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Chapter
1

Chemistry Of Representative Elements

GENERAL GROUP TRENDS OF REPRESENTATIVE ELEMENTS

Elements in the long form of periodic table are arranged according to their increasing atomic number and electronic configuration in such a manner that their general properties are correlated to each other.
They exhibit a regular trend in properties within each group, with some exceptions or anomalies occurring in specific positions.

Group Trend

The regular variations in the properties of elements in a group of periodic table is called group trend

Atomic Radii

Atomic radius is the distance between the nucleus of an atom to its outermost electron shell.

Group Trends

IA and IIA Groups

- ✓ Elements of group IA are termed as alkali metals.
- ✓ They possess the largest atomic radii in their respective periods.
- ✓ However the atomic radii increase regularly from lithium to francium.
- ✓ It is because the number of energy levels occupied by electrons increases, resulting in an increase in the distance between the nucleus and the outermost electronic shell.
- ✓ The same trend applies to the elements of group IIA (Be to Ra).
- ✓ That means beryllium is the smallest alkaline earth metal (IIA) and barium is the largest.

Alkali Metals (Group IA)	**Atomic Radii (pm)**
Li	152
Na	186
K	227
Rb	248
Cs	264
Fr	348

Alkaline Earth Metals (Group IIA)	**Atomic Radii (pm)**
Be	112
Mg	145
Ca	194
Sr	219
Ba	253
Ra	215

IIIA Group

- ✓ Atomic radii of the elements of Boron family (Group IIIA) generally increase down the group (from boron to thallium).
- ✓ There is an exception to the trend between aluminium and gallium. Gallium has slightly smaller atomic radii than aluminium despite being located below it in the group.
- ✓ It is because of poor shielding effect caused by electrons of d-orbitals.

IVA to VIIIA Groups

- ✓ The atomic radii of elements of Group IVA to Group VIIIA follow the similar group trend, increasing regularly from top to bottom within the group.
- ✓ The same reason for this trend is discussed as in the group trend of alkali metals.

IIIA	IVA	VA	VIA	VIIA	VIIIA
B	**C**	**O**	**N**	**F**	**Na**
-85	-77	-75	-73	-72	-71
Al	**S**	**P**	**S**	**CI**	**Ar**
-143	-118	-110	-103	-100	-98
Ga	**Ge**	**As**	**Se**	**Br**	**Kr**
-135	-122	-120	-119	-114	-112
In	**Sn**	**Sb**	**Te**	**I**	**Xe**
-167	-140	-140	-142	-133	-131
TI	**Pb**	**Bi**	**Po**	**At**	**Rn**
-170	-146	-150	-168	-140	-141

Ionization Energy

"It is the energy needed to remove an electron from a neutral atom in the gas phase".

Group Trends

IA and IIA Groups

- ✓ The ionization energy of alkali metals (Group IA) and alkaline earth metals (Group IIA) decreases as we move down the group.
- ✓ This is because the outermost electrons of these elements are located farther away from the nucleus as we go from top to bottom, leading to weaker attractive forces between the electrons and the nucleus.
- ✓ As a result, it requires less energy to remove the outer shell electrons from the atom, that is why the ionization energy decreases.

IIIA Group

- ✓ The ionization energy (IE) trend in group IIIA elements has irregularities as we move down the group.
- ✓ Two exceptions highlight this irregularity. Firstly, gallium (Ga) has a higher ionization energy than aluminium (A). Secondly, thallium (TI) exhibits a higher ionization energy than indium (n). These irregularities occur due to insufficient shielding of the nuclear charge in gallium
- ✓ by 3d electrons and in thallium by 4f electrons.

IVA Group

- ✓ The ionization energy of group IVA elements generally decreases from top to bottom in the group. There are irregularities observed between Tin (Sn) and Lead (Pb).
- ✓ This is because both tin and lead have nearly the same atomic radii, which is a result of the lanthanide contraction.
- ✓ Due to this, the attraction between the nucleus and the outer electrons becomes stronger and requires more energy to remove these electrons.

VA, VIA, VIIA and VIIIA Groups

- ✓ The ionization energy of the remaining groups of representative elements (group VA, VIA, VIIA, VIIIA) follows a regular pattern.
- ✓ It decreases progressively from top to bottom as the atomic radii increase,

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
-520	-900	-800	-1090	-1400	-1310	-1680	-2080
Ne	**Mg**	**Al**	**Si**	**P**	**S**	**CI**	**Ar**
-490	-730	-577	-780	-1060	-1001	-1250	-1520
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
-420	-590	-580	-762	-960	-950	-1140	-1350
R	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
-400	-550	-560	-700	-830	-870	-1010	-1170
Cs	**Ba**	**TI**	**Pb**	**Bi**	**Po**	**At**	**Rn**
-380	-500	-590	-710	-800	-810	-920	-1030

Electronegativity (EN)

"It is the measure of the tendency of an atom to attract the shared pair of electrons towards itself when it is involved in a covalent bond".

Group Trends

IA and IIA Groups

- ✓ The electronegativity (EN) of alkali metals (Group IA) and alkaline earth metals (Group IIA) follows a regular decreasing trend from top to bottom.
- ✓ This trend can be explained by the regular increase in atomic radii as we move down the group.
- ✓ The larger atomic size results in a decreasing tendency for the atom to attract the shared pair of electrons towards itself.

IIIA Group

- ✓ The electronegativity (EN) of group III elements initially decreases from Boron (B) to Aluminium (Al) and then increases from gallium (Ga) to tellurium (Te).
- ✓ This irregular increase in EN can be attributed to the poor shielding effect of the electrons in the d-orbital and f-orbitals, respectively.

IVA, VA, VIA and VIIA Groups

- ✓ The electronegativity of groups IVA, VÀ, VIA, and VIIA decreases regularly from top to bottom.
- ✓ This trend can be explained by the same reason as discussed for alkali metals

IA	**IIA**	**IIA**	**IVA**	**VA**	**VIA**	**VIIA**
Li	**Be**	**B**	**C**	**N**	**O**	**F**
-1	-1.5	-2	-2.5	-3	-3.5	-4
Na	**Mg**	**Al**	**Si**	**P**	**S**	**CI**
-0.9	-1.2	-1.5	-1.9	-2.1	-2.5	-3
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**
-0.8	-1	-1.6	-1.8	-2	-2.4	-2.8
Rb	**S**	**In**	**Sn**	**Sb**	**Te**	**I**
-0.8	-0.95	-1.7	-1.8	-1.9	-2.1	-2.5
Cs	**Ba**	**TI**	**Pb**	**Bi**	**Po**	**At**
-0.7	-0.9	-1.8	-1.8	-1.9	-2	-2.2

Electrical Conductivity

"Electrical conductivity is the measurement of a material's capability to conduct electric current".

- ✓ Materials with high electrical conductivity allow electric current to pass through them easily, while materials with low electrical conductivity hinder the flow of electric charges.
- ✓ The electrical conductivity of representative elements can vary widely. Alkali metals and alkaline earth metals generally exhibit high electrical conductivity due to their ability to easily transfer electrons.
- ✓ Group IIA elements display moderate electrical conductivity, while elements in Group IVA can have variable conductivity ranging from poor (e.g., carbon and lead) to moderate (e.g., silicon and tin). Group VA, VIA, and VILA elements typically have poor electrical conductivity.

- ✓ Noble gases, on the other hand, have extremely low electrical conductivity as shown in Table

Electrical conductivity trends of representative elements

Group Number	Trend of Electrical Conductivity
Group I and IIA	High electrical conductivity
Group IIIA	Moderate electrical conductivity
Group IVA	Variable electrical conductivity (Carbon: poor, Silicon: moderate, Germanium: moderate, Tin: moderate, Lead: poor)
Group VA	Moderate electrical conductivity
Group VIA	Poor electrical conductivity
Group VIIA	(Halogens) Poor electrical conductivity
Group VIIIA	(Noble gases) Extremely low electrical conductivity

Oxidation State

"An oxidation number is a value assigned to an element in a chemical compound or combined state".

The oxidation states of representative elements depend on their position in a particular group of periodic table.

Oxidation states of representative elements

Group	**Elements**	**Oxidation States**
IA (Alkali Metals)	Li, Na, K, Rb, Cs	1
IIA (Alkaline Earth Metals)	Be, Mg, Ca, Sr, Ba	2
IIIA	B, Al, Ga, In, TI	3
IVA	C, Si, Ge, Sn, Pb	-4, -2, +2, +4
VA	N, P, As, Sb, Bi	-3, -2, +3, +5
VIA	O, S, Se, Te, Po	-2, +2, +4, t6
VIIA (Halogens)	F, CI, Br, I, At	-1, +1, +3, +5, +7
VIIIA (Noble Gases)	He, Ne, Ar, Kr, Xe, Rn	0

Melting and Boiling Point

- ✓ The melting and boiling points of representative elements can vary widely across the periodic table.
- ✓ Alkali metals have low melting and boiling points due to weak metallic bonding,
- ✓ while alkaline earth metals have higher melting and boiling points due to stronger metallic bonding
- ✓ Moving across the p-block elements, the melting and boiling points generally increase gradually.

- ✓ However, there are exceptions in groups IVA and VA. Carbon has a high melting point due to strong covalent bonds, while nitrogen has low melting and boiling points because it exists as diatomic molecules with weak intermolecular forces.
- ✓ Halogens have low melting and boiling points due to weak intermolecular forces, and noble gases have extremely low melting and boiling points due to weak interatomic forces.
- ✓ The melting and boiling points of representative elements reflect the different bonding types and intermolecular forces within each group, resulting in a wide range of physical properties.

Melting point of representative element in °C

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
-180	-1278	-2300	-3700	-210	-219	-220	-248
Na	**Mg**	**Al**	**Si**	**P**	**S**	**CI**	**Ar**
-97.8	-651	-658	-1410	-34	-119	-102	-186
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
-63.7	-843	-297	-937	-814	-217	-7.2	-157
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
-39	-769	-155	-232	-630	-450	-114	-112
Cs	**Ba**	**TI**	**Pb**	**Bi**	**Po**	**At**	**Rn**
-28.6	-725	-303	-327	-271	-	-302	-71

Unique behaviour of Beryllium in group IIA

- ✓ Beryllium differs markedly from its other members because of its smaller atomic radii and high electronegativity.
- ✓ Some unique characteristics shown by beryllium in comparison to other elements of group IIA are given as:
- ✓ Beryllium is harder and more rigid than other members of group IIA.
- ✓ Beryllium has relatively low density and high melting point compared with other group members.
- ✓ Beryllium exhibits chemical stability due to the formation of protective oxide layer on its surface which prevents further oxidation and corrosion.
- ✓ Beryllium has tendency to form covalent bonds with other elements due to its smaller atomic size while other members of the group form ionic bonds.

REACTIONS OF REPRESENTATIVE ELEMENTS

s-block elements

Some common reactions of the elements of group IA and IIA are given as.

1. With oxygen

Alkali metals rapidly react with oxygen to produce oxides. Lithium forms normal oxide (oxidation state of oxygen -2), sodium forms peroxide (oxidation state of oxygen is -1) in excess of air while the rest of the elements of group IA form superoxides (oxidation state of oxygen is).

$4Li + O_2 \longrightarrow 2Li_2O$ (Normal Oxide)
$2Na + O_2 \longrightarrow Na_2O_2$ (Per Oxide)
$4K + O_2 \longrightarrow 2KO_2$ (Super Oxide)
$4Rb + O_2 \longrightarrow RbO_2$ (Super Oxide)
$4Cs + O_2 \longrightarrow CsO_2$ (Super Oxide)

The reaction of alkaline earth metals with oxygen takes place at high temperature. However, on oxidation, beryllium, magnesium and calcium form normal oxides while strontium and barium form peroxides.

General Reactions

$2M + 0_2 \longrightarrow 2MO$ (Where M = Be, Mg, Ca)
$2Be + 0_2 \longrightarrow 2BeO$
$2Mg + 0_2 \longrightarrow 2MgO$
$2Ca + 0_2 \longrightarrow 2CaO$

General Reactions

$M + 0_2 \longrightarrow MO_2$ (Where M = Sr, Ba)
$Sr + 0_2 \longrightarrow MO_2$
$Ba + 0_2 \longrightarrow MO_2$

2. With Water

Alkali metals react with water to produce metal hydroxides with the liberation of hydrogen gas.

General Reaction

$2M + 2H_20 \longrightarrow 2MOH + H_2$
(Where M= Li, Na, K, Rb, Cs).

$2Li + 2H_20 \longrightarrow 2LiOH + H_2$
$2Na + 2H_20 \longrightarrow 2NaOH + H_2$
$2K + 2H_20 \longrightarrow 2KOH + H_2$
$2Rb + 2H_20 \longrightarrow 2RbOH + H_2$
$2Cs + 2H_20 \longrightarrow 2CsOH + H_2$

Among alkaline earth metals beryllium does not react with either cold or steam, but magnesium reacts with steam.

General Reactions

$M + 2H_2O \longrightarrow M(OH)_2 + H_2\uparrow$
(Where M = Mg, Ca, Sr and Ba).

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2\uparrow$$
$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2\uparrow$$
$$Sr + 2H_2O \longrightarrow Sr(OH)_2 + H_2\uparrow$$
$$Ba + 2H_2O \longrightarrow Ba(OH)_2 + H_2\uparrow$$

3. With halogens

Alkali metals react vigorously with halogens to form metal halides. The reaction involves the transfer of electron from an alkali metal to a halogen.

General Reaction With Group IA

$$2M + X_2 \longrightarrow 2MX$$

(Where M= Li, Na, K, Rb, Cs) & (X = Cl, Br I)

General Reaction With Group IIA

$$2M + X_2 \longrightarrow MX_2$$

(Where M= Be, Mg, Ca, Sr, Ba)

4. With nitrogen

Nitrides are formed when both alkali metals and alkaline earth metals react with nitrogen. The general formula for the nitrides of alkali metals is M_3N and for the nitrides of alkaline earth metals is the formula M_3N_2.

General Reaction

$$6M + N_2 \longrightarrow 2M_3N \text{ (M= Li, Na, K, Rb, Cs)}$$
$$3M + N_2 \longrightarrow M_3N_2 \text{ (M= Be, Mg, Ca, Sr, Ba)}$$

5. With hydrogen

Alkali and alkaline earth metals react with hydrogen at different temperatures to produce ionic hydrides.

General Reaction

$$2M + H_2 \longrightarrow 2MH \text{ (M=Li, Na, K, Rb, Cs)}$$
$$M + H_2 \longrightarrow MH_2 \text{ (M = Ca, Sr, Ba)}$$

6. With alcohols

Elements of group IA react vigorously with alcohols to form metal alkoxide with the liberation of hydrogen gas.

General Reaction

$$2M + 2C_2H_5OH \longrightarrow 2C_2H_5OM + H_2 \text{ (M= Li, Na, K, Rb, Cs)}$$

Alkaline earth metals have a very limited reactivity with alcohols.

7. With acids

Alkali metals react vigorously with acids to produce salt with the liberation of hydrogen gas. This reaction is highly exothermic and violent.

General Reaction

$$2M + 2HCl \longrightarrow 2MCl \text{ t } H2 \text{ (Where M = Li, Na, K, Rb, Cs)}$$

Alkaline earth metals can react with acids but their reactivity is generally lower compared to alkali metals.

FLAME TEST FOR S-BLOCK ELEMENTS

"Flame test is a qualitative method used to identify the presence of alkali metals based on their characteristic flame colours".

Colour flames of alkali and alkaline earth metals

Elements	Flame Colour
Lithium	Red
Sodium	Yellow
Potassium	Violet
Rubidium	Red Violet
Cesium	Blue Violet
Beryllium	No characteristic flame colour
Magnesium	Silver white
Calcium	Orange red
Strontium	Deep Red
Barium	Pale Green

CHEMISTRY OF IMPORTANT COMPOUNDS OF S-BLOCK ELEMENTS

Sodium Hydroxide or Caustic Soda (NaOH)

Sodium hydroxide is one of the most important chemicals. Sodium hydroxide is commonly known as 'Caustic Soda' because it is caustic (able to burn) to touch and causes painful burns, therefore it must be handled with care.

Manufacture of Sodium hydroxide by Castner-Kellner's Process:

Sodium hydroxide is manufactured by an electrolytic process, known as Castner-Kellner's process.

Raw Material:

25% (W/W) solution of sodium chloride.

Apparatus:

Castner-Kellner's cell

Construction of Castner-Kellner's Cell:

Castner-Kellner's cell is an electrolytic cell in which anode consist of number of titanium plates dipped in sodium chloride solution. The cathode is a moving mercury layer at the bottom of the cell. Mercury flows from left to right. Saturated solution of NaCl also flows in the same direction. There is another lower chamber known as denuder, which is filled with water and packed with graphite blocks as hydrogen is easily liberated over graphite surface.

Process in the Cell:

Ionization:

$$2NaCl \longrightarrow 2Na^+ + 2Cl^-$$

Reaction at Anode:

On passing electric current Cl- ions migrate towards anode and after oxidation liberated as chlorine gas.

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

Reaction at Cathode:

Na+ ions are discharge over mercury surface and dissolved in it forming sodium amalgam.

$$2Na^+ + 2e^- \longrightarrow 2Na$$

$$2Na + 2Hg \longrightarrow 2Na/Hg \text{ (sodium amalgam)}$$

Reaction in Denuder:

The mercury containing dissolved sodium is sent to denuder chamber where sodium reacts with water forming sodium hydroxide and hydrogen gas is liberated.

$$2Na/Hg + 2H_2O \longrightarrow 2NaOH + H_2 + 2Hg$$

The mercury is recycled to upper cell to dissolve more sodium

Advantages of the Process:

- ✓ The process is very efficient.
- ✓ The products are of high purity.

- ✓ The possible reaction between NaOH andCl2 is avoided by obtaining NaOH and Cl_2 in separated compartment.

Disadvantages of the Process:

- ✓ This process consumes large amount of electricity.
- ✓ In spite of strict control some mercury vapors escapes into environment and producing the pollution of food
- ✓ chains.
- ✓ The use of this process has been banned and is being replaced by Gibb's diaphragm cell process which does not use
- ✓ mercury but gives the products of high purity.

Physical Properties

- ✓ **State:** It is a solid at room temperature, typically appearing as white pellets, flakes, or granules.
- ✓ **Odor:** It is odorless.
- ✓ **Melting Point:** Its melting point is approximately 318 °C (604 °F). At this temperature, it melts and forms a liquid.
- ✓ **Solubility:** It is highly soluble in water.
- ✓ **Density:** The density of NaOH depends on its concentration and temperature. For a 50% concentration at room temperature, the density is approximately 1.52 g/cm³.
- ✓ **Corrosiveness:** It is highly corrosive and can cause burns and irritation to the skin, eyes, and respiratory system.

Chemical Properties

1. Reaction with acids

Being a strong base, it reacts with all acids to produce sodium salt and water.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$
$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_20$$

2. Reaction with Ferric Chloride

On reaction with aqueous ferric chloride, it gives brown ppt of ferric hydroxide.

$$3NaOH + FeCl_3 \longrightarrow Fe(OH)_3 + 3NaCl$$

3. Reaction with Aluminium and Zinc

Caustic soda can react with aluminium and zinc to form aluminate and zincate salts.

$$2NaOH + 2Al + 2H_20 \longrightarrow 2NaAlO_2 + 3H_2$$
$$2NaOH + Zn \longrightarrow Na_2ZnO_2 + H_2$$

4. Reaction with Chlorine

The reaction of hot aqueous sodium hydroxide with chlorine gas gives sodium
chloride and sodium chlorate.

$$6NaOH + 3Cl_2 \longrightarrow NaClO_3 + 5NaCl + 3H_20$$

Uses of Sodium Hydroxide

- ✓ It is a key ingredient in the production of detergents and soaps.
- ✓ It is utilized in the production of bleach, such as chlorine bleach, which is commonly used as a disinfectant and stain remover.
- ✓ Its strong alkaline nature makes it effective for unclogging drains and pipes by breaking down organic matter.
- ✓ It is used to remove heavy metals and adjust pH levels in water, ensuring safe and clean drinking water.
- ✓ It is used as a food preservative to prevent bacterial and mold growth, enhancing the shelf life of certain food products.
- ✓ It is utilized in the canning process to remove the outer skin of fruits and vegetables, ensuring food safety and quality.

Bleaching Powder {Ca(OCl)Cl or CaOCl2}

The chemical formula bleaching powder suggested by Professor Odling is Ca(OCl)Cl or CaOCl2. It is a white amorphous powder with smell of chlorine.

Preparation:

In industrial scale bleaching powder is prepared by “Hasen Clever process”. The plant consist of number of iron cylinders in which chlorine is brought in contact with slaked lime {Ca(OH)2} and bleaching powder is formed

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

Reactions:

1. With Water:

In aqueous solution it liberates Cl_2 gas

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

2. With Acids:

When it reacts with acids, Cl2 gas is liberated.

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + Cl_2 + H_2O$$

3. With atmospheric CO_2 and moisture:

When it reacts with atmospheric CO_2 and moisture, HOCl is liberated.

$$2CaOCl_2 + CO_2 + H_2O \longrightarrow CaCl_2 + CaCO_3 + 2HOCl$$

Uses:

- ✓ It is used in sterilization of drinking water.
- ✓ It is used for bleaching of cotton, linen and paper pulp.
- ✓ It used for the preparation of Cl_2 gas and Chloroform ($CHCl_3$).
- ✓ It plays a role in the paper making industry, where is used for pulping wood fibers and paper recycling processes.

Selected s-block elements and Significant Uses their compounds

❖ Sodium Na

It helps to regulate the balance of fluids inside and outside our tissues and facilitates the absorption of various nutrients.

❖ Potassium K

It helps to balance the pH level in the body.

❖ Magnesium Mg

It helps in muscle contraction and maintain the bones and heart functions.

❖ Calcium Ca

It is essential for the growth of bones and teeth.

❖ Common Salt NaCl

It is a raw material for the synthesis of various chemicals such as soda ash, caustic soda and chlorine gas etc. It plays a vital role in maintaining electrolyte balance in the body.

❖ Washing Soda $Na_2CO_3. 10H_20$

It is used in the manufacturing of glass, soap and borax. It is also used for laundry purpose.

- **Backing Soda $NaHCO_3$**

It is used in bakeries to prepare various food items.

- **Potassium Nitrate KNO_3**

It is used in fireworks and fertilizer.

REACTIONS OF p-BLOCK ELEMENTS

Some important chemical reactions involving p-block elements are given below.

1. With oxygen

The reactions of p-block elements with oxygen produce either normal Oxides or in some cases peroxides.

Elements of group IIIA react with oxygen to produce oxides of the formula M_20_3.

$$4B + 30_2 \longrightarrow 2B_20_3$$
$$4Al + 30_2 \longrightarrow 2Al_20_3$$

In group IVA, carbon forms carbon monoxide and carbon dioxide when it reacts with oxygen while silicon form only one stable silicon oxide($Si0_2$).

$$C + O_2 \longrightarrow CO_2$$
$$2C + O_2 \longrightarrow 2CO$$
$$Si + O_2 \xrightarrow{\text{above } 900°C} SiO_2$$

In group VA, nitrogen forms NO, N,O and NO, when reacts with oxygen depending upon the conditions applied. Phosphorus may form P,0, in limited supply of Oxygen whereas P,0, in excess of oxygen.

$$N_2 + O_2 \xrightarrow{\text{High temp}} 2NO$$
$$2N_2 + O_2 \xrightarrow{\textit{Catalyst}} 2N_2O$$
$$4P + 30_2 \xrightarrow{\textit{Limited oxygen}} 2P_20_3$$
$$4P + 50_2 \xrightarrow{\textit{Excess oxygen}} 2P_2O_5$$

A In group VIA, sulphur oxidized in air to give sulphur dioxide.

$$S + O_2 \longrightarrow SO_2$$

Halogens can also react with oxygen however their oxides are mostly highly reactive.

For example the oxide of fluorine is a highly reactive yellow gas.
The oxides of halogens are very unstable.

$$2F_2 + O_2 \longrightarrow 2F_2O$$

2. With water

The reaction of p-block elements with water depends on the nature of element and the group to which it belongs.

Aluminium reacts with water but the reaction is slow due to the presence of a thin oxide film on its surface.

$$2Al + 6H_20 \longrightarrow 2AI(OH)_3 + 3H_2$$

Silicon reacts with steam and forms silicon dioxide.

$$Si + 2H_20 \longrightarrow SiO_2 + 2H_2$$

Phosphorus reacts vigorously with water to produce phosphoric acid and phosphine.

$$2P_4 + 12H_2O \longrightarrow H_3PO_4 + 5PH_3$$

Sulphur reacts if it is heated to a high temperature.

$$S + 2H_2Oo) \xrightarrow{high\ temp} SO_2 + 2H_2$$

Halogens such as chlorine and bromine react with water to form a mixture of two acids.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$
$$Br_2 + H_2O \longrightarrow HBr + HOBr$$

3. With halogens

Majority of p-block elements have the capability to react with halogens, resulting in the formation of binary compounds.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$
$$C + 2Cl_2 \longrightarrow CCl_4$$
$$N_2 + 3Cl_2 \longrightarrow 2NCl_3$$
$$O_2 + 2F_2 \longrightarrow 2F_2O$$

4. With nitrogen

The reaction of p-block elements with nitrogen can vary depending on the specific element and the reaction conditions.

Boron and aluminium react with nitrogen to form their nitrides.

$$2B + N_2 \longrightarrow 2BN$$
$$2Al + N_2 \longrightarrow 2AIN$$

Carbon and Silicon can form nitrides when heated with nitrogen at high temperatures.

$$3C + 2N_2 \xrightarrow{\Delta} C_3N_4$$
$$3Si + N_2 \longrightarrow Si_3N_4$$

Phosphorus reacts with nitrogen at high temperatures to form phosphorus nitride (P_3N_5).

$$6P + 5N_2 \longrightarrow 2P_3N_5$$

Halogen (Cl_2 ,Br_2) can react with nitrogen to form nitrogen trihalide.

$$3Cl_2 + N_2 \longrightarrow 2NCl_3$$

5. With hydrogen

Elements of group IIA and IVA do not directly react with hydrogen, however silicon at high temperatures may form silicon hydrides.

$$Si + 2H_2 \xrightarrow{High\ Temperature} SiH_4$$

Nitrogen reacts with hydrogen under high pressure to form ammonia.

$$N_2 + 3H_2 \xrightarrow{400-450°C} 2NH_3$$

Sulphur reacts with hydrogen at high temperatures to form hydrogen sulphide.

$$S + H_2 \xrightarrow{850°C} + H_2S$$

The reaction of halogen with hydrogen can result in the formation of hydrogen halides.

$$Cl_2 + H_2 \longrightarrow 2HCl$$

CHEMICAL BEHAVIOR OF HALOGENS

Halogens include fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). The reactivity of halogens is determined by their bond enthalpies and their ability to undergo redox reactions.

Bond enthalpies in halogens

The enthalpy is required for the dissociation of halogen-halogen bond in gaseous state and it varies according to size of halogen atom, bond length and the intermolecular attraction.

Halogen	**Atomic radii (pm)**	**Bond Length (in gaseous phase) pm**	**Bond enthalpies (kj/mol)**
F – F	72	143	159
Cl – Cl	100	199	242
Br – Br	114	228	193
I – I	133	266	151

Acidity of Hydrogen Halides

Hydrogen halides (HX) are strong mineral acids and their acidity follows an increasing trend from HF to HI (HF < HCl< HBr < HI). The increasing order of acidity of hydrogen halides can be attributed to their bond energies. Since the bond energy of H-I is the smallest, it can easily donate a proton and serves as the strongest acid compared to other halogen acids.

Halogen acids	**H – F**	**H – Cl**	**H – Br**	**H – I**
Bond energies (KJ/mol)	565	432	366	299

Strength of Halogens as oxidizing agent

Halogens are good oxidizing agents due to their high electronegativities and ability to readily accept electrons. The strength of halogens as oxidizing agent decreases from top to bottom in group VIIA.

$$F_2 > Cl_2 > Br_2 > I_2$$

Halide ions as a reducing agent

Halide ions (Cl, Br, I) can serve as reducing agents in chemical reactions due to their ability to readily donate electron to an oxidizing species thereby undergoing oxidation.

Among halide ions, there is a trend in relative strength of reducing agents I> BF > Cl > F. This means that iodide ion is the strongest reducing agent while fluoride ion is the weakest.

Chlorine as an auto oxidizing and reducing agent

Chlorine reacts with water to form hydrochloric acid and hypochlorous acid. In this reaction chlorine itself reduces into hydrochloric acid and oxidizes into hypochlorous acid and hence serves as auto oxidizing and reducing agent.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

(Chlorine) (Hydrochloric acid) (Hypochlorous acid)

MANUFACTURING OF SULPHURIC ACID (OIL OF VITRIOL) BY CONCTACT METHOD:

Raw Materials:

- ✓ Sulphur or iron pyrites (FeS_2)
- ✓ Air (O_2)
- ✓ Water (H_2O)
- ✓ Catalyst: Vanadium penta oxide (V_2O_5)

Details of Process:

Formation of 'SO_2':

In first step SO_2 is formed by the combustion of sulphur or iron pyrite in pyrite burner.

$$S + O_2 \longrightarrow SO_2$$

OR

$$4FeS_2 + 11O_2 \longrightarrow 3Fe_2O_3 + 8SO_2$$

Mixture of SO_2 and air is passed through special filters, washing and drying towers. As a result of this impurities are left behind and purified mixture of SO_2 and air is entered into contact tower.

Reaction in contact tower:

In contact tower SO_2 is oxidized to SO_3 in presence of catalyst vanadium penta oxide

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3 \ \Delta H = -45 \text{ K.cal}$$

Favorable conditions:

Since, reaction is reversible and exothermic so, the favorable conditions for obtaining maximum yield of SO3 are:

a) Low temperature (400^{0}C to 450^{0}C)
b) High pressure (1.5 to 1.7 atm)
c) Excess of oxygen.

Under these conditions, the equilibrium mixture contains 98% of SO_3.

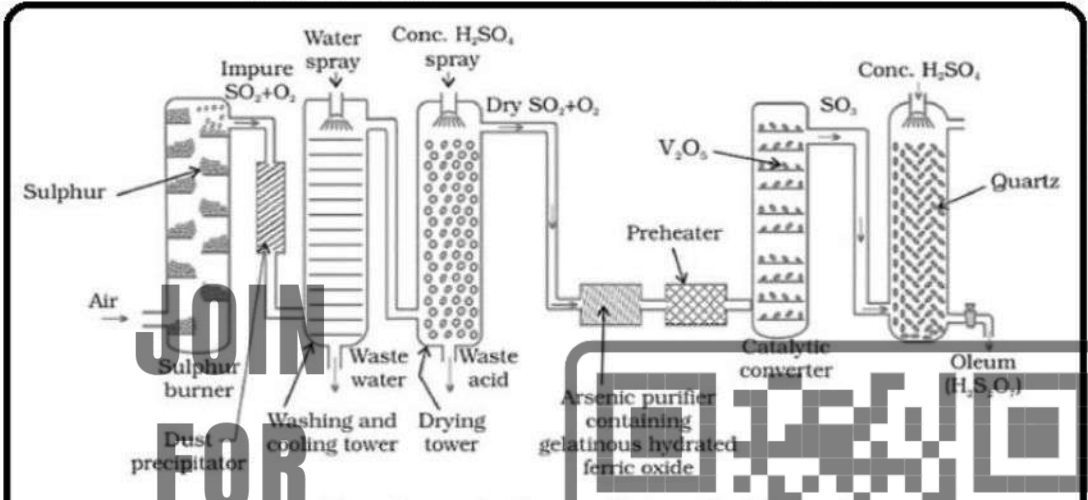
Formation of oleum:

The SO_3 produced in contact tower absorbed H_2SO_4 in absorption tower to form oleum.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

Formation of H_2SO_4:
Oleum absorbed calculated amount of water in last absorption tower to form sulphuric acid of desired concentration.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$



Flow diagram for the manufacture of sulphuric acid

Physical Properties

- ✓ Density: Sulphuric acid has a high density, typically around 1.84 g/cm³.
- ✓ Melting Point: Sulphuric acid has no distinct melting point since it can
- ✓ Supercool below its freezing point. The freezing point of sulphuric acid is approximately 10°C but it can vary depending on the concentration.
- ✓ Boiling Point: Commercial sulphuric acid has a boiling point of 290°C. However, the boiling point increases with increasing concentration.
- ✓ Solubility: Sulphuric acid is highly soluble in water.
- ✓ Corrosive Nature: Sulphuric acid is a highly corrosive substance and can react with metals and organic compounds etc.

Chemical Properties of H_2SO_4

1. An oxidizing agent

In sulphuric acid, sulphur exists in its highest oxidation state of +6. This highest oxidation state of sulphur makes the sulphuric acid to serve as an oxidizing agent when reacts with metals and non metals.

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2S0_2 + 2H_20$$
$$S + 2H_2SO_4 \longrightarrow 3S0_2 + 2H_2O$$
$$Cu + 2\,H_2SO_4 \xrightarrow{(conc.)} CuSO_4 + SO_2 + 2H_2O$$
$$2Al + 6\,H_2SO_4 \xrightarrow{(conc.)} Al_2\,(S0_4)_3 + 3S0_2 + 6H_20$$

2. A dehydrating agent

The dehydrating ability of sulphuric acid can be attributed to its capability to extract water molecules from other substances.

$$C_6H_{12}0_6 \xrightarrow{H_2SO_4(conc)}. 6C + 6H_2O$$
(glucose)

$$C_{12}H_{22}0_{11} \xrightarrow{H_2SO_4(conc)} 12C + 11H_2O$$
(sugar)

$$(C_6H_{12}0_5)_n + \xrightarrow{H_2SO_4(conc)} 6nC + 5nH_2O$$
(wood)

3. As sulphonating agent

Sulphonation involves the introduction of sulphonic group (SO_3H) into a molecule. Sulphuric acid serves as a source of sulphonic group which can be added to organic compounds to create new molecules.

$$C_6H_6 + H_2SO_{4\ (conc)} \longrightarrow C_6H_5S0_3H + H_2O$$
(Benzene) (Benzene sulphonic acid)

$$C_7H_8 + H_2SO_{4\ (conc)} \longrightarrow C_6H_4(CH_3)S0_3H + H_2O$$
(Toluene) (p-toluene sulphonic acid)

4. As dibasic acid

Sulphuric acid has the ability to donate two protons in water in two dissociation steps and serves as dibasic acid.

$$H_2SO_4 \rightarrow H_30^+ + HSO_4^-$$
$$HSO_4^- \rightarrow H_30+ + SO_4^{-2}$$

Uses of Sulphuric acid

- ✓ Sulphuric acid is used in various industries for:
- ✓ Producing fertilizers, dyes, pigments, detergents, pharmaceuticals, and synthetic fibers.
- ✓ Refining petroleum to make high-octane gasoline additives.
- ✓ Processing and purifying metals, including removing rust and scale.
- ✓ Etching and electroplating processes.
- ✓ Manufacturing lead-acid batteries.

Diagonal Relationship

The diagonal relationship refers to the resemblance in the properties exhibited by certain pairs of elements that are located diagonally to each other within the periodic table.

Periods	**Groups**			
	IA	**II A**	**III A**	**IV A**
Second	Li	Be	B	C
Third	Na	Mg	Al	Si

There are three pairs of elements that exhibit the diagonal relationship in the second and third periods of representative elements.

Diagonal relationship between

- ✓ lithium and magnesium,
- ✓ Beryllium and Aluminium,
- ✓ Boron and Silicon

Li and Mg

- ✓ Both have almost similar atomic radii (Li = 152pm and Mg =160pm).
- ✓ Both have almost similar electronegativities (Li = 1.0 and Mg 1.2)
- ✓ Both are lighter in their respective group.
- ✓ Oxide of both Li and Mg are very less soluble in water compared to other elements of the respective group.

Be and Al

- ✓ Both Be and Mg have same EN (1.5).
- ✓ Both show passivity with conc. Nitric acid.
- ✓ $BeCl_2$ and $AlCl_3$ both acts as Lewis acid.

B and Si

- ✓ Both B and Si have closer EN (B 2.0 and Si 1.8).
- ✓ Both B and Si have nearly same density (B=2.35g/cm_3, Si= 2.34g/cm_3).
- ✓ Both B and Si are metalloids and both of these do not form cation.

Element/Compound Significant Uses

❖ Aluminium

- ✓ It is used in making coils, alloys, kitchen utensils, window frames, chocolate foils etc.

❖ Sulphur

- ✓ It is used in the manufacturing of sulphuric acid, hydrogen sulphide and pesticides.

❖ Chlorine

- ✓ It is used in the manufacturing of plastic, bleaching powder and in the purification of drinking water.

❖ **Borax ($Na_2B_4O_7.10H_2O$)**

- ✓ It is used in cleaning, laundry, cosmetics and as flux in welding.

❖ **Alum ($K_2SO_4.Al_2SO_4.24H_2O$)**

- ✓ It is used for the purification of water, tanning of leather, fire extinguishers and as an antiseptic for minor cuts and wounds.

❖ **Ammonia (NH_3)**

- ✓ It is used in the manufacturing of fertilizers, nitric acid and refrigeration.

Short Question Answers

Q1. Give Reasons Of the following.

(i) Ionization energy decreases from top to bottom in s-block elements?

This is because as we move down the group, the valence electrons are added to higher and higher energy shells. As a result, they are further away from the nucleus and are less strongly attracted to it. This makes them easier to remove, which corresponds to a lower ionization energy.

(ii) Boiling point of halogens increase down the group in the periodic table?

This is because the boiling point of a substance is determined by the strength of the intermolecular forces between its molecules. Halogens are non-polar molecules, and the main intermolecular force between them is van der Waals forces. Van der Waals forces are weak forces, but they increase in strength as the size and mass of the molecule increases. As we move down the halogen group, the size and mass of the atoms increase, so the van der Waals forces between them increase. This results in a higher boiling point.

(iii) Gallium has smaller atomic radii than aluminium despite being below the aluminium in group IIIA?

This is because of the lanthanide contraction. The lanthanides are a group of 15 elements that come between lanthanum and lutetium in the periodic table. They have a very similar atomic structure, and as a result, their atomic radii decrease gradually from left to right. This contraction also affects the elements below the lanthanides, causing their atomic radii to be smaller than expected.

(iv) Electronegativities of alkali metals decrease from Li to Cs?

Electronegativity is a measure of how strongly an atom attracts electrons. Alkali metals have a single valence electron in the outermost s shell. This valence electron is relatively loosely held, so alkali metals are not very electronegative. As we move down the alkali metal group, the size of the atom increases. This means that the valence electron is further away from the nucleus, which makes it even less strongly attracted. As a result, the electronegativity of alkali metals decreases from Li to Cs.

(v) Alkali metals are good conductor of electricity.?

Alkali metals are good conductors of electricity because they have a low ionization energy and a large atomic radius. This means that their valence electrons are loosely held and can easily move around. When an electric current is applied, these valence electrons flow towards the positive terminal, creating an electric current.

(vi) Acidity of hydrogen halides increase from HF to HI?

The acidity of a hydrogen halide is determined by the strength of the bond between the hydrogen atom and the halogen atom. As we move down the halogen group, the size of the halogen atom increases. This makes the bond between the hydrogen atom and the halogen atom weaker. As a result, the hydrogen atom is more easily lost, and the hydrogen halide is more acidic.

(vii) Fluorine is the strongest oxidizing agent?
Fluorine is the strongest oxidizing agent because it has the highest electronegativity of all the elements. This means that it has a very strong tendency to attract electrons from other atoms. When fluorine reacts with another atom, it often strips the other atom of its electrons, forming an ion. This is why fluorine is such a powerful oxidizing agent.

Q2. What is flame test? Mention the colour of flame of alkali metals.

"Flame test is a qualitative method used to identify the presence of alkali metals based on their characteristic flame colours".

Colour flames of alkali

Elements	Flame Colour
Lithium	Red
Sodium	Yellow
Potassium	Violet
Rubidium	Red Violet
Cesium	Blue Violet

Q3. Explain the auto oxidizing and reducing properties of chlorine.

Auto-oxidation and reduction of chlorine

Auto-oxidation and reduction is a type of redox reaction in which a substance reacts with itself to produce both oxidized and reduced forms of the substance. Chlorine can undergo auto-oxidation and reduction, as shown in the following equation:

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

In this reaction, one chlorine molecule is oxidized to hypochlorous acid (HOCl), while the other chlorine molecule is reduced to chloride ions (Cl-). The hypochlorous acid produced in this reaction is also a strong oxidizing agent, and it can be used to bleach and disinfect.

Examples of the auto-oxidizing and reducing properties of chlorine

- **Auto-oxidation:**
  When chlorine gas is bubbled into water, it reacts with water to form hydrochloric acid and hypochlorous acid. The hypochlorous acid is a strong oxidizing agent, and it can be used to bleach and disinfect.
- **Auto-reduction:**
  When chlorine gas is reacted with hot sodium hydroxide solution, it is reduced to chloride ions. This reaction is used to produce sodium hypochlorite (NaClO), which is a common bleaching agent and disinfectant.

Q4. What is meant by a diagonal relationship? Mention three pairs of representative elements that show diagonal relationship.

Diagonal Relationship

The diagonal relationship refers to the resemblance in the properties exhibited by certain pairs of elements that are located diagonally to each other within the periodic table.

There are three pairs of elements that exhibit the diagonal relationship in the second and third periods of representative elements.

Diagonal relationship between
- ✓ lithium and magnesium,
- ✓ Beryllium and Aluminium,
- ✓ Boron and Silicon

Q5. Discuss the group trend of lionization energy in group IIIA of periodic table.

The ionization energy of an element is the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom. The ionization energy of group IIIA elements decreases from top to bottom in the periodic table.

This is because as we move down the group, the valence electrons are added to higher and higher energy shells. As a result, they are further away from the nucleus and are less strongly attracted to it. This makes them easier to remove, which corresponds to a lower ionization energy.

The following table shows the ionization energies of the group IIIA elements:

Element	Ionization energy (kJ/mol)
Boron	800.6
Aluminum	577.6
Gallium	599.9
Indium	558.2
Thallium	589.5

As can be seen from the table, the ionization energy of gallium is slightly higher than that of Aluminum, even though gallium is below Aluminum in the group. This is due to the lanthanide contraction. The lanthanides are a group of 15 elements that come between lanthanum and lutetium in the periodic table. They have a very similar atomic structure, and as a result, their atomic radii decrease gradually from left to right. This contraction also affects the elements below the lanthanides, causing their atomic radii to be smaller than expected.

Gallium is below the lanthanides, so its atomic radius is smaller than expected. This means that the valence electrons in gallium are closer to the nucleus than expected, and they are therefore more strongly attracted to it. This is why the ionization energy of gallium is slightly higher than that of Aluminum.

Overall, the ionization energy of group IIIA elements decreases from top to bottom in the periodic table. This is because the valence electrons are added to higher and higher energy shells as we move down the group. However, there is a slight anomaly in the trend due to the lanthanide contraction.

Q6. Write down three properties of beryllium that show its unique behaviour in group IIA.

- High ionization energy: Beryllium has the highest ionization energy of all the group IIA elements. This is because beryllium is a very small atom, and its valence electrons are close to the nucleus.
- High melting and boiling points: Beryllium has the highest melting and boiling points of all the group IIA elements. This is because beryllium has a strong covalent character, and its atoms are bonded together very tightly.
- Amphoteric nature: Beryllium is the only group IIA element that is amphoteric. This means that it can react with both acids and bases.

Here are some examples of the unique behaviour of beryllium:

- Ionization energy:

Beryllium has an ionization energy of 899.5 kJ/mol, while the other group IIA elements have ionization energies in the range of 577.6 to 589.5 kJ/mol.

- Melting and boiling points

Beryllium has a melting point of 1278 K and a boiling point of 2970 K, while the other group IIA elements have melting and boiling points in the range of 933 to 1115 K and 1807 to 2795 K, respectively.

- Amphoteric nature

Beryllium can react with acids to form beryllium salts, such as beryllium chloride ($BeCl_2$). It can also react with bases to form beryllate ions, such as beryllate ions (BeO_2^-).

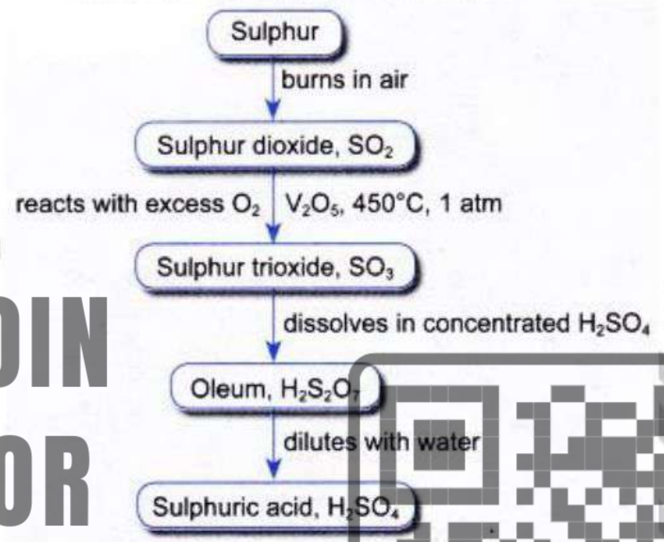
The unique properties of beryllium are due to its small size and high electronegativity. Beryllium is the smallest atom in group IIA, and it has the highest electronegativity of all the group IIA elements. This is because beryllium has a very effective nuclear charge, which attracts its electrons very strongly.

The unique properties of beryllium make it a very useful material. For example, beryllium is used in aerospace applications because of its high melting point and low weight. It is also used in nuclear reactors because of its ability to absorb neutrons.

Descriptive Questions

Q1. Draw a flow diagram of contact process and describe various steps involved in the manufacturing of sulphuric acid.

Flow chart of the Contact process



Q2. Explain with the help of a diagram of Castner Kellner cell, how caustic soda is obtained by the electrolysis of aqueous sodium chloride?

See Answer On Pg #

Q3. Write the balance equations for the following chemical process.

(i) A piece of Aluminum is dipped into concentrated sulphuric acid.

$$Al_{(s)} + 6H_2SO_{4(aq)} \longrightarrow Al_2(SO_4)_{3(aq)} + 3H_{2(g)}$$

(ii) Ferric chloride is mixed with an aqueous solution of caustic soda.

$$FeCl_{3(aq)} + 3NaOH_{(aq)} \longrightarrow Fe(OH)_{3(s)} + 3NaCl_{(aq)}$$

(iii) Sodium burns in excess of air.

$$2Na_{(s)} + O_{2(g)} \longrightarrow 2Na2O_{(s)}$$

(iv) Magnesium is heated with nitrogen gas.

$$3Mg_{(s)} + N_{2(g)} \longrightarrow Mg_3N_{2(s)}$$

(v) Potassium is put into ethyl alcohol.

$$2K_{(s)} + 2C_2H_5OH_{(l)} \longrightarrow 2C_2H_5OK_{(l)} + H_{2(g)}$$

(vi) Chlorine gas is passed through an aqueous solution of caustic soda.

$$Cl_{2(g)} + 2NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + NaClO_{(aq)} + H_2O_{(l)}$$

Q4. What is bleaching powder? How is prepared? Give the reaction of bleaching powder with water and hydrochloric acid.

See Answer On Pg #

Q5. Discuss the group trend of atomic radii, ionization energy and electronegativity of alkali metals.

See Answer On Pg #

Chapter
2

CHEMISTRY OF OUTER TRANSITION ELEMENTS

INTRODUCTION

- The elements that possess partially occupied d-orbitals, either in their atomic state or any of their ionic states, are commonly referred as outer transition elements or d-block elements.
- These elements are positioned in the middle section of the periodic table and are recognized for their intermediate characteristics between s-block and p-block elements.
- The elements are called d-block elements because they possess partially filled d-electrons in their valence shell.
- These elements hold considerable significance across numerous domains of chemistry and industries due to their versatile oxidation states, catalytic activity, alloy forming ability, colour, complex forming ability, magnetic behavior and electrical conductivity.
- The unique electronic structure and broad range of oxidation states exhibited by these elements make significant contributions to the advancement of technology in industry and various scientific fields.
- There are total four series of d-block elements found in the 4th, 5th, 6th and 7th periods.

3d- series:

- ✓ This ten elements series is located in the 4th period. It includes elements from scandium (Sc) to zinc (Zn).

4d - series:

- ✓ This series is placed in 5th period and consists of elements from yttrium(Y) to cadmium (Cd).

5d– series:

- ✓ This series is situated in the sixth period and consists of elements from lanthanum (La) to mercury (Hg).

6d- series:

- ✓ This series consists of elements from actinium (Ac) to copernicium (Cn).

Elements	**Sc**	**T**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Atomic No. (z)	21	22	23	24	25	26	27	28	29	30
Atomic size (pm)	144	132	122	117	117	117	116	115	117	125
1st ionization potential (KJ/mol)	632	661	648	653	716	762	757	736	745	908
Melting Point (°C)	1539	1668	1760	1875	1245	1535	1480	1452	1083	419
Boiling point (°C)	3900	3130	3000	2480	2087	2450	2900	2900	2310	907
Electronegativity	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6

Electronic Structure

d-block elements have valence electrons both in outer most and second outer most shells (penultimate) therefore the general valence electronic configuration of these elements is represented by **ns^2, $(n-1)d^1$ till ns^2, $(n-1)d^{10}$**, where "n" is the outermost shell and n-1 is the penultimate shell.

Binding Energy

The amount of energy required to separate the constituents of a bound system, such as atoms, nuclei, or particles.

- It represents the strength of the attractive forces holding the system together.
- The d-block elements have partially filed d orbitals, which contribute to their unique properties.
- Their binding energy is higher than that of other elements due to the strong attraction to their outermost d electrons.
- The binding energy increases across a period from left to right in the d-block elements due to increasing nuclear charge and decreasing atomic radius.
- The stronger positive charge attracts the d electrons more, requiring more energy to remove them.
- Down a group, the binding energy tends to decrease in the d-block elements.
- This is because the increasing atomic size and shielding effect reduce the effective nuclear charge felt by the outermost d electrons, making them easier to remove.

Variable Oxidation States

- The variable oxidation states displayed by transition elements are recognized as one of their distinctive properties.
- The oxidation states of transition metal ions are in the range of +1 to +7.
- This variation is due to very small energy difference between 3d and 4s orbitals".

