silicones :** These are formed when many molecules of $R_2Si(OH)_2$ undergo polymerisation.



Three molecules of $R_2Si(OH)_2$

Properties of silicones

The important general characteristic properties of silicones are :

1. **Thermal stability :** The most important property of silicones in their thermal stability. These polymers can withstand a temperature upto 250° – 300°C. This stability is associated to the relatively high bond strength of Si – O bond. Silicone polymers have low glass transition temperature (Tg). i.e., below this temperature, the silicon polymers behave like a rigid glass, and above this temperature, the polymers behave like a **quasi liquid** i.e., like an elastomers.

   All silicones have good insulating properties. These polymers can withstand at high temperature without charring. It is due to insulating properties that silicones are used in insulating materials for electric motors and other electric appliances.

2. **Chemical stability :** Silicones are not only thermally stable, they are stable towards weak acids, alkalies, salt solutions or water at room temperature. Strong bases and conc. acids may cause depolymerisation. Si – O bond is fairly ionic (about 51%) and can be cleaved by strong acids and strong bases. Many of low molecular weight silicones dissolve in solvents like CCl_4, ether and benzene. They are quite stable to attack by oxygen although some oxidation may occur at higher temperatures. However, the presence of aromatic groups on silicones increases the oxidative stability of the polysiloxanes.

Uses of Silicone polymers

(1) Silicone polymers are used for high temperature oil baths.
(2) Silicone polymers are used as lubricants at both low and high temperature.
(3) They have low toxicity and therefore, these are used in medicinal implants.
(4) They are used as good electrical insulators for electric motors.
(5) Silicone polymers are used for water proofing and in electrical condensers.
(6) Silicone rubbers are useful because they retain their elasticity even at low temperature as compared to other rubbers. They are also mixed with paint to make them damp resistant.
(7) Silicone polymers are used in greases, and varnishes even at low temperature.

Silicone Resins

The silicone resins have ring structures. Their properties depend upon R/Si ratio (R = alkyl group). If the ratio is lowered from 2.0 to 1.0, the polymers becomes progressively less fluid less fusible and less soluble. If the ratio is 1.0, highly cross-linked structure is obtained. Cross-linked polymers have higher density than silicone elastomers. In a stretched elastomer, the molecular chain uncoils through rotation about the – Si – O – bonds. Such rotations are highly restricted. If the R/Si ratio is between 1.0 and 1.6, resin properties become intermediate

Polysiloxane Copolymers

Polysiloxane copolymers of desired properties can be obtained by combining polysiloxanes structures with organic polymer structures. There are two types of co-polymers :

(i) Block copolymer
(ii) Graft copolymer

(i) **Block copolymers :** These are those polymer in which shorter or longer siloxane units are connected by blocks of organic polymer.

$$-x-x-x-x-y-y-y-y-x-x-x-x-$$

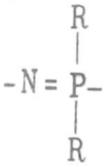
Polysiloxane block copolymers can be similarly represented as

$$\boxed{\text{Siloxane}}-\boxed{\text{Organic polymer}}-\boxed{\text{Siloxane}}-\boxed{\text{Organic polymer}}$$

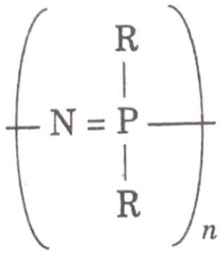
(ii) **Graft copolymers :** These are those polymers in which there are continuous polysiloxane chains which are either connected or substituted by organic polymer blocks.

Poly phosphazenes

These are inorganic polymers containing alternate phosphorous and nitrogen atoms with two substituents on each phosphorous atom. These are chain or cyclic polymers which contain



$-N=\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{P}}-$ as the repeating unit. Their structural formula



$$\left(-N=\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{P}}-\right)_n$$

where substituents R may be inorganic, organic or organometallic units. It may be written as $(NPR_2)_n$, Each macromolecule may contain 15000 or more repeating units linked end to end so that their molecular weight of these macromolecules are in the range of 2 million to 10 million.