Elements	Outer Electronic Configuration	Oxidation States
Scandium (Sc)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1, 4s^2$	+2, +3
Titanium (Ti)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^2, 4s^2$	+2, +3, +4
Vanadium (V)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^3, 4s^2$	+2, +3, +t4, +5
Chromium (Cr)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$	+1, +2, +3, +4, +5, t6
Manganese (Mn)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^2$	+2, +3, t4, +5, +6, +7
Iron (Fe) [Ar	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$	+2, +3, +4, +5, +6
Cobalt (Co)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^7, 4s^2$	+2, +3, +4
Nickel (Ni)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8, 4s^2$	+2, +3, +4
Copper (Cu)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$	+1, +2

Zinc (Zn)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2$		+2

Catalytic Activity

Most of the transition elements and their compounds serve as catalysts in numerous chemical splitting reactions

The property of transition metals to serve as catalyst can be explained by the following factors.

(i) Transition elements have variable oxidation states. They can easily withdraw or lend electrons from the reagent to form unstable intermediate which then changes into the final product.

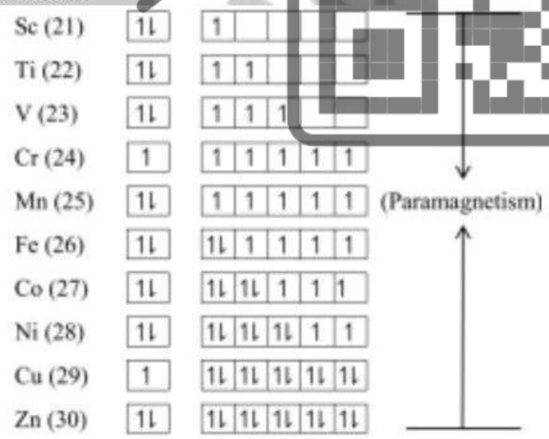
(ii) The surfaces of transition metals offer many active sites where reactant molecules can adsorb.

Magnetic Behavior

Atoms, ions or molecules when exposed to a strong external magnetic field, exhibit two distinct behaviors, either they are weakly attracted or repelled by the magnetic field.

The substances that are attracted by the magnetic field are called paramagnetic substances and those which are repelled by magnetic field are known as diamagnetic substances".

Most of the transition elements and their ions show paramagnetic behavior. This is due to the fact that d-orbitals of these elements possess one or more unpaired electrons and the spinning of unpaired electrons generates a magnetic moment. This magnetic moment causes the ion to interact with the external magnetic field.



The paramagnetic behavior is more pronounced in the middle of 3d series due to the maximum spin of electrons.

However, zinc is diamagnetic since it lacks unpaired electrons in its d-orbitals.

Alloy Formation

"Alloy is a homogenous mixture of two or more elements with at least one of them being a metal".

- Transition elements have the tendency to form alloys because of their similarities in atomic size which enable them to mix easily with one another.
- Alloys of transition metals exhibit greater rigidity, strength, light weight and shine compared to pure metals.
- Moreover, they possess enhanced resistance against corrosion. The composition and uses of some alloys are given below.
- Compositions and important uses of some alloys of transition-elements

Alloy	Stainless steel
Compositions	Iron, Chromium and Nickel.
Important Uses	In making cutlery, and surgical instruments
Alloys	Duralumin
Compositions	Aluminum, Copper Magnesium and Manganese
Important Uses	In making utensils, aero plane etc.
Alloys	Brass
Compositions	Copper and Zinc
Important Uses	In plumbing and automotive parts etc
Alloys	Bronze
Compositions	Copper and Aluminum
Important Uses	In making medals, statues, coins etc

Colour of Complexes

When a transition metal cation interacts with ligand, its five degenerate d-orbitals split into two sets of energy levels known as t_2g (lower energy level) and eg (higher energy level)"

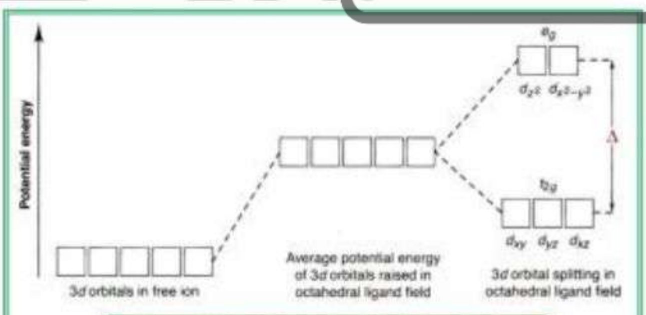
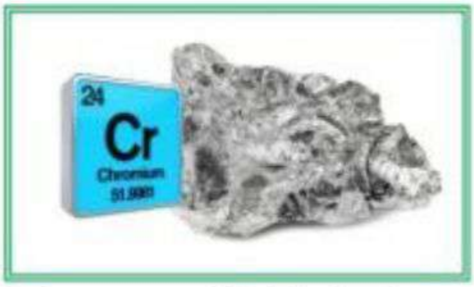


Fig 2.1: Splitting of five degenerate d-orbitals into t_2g and eg energy level

CHEMISTRY OF SOME IMPORTANT TRANSITION ELEMENTS

Chromium



- Chromium is the fourth member of 3d series of transition elements.
- It is characterized by its silvery grey colour and metallic luster.
- It is widely used as Cr protective coating on metal surfaces to prevent them from corrosion.
- Chromium exhibits various Oxidation states (+2, +3, +4, +5, +6) due to the electronic configuration of its atom (3d, 4s).
- The multiple oxidation states of chromium allow it to play a versatile role in redox reactions.
- In lower oxidation states, it serves as a reducing agent while in higher oxidation state works as an oxidizing agent.
- Chromium reacts with dilute hydrochloric acid to liberate hydrogen gas.

$$2Cr + 6HCl \longrightarrow 2CrCl_3 + 3H_2$$

Chromium reacts with oxygen to form chromium oxide

$$4Cr + 30_2 \xrightarrow{Heat} + 2Cr20_3$$

Chromium reacts with steam at high temperatures to form chromium oxide with the liberation of hydrogen.

$$2Cr + 3H_20 \xrightarrow{Heat} Cr_20_3 \text{ t+ } 3H_2$$

Chromium is used in the production of stainless steel, chrome plating, pigments and as a catalyst in certain chemical reactions.

Chemistry of Potassium dichromate

Potassium dichromate is a red crystalline solid that is highly soluble in water. If it dissolves in water at neutral pH, a chromate and dichromate equilibrium is formed which shows an orange red colour.

$Cr_20_7^{-2} + H_2O \longrightarrow 2Cr0_2 + 2H^+$
(red) (yellow)

The preparation of Potassium dichromate is commonly done by using chromates and these chromates are formed by the reaction of chromite ore with sodium or potassium carbonate.

Potassium dichromate is used as an oxidizing agent in various chemical reactions since it possesses the highest oxidation state of chromium (+6). The redox titration of potassium dichromate with oxalic acid ($H_2C_20_4$) and Mohr's salt (Fe(NH,),(So)2.6H,0) is commonly carried out in the laboratories for determining the concentration of analyte. The end point of this titration is indicated by the colour change from orange (Cr^{+6}) to green (Cr^{+3}).

$2Cr_20_7^{-2} + 3H_2C_20_4 + 8H^+ \longrightarrow 4Cr^{+3} + 6C0_2 + 7H_20$
(orange) (green)

$Cr_20_7^{-2} + 6Fe^{+2} + 14H^+ \longrightarrow 2Cr^{+3} + 6Fe^{+3} + 7H_20$
(orange) (green)

Manganese

Manganese is a greyish white, hard and brittle metal. It ranks as the twelfth most prevalent element within the Earth crust.
It exists in various oxidation states.
For example the oxidation state of manganese in potassium permanganate

($KMn0_4$) is +7 and in manganese dioxide ($Mn0_2$) it is +4, where as in manganese chloride ($MnCl_2$) it is +2.

Manganese reacts with air to form manganese oxide Mn_20_4.

$$3Mn + 20_2 \longrightarrow Mn_20_4$$

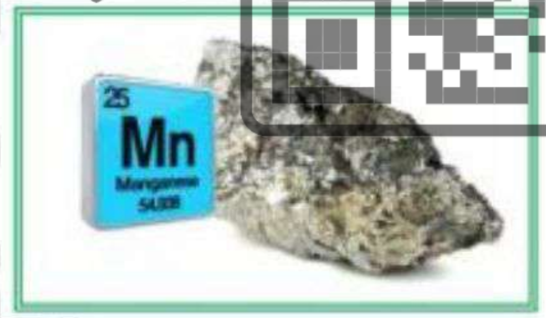
Manganese reacts with chlorine to form manganese chloride.

$$Mn + Cl_2 \longrightarrow MnCl_2$$

Manganese when dissolves in dilute sulphuric acid, it liberates hydrogen gas.

$$Mn + H_2SO_4 \longrightarrow MnSO_4 + H_2$$

Manganese is used in the production of steel, alloys, batteries, ceramics and glasses etc. It is an essential nutrient and play vital role in metabolism, bone development and enzyme function.



Chemistry of Potassium Permanganate

Potassium permanganate is a deep purple crystalline solid. Commercially, potassium permanganate ($KMnO_4$) is prepared by mixing a solution of potassium hydroxide (KOH) with powdered manganese dioxide (MnO_4) along with an oxidizing agent such as potassium chlorate ($KCIO_3$). It is highly soluble in water, forming a pink solution, potassium permanganate is a powerful oxidizing agent. It works cither in acidic, alkaline or neutral medium.

In acidic solutions permanganate ion accept five electrons and change from $Mn0_4^-$ to Mn^{+2}

$$Mn0_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_20$$

In basic or neutral medium it accepts three electrons and changes from $Mn0_4^-$ to $Mn0_2$

$$Mn0_4^- + 2H_20 + 3e^- \longrightarrow Mn0_2 \text{ t } 40H^-$$

The reaction of potassium permanganate with ferrous sulphate and Mohr's salt is given as;

$$Mn0_4^- + 5Fe^{+2} + 8H^+ \longrightarrow Mn^{+2} + 5Fe^{+3} + 4H_20$$

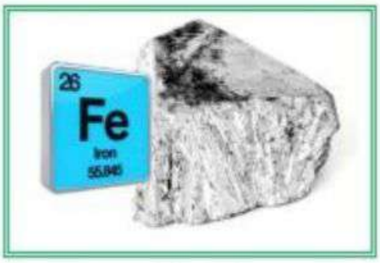
The reaction of potassium permanganate with oxalic acid is given as

$$2\ Mn0_4^- + 5C_20_4^{-2} + 16H^+ \longrightarrow 2Mn^{+2} + 10C02 + 8H20$$

Potassium permanganate is used as a powerful Oxidizing agent in various applications, including water treatment for purification and disinfection, and as a chemical reagent in organic synthesis and laboratory experiments.

Iron

Iron is the fourth most abundant element in the Earth crust. Its strength and magnetic properties make it valuable in industries such as Construction and manufacturing.



Furthermore, iron is an indispensable Component of hemoglobin, emphasizing its critical role in the biological system.

When iron is exposed to air, it oxidizes and forms an oxide film on its surface which is rusting of iron.

$$4Fe + 30_2 \longrightarrow 2Fe_20_3$$

When it reacts with excess of chlorine, it forms ferric chloride.

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

Iron is mainly used in the construction of buildings and flyovers. It is used in industries for making tools, weapons, appliances, rail tracks, trains, automobiles etc.

Steel Types and Applications

Steel is a widely used alloy comprised primarily of iron combined with some other elements. By the inclusion of carbon and other alloying elements in steel enhances its mechanical, thermal and chemical properties compared with simple iron.

There are several types of steel each characterized by unique compositions and properties suited for specific applications.

Type of Steel	**Applications**
Carbon Steel	Construction tools, machinery, pipes, tubes, automotive etc.
Stainless Steel	Kitchen appliances, Cutlery and Medical equipment
Tool Steel	Cutting and drilling equipment
Alloy Steel	Fry pan, Toaster etc

Copper

- ✓ Copper is a dense metal with a reddish brown colour.
- ✓ It is malleable and ductile, allowing it to be easily shaped and wired.
- ✓ Copper is known for its excellent electrical conductivity and it ranks as second highest (after silver) electrical conductor among pure metals.

Copper reacts with conc. sulphuric acid to form copper sulphate and sulphur dioxide.

$$Cu + 2H_2SO_{4(conc)} \longrightarrow CuSO_4 + S0_2 + 2H_20$$

Copper reacts with conc. nitric acid to form copper nitrate and nitrogen dioxide.

$$Cu + 4HNO_{3(conc.)} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_20$$

Copper is primarily used in making electric wires, cables, motors and other electrical equipment's. It is also used in plumbing, piping, telecommunication, coinage and alloy formation.

Metallurgy of Copper

Copper is present in Earth's crust in the combined form referred to as ore. The most abundant ore of copper is chalcopyrite ($CuFeS_2$). The process of extracting metal like copper from its ore is called metallurgy. The metallurgical operations associated with chalcopyrite ore include series of steps: such as crushing, grinding, Concentration, roasting, smelting and refining.

Concentration

In this stage, the objective is to eliminate gangue impurities from the powdered chalcopyrite ore. This is accomplished through a froth floating process, where the ore is blended with water that has pine oil added to it. Subsequently, air is introduced into the water, causing the ore particles to become coated with froth, while the gange particles settle to the bottom as shown in figure

Roasting

This process involves the heating of ore in the presence of excess air at an elevated temperature in a roasted kiln. As a result, the impurities oxidizes and the ore undergoes decomposition, leading to the formation of cupreous sulphide and ferrous oxide while sulphur dioxide is simultaneously eliminated.

$$2CuFeS_2 + 40_2 \longrightarrow Cu_2S + 2Fe0 + 3S0_2$$

Smelting

Roasted ore along with silica and coal is charged into a blast furnace. The combustion of coal elevates the furnace temperature to approximately 1200°C to 1500°C. Within this environment, ferrous oxide (Fe0) present in the ore reacts with silica, resulting in the formation of iron silicate ($FeSi0_3$) commonly referred to as slag. The slag floats on the surface of the molten matte while the matte (consisting of Cu,S and some impurities) is separately collected from the slag.

$$FeO + SiO_2 \rightarrow \xrightarrow{1200°C - 1500°C} FeSiO_3$$

(Iron oxide) (Silica) (Slag)

Bessemerization

The matte is subsequently fed into a pear shaped Bessemer converter, where hot gases are introduced from the mid lower portion. Within this converter, cupreous sulphide (Cu_2S) is partly converted into cupreous oxide (Cu_2O), which then reacts with the remaining cupreous sulphide, resulting in the production of molten metallic copper.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

The copper thus produced is called blister copper because as it solidifies hidden Sulphur dioxide gas escapes producing blisters on its surface. It is about 99% pure. The blister copper contains impurities mainly iron but small amount of arsenic, zinc, lead, silver and gold. Blister copper is not suitable especially for electrical purposes; therefore, it undergoes a refining process to remove all remaining impurities as shown in figure.

Fig.: Structure of Bessemer Converter

Refining of Copper

Copper is refined by electrolysis in an electrolytic tank. The blocks of blister copper are used as anodes and thin sheets of pure copper act as cathodes as shown in figure. The electrolyte is copper sulphate which is acidified with sulphuric acid. By passing electricity through the electrolytic solution, the blister copper undergoes oxidation and the Cu^{+2} ions produced in this oxidation process are then deposited onto cathode. The impurities are left behind which fall to the bottom of the cell as anode mud.

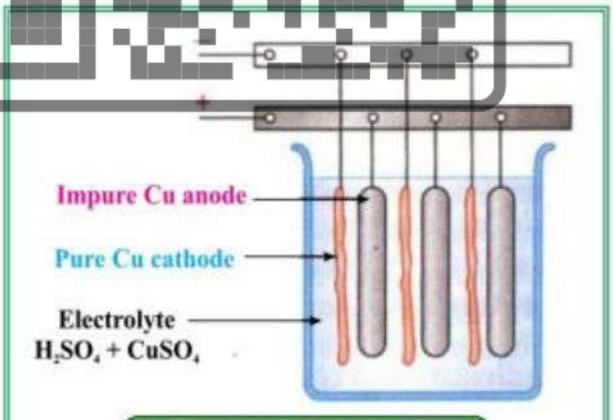


Fig: Electrolytic refining of blister copper

$$Cu \longrightarrow Cu^{+2} + 2e^- \text{ (oxidation at anode)}$$

(Blister copper)

$$Cu^{+2} + 2e^- \longrightarrow Cu \text{ (reduction at cathode)}$$

Copper obtained after electrolytic refining is 99.99% pure.

Commercial applications of some common transition elements

Transition	**Elements Commercial Applications**
Titanium	In making artificial joints, bone plates, screws and dental implants.
Vanadium	Use in batteries, as a catalyst and as a pigment in glass making
Iron	Building and bridge construction and tool making.
Copper	In making copper wires, alloys and sanitary works.
Zinc	Galvanizing, alloying and also use in batteries
Platinum	In making jewellery and also serves as a catalyst.
Mercury	Use in thermometers, B.P. apparatus, and amalgam formation

Short Questions

1. Write the IUPAC names of the following:

(i) $Na_2[Pt(OH)_4]$	Sodium tetra hydroxo platinate (II)
(ii) $K_2[Fe(CN)_5 NO]$	Potassium penta cyano nitrosyl ferrate (II)
(ii) $(Zn(NH_3)_4]^{+2}$	Tetra ammine zinc (II) ion
(iv) $[Ni(SCN)_4]^{-2}$	Tetra thio cyanato nickelate (II) ion

2. Give reasons for the following:

i) Why do transition elements show variable oxidation states?

Transition elements show variable oxidation states because their valence electrons are in two different sets of orbitals, i.e. in (n - 1) d and ns orbitals. The energy difference between these orbitals is very less. This means that transition metals can lose electrons from either the (n - 1) d or ns orbitals, or from both, depending on the conditions.

(ii) Why transition elements have ability to form alloys?

Transition elements have the ability to form alloys because their atoms have similar sizes and similar electronic configurations. This allows them to mix together and form solid solutions. Alloys are often stronger and more durable than pure metals, and they can also have other desirable properties, such as resistance to corrosion or high melting points.

(iii) Why Cu^{+2} ion is blue but Zn+2 is colourless?

Copper(II) ion (Cu^{+2}) is blue in color because it can absorb visible light of the orange-red wavelength. This absorption is due to a phenomenon called d-d transition. In a d-d transition, an electron is excited from one d orbital to another d orbital of higher energy.

Zinc(II) ion (Zn^{+2}), on the other hand, is colorless because it does not have any d orbitals. All of its valence electrons are in s orbitals. This means that there are no d-d transitions possible, and therefore Zn^{+2} does not absorb visible light.

(iv) Why chromium exists in $4s^1$, $3d^5$ configuration but not in $4s^2$, $3d^4$?

Chromium exists in the $4s^1$,$3d^5$ configuration because it is more stable than the $4s^2$, $3d^4$ configuration. This is due to the phenomenon of Hund's rule, which states that electrons will occupy different orbitals of the same energy level before they pair up. In the $4s^1$, $3d^5$ configuration, all of the electrons in the 3d orbital have unpaired spins. This is more stable than the $4s^2$, $3d^4$ configuration, in which two of the electrons in the 3d orbital would have to pair up.

(v) Why binding energy of zinc is least in 3d series?

The binding energy of zinc is the least in the 3d series because it has the smallest atomic radius. Atomic radius is the distance from the nucleus of an atom to its outermost valence electrons. The smaller the atomic radius, the more tightly the valence electrons are held to the nucleus. This means that it takes more energy to remove an electron from a zinc atom than from any other atom in the 3d series.

In addition, zinc has a filled 3d subshell. Filled subshells are more stable than incomplete subshells. This also contributes to the high binding energy of zinc.

However, it is important to note that the binding energy of zinc is still relatively low. This is because the energy difference between the 4s and 3d orbitals in zinc is very small. This allows zinc to lose electrons from either the 4s or 3d orbital, or from both, depending on the conditions.

(i) Reaction of conc. nitric acid with copper

$$Cu_{(s)} + 4HNO_{3(conc.)} \longrightarrow Cu(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

(ii) Reaction of conc. sulphuric acid with copper

$$Cu_{(s)} + 2H_2SO_{4(conc.)} \longrightarrow CuSO_{4(aq)} + SO_{2(g)} + 2H_2O_{(l)}$$

(iii) Reaction of permanganate with oxalic acid

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2KHSO_4 + 5CO_2 + 2MnSO_4 + 8H_2O$$

(iv) Reaction of dichromate with ferrous sulphate

$$2Cr_2O_7^{2-} + 6Fe^{2+} + 14H_{+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

(v) Reaction of manganese with dilute sulphuric acid

$$Mn_{(s)} + H_2SO_{4(aq)} \longrightarrow MnSO_{4(aq)} + H_{2(g)}$$

(vi) Reaction of iron with chlorine

$$Fe_{(s)} + Cl_{2(g)} \longrightarrow FeCl_{2(s)}$$

4. **Why d-block elements are called outer transition elements?**

The d-block elements are called outer transition elements because they are located in the middle of the periodic table, between the s-block and p-block elements. They are also called transition elements because their properties show a gradual transition from the properties of the s-block elements to the properties of the p-block elements.

5. **Write down the effect of pH changes on dichromate equilibrium in water.**

The equilibrium between dichromate (Cr2O72−) and chromate (CrO42−) ions in water is pH-dependent. At low pH, the dichromate ion is the predominant species. As the pH increases, the equilibrium shifts to the right, and the chromate ion becomes the predominant species. This is because the chromate ion is more stable at higher pH values.

The following equation shows the equilibrium between dichromate and chromate ions in water:

$$2Cr_2O_7^{2-} + 2H_2O \longrightarrow CrO_4^{2-} + 2H^{+} + 2CrO_4^{2-}$$

6. **Melting point of d-block elements increase up to middle of the series and then decrease why?**

The melting point of d-block elements increases up to the middle of the series and then decreases because of the increasing number of d electrons. The d electrons can participate in metallic bonding, which strengthens the metal and increases its melting point. However, as the number of d electrons increases, the electrons become more delocalized and less involved in metallic bonding. This leads to a decrease in the melting point.

Another factor that contributes to the decrease in melting point after the middle of the series is the increasing size of the atoms. The larger atoms have more space between them, which makes it easier for them to slide past each other and melt.

7. **Give the composition and applications of stainless steel, brass and bronze.**

Stainless steel is a type of steel that is resistant to corrosion. It is typically made up of iron, chromium, and nickel. Stainless steel is used in a wide variety of applications, including:

- Food processing equipment
- Medical devices
- Chemical processing equipment
- Automotive parts
- Architectural components

Brass is an alloy of copper and zinc. It is typically made up of 60-70% copper and 30-40% zinc. Brass is a strong and durable material that is also resistant to corrosion. It is used in a wide variety of applications, including:

- Plumbing hardware
- Electrical connectors
- Musical instruments
- Decorative items

Bronze is an alloy of copper and tin. It is typically made up of 80-90% copper and 10-20% tin. Bronze is a strong and durable material that is also resistant to corrosion. It has been used for centuries to make a variety of items, including:

- Sculptures
- Statues
- Bells
- Coins
- Bearings

Note: The composition and applications of stainless steel, brass, and bronze can vary depending on the specific alloy.

Descriptive Questions

1. Explain the trend of following properties of 3d-series of transition elements.

(a) Paramagnetic behavior (b) Variable oxidation state (c) Colour formation.

(a) Paramagnetic behavior

Paramagnetism is a type of magnetism in which materials are attracted to magnetic fields. It is caused by the presence of unpaired electrons.

Transition elements are paramagnetic because they have unpaired electrons in their d orbitals. The number of unpaired electrons in a transition element depends on its oxidation state. For example, scandium (Sc) has no unpaired electrons in its +3 oxidation state, so it is diamagnetic (not attracted to magnetic fields). However, titanium (Ti) has one unpaired electron in its +3 oxidation state, so it is paramagnetic.

The trend of paramagnetic behavior in the 3d series of transition elements is as follows:

- The maximum number of unpaired electrons is five, and this occurs at the middle of the series (from chromium (Cr) to manganese (Mn)).
- The number of unpaired electrons decreases on either side of the series.

- Elements at the end of the series (from nickel (Ni) to zinc (Zn)) have no unpaired electrons, so they are diamagnetic.

(b) Variable oxidation state

Transition elements show variable oxidation states because they have unpaired electrons in their d orbitals. These unpaired electrons can be lost or gained to form different oxidation states.

The trend of variable oxidation state in the 3d series of transition elements is as follows:

- The maximum number of oxidation states is seven, and this occurs at the middle of the series (from manganese (Mn) to chromium (Cr)).
- The number of oxidation states decreases on either side of the series.
- Elements at the beginning of the series (from scandium (Sc) to titanium (Ti)) have only one or two oxidation states. Elements at the end of the series (from nickel (Ni) to zinc (Zn)) have only one oxidation state.

(c) Colour formation

Transition elements are colored because they can absorb visible light. This absorption is due to a phenomenon called d-d transition. In a d-d transition, an electron is excited from one d orbital to another d orbital of higher energy.

The energy of the absorbed light depends on the energy difference between the two d orbitals. The greater the energy difference, the shorter the wavelength of the absorbed light.

The trend of colour formation in the 3d series of transition elements is as follows:

- Elements at the beginning of the series (from scandium (Sc) to titanium (Ti)) are colorless because their d-d transitions are too high in energy to be absorbed in the visible region of the spectrum.
- Elements at the middle of the series (from chromium (Cr) to manganese (Mn)) are colored because their d-d transitions are in the visible region of the spectrum.
- Elements at the end of the series (from nickel (Ni) to zinc (Zn)) are colorless because their d orbitals are filled, so there are no d-d transitions possible.

Conclusion

The paramagnetic behaviour, variable oxidation state, and colour formation of transition elements are all due to the presence of unpaired electrons in their d orbitals. The trends in these properties can be explained by the energy levels of the d orbitals and the energy of the absorbed light.

2. How can you define a coordination complex and a chelating ligand? Explain various types of ligands with examples.

Coordination complex

A coordination complex is a chemical compound consisting of a central atom or ion, which is usually metallic and is called the coordination centre, and a surrounding array of bound molecules or ions, that are in turn known as ligands or complexing agents. Many metal-containing compounds, especially those that include transition metals (elements like titanium that belong to the periodic table's d-block), are coordination complexes.

Examples of coordination complexes include:

- Haemoglobin, which contains an iron atom coordinated to four nitrogen atoms in a porphyrin ring, and two oxygen molecules.
- Chlorophyll, which contains a magnesium atom coordinated to four nitrogen atoms in a porphyrin ring.
- Cisplatin, a cancer drug that contains a platinum atom coordinated to two chloride ions and two ammonia molecules.

Chelating ligand

A chelating ligand is a ligand that can bond to a central metal atom through two or more donor atoms. This forms a ring structure called a chelate ring. Chelating ligands are typically more stable than monodentate ligands, which can only bond to a central metal atom through one donor atom.

Examples of chelating ligands include:

- Ethylenediamine (en)
- Bidentate (bipy)
- Triphenylphosphine (PPh3)
- Oxalate (ox)
- Glycinate (gly)

Types of ligands

Ligands can be classified into two main types: monodentate and polydentate.

- Monodentate ligands can only bond to a central metal atom through one donor atom. Examples of monodentate ligands include water (H2O), ammonia (NH3), chloride (Cl−), and fluoride (F−).
- Polydentate ligands can bond to a central metal atom through two or more donor atoms. Examples of polydentate ligands include ethylenediamine (en), bidentate (bipy), triphenylphosphine (PPh3), oxalate (ox), and glycinate (gly).

3. Describe how 99.99% pure copper is obtained from its chalcopyrite ore.

Notes Pg no 53

4. Explain why transition elements and their compounds serve as catalysts in many chemical reactions

Transition elements and their compounds serve as catalysts in many chemical reactions because of the following reasons:

- **Variable oxidation state:** Transition elements can exist in a variety of oxidation states, which allows them to act as electron donors or acceptors in chemical reactions. This can help to lower the activation energy of the reaction and speed it up.
- **Formation of coordination complexes:** Transition elements can form coordination complexes with other molecules, which can change the reactivity of the transition metal. For example, the coordination complex cisplatin is a cancer drug that is much more effective than platinum metal alone.

- **Presence of d orbitals:** Transition elements have d orbitals, which can overlap with the orbitals of other molecules to form bonds. This can help to activate reactants and speed up reactions.

5. What is meant by binding energy? Write down the trend of binding energy in 3d series of transition elements.

Binding energy

Binding energy is the energy required to break a bond between two atoms. It is a measure of the strength of the bond. The higher the binding energy, the stronger the bond.

The binding energy of a transition metal atom is the energy required to remove an electron from the outermost shell of the atom. The binding energy of a transition metal atom depends on the number of protons in the nucleus, the number of electrons in the outermost shell, and the shielding effect of the inner electrons.

The trend of binding energy in the 3d series of transition elements is as follows:

- The binding energy increases up to the middle of the series, and then decreases.
- The maximum binding energy occurs at chromium (Cr).
- The minimum binding energy occurs at zinc (Zn).

Chapter # 3

Organic Chemistry

INTRODUCTION

Organic chemistry is the study of properties and structure of carbon containing compounds. Thus

"Organic chemistry deals with hydrocarbons and their derivatives".

- ✓ However, a few numbers of carbon containing compounds are excluded from organic chemistry either by their properties or nature of bonding.
- ✓ These are carbonates, bicarbonates, cyanides, carbides, carbon dioxide, carbon monoxide and carbon disulphide etc.
- ✓ Organic chemistry is probably the biggest sub-field in chemical sciences and is recognized as the fundamental field for all chemists to study. It serves as a bridge between chemistry and biology.

Old Concept of Organic Chemistry(Vital Force Theory)

Before the 18h century, the term organic chemistry was used only for those substances that were obtained from animals and plants and could not be prepared in laboratory.

It was extensively believed by chemists that there existed a vital force in all living things that was required for the production of organic compounds.

End of Vital Force Theory (Preparation of Urea)

In 1828, a German chemist Friedrich Wohler prepared urea in the laboratory by boiling ammonium cyanate with water.

$$NH_4CNO \xrightarrow{Heat} CO(NH_2)_2$$

(ammonium cyanate) (urea)

Urea is a typical organic compound that is excreted from urine.

Laboratory synthesis of urea by Wohler disapproved the vital force theory and turned the minds of chemists towards synthetic organic chemistry and since then millions of organic compounds have been synthesized.

SOURCES

- ✓ Organic compounds are abundant in nature and can be found in various natural sources such as fossil fuels, plants, animals and microorganisms.
- ✓ They play an important role in our society in various aspects.
- ✓ Fossil Remains (Coal, Petroleum, Natural Gas)
- ✓ Fossil remains refer to the remnants of ancient animals and plants that have been preserved in rocks and sediments.
- ✓ These remains can include bones, teeth, shells imprints of leaves or other plant parts and provide important clues about the history of life on earth.
- ✓ Fossils are formed when an organism dies and its remains are quickly buried by sediment without decomposition.

- ✓ The buried remains become compressed and the organic material in the remains is slowly transformed into fossil fuel leaving behind the minerals of the rock.
- ✓ Fossil fuels are nonrenewable energy source.

The three main types of fossil fuels are coal, petroleum and natural gas.

Coal

Coal is a plant-derived black mineral found beneath the earth's crust and is a solid fossil fuel that has significance all over the world. Plants that were buried underneath the earth crust millennia ago were slowly turned to coal under high temperature and pressure owing to bacterial and chemical processes.
The coal types and their some uses are:

Peat 45– 60%
It is the earliest stage of coal formation resulting from the decomposition of fossilized remains. It has very low heat contents and use for domestic heating as an alternate of fire wood.

Lignite 60-70%
It is a brownish black coloured soft coal. It is typically used to generate electricity in power plants.

Bituminous 70– 85%
It is a black coloured soft coal. It has a higher carbon content than lignite. It is often used for electric generation and steel production.

Anthracite 90–95%
It is a dark black coloured hard coal. It is the highest ranking coal with the highest carbon content. It is used in furnaces, power stations and as a domestic fuel.

Petroleum

The term petroleum refers to rock oil or crude oil since it is a thick black liquid that oozes out of the earth.
It is a complex combination of alkanes, cycloalkanes and aromatic hydrocarbons etc.
Petroleum is formed from the ancient marine animals that were buried millions of years ago in the earth's crust.
It is used for transportation, power generation and many other purposes.
Some important products that are extracted from petroleum include gasoline, kerosene, diesel, naphtha, parafin wax etc.

Natural Gas

Natural gas produced by the decomposition of marine microorganisms over the millions of years.

Natural gas is a mixture of methane, ethane, propane and butane. The highest composition in natural gas is methane (85 - 90% approximately). Natural gas is a more beneficial source of energy than coal and petroleum because its combustion causes less pollution.

Natural Products (Plants and Animals)

Many organic compounds are isolated from plants, animals and microbes. These are referred to as natural products.

These products are typically produced by living organisms through natural metabolic processes and extracted out through various methods such as distillation, fermentation, purification etc.

Natural products have been utilized for millennia for medicinal, cosmetic, and nutritional reasons.

Some examples of natural products are glucose, cellulose, insulin, cholesterol, caffeine, nicotine, menthol and peppermint oil etc.

Partial and Total Synthesis

Partial Synthesis:

Partial synthesis involves starting with a simpler molecule and modifying it through a series of chemical reactions to create a more complex target molecule.

This method is particularly useful when the target molecule challenging to synthesize directly or requires multiple steps.

One example of partial synthesis is the production of the anti-inflammatory drug ibuprofen from a compound called cumene. Cumene undergoes several chemical transformations, including oxidation and rearrangement, to yield ibuprofen.

Total Synthesis:

Total synthesis involves building a complex target molecule entirely from simple starting materials.

It requires designing a route that carefully selects and assembles the necessary building blocks through a series of chemical reactions.

Total synthesis is often used to produce natural products or pharmaceutical compounds that are not readily available from natural sources.

For example, the total synthesis of the anti-cancer drug paclitaxel (Taxol) involves numerous steps to construct the molecule from simple building blocks.

Products of Biotechnology

“Products that are made by using living organisms or their constituents such as cells enzymes, DNA, etc called as products of biotechnology."

Destructive Distillation of Coal

The process in which coal is heated in the absence of air to produce a range of useful products is known as destructive distillation".

The process requires an elevated temperature typically 400°C to 900°C in a closed container. The four principal products of destructive distillation of coal are coke, coal tar, coal gases and ammonia liquor.

Coke

It is a greyish black hard solid contain 98-99% carbon. It is used as fuel and reducing agent.

Coaltar

It is thick black liquid. Its fractional distillation gives many useful organic compounds such as benzene, toluene, xylene, naphthalene and phenol etc.

Coal Gases

It is a mixture of methane and water gas. It is highly flammable and is employed for heating and municipal lighting.

Ammonia Liquor

It is a mixture of ammonium compounds and liquid ammonia and is usually obtained from bituminous coal.

Reforming of Petroleum

"The process of conversion of hydrocarbons (gasoline) with low octane rating into those with higher octane rating that can be utilized as a fuel in internal combustion engine is known as reforming".

The process of reforming is carried out under high pressure and temperature using platinum catalyst.

CHARACTERISTICS OF ORGANIC COMPOUNDS

Catenation

Organic compounds are made up of carbon atoms. Carbon is distinctive in its ability to bond covalently with other carbon atoms in many different ways to form long chain, branch chain and cyclic compounds. This unique property of organic compounds is known as catenation.

Non Ionic Nature

Organic compounds are made up of carbons and a carbon atom contains four valence electrons.

It does not have the ability to lose or gain four electrons since it requires very high energy. Therefore, in contrast with inorganic compounds, it forms covalent bonds by the sharing of electrons.

Solubility

The solubility of organic compounds can vary widely depending on their chemical structure and the solvent in which they are dissolved. For examples:

Water-soluble organic compounds:

Organic compounds that contain polar functional groups, such as hydroxyl (-OH) or carboxyl (-COOH) groups, tend to be soluble in water due to the ability to form hydrogen bonds with water molecules.

For example, ethanol (C_2H_5OH) and acetic acid (CH_3COOH) are both water-soluble organic compounds.

Nonpolar organic compounds:

Nonpolar organic compounds, such as hydrocarbons, generally have low solubility in water but are soluble in nonpolar solvents like hexane or diethyl ether.

For instance, hexane (C_6H_{14}) and toluene ($C_6H_5CH_3$) are nonpolar organic compounds that exhibit poor solubility in water but dissolve readily in nonpolar solvents.

Low Melting and Boiling Point

Organic compounds in comparison to inorganic compounds have lower melting and boiling points. This is due to the comparatively weak intermolecular forces found in these molecules. They exist as gases, liquids and soft solids.

Flammability

The majority of organic compounds are combustible and readily react with oxygen to form carbon dioxide and water, thereby releasing heat. As a result, most fuels are organic, such as wood, coal, oil, gasoline, and natural gas. Burning of organic compounds provide heat energy. The combustion reaction for methane (CH_4) is as follows:

$$CH_4 + 20_2 \rightarrow CO_2 + 2H_2O + \text{Heat energy}$$

Reactivity

Organic compounds react at a substantially slower rate than the ionic reactions that are often found in inorganic compounds. To accelerate the reaction, they generally require heating, mixing, and a catalyst.

Isomerism

Isomerism is a characteristic of organic compounds where compounds with the same number of atoms of each element can arrange those atoms in different ways, resulting in distinct structures and properties. These compounds with different structures but the same molecular formula are called isomers.

For example:

There are two isomers of butane: n-butane and isobutane.

In n-butane, the carbon atoms form a straight chain, while in isobutane, the carbon atoms form a branched structure.

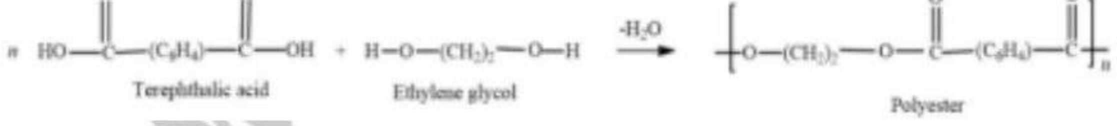
n-Butane: $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$

Isobutane: $CH_3\text{-}CH(CH_3)\text{-}CH_3$

Polymerization

Many small organic molecules (monomers) can unite through addition or condensation process to form a single large molecule. This process is known as polymerization and the macromolecule thus formed is called as a polymer.

For example, the polymerization of terephthalic acid (a dicarboxylic acid) with ethylene glycol (a diol) forms polyethylene terephthalate (PET), which is a common type of polyester used in various applications, including textiles, packaging, and beverage containers.



USES OF ORGANIC COMPOUNDS

Organic compounds are widely used in various applications, including pharmaceuticals, agriculture, plastics, fuel, material production, and energy generation.

Use of common organic compounds

Organic Compounds	Common Use
Gasoline	Fuel for automobiles
Natural gas	Domestic fuel
Ethene	Ripening of fruits
Ethyne	Gas Welding
Formalin	Preservative of biological specimen
Ethylene glycol	Antifreeze and coolant in automobiles
Phenol	Antiseptics and ink preservatives
Diethyl ether	Anesthesia
Acetic acid	Vinegar
Ethyl acetate	Artificial flavors and essences
Acetone	Nail polish remover
Nylon	Ropes and fish nets
Poly ester	Fabrics
Carbohydrate, protein, fats, vitamins	Food components

NEW ALLOTROPIC FORM OF CARBON (BUCKY BALLS)

It has been known for centuries that pure carbon exists in two allotropic forms with diamond and graphite.
In 1985, Richard Smalley and Harry Kroto introduced a new allotropic form of carbon that consists of 60 carbons.
The shape of this newly discovered form of carbon was similar to the geodesic dome developed by American architect and scholar Richard Buckminster Fuller. The name of this new form of C_{60} was suggested as Fullerene or Bucky Ball.
It consists of twelve (12) five membered ring and twenty (20) six membered ring. Structurally each pentagon is surrounded by hexagon. Forming a hollow cage-like structure.

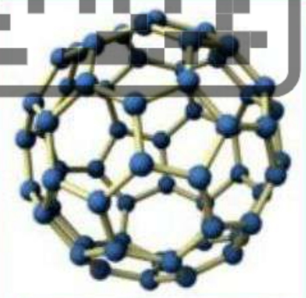
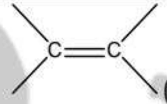
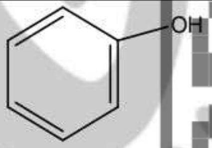
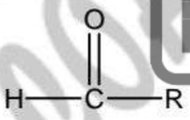
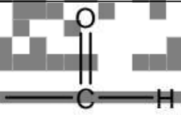
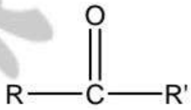
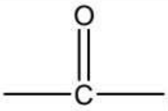


Fig 3.2: Structure of Bucky Ball

Functional Group

“A functional group is a specific group of atoms within the molecule that is responsible for unique chemical properties and determines its characteristic reactions".

HOMOLOGUES SERIES	**GENERAL FORMULA**	**FUNCTIONAL GROUP**
Alkane	R — H or C_nH_{2n+2}	—
Alkene	R = H or C_nH_{2n}	 (double bond)
Alkyne	R ≡ H or C_nH_{2n-2}	$—C\equiv C—$ (triple bond)
Haloalkane	R — X (where X = F, Cl, Br, I Or $C_nH_{2n+1}X$	—X (halide group)
Alcohol	R — OH or $C_nH_{2n+1}OH$	— OH (hydroxyl group)
Phenol	 Or R — O —R' or C_6H_5OH	— OH (hydroxyl group)
Ether	R — O —R' or $C_nH_{2n+2}O$	— OR' (alkoxyl group)
Aldehydes	 $H—\overset{\overset{\displaystyle O}{\|}}{C}—R$	 $—\overset{\overset{\displaystyle O}{\|}}{C}—H$ (carbonyl group or —CHO) aldehyde group
ketone	 $R—\overset{\overset{\displaystyle O}{\|}}{C}—R'$	 $—\overset{\overset{\displaystyle O}{\|}}{C}—$ (carbonyl group) (Ketonic group)

Homologous Series

"A series refers to group of organic compounds with similar structural characteristics but differing from each other by the addition of a methylene group ($-CH_2-$) in their structure is called homologous series".

The general characteristics of homologous series are given below:

(i) The composition of all the members of a homologous series can be expressed by a general formula.

Alkane C_nH_{2n+2}
Alkene C_nH_{2n}
Alkynes C_nH_{2n-2}
Alcohol C_nH_{2n+1} OH
Alkyl halide C_nH_{2n+1} X
Amine C_nH_{2n+1} NH_2

(ii) The molecular mass of each member of homologous series differs from the next higher or lower member by 14 a.m.u.

(ii) All the members of homologous series show similar chemical properties due to the presence of similar functional group.

(iv) There is a gradual variation in the physical properties such as physical state, solubility, melting and boiling points etc as the number of carbon atoms per molecule increases.

Short Questions

1. Define organic chemistry and give the significance of some organic compounds in everyday life

Organic chemistry is the study of the structure, properties, composition, reactions, and preparation of organic compounds. Organic compounds are chemical compounds that contain carbon atoms. They are the basis of all life on Earth, and they are also found in many non-living things, such as petroleum, coal, and natural gas.

Some of the most important organic compounds in everyday life include:

- **Food:** Organic compounds make up all of the food that we eat. Carbohydrates, proteins, fats, and vitamins are all organic compounds.
- **Clothing:** Many of the fibers that are used to make clothing, such as cotton, wool, and polyester, are organic compounds.
- **Plastics:** Plastics are synthetic organic compounds that are used to make a wide variety of products, from food packaging to medical devices.
- **Fuels:** Petroleum and coal are both organic compounds. They are used to generate electricity and power vehicles.
- **Medicines:** Many medicines are organic compounds. For example, aspirin, ibuprofen, and penicillin are all organic compounds.

2. What is Vital force theory? Why was it disapproved?

Notes pg #

3. Define functional group and write the structure of three oxygen containing functional group.

Notes pg #

4. Define the following terms: (a) Catenation (b) Isomerism

Notes pg #

5. How can you differentiate between total and partial synthesis of organic compounds?

Notes Pg #

6. What is meant by Reforming? Why is it considered a useful technique?

Reforming is a chemical process that converts low-octane hydrocarbons into high-octane hydrocarbons. It is a widely used process in the petroleum industry to produce gasoline and other high-value products.

Reforming is a useful technique because it allows refiners to produce high-octane gasoline from low-octane hydrocarbons. This is important because high-octane gasoline produces less emissions and less engine knocking.

Here are some of the specific benefits of reforming:

- Improved octane rating: Reforming produces high-octane gasoline, which is better for engines and produces less emissions.
- Increased yield of high-value products: Reforming also produces other high-value products, such as benzene, toluene, and xylene, which can be used to make a variety of other products, such as plastics and petrochemicals.
- Reduced environmental impact: Reforming can help to reduce the environmental impact of gasoline production by reducing the amount of waste products that are produced.

7. Write down some examples of products that can be produced using biotechnology?

- **Food:**

Biotechnology can be used to produce food that is more nutritious, pest-resistant, or drought-tolerant. For example, genetically modified (GM) crops such as soybeans, corn, and rice are widely grown around the world. Biotechnology can also be used to produce food additives and enzymes, such as rennet for cheesemaking and aspartame for sweeteners.

- **Medicine:**

Biotechnology is used to produce a wide range of medicines, including vaccines, antibiotics, and hormones. For example, recombinant insulin is produced using biotechnology, and it is used to treat diabetes. Biotechnology is also being used to develop new treatments for cancer and other diseases.

- **Biofuels:**

Biotechnology can be used to produce biofuels such as ethanol and biodiesel from renewable resources such as corn and soybeans. Biofuels can help to reduce our reliance on fossil fuels and reduce greenhouse gas emissions.

- **Industrial chemicals:**

Biotechnology can be used to produce a variety of industrial chemicals, such as bioplastics, detergents, and solvents. Biobased chemicals can help to reduce our reliance on petroleum and other fossil fuels.

- **Environmental products:**

Biotechnology can be used to produce a variety of environmental products, such as bioremediation agents and wastewater treatment products. Bioremediation agents can be used to clean up contaminated soil and water, and wastewater treatment products can be used to remove pollutants from wastewater.

8. Write down some common uses of organic compounds?

Organic compounds are used in a wide variety of products and applications.

- **Food:** Organic compounds make up all of the food that we eat. Carbohydrates, proteins, fats, and vitamins are all organic compounds.
- **Clothing:** Many of the fibers that are used to make clothing, such as cotton, wool, and polyester, are organic compounds.
- **Plastics:** Plastics are synthetic organic compounds that are used to make a wide variety of products, from food packaging to medical devices.
- **Fuels:** Petroleum and coal are both organic compounds. They are used to generate electricity and power vehicles.
- **Medicines:** Many medicines are organic compounds. For example, aspirin, ibuprofen, and penicillin are all organic compounds.
- **Personal care products:** Organic compounds are used in a wide variety of personal care products, such as soaps, shampoos, conditioners, and cosmetics.
- **Cleaning products:** Organic compounds are used in a variety of cleaning products, such as detergents, dishwashing liquids, and all-purpose cleaners.
- **Construction materials:** Organic compounds are used in a variety of construction materials, such as asphalt, roofing materials, and insulation.
- **Industrial products:** Organic compounds are used in a variety of industrial products, such as paints, solvents, and adhesives.

Descriptive Questions

1. Describe the natural sources of organic compounds.

Notes pg #

2. Define Bucky Ball? Explain its structure and mention its some properties.

Notes pg #

3. Explain destructive distillation of coal? What are the various products obtained from it?

Notes pg #

4. Describe homologous series of organic compounds? Write three main properties of homologous series.

Notes pg #

5. Explain various unique characteristics associated with organic compounds.

- **Carbon-based:**

All organic compounds contain carbon. Carbon is a unique element because it can form four bonds with other atoms, which allows it to form a wide variety of complex structures.

Covalent bonding: Organic compounds are held together by covalent bonds. Covalent bonds are strong bonds that are formed when two atoms share electrons.

- **High molecular weights:**

Organic compounds can have very high molecular weights, which means that they can be made up of millions of atoms. This allows organic compounds to form complex structures with a variety of properties.

- **Isomerism:**

Organic compounds can exhibit isomerism. Isomers are compounds that have the same molecular formula but different structures and properties.

- **Functional groups:**

Organic compounds contain functional groups, which are groups of atoms that have specific chemical properties. The presence or absence of functional groups can have a significant impact on the properties of an organic compound.

6. Describe natural product chemistry and explain the use of plants and animals as sources of organic compounds.

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7. Write down the different types of coal and how do they differ from each other?

Notes pg # 71, 72

Chapter
4

Nomenclature of Organic Compounds

INTRODUCTION

- ✓ Organic compounds exhibit a great diversity with millions of known compounds and an infinite number of possible isomers.
- ✓ These compounds can possess distinct functional groups, different type of substituents, and variable lengths, branches and cyclic structure of carbon chains leading to a wide range of structural possibilities.
- ✓ it was a big challenge for organic chemists to establish a systematic and simplified method for naming the vast number of organic compounds in a consistent and uniform manner.
- ✓ However this challenge was successfully addressed with the introduction of IUPAC (international union of pure and applied chemistry) naming system which provides comprehensive solution for the nomenclature of organic compounds and allows chemists to identify and understand the vast array of organic compounds that exists in nature or are synthesized in the laboratory.

HYDROCARBONS AND THEIR DERIVATIVES

Organic compounds are mainly made up of carbon and hydrogen, however certain other elements such as oxygen, nitrogen, Sulphur and halogen may also be present in their structures.

Number of carbon atoms in chain	**prefixes**	**Alkane**	**Alkene**	**Alkyne**
1	Meth-	Methane		
2	Eth-	Ethane	Ethene	Ethyne
3	Prop-	Propane	Propene	Propyne
4	But-	Butane	Butene	Butyne
5	Pent-	Pentane	Pentene	Pentyne
6	Hex-	Hexane	Hexene	Hexyne
7	Hept-	Heptane	Heptene	Heptyne
8	Oct-	Octane	Octene	Octyne
9	Non-	Nonane	Nonene	Nonyne
10	Dec-	Decane	Decene	Decyne
11	Undec-	Undecane	Undecene	Undecyne
12	Dodec-	Dodecane	Dodecene	Dodecyne

HISTORY OF NOMENCLATURE

Every organic compound found on Earth possesses a distinct structural feature. Initially the names of organic compounds were assigned on the basis of origin or the person who discovered.

These specific designations are referred to as common names or trivial names.

With the rapid growth of organic chemistry, the number of compounds increased tremendously, where it became impossible to assign a common name to such an extensive range of compounds and scientists felt the need for a structural or systematic name, that one would accurately reflect the molecular structure of organic compound.

An attempt was made at Geneva conference (1892) to create unique nomenclature wherein only one official name would be assigned to each compound. In 1958, a new commission on nomenclature was appointed by the international union of pure and applied chemistry (IUPAC) for further work on the nomenclature.

This new system of nomenclature has set rules for naming organic molecules on the basis of their structures.

IUPAC SYSTEM

The systematic or scientific system for the naming of organic compound is referred as IUPAC method. This system provides distinct names for over fifteen millions reported organic compounds and can be devised for the millions of organic compounds yet to be synthesized.

IUPAC method considers the arrangement of carbon atoms, types and positions of functional groups and other distinctive features of the compound to generate a standard name.

1) The general rules set for IUPAC method of naming organic compounds are as follow:
2) Identify the longest unbroken carbon chain within the molecule which will act as parent chain.
3) Allocate numerical designations to the carbon atoms within the parent chain to the terminal side, to which functional group is nearer.
4) ldentify substituents and name them using prefix such as methyl, ethyl, methoxy, chloro, bromo etc. and mention their position in the longest carbon chain.
5) If any functional group is present in the molecule, name it by using appropriate suffix such as "one" for ketone, "-al" for aldehyde and -ol" for alcohol etc.
6) If there are more than one functional group present in the molecule, write their name on priority basis set by priority rules i.e.
   (-COOH) > (-CHO) > (C=O) > (-OH) > (-NH2) > (-O-) > (=)> (≡).

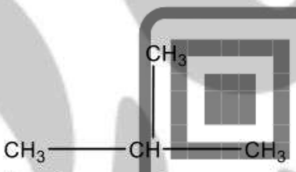
NOMENCLATURE OF ALKANES

In this system, all the carbon atoms present in the structure are included in the name, regardless of whether these carbon atoms are attached to each other in straight chain or in a branch form.

1) The prefix n- is utilized for alkanes where all the carbon atoms are arranged in a single uninterrupted straight chain.
2) The prefix Iso- is utilized if in the structure of alkane molecule one branch (e.g. CH_3) is attached to the second last carbon atom of the chain.
3) The prefix Neo- is utilized if two branches are attached on the second last carbon of alkanes.

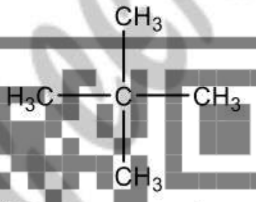
$CH_3-CH_2-CH_2-CH_3$

(n-Butane)



$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_3$

(Isobutane)



$H_3C-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

(Neopentane)

IUPAC System

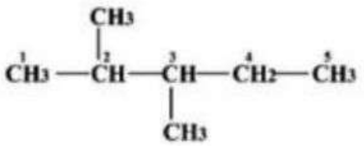
- ✓ The IUPAC names of alkane family is ended with the suffix "ane".
- ✓ The first four members of this group of organic compounds are written by their trivial names (methane ethane, propane and butane).
- ✓ From the fifth onwards alkanes are named by prefixing the Greek numerals pent (five), hex (six), hept (seven), oct (eight) etc. indicating the number of carbons presents in the molecule to the suffix "ane",

When naming a specific alkane, by IUPAC system it is important to consider the following fundamental rules.

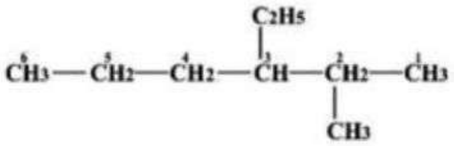
1) Select the longest continuous carbon chain in the molecule and number the carbon chain from one of its terminal. The name of the chain is retained as propane, butane, pentane, hexane etc.
2) The numbering of carbon chain should be assigned, starting from the terminal where functional group or an alkyl group (substituent) is nearest.
3) If the identical substituents are attached at the same position from both ends of main carbon chain, numbering can be done from either terminal. However, if the identical substituents are attached at different positions, the numbering should be done from the side where the substituent is nearer.
4) When two different substituents are attached at the same position from either side of the carbon chain, the numbering of chain is determined

from the terminal where the substituent with the lower alphabetical order is nearer.

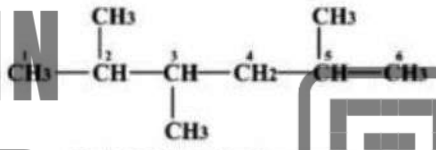
5) When two or more same substituents are attached to the carbon chain, indicate the quantity of each substituent by using di, tri and so forth.
6) Prefix cyclo is used to name cycloalkanes.


$CH_3-\overset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2-CH_3$

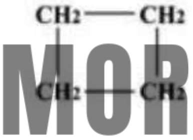
(2, 3-Dimethylpentane)

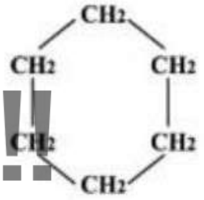

$CH_3-CH_2-CH_2-\overset{C_2H_5}{CH}-\underset{CH_3}{CH_2}-CH_3$

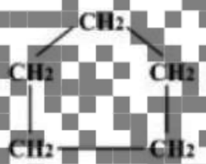
(3-Ethyl-2-methylhexane)


$CH_3-\overset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-CH_3$

(2, 3, 5-Trimethylhexane)


(Cyclobutane)


(Cyclohexane)


(Cyclopentane)

NOMENCLATURE OF ALKENES

Common system

In common system, alkenes are named by replacing the suffix "ane" with "ylene" for example ethylene, propylene, butylene.

$CH_2 = CH_2$,
(Ethylene)

$CH_3 - CH = CH_2$
(Propylene)

An alternative way of naming alkenes is by considering them as derivatives of ethylene.
For example

$C_2H_5 - CH = CH - C_2H_5$,
(Diethylethylene)

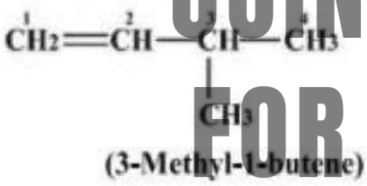
$CH_3 - CH = CH_2$
(Methylethylene)

IUPAC System

In the IUPAC naming of alkene the suffix "ene" is used to indicate the presence of double bond.

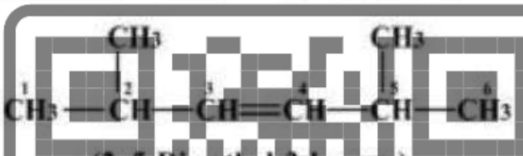
Consider the following general rules as a guideline for naming alkene molecule according to IUPAC system.

a. Select the longest carbon chain which must contain double bonded carbon atoms.
b. The numbering of the longest chain starts from that end nearest to the carbon-carbon double bond irespective of the location of alkyl radicals.
c. Indicate the position of double bond by specifying the location of carbon atoms involved in the double bond.
d. If there are more than one double bonds present within the carbon chainthey are indicated by adding the prefixes di, tri etc. before the suffix "ene".



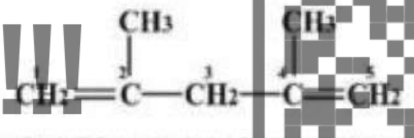
$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\underset{CH_3}{\overset{3}{C}H}{-}\overset{4}{C}H_3$

(3-Methyl-1-butene)



$\overset{1}{C}H_3{-}\overset{CH_3}{\overset{2}{C}H}{-}\overset{3}{C}H{=}\overset{4}{C}H{-}\overset{CH_3}{\overset{5}{C}H}{-}\overset{6}{C}H_3$

(2, 5-Dimethyl-3-hexene)



$\overset{1}{C}H_2{=}\overset{CH_3}{\overset{2}{C}}{-}\overset{3}{C}H_2{-}\overset{CH_3}{\overset{4}{C}}{=}\overset{5}{C}H_2$

(2, 4-Dimethyl-1, 4-pentadiene)

NOMENCLATURE OF ALKYNES

Common System

In common system, the first member of alkyne family is named as acetylene (CzH). The name of higher alkynes are derived from acetylene by considering the branched carbon atoms as alkyl radicals.

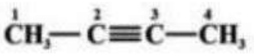
For example

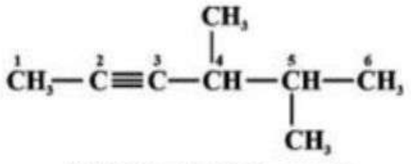
$HC = CH$ (Acetylene)	$H_3C- C \equiv CH$ (Methylacetylene)	$CH_3 - C \equiv C - CH_3$ (Dimethylacetylene)
$C_2H_5 - C \equiv C - CH_3$ (Ethylmethylacetylene)	$CH_2 = CH -C = C- CH = CH_2$ (Divinylacetylene)	

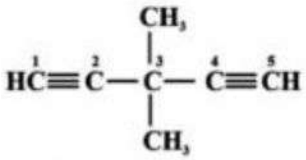
IUPAC System

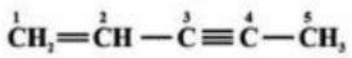
To write IUPAC names of alkynes, it is necessary to consider the following essential rules.

a. Select the longest continuous carbon chain which must include both the carbon atoms containing triple bond.
b. The numbering of carbon chain starts from the terminal which is nearest to the carbon-carbon triple bond.
c. Write the name of parent alkanes for the same number of carbon atoms, replacing suffix "ane" with "yne" to indicate the presence of triple bond.
d. Indicate the position of triple bond by specifying the location of the carbon atom involved in the bond.
e. If two or more triple bond are present in the chain then they are indicated by adding the prefix di, tri etc. before the suffix -yne.
f. When both double and triple bonds are present in the molecule at different positions then the numbering starts from the end where the bond (double or triple) is nearest.
g. When double and triple bonds are present in the molecule at equal positions from the end, then the preference of numbering is given to double bond.


(2-Butyne)


(4,5-Dimethyl-2-hexyne)


(3,3-Dimethyl-1, 4-pentadiyne)


(1- Pentene-3-yne)

NOMENCLATURE OF ALKYL HALIDES

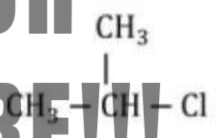
Alkyl halides are the derivatives of alkanes in which one or more hydrogen of alkanes are replaced by halogen atom.

Common System

The common name of an alkyl halide is formed by naming the alkyl group first, followed by the term "halide".

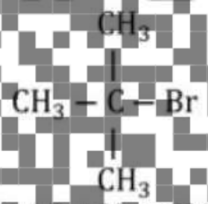
$CH_3 - Cl$	$CH_3 - CH_2 - Br$	$CH_3 - CH_2 - CH_2 - I$
(Methyl chloride)	(Ethyl bromide)	(Propyl iodide)

The term secondary (sec.) and tertiary (tert..) are used as prefix if the carbon atom bonded to halogen is further attached to two and three other carbon atoms respectively.



$$\begin{array}{c} \phantom{CH_3 - {}}CH_3\phantom{{} - Cl} \\ \phantom{CH_3 - {}}|\phantom{{} - Cl} \\ CH_3 - CH - Cl \end{array}$$

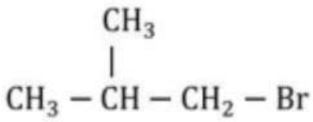
(sec-Propyl chloride)



$$\begin{array}{c} \phantom{CH_3 - {}}CH_3\phantom{{} - Br} \\ \phantom{CH_3 - {}}|\phantom{{} - Br} \\ CH_3 - C - Br \\ \phantom{CH_3 - {}}|\phantom{{} - Br} \\ \phantom{CH_3 - {}}CH_3\phantom{{} - Br} \end{array}$$

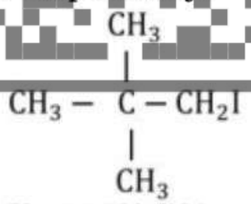
(tert-Butyl bromide)

The term iso and neo are also used as prefix when penultimate carbon is further attached to two or three other carbon atoms respectively.



$$\begin{array}{c} \phantom{CH_3 - {}}CH_3\phantom{{} - CH_2 - Br} \\ \phantom{CH_3 - {}}|\phantom{{} - CH_2 - Br} \\ CH_3 - CH - CH_2 - Br \end{array}$$

(Isobutyl bromide)



$$\begin{array}{c} \phantom{CH_3 - {}}CH_3\phantom{{} - CH_2I} \\ \phantom{CH_3 - {}}|\phantom{{} - CH_2I} \\ CH_3 - C - CH_2I \\ \phantom{CH_3 - {}}|\phantom{{} - CH_2I} \\ \phantom{CH_3 - {}}CH_3\phantom{{} - CH_2I} \end{array}$$

(Neo pentyl iodide)

IUPAC System

In IUPAC system alkyl halides are named as haloalkanes, where halo is chloro, bromo, iodo etc. When naming alkyl halides according to IUPAC system, it is important to adhere to the following rules.

a. Determine the longest carbon chain that contains the carbon atom directly bonded to halogen.
b. Number the carbon atoms in the chain from the end closest to the halogen atom.

c. When a double or triple bond is present in the halogenated carbon chain it is recommended to number the chain from the end nearest to the double or triple bond.

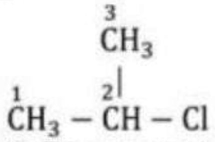
d. Prefix di, tri, tetra etc. are used to indicate the number of halogens attached to the main carbon chain.

e. When two different halogens are attached to the carbon chain at the same position from opposite ends, the halogen name will be written by its alphabetical order.

alphabetical order.

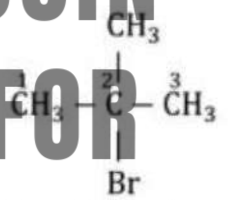
$CH_3 - CH_2 - Br$

(Bromoethane)



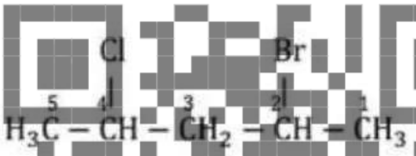
$\overset{1}{C}H_3 - \overset{2}{C}H(\overset{3}{C}H_3) - Cl$

(2-Chloropropane)



$\overset{1}{C}H_3 - \overset{2}{C}(CH_3)(Br) - \overset{3}{C}H_3$

(2-Bromo-2-methylpropane)



$H_3\overset{5}{C} - \overset{4}{C}H(Cl) - \overset{3}{C}H_2 - \overset{2}{C}H(Br) - \overset{1}{C}H_3$

(2-Bromo-4-chloropentane)

CF_2Cl_2

(Dichlorodifluromethane)

NOMENCLATURE OF AMINES

Amines are organic compounds that contain a nitrogen atom bonded to one or more alkyl or aryl groups. Primary amines contains one alkyl group bonded to the nitrogen atom while secondary and tertiary amine are identified by the direct attachment of two and three alkyl groups with the nitrogen atom respectively.

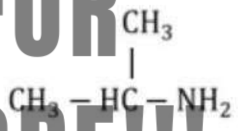
Common System

The common name of a primary amine is formed by combining the name of alkyl group with the suffix "amine".

$CH_3 - NH_2$ (Methyl amine)

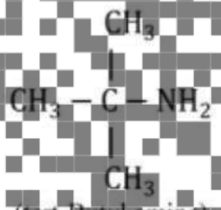
$CH_3 - CH_2 - NH_2$ (Ethyl amine)

The prefix sec. and tert. are used if the carbon atom bonded to nitrogen is further attached with two or three alkyl radicals.



$$CH_3 - \overset{\displaystyle CH_3 \atop |}{HC} - NH_2$$

(sec-Propyl amine)



$$CH_3 - \underset{\displaystyle | \atop CH_3}{\overset{\displaystyle CH_3 \atop |}{C}} - NH_2$$

(tert-Butyl amine)

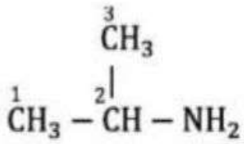
IUPAC System

In IUPAC system, primary amines are named as alkanamine and based on the following rules.

1) Select the longest carbon chain that contain the carbon atom directly bonded to $-NH_2$ group.
2) Write the name of compound by replacing the ending “e" of alkane chain by adding the suffix "amine".

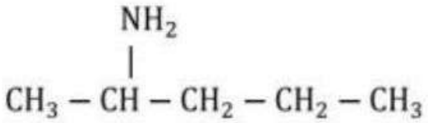
$CH_3 - CH_2 - NH_2$

(Ethanamine)



$$\overset{1}{C}H_3 - \overset{\displaystyle \overset{3}{C}H_3 \atop {}^{2}|}{C}H - NH_2$$

(2-Propanamine)



$$CH_3 - \overset{\displaystyle NH_2 \atop |}{CH} - CH_2 - CH_2 - CH_3$$

(2-Pentanamine)

NOMENCLATURE OF ALCOHOLS

Organic compounds that contain one or more hydroxyl (-0H) functional group attached to the carbon chain are called alcohols.

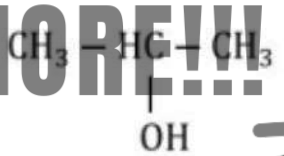
Common System

Since alcohols are hydroxyl derivatives of hydrocarbons, their common names are formed by combining the name of alkyl group with the suffix “alcohol".

$CH_3 - OH$
(Methyl alcohol)

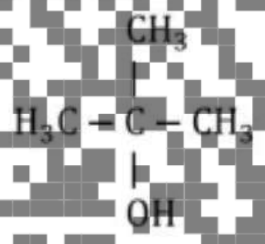
$CH_3 - CH_2 - CH_2 - OH$
(Propyl alcohol)

If the carbon atom bearing the hydroxyl group is directly connected to two or three other carbon atoms, the term secondary and tertiary is used as a prefix.



$$CH_3 - \underset{\displaystyle OH}{\underset{|}{HC}} - CH_3$$

(sec-Propyl alcohol)



$$H_3C - \underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - CH_3$$

(tert-Butyl alcohol)

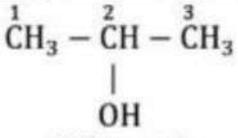
IUPAC System

The set of rules established by IUPAC system for the naming of alcohol is given as follow:

a. Identify the longest continuous carbon chain that include the carbon atom bearing the hydroxyl group (-OH).
b. Number the carbon atoms in the chain starting from the end nearest to the hydroxyl group.
c. The end “e of the parent alkane is replaced by "ol".
d. If the molecule of alcohol has substituents (CH_3, Br, Cl, I etc), name them as prefixes.
e. If two or more hydroxyl groups are present in the carbon chain, use di, tri etc. before the suffix -ol".
f. The positions of substituents should be written in alphabetical order.

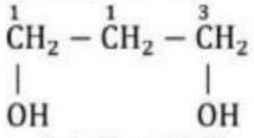
$CH_3 - CH_2 - OH$

(Ethanol)



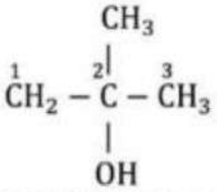
$\overset{1}{C}H_3 - \underset{\displaystyle OH}{\underset{|}{\overset{2}{C}H}} - \overset{3}{C}H_3$

(2-Propanol)



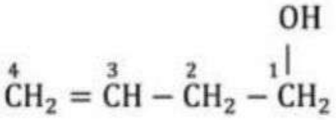
$\underset{\displaystyle OH}{\underset{|}{\overset{1}{C}H_2}} - \overset{1}{C}H_2 - \underset{\displaystyle OH}{\underset{|}{\overset{3}{C}H_2}}$

(1, 3-Propandiol)



$\overset{1}{C}H_2 - \underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{\overset{2}{C}}}}} - \overset{3}{C}H_3$

(2-Methyl-2-propanol)



$\overset{4}{C}H_2 = \overset{3}{C}H - \overset{2}{C}H_2 - \overset{\displaystyle OH}{\overset{|}{\overset{1}{C}H_2}}$

(3-Buten-1-ol)

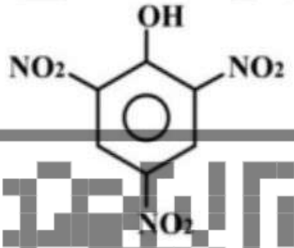
NOMENCLATURE OF PHENOLS

The class of organic compounds in which one or more hydroxyl group are directly attached with the benzene ring are called as phenols.

In the IUPAC nomenclature system, the parent molecule is referred phenol while numbering the substituents, the hydroxyl group (OH) is assigned the default first position. The term ortho, (-o), meta (-m) and para (-p) may be used for mentioning the position of substituents. It is important to note that certain phenols are still used by their trivial names in IUPAC system of nomenclature.

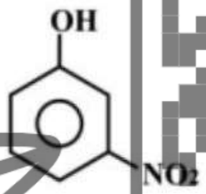
(2-Chlorophenol)
(o-Chlorophenol)

(4-Methylphenol)
(p-Cresol)

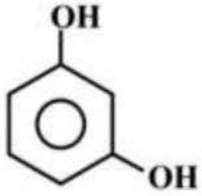


(2, 4, 6-Trinitrophenol)
(Picric acid)

(1, 2-Benzenediol)
(Catechol)

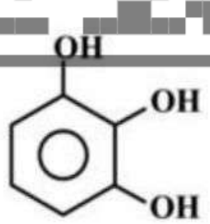


(3-Nitrophenol)
(m-Nitrophenol)



(1, 3-Benzenediol)
(Resorcinol)

(1, 4-Benzenediol)
(Hydroquinone)



(1, 2, 3-Benzenetriol)
(Pyrogallol)

NOMENCLATURE OF ETHERS

Ether is a family of organic compounds in which two alkyl or aryl radicals are attached to an oxygen atom. These compounds are represented by R-0-R.

Common System

In the common system of naming of ethers, the two alkyl groups are written in alphabetical order and the term ether is added at the end of the name.

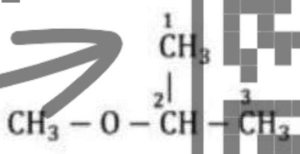
$CH_3 -O - C_2H_5$	C_2H_5 -O- C_2H_5	$C_6H_5 -O - CH_3$
(Ethyl methyl ether)	(Diethyl ether)	(Methyl phenyl ether)

IUPAC System

In IUPAC system of nomenclature, ethers are referred to as alkoxy derivatives of alkanes. The alkyl group of larger number of carbon atoms is considered as the main carbon chain whereas the smaller alkyl group, along with its oxygen is named as alkoxy group. The alkoxy group is taken as prefix.

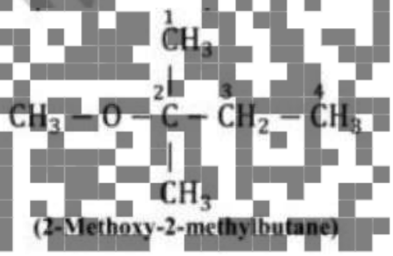
$CH_3 - O - CH_2 - CH_3$

(Methoxyethane)



$CH_3 - O - \overset{2}{C}H(\overset{1}{C}H_3) - \overset{3}{C}H_3$

(2-Methoxypropane)



$CH_3 - O - \overset{2}{C}(\overset{1}{C}H_3)(CH_3) - \overset{3}{C}H_2 - \overset{4}{C}H_3$

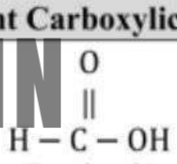
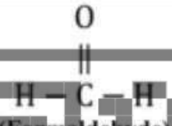
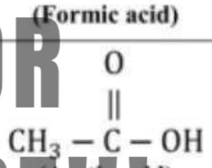
(2-Methoxy-2-methylbutane)

NOMENCLATURE OF ALDEHYDES AND KETONES

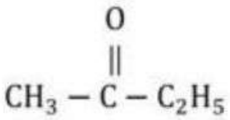
Aldehydes and ketones are characterized by the presence of a carbonyl group. (C-O). Aldehydes have carbonyl group at the end of carbon chain whereas ketones have the carbonyl group within the carbon chain.

Common System

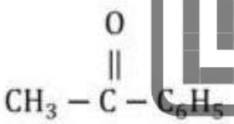
The common name of aldehyde is derived from the corresponding parent carboxylic acid by replacing -ic acid with the aldehyde.
For example

Parent Carboxylic Acid	Aldehyde
 $H-\overset{\overset{O}{\Vert}}{C}-OH$ (Formic acid)	 $H-\overset{\overset{O}{\Vert}}{C}-H$ (Formaldehyde)
 $CH_3-\overset{\overset{O}{\Vert}}{C}-OH$ (Acetic acid)	 $CH_3-\overset{\overset{O}{\Vert}}{C}-H$ (Acetaldehyde)

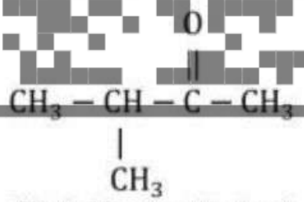
The common naming system of ketones is quite similar to that of ether. The two alkyl groups attached to the carbonyl carbon are named in alphabetical order and the term ketone is added at the end of the name.


$CH_3-\overset{\overset{O}{\Vert}}{C}-C_2H_5$

(Ethyl methyl ketone)


$CH_3-\overset{\overset{O}{\Vert}}{C}-C_6H_5$

(Methyl phenyl ketone)

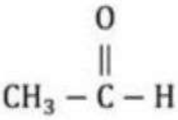

$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\Vert}}{C}-CH_3$

(Methyl isopropyl ketone)

IUPAC System

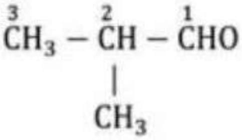
In this system aldehydes are named after the name of corresponding alkanes. The ending "e" of alkane being replaced by suffix -al. The longest carbon chain containing the CHO group is chosen as the parent chain. The position of substituents are indicated by the numbers of carbon atoms to which they are attached and the carbon atom of the -CHO group is given number one.

The hydroxyl group take preference over double bond and double bond take preference over halogens and alkyl groups if present in the molecule.



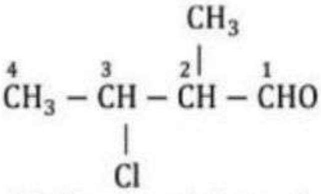
$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - H$

(Ethanal)



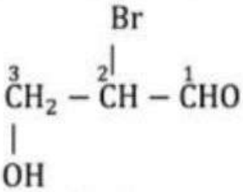
$\overset{3}{C}H_3 - \underset{\underset{\displaystyle CH_3}{|}}{\overset{2}{C}H} - \overset{1}{C}HO$

(2-Methylpropanal)



$\overset{4}{C}H_3 - \underset{\underset{\displaystyle Cl}{|}}{\overset{3}{C}H} - \overset{\overset{\displaystyle CH_3}{|}}{\overset{2}{C}H} - \overset{1}{C}HO$

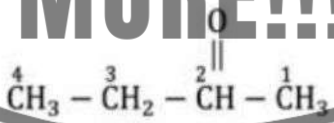
(3-Chloro-2-methylbutanal)



$\underset{\underset{\displaystyle OH}{|}}{\overset{3}{C}H_2} - \overset{\overset{\displaystyle Br}{|}}{\overset{2}{C}H} - \overset{1}{C}HO$

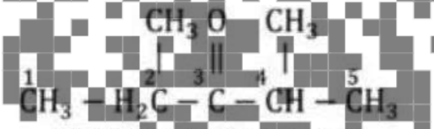
(2-Bromo-3-hydroxypropanal)

In the IUPAC naming of ketones, the longest carbon chain having the ketonic functional group is chosen as the parent chain and the ketone is named by replacing -e" of the parent alkane with the suffix "one". The position of substituents are indicated by numbers of the carbon atoms to which they are attached and the carbon of carbonyl group is given the lowest possible number.



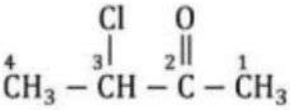
$\overset{4}{C}H_3 - \overset{3}{C}H_2 - \overset{\overset{\displaystyle O}{\|}}{\overset{2}{C}H} - \overset{1}{C}H_3$

(2-Butanone)



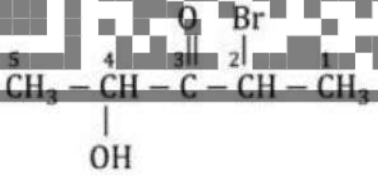
$\overset{1}{C}H_3 - \overset{\overset{\displaystyle CH_3}{|}}{\overset{2}{H_2C}} - \overset{\overset{\displaystyle O}{\|}}{\overset{3}{C}} - \overset{\overset{\displaystyle CH_3}{|}}{\overset{4}{C}H} - \overset{5}{C}H_3$

(2, 4-Dimethyl-3-pentanone)



$\overset{4}{C}H_3 - \overset{\overset{\displaystyle Cl}{|}}{\overset{3}{C}H} - \overset{\overset{\displaystyle O}{\|}}{\overset{2}{C}} - \overset{1}{C}H_3$

(3-Chloro-2-butanone)



$\overset{5}{C}H_3 - \underset{\underset{\displaystyle OH}{|}}{\overset{4}{C}H} - \overset{\overset{\displaystyle O}{\|}}{\overset{3}{C}} - \overset{\overset{\displaystyle Br}{|}}{\overset{2}{C}H} - \overset{1}{C}H_3$

(2-Bromo-4-hydroxy-3-pentanone)

NOMENCLATURE OF CARBOXYLIC ACIDS

Organic compounds which contain carboxyl group (–COOH) are known as carboxylic acids.

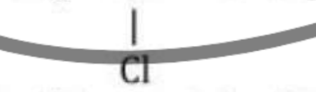
Common System

The common names of mono carboxylic acids refers to their sources rather than their chemical structures. Positions of substituents is designated by, B and Y etc.

Common names of some carboxylic acids are given below.

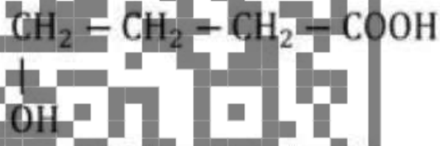
Structure	**Common name**
HCOOH	Formic acid
CH_3COOH	Acetic acid
CH_3CH_2COOH	Propionic acid
$CH_3(CH)_2COOH$	Butyric acid
$CH_3\ (CH_2)_2COOH$	Valeric acid
$CH_3(CH_2)_4COOH$	Caproic acid

Common names of carboxylic acid are given as



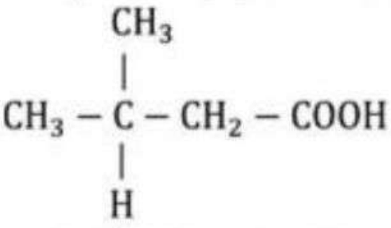
$$CH_3-\underset{\overset{|}{Cl}}{CH}-COOH$$

(∝-Chloro propionic acid)



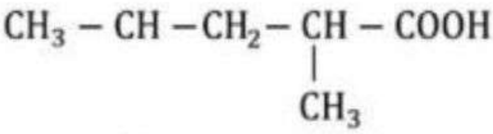
$$\underset{\overset{|}{OH}}{CH_2}-CH_2-CH_2-COOH$$

(γ-Hydroxy butyric acid)



$$CH_3-\overset{\underset{|}{CH_3}}{\underset{\overset{|}{H}}{C}}-CH_2-COOH$$

(β-Methyl butyric acid)



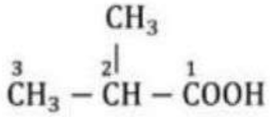
$$CH_3-CH-CH_2-\underset{\overset{|}{CH_3}}{CH}-COOH$$

(∝, β-Dimethyl valeric acid)

IUPAC System

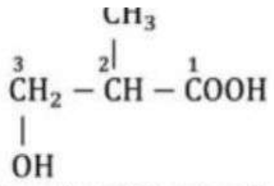
The name of carboxylic acid in IUPAC system is referred as alkanoic acid. The longest continuous carbon chain containing the -COOH group is considered the parent chain and the acid is named by replacing -e of the corresponding alkane with "oic acid".

Double bond in the main chain are written by the ending -enoic acid and its position is designated by numerical prefix. When two -COOH groups are present in the main chain, use the prefix 'di' before the suffix oic acid. When a carboxylic acid is attached to benzene ring the parent ring, named as benzoic acid.



$$\overset{3}{C}H_3-\overset{2}{C}H(CH_3)-\overset{1}{C}OOH$$

(2-Methyl propanoic acid)

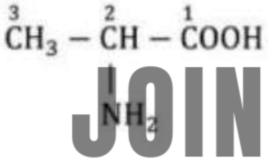


$$\overset{3}{C}H_2(OH)-\overset{2}{C}H(CH_3)-\overset{1}{C}OOH$$

(3-Hydroxy-2-methyl propanoic acid)

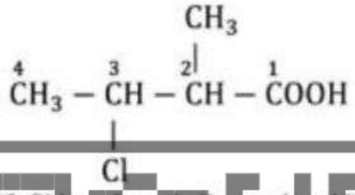
$$HOO\overset{4}{C}-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}OOH$$

(2-Buten-1,4dioic acid)



$$\overset{3}{C}H_3-\overset{2}{C}H(NH_2)-\overset{1}{C}OOH$$

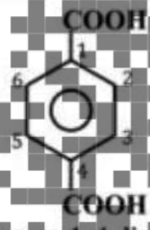
(2-Aminopropanoic acid)



$$\overset{4}{C}H_3-\overset{3}{C}H(Cl)-\overset{2}{C}H(CH_3)-\overset{1}{C}OOH$$

(3-Chloro-2-methylbutanoic acid)

(3-Bromobenzoic acid)



(Benzen-1, 4-dioic acid)

NOMENCLATURE OF ESTERS

Esters are named as alkyl derivatives carboxylic acids. Following steps should be noted for the naming of ester molecules.

1) Find the longest carbon chain which contains -CO0- group.
2) Write the name of alkyl group which is attached to R-CO0- chain.
3) Name the carbon chain that contain ester functional group using "oate" as a suffix.

Common system of nomenclature of ester is quite similar with IUPAC method. Here "ate is used as suffix with the main carbon chain.

Structure of Ester	**Common Name**	**IUPAC Name**
$HCOOC_2H_5$	Ethyl formate	Ethyl methanoate
$CH_3 - CH_2 - COO - CH_3$	Methyl propionate	Methyl propanoate
$CH_3(CH_2)_2COOC_2H_5$	Ethyl butyrate	Ethyl butanoate
$CH_3COOCH(CH_3)_2$	Isopropyl acetate	Isopropyl ethanoate

NOMENCLATURE OF AMIDE

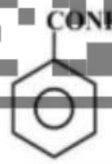
Amides are the derivate of carboxylic acids formed by replacing -OH group of carboxylic acid by NH_2 group. The nomenclature of amide is based on replacing the suffix -oic acid with amide. For example

$CH_3 - CH_2 - CONH_2$

(Propanamide)

$CH_3 - (CH_2)_2 - CONH_2$

(Butanamide)



(Benzamide)

NOMENCLATURE OF ACYL HALIDE S

Acyl halides or acid halides are derived from carboxylic acids. They are characterized by the presence of a halogen atom attached to acyl group(R-CO-).

When naming an acyl halide, the work begins with the name of the corresponding carboxylic acid. In both common and IUPAC method the ic acid ending the carboxylic acid is replaced by -yl, and then name the specific halide group.

For example

$CH_3 - CH_2 - CO - Br$
Propanoyl bromide (IUPAC)
Propionyl bromide (common)

$CH_3 - COCl$
Ethanoyl chloride (IUPAC)
Acetyl chloride (common)

Short Questions

1. Why IUPAC system of nomenclature is preferred on common system of naming of organic compounds?

The IUPAC system of nomenclature for organic compounds is preferred over the common system of naming for several reasons:

- Unambiguousness: The IUPAC system provides a unique and unambiguous name for every organic compound, regardless of its complexity. This is because the name is based on the structure of the compound, rather than on any arbitrary or historical criteria.
- Systematic: The IUPAC system is a systematic approach to naming organic compounds. This means that there are a set of rules that can be followed to generate a name for any compound. This makes it easy to learn and apply the system.
- International: The IUPAC system is an internationally accepted standard for naming organic compounds. This means that chemists from all over the world can communicate with each other using the same nomenclature system.

2. Write the name of five organic families and mention the functional group present in them.

Family	**Functional group**
Alkanes	Alkyl group (C–C)
Alkenes	Carbon-carbon double bond (C = C)
Alkynes	Carbon-carbon triple bond (C ≡ C)
Alcohols	Hydroxyl group (– OH)
Carboxylic acids	Carboxyl group (– COOH)

3. Write down basic rules for IUPAC naming of organic compound.

Notes Pg #

4. We often use the term Iso and Neo in the common system of naming of alkanes. Explain with example

The terms "iso" and "neo" are used in the common system of naming alkanes to indicate specific branching patterns.

- Iso: The prefix "iso" is used to indicate that the compound is a branched alkane with a methyl group attached to the second carbon atom. For example, isobutane is a branched alkane with a methyl group attached to the second carbon atom of a three-carbon chain.

- Neo: The prefix "neo" is used to indicate that the compound is a branched alkane with a tertiary butyl group attached to a carbon atom. For example, neopentane is a branched alkane with a tertiary butyl group attached to the second carbon atom of a three-carbon chain.

Here are some more examples:

Compound	**Common name**	**IUPAC name**
$CH_3CH(CH_3)_2$	Isobutane	2-Methylpropane
$(CH_3)\ _3CH$	Neopentane	2,2-Dimethylpropane
$(CH_3CH_2CH(CH_3))_2$	Isoheptane	2-Methylhexane
$(CH_3)\ _3CCH_2(CH_3)\ _3$	Neooctane	2,2,4-Trimethylpentane

5. Write the common names of first five members of carboxylic acid.

The common names of the first five members of the carboxylic acid family are:

Formic acid	(HCO_2H)
Acetic acid	(CH_3COOH)
Propionic acid	(CH_3CH_2COOH)
Butyric acid	($CH_3(CH_2)_2COOH$)
Valeric acid	($CH_3(CH_2)_3COOH$)

6. If an organic compound contains both double and triple bond, in the main carbon chain, what rules you follow to write its IUPAC name. Explain by giving an example.

When naming an organic compound that contains both a double and a triple bond in the main carbon chain, the following rules are followed:

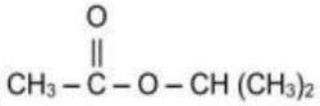
1. Choose the longest carbon chain that contains both the double and triple bond.
2. Number the carbon atoms in the longest chain, starting from the end that is closest to the multiple bonds.
3. If the double and triple bonds have the same number, the double bond is given the lower number.
4. The suffixes "-ene" and "-yne" are added to the end of the parent chain name, in that order.
5. The numbers of the carbon atoms where the double and triple bonds occur are placed in front of the suffixes, and separated by a hyphen.

Example:

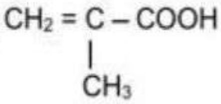
The IUPAC name of the compound CH3 – CH = CH – C ≡ C is: **2-buten-4-yne**

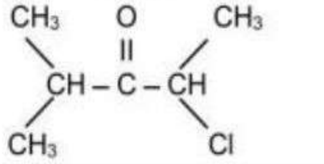
Descriptive Questions

1. Give the IUPAC names of the following organic molecules.

(a)

$CH_3-\overset{\overset{O}{\|}}{C}-O-CH(CH_3)_2$

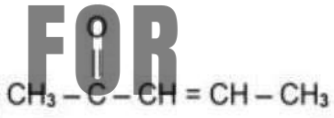
(b) $HC\equiv C-CH(CH_3)-CH=CH_2$

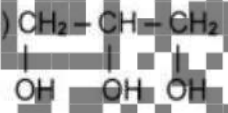
(c)

$CH_2=\underset{\underset{CH_3}{|}}{C}-COOH$

(d)


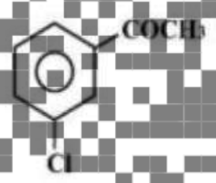
(e) $CH_3-CH_2-OC(CH_3)_2C_2H_5$

(f) $(CH_3)_2CBrCHO$

(g)

$CH_3-\overset{\overset{O}{\|}}{C}-CH=CH-CH_3$

(h)

$\underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$

(i)


(j)


2. Outline the structure of each of the following molecules.

(a) Ethyl neo-pentyl ether (b) Resorcinol

(c) Picric acid (d) Isopropylbutanoate

(e) 1-Bromo-3-methyl hexane-2-one () a, B-dimethyl butyric acid

(g) Butyraldehyde (h) 3-Chlorobenzamide

(i) Butanoyl iodide (j) 1, 2,3-benzentriol

(k) Ethyl isopropyl ketone (l) -Mthyl butyraldehyde

(m) -Chloro-ß-methyl valeric acid

Chapter

5

Hydro Carbon

INTRODUCTION

- Organic compounds made up of hydrogen and carbon atoms are known as hydrocarbons.
- Hydrocarbons are obtained from fossil fuels like coal, petroleum and natural gases which serve as the primary source of energy for generating heat, electricity and fuel for transportation.
- The refining of crude oil yields hundreds of hydrocarbons.
- Methane is the most basic hydrocarbon.
- It is the main constituent of natural gas and is commonly found in marshy areas.

TYPES OF HYDROCARBONS

Hydrocarbons are classified based on their molecular structure and the types of bonds present between carbon atoms.

They can be categorized into two main groups; aliphatic hydrocarbons and aromatic hydrocarbons.

Aliphatic Hydrocarbons

It is a class of hydrocarbon in which carbon atoms are arranged in straight or branched chain through single, double or triple bonds. These are often called as open chain hydrocarbons.

Aliphatic hydrocarbons can be further classified into saturated and unsaturated hydrocarbons. number.

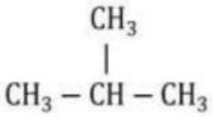
Saturated Hydrocarbons

"In these hydrocarbons, all carbon atoms are attached to each other by a single bond only".

These are further classified into alkanes and cyclo alkanes.

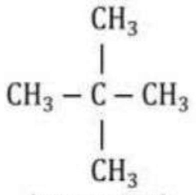
$H_3C-CH_2-CH_2-CH_3$

(n – butane)



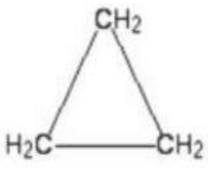
$CH_3-CH(CH_3)-CH_3$

(iso butane)

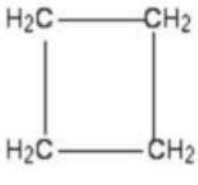


$CH_3-C(CH_3)_2-CH_3$

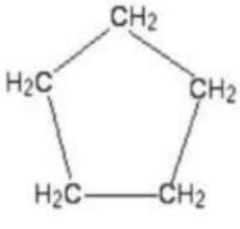
(neo pentane)



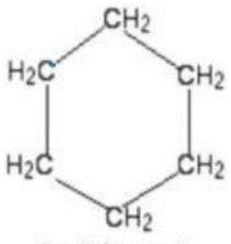
(cyclopropane)



(cyclobutane)



(cyclopentane)



(cyclohexane)

Unsaturated Hydrocarbons

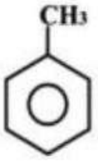
These hydrocarbons contain one or more double or triple bonds between the two adjacent carbon atoms in their structure".

$CH_2 = CH- CH_3$	$CH_3 - C = C - CH_3$	$CH_2 = CH - CH = CH_2$
(1-propene)	(2-butyne)	(1,3-buta diene)

Aromatic Hydrocarbons

"Aromatic compounds are those which characterized by a cyclic arrangement of atoms that are connected by alternating double bonds they generally follow the Huckle rule (4n+2π electrons)".


(Benzene)



(Toluene)

(Phenol)

(Benzoic acid)

ALKANES AND CYCLO ALKANES

ALKANES

Alkanes have open-chain or straight chain structures.

CYCLO ALKANES

Cycloalkanes on the other hand, have a close-ring or cyclic structure. Cycloalkanes are typically nonpolar similar to alkanes.

Despite both being saturated hydrocarbons, cyclopropane exhibits distinct properties compared to alkanes.

Physical properties of alkanes

(i) Alkanes are nonpolar organic compounds that are insoluble in water but soluble in organic solvents.

(ii) Boiling point of alkanes is very low, it increases with the length of the carbon chain.

(iii) The boiling point of straight chain alkanes is higher than that of branched chain alkanes because straight chain alkanes are more extended, which allows the greater surface arca.

(iv) Alkanes which consist of C_1 to C_4 are gases C_5 to C_{17} are liquids and above C_{I7} are waxy solids.

Physical properties of cycloalkanes

(i) Cycloalkanes of C_3 and C_4 carbons are gases, while cycloalkanes of C_5 or more carbon atoms are liquids.

(ii) The boiling point of cycloalkanes is lower than that of straight chain alkanes of comparable molar mass due to the ring strain.

Structure of Alkanes

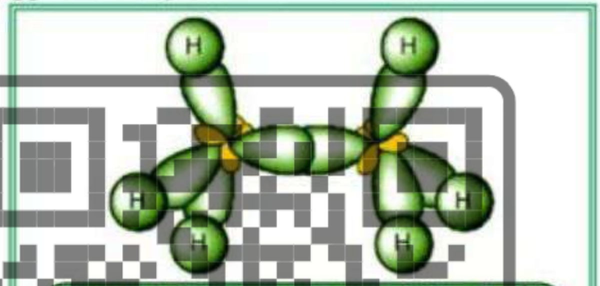
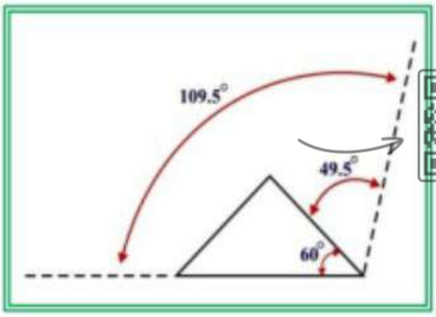


Fig. 5.17 Orbital structure of ethane showing all sp^3-s and sp^3-sp^3 sigma bonds

Alkanes are open chain saturated hydrocarbons. Each carbon atom in alkanes is tetrahedrally bonded with hydrogen atoms and other carbon atoms.
To illustrate the structure of alkanes, the molecule of ethane is taken as a representative example.
Ethane is composed of two carbon atoms and six hydrogen atoms(C_6H_6). Each carbon atom in ethane is sp^3 hybridized containing four sp^3 hybrid orbitals. These four sp^3 hybrid orbitals are arranged in a tetrahedral fashion. Out of four sp^3 hybrid orbitals of each carbon atom, three sp^3 hybrid orbitals are utilized in the formation of sigma bonds with three hydrogen atoms whereas the remaining sp^3 hybrid orbital of one carbon atom overlaps with the sp^3 hybrid orbital of another carbon atom. The bond length between the carbon and carbon atoms is approximately 1.54 ^{o}A, and the bond angle between carbon, carbon and hydrogen atoms is approximately 109.5^{o}.

Structure of Cycloalkanes

Cyclopropane is the smallest and simplest cycloalkanes with a ring composed of three carbon atoms and six hydrogen atoms. The carbon atoms in cyclopropane are arranged in a trigonal geometry with an internal angle of 60°, which is quite smaller than the bond angle (109.5°) exist in alkanes.



Reactivity

Reactivity of Alkanes

Alkanes are less reactive under normal conditions. This is because they are non polar in nature and hence a polar reagent finds no reaction site. Further, the stronger carbon-carbon bond requires high bond energy for its breaking.

Reactivity of Cycloalkanes

Cycloalkanes are very similar to the alkanes in reactivity, except for the very small ones - especially cyclopropane. Cyclopropane is much more reactive due bond angle strain in ring structure.

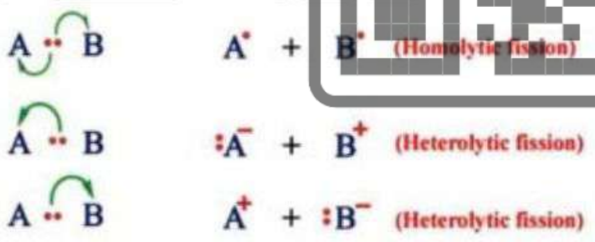
RADICAL SUBSTITUTION REACTIONS

Homolytic fission

In homolytic fission the bond cleavage takes place evenly, with each atom receiving one of the electron from the bond.

Heterolytic fission

In heterolytic fission, the cleavage is uneven with one atom receiving both electrons from the bond and the other atom receiving none.



The mechanism of free radical reaction consists of following three steps.

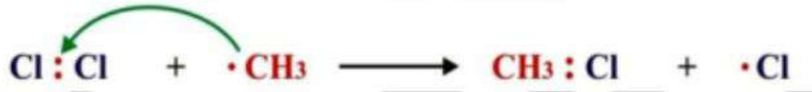
Step-1: Chain Initiation

The reaction begins with the breaking of the chlorine-chlorine bond in the presence of U.V light producing two chlorine free radicals.

Step-2: Chain Propagation

The chlorine radical is produced during chain initiation by attacking the methane molecule and abstracting a hydrogen atom. This process results in the formation of a molecule of hydrogen chloride and a methyl free radical.

The methyl free radical then attacks another chlorine molecule, removing a chlorine atom to produce methyl chloride.



Step-3: Chain Termination

This step leads to the completion of reaction when all free radicals combine to form three possible stable molecules.

$$Cl\cdot + \cdot Cl \longrightarrow Cl:Cl$$

$$CH_3\cdot + \cdot Cl \longrightarrow CH_3:Cl$$

$$CH_3\cdot + \cdot CH_3 \longrightarrow CH_3:CH_3$$

In reality, the reaction does not halt after the production of methyl chloride; rather, the remaining three hydrogen atoms in the methyl chloride molecule are substituted by chlorine atoms before the reaction stops.

$$\underset{\text{(Methane)}}{CH_4} + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{(Methyl chloride)}}{CH_3Cl} + HCl$$

$$CH_3-Cl + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{(Methylene dichloride)}}{CH_2Cl_2} + HCl$$

$$\underset{\text{(Methylene dichloride)}}{CH_2Cl_2} + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{(Chloroform)}}{CHCl_3} + HCl$$

$$\underset{\text{(Chloroform)}}{CHCl_3} + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{(Carbon tetrachloride)}}{CCl_4} + HCl$$

ALKENES

Alkenes are a class of unsaturated hydrocarbons, they contain one or more carbon-carbon double bonds in the chain.

Olefins is another term used to refer alkenes. The term olefin derives from Latin oleum meaning oil. This is because some of early discovered alkenes were oil like.