Preparation of Phosphazenes

(1) Preparation of polyhalophosphazenes : $(NPCl_2)_n$

(i) These compounds can be prepared by the reaction between phosphorous pentachloride, PCl_5 and ammonium chloride, NH_4Cl in the presence of $C_2H_4Cl_2$ or C_6H_5Cl or by heating PCl_5 with solid NH_4Cl at 140 – 160°C.

$$nPCl_5 + nNH_4Cl \xrightarrow[\text{or } C_6H_5Cl]{C_2H_4Cl_2} (NPCl_2)_n + 4\,nHCl$$

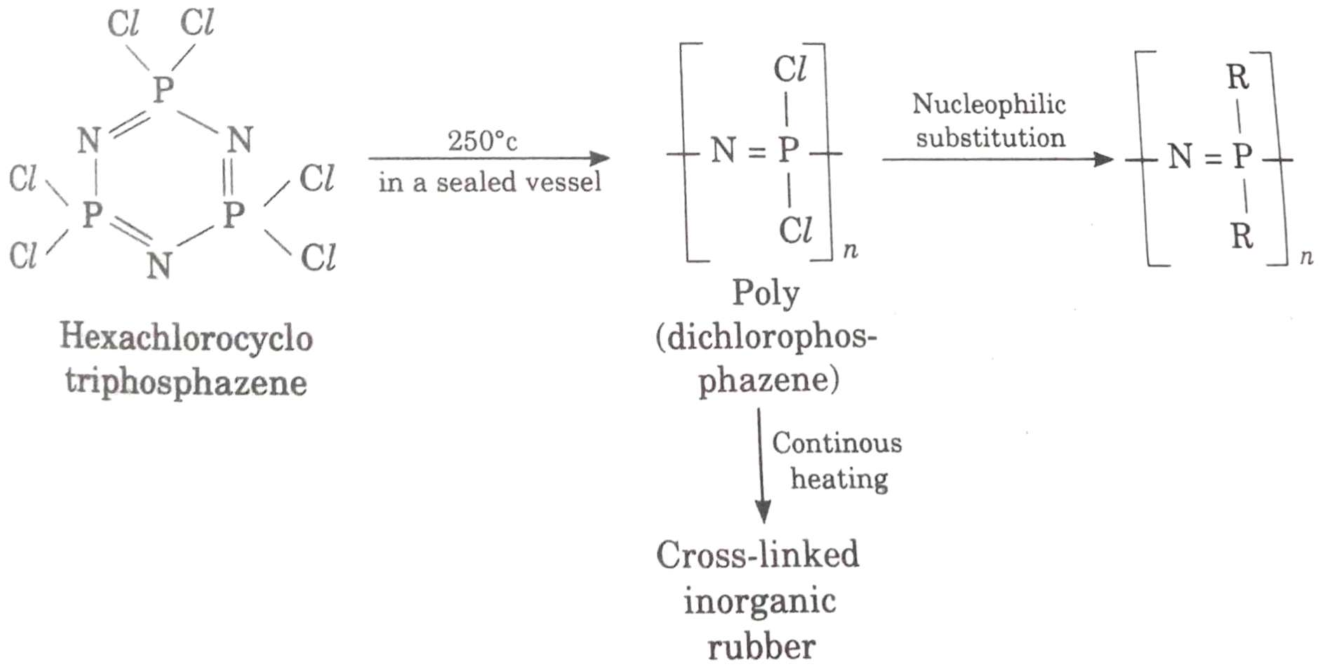
$$nPCl_5 + nNH_4Cl(s) \xrightarrow{140-160^\circ C} (NPCl_2)_n + 4\,nHCl$$

Both these reactions produce a mixture of various phosphonitric chlorides, but under controlled conditions, high yields of $(NPCl_2)_3$ and $(NPCl_2)_4$ can be obtained.

These two compounds can be separated from each other by using the fact that $(NPCl_2)_3$ sublimes in vacuum at 50°C as a white crystalline solid whereas $(NPCl_2)_4$ does not do so under these conditions. The formation of $(NPCl_2)_n$ takes places through the following steps :

(a) $NH_4Cl + PCl_5 \longrightarrow \underset{\text{Amm · hexachloro phosphate (unstable compounds)}}{NH_4PCl_6}$

2 **Preparation of other polyphosphazenes :** The other types of polyphosphazenes are obtained from trimer i.e., hexachlorocyclotriphosphazene. In this method, a timer, $(NPCl_2)_3$ is heated in a molten state in a sealed vessel in the absence of moisture continuously for several days at a temperatures between 200 – 250°C to induce ring opening and polymerisation. This originated in the ring opening of cyclic compound. The originating polydichlorophosphazene when dissolved in a suitable solvent behaves as an excellent macromolecular reactant which gives nucleophilic substitution reaction as given below :



The treatment of poly (dichlorophosphazene) with organic nucleophiles such as sodium salts of alcohols or phenols or with primary amines or secondary amines results in the replacement of chlorine atoms by organic units thereby giving stable drivatives which possess useful properties.