Structure of Ethene

The structure of ethene is characterized by two sp^2 hybrid carbon atoms that are arranged in a trigonal planar geometry. The double bond between the carbon atoms is composed of a sigma bond, which arises from the overlap of two sp^2 hybrid orbitals from each carbon atom and a pi bond which forms due to lateral overlapping of two un hybrid p orbitals, one from each carbon atom. Each carbon in ethene is also bonded with two hydrogen atoms through sp^2-s sigma bonding. The bond length for the C-C single sigma bond is approximately 1.34 °A and bond angle between the two carbon-hydrogen (C-H) bonds is approximately 120°

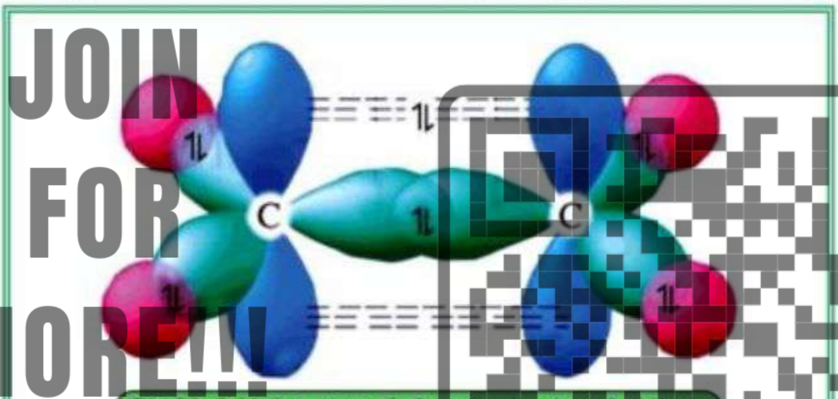


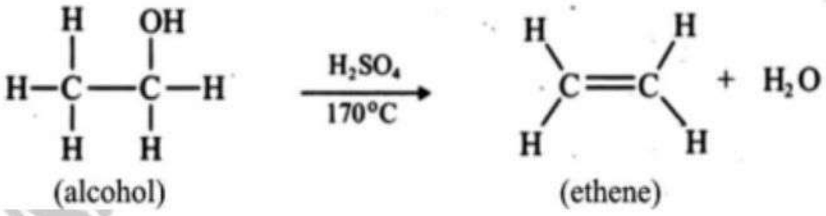
Fig. 5.2: Orbital structure of ethene showing sigma & pi bonds

Preparation of Alkenes

Alkenes can be prepared by dehydration of alcohol and dehydrohalogenation of alkyl halides.

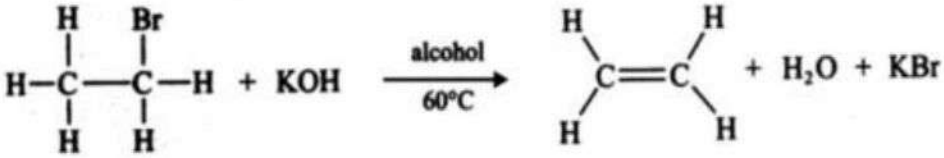
Dehydration of Alcohol

When an alcohol is heated in the presence of a dehydrating agent such as concentrated sulphuric acid, it undergoes elimination of water molecule and gives an alkene.



Dehydrohalogenation of an Alkyl halide

When ethyl halide is treated with an alcoholic solution of potassium hydroxide (KOH), the elimination of a hydrogen and a halogen atom takes place from two adjacent carbon atoms of alkyl halide, giving an alkene.



(ethyl bromide) (ethene)

Reactivity of Alkenes

The higher reactivity of alkene as compared to alkane is attributed to the presence of a pi bond between the carbon atoms.

The pi bond relatively weaker and requires less energy to break.

Additionally the electron density associated with the pi bond is distributed above and below the carbon-carbon axis, making the pi electrons more exposed to an Electrophilic species.

Consequently, alkenes readily react with electrophile making them more reactive than alkanes.

Reactions of Alkenes

Even though alkenes can undergo oxidation and polymerization reactions, the most frequently observed reactions for alkenes are those involving addition reactions.

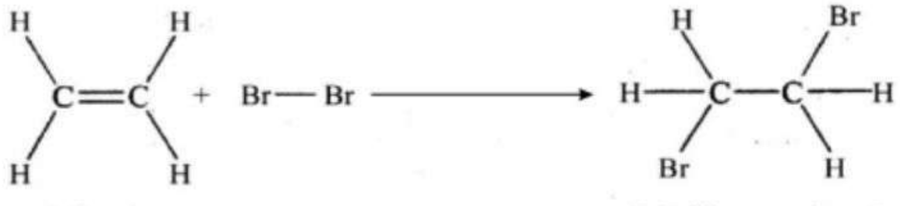
Hydrogenation

In this reaction, hydrogen gas (H_2) is added across a carbon-carbon double bond of alkene. The reaction is carried out in the presence of metal catalyst such as platinum (P), palladium (Pd) or nickel (N)) at a temperature of 250°C to 300 °C.

$$\underset{\text{(ethene)}}{H_2C=CH_2+H_2} \xrightarrow[\text{Ni.Pt or Pd}]{250\text{-}300^{\circ}C} \underset{\text{(ethane)}}{CH_3-CH_3}$$

Halogenation

The reaction of ethene with halogen is an addition reaction which gives a dihaloalkane. This reaction takes place in the presence of an inert solvent such as carbon tetrachloride or chloroform.



(ethene) (1,2-dibromo ethene)

Hydrohalogenation

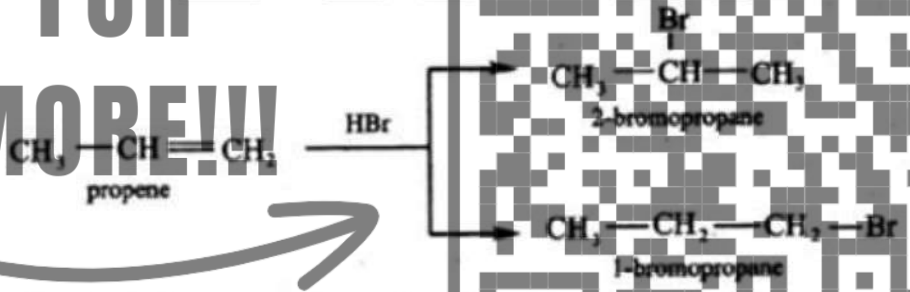
The addition of a halogen acid (HX) on an alkene to give an alkyl halide is known as hydrohalogenation of alkene.

$$\underset{\text{(ethene)}}{CH_2=CH_2} + H-Br \longrightarrow \underset{\text{(ethyl bromide)}}{CH_3-CH_2-Br}$$

The addition of halogen acid on an unsymmetrical alkene is governed by Markovnikov's rule which states that

"When an unsymmetrical alkene undergoes addition reactions, the negative part of attacking reagent is added to that double bonded carbon atom which holds lesser number of hydrogen atoms while the hydrogen atom is attached to the carbon atom with the highest number of hydrogen substituents".

For example the reaction of propene with hydrogen bromide (HBr) gives 2-bromo propane as a major product.



The order of reactivity of halogen acid HX is HI > HBr > HCl

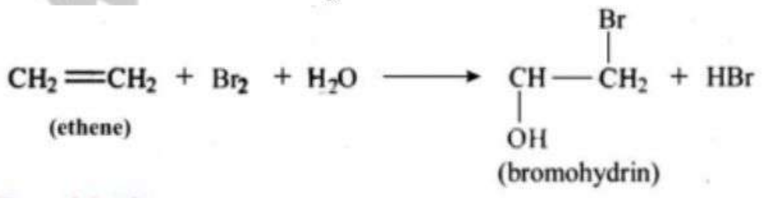
Hydration

The addition of water on an alkene to give alcohol is known as hydration of alkene. This reaction is carried out by acid catalysis at 80-100°C.

$$\underset{\text{(ethene)}}{H_2C=CH_2} + H_2O \xrightarrow[100^\circ C]{H_2SO_4} \underset{\text{(ethyl alcohol)}}{CH_3-CH_2-OH}$$

Halo hydration

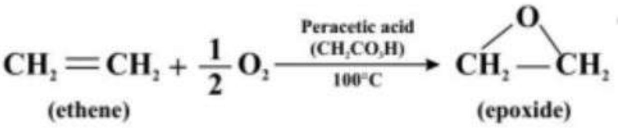
Halo hydration is a reaction in which a halogen reacts with alkene in presence of water and forms halohydrin.



$$\underset{\text{(ethene)}}{CH_2=CH_2} + Br_2 + H_2O \longrightarrow \underset{\text{(bromohydrin)}}{\underset{OH}{CH}-\overset{Br}{CH_2}} + HBr$$

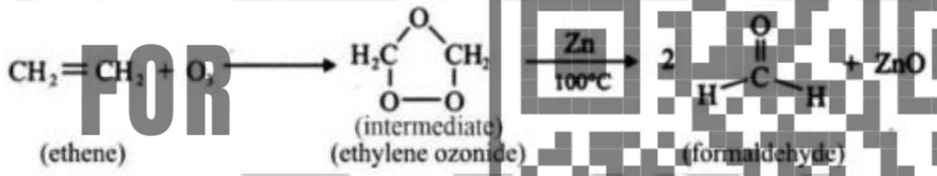
Epoxidation

The addition of oxygen to the double bond of an alkene is known as epoxidation. The product of this reaction is an epoxide which is a three membered cyclic ether.



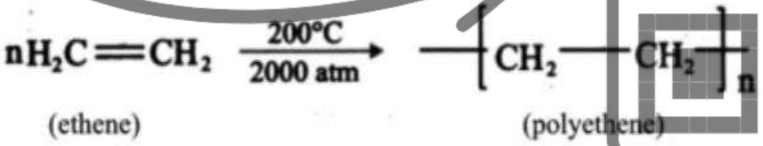
Ozonolysis

Ozonolysis is a chemical reaction that involves the cleavage of an alkene or alkyne by ozone in the presence of reducing agent such as zinc. The reaction results in the formation of ozonide intermediates which are unstable and quickly decompose to form an aldehyde.



Polymerization

Polymerization of alkene involves the linking of many alkene monomers together to produce a polymer chain.



ALKYNES

Alkynes are hydrocarbons that contain a triple bond between the two carbon atoms.

Structure of Ethyne

Ethyne is the first member of alkynes family in which both carbon atoms are sp hybridized. Each carbon has two sp hybrid orbitals and two unhybrid 'p' orbitals (Py and Pz). Two hybrid orbitals form two sigma bonds, one with carbon and other with hydrogen, whereas two unhybrid orbitals form two pi bonds by parallel overlapping. Hence the shape is linear with an angle of 180° The bond length of the carbon-carbon triple bond (C=C) in ethyne is approximately 1.20 ^{o}A

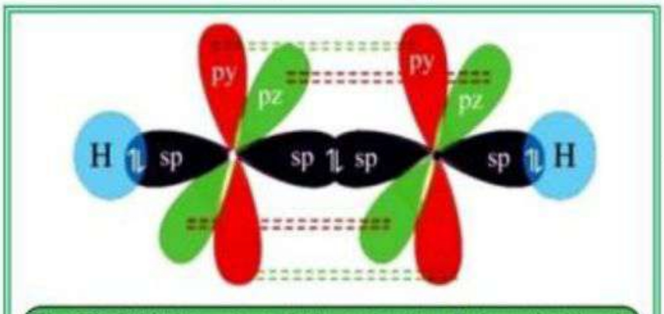


Fig. 5.3: Orbital structure of ethyne showing all sigma & pi bonds

Physical Properties

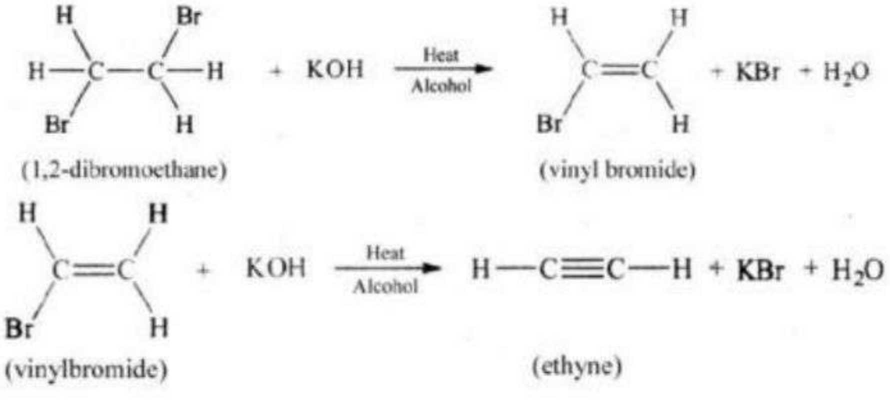
1. Alkynes are colourless and odourless except for acetylene gas which has garlic like odour.
2. Alkynes are insoluble in water but soluble in the organic solvents like acetone, ether, Ethyl acetate etc.
3. Melting and boiling points increase with increasing molecular mass of alkynes.
4. First three members are gases and next members up to 12 carbons are liquids.

Preparation of Alkynes by elimination reaction

Alkynes are generally synthesized through elimination reactions, which involve the removal of atoms or groups from two adjacent carbon atoms.

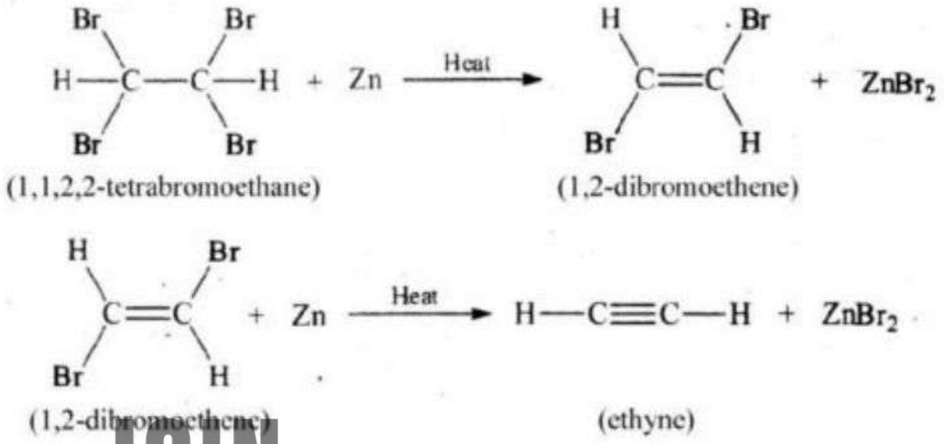
Dehydrohalogenation of Vicinal dihalide

When vicinal dihalide is heated with an alcohol solution of potassium hydroxide (KOH) to give an ethyne. This reaction involves the removal of two halogens and two hydrogens from adjacent carbon atoms.



Dehalogenation of Tetrahalides

A tetrahalide on heating with zinc dust forms ethyne.



Addition reaction of alkynes

Alkynes undergo addition reactions similar to alkenes however, the reactivity of alkynes towards electrophilic reagents is relatively less than that of alkenes.

Hydrogenation

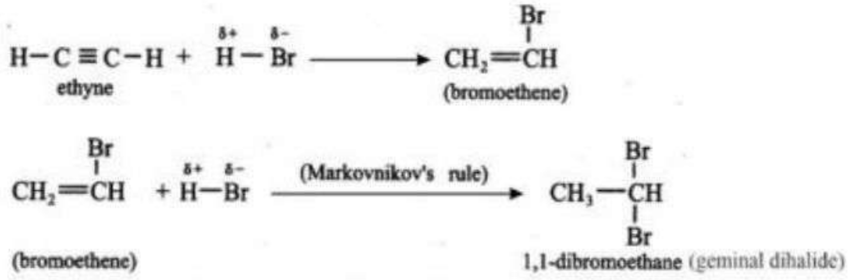
Alkyne reacts with hydrogen in the presence of metal catalysts such as nickel (N), platinum (Pt) and palladium (Pd) to give an alkene which then further reacts with another molecule of hydrogen to produce an alkane.

$$\underset{\text{(ethyne)}}{HC\equiv CH} + H_2 \xrightarrow[\text{Ni,Pt or Pd}]{250\text{-}300^\circ C} \underset{\text{(ethene)}}{H_2C=CH_2}$$

$$\underset{\text{(ethene)}}{H_2C=CH_2 + H_2} \xrightarrow[\text{Ni,Pt or Pd}]{250\text{-}300^\circ C} \underset{\text{(ethane)}}{CH_3-CH_3}$$

Hydrohalogenation

The final product of the reaction of an alkyne with hydrogen halide is a dihaloalkane, however, the reaction completes in two steps. The second step involves the Markovnikov's rule.

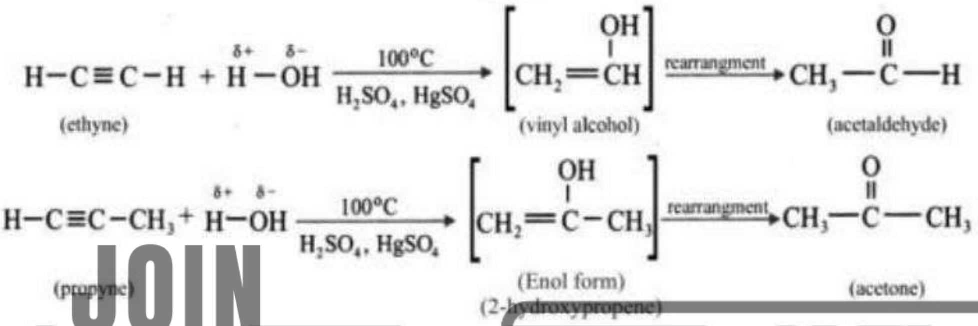


$$\underset{\text{ethyne}}{H-C\equiv C-H} + \overset{\delta+}{H}-\overset{\delta-}{Br} \longrightarrow \underset{\text{(bromoethene)}}{CH_2{=}\overset{\overset{\displaystyle Br}{|}}{CH}}$$

$$\underset{\text{(bromoethene)}}{CH_2{=}\overset{\overset{\displaystyle Br}{|}}{CH}} + \overset{\delta+}{H}-\overset{\delta-}{Br} \xrightarrow{\text{(Markovnikov's rule)}} \underset{\text{1,1-dibromoethane (geminal dihalide)}}{CH_3-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle Br}{|}}{CH}}}$$

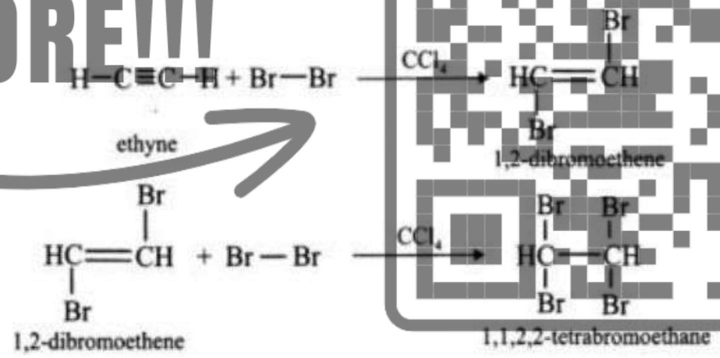
Hydration

When an alkyl halide undergoes reaction with water in the presence of mercurous sulphate and sulphuric acid, it forms an enol. This enol subsequently undergoes rearrangement, resulting in the formation of an aldehyde or ketone.



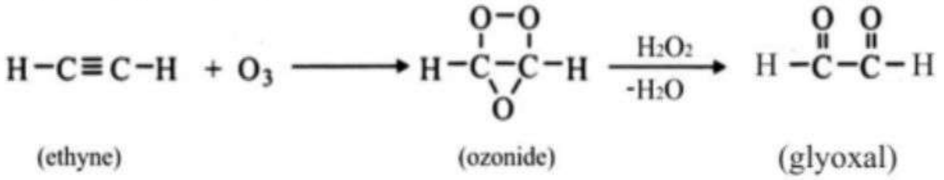
Bromination

The addition of bromine to an alkyne molecule gives a dibromo alkene which then absorbs another bromine molecule to produce tetrabromo alkane.



Ozonolysis

Ozonolysis is a reaction in which the pi bonds between carbon-carbon atoms are broken down by the addition of ozone (O_3). The ozonolysis of an alkyne initially gives an ozonide, which subsequently undergoes oxidation with hydrogen peroxide. This oxidation results in the formation of glyoxal.



Alkanes	Alkenes	Alkynes
Alkanes are chemically less reactive since the	Alkenes are more reactive because the	Alkynes display higher reactivity than alkanes

Sigma bond between carbon-carbon requires high energy to break.	electron density of pi electrons spreads above and below the axis which offers an electrophile to attack on the substrate molecule.	but lower reactivity than alkenes because electrons are not entirely exposed owing to the short length of triple bond.
They do not oxidized by $KMnO_4$.	They oxidize by $KMnO_4$.	They oxidize by $KMnO_4$.

ISOMERISM

"A wide range of organic compounds studied in organic chemistry exhibit the same molecular formula, yet differ in their structure or sterio chemistry. These compounds are known as isomers and the phenomenon is referred as isomerism".

Isomers are initially classified into following two categories.
(i) Structural isomers (ii) Stereo isomers

Structural Isomerism

Organic molecules having the same molecular formula but differing in the way their atoms are connected to each other are called as structural isomers.

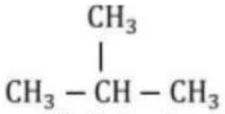
These are further classified into the following types.

Chain isomers

"It is a type of structural isomer in which the molecules differ from each other with respect to carbon skeleton".

For example C_4H_{10} exists in the following two chain isomers.

$H_3C - CH_2 - CH_2 - CH_5$
(n – butane)

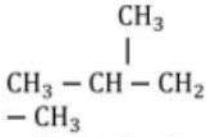


$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3$$

(isobutene)

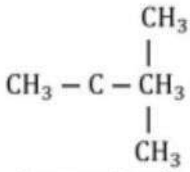
Similarly C_5H_{12} has the following three possible chain isomers.

$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$
(n - pentane)



$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_2 - CH_3$$

(isopentane)



$$CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} - CH_3$$

(neopentane)

Position isomerism

"In this type of isomerism, the structural difference is based on the change in the position of functional group".

For example C_4H_8 has two position isomers.

$CH_3 - CH = CH - CH,$ $CH_3 - CH_2 - CH = CH_2$
(2-butene) (1- butane)

Similarly the two possible position isomers of C_3H_7Cl are given as.

$Cl - CH_2 - CH_2 - CH_3$ $CH_3 - CHCl - CH_3$
(1- chloropropane) (2- chloropropane)

Functional group isomers

"Two molecules having the same molecular formula but differing from each other by the change of functional groups are called functional group isomers",

For example the two possible functional group isomers of C_2H_60 are given as.

$CH_3 - CH_2 - OH$ $CH_3 - 0 - CH_3$
(ethyl alcohol) (Dimethyl ether)

Another example of molecule exhibiting functional group isomerism is C_3H_60.

$H_3C- CH_2 - CO - H$ $H_3C - CO - CH_3$
(propanal) (2- propanone)

Metamerism

"Organic molecule which exhibits unequal distribution of alkyl group on either side of functional group is known as metamerism".

For example two possible metamers of the formula C4Ho0 are.

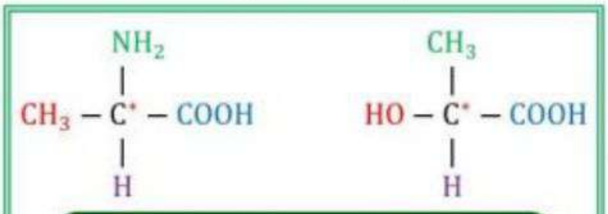
$CH_3 - 0 - C_3H_7$ $C_2H_5 - 0 - C_3H_5$
(methyl propyl ether) (Diethyl ether)

Chiral Centre

"A chiral centre is formed in a molecule when a carbon atom is bonded to four different atoms or groups".

The carbon atom on which these different groups are attached is called chiral carbon and the phenomenon is referred as chirality.

For example, in the molecules of amino acid and lactic acid four different groups are attached with the ∝-carbon as given in figure 5.4.



$$\underset{H}{\overset{NH_2}{CH_3-C^*-COOH}} \qquad \underset{H}{\overset{CH_3}{HO-C^*-COOH}}$$

Fig 5.4: Structure of (a) amino acid and (b) lactic acid showing chiral carbon

Optical Activity

When a plane of polarized light is passed through a solution of organic compound that contain chiral carbon, the light is rotated either clockwise or anticlockwise direction at a certain degree. This property of rotating plane of polarized light when passes through a solution of a compound is known optical activity.

The device used to measure the optical activity is known as polarimeter. The components of a polarimeter is shown in figure

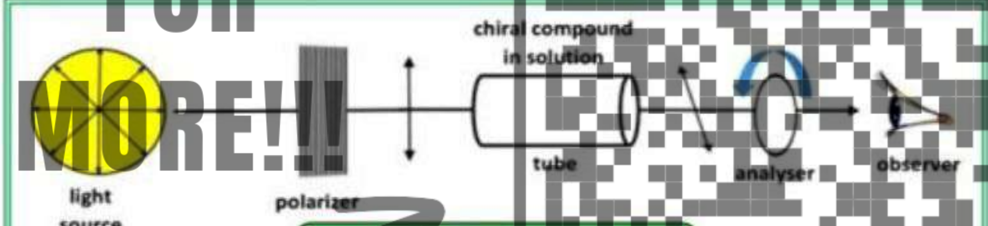


Fig 5.5: Components of a polarimeter

Optical Isomers

Two compounds having the same molecular formula, same structure but differing from each other by the optical rotation of plane of polarized light are enantiomers".

The compound that rotates the plane of polarized light in a clockwise direction is known as dextrorotatory or D-isomer while the compound that rotates the plane of polarized light in anticlockwise direction is referred as levorotatory or L-isomer. These two optical isomers are mirror images to each other but not superimposable and are known as enantiomers.

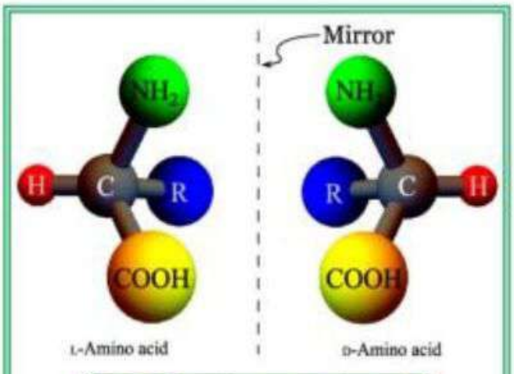


Fig 5.6: Enantiomers of amino acids

Stereoisomerism (Geometrical isomers)

Stereoisomers are a type of isomers that have the same molecular formula and connectivity of atoms but differ in the spatial arrangement of atoms in three-dimensional space, resulting in distinct physical and chemical properties.

"Geometrical isomers are of two types, one is called cis and other is called trans".

If the same groups lie on the same side of molecule, this is called cis isomer where as if the same groups lie on opposite direction in the molecule, this is referred as trans-isomer.

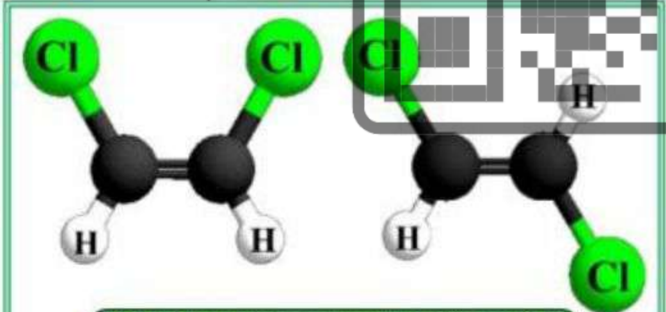


Fig 5.7: Cis and trans isomers of 1,2-dichloro ethene

BENZENE AND ITS DERIVATIVES

- Benzene is the simplest aromatic compound.
- It is a colourless, carcinogenic and highly inflammable liquid.
- It burns with black flames due to the presence of high carbon contents in the molecule.
- Its molecular formula is C_6H_6.
- It was first isolated by Michael Faraday in 1825.
- The structure of benzene was suggested by Kekule in 1865.

- According to him "Benzene is a cyclic hexagonal molecule with alternative double bonds".
- Huckel and certain other chemists studied on Kekule structures of benzene and introduced the term resonance" within the benzene molecule.
- Hence the additional stability shown by benzene arises from the presence of delocalized pi electrons.

Physical Properties

1. Benzene is a colorless liquid having molecular mass 78 g/mol.
2. The melting point of benzene is 5.5°C and boiling point is 80°C.
3. The density of benzene is 0.88 g/cm^3.
4. Benzene is insoluble in water but soluble in organic solvents such as ether, acetone and chloroform.

Molecular orbital structure of benzene

Benzene consists of six carbon atoms in a ring, each carbon is sp^2 hybridized and has three sp^2 hybrid orbitals.
Two hybrid orbitals of each carbon atoms are used to make sigma bond with the adjacent carbon atom, through sp^2 – sp^2 overlapping. The third sp^2 hybrid orbital is involved in sigma bonding with hydrogen atoms through sp^2 S overlapping. All sigma bonds in benzene are coplanar and have bond angle of 120°. In benzene, the carbon-carbon (C-C) bond length as well as carbon-carbon double bond (C = C) length is approximately 1.39 °A.
The six carbon atoms in benzene possess six non hybridized p orbitals that are oriented perpendicular to the sigma bonds. The side wise overlapping of these p orbitals gives six delocalized pi molecular orbitals where half of them are located above the plane while other half below the plane of sigma bonds. The six electrons present in pi molecular orbitals are delocalized over all six carbon atoms in the molecule.

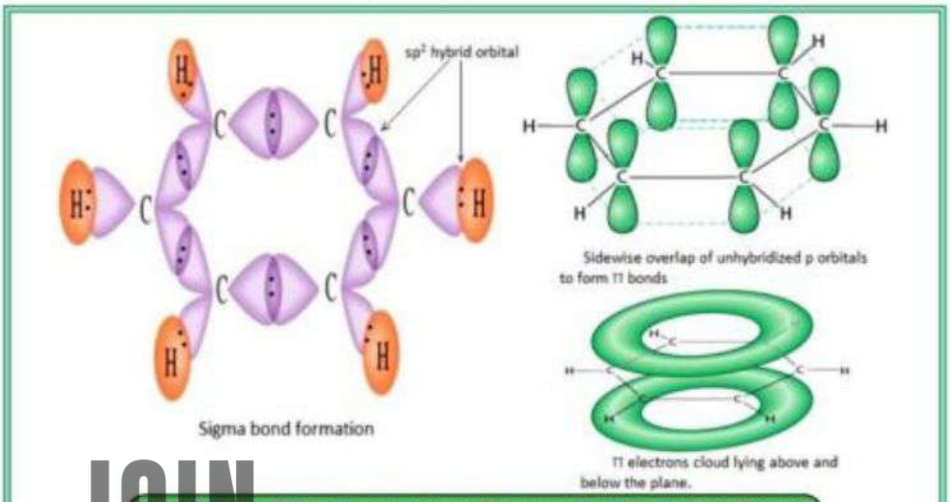
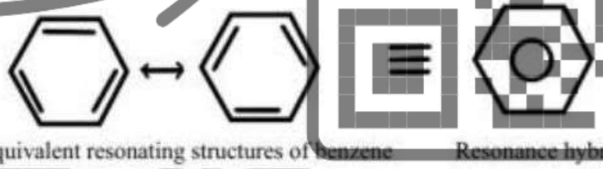


Fig 5.8: Molecular orbital structure of benzene showing sigma & pi bonds

The molecular orbital structure of benzene provides the following information.

1. Benzene is a planar hexagonal molecule.
2. Pi electrons of benzene are delocalized and responsible for the extra stability of molecule.
3. Actual structure of benzene is a hybrid of two resonating structures described by Kekule.

Kekule Structures



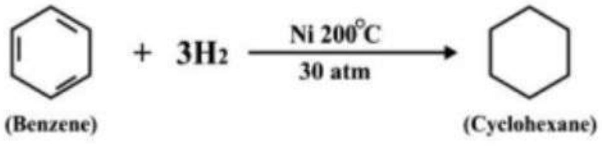
Two equivalent resonating structures of benzene Resonance hybrid

Addition reactions of benzene

Benzene, being an aromatic compound, is highly resistant to addition reactions due to its stability. However, under specific conditions, it can undergo addition reactions. So far only the addition of hydrogen and chlorine to benzene has been observed.

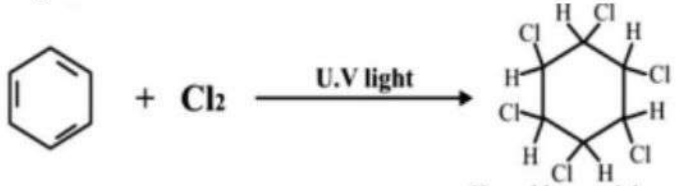
Addition of Hydrogen

Benzene undergoes an addition reaction with hydrogen to produce cyclohexane. It is a catalytic hydrogenation carried out in the presence of Nickel at 200°C and 30 atmospheric pressure.



Addition of Halogen

Chlorine and bromine are added to benzene under sunlight and at high temperature and pressure.



Hexachlorocyclohexane

Electrophilic substitution reactions of benzene

Electrophilic substitution reactions type of organic reaction in which an electrophile reacts with an electron-rich compound and replaces an electrophile in the compound.

The proposed general mechanism of Electrophilic substitution reaction of benzene consists of following steps.

Step-1: Generation of an electrophile

An electrophile (E^+) is generated by reaction of catalyst with the reagent.

$E - Z + \text{Catalyst} \rightarrow E^+ + [Z - \text{catalyst}]$

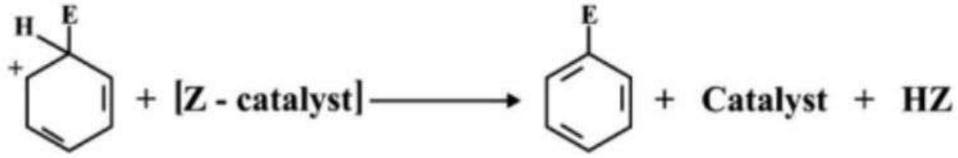
Step-2: Formation of Arenium ion

The electrophile attacks on pi system of benzene and forms a carbocation known as arenium ion.

In this attack, one carbon of benzene becomes sp^3 hybridized and hence the aromaticity of benzene has lost.

Step-3: Abstraction of proton

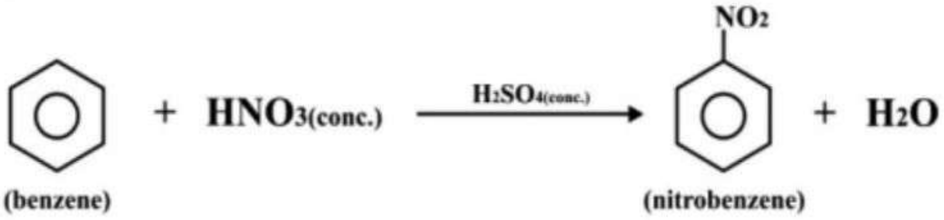
The unstable non aromatic arenium ion then loses a proton and changes into the product.



In this stage aromaticity of benzene is restored. Benzene undergoes following types of Electrophilic substitution reactions.

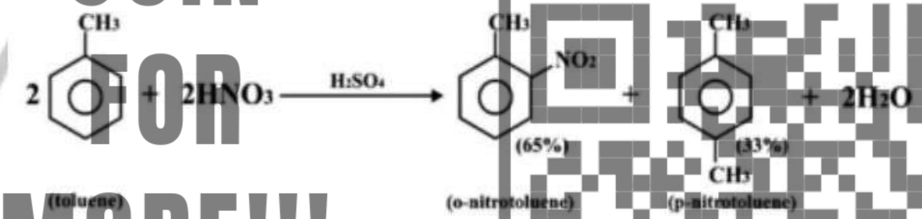
1. Nitration

The reaction of benzene with conc. nitric acid to produce nitrobenzene is known as nitration. This reaction is carried out at 50°C in the presence of conc. sulphuric acid.



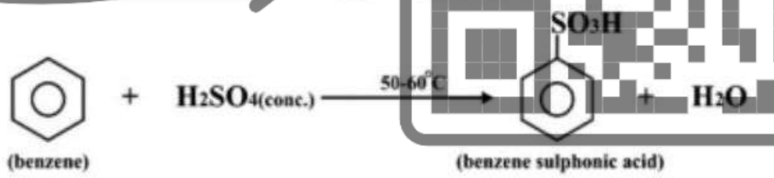
In this reaction, one hydrogen of benzene is replaced by a nitronium ion (NO_2^+).

Similar to benzene, toluene also undergoes nitration, but the product is a mixture of ortho and para nitro toluene.

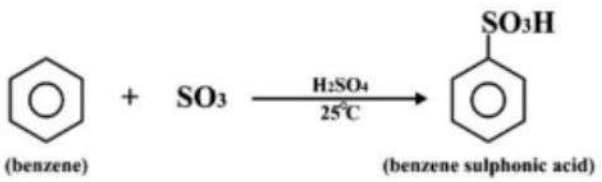


Sulphonation

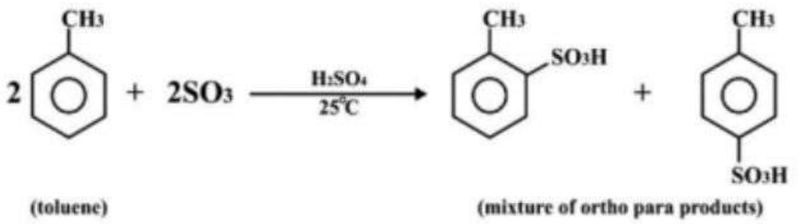
Benzene reacts with conc. sulphuric acid at 50 to 60°C to give benzene sulphonic acid.



This reaction may also be carried out at room temperature if fuming sulphuric acid is used.

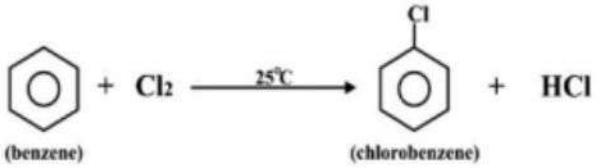


Sulphonation of toluene gives a mixture of ortho, para methyl benzene sulphonate.

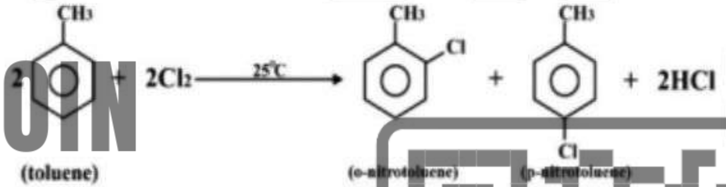


Halogenation

Benzene reacts with halogens (Cl_2, Br_2) at room temperature in the presence of a Lewis acid ($FeCl_3$) to give a halobenzene.



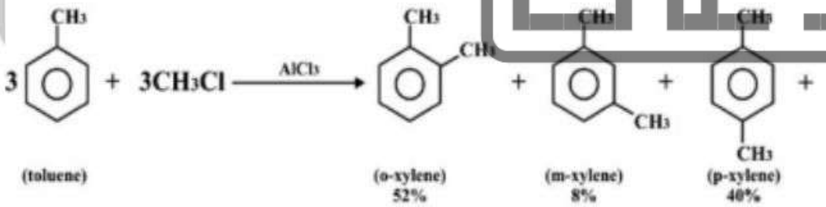
If toluene is allowed to undergo halogenations, it give a mixture of ortho, para chlorotoluene.



Friedal Craft Alkylation

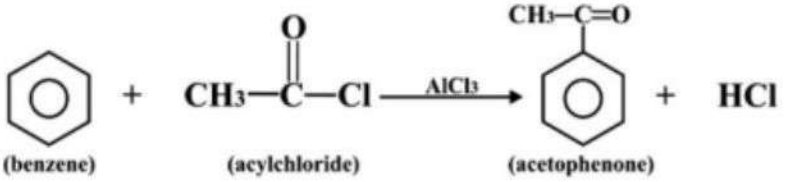
Benzene undergoes reaction with an alkyl halide in the presence of a Lewis acid (AlCl;) to produce an alkyl benzene.

The reaction of toluene with an alkyl halide gives a mixture of ortho, para and meta products.

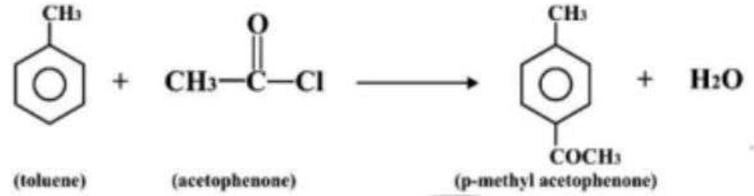


Friedal Craft Acylation

The reaction of benzene with an acylhalide (RCOCl) in the presence of lewis acid ($AlCl_3$) is known as Friedal Craft acylation.

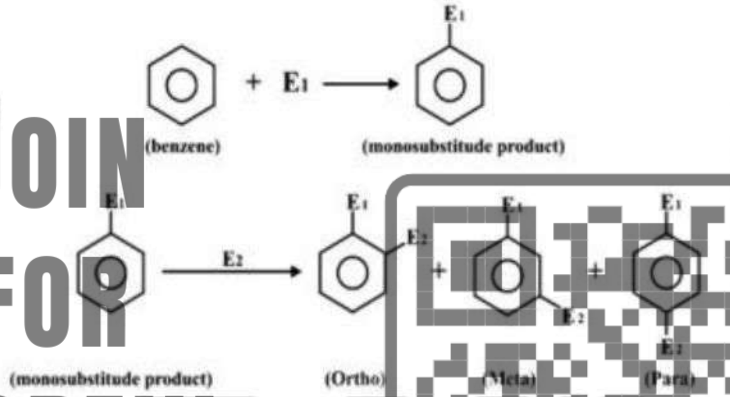


The attacking electrophile in this reaction is acyl cation (RCO^+) which is produced by the reaction of acyl chloride with Lewis acid ($AlCl^3$). Acylation of toluene give only the para product.



Substituent Effect

The effect of the first substituent on the incoming electrophilic reagent is known as substitution effect or orientation of benzene.

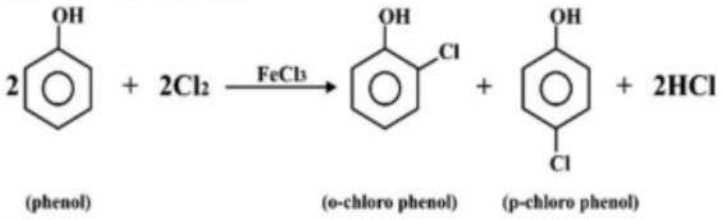


(i) Ortho, para directing groups

"These substituent groups when attached to benzene ring, direct incoming Electrophilic substituents to the ortho and para positions".

They increase the electron density on ortho and para positions through resonance effect. The increased electron density on these positions make more attraction for the incoming electrophile to attack.

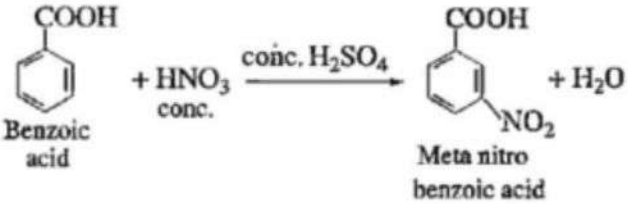
For example the – OH group of phenol is orth0, para director and when reacted with chlorine in presence of ferric chloride ($FeCl_3$), it gives a mixture of ortho para chloro phenol.



(ii) Meta direction group

The presence of these groups in benzene ring decreases the electron density at ortho and para positions due to inductive effect and hence the incoming electrophile attacks on meta position.

For example the -COOH part of benzoic acid is meta directing. Thus, when benzoic acid reacts with nitric acid, it produces a meta product.



Comparative studies of ortho, para and meta directing group

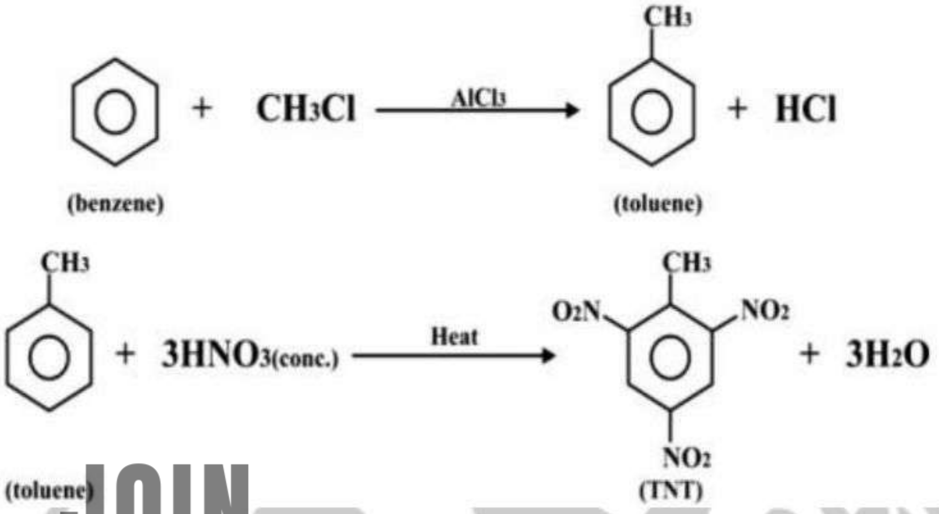
Ortho para directors	Meta director
They release electron to the aromatic ring and increasing the electron density on ortho para position.	They withdraw electron from benzene ring and decrease the electron density on ortho para position.
When they attached with the benzene rings they allow the incoming electrophilic reagent toward ortho and para positions.	When they attached with the benzene ring, they invite the incoming electrophilic reagent towards meta positions.
Example are – R, – RCO, – OR, –Cl, – Br, – CH_3, – OH etc	Examples are – COOR, – CHO COOH, – NO_2,– $COCH_3$, – SO_3H etc

Preparation of poly substituted benzene

Poly substituted benzene is formed by the replacement of two or more hydrogen atoms of benzene ring with Electrophilic reagents.
These are also called derivatives of benzene.

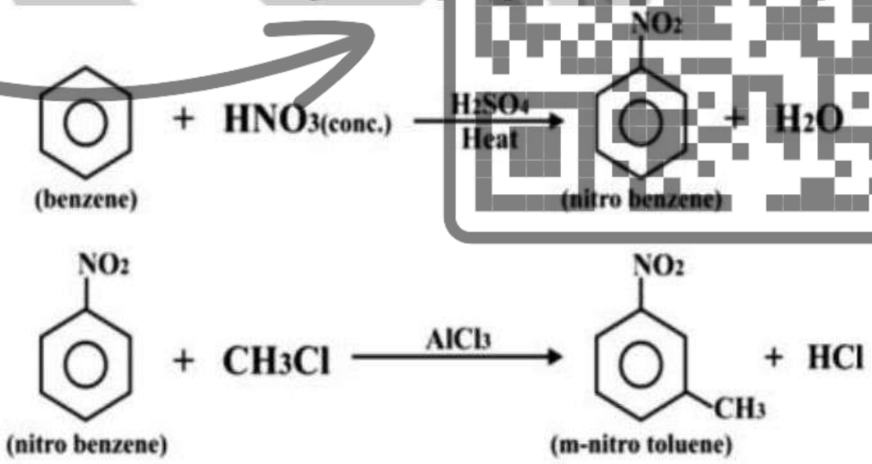
Preparation of trinitro toluene (TNT)

Trinitro toluene is an explosive organic material. During its preparation from benzene, the benzene is first converted into toluene and then toluene treated with hot concentrated nitric acid. Since – CH_3 group of toluene is ortho para directing, it invites the NO} group of nitric acid towards ortho and para positions.



Preparation of m-nitro toluene

In order to synthesize m-nitro toluene, the first step is to transform benzene into nitrobenzene. Due to the meta directing nature of nitro group of nitro benzene, it directs the incoming – CH_3 group towards the meta position.



Short Questions

1. Give three differences between aliphatic and aromatic hydrocarbons

Feature	Aliphatic Hydrocarbons	Aromatic Hydrocarbons
Bonding	Single C-C bonds	Alternating single and double C-C bonds in a ring structure
Reactivity	Generally more reactive	Less reactive due to the stabilizing aromatic ring system

Examples	Methane, Ethane, Propane, Hexane, Cyclohexane, Ethene, Propene, Butyne	Benzene, Toluene, Xylene, Naphthalene, Anthracene

2. Give the mechanism of free radical reaction between methane and chlorine in the presence of sunlight.

Notes

3. Complete the following reactions and name the major product formed in each reaction.

1. $C_2H_5OH \xrightarrow{H_2SO_{4(conc)}\,170^0C} CH_2{=}CH_2 + H_2O$
2. $C_2H_5Br + KOH$ Alcohol, heat $\xrightarrow{Heat} C_2H_4 + KBr + H_2O$
3. $CH_3 - CH = CH_2 + HBr \longrightarrow CH_3 - CH_2 - CH_2Br$ (major) + $CH_3CHBrCH_3$ (minor)
4. $CH_2 = CH_2 + O_3 \longrightarrow HCOOH + H_2O_2$

4. Define a chiral carbon? Give an example to justify your answer.

Notes

5. Write the equations with all required conditions for the reaction of benzene with the following:

()) H_2 (ii) CH_3COCI (ii) $HNO_{3(conc.)}$ (iv) $H_2SO_{4(conc.)}$

6. Bring about the following conversions.

(i) Toluene to ortho-para nitro benzoic acid

(i) Benzene to m-nitro toluene

Notes

Notes

8. Alkanes are generally referred as parafins due to their less reactivity, why are they stable towards chemical reactions?

Alkanes are generally referred to as paraffins due to their low reactivity, which is attributed to several factors:

1. Strong covalent bonds:
   - Alkanes have strong carbon-carbon (C-C) and carbon-hydrogen (C-H) bonds, which require a significant amount of energy to break.
2. Non-polarity:
   - Alkanes are non-polar molecules, meaning they have an even distribution of electrons and no significant positive or negative charges.
3. Saturated carbon atoms:
   - Each carbon atom in an alkane has four single bonds, which means it has achieved a full octet of electrons.

4. Lack of functional groups:
   - Alkanes are hydrocarbons that only contain carbon and hydrogen atoms.

5. High kinetic stability:
   - Alkanes have a high activation energy, which is the minimum amount of energy required for a chemical reaction to occur.

Descriptive Questions

1. Draw the orbital structures of the following hydrocarbons.

(i) Ethane (i) Ethylene (ii) Acetylene

Notes

2. Write the equations of the following chemical processes.

(i) Ethylene is heated at high temperature and pressure.

$nC_2H_4 \rightarrow (-CH_2-CH_2-)n$ (Polyethylene)

(ii) Ethene is burnt in air in the presence of per acetic acid.

$C_2H_4 + 3O_2 + CH_3COOOH \rightarrow 2CO_2 + 4H_2O + CH_3COOH$

(iii) 1,2-di bromo butane is heated with alcoholic potassium hydroxide.

$C_4H_8Br_2 + 2KOH$ (alc.) $\rightarrow C_4H_8 + 2KBr + 2H_2O$

(iv) 1,1,2,2 tetra bromo ethane is heated with zinc powder.

$C_2H_2Br_4 + 2Zn \rightarrow C_2H_2 + 2ZnBr_2$

(v) Reaction of chlorine with acetylene

$C_2H_2 + Cl_2 \rightarrow C_2H_2Cl_2$ (1,1-dichloroethene)

3. Ethene is more reactive than ethane but less reactive than ethyne, how can you explain this behavior?

The different reactivities of ethane ($C2H6$), ethene ($C2H4$), and ethyne ($C2H2$) can be explained by the different types of bonds present in their molecules:

1. Types of bonds:

- Ethane: Contains only single C-C and C-H bonds. These are strong covalent bonds but are less reactive due to their stability.
- Ethene: Contains one double C=C bond and four single C-H bonds. The double bond is composed of a stronger sigma bond and a weaker pi bond. The pi bond is more susceptible to attack by other molecules and is responsible for the increased reactivity of ethene compared to ethane.
- Ethyne: Contains one triple C≡C bond and four single C-H bonds. The triple bond consists of one sigma bond and two weaker pi bonds. These pi bonds are even more vulnerable to attack than the pi bond in ethene, making ethyne the most reactive of the three hydrocarbons.

2. Bond strength and stability:

- Single bonds are the strongest and most stable type of bond.
- Double and triple bonds are weaker than single bonds but are still relatively strong.
- The presence of pi bonds, especially multiple pi bonds, makes the molecule more reactive because the electrons in the pi bonds are less tightly held and are more easily attracted to other molecules.

3. Availability of electrons:

- Ethane has all its electrons involved in strong single bonds, making them less available to participate in chemical reactions.
- Ethene and ethyne have pi bonds where the electrons are not as tightly held, making them more accessible and reactive.

4. Hybridization:

- Ethane has sp3 hybridized carbon atoms, which means the electron orbitals are arranged in a tetrahedral geometry, making it difficult for other molecules to approach and react with them.
- Ethene and ethyne have sp2 and sp hybridized carbon atoms, respectively, which result in a more linear geometry, making the carbon atoms more accessible for attack by other molecules.

In summary:

- The presence of pi bonds, especially multiple pi bonds, increases reactivity due to the weaker electron density and greater accessibility of the electrons.
- The stronger the bond, the less reactive the molecule.
- The availability of electrons for participation in reactions plays a crucial role in determining reactivity.
- The hybridization of carbon atoms also influences the accessibility of the molecule for reaction.

Therefore, the trend in reactivity from least to most reactive is:

Ethane < Ethene < Ethyne

4. What is meant by isomerism? Explain four different types of structural isomers and give one example of each.

Notes

5. Explain the following with suitable examples. (a) Optical isomers (b) Geometrical isomers

Notes

6. Describe the molecular orbital structure of benzene.

Notes

7. Give the mechanism of following Electrophilic substitution reaction of benzene.

(a) Nitration (b) Acylation (c) Chlorination

8. What is meant by ortho, para and meta directing groups. Explain the influence of substituent of benzene to the incoming Electrophile.

Notes

9. Why ethyne terminal hydrogen is acidic in nature? Give two reactions of ethyne to show their acidic behavior.

Ethyne's Terminal Hydrogen is acidic due to:
1. High s-character in sp-hybridized carbon:
2. Stability of the conjugate base (acetylide ion):

Reactions of Ethyne demonstrating its acidity:
1. Reaction with strong bases:
   - Ethyne reacts with strong bases like sodium metal or sodium amide to form sodium acetylide and release hydrogen gas.

$$C_2H_2 + 2Na \rightarrow C_2H_2Na_2 + H_2$$

$$C_2H_2 + NaNH_2 \rightarrow C_2H_2Na + NH_3$$

2. Reaction with Grignard reagents:
   - Ethyne reacts with Grignard reagents (R-MgX) to form addition products with the acetylide ion.

$$C_2H_2 + RMgX \rightarrow RC_2H_2MgX$$

Chapter # 6

ALKYL HALIDES AND AMINES

INTRODUCTION

"Organic compounds that contain at least one halogen atom (fluorine, chlorine, bromine, or iodine) bonded to an alkyl group are called haloalkanes".

These compounds are classified on the basis of number of halogen atoms attached to alkyl group.

- Mono haloalkanes have only one halogen atom,
- Dihaloalkanes have two halogen atoms and
- Tri haloalkanes have three halogen atoms.

Mono haloalkanes are usually called alkyl halides and represented by a formula R-X, where R is an alkyl group and X is halogen atom (functional group).

The general formula of mono haloalkanes is $CH_{2n+1}X$ where n, represents the number of carbon atoms.

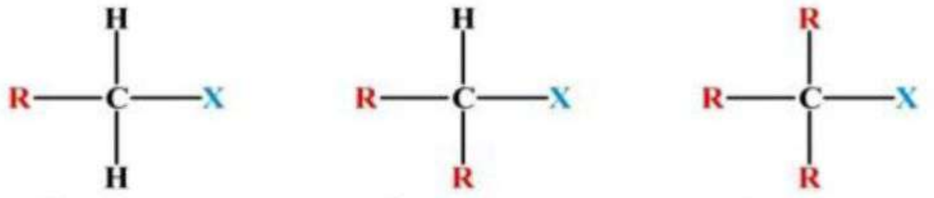
ALKYL HALIDES

Alkyl halides can be classified according to the carbon atom to which the halogen atom is attached.

A primary (1°) alkyl halide refers to an alkyl halide where the halogen-bearing carbon is bonded to only one other carbon atom.

When two carbon atoms are attached to the halogen-bearing carbon, it is known as a secondary (2°) alkyl halide.

Finally, a tertiary (3°) alkyl halide is characterized by the halogen-bearing carbon being bonded to three carbon atoms.



(1°- Alkyl halide) (2°- Alkyl halide) (3°- Alkyl halide)

Examples of alkyl halides are given below

1. Primary alkyl halide: 1-Bromopropane ($CH_3CH_2CH_2Br$)
2. Secondary alkyl halide: 2-Bromopropane ($CH_3CHBrCH_3$)
3. Tertiary alkyl halide: 2-Bromo-2-methylpropane ($CH_3C(CH_3)_2Br$)

Structure of Alkyl Halide

Let us consider methyl chloride (CH_3-Cl) as an alkyl halide.

Carbon of methyl halide is bonded with four atoms which means carbon is utilizing its all four valence electrons to produce four sp^2 hybrid orbitals, which are oriented at an angle of 109° to give a tetrahedral geometry. These four sp^3 hybrid orbitals are shared with three s-orbitals of hydrogen atoms and one p-orbital of chlorine by head on overlapping to make four sigma bonds.

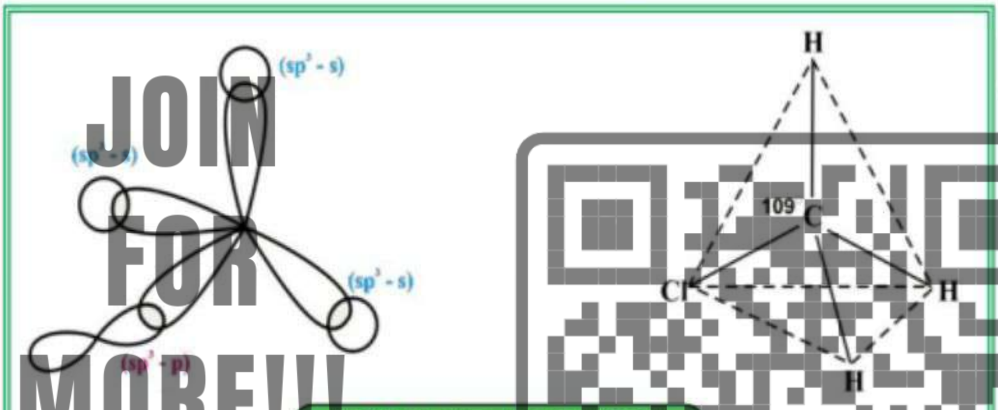


Fig 6.1: Structure of methyl chloride

Physical Properties of Alkyl Halides

(i) Physical state

Alkyl halides with lower number of carbon atoms and different halogen atoms exist as gas or liquid at room temperature, whereas alkyl halides with higher carbon atoms i.e. beyond 18-carbon atoms are colorless solids.

(ii) Solubility

Alkyl halides are soluble in organic solvents but are slightly soluble in water, this is due to the inability of alkyl halides to form hydrogen bonds with water.

(iii) Melting and boiling points

Alkyl halides possess higher melting and boiling points than alkanes of comparable molecular weight, this is due to increasing strength of intermolecular forces.

Preparation of Alkyl Halides

Alkyl halides can be prepared by various methods. Some of which are given below:

Reaction of Alcohol with Hydrogen Halides:

Alcohols can be converted to alkyl halides by the reaction with hydrogen halides. The reactivity of an alcohol with halogen acid follows the trend HI >HBr > HCI. When producing an alkyl halide from hydrogen chloride, anhydrous zinc chloride ($ZnCl_2$) is used as a catalyst.

$$R-OH + HX \longrightarrow R-X + H_2O$$

$$\underset{\text{(Ethyl alcohol)}}{CH_3CH_2OH} + \underset{\text{(Hydrogen chloride)}}{HCl} \xrightarrow{ZnCl_2} \underset{\text{(Ethyl chloride)}}{CH_3CH_2Cl} + H_2O$$

Reaction of Alcohols with other halogenated agents

Alcohols react with phosphorous trihalide (PCl_3, PBr_3, PI_3) to form alkylhalides. Since phosphorus trichloride is more easily available, the reaction is generally carried out by using this reagent.

$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$$

$$\underset{\text{(Ethyl alcohol)}}{3CH_3CH_2OH} + \underset{\text{(Phosphorous tri chloride)}}{PCl_3} \longrightarrow \underset{\text{(Ethyl chloride)}}{3CH_3CH_2Cl} + \underset{\text{(Phosphorous acid)}}{H_3PO_3}$$

Alcohols reacts with thionyl halide (SOX_2) in the presence of pyridine as catalyst to produce an alkyl halides. This is preferred method for the preparation of alkyl halide because both the by products are in gaseous state.

$$R-OH + SOX_2 \longrightarrow R-X + SO_2 + HX$$

$$\underset{\text{(Ethyl alcohol)}}{CH_3CH_2OH} + \underset{\text{(Thionyl chloride)}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\text{(Ethyl chloride)}}{CH_3CH_2Cl} + SO_2 + HCl$$

By the halogenation of alkane

The reaction between alkanes and halogens in the presence of sun light or high temperature produces alkyl halides. This reaction involves the substitution of one or more hydrogen atoms in alkanes by halogen atoms, resulting in the formation of a mixture of different haloalkanes. However, due to the production of a mixture of different halogenated alkanes, this method is not considered efficient for the preparation of alkyl halides.

$$\underset{\text{(Methane)}}{CH_4} + \underset{\text{(Chlorine)}}{Cl_2} \xrightarrow{UV} \underset{\text{(Methyl chloride)}}{CH_3Cl} + HCl$$

Nucleophile

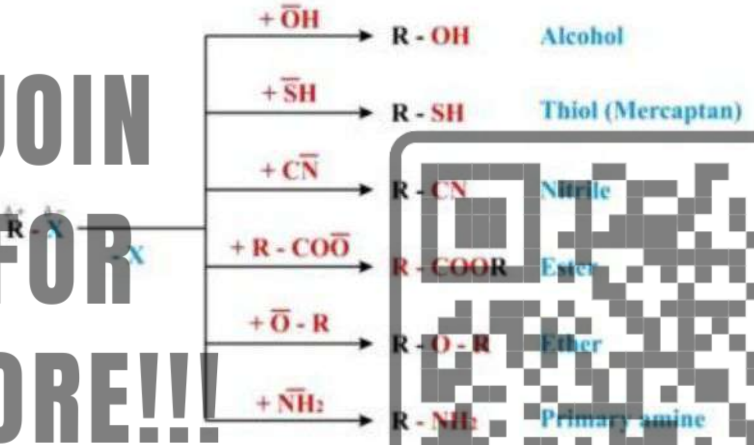
Nucleophile is a chemical species within a molecule that can donate a pair of a electrons to forma covalent bond with another atom or molecule.

Nucleophilic Substitution Reactions

“A type of chemical reactions in which strong nucleophile (electron efficient species) replaces the weak nucleophile of the substrate is termed as nucleophilic substitution reactions".

$$R-X + Nu \longrightarrow R-Nu + X^-$$

Different strong nucleophilic can produce a variety of organic compounds when treated with an alkyl halide.



Some common strong Nucleophiles along with their typical reagents.

Nucleophiles	Typical Reagent
^-OH	NaOH, KOH
^-SH	KSH
CN^-	NaCN
CH_3-COO^-	CH_3-COONa
CH_3-CH_2-O^-	CH_3-CH_2-ONa
NH_2^-	$NaNH_2$

Mechanism of nucleophilic substitution reactions

The mechanism of nucleophilic substitution reaction is divided into:

(i) SN^1 Reactions

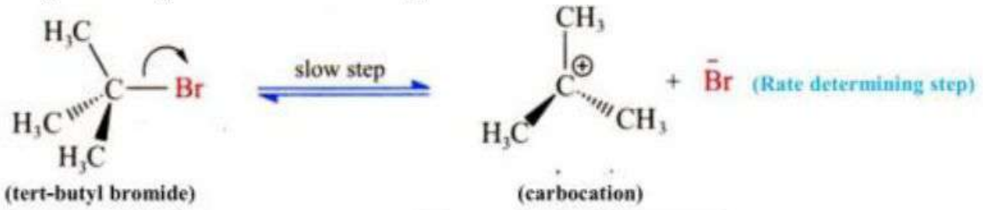
(ii) SN^2 Reactions

SN^1 mechanism

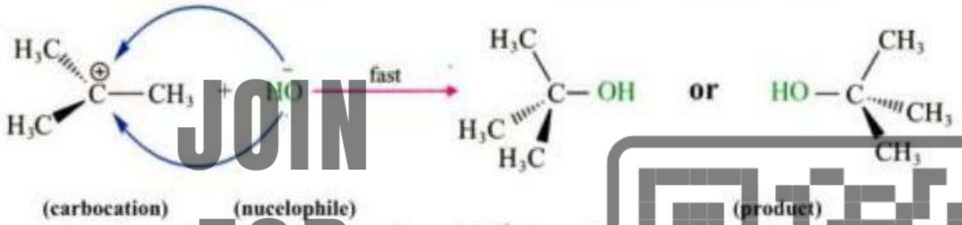
It is unimolecular bi-step SN reaction,

“The SN^1 reaction mechanism proceeds in two distinct steps, with the first step involving the departure of the leaving group (the halogen atom) from the substrate molecule, leading to the formation of a carbocation intermediate, followed by nucleophilic attack in the second step".

Step-1: Departure of halogen from substrate to form carbocation



Step-2: Attack of strong nucleophile on carbocation to form product



Tertiary alkyl halides undergo SN^1 reactions more readily than primary or secondary alkyl halides due to the stabilizing effect of electron-donating alkyl groups, and favoring the formation of the carbocation intermediate, thus facilitating the SN^1 reaction.

Chemical reactions that processed via the SN^1 mechanism exhibit first-order Kinetics, and the rate of the reaction is dependent on the concentration of the substrate, not on the nucleophile involved in the reaction.

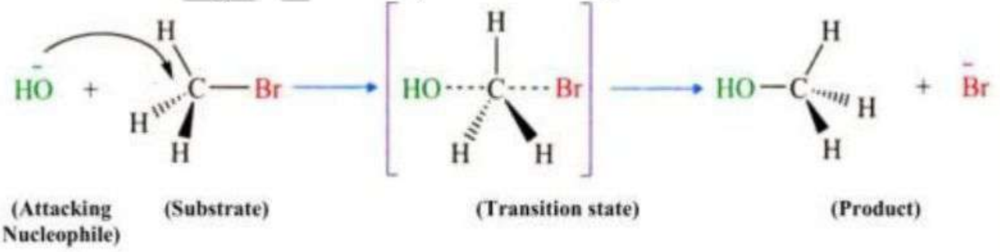
R = K [Substrate]

SN^2 mechanism

It is bimolecular single step SN reaction

> "In the SN^2 mechanism, bond formation and bond breaking occur simultaneously in a single step process".

The nucleophile directly attacks the electrophilic carbon atom of the substrate, leading to the departure of the halogen atom attached to the electrophilic carbon. The nucleophile attacks from the back side because the front side is sterically hindered by the nucleophile of the substrate.

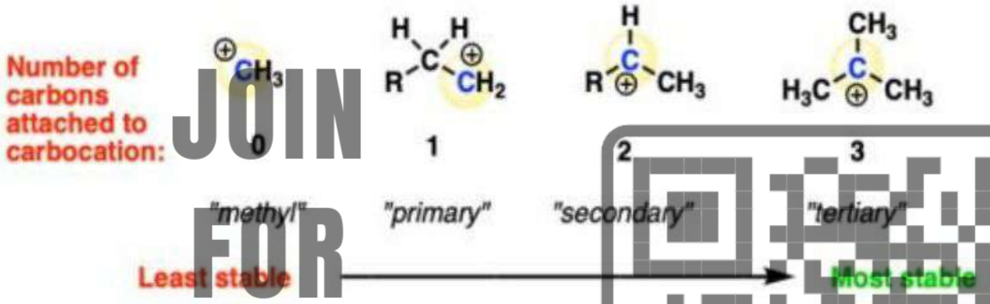


The SN^2 mechanism is typically observed in primary alkyl halides and methyl halides because primary carbocation and methyl carbocation are highly unstable due to the lack of electron donating alkyl groups.

The SN^2 mechanism is followed by second order kinetics which means that the reaction rate is dependent upon the concentration of both substrate and attacking nucleophile.
R=K [Substrate] [Nu]

Carbocations and their stability

"Carbocations are organic ions that have a positively charged carbon atom. They are formed when a carbon atom loses a pair of electrons".

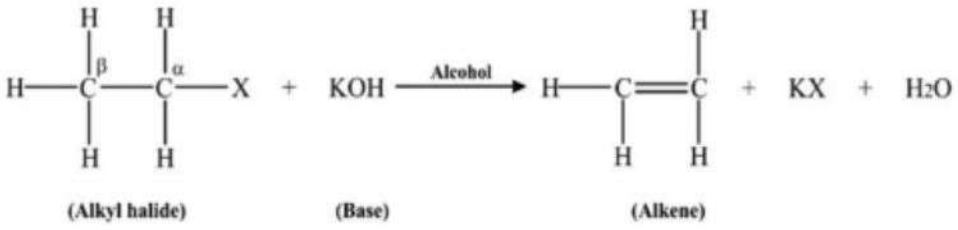


Elimination Reactions

An elimination reaction refers to a type of organic reaction where the substituents are removed from the adjacent carbon atoms of substrate molecule.

"When an alkyl halide reacts with alcoholic potassium hydroxide, the removal of hydrogen and halogen atoms from two adjacent carbon atoms of substrate takes place, giving a multiple bond product". It is referred as 1, 2-elimination or β-elimination reaction.

In β-elimination reaction, base initiates the reaction by abstracting a proton from substrate. leads to the formation of carbocation intermediate, which then eliminated a halogen atom from the adjacent carbon to from a new Pi bond.



There are two common types of β-elimination reactions named as E_1 and E_2.

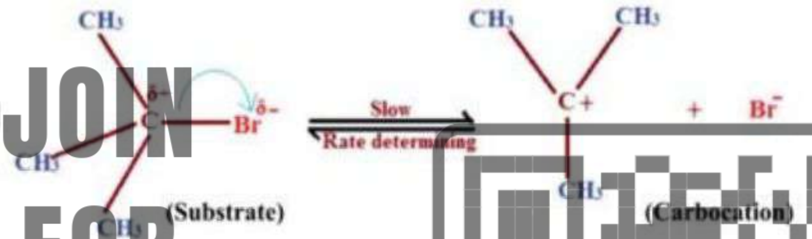
Mechanism of E_1 Reaction

E_1 reactions, known as unimolecular elimination reactions, occur in two steps.

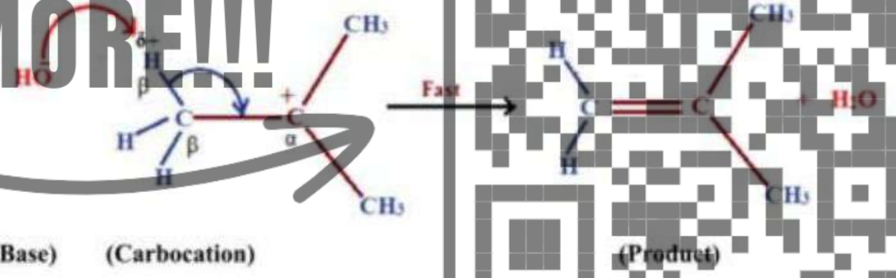
In the first step, the halogen atom departs from the substrate, forming a carbocation intermediate, which is the slow and rate-determining step.

In the second step, a base abstracts a proton from the carbon next to the halogenated carbon, leading to the formation of a double bond between the two adjacent carbon atoms.

Step-1: Formation of carbocation



Step-2: Attack of Base on B-H & formation of multiple bond

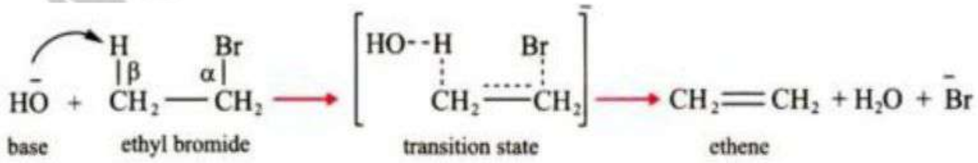


The rate determining step in E' mechanism involves the unimolecular ionization of the substrate molecule. Therefore, the rate of the reaction depends only on the concentration of reactant, and not on the concentration of base.

R = K [Substrate]

Mechanism of E_2- reaction

E_2-reaction is referred as bimolecular elimination reaction. The mechanism completes in single step in which both substrate and attacking base are involved.



Mechanism of E_2 reaction is feasible in primary alkyl halides for example when ethyl bromide is allowed to react with hot alcoholic potassium hydroxide, it gives ethene followed by E_2-mechanism. Base first attacks on ethyl bromide and abstracts a proton from B-carbon. Simultaneous halide ion eliminates from c-carbon and the lone pair of electrons is shifted between α and β carbon to give an ethene.

Therefore, as far as kinetics of E_2 reaction is concerned, the rate of this reaction depends upon the concentration of both substrate and attacking base, the rate law may be written as
R=K[Sub] [base]

Substitution Versus Elimination Reactions

Nucleophile substitution reactions can occur alongside the elimination reactions because nucleophile can also act as a base. However, nucleophilic substitution reactions occur when the nucleophile attacks on the c-carbon atom where as elimination reaction occurs when the nucleophile attacks on the B- hydrogen. Several factors can influence the formation of products via either substitution or elimination mechanisms.

Solvent effect:

Substitution reactions are favored in polar solvents while elimination reaction are favored in non polar solvents.

Base effect:

A strong base promotes elimination reaction and hinders substitution reaction.

Temperature effect:

The rise in temperature encourages elimination reaction over substitution reaction.

Substrate effect:

If the substrate molecule is a tertiary alkyl halide, it favors elimination reaction while if it is primary alkyl halide, it favors substitution reaction. Secondary alkyl halide is consented to both substitution and elimination.

GRINGARD'S REAGENTS DOYOU (ORGANOMETALLIC COMPOUNDS)

"Organic compound that possess at least one bond between a carbon atom and a metal atom".

Some common examples of organometallic compounds are given as:

(i) Grignard reagent: It is a highly reactive organic compound and used in organic synthesis.

(ii) Methyl cobalamine: It is a derivative of vitamin B-12.

(ii) Dimethyl Zinc: It is used as insecticide.

(iv) Tetraethyl lead: It is used as knock inhibitor in petroleum industry.

Preparation of Grignard Reagent

"Grignard reagent is an organometallic compound that contains a carbon-magnesium (C-Mg) bond".

Grignard reagents are prepared in the laboratory by the reaction of an alkyl halide with magnesium metal in the presence of anhydrous ether.

$$R - X + Mg \xrightarrow{\text{anhydrous ether}} R - MgX$$

Where R = alkyl group,

X= halogen, for example — Cl, — Br, — I

The formation of Grignard reagent depends on two factors that determine its case of production.

(i) Size of alkyl group:

The larger the size of alkyl group, the more difficult is the formation of Grignard reagent.

(ii) Nature of halogen atom:

The ease of formation of Grignard reagent also depends upon nature of halogen atom attached to an alkyl group of alkyl halide. The order is I> Br > CI because the bond between iodine and carbon is weaker than corresponding bond with other halogens.

Reactivity

In Grignard reagent the carbon-magnesium bond is covalent and highly polar due to high electronegativity of carbon atom than magnesium metal, which creates more electron density on carbon of alkyl group.

As a result the carbon atom bears a partial negative charge and acts as nucleophile. Due to this nucleophilic nature of alkyl parts, Grignard reagent reacts with polarized molecules either by nucleophilic substitution or nucleophilic addition.

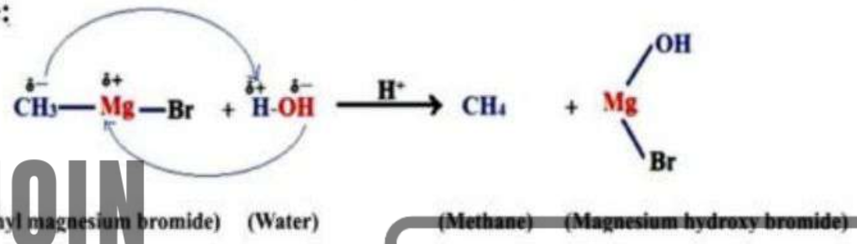
Reactions of Grignard Reagent

Grignard reagent is a versatile chemical; it is used as starting material for the synthesis of various organic compounds such as alkanes, alcohols, carboxylic acids and ketones.

Reaction with Water

When Grignard reagent reacts with water in an acidic medium, it yields alkanes.

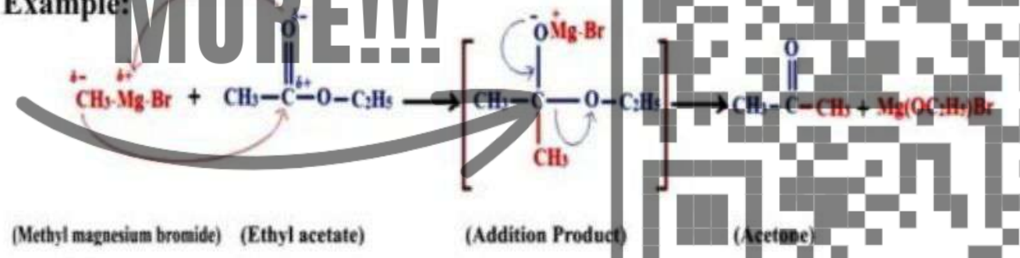
Example:



Reaction with ester

Grignard reagent when reacts with ester, it first forms unstable addition product which is later on stabilized with the formation of ketone.

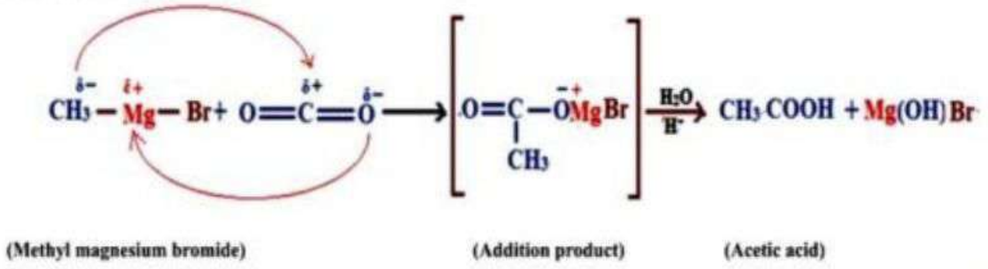
Example:



Reaction with carbon dioxide

Grignard reagent when reacts with carbon dioxide, it gives unstable addition product, later on hydrolysis in an acidic medium produces carboxylic acid.

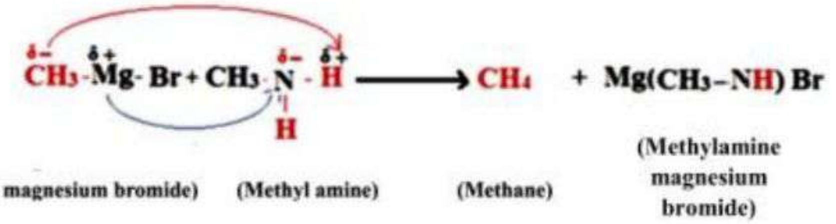
Example:



Reaction with primary amine

Grignard reagent reacts with primary amine to produce an alkane.

Example:

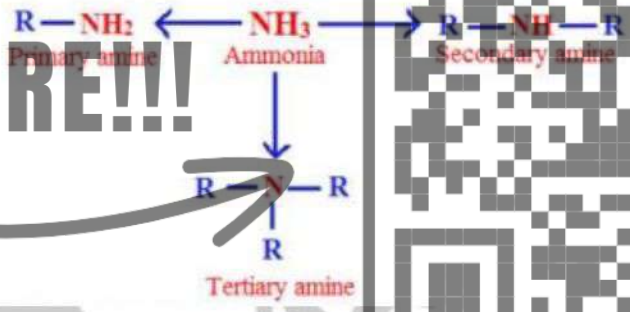


AMINES

Many drugs including antibiotics, anti-depressant and antihistamine contain amine functional groups.

"Organic compounds that contain nitrogen atom bonded to one or more alkyl or aryl groups are known as amines".

These are derivatives of ammonia where one or more hydrogen atoms of ammonia are replaced by an alkyl or aryl group.



Physical Properties

Physical state:

Lower members exist in gaseous states (i.e. Methylamine CH_3NH_2) at room temperature whereas higher members are liquids (i.e. Ethylamine $C_2H_5NH_2$).

Odour and Colour:

Mostly they are colorless with an unpleasant smell.

For example: Trimethylamine ($N(CH_3)_3$) has a strong fishy odor and is found in decaying fish and other organic matter.

Solubility:

Amines are soluble in water, their solubility decreases with the increase in non-polar hydrocarbon chain.

For example: Methylamine (CH_3NH_2) is soluble in water and Trimethylamine ($N(CH_3)_3$) has limited solubility in water as the presence of three methyl groups hinders its interaction with water molecules.

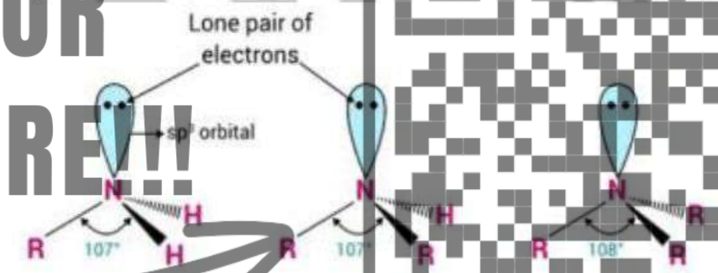
Melting and Boiling Points:

Amines are polar in nature and form hydrogen bonds with each other that is why their melting and boiling points are relatively higher than those hydrocarbons of comparable molecular mass.

For example: Diethyl amine $(C_2H_5)_2NH$ has a higher boiling point compared to ethylamine due to the presence of two ethyl groups.

Structure

The nitrogen of amines is sp^3 hybridized and contains four sp^3 hybrid orbitals, out of which three sp^3 hybrid orbitals involved in formation of sigma bond whereas fourth sp^3 hybrid orbital contains lone pair of electrons. These four sp^3 hybrid orbitals are oriented in space in tetrahedral pyramidal geometry.



Basicity of Amines

Compounds of all classes of amines are basic in nature.

"The basicity of amines is explained by the presence of non-bonding lone pair of electrons on nitrogen atom".

$$\underset{\text{(Primary amine)}}{R-NH_2} + HCl \longrightarrow \underset{\text{(Alkylammonium chloride salt)}}{[R-NH_3]^+ Cl^-}$$

Preparation of Amines

Amines are prepared by different methods:

Alkylation of Ammonia by Alkyl Halides

When alkyl halides are heated with alcoholic ammonia in a sealed tube, a mixture of primary, secondary and tertiary amines are obtained.

$$CH_3-I + NH_3 \longrightarrow \underset{\text{(Primary amine)}}{CH_3-NH_2} + HI$$

$$CH_3-NH_2 + CH_3-I \longrightarrow \underset{\text{(Secondary amine)}}{CH_3-NH-CH_3} + HI$$

$$CH_3-NH-CH_3 + CH_3-I \longrightarrow \underset{\text{(Tertiary amine)}}{CH_3-N(CH_3)-CH_3} + HI$$

Reduction of Nitrogen Containing Functional Group

Reduction of Nitriles:

Methyl cyanide (Nitrile) on catalytic hydrogenation can produce ethyl amine.

$$\underset{\text{(methyl cyanide)}}{CH_3-C\equiv N} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{(Ethyl amine)}}{CH_3-CH_2-NH_2}$$

Reduction of Amides:

Primary amines can be produced by the reduction of amides with lithium aluminum hydrides.

$$\underset{\text{(Amide)}}{CH_3-\overset{O}{\overset{\|}{C}}-NH_2} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{(Ethyl amine)}}{CH_3-CH_2-NH_2} + H_2O$$

153)

Reactivity

Amines are reactive due to the presence of lone pair of electrons on nitrogen atom and behave as nucleophile or a base. However, the reactivity of amines can be influenced by the nature and number of alkyl groups attached to nitrogen atom.

Reactions of Amines

Alkylation of Amines by Alkyl halides

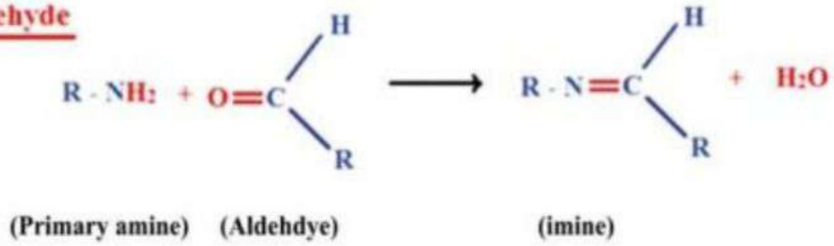
Primary amines react with alkyl halides to form secondary and tertiary amines. In this reaction hydrogen atoms of amines are replaced by alkyl groups.

$$\underset{\text{(Methylamine)}}{CH_3-NH_2} \xrightarrow[-HI]{CH_3I} \underset{\text{(Dimethylamine)}}{(CH_3)_2NH} \xrightarrow[-HI]{CH_3I} \underset{\text{(Trimethylamine)}}{(CH_3)_3N}$$

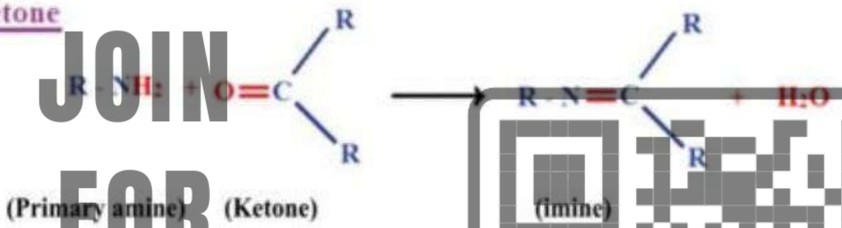
Reactions of amine with Aldehydes & Ketones

Primary amines can react with aldehydes and ketones to produce imines" which also referred as Schiff bases.

with Aldehyde

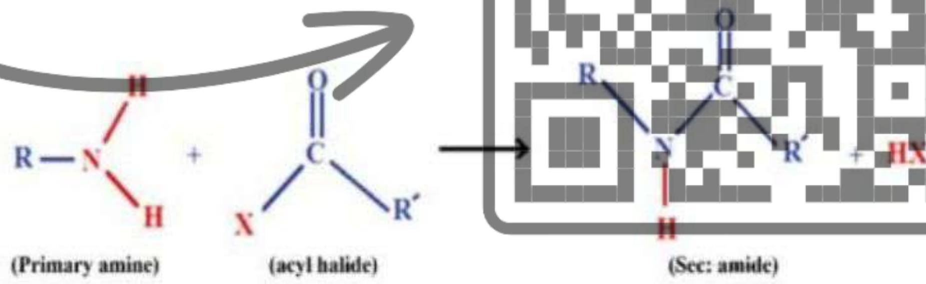


with ketone

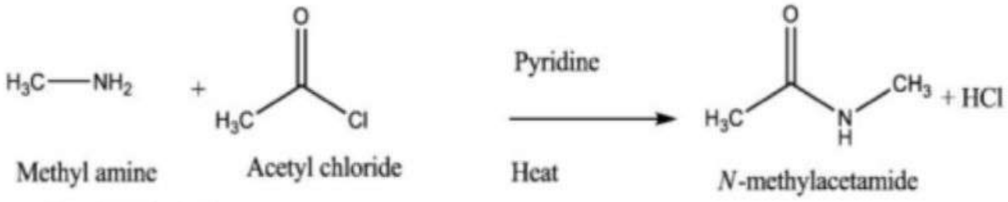


Preparation of Amides

When primary amines are reacted with Acyl halide or Acid anhydride, they form amides.



When methyl amine reacts with acetyl chloride to form:

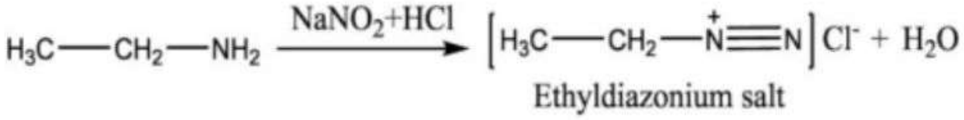


Preparation of Diazonium Salt

When amines react with nitrous acid in the presence of hydrochloric acid at below 10°C, a diazonium salt will be obtained.

$$\underset{\text{(Amine)}}{R-NH_2} + \underset{\text{(Nitrous acid)}}{HNO_2} + HCl \xrightarrow{\text{Below } 10^{\circ}C} \underset{\text{(Diazonium chloride)}}{R-N^{+}\equiv NCl^{-}} + 2H_2O$$

The reaction of ethylamine with nitrous acid in the presence of hydrochloric acid forms ethyl diazonium, as shown below:



$$H_3C-CH_2-NH_2 \xrightarrow{NaNO_2+HCl} \left[H_3C-CH_2-\overset{+}{N}\equiv N\right]Cl^- + H_2O$$

Short Questions

1. How are alkyl halides prepared by the reaction of alcohol with (i) HX (ii) PX_3 (iii) $SOCl_2$. Give the equations.
2. How are amines prepared from nitriles, give the equations.
3. Why are secondary and tertiary amines more alkaline than primary amines?

4. Why the alkyl part of Grignard reagent is nucleophilic in nature?

Despite not being a strong nucleophile on its own, the alkyl group in a Grignard reagent reacts with electrophiles due to several factors:

- **Strong basic character of the Grignard reagent:** The negative charge on the magnesium atom makes the Grignard reagent a strong base. It readily reacts with protic solvents like water (H_2O) to form the corresponding alkane and a magnesium hydroxide byproduct.
- **Favorable thermodynamics of the reaction product:** When the alkyl group of the Grignard reagent reacts with an electrophile (often a carbonyl compound), a new carbon-carbon bond is formed. This C-C bond is typically much stronger than the C-Mg bond in the Grignard reagent. The formation of a stronger bond drives the reaction forward even though the alkyl carbon itself isn't a strong nucleophile.

5. Convert the followings:

(a) Methyl magnesium bromide into acetone
(b) Ethyl chloride into ethyl amine
(c) Ethyl chloride into ethyl alcohol
(d) Ethylamine into imine

6. How is primary amine converted into secondary and tertiary amines, give the equations.

7. Give an account on the basicity of amines.

more hydrogen atoms with alkyl or aryl groups. They exhibit basic character due to the presence of a lone pair of electrons on the nitrogen atom. Here's a detailed look at factors affecting the basicity of amines:

Factors Influencing Basicity:

1. **Availability of the Lone Pair:**
   - The ability of the lone pair on nitrogen to donate electrons determines the basicity of an amine. This availability is influenced by surrounding atoms and electron-withdrawing/donating effects.
2. **Inductive Effect (-I or +I effect):**

- Substituent groups attached to the nitrogen atom can influence the electron density around nitrogen through inductive effects.
    - **Electron-withdrawing groups (-I effect):** Groups like carbonyl (C=O), nitro (NO2), or cyano (CN) withdraw electrons from the nitrogen atom, reducing its electron density and weakening its ability to donate electrons as a base. Thus, amines with electron-withdrawing groups are less basic.
    - **Electron-donating groups (+I effect):** Alkyl groups (like CH3, C2H5) have a slight electron-donating effect. They slightly increase the electron density around nitrogen, making the lone pair more available for donation. However, the effect is relatively weak compared to electron-withdrawing groups.

3. **Steric Hindrance:**

- Bulky substituent groups around the nitrogen atom can create steric hindrance. This hindrance can interfere with the lone pair's ability to interact with a proton (H+) from an acid, thereby affecting basicity. As steric hindrance increases, the basicity of the amine may decrease

8. How can you justify the fact that alkyl halides are water insoluble?

lkyl halides (RX, where R is an alkyl group and X is a halogen) are generally insoluble in water due to a fundamental difference in the intermolecular forces between the two:

- **Alkyl Halides:** Rely on weaker **dispersion forces** (also known as London dispersion forces) for intermolecular attraction. These forces arise from temporary fluctuations in electron distribution within the molecule, creating instantaneous dipoles that induce weak attractions with neighboring molecules.
- **Water:** Highly polar molecule due to the presence of a bent shape and electronegative oxygen atom. This polarity allows water molecules to participate in strong **hydrogen bonding** with each other. In hydrogen bonding, a hydrogen atom bonded to a highly electronegative atom (like oxygen in water) is attracted to the lone pair of electrons on another electronegative atom in a nearby molecule.

Here's a breakdown of why these differences lead to water insolubility:

1. **Energy Considerations:** Breaking the strong hydrogen bonds in water requires a significant amount of energy. When an alkyl halide dissolves in water, it would need to disrupt these hydrogen bonds to be surrounded by water molecules. The energy released by the dispersion forces between the alkyl halide and water molecules is insufficient to overcome the energy required to break the hydrogen bonds.

2. **Favorable Interactions:** Water molecules prefer to interact with each other through hydrogen bonding, forming a stable network. Alkyl halides, lacking the ability to participate in hydrogen bonding, offer a less favorable interaction for water molecules.

9. How can you define a nucleophile? Write the names of four nucleophiles along with their typical reagents.

A nucleophile is a chemical species that has an electron-rich center and can donate an electron pair to form a new covalent bond.

Here are four common nucleophiles and their typical reagents:

1. **Ammonia (NH_3) and Amines (RNH_2, R_2NH, R_3N):**
    - These Lewis bases possess a lone pair of electrons on the nitrogen atom readily available for donation.
    - **Typical reagents:** Ammonia is often used directly. Amines can be used directly or as their conjugate acid salts (e.g., ammonium chloride, NH_4Cl).
2. **Hydroxide Ion (OH^-):**
    - This negatively charged oxygen atom has a lone pair and readily acts as a nucleophile in many reactions.
    - **Typical reagents:** Aqueous solutions of sodium hydroxide (NaOH) or potassium hydroxide (KOH) are common sources of hydroxide ions.
3. **Alkoxide Anions (RO^-):**
    - These negatively charged oxygen atoms in alkoxides (e.g., methoxide, CH_3O^-; ethoxide, $C_2H_5O^-$) possess lone pairs and can act as nucleophiles.
    - **Typical reagents:** They are often generated in situ (at the reaction site) by reacting alcohols (ROH) with strong bases like sodium hydride (NaH) or lithium diisopropylamide (LDA).
4. **Grignard Reagents (RMgX):**
    - These organometallic compounds contain a carbon-magnesium bond (C-Mg) with a partial negative charge on the carbon due to the highly electronegative magnesium atom. While not strictly a classical nucleophile with a lone pair, the carbanion character of the carbon allows it to act as a nucleophile.
    - **Typical reagents:** Grignard reagents are prepared by reacting magnesium metal (Mg) with alkyl halides (RX) in an anhydrous ether solvent (e.g., diethyl ether)

10. Why the mechanism of SN^2 reaction completes in one step?
Notes

Descriptive Questions

1. How can you define nucleophilic substitution reactions? Describe the mechanisms of SN^1 and SN^2 reactions.

Notes

2. What is β-elimination? Discuss the mechanisms of E_1 and E_2 reactions.

Notes

3. What are organometallic compounds? How is Grignard reagent prepared? Write down the reactions of Grignard reagent with water, carbon dioxide, ester and amines.

Notes

4. What are alkyl halides? Define primary, secondary and tertiary alkyl halides.

Notes

5. Draw the orbital structure of methyl iodide and explain the type of hybridization in it.

Notes

6. Give a comparative study between nucleophilic substitution reactions and elimination reactions of alkyl halides.

Notes

Chapter # 7

Alcohols, Phenols and Ethers

INTRODUCTION

- Alcohols, Phenols and Ethers are three classes of oxygen containing organic compounds.

- Alcohols and Phenols are derived by replacing one hydrogen atom of water with an alkyl and aryl group respectively but ethers are formed by replacing both hydrogen atoms of water with alkyl or aryl groups.

- Alcohols, phenols and ethers have a wide range of industrial as well as pharmaceutical applications.

- Methanol and Ethanol are good car fuels with high octane rating,
- Isopropyl alcohol is a common sanitizer, Ethylene glycol is frequently used as automotive antifreeze.

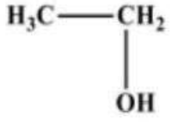
- Phenol is the oldest mild antiseptic agent and ethers are known for their anesthetic properties.

ALCOHOL

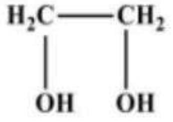
Alcohol is a class of organic compounds in which hydroxyl group (-0H) is attached aliphatic carbon atom.

They are classified according to the number of hydroxyl groups present in the molecule.

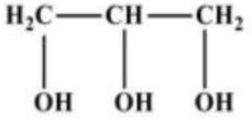
Monohydric alcohols contain one hydroxyl group.
If two or more hydroxyl groups (-OH) are present in the molecule, these are identified as dihydric and polyhydric alcohols respectively.



Ethanol
(monohydric alcohol)

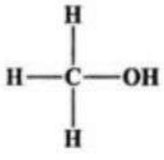


Ethylene glycol
(Dihydric alcohol)

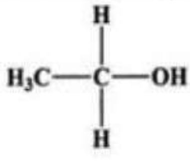


Glycerol
(Trihydric alcohol)

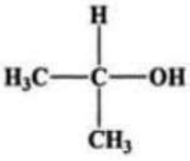
Monohydric alcohols are represented by a general formula R-OH or C_nH_{2n+1} OH.
Monohydric alcohols are further classified into primary (1°- alcohol), secondary (2° -alcohol) and tertiary (3° -alcohol) depending upon whether the hydroxyl group is attached to primary, secondary or tertiary carbon atom.



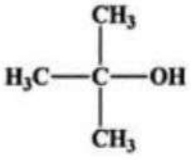
(Methyl alcohol)



(1° - alcohol)
(ethyl alcohol)



(2° - alcohol)
(isopropyl alcohol)



(3° - alcohol)
(t-butyl alcohol)

Structure of Alcohol

The structure of an alcohol molecule is similar to that of water molecule. The carbon atom which is bonded to hydroxyl group is sp^3-hybridized. The oxygen atom of – OH group is also sp^3 hybridized. Oxygen atom utilizes its two sp^3 hybrid orbitals in the formation of sigma bond with carbon and hydrogen atoms while the remaining two sp^3 hybrid orbitals of oxygen contain lone pairs of electrons. The C-O-H bond angle is 108.9°, which is slightly higher than exists in water molecule (104.5°).

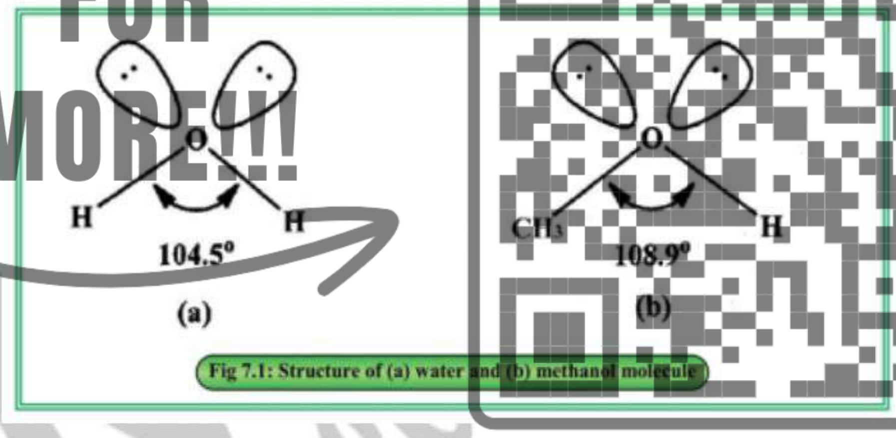


Fig 7.1: Structure of (a) water and (b) methanol molecule

Physical Properties

Physical State:

Alcohols of lower molecular mass (up to butanol) are colorless liquids with characteristic sweet smell.

Boiling Point:

Boiling point of alcohol is much higher than that of alkanes and ethers of comparable molecular mass.

Solubility:

Alcohols are generally soluble in water since they form hydrogen bonds with water molecules. However, solubility decreases with increasing the number of alkyl groups in the molecule

Acidity of Alcohol:

Alcohols are generally classified as weak acids due to their ability to donate a proton to a strong base.

Preparations of Alcohols

Hydration of an Alkene

Alkene when boils with water in the presence of concentrated sulphuric acid to give corresponding alcohol.

$$H_2C{=}CH_2 + H_2O \xrightarrow[100^\circ C]{H_2SO_4\ (conc.)} H_3C{-}CH_2{-}OH$$

(Ethene) (Ethyl alcohol)

Hydrolysis of an Alkyl halide

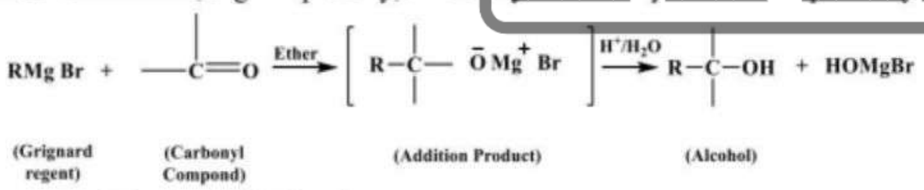
When an alkyl halide is heated with aqueous alkali (NaOH, KOH), it gives corresponding alcohol.

$$C_2H_5Cl + NaOH \xrightarrow[Heat]{H_2O} C_2H_5OH + NaCl$$

(Ethyl Chloride) (Ethyl alcohol)

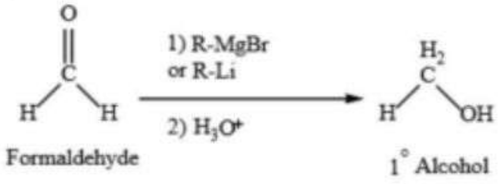
Reaction of Grignard reagent with Aldehyde and Ketone

Grignard reagent when reacts with a formaldehyde, acetaldehyde and acetone molecule, it gives primary, secondary and tertiary alcohols respectively.