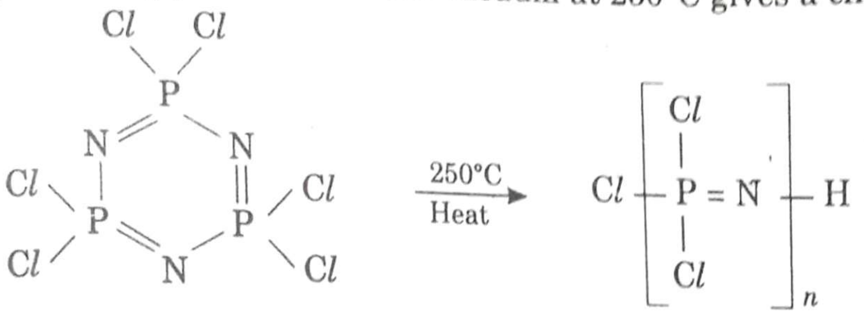
PROPERTIES AND STRUCTURES

Physical properties

(i) $(NPCl_2)_3$ melts at 114°C, boils at 256°C at one atmosphere pressure. It is readily soluble in ether, benzene and carbon tetrachloride. $(NPCl_2)_4$ melts at 123.5°C, boils at 328.5°C. Its solubility is less in ether, benzene or carbon tetrachloride.

(ii) $(NPCl_2)_3$ and $(NPCl_2)_4$ are irritating and some what toxic also.

(iii) $(NPCl_2)_3$ or $(NPCl_2)_4$, when heated in vacuum at 250°C gives a chain polymer.



Chemical Properties

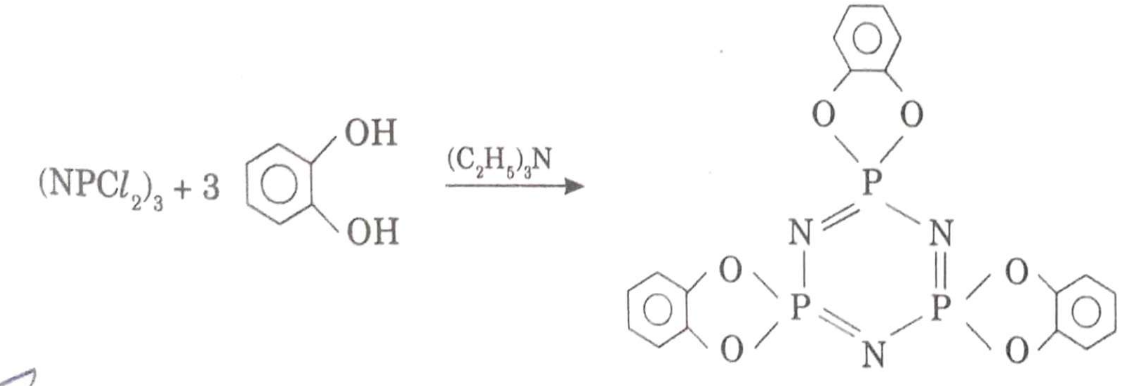
(1) **Reaction involving replacement of chlorine atom of P – Cl bond :** Chlorine atom in P – Cl bond is fairly reactive and can be replaced by many nucleophiles. The mechanism of this replacement is not well understood. However, it appears to involves S_N^2 attack on P – atom.

The following reactions involves the replacement of Cl-atom.

(i) $(NPCl_2)_3 + 6NaF \xrightarrow[(CH_3CN)]{\text{Acctonitrile}} (NPF_2)_3 + 6NaCl$

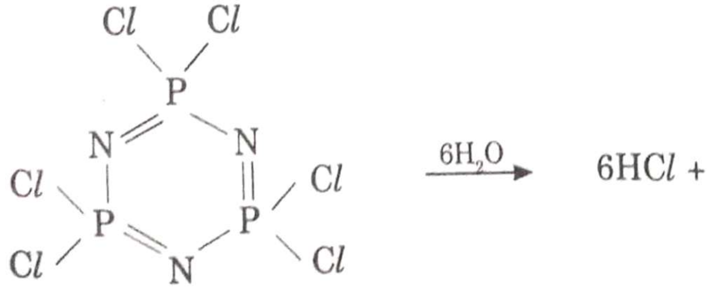
(ii) $(NPCl_2)_3 + 2NaOCH_3 \longrightarrow \underset{\text{Tridimethoxy phosphazene}}{[NP(OCH_3)_2]_3} + 2NaCl$

(iii) $(NPCl_2)_3 + 6C_6H_5MgBr \xrightarrow[\text{toluene}]{\text{Boiling}} [NP(C_6H_5)_2]_3 + 3MgBr_2 + 3MgCl_2$



(2) **Hydrolysis**

(a) $(NPCl_2)_3$ reacts with H_2O in aqueous ether, its all the Cl-atoms are replaced by – OH groups



$(NPCl_2)_3$