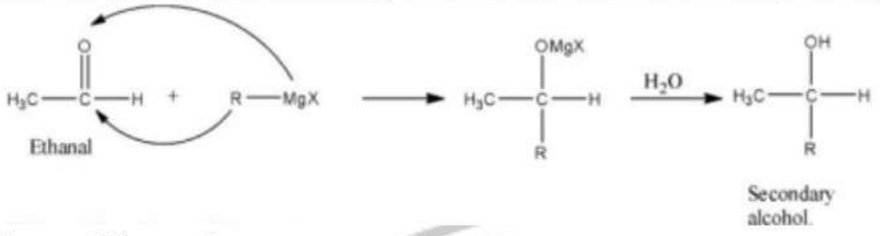


Preparation of primary, secondary and tertiary alcohol

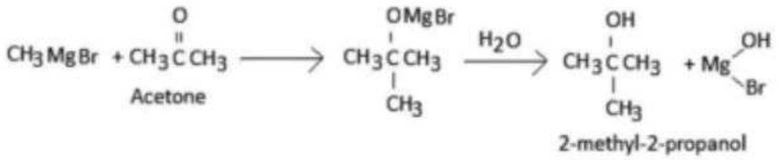
(i) Reaction with formaldehyde



(ii) Reaction with acetaldehyde (ethanal)



(iii) Reaction with acetone

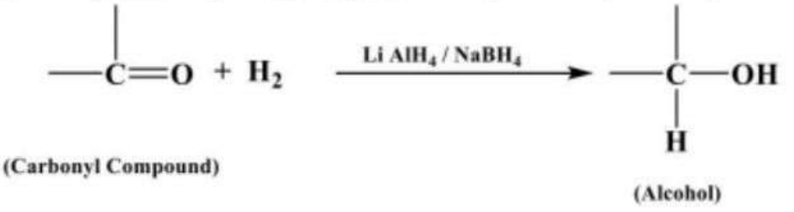


Reduction of Aldehydes and Ketones

Aldehydes and Ketones can be reduced to alcohols by using any one of the following two methods:

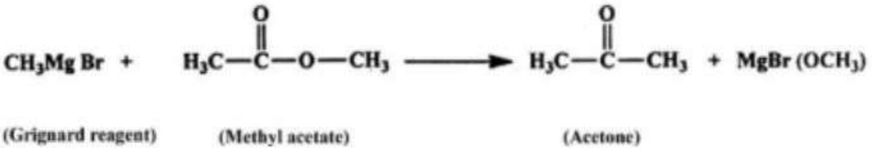
(a) Hydrogenation of aldehyde and ketone at high temperature and pressure in the presence of catalyst like nickel (Ni), platinum (Pt) or palladium (Pd).

(b) Reaction of aldehyde and ketone with a reducing agent like lithium aluminum hydride (Li AlH_4) or sodium borohydride ($NaBH_4$).

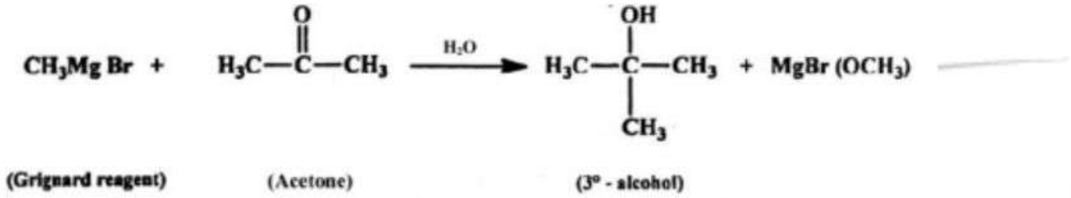


Reaction of Grignard reagent with Esters

When a Grignard reagent is mixed with an ester, it chemically changes into carbonyl compound (aldehyde or ketone).



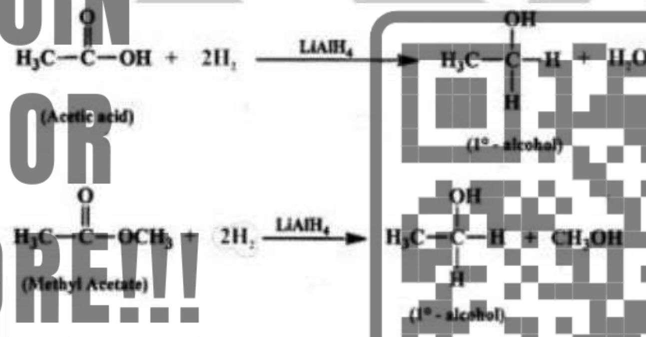
The carbonyl compound thus formed then reacts with another molecule of Grignard reagent and finally gives an alcohol (Discussed in Chap. 18).



$$CH_3MgBr + H_3C-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{H_2O} H_3C-\overset{OH}{\underset{CH_3}{C}}-CH_3 + MgBr(OCH_3)$$

Reduction of Carboxylic acids and Esters

Carboxylic acids and esters can be reduced to the primary alcohols (1°-alcohols) in the presence of a very strong reducing agent such as lithium aluminum hydride.



$$H_3C-\overset{O}{\overset{\|}{C}}-OH + 2H_2 \xrightarrow{LiAlH_4} H_3C-\overset{OH}{\underset{H}{C}}-H + H_2O$$

$$H_3C-\overset{O}{\overset{\|}{C}}-OCH_3 + 2H_2 \xrightarrow{LiAlH_4} H_3C-\overset{OH}{\underset{H}{C}}-H + CH_3OH$$

Reactivity of Alcohol

The reactivity of alcohol can be attributed to the breaking of either C-OH bond with the removal of OH group or by the breaking 0- H bond with the removal of hydrogen (H). The common reactions of alcohol are substitution, elimination and oxidation.

Reactions of Alcohols

Reaction with Halogen acids (HX)

In the presence of a catalyst, zinc chloride ($ZnCl_2$), ethyl alcohol reacts with hydrochloric acid (HCl) to produce ethyl chloride.

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

(Ethyl alcohol) (Ethyl chloride)

The mixture of concentrated HCl $ZnCl_2$ is called "Lucas reagent" and used to distinguish between primary, secondary and tertiary alcohol.

Reaction with $SOCl_3$ and PX_3

When alcohol is treated with Phosphorus tri halide (PX3) or thionyl chloride ($SOCl_3$), it gives corresponding alkyl halide

$$\underset{\text{(Ethyl alcohol)}}{3\,C_2H_5OH} + PCl_3 \longrightarrow \underset{\text{(Ethyl chloride)}}{3\,C_2H_5Cl} + H_3PO_3$$

$$\underset{\text{(Ethyl alcohol)}}{C_2H_5OH} + SOCl_2 \xrightarrow{\text{Pyridine}} \underset{\text{(Ethyl chloride)}}{C_2H_5Cl} + SO_2 + HCl$$

Acid Catalyzed Dehydration

When an alcohol is heated with concentrated sulphuric acid at 170°C, it undergoes a dehydration process, resulting in the formation of an alkene. In this process, a water molecule is eliminated.

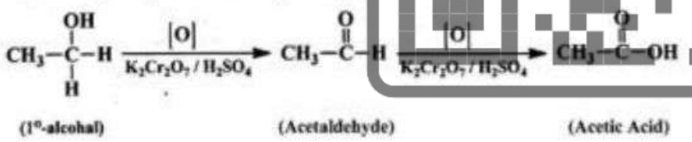
$$\underset{\text{(Ethyl alcohol)}}{C_2H_5OH} \xrightarrow[170°C]{\text{Conc. } H_2SO_4} \underset{\text{(Ethene)}}{H_2C{=}CH_2} + H_2O$$

The ease of acid catalyzed dehydration of alcohol is given as 3°-alcohol > 2°-alcohol > 1°-alcohol

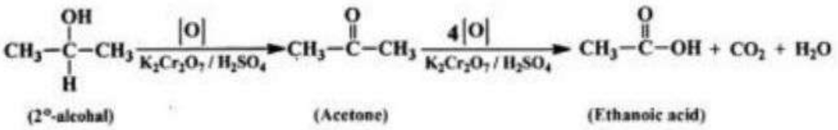
Oxidation Reaction

Primary and secondary alcohols oxidize in the presence of strong oxidizing agents such as acidified potassium dichromate ($K_2Cr_2O_7$) or potassium per manganate ($KMnO_4$) to give carboxylic acid through an aldehyde or ketone intermediate.

Tertiary alcohol cannot be oxidized due to the unavailability of hydrogen on its hydroxyl-bearing carbon.



$$\underset{\text{(1°-alcohal)}}{CH_3-\underset{H}{\overset{OH}{C}}-H} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{|O|} \underset{\text{(Acetaldehyde)}}{CH_3-\overset{O}{\overset{\|}{C}}-H} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{|O|} \underset{\text{(Acetic Acid)}}{CH_3-\overset{O}{\overset{\|}{C}}-OH}$$



$$\underset{\text{(2°-alcohal)}}{CH_3-\underset{H}{\overset{OH}{C}}-CH_3} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{|O|} \underset{\text{(Acetone)}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{4|O|} \underset{\text{(Ethanoic acid)}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + CO_2 + H_2O$$

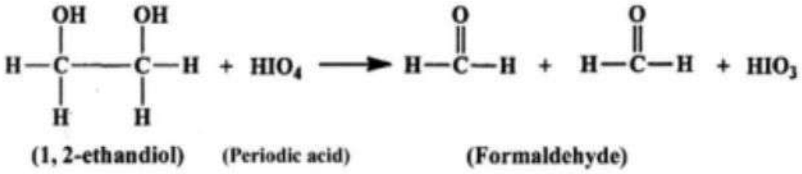
Since the oxidation of ketone involves the breaking of carbon-carbon sigma bond, it is a relatively slow process.

Cleavage of 1, 2-diols

An alcohol molecule in which two hydroxyl groups (-OH) are attached on position 1 and 2 is called as 1, 2 diol or vicinal diol.

When a 1, 2-diol molecule is treated with per iodic acid (HIO_4), an oxidative cleavage occurs between carbon 1 and carbon 2 atoms resulting in the formation of two carbonyl molecules. These carbonyl molecules may be aldehyde or Ketone depending upon the number of alkyl groups attached to the carbon atom bearing hydroxyl groups. In this reaction periodic acid (HIO_4) is reduced into iodic acid (HIO_3).

For example, ethylene glycol (1, 2- ethanediol) is broken down into two formaldehydes molecules if treated with per iodic acid.



Uses of Alcohol

(i) Methanol is used as antifreeze solution and also in the preparation of perfumes, dyes, drugs etc.

(ii) Ethanol is used as a raw material in the synthesis of a variety of organic compounds such as gums, resins, tinctures, chloroform, esters, acetone and acetic acid.

(iii) The mixture of isopropyl alcohol in water is used as rubbing alcohol (antiseptic).

PHENOLS

Organic compounds in which hydroxyl group (-OH) is directly attached to benzene ring are called Phenols.

The parent compound of this family is monohydroxy benzene which is also known as carbolic acid or benzenol.

On the basis of number of hydroxyl groups (-OH) attached to aromatic ring, Phenols are classified into monohydric, dihydric and trihydric Phenols

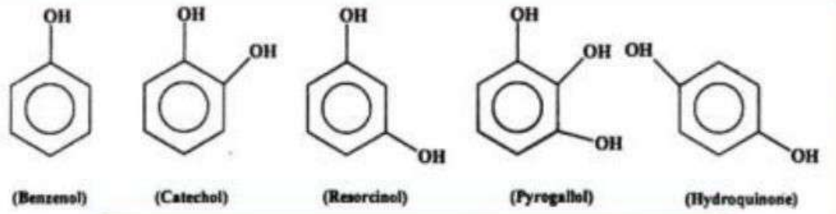


Fig 7.4: Structure of various monohydric, dihydric and trihydric phenols

Structure of Phenol

In the molecule of phenol, the carbon atom of aromatic ring is attached to an OH group. The oxygen atom in the -OH group is sp^3 hybridized, while the carbon atoms in the aromatic ring are sp^2 hybridized. An sp^3-sp^2 sigma bond is formed between oxygen atom of -OH group and carbon atom of aromatic ring.

The C -0- H bond angle is set at 109° which is almost the same as the bond angle of tetrahedral geometry (109.5") but due to two non-bonded electrons 109° pairs of oxygen atom, the geometry is slightly distorted from a normal tetrahedron and exists in a bent shape.

Physical Properties

(i) Physical State:

Pure phenol is a white crystalline solid at room temperature however it may appear in red colour due to the presence of some oxidized products as impurities.

(ii) Boiling Point:

The boiling point of phenol is higher than that of other compounds of comparable size because the presence of OH group

(iii) Toxicity:

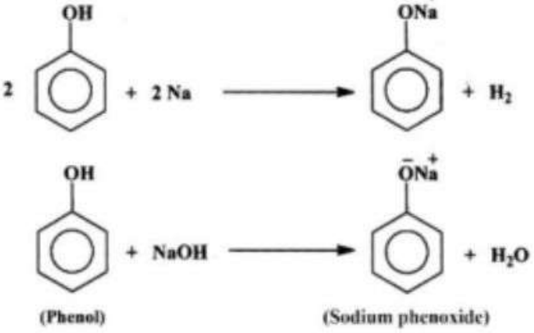
Phenol is toxic and corrosive in nature. When it comes into contact with skin it can lead to a severe burns and tissue damage.

(iv) Solubility:

The hydroxyl group attached to the aromatic ring allows phenol to make hydrogen bond with water molecules that is why it is soluble in water.

Acidity of Phenol

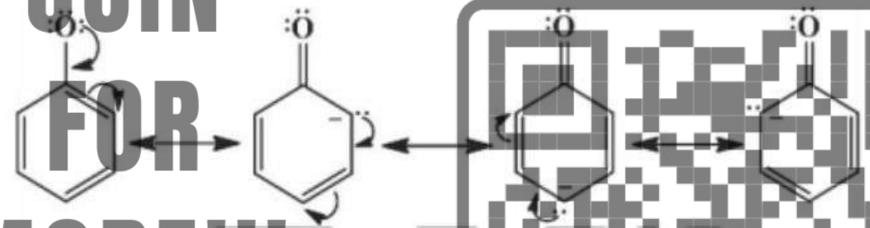
Phenol is fairly acidic since it reacts with an alkali or alkali metal to form salt.



The pka value of phenol is approximately 10, which is far less than carboxylic acid (pka 5) but much higher than alcohol (pka = 15 – 18) that is why phenol is much weaker acid than carboxylic acid but stronger than alcohol.

Comparing phenoxide ion with ethoxide ion, it is noted that the negative charge on oxygen atom of phenoxide ion is delocalized over the entire ring through a process called as resonance and make the phenoxide ion stable.

$$\underset{\text{(Phenol)}}{C_6H_5OH} + H_2O \rightleftharpoons \underset{\text{(Phenoxide ion)}}{C_6H_5\overline{O}} + H_3O^+$$



On the other hand, in ethoxide ion the negative charge is localized on the Oxygen atom due to the absence of aromatic ring result in a less stable structure compared to phenoxide ion.

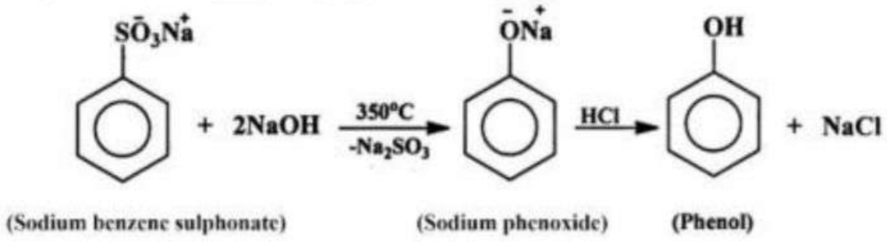
$$\underset{\text{(Ethanol)}}{C_2H_5OH} + H_2O \rightleftharpoons \underset{\text{(Ethoxide ion)}}{C_2H_5\overline{O}} + H_3O^+$$

Preparation of Phenol

Phenol can be prepared by various methods. The two most common methods are described below.

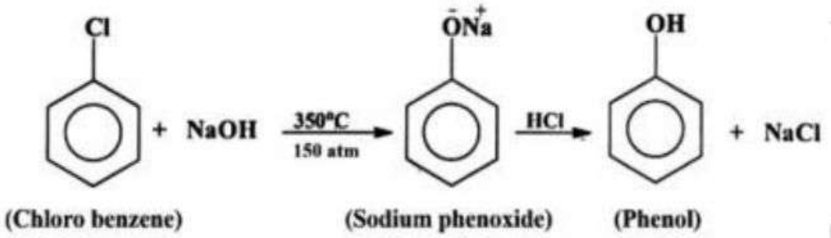
From Sodium Benzene Sulphonate

Sodium benzene sulphonate when fused with sodium hydroxide at 300 - 350°C, produces sodium phenoxide which on acidification yield phenol.



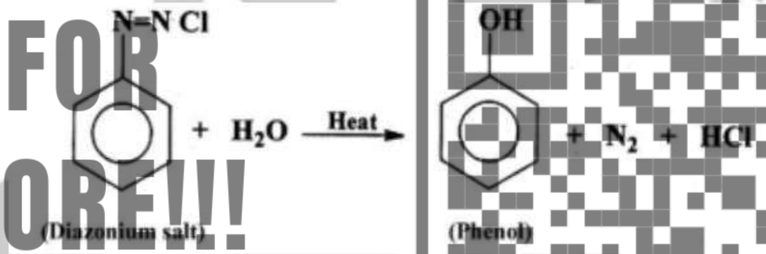
From Chlorobenzene (Dow's Process)

Chlorobenzene when fused with aqueous sodium hydroxide (NaOH) at 350°C and 150 atmospheric pressures, it gives sodium phenoxide which then acidified with dilute hydrochloric acid to yield phenol.



Hydrolysis of Diazonium salt

It is a laboratory method for the preparation of phenol. Benzene diazonium chloride on heating with water, changes into phenol with the release of nitrogen gas.



Diazonium salt is a class of organic compounds that contain a functional group –N_2Cl attached with alkyl or aryl carbon chain.

Reactivity of Phenol

The aromatic part of phenol is similar to benzene which favors the electrophilic substitution reactions.

Reactions of Phenol

Phenol typically undergoes two types of reactions; those involving the hydroxyl group and those involving the aromatic ring.

In the first type of reactions, the -OH part usually broken to form substances such as salts and esters, which are similar to those of alcohols.

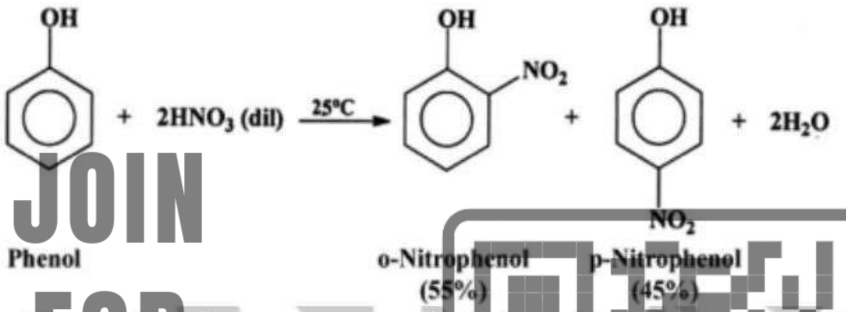
In the second type of reactions, the aromatic ring of phenol undergoes electrophilic substitution reactions.

Electrophilic Aromatic Substitutions

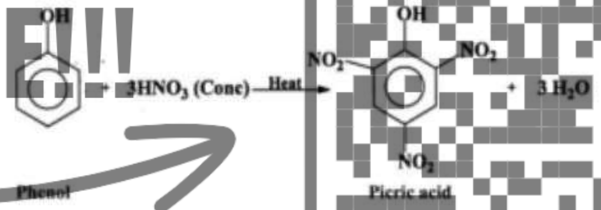
These reactions occur due to aromatic part of molecule. Most common electrophilic aromatic substitution reactions of phenol are nitration, Sulphonation and halogenation.

Nitration

Phenol on treating with dilute nitric acid at 25°C gives a mixture of o-nitrophenol and p- nitrophenol.



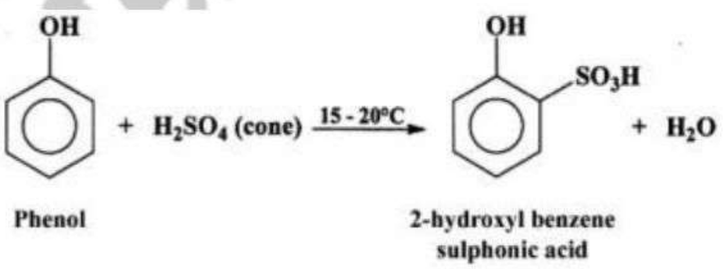
When phenol heated with concentrated nitric acid, it gives 2, 4, 6-trinitrophenol (picric acid).



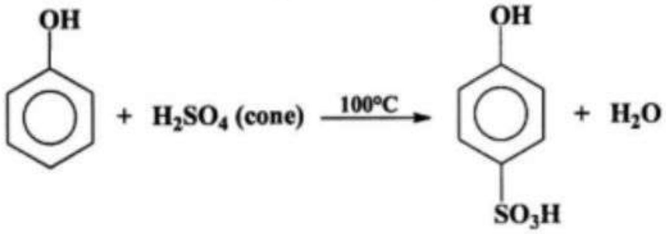
Sulphonation explosion.

When phenol is treated with sulphuric acid, it gives Phenol sulphonic acid, however the relative proportion of isomers depends upon temperature.

(a) On heating at 15° - 20°C, ortho phenol sulphonic acid is formed as major proportion.



(b) On heating at 100°C it gives major product of para phenol sulphonic acid.

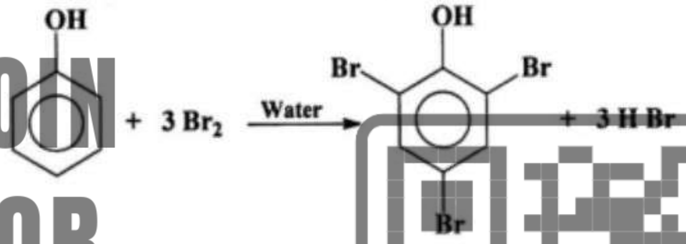


Phenol

4-hydroxyl benzene sulphonic acid

Halogenation

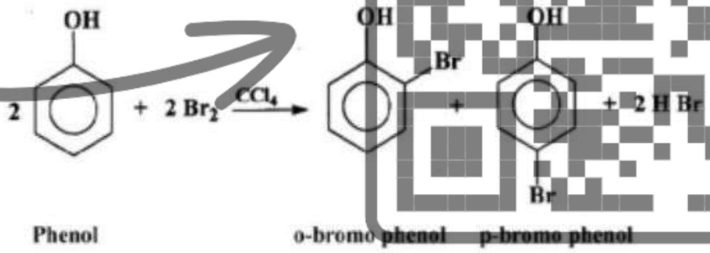
Phenol if reacts with aqueous bromine, it produces 2, 4, 6 - tribromophenol



Phenol

2, 4, 6-tribromo phenol

Phenol reacts with Bromine in carbon tetra chloride, it gives a mixture of ortho and para bromophenol.



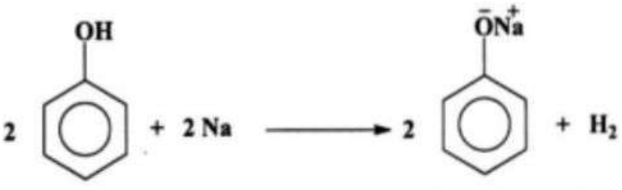
Phenol

o-bromo phenol

p-bromo phenol

Reaction with Sodium Metal

Phenol when reacts with highly active metal such as sodium, the sodium donate an electron to the Oxygen atom of the hydroxyl group in phenol forming sodium phenoxide

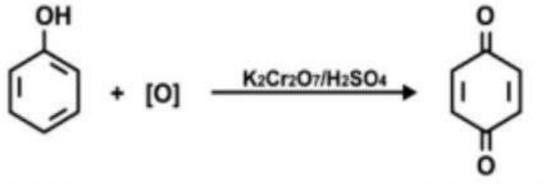


(Phenol)

(Sodium Phenoxide)

Oxidation of Phenol

In this reaction potassium dichromate acts as oxidizing agent and the Sulphruic acid serves as catalyst. Phenol is oxidized to yellow colored benzoquinone (conjugated diketone).



(Phenol) (Benzoquinone)

Difference between Alcohol and Phenol

Property	Alcohol	Phenol
Functional Group	-OH attached to alkyl carbon (R-OH)	-OH attached to aryl carbon (Ar-OH)
Hydrogen Bonding	Can form intermolecular hydrogen bonding	Can form stronger hydrogen bonding
Boiling Point	Generally lower than phenol	Generally higher than alcohols
Acidity	Weaker acids (higher pKa values)	Stronger acids (lower pKa values)
Solubility in Water	Readily soluble in water	Lower solubility in water
Aromatic Properties	Lacks aromatic properties Contains an aromatic ring	Contains an aromatic ring

Uses of Phenol

(i) It is used as an antiseptic and disinfectant

(ii) It is used in the manufacturing of soap, Plastics, ointments and lozenges etc.

(ii) It is used in the preparation of picric acid and, phenolphthalein.

(iv) It is used as ink preservative.

Identification tests for Alcohols and Phenols

Tests of identification of Alcohol

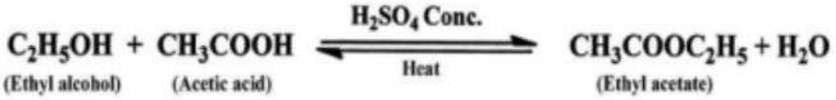
(i) Sodium metal test

Alcohol readily reacts with sodium metal at room temperature to form sodium alkoxide with the liberation of hydrogen gas.

$$\underset{\text{(Phenol)}}{2\ C_6H_5OH} + 2\ Na \rightleftharpoons \underset{\text{(Sodium Phenoxide)}}{2\ C_6H_5ONa} + H_2\uparrow$$

(ii) Ester test

Alcohol when heated with acetic acid in the presence of small amount of concentrated sulphuric acid, it forms an ester.



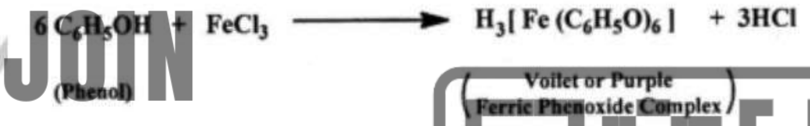
$$\underset{\text{(Ethyl alcohol)}}{C_2H_5OH} + \underset{\text{(Acetic acid)}}{CH_3COOH} \xrightleftharpoons[\text{Heat}]{H_2SO_4\text{ Conc.}} \underset{\text{(Ethyl acetate)}}{CH_3COOC_2H_5} + H_2O$$

Fruity smell of ester indicates the presence of alcoholic group in the given organic compound.

Tests for identification of Phenol

(i) Ferric chloride test

When freshly prepared aqueous solution of ferric chloride (FeCl3) is added to phenol, it forms a ferric phenoxide complex.

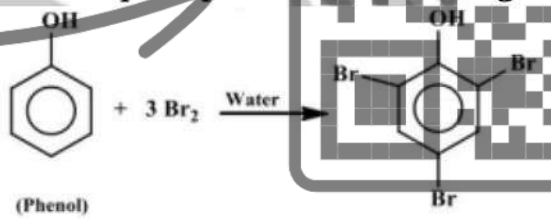


$$\underset{\text{(Phenol)}}{6\,C_6H_5OH} + FeCl_3 \longrightarrow \underset{\text{(Voilet or Purple Ferric Phenoxide Complex)}}{H_3[Fe(C_6H_5O)_6]} + 3HCl$$

Appearance of violet, blue or purple coloration indicates the formation of complex and identifies the presence of phenol.

(ii) Bromine water test

When bromine water is added to phenol, an electrophilic substitution reaction occurs on orho and para positions of the ring.



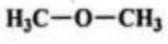
(Phenol) (2,4,6-tribromo Phenol)

Disappearance of brown color of bromine and appearance of white precipitates of 2,4,6-tribromophenol identifies the presence of phenols

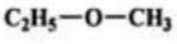
ETHERS

Ethers are an organic compounds having a general formula R-O-R, characterized by an Oxygen atom bonded to two alkyl or aryl groups

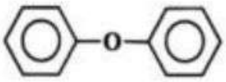
A symmetrical or simple ether is that in which both groups are of same type whereas unsymmetrical or mixed ether consists of two different groups.



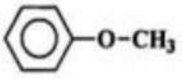
Dimethyl ether
(symmetrical ehter)



Ethyl methyl ether
(unsymmetrical ether)



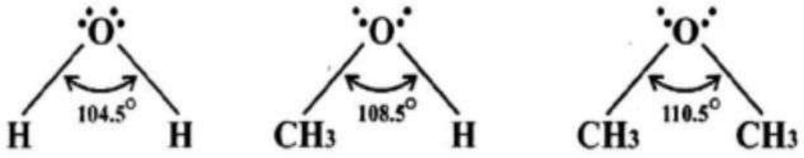
Diphenyl ether
(symmetrical ether)



Phenyl methyl ether
(unsymmetrical ether)

Structure of Ether

The geometry of ether molecule is bent shaped similar to alcohol and water, however the bond angle of C-0-C in ether molecule is 110.5° which is larger than water (104.5°) and alcohol (108.5°). The hybridization of oxygen atom is sp^2 while the hybridization of carbon depends on the nature substituent group (alkyl or aryl) attached to the oxygen atom.



The greater (C-O-C) bond angle in ether is due to greater internal repulsion of hydrocarbon part than the external repulsion of lone pair on Oxygen.

Preparation of Ether

(i) Dehydration of alcohol

Excess of alcohol when heated with concentrated H_2SO_4 at 140°C, an intermolecular dehydration occurs to give ether.

$$\underset{\text{(Ethyl alcohol)}}{C_2H_5OH} + \underset{\text{(Ethyl alcohol)}}{HOC_2H_5} \xrightarrow[140^\circ C]{H_2SO_4} \underset{\text{(Diethyl ether)}}{C_2H_5—O—C_2H_5} + H_2O$$

(ii) Williamson synthesis

It is a well-known method for the preparation of ethers. In this method an alkoxide ion acts as a nucleophile and reacts with an alkyl halide to produce ether.

$$\underset{\text{(Sodium ethoxide)}}{C_2H_5\bar{O}\overset{+}{Na}} + \underset{\text{(Ethyl chloride)}}{C_2H_5Cl} \longrightarrow \underset{\text{(Diethyl ether)}}{C_2H_5—O—C_2H_5} + NaCl$$

The alkoxide is obtained by treating an alcohol with sodium metal.

$$\underset{\text{(Ethyl alcohol)}}{2\,C_2H_5OH} + 2\,Na \longrightarrow \underset{\text{(Sodium ethoxide)}}{2\,C_2H_5ONa} + H_2\uparrow$$

Physical Properties

(i) Dimethyl ether and ethyl methyl ether are gases, however other higher members of ether family exist in volatile liquid state at room temperature.

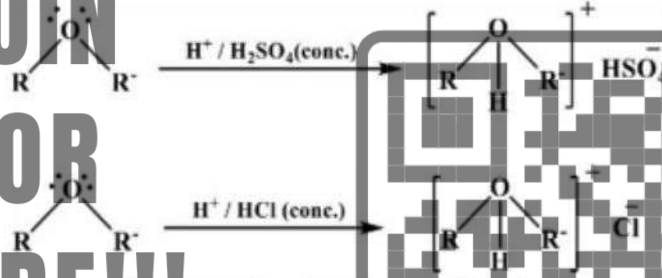
(ii) The boiling point of ether is lower than alcohol due to the absence of intermolecular hydrogen bond.

(iii) Ethers are moderately soluble in water since the presence of oxygen makes the molecule polar. However, solubility decreases with increasing the number of carbons of alkyl or aryl groups.

Chemical Reactivity

Ethers are relatively less reactive organic compounds compared to other functional group because the C-0 bond of ether is stable and shows low reactivity towards nucleophile or electrophile. The relatively low reactivity of ethers makes them useful as solvents and anesthetics.

Since oxygen atom of ether possess lone pairs of electrons, they serve as weak base and hence can react with strong acids to form oxonium salt.



The oxonium salt of ether remains stable if acid is concentrated but on dilution with water, it dissociates to reform ether and acid. The reason is that water is stronger Lewis acid than ether.

Uses of Ethers

(i) Ether is used as solvent in the manufacturing of waxes, gums, resins, oils etc.

(ii) Diethyl ether is used as solvent in Wurtz reaction and in the preparation of Grignard reagent.

Short Questions

1. Define Phenol? Write the equations for the preparation of Phenol from.

(i) Chlorobenzene

(ii) Sodium benzene sulphonate

Notes

2. Write the equations for the following chemical Process

Reduction of acetic acid with $LiAlH_4$:

$$CH_3COOH + LiAlH_4 \longrightarrow CH_3CH_2OH + AlCl_3 + LiH$$

Hydration of ethene with hot concentrated H_2SO_4:

$$C_2H_4 + H_2O \longrightarrow CH_3CH_2OH + H_2SO_4$$

Oxidation of ethanol with acidified dichromate:

$$CH_3CH_2OH + Cr_2O_7^{-2} + H_2SO_4 \longrightarrow CH_3COOH + Cr_2(SO_4)_3 + H_2O$$

Hydrolysis of diazonium salt:

$$ArN_2+ + H_2O \longrightarrow ArOH + N_2 + H^+$$

3. Explain the following with scientific reason

(i) Boiling point of ether is less than alcohol?

(ii) Alcohols are soluble in water?

(ii) Ethanol is liquid but ethyl chloride is gas at room temperature?

(i) Boiling Point of Ether vs. Alcohol:

The key lies in **intermolecular forces**:

- **Alcohol:** Has an -OH group, allowing **hydrogen bonding** between molecules. These bonds are strong and require more energy to break, leading to a **higher boiling point**.
- **Ether:** Contains an oxygen atom but lacks the -OH group, preventing hydrogen bonding. Instead, weaker **dispersion forces** exist. Breaking these weaker forces requires less energy, resulting in a **lower boiling point** compared to alcohol.

For example, ethanol (alcohol) boils at 78.5°C, while diethyl ether (comparable-sized ether) boils at 34.6°C.

(ii) Solubility of Alcohols in Water:

It's about **intermolecular forces**:

- **Alcohol:** The -OH group in alcohols can form **hydrogen bonds** with water molecules. These bonds pull the alcohol molecules into the water structure, making them **soluble**.
- **Water:** Highly polar molecule with strong hydrogen bonding ability.

The more carbon atoms in an alcohol, the fewer -OH groups relative to the hydrocarbon chain, reducing solubility.

(iii) Ethanol vs. Ethyl Chloride:

Intermolecular forces and molecular size play a role:

- **Ethanol:** Polar molecule with -OH group for hydrogen bonding and a larger size. Hydrogen bonding dominates, leading to a **liquid** state at room temperature.
- **Ethyl Chloride:** Smaller molecule with polar C-Cl bond but no hydrogen bonding capacity. Weaker dispersion forces are insufficient to overcome thermal energy at room temperature, resulting in a **gas** state.

4. Identify each of following with two laboratory tests.
(i) Phenol
(ii) Alcohol

Notes

5. What is Lucas reagent? Describe its use to distinguish between primary, secondary and tertiary alcohol.

Notes

6. What is oxonium ion? How can ether form oxonium ion?

Notes

Descriptive Questions

1. (a) What are alcohols? How alcohols are they classified?
(b) Starting from Grignard reagent how is primary, secondary and tertiary alcohol prepared?

Notes

2. Write the equations for the following possible conversions.
(i) Ethyl alcohol to diethyl ether
(ii) Phenol to benzoquinone
(iii)) Ethyl bromide to ethanol
(iv) 2°- alcohol to carboxylic acid

3 Differentiate between alcohol and phenol on the basis of
(i) Solubility in water
(ii) Boiling Point

(ii) Acidic character

Notes

4. Write the equation and name the final product when phenol reacts with the following

(i) Hot and concentrated nitric acid.

(ii) Concentrated sulphuric acid at 100°C

(ii) Bromine water

(iv) Sodium metal

Notes

5. Enlist the commercial applications of Alcohol, Phenol and ether

Alcohols

- **Ethanol (CH_3CH_2OH)**: The most common alcohol, ethanol is used in a variety of products, including:
  - **Beverages:** As the alcohol in alcoholic drinks such as beer, wine, and liquor.
  - **Fuel:** As a biofuel, either blended with gasoline or used pure in specially designed engines.
  - **Solvents:** In paints, varnishes, cosmetics, and pharmaceuticals.
  - **Disinfectants:** To kill bacteria and viruses.
  - **Antiseptic:** To clean and sterilize wounds.

Methanol (CH_3OH): Also known as wood alcohol, methanol is used in a variety of products, including:

- **Antifreeze:** To prevent car engines from freezing in cold weather.
- **Solvents:** In paints, varnishes, and plastics.
- **Fuels:** As a racing fuel and in fuel cells.
- **Chemicals:** In the production of formaldehyde, acetic acid, and other chemicals.

Isopropanol ($CH_3CHOHCH_3$): Also known as rubbing alcohol, isopropanol is used in a variety of products, including:

- **Disinfectants:** To clean and sterilize wounds and surfaces.
- **Solvents:** In paints, varnishes, and electronics.
- **Cosmetics:** In astringents and toners.
- **Antifreeze:** In some windshield washer fluids.

Phenols

- **Phenol (C_6H_5OH)**: Also known as carbolic acid, phenol is a powerful disinfectant that is used in a variety of products, including:

- **Medical disinfectants:** To sterilize surgical instruments and medical equipment.
- **Household disinfectants:** In cleaners and sanitizers.
- **Chemical industry:** In the production of plastics, resins, and nylon.
- **[Pharmaceuticals:** In the production of aspirin and other drugs

Ethers

- **Diethyl ether ($CH_3CH_2OCH_2CH_3$)**: Also known as ether, diethyl ether is a volatile solvent that was once widely used in anaesthesia. Today, it is used in a variety of products, including:
- **Solvents:** In paints, varnishes, and adhesives.
- **Starting materials:** In the production of other chemicals.
- **Fuels:** As a racing fuel and in fuel cells.

CHAPTER # 8

CARBOYNL COMPOUNDS I: ALDEHYDES AND KETONES

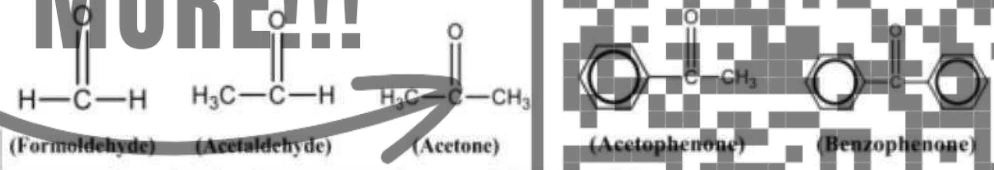
INTRODUCTION

Aldehydes and ketones hold significant importance, with widespread usage in several industries. They are the simplest carbonyl compounds; both contain a carbonyl group, which is a functional group consisting of a carbon atom double-bonded to an oxygen atom.

Aldehyde contain a carbonyl group at the terminal carbon of their carbon chain,
whereas ketone have a carbonyl group located on the carbon within their carbon chain.

Both types of compounds have unique properties and reactivity due to the presence of the carbonyl group, which makes them useful in a variety of applications.

The typical representatives of this class of compounds are formaldehyde, acetone, benzaldehyde and acetophenone. Formaldehyde is exceptional since it carries two hydrogen atoms instead of alkyl substituents.



Organic chemistry emphasizes the study of aldehyde and ketones due to their significant applications in various industrial sectors.

For example, formaldehyde is used to produce resins, synthetic plastic and urea formaldehyde. Acetone is used in the preparation of iodoform, chloroform and nail polish remover Benzaldehyde is used in the manufacturing of dyes etc.

PHYSICAL PROPERTIES

Physical State:

Methanal and ethanal are gases; the other lower aldehydes and ketones are colourless liquids at room temperature. The higher aldehydes and ketones (more than C_{20}) are solids at room temperature.

Odour:

Lower aldehydes have a pungent smell whereas ketones and higher aldehydes have a pleasant smell.

Boiling Point:

Carbonyl compounds have higher boiling points than alkanes of similar molecular weights due to the polar nature of the carbonyl group, enabling intermolecular forces.

However, they have lower boiling points compared to alcohols and carboxylic acids due to the absence of intermolecular hydrogen bonding.

Solubility:

Carbonyl compounds are generally polar, and they are soluble in polar solvents such as water and ethanol. However, their solubility decreases as the size of the hydrophobic group (hydrocarbon chain) attached to the carbonyl carbon increases.

STRUCTURE OF ALDEHYDES AND KETONES

In aldehyde and ketone, the carbonyl group comprises a carbon atom that is double bonded to an oxygen atom. The carbon atom in the carbonyl group is sp^2 hybridized, with one of its sp^2 hybrid orbitals participating in sigma bond formation with the oxygen atom, while the other two sp^2 hybrid orbitals form sigma bonds with other atoms. The un hybrid p orbital of the carbon atom in the carbonyl group forms a pi bond with the Oxygen atom.

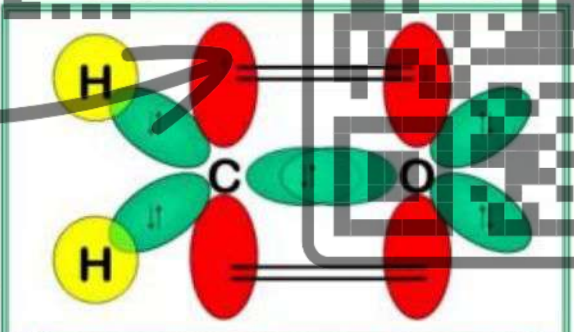
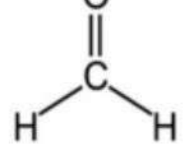
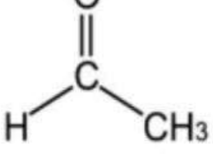


Fig. 8.1: Structure of formaldehyde showing sigma and pi bonding

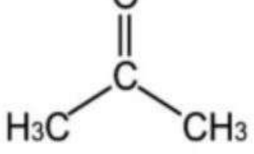
The sp^2 hybridization of the carbon atom the carbonyl group allows it to acquire a trigonal planar geometry, with bond angles of approximately 120°.



(Formaldehyde)



(Acetaldehyde)

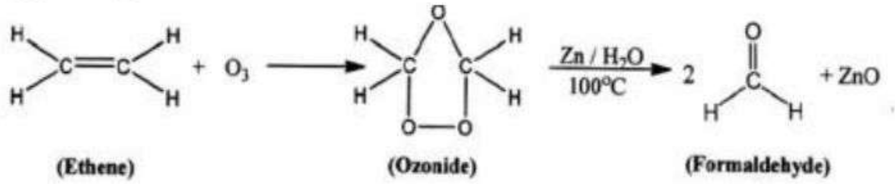


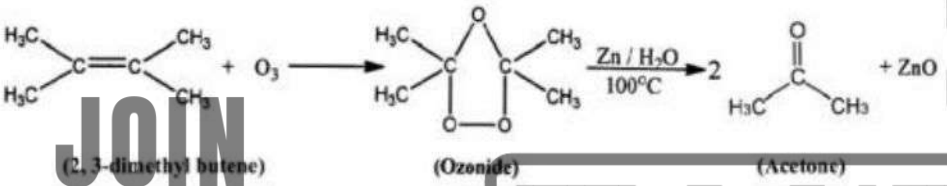
(Acetone)

PREPARATION OF ALDEHYDES AND KETONES

Ozonolysis of Alkenes

Alkenes can be ozonolyzed to yield aldehydes and ketones. This reaction involves the breaking of C-C of alkene by the use of ozone and reducing agent such as Zinc.

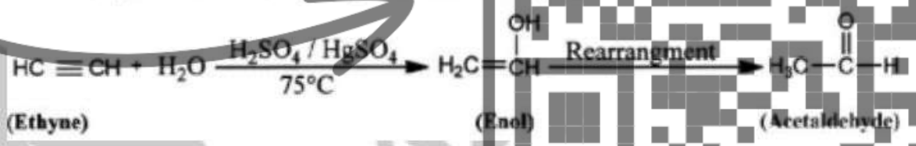




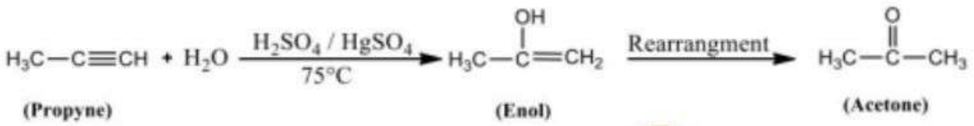
Hydration of Alkyne

Alkynes when heated with water in the presence of H_2SO_4 and $HgSO_4$, an acid catalyzed addition reaction occur on C≡C to form an unstable enol which then on tautomerization, gives aldehyde or Ketone.

(i) The hydration of ethyne gives acetaldehyde

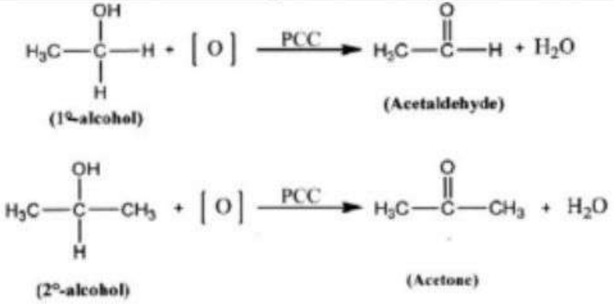


(ii) The hydration of propyne gives propanone



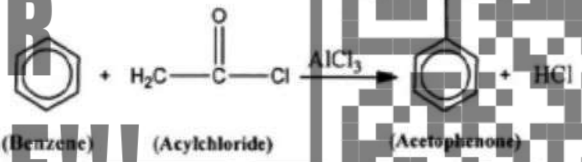
Oxidation of Alcohol

In the Oxidation of alcohols, the -OH functional groups are converted to carbonyl groups (C=0). Primary alcohols are oxidized to aldehydes, and secondary alcohols are oxidized to ketones, which can be achieved using pyridinium chlorochromate (PCC) as an oxidizing agent. However, tertiary alcohols do not undergo oxidation. This controlled process is valuable in obtaining specific carbonyl compounds in organic synthesis.



Friedel-Craft Acylation of Aromatic Compounds

Aromatic ketones can be synthesized through the Friedal Craft acylation method. In this reaction, an acyl chloride reacts with benzene or its derivatives in the presence of a Lewis acid catalyst, typically aluminum chloride ($AlCl_3$).



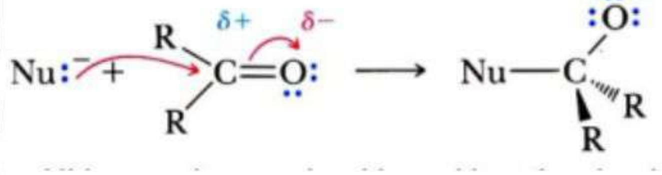
REACTIONS OF ALDEHYDE AND KETONES

Aldehyde and ketone undergo following types of reactions.

(i) Nucleophilic addition reactions
(ii) Reduction reaction
(iii) Oxidation reaction

Nucleophilic addition reaction

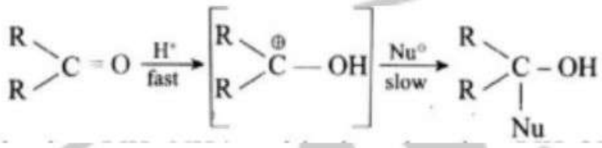
In these reactions, nucleophiles attack the carbonyl carbon of aldehydes and ketones, leading to a change in the hybridization of the carbon atom from sp^2 to Sp^3. The pi electron pair of C-0 shifts towards the oxygen atom, forming an alkoxide intermediate, which is subsequently protonated to yield the addition product.



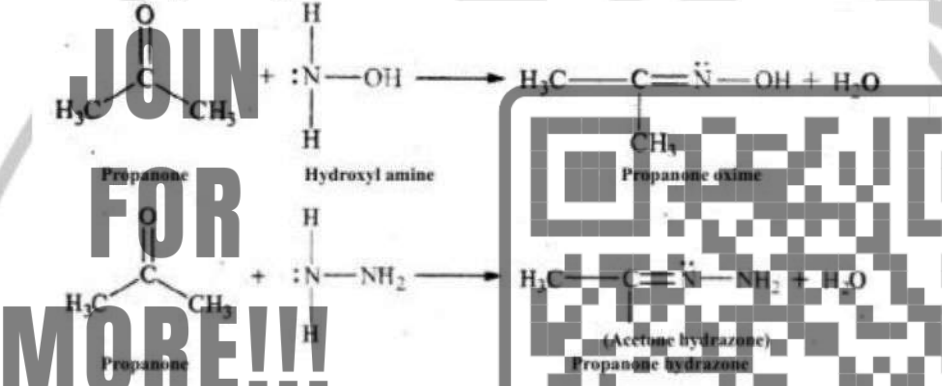
Nucleophilic addition reactions can be either acid-catalyzed or base-catalyzed, depending on the nature of reactants and the reaction conditions.

(i) Acid catalysed Nucleophilic addition reactions

An acid catalyst is employed in a case where a carbonyl compound reacts with weak nucleophile for addition. The acidic proton, attacks the carbonyl atom, resulting in the formation of a protonated carbonyl group. The general mechanism of acid catalyzed nucleophilic addition on aldehyde and ketone is written as.

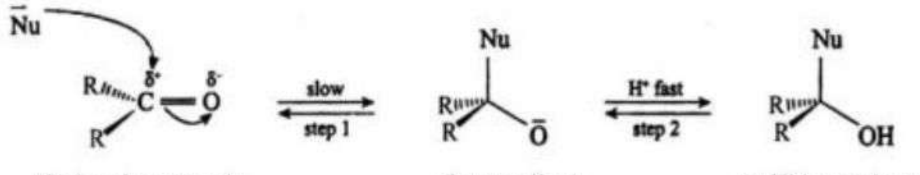


Addition of hydrazine (NH_2-NH_2) and hydroxyl amine (NH_2–OH) on aldehyde and ketone is catalyzed by an acid.



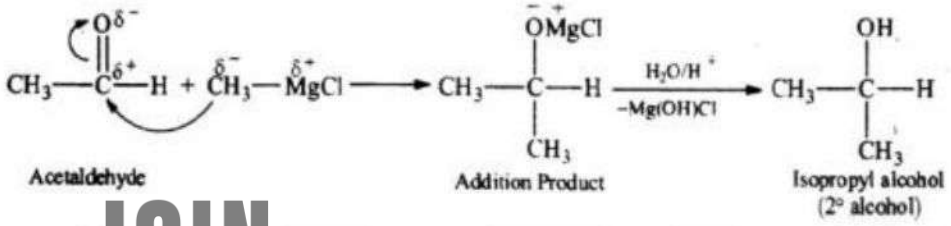
(ii) Base catalyzed Nucleophile addition reaction

Addition of strong nucleophilic reagents on aldehyde and ketone is catalysed by base. The base first reacts with the reagent to generate a nucleophile. The nucleophile then attacks on carbonyl carbon. The pi electron of C-0 is then shifted towards oxygen atom to form tetrahedral alkoxide ion as intermediate. These intermediate captures a proton or the electrophile to give the product. General mechanism of base catalyzed Nucleophilic addition reaction is given as.



(Carbonyl compound) (Intermediate) (Addition product)

Addition of HCN and Grignard reagent is catalysed by base.

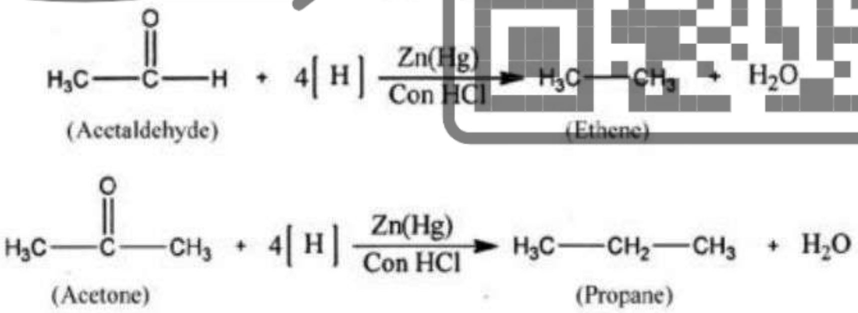


Reduction of Aldehyde and Ketone

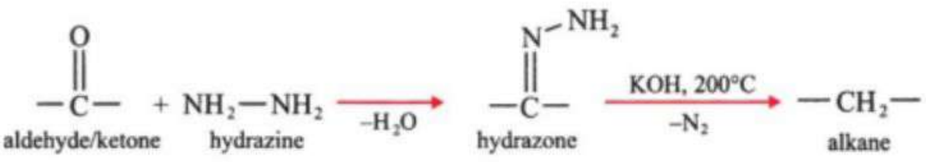
The reduction of aldehydes and ketones involves the addition of hydrogen to the carbonyl group resulting in the formation of an alkane or alcohol depending upon the suitable reducing agent used in the reaction.

Reduction to Hydrocarbon

The reduction of aldehyde and ketone into saturated hydrocarbons is carried out if a mixture of zinc amalgam and concentrated HCI is used. This is known as Clemmensen reduction.

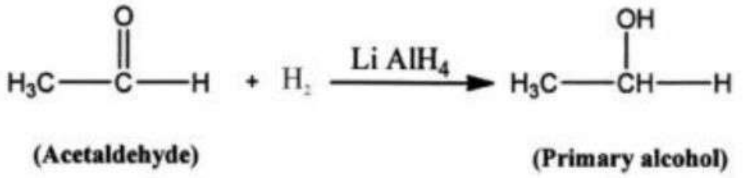


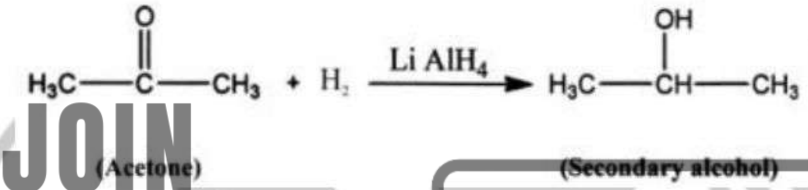
Aldehyde and ketone can also be converted into alkane by using hydrazine (NH_2-NH_2) and potassium hydroxide. This is known as Wolf Kishner reaction.



Reduction to Alcohol

Aldehyde and ketone when treated with strong reducing agents such as $NaBH_4$ or $LiAlH_4$, they reduce into primary and secondary alcohols respectively.

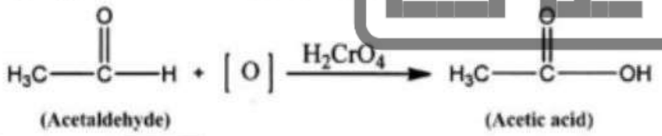




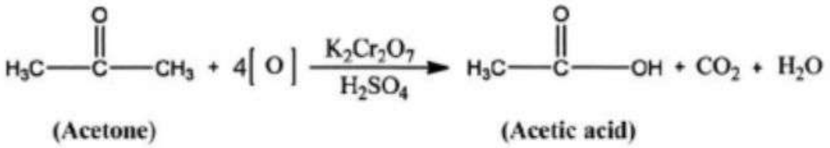
Oxidation Reaction

Aldehydes and ketones undergo oxidation with an oxidizing agent to give carboxylic acid. However, the reactivity of aldehyde towards oxidation reaction is quite easy due to the availability of active hydrogen atom at the carbonyl position, thus

i. A variety of mild oxidizing agents such as chromic acid (H_2CrO_4), Tollen's reagent, Fehling reagent and Benedict reagent can be used to convert aldehyde into corresponding carboxylic acid. Aldehydes can also be Oxidized by strong oxidizing agents.



ii. Oxidation of ketone is relatively slow and it involves the breaking of carbon-carbon sigma bond and it happens only in the presence of strong oxidizing agent.



Laboratory test to distinguish between aldehydes and ketones

(i) Silver mirror test

The reagent used for this test is ammoniacal silver nitrate (Tollen's reagent). Since this reagent has short shelf life, it should be freshly prepared in laboratory by mixing silver nitrate and ammonium hydroxide.

$$\underset{\text{(Aldehyde)}}{RCHO} + \underset{\text{(Tollen's reagent)}}{2[Ag(NH_3)_2]OH} \xrightarrow{\text{Heat}} \underset{\text{Ammonium}}{RCOO^{-}NH_4^{+}} + 3NH_3 + H_2O + \underset{\text{(Silver mirror)}}{2Ag\downarrow}$$

While performing the test, tollens's reagent is mixed with the given carbonyl compound and heated to boiling. If aldehyde is present, a silver mirror will form on the inside of the test tube.

(ii) Fehling test

There are two Fehling solutions available in laboratory. Fehling A is an aqueous copper (II) sulphate solution while Fehling B is an aqueous solution of sodium hydroxide (NaOH) with sodium potassium tartrate.
To carry out the Fehling's test, mix equal volumes of Fehling A andB in a test tube, heat the mixture to boiling and then add a small amount of given carbonyl compound into the test tube. If aldehyde is present, the blue colour of Fehling solution (Cu?) changes to red precipitates (ppt) of copper (l) oxide.

$$\underset{\text{(Aldehyde)}}{RCHO} + \underset{\text{(Fehling Solution)}}{2Cu^{+2}} + 5\bar{O}H \longrightarrow RCOO^{-} + \underset{\text{(Red-brown ppt.)}}{Cu_2O} + 3H_2O$$

Difference between Aldehyde and Ketone

Basic Structure:

Both aldehydes and ketones are carbonyl compounds but in aldehydes, the carbonyl carbon is attached with at least one alkyl or aryl group while in ketones, carbonyl carbon is attached with two alkyl or aryl groups.

Physics Properties:

The boiling point of ketones is relatively higher than aldehydes since carbonyl group of ketones is more polarized than aldehydes.

Reactivity:

The reactivity of aldehydes towards nucleophilic addition is greater than ketones because of less steric hindrance and less electronic effect.

Oxidation into Carboxylic acid:

Ketones oxidizes to carboxylic acid with strong oxidizing agent such as potassium dichromate ($KCr0_7$) and potassium permanganate ($KMnO_4$) while aldehydes can casily be oxidized to carboxylic acid with mild oxidizing agent such as chromic acid (H_2CrO_4), Tollen's reagent and Fehling solution and Benedict solution.

Reduction into alcohol:

Reduction of aldehydes in the presence of strong reducing agents such as lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$) gives primary alcohol while the reduction of ketones gives secondary alcohol.

Some applications of aldehydes and ketones

Application	Aldehydes	Ketones
Organic Synthesis	Used as key intermediates in various organic reactions.	Important starting materials for creating complex organic compounds.
Flavor Fragrance	Provide characteristic aroma and taste to many natural and synthetic products, e.g., vanillin and benzaldehyde.	Used as flavouring agents and fragrances in the food, cosmetic, and perfume industries.
Pharmaceuticals	Serve as building blocks for Some various pharmaceuticals, such as anti-inflammatory drugs and antihistamines.	ketones are used as active pharmaceutical ingredients in medicines.
Solvents	Formaldehyde is used as solvent for certain reactions.	Acetone is a widely used a solvent for chemical reactions and as a nail polish remover.

Short Questions

1. Give reasons for the following:

i. The boiling point of aldehydes and ketones is lower than alcohol.

Aldehydes and ketones have **weaker intermolecular forces** compared to alcohols. Here's why:

- **Alcohols:** Possess an -OH group, enabling **hydrogen bonding** between molecules. These hydrogen bonds are strong and require significant energy to break, leading to a **higher boiling point**.
- **Aldehydes and Ketones:** Contain a carbonyl group (C=O) but lack the -OH group. This absence prevents hydrogen bonding. Instead, they rely on weaker **dipole-dipole interactions** for intermolecular attraction. These weaker forces require less energy to overcome, resulting in a **lower boiling point** compared to alcohols.

ii. Formaldehyde is highly soluble in water as compared to other aldehydes.

High Water Solubility of Formaldehyde:

Formaldehyde (HCHO) has a significantly higher water solubility compared to other aldehydes due to its **smaller size and the presence of two hydrogen atoms** in its functional group:

- **Smaller size:** Formaldehyde has the simplest aldehyde structure (HCHO). With a smaller molecule, there's a greater surface area available for hydrogen bonding with water molecules, leading to higher solubility.
- **Two hydrogen atoms:** Formaldehyde has two hydrogens directly attached to the oxygen atom (O) in the carbonyl group. These hydrogens can participate in more extensive hydrogen bonding with water compared to aldehydes with only one hydrogen on the O atom.

iii. Oxidation of aldehydes is faster than ketones.

Oxidation Rate of Aldehydes vs. Ketones:

i. Faster Oxidation of Aldehydes:

Aldehydes generally undergo oxidation reactions **faster** than ketones. This can be attributed to several factors:

- **More reactive carbonyl carbon:** In aldehydes, the carbonyl carbon atom has only one bulky substituent (a hydrogen) attached. This allows for easier access by the oxidizing agent to the carbon-oxygen double bond, facilitating oxidation.
- **Formation of a more stable intermediate:** During oxidation, aldehydes form a resonance-stabilized intermediate (a gem-diol) due to the presence of two hydrogens on the carbonyl carbon. This

intermediate is more stable than the corresponding intermediate formed in ketone oxidation, lowering the activation energy barrier and speeding up the reaction.

2. Write the equation for the reaction of acetaldehyde with the following:

i. Chromic acid (H_2CrO_4)

$$CH_3CHO + H_2CrO_4 \rightarrow CH_3COOH + Cr_2O_3 + H_2O$$

ii. Lithium Aluminum hydride ($LiAIH_4$)

CH3CHO + 4LiAlH4 -> CH3CH2OH + Al(OH)4Li + 3H2

ii. Zinc mercury amalgam

3. How is formaldehyde prepared by ozonolysis?

Notes

4. Why is formaldehyde more reactive towards Nucleophilic addition reactions compared with ketones.

Formaldehyde exhibits greater reactivity towards nucleophilic addition reactions compared to ketones due to two key factors:

1. **Steric Hindrance:**
- **Formaldehyde:** Has only one hydrogen atom attached to the carbonyl carbon (C=O). This results in **less steric hindrance** around the electrophilic carbon center. Nucleophiles can approach and attack this carbon more easily due to the absence of bulky substituents.
- **Ketones:** Contain two bulky substituent groups (alkyl or aryl groups) attached to the carbonyl carbon. This creates **more steric hindrance** around the electrophilic carbon. The bulky groups can physically hinder the nucleophile's approach and make the reaction slower.

2. **Electronic Effect:**
- **Formaldehyde:** The presence of two hydrogen atoms bonded to the oxygen atom in the carbonyl group creates a **greater electron-withdrawing effect** through inductive electron donation. This effect pulls electron density away from the carbon-oxygen double bond, making the **carbonyl carbon more positive (electrophilic)**. A more positive carbon is more attractive to electron-rich nucleophiles.
- **Ketones:** Generally have only one alkyl group attached to the oxygen atom. This group's electron-withdrawing effect is weaker compared to two hydrogens in formaldehyde. Consequently, the carbonyl carbon in ketones is **slightly less positive** than in formaldehyde, leading to a lower electrophilic character and reduced reactivity towards nucleophiles.

In summary, the combination of less steric hindrance and a more electrophilic carbonyl carbon makes formaldehyde a more reactive nucleophile acceptor compared to ketones. This allows for faster and more efficient nucleophilic addition reactions with formaldehyde.

5. How does the oxidation of ketones differ from the oxidation of aldehydes?

The key differences between the oxidation of ketones and aldehydes lie in the ease of oxidation and the products formed:

Ease of Oxidation:

- **Aldehydes (RCHO):** Generally much **easier to oxidize** than ketones. This is due to the presence of a more reactive carbonyl carbon atom.
  - **Reason:** In aldehydes, the carbonyl carbon has only one bulky substituent (a hydrogen atom). This allows for easier access by oxidizing agents to the carbon-oxygen double bond, facilitating oxidation.
- **Ketones (R_2CO):** Considerably **more resistant to oxidation** compared to aldehydes.
  - **Reason:** Ketones have two bulky substituents on the carbonyl carbon, creating steric hindrance. This hindrance makes it more difficult for oxidizing agents to approach and attack the carbon-oxygen double bond.

Products of Oxidation:

- **Aldehydes:** When oxidized, aldehydes are readily converted to **carboxylic acids (RCOOH)**. This process involves the breaking of the carbon-hydrogen bond in the carbonyl group and the addition of an oxygen atom (from the oxidizing agent) to form a new C-O bond.

Example: CH_3CHO (acetaldehyde) + O_2 -> CH_3COOH (acetic acid)

- **Ketones:** Cleavage of the carbon-carbon bond adjacent to the carbonyl group is the typical mode of oxidation for ketones under harsher conditions (strong oxidizing agents and often heat). This cleavage results in the formation of a carboxylic acid with a smaller carbon chain and another carboxylic acid or a ketone with a shorter chain depending on the position of the cleavage.

Example:

$$\underset{\text{(acetone)}}{CH_3COCH_3} + \underset{\text{(strong oxidizing agent)}}{K_2Cr_2O_7 + H_2SO_4} \rightarrow \underset{\text{(acetic acid)}}{CH_3COOH} + CO_2$$

6. Why are ethers considered as good solvents in organic reactions?

- **Polarity:** The polar nature allows them to solvate (dissolve) other polar molecules through dipole-dipole interactions.

- **Hydrogen Bonding Acceptance:** Enables interaction with a broader range of organic compounds containing O-H or N-H groups.
- **Inertness:** Minimizes interference with the desired reaction.
- **Moderate Water Solubility:** Provides versatility for reactions involving water or water-soluble components.
- **Volatility:** Facilitates solvent removal after the reaction.

Descriptive Questions

1. What are aldehydes and ketones? Describe the structure and type of hybridization in them.

Notes

2. Explain the acid-catalyzed and base-catalyzed nucleophilic addition reactions in aldehydes and ketones.

Notes

3. Describe how aldehydes are distinguished from ketones by the following laboratory test.

(i) Tollen's reagents (ii) Fehling solution

Notes

4. Write the equation and give the name of major product in the following chemical process.

i. Oxidation of acetone with acidified $K_2Cr_20_7$.
ii. Reduction of acetaldehyde with $NaBH_4$.
iii. Hydration of ethyne in the presence of $H_2SO_4/HgSO_4$
iv. Acylation of benzene in the presence of $AlCl_3$.

5. Give four differences between aldehydes and ketones.

Notes

6. Write the equation for the nucleophilic addition reaction if formaldehyde treated with

i. Hydrogen cyanide

$$HCHO + HCN \longrightarrow HC(OH)(CN)\ \text{(Hydroxyacetonitrile)}$$

ii Primary alcohol

$$HCHO + RCH_2OH \longrightarrow HOCH_2CH_2OR\ \text{(Hemiacetal)}$$

iii. Methyl magnesium bromide

$$HCHO + CH_3MgBr \longrightarrow CH_3CH_2OH\ \text{(Ethanol)}$$

iv. Ammonia

$$HCHO + NH_3 \longrightarrow CH_2{=}NH + H_2O\ \text{(Methylamine and water)}$$

7. Explain the factors that influence the reactivity of carbonyl compounds towards nucleophilic addition reaction.

Notes

Chapter # 9

Carbonyl compound II Carboyclic acid and functional derivatives

INTRODUCTION

"Organic compounds which contain carbonyl group (C = 0) attached to hydroxyl group (-OH) are referred as carboxylic acid".

PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

i) Colour and odour

Aliphatic monocarboxylic acids are generally colorless. They have a pungent odour.

ii) Solubility

Carboxylic acids are soluble in polar solvents such as water and alcohols, due to their ability to form hydrogen bonds with these solvents.

iii) Boiling points

Compared to alcohols, carboxylic acids are more polar and have a high tendency to form hydrogen bonds among themselves.

STRUCTURE OF CARBOXYLIC ACID

Structure of carboxylic acid is explained by the hybrid orbital theory. The carbonyl carbon is sp^2 hybridized, possessing three sp^2 hybrid orbitals and one pz unhybridized orbital. These three sp^2 hybrid orbitals are oriented almost at an angle of 120° to give trigonal geometry whereas pz unhybridized orbital of carbonyl carbon form pi bond with pz orbital of oxygen atom.

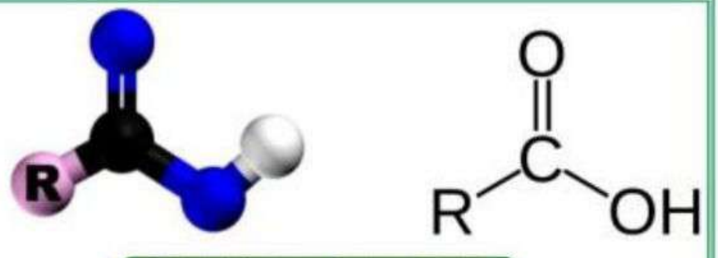


Fig 9.1: Structure of carboxylic acid

ACIDITY OF CARBOXYLIC ACID

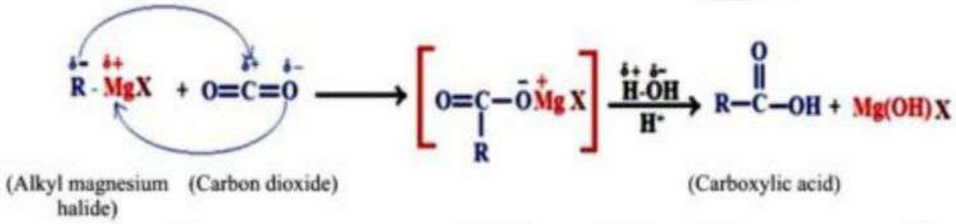
"Carboxylic acids are considerably stronger acids than alcohols, phenols and water. However, they are weaker acids compared to mineral acids",

PREPARATION OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES

Carboxylic acids are prepared by the following different methods.

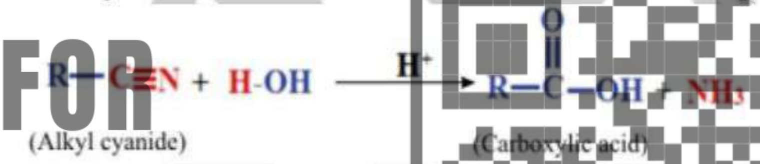
By the Carbonation of Grignard Reagent

When Grignard reagent reacts with carbon dioxide, it changes into an addition product which on hydrolysis in acidic medium produce carboxylic acid.



By the Hydrolysis of Nitriles

Alkyl cyanide (nitrile) when reacts with water in the presence of acid, it changes into carboxylic acid with the liberation of ammonia gas.



By the Oxidation of Primary Alcohols

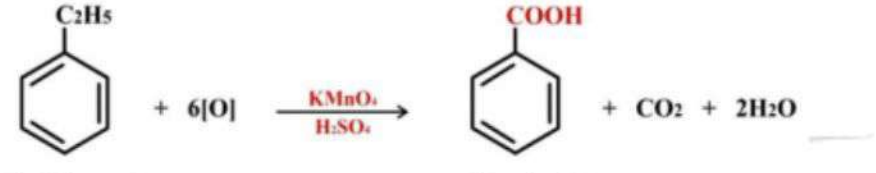
By using acidified oxidizing agents such as $K_2Cr_2O_7$ or $KMnO_4$ primary alcohols can be oxidized to form carboxylic acids. This process occurs through an intermediate stage where the alcohol is converted into an aldehyde.

By the Oxidation of Aldehyde

Aldehydes oxidized when mixed with Potassium dichromate and sulphuric acid to produce carboxylic acid.

By the Oxidation of Alkyl Benzene

When an alkyl benzene reacts with potassium permanganate ($KMnO_4$) under acidic conditions, the alkyl group is oxidized to-COOH group.



(Ethyl benzene) (Benzoic acid)

REACTIONS OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES

Certain compounds are structurally derived from carboxylic acids by replacing a part of functional group of the carboxylic acid. Some common derivatives of carboxylic acids are given as.

(i) Esters:

They are formed by replacing the hydroxyl group of carboxylic acid with an alkyl or aryl group. Their general formula is R-COOR e.g. Ethyl acetate ($CH_3COOCH_2CH_3$), Methyl propionate ($CH_3CH_2CO0CH_3$).

(i) Acid halides:

They are formed by replacing the hydroxyl group of carboxylic acid with a halogen (X) atomn. Their general formula is RCOX e.g. Acetyl chloride (CH_3COCl), Propionyl chloride (CH_3CH_2COCl).

(iii) Amides:

They are formed by replacing the hydroxyl group of carboxylic acid with an amino group. Their general formula is RCONH e.g. Acetamide (CH_3CONH_2), Benzamide ($C_6H_5CONH_2$).

(iv) Anhydrides:

They are formed by the removing a water molecule from two carboxylic acid molecules. Their general formula is $(RCO)_20$ e.g. Acetic anhydride $(CH_3CO)_2O$, Maleic anhydride ($C_4H_20_3$).

Conversion of carboxylic acids into acyl halides

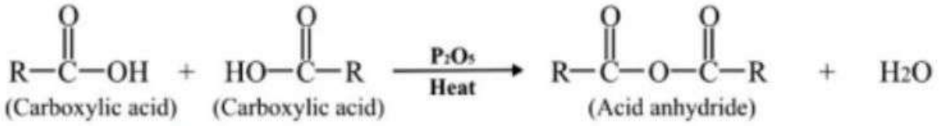
Like alcohols, the hydroxyl groups of carboxylic acids are easily replaced by halogen atom on heating with PCl_5, PCl_3, or $SOCl_2$

$$\underset{\text{(carboxylic acid)}}{R-COOH} + PCl_5 \longrightarrow \underset{\text{(Acyl halide)}}{R-CO-Cl} + POCl_3 + HCl$$

$$\underset{\text{(carboxylic acid)}}{3R-COOH} + PCl_3 \longrightarrow \underset{\text{(Acyl halide)}}{3R-CO-Cl} + H_3PO_3$$

Conversion of Carboxylic Acids into Acid Anhydrides

The formation of an acid anhydride involves a condensation reaction between two carboxylic acid molecules. This reaction is typically conducted in the presence of a dehydrating agent like phosphorus pentoxide (P_2O_5).



$$\underset{\text{(Carboxylic acid)}}{R-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{(Carboxylic acid)}}{HO-\overset{\overset{O}{\|}}{C}-R} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{(Acid anhydride)}}{R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R} + H_2O$$

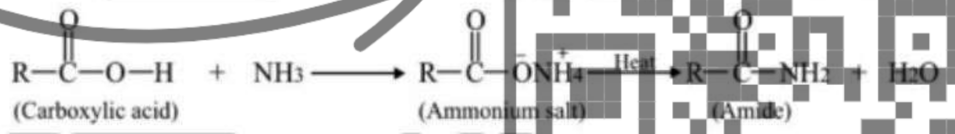
Conversion of Carboxylic Acids into Ester

Esters are produced from carboxylic acids through a reaction called esterification. In this reaction carboxylic acid reacts with an alcohol in the presence of a catalyst usually concentrated Sulphruic acid to produce an ester and water.

$$\underset{\text{(Carboxylic acid)}}{R-\overset{\overset{O}{\|}}{C}-O-H} + \underset{\text{(Alcohol)}}{C_2H_5-OH} \overset{H^+}{\rightleftharpoons} \underset{\text{(Ester)}}{R-\overset{\overset{O}{\|}}{C}-OC_2H_5} + H_2O$$

Conversion of Carboxylic Acids into Amides

Amides can be produced by the reaction between carboxylic acid and ammonia, where an ammonium salt is formed, which upon heating yields the corresponding acid amide.



$$\underset{\text{(Carboxylic acid)}}{R-\overset{\overset{O}{\|}}{C}-O-H} + NH_3 \longrightarrow \underset{\text{(Ammonium salt)}}{R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{N}H_4} \xrightarrow{\text{Heat}} \underset{\text{(Amide)}}{R-\overset{\overset{O}{\|}}{C}-NH_2} + H_2O$$

Conversion of Carboxylic Acids into Alcohols

Carboxylic acids upon catalytic reduction with lithium aluminum hydrides produce primary alcohols.

$$\underset{\text{(Carboxylic acid)}}{R-COOH} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{(Alcohol)}}{R-CH_2-OH} + H_2O$$

Conversion of Carboxylic Acids into Alkane

Carboxylic acids when reacted with caustic soda (base) they form salt of carboxylic acid which on further heating with soda-lime yield alkanes.

$$\underset{\text{(Acetic acid)}}{CH_3\text{-}COOH} + NaOH \longrightarrow \underset{\text{(Sod. acetate)}}{CH_3\text{-}COONa} + H_2O$$

$$\underset{\text{(Sod. acetate)}}{CH_3\text{-}COONa} + NaOH \xrightarrow{CaO/Heat} \underset{\text{(Methane)}}{CH_4} + Na_2CO_3$$

Uses of some common carboxylic acids and their derivatives

Citric Acid ($C_6H_8O_7$)

It is used as a preservative, flavor enhancer acidity regulator.

Malic Acid ($C_4H_6O_5$)
It is used as a food additive and pH control agent.

Tartaric Acid ($C_4H_6O_6$)
It is commonly used in food and beverage industry. products.

Acetic Acid (CH_3COOH)
It is used as a preservative and as a raw material of various chemicals.

Salicylic Acid (HOC_6H_4COOH)
It is used in the preparation of skin care products and in the production of aspirin.

Benzoic Acid (C_6H_5COOH)
It is used in the production of dyes, perfumes and plastics.

Acetamide (CH_3CONH_2)
It is used as a raw material in pharmaceuticals and drug synthesis.

Acetic anhydride ($C_4H_6O_3$)
It is used in making cellulose acetate and in the manufacturing of dyes.

Short Questions

1. Explain why?

i) The boiling points of carboxylic acids are high than alcohol?
Intermolecular hydrogen bonding between carboxylic acid molecules is responsible for their higher boiling points compared to alcohols.

ii) The structure of carboxylic acid is trigonal planar?
The functional group (COOH) in a carboxylic acid has a trigonal planar geometry due to sp2 hybridization of the central carbon atom.

2. What happens when:

i) Formaldehyde reacts with a mixture of Potassium dichromate & Sulphruic acid.

$$HCHO + K_2Cr_2O_7 + H_2SO_4 \longrightarrow HCOOH + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$

ii) Carboxylic acid reacts with thionyl chloride

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

ii) Carboxylic acid reacts with ammonia

iv) Ethyl magnesium bromide reacts with carbon dioxide

$$C_2H_5MgBr + CO_2 \longrightarrow CH_3CH_2COOH + MgBr_2$$

3. Write down the commercial applications of carboxylic acids.

Carboxylic acids are a diverse group of organic compounds with a wide range of commercial applications. Here are some of the most important ones:

Food and Beverages: Many carboxylic acids are found naturally in food and beverages or are added as ingredients.

Chemicals and Polymers: Carboxylic acids are essential starting materials for the production of various chemicals and polymers.

Pharmaceuticals and Cosmetics: Many carboxylic acids are used in the production of medicines and cosmetics.

Other Applications: Carboxylic acids have numerous other industrial applications, including:

- **Formic acid:** Used in the textile industry for dyeing and finishing fabrics.
- **Oxalic acid:** Used as a bleaching agent and rust remover.
- **Acetic acid:** A solvent for paints, inks, and adhesives.

4. Write the natural sources of following carboxylic acids.

(a) Formic acid (b) Acetic acid (c) Valeric acid (d) Caproic acid

Here are the natural sources of the following carboxylic acids:

(a) Formic Acid (HCOOH):

- **Insects:** Formic acid is found in the venom of some ant and bee species. It's responsible for the stinging sensation and irritation caused by their bites.
- **Plants:** Stinging nettles and pine needles contain small amounts of formic acid.

(b) Acetic Acid (CH_3COOH):

- **Vinegar:** The most common source of acetic acid is vinegar, produced by the fermentation of alcoholic beverages (like wine) or sugary solutions using acetic acid bacteria.

(c) Valeric Acid ($C_5H_{10}O_2$):

- **Valeriana officinalis (Valerian Root):** This herb is a natural source of valeric acid, which is thought to contribute to its sedative and calming effects.

- **Other Plants:** Valeric acid is also found in some other plants, including catnip and cheese rind.

(d) Caproic Acid ($C_6H_{12}O_2$):

- **Milk:** Caproic acid is a short-chain fatty acid found in goat's milk and cow's milk, contributing to their characteristic flavor and odor.
- **Other Dairy Products:** It's also present in some cheeses and other dairy products.
- **Coconut Oil:** Caproic acid is a minor component of coconut oil

Descriptive Questions

1. How is carboxylic acid prepared by:

i) Carbonation of Grignard reagent

$$RMgX + CO_2 \rightarrow RCOOH + MgX_2$$

ii) Hydrolysis of alkyl nitriles

$$RCN + 2H_2O + H^+ \rightarrow RCOOH + NH_4^+$$

ii) Oxidation of primary alcohols

$$RCH_2OH + H_2CrO_4 + H_2SO_4 \rightarrow RCOOH + Cr_2(SO_4)_3 + H_2O$$

2. Explain the structure of carboxylic acid.

Notes

3. Discuss the acidic nature of carboxylic acid. How is it stronger than other organic compounds and weaker than mineral acids?

Carboxylic acids are acidic due to the stability of the carboxylate ion formed upon proton donation. This stability is a result of both electron donation from the oxygen atoms and resonance stabilization. While stronger acids than most organic compounds like alcohols, they are weaker than mineral acids due to the limitations of single proton donation and the nature of their conjugate bases.

4. Convert the followings:

i) Carboxylic acid into acid anhydride

ii) Ester into carboxylic acid

iii) Toluene into benzoic acid

5. Explain the following physical properties of carboxylic acids:

(a) Solubility (b) Boiling point

Notes

6. Write the names of four derivatives of carboxylic acids and give the equation for their preparation from acetic acid.

Notes

Chapter # 10

Bio-Chemistry

INTRODUCTION

"Biochemistry is the branch of science that deals with the chemical processes taking place in the organisms".

It focuses on the study of structure, function and interaction of biological macromolecules such as proteins, carbohydrates and lipids as well as the chemical reactions and pathways that Occur within cells.

CARBOHYDRATES

Carbohydrate is an essential group of foods in human and animal diets. It is more realistic to define a carbohydrate as

“Polyhydroxy aldehydes and ketones or the substances that yield such compounds when they react with water on hydrolysis.”

Classification based on structure

"Carbohydrates are classified as monosaccharides, disaccharides, oligosaccharide and polysaccharides".

This classification is based on the number of sugar unit present in carbohydrates.

Monosaccharides contain a single sugar unit for example glucose, fructose, and galactose.

Disaccharides contain two sugar units, examples are sucrose, lactose and maltose.

Oligosaccharide are carbohydrates that are made up of 3 to 10 sugar units, for example ketose (glucose-fructose-fructose) and melezitose (glucose-fructose-glucose).

Polysaccharides Contain more than 10 sugar units, Cellulose, starch and glycogen are examples of polysaccharides.

Monosaccharides are classified on the basis of the number of carbons present in the molecule. In this classification prefix is used to indicate number of carbon atoms in the molecule and the suffix -ose, is used to indicate carbohydrate as a class of biomolecule.

Class of Monosaccharid	**Formula**	**Examples**
Triose	$C_3H_6O_3$	Glyeeraldehyde
Tetrose	$C_4H_8O_4$	Erythrose
Pentose	$C_5H_{10}O_5$	Ribose
Hexose	$C_6H_{12}O_6$	Glucose

Among these monosaccharide, hexose sugar is important since it plays a crucial role in biological system. Hexose sugars are classified into aldohexose and ketohexose. An example of aldohexose is glucose where as ketohexose is fructose.

Glucose and fructose exist in both open chain and close chain form however, the open chain form is relatively unstable. The close chain form of glucose is called pyranose since it resembles with pyran where as the close chain form of fructose is known a furanose since it resembles with furan.

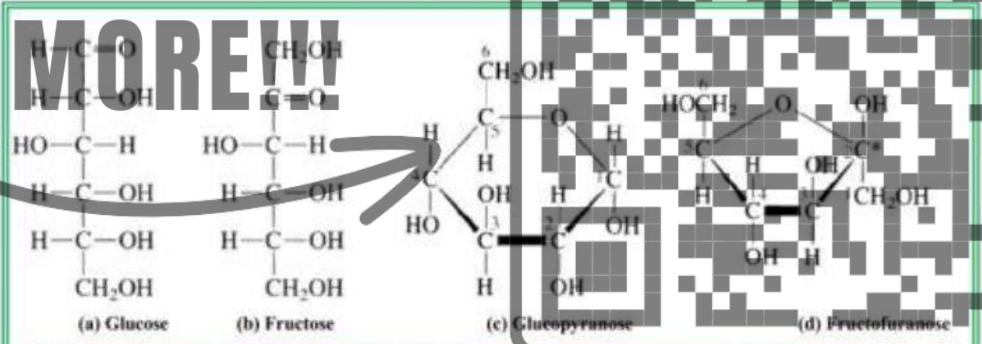


Fig 10.1: (a) Open structure of glucose (b) open structure of fructose (c) pyranose structure of glucose (d) furanose structure of fructose

Disaccharides are carbohydrates consisting of two monosaccharide units join together through glycosidic bond. “A glycosidic bond (0-C-0) is a type of covalent bond that join two monosaccharide units together to form a larger carbohydrate molecule". It is formed through a condensation reaction with the elimination of water molecule (Fig.10.2). Disaccharides are water soluble crystalline solids and represented by molecular formula $C_{12}H_2O_{11}$.

“Polysaccharides are macro bio molecules. They are amorphous, water insoluble and made up of more than hexose sugars”.

Plant polysaccharide are the reserved carbohydrates of plants. Example of plant polysaccharides are starch and cellulose which are composed of thousands glucose units.

Starch is a main component of our carbohydrate intake. It is found in potato, wheat, burley etc. cellulose is found n the cell wall of plant. It is used in making cotton, cellulose fiber and paper etc.

Importance of Carbohydrates
Carbohydrates are nutritionally significant bio molecules and are essential part of our balanced diet.

Carbohydrates such as starch, sucrose, maltose etc convert into glucose in our digestive system which then absorbed into the bloodstream and transported various cells where is utilized for the biological processes.

$$C_6H_{12}O_{6\,(glucose)} + 60_2 \longrightarrow 6CO_2 + 6H_20 + Energy$$

Glucose plays a vital role in energy storage within the body. The extra glucose of the bloodstream is converted into glycogen which serves as a primary form of energy storage in animals including humans. Glycogen is stored in muscles and liver. Another way glucose can be stored by converting it into triglycerides which are then stored as body fat.

Role of Common Carbohydrates in Health and Disease
Glucose: It is a vital component of our blood. Typically, the normal range of glucose in blood ranges between 70 to 110mg per 100 dl. However, if glucose level exceeds this range, it can lead to the Diabetes which can be managed through insulin control.

Fructose:
Fructose is a simple sugar that found in many fruits and honey. It is the sweetest among all other carbohydrates. Its main function is to provide energy during metabolism in the body. However, a high intake of fructose has been associated with weight gain and obesity.

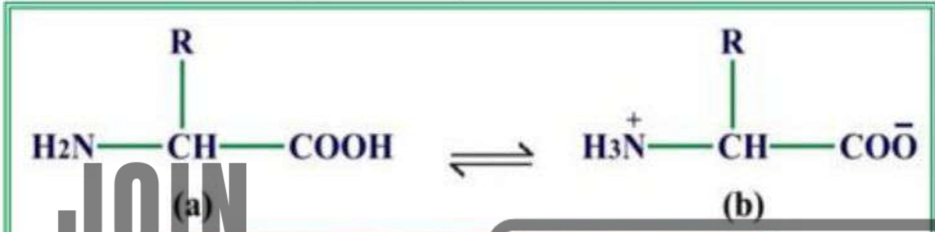
Lactose:
It is a disaccharide. It is found in milk and hence also known as milk sugar. During intake, it is broken down into glucose and galactose in the alimentary canal by the enzymatic activity.

Sucrose:
It is also a disaccharide and made up of a glucose and a fructose sugar. It is known as table sugar or cane sugar. An excess amount of sucrose in our

diet can cause the development of gum disease such as fatness, plaque formation in the teeth, and even tooth decay.

PROTEINS

Proteins are naturally occurring macromolecules made up of long chain of amino acids that fold into precise three dimensional configurations. All living organisms including plants, animals and bacteria contain proteins and their presence is vital for the life.



$$\underset{\text{(a)}}{H_2N-\overset{\overset{\displaystyle R}{|}}{C}H-COOH} \rightleftharpoons \underset{\text{(b)}}{H_3\overset{+}{N}-\overset{\overset{\displaystyle R}{|}}{C}H-CO\bar{O}}$$

Fig 10.3: Structure of (a) amino acid (b) zwitter ion of amino acid

There are twenty-two (22) different types of alpha amino acids that can be used to build proteins. Each amino acid consists of an amino group as well as a carboxyl group. These amino acids are associated with each other through poly peptide linkage (CONH). The specific arrangement and sequence of these amino acids determine the structure and function of the protein.

Fig 10.4: Formation of dipeptide by the condensation of two amino acids

Classification of proteins

Proteins may be classified into several groups based on their functions and structures. Based on functions, proteins are classified into following types.

(i) Catalytic proteins (Enzymes):

Enzymes are biological catalysts. They increase the rate of the biological reaction multiple fold as compared to a chemical catalyst. Our bodies contain numerous catalytic proteins which facilitate the chemical reactions inside the body. For example, lipase catalysis the decomposition of lipids into fatty acids in our alimentary canal.

$$\text{Starch} + H_2O \xrightarrow{\text{Amalyase}} \text{Glucose}$$

$$\text{Protein} + H_2O \xrightarrow{\text{Protease}} \text{Amino acid}$$

$$\text{Lipid} + H_2O \xrightarrow{\text{Lipase}} \text{Fatty acid}$$

(ii) Storage proteins:

These proteins store nutrients or metal ions in a particular part of plants or animals. For example, Albumin, Globulin and Casein etc.

(iii) Transport proteins:

These proteins facilitate the movement of molecules, ions and other substances across cellular membranes and in the blood stream. For example, hemoglobin.

(iv) Regulatory or hormonal proteins:

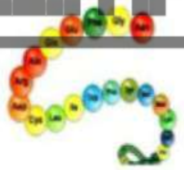
These proteins play a critical role in regulating the function of body by transmitting signals between the cells.

Classification of proteins on the basis of their structure

Proteins are essential macromolecules classified into four main types based on their structure.

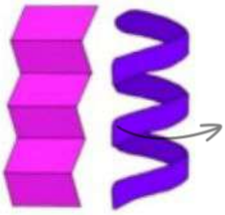
Classification of proteins

Primary



- ✓ It is a linear sequence of amino acids in the protein chain.
- ✓ This sequence plays a crucial role in determining the overall shape and function of the protein.

Secondary



- ✓ It refers to the folding patterns in polypeptide chains due to interactions between nearby amino acids.
- ✓ The two secondary common structures are alpha helix and beta sheets.
- ✓ The Stabilization of secondary structure is due formation of hydrogen bonds between N-H and C-0 groups of amino acids

Tertiary

- ✓ It refers to three-dimensional arrangement of a protein molecule having folded and refolded polypeptide chain.
- ✓ The stability of molecule is due to the presence of following types of forces among polypeptide chain:
- ✓ Salt bridge (ionic bond)
- ✓ Disulfide bridge (covalent bond)
- ✓ Van der Waals forces
- ✓ Hydrogen bond
- ✓ Example: Myoglobin exhibits tertiary structure.

Quaternary

- ✓ It is a large complex protein molecule and formed by the interaction of multiple protein subunits.
- ✓ Example: Hemoglobin, which consists of four subunits and illustrates the quaternary structure.

Properties of proteins

(i) Proteins are water soluble due to the di polar terminal of amino acids in the polypeptide chain.

(ii) Proteins are amphoteric in nature because of the presence of COOH as well as NH_2 group in their structure of amino acid sequences.

(ii) Proteins exhibit flexibility due to the ability of amino acid chain rotation.

(iv) Certain proteins exist in various colours i.e. hemoglobin.

(v) Proteins are thermally stable, however the structure of proteins are disrupted by heating, at elevated temperature or by a sharp change in the pH.

Importance of proteins

(i) Proteins provide energy for the body and in a rough estimation, 1g of protein provides four calories.

(i) Hemoglobin is a protein, it transports oxygen from the lungs to every tissue of the body.

(ii) Harmons are proteins which regulate various physiological functions in the body.

(iv) Antibodies are proteins which play a very important role in the immune system of the body.

LIPIDS

"Lipids are naturally occurring heterogeneous organic compounds that are insoluble in water but soluble in Bloor’s Bloor's reagent".

The term "lipid" originates from the Greek word "Lipos"" meaning "fat like" due to their greasy or oily texture when touched.

Lipids are vital components of our diet and can be obtained from various sources such as animal fat (e.g. butter, ghee) vegetable oil etc.

Classification of lipids

On the basis of chemical composition lipids are classified into three main groups, named as simple lipids, compound lipids and steroids.

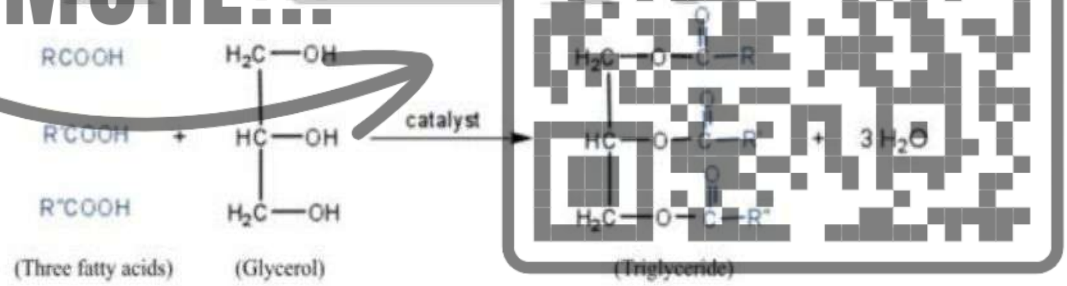
Simple Lipids

These lipids are chemically esters, made up of fatty acids and alcohols, mainly serve as energy source to the body.

Simple lipids are further classified into fat, oil and waxes.

Fats and Oils

"These lipids are abundantly found in nature and chemically known as triglycerides or triesters", They are formed by the condensation of three fatty acid and a glycerol molecule.



The fatty acid chains in the molecules of fat and oil consists of C_{12} to C_{24} carbon atoms which may be saturated or unsaturated. Vegetable oil contains unsaturated fatty acids and are liquid at room temperature. Animals fats are composed of saturated fatty acids and usually solids at room temperature.

Types of fatty acids

Saturated Fatty Acid

Contains only single bonds between carbon atoms

Example: Stearic Acid, Palmitic Acid

Unsaturated Fatty Acid

Contains at least one double bond between carbon atoms

Example: Oleic Acid, Linoleic Acid.

Waxes

"Waxes are the naturally occurring esters of long-chain fatty acids and long chain alcohols".

Waxes are solids with water repellent nature. In plants they form coating on the surface of leaves, fruits and other parts helping to prevent water loss and protect against environment. Honey bees produce wax to build honey combs for the protection of hives.

$$C_{15}H_{31} - COO - C_{16}H_{33}$$

(Bees wax)

Compound lipids

These are esters of glycerol with two fatty acids and some other compounds such as carbohydrates, amino acids, phosphoric acid etc".

These are classified into phospho lipids, glyco lipids and lipo proteins on the basis of introduction of dditional groups like phosphoric acid, glycogen and protein etc.

Example: LDL (low-density lipoprotein).

Steroids

These are derived lipids that are composed of specific structure of four interconnected carbon rings (Cyclopentanophenanthrene nucleus). Examples of steroids are cholesterol and cholic acid.

The structure of lipids varies depending on their classification. However the basic structure consists of a hydrophilic head and a hydrophobic carbon tail.

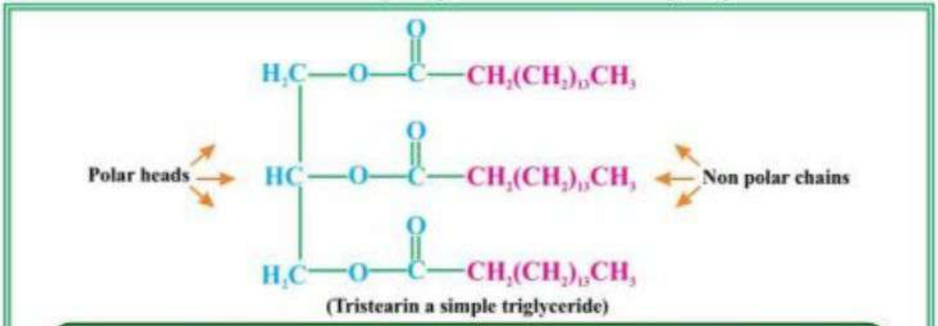


Fig. 10.5: Structure of a simple lipid showing its polar heads and non polar carbon chains

Properties of lipids

Physical Properties

- ✓ Lipids exist in different physical states depending upon their chemical nature and temperature.

- ✓ For example, fat exists in solid state, wax is semisolid state and oil in liquid state at room temperature.
- ✓ Lipids are translucent or opaque in nature.
- ✓ Lipids are insoluble in water and soluble in the organic solvents; like Bloor's reagent.
- ✓ Lipids have low density which enables them to float on water.
- ✓ Melting point of saturated lipids is higher than unsaturated lipids.
- ✓ Lipids are poor conductors of heat and electricity therefore serve as insulators for the animal body.

Chemical Properties

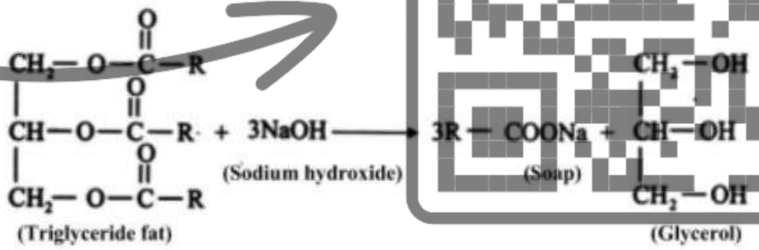
Addition reactions

Oils undergo addition reactions with hydrogen in the presence of nickel (catalyst) to produce fats. In this chemical reaction, unsaturated fatty acids of oil convert into saturated fatty acids.

$$R\text{-}CH\text{-}CH\text{-}COOH + H_2 \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}COOH$$

Saponification

Fat and oil are hydrolyzed when heated with an alkali to produce soap and glycerol, this process is known as saponification.



Rancidity

When animal fats are exposed to moist air, they undergo oxidation and hydrolysis reactions simultaneously leading to the development of an unpleasant taste and Odour. This process is commonly referred to as rancidity.

Importance of lipids

Lipids play important role in human body.

(iv)They store chemical energy in the form of triglycerides in adipose tissues. They store more than twice energy as compared to carbohydrates and proteins. This stored energy is used during fasting.

(ii) They are fundamental building blocks of cell membranes. Due to their water insolubility, they protect the cell by forming a phospholipid layer which allows the movement of substances in and out of the cell.

(iii) Lipids in adipose tissues help maintaining the body temperature and serve as insulation of the body.
(iv) They help in the absorption and utilization of fat soluble vitamins such as vitamin A, D, E and K.

MINERALS OF BIOLOGICAL SIGNIFICANCE

"Minerals are inorganic substances that are required to maintain physical health and prevent us from certain diseases".

Sources of important minerals

Minerals are generally found in fruits, vegetables, whole grains, dairy products, meats, sea food and water etc.

Sources of some minerals are listed

Minerals	Sources
Calcium	Milk, Cheese, Yogurt, Leafy greens
Iron	Red meat, Poultry, Sea Food, Bean, Lentils
Zinc	Beef, Chicken, Sea Food, Beans
Phosphorous	Meat, fish, dairy products, nuts, seeds, and whole grains.

Short Questions

1. Mention the three main functions of lipids.

Notes

2. Comparing with other nutrients, why lipids are better source of energy?

Energy Density:

- **Lipids:** One gram of fat provides about 9 calories of energy, while carbohydrates and proteins only offer around 4 calories per gram. This means lipids pack more energy per unit weight.

Storage:

- **Lipids:** Our bodies can store excess energy in the form of triglycerides (fats) in adipose tissue. These fat deposits act as a reserve fuel source, especially during times of limited food intake or high energy expenditure.
- **Carbohydrates:** The primary storage form of carbohydrates is glycogen, mainly stored in the liver and muscles. However, glycogen storage capacity is limited compared to fat storage.
- **Proteins:** Proteins are primarily used for building and repairing tissues and are not a preferred source of energy. While the body can break down proteins for energy in extreme situations, this process is less efficient and can have negative consequences like muscle breakdown.

Slow and Sustained Energy Release:

- **Lipids:** The breakdown of fats for energy is a slower process compared to carbohydrates. This slower release of energy provides a more sustained source of fuel, helping to regulate blood sugar levels and prevent energy crashes.

Essential Fatty Acids:

- **Lipids:** Some essential fatty acids cannot be synthesized by the body and must be obtained from the diet. These fats play crucial roles in various bodily functions, including hormone production and cell membrane structure.

However, it's important to note:

- Not all fats are created equal. Saturated and trans fats can contribute to health problems like heart disease. Unsaturated fats, particularly polyunsaturated and monounsaturated fats, are considered healthier options.
- A balanced diet needs all three macronutrients (carbohydrates, proteins, and lipids) for optimal health. Carbohydrates provide readily available energy for the brain and other organs, while proteins are essential for building and maintaining tissues.

In summary:

Lipids offer a concentrated source of energy, efficient storage capacity, and sustained energy release. However, it's crucial to consume healthy fats in moderation as part of a balanced diet.

3. Carbohydrates are necessary component of our diet. Give two dietary importance of carbohydrates.

Here are two key dietary importances of carbohydrates:

1. **Primary Source of Energy:** Carbohydrates are the body's preferred source of readily available energy. They are broken down into glucose (blood sugar) through digestion and absorption. Glucose enters the bloodstream and is transported to cells throughout the body, where it fuels various cellular processes.

- **Brain Function:** The brain relies heavily on a constant supply of glucose for proper functioning. Carbohydrates provide the necessary fuel for cognitive activities, memory, concentration, and mood regulation.
- **Muscular Activity:** During physical activity, especially moderate to high-intensity exercise, glucose is the primary source of energy for muscles. Carbohydrates ensure sustained energy levels for workouts and daily activities.

2. **Fiber for Digestive Health and Satiety:** Not all carbohydrates are created equal. Complex carbohydrates, particularly those rich in fiber, play a vital role in digestive health and promoting a feeling of fullness.

- **Fiber:** Dietary fiber, a type of complex carbohydrate, helps regulate digestion by adding bulk to stool and promoting smooth passage through the digestive tract. It also aids in the growth of beneficial gut bacteria, contributing to overall gut health.
- **Satiety:** Complex carbohydrates, especially those with high fiber content, take longer to digest and absorb compared to simple carbohydrates. This slower digestion process helps you feel fuller for longer, promoting satiety and potentially aiding in weight management.

4. What is meant by saponification? Give the reaction.

Saponification

Saponification refers to the chemical reaction between a **triglyceride (fat or oil)** and an **alkali (base)**, typically sodium hydroxide (NaOH) or potassium hydroxide (KOH), to produce **soap (a fatty acid salt)** and **glycerol**.

Here's the general reaction for saponification:
Triglyceride + 3 NaOH → 3 Soap + Glycerol
(fat/oil) (or 3 KOH) (fatty acid salt)

5. What is rancidity which chemical reaction involves in this process?

Rancidity refers to the spoilage of fats and oils that leads to unpleasant odors and flavors. It's caused by a group of chemical reactions that break down the fats and oils, primarily involving:

1. Oxidation:

This is the main culprit behind rancidity. Oxygen in the air reacts with the unsaturated fatty acids (fats with double bonds between carbon atoms) present in the fats and oils. This reaction is similar to how iron rusts in the presence of oxygen.

- **Free Radicals:** The oxidation process often starts with the formation of free radicals. These are highly reactive molecules with an unpaired electron, making them unstable and prone to further reactions.
- **Chain Reaction:** Free radicals can steal hydrogen atoms from unsaturated fatty acids, creating new free radicals and propagating the oxidation chain reaction. This chain reaction leads to the breakdown of the fatty acid molecules.

2. Hydrolysis:

While less prominent than oxidation, hydrolysis can also contribute to rancidity. This reaction involves the breakdown of fats and oils by water molecules. Enzymes naturally present in some foods or introduced by microorganisms (bacteria or mold) can accelerate hydrolysis.

Products of these reactions:

- The breakdown of fats and oils through oxidation and hydrolysis produces various volatile compounds with unpleasant odors and flavors. These can include aldehydes, ketones, and short-chain fatty acids.
- Additionally, the breakdown products can be irritating to the digestive system.

Factors affecting rancidity:

- **Unsaturation:** Fats and oils with a higher degree of unsaturation (more double bonds) are generally more prone to rancidity due to their increased reactivity with oxygen.
- **Light, Heat, and Air:** Exposure to light, heat, and air can accelerate the oxidation process, leading to faster rancidity.

- **Storage:** Proper storage methods like refrigeration or using airtight containers can help minimize exposure to these factors and slow down rancidity.

6. Write three essential functions of protein in the body.

Here are three essential functions of protein in the body:

1. **Building and Repairing Tissues:** Proteins are the building blocks of our body's tissues. They are crucial for:
   - ➢ **Growth and Development:** During childhood and adolescence, protein is essential for building new tissues like muscles, bones, skin, hair, and organs.
   - ➢ **Maintenance and Repair:** Throughout life, our bodies constantly repair and replace damaged tissues. Protein provides the necessary amino acids to rebuild and maintain these tissues.
   - ➢ **Cell Structure:** Proteins are major components of cell membranes and other cellular structures, providing support and shape.
2. **Enzymes:** Enzymes are biological catalysts that regulate and accelerate countless biochemical reactions within the body. Most enzymes are proteins with specific shapes that allow them to bind to particular molecules (substrates) and speed up their conversion into products. Without enzymes, these reactions would occur very slowly or not at all, hindering vital cellular processes. Examples include enzymes involved in digestion, energy production, and waste removal.
3. **Transportation and Storage:** Proteins play a vital role in transporting various molecules throughout the body. For instance:
   - ➢ **Hemoglobin:** This protein in red blood cells carries oxygen from the lungs to tissues throughout the body.
   - ➢ **Lipoproteins:** These transport molecules carry lipids (fats) like cholesterol in the bloodstream.
   - ➢ **Plasma Proteins:** Proteins present in blood plasma can also bind and transport various substances like hormones, vitamins, and metal ions. Proteins can also serve as storage molecules for essential amino acids. When dietary protein intake is insufficient, the body can break down stored proteins to access amino acids for building other proteins or generating energy.

7. Write down the sources from which we intake fructose and lactose.

Fructose Sources:

- **Fruits:**

A wide variety of fruits naturally contain fructose, including:

Apples, berries, grapes, citrus fruits (oranges, grapefruits), pears, mangoes, dates, etc.

- **Honey:**
  This natural sweetener from bees is a mixture of fructose and glucose.

Lactose Sources:

- **Milk:**
  Lactose, or milk sugar, is naturally found in milk from mammals like:
    - Cows, goats, sheep

- **Milk Products:**
  Lactose is present in various dairy products derived from milk, such as:
    - Cheese (amounts vary depending on the type)
    - Yogurt
    - Ice cream

- **Fortified Foods:**
  Some processed foods may be fortified with lactose or milk solids, adding it as an ingredient.

Descriptive Questions

1. What are Carbohydrates? Give their classification on the basis of structure.

Notes

2. Explain the role of glucose, fructose, sucrose and lactose in the health of human being.

Glucose:

- **Essential Energy Source:** Glucose is the primary source of energy for most cells in the body. It plays a crucial role in fueling various bodily functions, including:
    - Brain function
    - Muscle activity
    - Organ function
    - Cellular processes
- **Blood Sugar Regulation:** The body tightly regulates blood sugar (glucose) levels for optimal functioning. Hormones like insulin and glucagon work together to maintain blood sugar balance.
- **Excessive Intake Concerns:** While essential, chronically high blood sugar due to excessive intake of carbohydrates or impaired regulation can contribute to health problems like diabetes and metabolic syndrome.

Fructose:

- **Natural Sweetener:** Found in fruits and honey, fructose provides sweetness and contributes to the overall taste of these foods.
- **Moderate Intake:** In moderation, fructose from natural sources can be part of a healthy diet. However, excessive consumption, particularly from added sugars like high-fructose corn syrup (HFCS), has been linked to various health concerns, including:
    - Increased risk of obesity
    - Non-alcoholic fatty liver disease
    - Insulin resistance
    - Increased triglycerides (blood fats)

Sucrose (Table Sugar):

- **Common Sweetener:** Sucrose is a disaccharide composed of glucose and fructose. It's the most common table sugar and widely used as a sweetener in processed foods and beverages.
- **Health Effects:** Consuming large amounts of added sucrose can have similar health consequences as excessive fructose intake, including obesity, metabolic syndrome, and increased risk of chronic diseases.

Lactose:

- **Milk Sugar:** Lactose is a natural sugar found in milk from mammals. It provides some energy and nutrients like calcium.
- **Lactose Intolerance:** Some individuals lack sufficient lactase, the enzyme needed to break down lactose in the small intestine. This can lead to digestive discomfort like bloating, gas, and diarrhea after consuming milk or dairy products.

Overall:

- Moderate intake of natural sugars like fructose and lactose from whole fruits and dairy (for those without lactose intolerance) can be part of a healthy diet.
- Excessive consumption of added sugars, particularly from processed foods and beverages, can negatively impact health.
- Glucose is essential for energy but maintaining healthy blood sugar levels is crucial.

3. What are Proteins? Classify various types of proteins on the basis of their function.

Notes

4. What are Lipids? Give their classification, properties and biological significance.

Notes

5. How can you explain primary, secondary and tertiary structure of proteins?

Notes

6. Describe physical properties of proteins.

Notes

7. Why minerals are essential for our health? Give the biological significance of Calcium, Iron, Zinc, and phosphorus.

Minerals are essential for our health because they play a multitude of vital roles in various bodily functions. They cannot be produced by the body and must be obtained from our diet. Here's a breakdown of the biological significance of Calcium, Iron, Zinc, and Phosphorus:

Calcium (Ca):

- **Bone Health:** Calcium is the most abundant mineral in the body, constituting a major component of bones and teeth. It provides structural strength and rigidity to these skeletal structures.
- **Muscle Function:** Calcium is crucial for proper muscle contraction and relaxation, including both skeletal muscles for movement and smooth muscles for organ function.
- **Nerve Impulse Transmission:** Calcium ions play a vital role in transmitting nerve impulses throughout the nervous system.
- **Blood Clotting:** Calcium is necessary for blood clotting, helping to prevent excessive bleeding from injuries.
- **Enzyme Regulation:** Calcium acts as a cofactor for various enzymes, influencing essential biochemical reactions in the body.

Iron (Fe):

- **Hemoglobin Production:** Iron is a central component of hemoglobin, the protein in red blood cells responsible for transporting oxygen throughout the body. Deficiency can lead to anemia, characterized by fatigue, weakness, and shortness of breath.
- **Myoglobin Formation:** Iron is also involved in myoglobin, a protein in muscle cells that stores oxygen for energy production during physical activity.
- **Enzyme Function:** Iron is a cofactor for several enzymes essential for energy production, DNA synthesis, and cellular processes.

Zinc (Zn):

- **Immune Function:** Zinc plays a crucial role in supporting a healthy immune system. It helps with the development and function of immune cells that fight off infections.
- **Wound Healing:** Zinc is necessary for proper wound healing and tissue repair.

- **Enzyme Activity:** Zinc acts as a cofactor for over 300 enzymes involved in various bodily functions like metabolism, protein synthesis, and DNA replication.
- **Sense of Taste and Smell:** Zinc is essential for the proper functioning of taste and smell receptors.

Phosphorus (P):

- **ATP (Energy):** Phosphorus is a key component of adenosine triphosphate (ATP), the primary energy molecule in cells. ATP fuels all cellular processes, making phosphorus crucial for energy production and utilization throughout the body.
- **Bone Health:** Phosphorus, along with calcium, is a major building block of bones and teeth, providing strength and structure.
- **Nucleic Acids (DNA and RNA):** Phosphorus is a vital component of the backbone structure of DNA and RNA, the genetic material that carries instructions for protein synthesis and cellular function.
- **Cell Membranes:** Phospholipids, containing phosphorus, are essential components of cell membranes, maintaining their structure and function.

Chapter # 11

Industrial Chemistry

Industrial chemistry is the branch of chemistry which deals with the conversion of raw materials into useful product through chemical process.

INTRODUCTION TO CHEMICAL INDUSTRIES

"The term chemical industries refers to all those companies that manufacture chemicals".

Some well-established chemical industries are given below;

(i) Petrochemical Industries:

These industries are primarily focuses on the extraction, refining and processing of petroleum and natural gases.

They also produce many other chemicals as by products which then sold as a raw materials several useful substances.

(ii) Fertilizer Industries:

Fertilizer industries are responsible for the production of fertilizers, which are substances used to improve soil fertility and promote plant growth. Fertilizers provide essential nutrients to plants, enhancing crop yields and agricultural productivity.

There are two main types of fertilizers: organic fertilizers, which are derived from natural sources, and synthetic fertilizers, which are manufactured chemically.

Some common synthetic fertilizers are listed

Synthetic Fertilizer	Chemical Formula	Nutrients Provided	Uses
Ammonium Nitrate	NH_4NO_3	Nitrogen	Development of roots and maintaining pH soil
Urea	$CONH_2)_2$	Nitrogen	Development of leaf, steam and fruits
Diammonium Phosphate(DAP)	$(NH_4)_2HP0_4$	Nitrogen, Phosphorus	Development of early stage of plants growth
Potassium Chloride(MOP)	KCI	Potassium	Help enzyme activities and photosynthesis

(ii) Textile Industries:

Textile industries are sectors of the economy that involve the production of fabrics and textiles, including natural fibers like cotton and wool, as well as synthetic materials like polyester and nylon.

These industries play a vital role in providing a wide range of products, from clothing and household items to industrial materials

Synthetic Textile Products	Description	Uses
Polyester	A synthetic fiber made from petrochemicals	Clothing (shirts, pants, dresses, jackets), curtains, bedding etc.
Nylon	A strong and durable synthetic fiber	Stockings, hosiery, swimwear's, ropes, parachutes, and various sportswear's.
Acrylic	A soft and light weight synthetic fiber.	Sweaters, blankets, faux fur, carpets,

(iv) Paint Industries:

The paint industry is a sector that produces liquid or powdered substances used for coating surfaces, providing protection, decoration, and other functional purposes in various applications such as construction, automotive, and industrial sectors.

Paint Products	Description	Common Uses
Water-Based Paint	It is also known as latex. In this paint water is used as a carrier solvent	Interior and exterior walls, ceilings, and various surfaces.
Oil-Based Paint	It contains organic solvents as a carrier.	Woodwork, metal surfaces and surfaces that require durability.
Enamel Paint	A type of oil-based or water-based paint with a hard, glossy finish.	Metal surfaces, kitchen appliances, and surfaces that need high durability.
Epoxy Paint	A two-part paint that consists of a resin and a hardener, creating a tough and durable coating.	Industrial floors, garage floors, marine applications, and metal surfaces.

(v) Detergent Industries:

The detergent industry produces cleaning products, typically containing surfactants and other agents, designed for various applications like laundry, dishwashing, and surface cleaning. These products help to remove dirt, stains, and grease for improved hygiene and cleanliness.

Detergent Products	Composition	Main Uses
Laundry Detergent	Surfactants, builders, enzymes, fragrance, water softeners	Cleaning clothes in washing machines
Dishwashing Detergent	Surfactants, enzymes, fragrance, water softeners	Washing dishes by hand or in dishwashers
All-Purpose Cleaner	Surfactants, solvents, fragrance, water	Cleaning various surfaces and floors
Hand Soap	Surfactants, moisturizers, fragrance, antibacterial agents	Hand hygiene and cleansing

(vi) Cement Industries:

The cement industry involves the production of cement, a binding material used in construction, made primarily from limestone, clay, and other raw materials. Cement is a fundamental component of concrete and mortar, essential for building infrastructure and structures worldwide.

Cement Type	Composition	Main Applications
Ordinary Portland Cement (OPC)	Clinker (mainly composed of calcium silicates), gypsum, limestone, and small amounts of concrete and production. other materials.	Infrastructure construction,
Portland Slag Cement (PSC)	Clinker, slag, gypsum and limestone.	Underground construction marine works, and sewage works.
White Cement	Clinker, limestone, and gypsum with low iron content.	Tile grout and other decorative constructions.

PHARMACEUTICAL INDUSTRY

Pharmaceutical industries refers to the companies where drugs are manufactured.

“Drug is a substance that is used to treat or cure a disease in human or animals".

Classification of pharmaceutical products is based on various factors, such as chemical structure, mechanism of action, therapeutic use and biological activities. Some common drugs are described below.

Analgesics

“A drug that specifically targeted on central nervous system to provide pain relief without consciousness is known as analgesic drug".

"Asprin" is the oldest and the most common analgesic drug.

Antibiotics

This drug is produced from certain chemicals of microorganism.

“It suppress growth or kills microorganisms".

"Penicillin" was the first discovered antibiotic. Now a days a range of antibiotics are used depending upon doctors prescription.

Antipyretic medicines

*A drug which lower the body temperature to normal is known as antipyretic".

The most widely used antipyretic medicine is "paracetamol".

Anti fungal medicine

"These drugs use to kill fungi that cause infections on skin".

The most common skin infections are ringworm and dandruff. Example of antifungal drug is “fluconazole".

Anti inflammatory medicine

"These drugs helps reduce inflammation, and relieve pain".

Ibuprofen (Brufen) is an example of anti inflammatory medicine. However many other options are also available.

Anti allergic medicine

These are also called antihistamines. Histamine is a chemical produce in the body due to decarboxylation of an amino acid known as histidine.

“The administration of these drugs reduces the histamine level in the body". A wide range of anti-allergic medicines are available in the market, one example of anti-allergic medicine is diphenyl hydramine".

Anti malarial medicine

Anti protozoal or anti-Malarial drugs are use to treat mosquito bite infectious diseases such as malaria. Most commonly used anti material drug is chloroquine.

There are hundreds of pharmaceutical industries operating in Pakistan.

Health ministry of Govt. of Pakistan play important role in the availability and accessibility of drugs in public sector.

PESTICIDES

"Chemical which are used to control, repel or kill pets or insects or fungus are known as pesticides".

Types of Pesticides

Pesticides are classified into three major classes named as insecticides, fungicides and herbicides.

Insecticides

"Chemical substances which use to kill insects are called as insecticides". The best known insecticide is Dichlorodiphenyltrichloroethane (DDT),

Herbicides

Undesirable herbs often co-exist with crops creating problems for the growth and fertility of crops, by taking away their share of nutrient water and sunlight, these types of herbs are known as weeds. "Herbicides are the chemicals which either destroy or stop growing weeds". A very common herbicide which former prefer to use is 2,4-dichlorophenoxyaceticacid (abbreviated as 2, 4-D).

Fungicides

"Fungicides are chemical substances employed to eliminate undesired fungi that develop within crops". A very common fungicide Mancozeb (Manganese ethylenebis (dithiocarbamate) zinc salt) which is used to control various fungal diseases on crops like potatoes, tomatoes, and grapes.

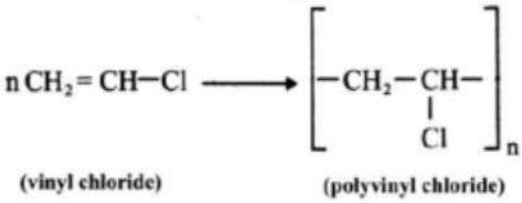
SYNTHETIC POLYMERS

"Polymer is a high molecular mass compound that forms by the combination of a large number of one or more types of molecules of low molecular mass". Polymers are either obtained from natural source such as rubber, cellulose, starch, etc or synthesized by chemical reactions.

Another classification of synthetic polymers is based on their behavior on heating. Thermoplastics soften on heating and regain their original properties on cooling, whereas thermoseting plastics undergo irreversible transformation, becoming hard and rigid upon heating.

Polyvinyl chloride (PVC)

Polyvinyl chloride (PVC) is a widely used thermoplastic due to its versatility and durability. It is known for its excellent electric insulation, light weight and low cost. PVC is an addition polymer of vinyl chloride it is prepared by heating vinyl chloride at 60-70°C in the presence of Hydrogenperoxide (H_2O_2).



$$n\,CH_2{=}CH{-}Cl \longrightarrow \left[-CH_2-\underset{Cl}{\underset{|}{CH}}-\right]_n$$

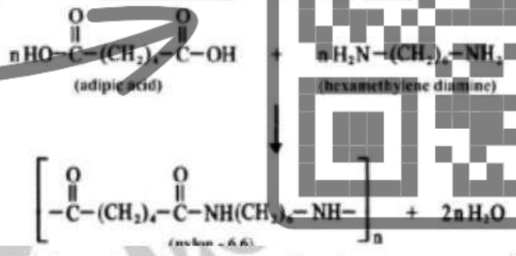
(vinyl chloride) (polyvinyl chloride)

PVC is used in the manufacturing of bottles, pipes, medical tubes, blood bags and insulation material on electric wires.

Nylon 6, 6

Nylon 6, 6 is a type of synthetic polymer. It is known due to its high strength, light weight and excellent mechanical properties.

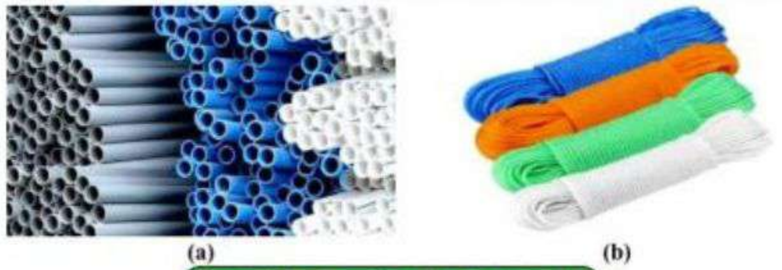
Nylon 6, 6 is chemically a polyamide and prepared by the process of condensation polymerization between hexamethylenediamine and adipic acid (hexanedioic acid) with the elimination of water molecules.



$$n\,HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + n\,H_2N-(CH_2)_6-NH_2 \longrightarrow \left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH(CH_2)_6-NH-\right]_n + 2n\,H_2O$$

(adipic acid) (hexamethylene diamine) (nylon - 6,6)

Nylon 6, 6 is used in making tents, parachutes, ropes, fish net, bristles of brushes and tires etc



(a) (b)

Fig 11.2: Product of (a) PVC (b) Nylon 6, 6

COSMETICS

The word cosmetic is derived from the Greek word "kosmetiko" meaning beautifying complexation of skin.

"Cosmetics are the products that are used to enhance or alter the appearance of face, body, nails or hairs". Thousands of cosmetic products are manufactured in the industries, few very common are briefly described below.

(i) Lipstick:
"Lipstick is a chemical used to colour, moisturization and protection of the lips".
It is a type of makeup that usually available in a stick and is applied directly to the lips. Lipstick is typically made from a mixture of oils, waxes, pigments, fragrance and moistening agent.

(ii) Nail Polish:
It is a type of lacquer that is used to enhance the appearance of nails in women. comes in a variety of colours including red, pink, brown and others. The basic components of nail polish include pigments, resin, plasticizers and film former.

(iii) Nail Polish Remover: It is an organic solvent such as "acetone" along with some other ingredients such as scent.

(iv) Hair Dyes:
These are chemicals that change the colour of hairs. Hair dyes are classified into temporary and permanent hair dyes.

Temporary hair dye last for a short period of time, typically a few washes. It is available in various form such as spray, gels and shampoos.

Permanent hair dye refers to a coloring product that last for long period of time. It mainly consists of colourent and developer. The developer is an oxidizing agent generally, hydrogen per oxide is used as developer.

(v) Perfumes:
These are complex mixtures of aromatic compounds, solvents, and fixatives that create pleasant and distinctive scents. They typically consist of top, middle, and base notes, which work together to provide a well-balanced and long-lasting fragrance.

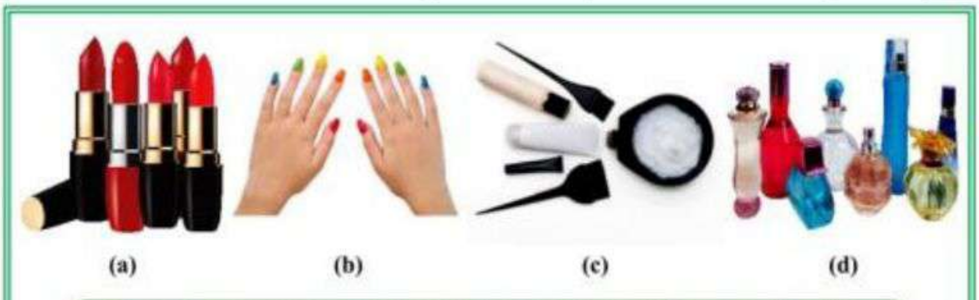


Fig 11.3: Various cosmetics (a) Lipsticks (b) Nail polishes (c) Hair dyes (d) Perfume

ADHESIVES

“Adhesives or glue are chemical substance that use to stick materials together".

They are liquids or semi solids. They create a bond between the two surface through either physical or chemical processes. A wide variety of adhesive are available, each possessing unique properties and appropriate applications. Some of frequently used adhesive are described below.

Starch

It is a natural adhesive and prepared by heating starch suspension in water. It has low adhesive strength but widely used because it is easily prepared and low cost. Starch is used as a thickening agent in various food products and as a raw material for the production of biodegradable plastics.

Epoxy Resins

These are strong synthetic adhesives and commonly used for bonding metals, plastics, glasses and ceramic items.

Silicon Resins

These are known with their high strength, high thermal stability and water repellent ability. These are use in sealing of engines, gasket making, bonding of optical instruments and medical instruments.

Super Glue

It is chemically named as cyanoacrylate. It is fast acting adhesive that bond quickly of broken items such as jewellery, toys, automotives etc.

Wood Glue

It is chemically named as polyvinyl acetate. It is a water based adhesive. It form a strong and durable bond between pieces of woods when compressed them under high pressure.

Short Questions

1. Give the scope of pharmaceutical industries in Pakistan.

1. **Pharmaceutical Industry in Pakistan:**

The pharmaceutical industry in Pakistan is a significant contributor to the country's healthcare sector. Here's a general overview:

- **Market Size and Growth:** The Pakistani pharmaceutical market is estimated to be worth several billion dollars and is experiencing steady growth.
- **Local Production:** A significant portion of the medicines consumed in Pakistan are produced domestically by local pharmaceutical companies.
- **Generic Drugs:** Generic drugs, which are more affordable versions of brand-name medications, form a major segment of the Pakistani pharmaceutical market.
- **Challenges:** The industry faces challenges such as counterfeiting, price control regulations, and competition from imported drugs.

2. What is antihistamine drug? Give the symptoms in which it is used.

2. **Antihistamine Drugs:**

Antihistamines are a class of medications used to treat symptoms associated with allergies, such as:

- **Runny or stuffy nose**
- **Itchy, watery eyes**
- **Sneezing**
- **Hives**
- **Skin rash**

They work by blocking the action of histamine, a chemical released by the body's immune system during an allergic reaction.

3. Write the names of two synthetic and two natural polymers.

- **Synthetic Polymers:** Examples include:
    - **Nylon:** Used in textiles, clothing, carpets, and engineering applications.
    - **Polyvinyl chloride (PVC):** Used in pipes, tubing, flooring, and building materials.
- **Natural Polymers:** Examples include:
    - **Cellulose:** Found in plant cell walls, used in paper, textiles, and food additives.
    - **DNA:** The genetic material in all living organisms.

4. Write the name of four main components of Nail polish?

Nail polish typically consists of several key components:

- **Film Formers:** These create the hard, protective coating on the nail. Examples include nitrocellulose and various resins.
- **Solvents:** These help dissolve the film formers and allow for smooth application. Examples include acetone, ethyl acetate, and butyl acetate.
- **Plasticizers:** These improve flexibility and prevent the polish from becoming brittle.
- **Pigments and Dyes:** These provide color to the nail polish.

Descriptive Questions

1. How can you define Cosmetics? Describe four cosmetics which are commonly used.

Notes

2. What are pesticides? Explain various types of pesticides along with their specific use.

Notes

3. Describe the preparation, properties and uses of Nylon and polyvinyl chloride.

Notes

4. What are adhesives? Explain the significance of super glue and silicon resins.

Notes

Chapter # 12

Environmental chemistry

"It deals with the study of chemical processes happening in Earth's environment and their direct or indirect impact on organisms that live on Earth".

"The presence of undesirable substances in the environment that harm the natural balance of eco systems is known as environmental pollution".

There are several types of pollution that can negatively impact the environment and human health such as air pollution, water pollution, soil pollution, noise pollution, radioactive pollution etc.
Earth's environment consists of four interconnected parts that work together to sustain life. These parts include;

- Lithosphere which comprises Earth crust and soil covering with the rocks.
- Hydrosphere which consists of all surface and underground water.
- Biosphere which includes the entire living being on the Earth.
- Atmosphere which is extended to 500 km above the Earth's surface and consists of gases.

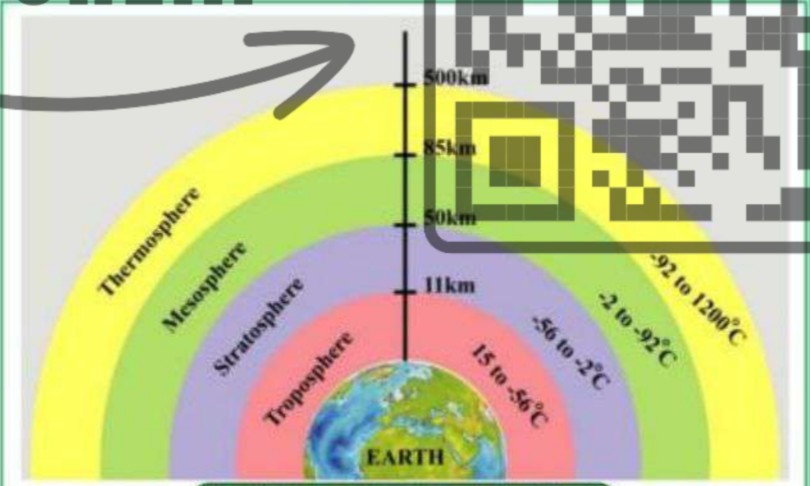


Fig 12.1: Four regions of earth atmosphere

The Earth's atmosphere is further divided into four major regions based on variation in the temperature and compositions. These regions are commonly known as atmospheric layers.

Troposphere:
It is the lowest layer of atmosphere extending from Earth's surface up to an altitude of 11km.
Stratosphere:

It starting from the top of troposphere and extending up to 50km above the Earth's surface.

Mesosphere:

It lies above stratosphere stretching from 50km to 85km above the Earth's surface.

Thermosphere:

It is the upper most layer of the Earth's atmosphere extending from 85km to 500km.

CHEMISTRY OF THE TROPOSPHERE

Troposphere is the lowest layer of Earth's atmosphere, where we experience our daily weather conditions such as rain, snow, winds, storms, thunders, clouds.

Reactions of CO_x, NOx, VOC_s, SOx, and O_3; with the atmosphere

Gases like nitrogen (N_2) and oxygen (O_2) form a protective layer in the Earth's atmosphere. However, certain toxic substances, including nitrogen oxides (NO_x) sulphur oxides (SO_x), volatile organic compounds ((VOC_s) and ozone (O_3) can cause atmospheric pollution.

Chemistry of oxides of carbon (CO_x)

The oxides of carbon in troposphere are carbon monoxide (CO) and carbon dioxide (CO_2), collectively written as CO_x.

Carbon monoxide is very toxic gas, since it has great affinity for hemoglobin. It is released by the partial combustion of fuel in automobile, petroleum refining and forest fire etc. Carbon monoxide in troposphere is broken down by U.V radiation into free carbon particles which are responsible for the smog formation.

$$CO_{(g)} + h\upsilon \rightarrow C_{(s)} + \tfrac{1}{2} O_{2(g)}$$

Carbon dioxide is added to atmosphere due to the combustion of fossil fuels such as coal, wood, petroleum. It is also released during the respiration of animals. The increase level of carbon dioxide in atmosphere causes suffocation and respiratory disorders.

Chemistry of Oxides of Nitrogen (NO_x)

There are two main oxides of nitrogen which cause pollution of air. These are nitric oxide (N0) and nitrogen dioxide (NO_2) and are collectively written as NO_x. These oxides produce from the combustion of fuel such as coal, petrol and natural gases at high temperature.

$$N_{2(g)} + O_{2(g)} \xrightarrow{\text{U.V light}} 2NO_{(g)}$$
$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

These gases are also formed by photolytic reaction in atmosphere.

$$NO_{2(g)} + h\upsilon \longrightarrow NO_{(g)} + \frac{1}{2}O_{2(g)}$$
$$O + O_2 \longrightarrow O_3$$

The high concentration of NO and NO_2 gases in air is harmful because they form acid rain and ozone in the atmosphere.

Chemistry of Oxides of Sulphur (SO_x)

There are two oxides of sulphur found in air named as sulphurdioxide (SO_2) and sulphur trioxide (SO_3), these are together abbreviated as SO_x. The pollution of SO_x is equally due to volcanic eruption and the burning of sulphur containing coal in thermal power plants.
In atmosphere SO_3 gas can be produced by photochemical oxidation of SO_2 under the influence of sun light.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{\text{U.V light}} 2SO_{3(g)}$$

The presence of these gases in atmosphere causes cardial and respiratory diseases and also effect negatively on crops production.

Chemistry of Volatile Organic Compounds (VOC_s)

Volatile organic solvents are commonly used in various chemical industries such as paints, varnishes, cosmetics, aerosols, air freshener and gasoline. "All those solvents which evaporate into atmosphere and contribute the atmosphere pollution are known as volatile organic compound (VOC_s)". Examples of VOC_s include formaldehyde, benzene, and toluene.

Chemistry of Ozone (O_3)

Ozone is an allotropic form of oxygen. It is present in a very low concentration in troposphere. Its presence is hazardous to both human health and the environment. Its side effects include respiratory issues, cardiac issues and irrigation of plants and crops.

Automobile Pollutants and the Catalytic Converter

The burning of gasoline in a car engine results in the formation of carbon monoxide (CO), nitric oxide (NO) and various unburnt volatile hydrocarbons. These substances, when released into the air, contribute to atmospheric pollution and have a direct impact on life. To solve this issue, modern car engines are equipped with catalytic converter "The purpose of catalytic converter is to transform the harmful chemicals produced during internal combustion of engine into less harmful or non harmful substances such as carbon dioxide (CO_2), nitrogen (N_2), oxygen (O_2) and water (H_2O)", Catalytic converter contain a mixture metals such as platinum and palladium which serves as catalyst.

Fig 12.2:
Catalytic converter of automobile engine

Industrial Smog

Smog is a type of air pollution. This term is the combination of smoke and fog.

In the industrial zones of a country, numerous industries are operational, manufacturing various valuable commercial products. However, during the chemical processes involved, a significant number of harmful by-products are emitted into the atmosphere. Some industries release sulphurdioxide (SO_2) when burning coal and oil while other introduce harmful solid to industrial smog particles like metal oxides, salt particles and even soil into the air. The mixing of these harmful substances contributes to the formation of smog

"Smog is a mixture of SO_2, aerosols and volatile organic compounds". It forms a brown-yellow layer usually in industrial areas. Smog has many harmful side effects on human health, plant growth and overall a major contributor of environmental pollution.

Global warming and Climate Change

"Global warming refers to the gradual rise in Earth's average surface temperature".

The average temperature of earth is approximately 15°C but due to long term climate change resulting from global warming is causing shifts in average temperature worldwide atmosphere.

"The temperature of our earth is regulated by certain gases present in the atmosphere such as CH_4, CO_2, N_20 and H_20 known as green house gases". The change in concentration of these gases can lead to alterations in the Earth's climate.

To prevent global warming, we need to reduce greenhouse gas emissions by alternating to renewable energy sources, promoting energy efficiency, and implementing sustainable practices in sectors like transportation and agriculture.

Green House Effect

It is an essential natural process that helps in regulating the Earth's temperature enabling the existence of life on our planet Sun release energy in the form of sunlight, which then reaches the earth atmosphere and a portion of it (UV and visible radiation) is absorbed by the earth which makes the earth warm. The warm surface of earth is then emitting radiation of IR frequency.

The green house gases in the atmosphere (CH_4, H_20, CO_2, etc) absorbs some of IR radiations emitted by the Earth's surface. The absorption of heat by green house gases prevents the escaping of heat into the space. The absorbed heat energy by green house gases is reemitted toward the earth surface and warms it.

Global warming causes a widespread rise in temperature all around the world. This has a significant impact on climate change leading to various consequences such as the melting of glaciers, rising sea levels, acid rain, irregular crop pattern and even changes in human life style.

Acid Rain

The term acid rain was first introduced by an English chemist Robert Angus in 1872.

"Acid rain refers to rainfall that has acidic components such as nitric acid, Sulphruic acid and carbonic acid".

The pH of normal rainfall generally ranges between 6 to 6.5 but the pH of acid rain is below 5 depending upon the concentration of acidic components present in it.

Pollutants like oxides of carbon, nitrogen and sulphur are present in the atmosphere. These oxides may undergo chemical reaction with atmospheric water to produced Sulphruic acid (H_2SO_4), nitric acid (HNO_4) and carbonic acid (H_2C0_3). These acidic components mixed with rainwater and fall to the earth as acid rain.

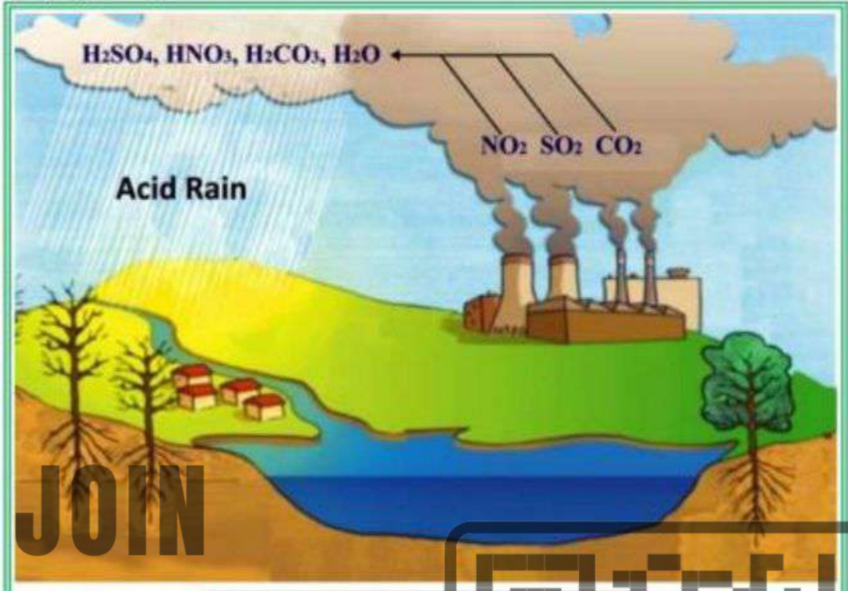


Fig 12.5: Global warming and climate change

Acid rain has several adverse effects on the environment and human life style for example.

(i) Acid rain increases the acidity of rivers, which affect negatively on aquatic animals and plants causing a disturbance of eco system.

(ii) Acid rain reduces soil fertility due to lowering in soil pH from their normal range and ultimately effect on crops production.

(iii) Acid rain causes corrosion of buildings, bridges and other concrete and metal made things.

(iv) Acid rain makes the underground water toxic and undrinkable.

CHEMISTRY OF STRATOSPHERE

The region from 11km to 50km above the Earth's surface is referred as stratosphere. This region is distinguished by the remarkable presence of ozone (0_2) layer. This layer plays a vital role in blocking and absorbing maximum portion of sun harmful radiations. The life on the Earth's would not be possible without the protection of this layer.

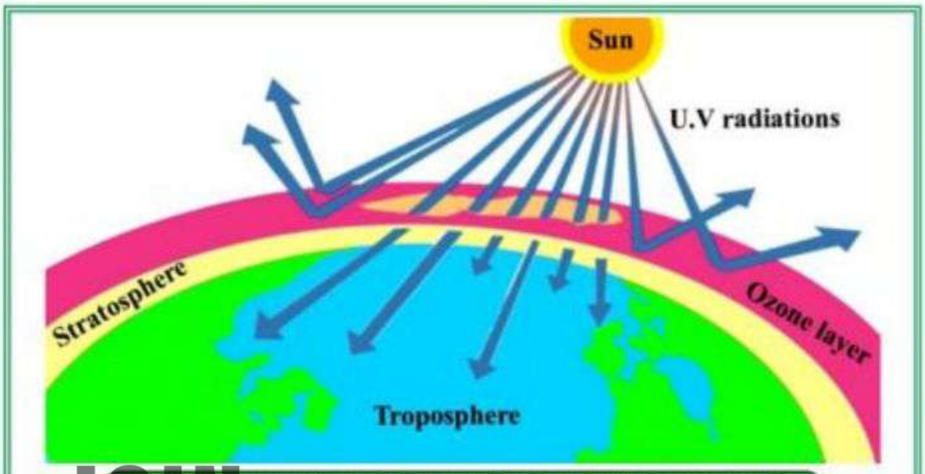


Fig 12.6: Protection of earth from hazardous U.V radiations by Ozone layer

Production and destruction of 0zone

Ozone is produced in stratosphere region due to photochemical reaction of sun rays and oxygen gas. Ultra-violet radiations of sunlight breaks oxygen molecule (0,) into free radicals. The oxygen free radicals are then combine with another oxygen molecule to produce 0zone.

$$O_2 \xrightarrow{\text{U.V radiations}} O\bullet + \bullet O$$

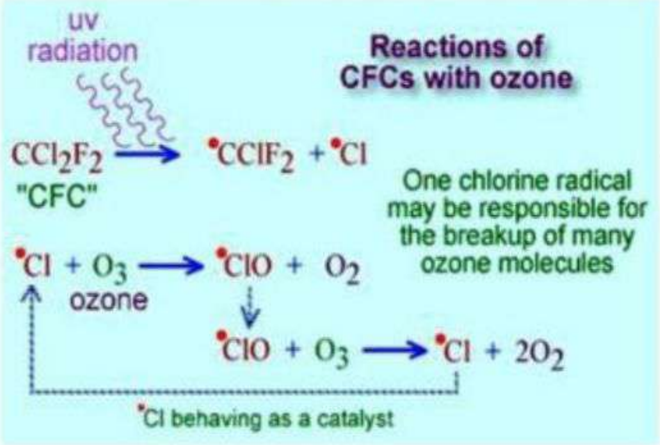
$$O\bullet + O_2 \longrightarrow O_3$$

Ozone in stratosphere also destroyed by solar energy but the two phenomena are in equilibrium and hence the thickness of ozone layer remain undisturbed.

Human activities can contribute the depletion of ozone layer through the emission of certain chemicals known as ozone-depletion substances (ODS). The most considerable human activity that have been responsible for ozone depletion is the release of gases from cooling devices such as refrigerator and air conditioners.

Chlorofluoro Carbon (CFC_s)

Chlorofluoro carbons is a highly stable gas used as coolant in refrigeration and also as repellent in aerosol spray. When (CFCs) reaches into stratosphere region, it breakdown into free chlorine and fluorine atoms which then react with 0zone in U.V light and decompose it into oxygen.



To address the problem of (CFC_s) causing ozone depletion, scientists have been working on developing alternatives to (CFCs) in order to prevent further damage to the ozone layer. The best alternative is hydrofluoro carbons (HFC_s) which do not have chlorine and do not contribute to ozone depletion.

WATER POLLUTION AND WATER ANALYSIS

About 75% of the Earth's is covered with water. Population explosion, industrialization, urbanization and many other human activities made the water polluted. Any undesirable change in the quality of water which affect the life adversely is known as water pollution".

Types of Water Pollution

The addition of pollutant substances alter the physical, chemical or biological properties of water and makes it unfit for the health of human. The substance which causes water pollution is classified into following three groups.

Suspended Solids and Sediments

"Small solid particles such as dust, coal microscopic organisms ete which remain suspended in the water are called colloids and the particles such as sand, clay which settle down to the bottom are called sediments".
These are the common pollutants of rivers, lakes and streams which produce turbidity in water and reduce the amount of sun light available to aquatic animals.

Dissolved Solids

Various organic and inorganic compound found in water. Inorganic solids consists of minerals, salts, metal cations like calcium, magnesium, sodium, potassium and anions such as chlorides, carbonates, bicarbonates, sulphates.

The organic solids originate from organic sources such as decomposition of animals, plants and microorganisms. Both inorganic and organic solids have very small particle size and hence soluble in water. They comes from industrial water and sewage. When they fall into the river or oceans, effect negatively on aquatic life.

Waste Water Analysis

Samples of waste water are collected from different areas and analysis them by involving through a series of tests.

(i) Physical test:

These include estimation of odour, colour and taste.

(ii) Chemical test:

These involve the checking of pH, presence of biocides and toxic chemical.

(iii) Microbiological test:

These tests involve checking for the presence of harmful bacteria and other microorganisms.

(iv) Organic test:

These tests are performed for the presence of pesticides and volatile organic solvents such as petrol, benzene, toluene etc.

GREEN CHEMISTRY

"The design and development of processes that minimize or eliminate the use of hazardous chemicals is known as green chemistry".

Green chemistry aims to create safer chemicals and processes to make the environment friendly. There are twelve rules of green chemistry.

(i) Prevent waste:

Design chemical synthesis to avoid waste. There should be no waste material left for treatment or clean up.

(ii) Maximize atom economy:

Design syntheses to get the maximum product out of the starting materials. Avoid un-reacted material.

(iii) Design less hazardous chemical syntheses:

Design synthetics techniques for the use and production of substances that are of little or no toxicity to humans and the environment.

(iv) Design safer chemicals and products:

Develop chemical products that are completely effective, yet have little or no toxicity.

(v) Use safer solvents and reaction conditions:

Avoid the use of solvents and other supporting chemicals. If any is unavoidable, use the safer ones.

(vi) Increase energy efficiency:

Design chemical reactions that can be carried out at room temperature and pressure.

(vii) Use renewable feedstock:

Use renewable raw materials in chemical industry rather depletable. The source of renewable raw materials is often agricultural products or by-product of industrial processes. Sources of depleting resources are often fossil fuels (oil, natural gas, or coal).

(vii) Use catalysts, not stoichiometric reagents:

Use catalytic reactions to minimize waste. The catalyst is effective in small amount and can carry out same reaction multiple times. They are preferred over stoichiometric reagents used in larger quantity and are carried out only once.

(ix) Design chemicals and products to degrade after use:

Design chemical products which decompose into harmless substances and do not accumulate in the environment.

(x) Analyze in real time to prevent pollution:

Include in-process, real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

(xi) Minimize the potential for accidents:

Design safer techniques for chemicals and their physical forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

Short Questions

1. Write the name of four segments of atmosphere and mention in which segment we live.

Notes

2. Explain the causes of depletion of ozone layer.

Notes

3. What is industrial smog and how is it formed?

Notes

4. What are the main gases responsible for green house effect?

Notes

5. Explain four fundamental methods for the testing of waste water.

Notes

Descriptive Questions

1. What is the effect of acid rain on human health and what measures can be taken to prevent acid rain?

Notes

2. WhNotesat is the main cause of Global warming? How does it effect on weather pattern?

Notes

3. Describe the chemistry involves due to the presence of oxides of nitrogen and sulphur in the troposphere.

Notes

4. What is Green house effect? How does human activities contributes to the enhancement of the green house effect?

Notes

5. What are ozone depletion substances (ODS)? What human activities have contributed to ozone depletion in the stratosphere?

Notes

6. What is a catalytic converter? What are the main pollution targeted by catalytic converter?

Notes

CHAPTER # 13

SPECTROSCOPY

"Spectroscopy is the study of interaction of electromagnetic radiation of light with matter".

Spectroscopy has a wide scope of applications in various fields of science and technology and significantly favored over conventional methods because;

- ➢ It is easier and takes very little time to analyze a sample.
- ➢ It requires a very small amount of substance which is to be analyzed.
- ➢ It provides more reliable information about chemical molecule.

Some applications of spectroscopy are given as:

(i) Analysis of chemical comnpounds
(i) Quality control of drugs syntheses
(iii) Analysis of water pollution
(iv) Determination of protein structure
(v) Analysis of forensic materials
(vi) It helps in structure analysis

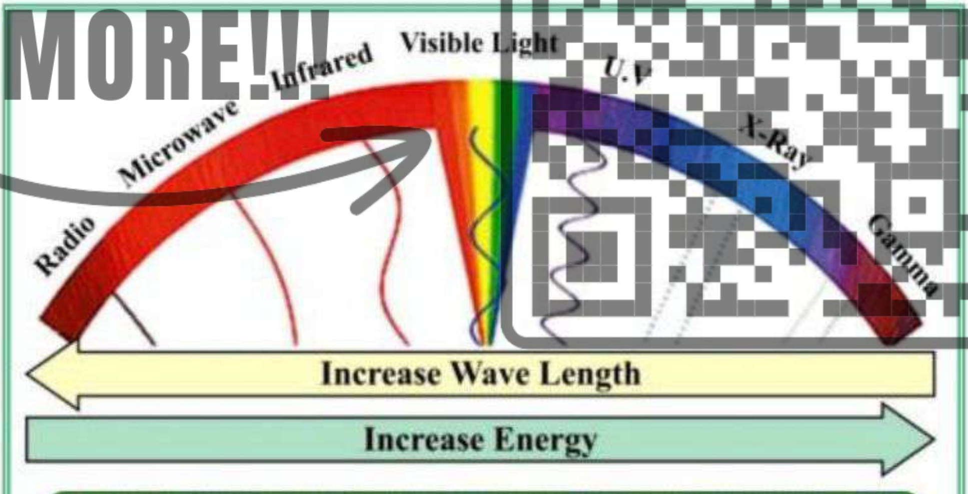


Fig 13.1: Electromagnetic spectrum from low-energy radiowaves to high energy gamma rays

METHODS OF SPECTROSCOPY

Sunlight consists of a wide range of electromagnetic waves including radio waves, microwaves, infrared radiations, visible radiations, ultra-violet radiations, etc. When electromagnetic radiations interact with molecule, some of the rays are absorbed by the molecules while other are transmitted. The wave length and frequency of absorbed light can provide valuable information about the structure of molecule. Various methods of spectroscopy are commonly used to analyze and characterize the compounds.

13.1.1 Infrared (IR) Spectroscopy

"Infrared spectroscopy is used to detect the type of bonds and the functional groups present in molecule".

I.R frequency is expressed in the unit of wave number (cm^{-1}). The most useful IR range lies between 4000-670 cm^{-1}.

Applications of IR Spectroscopy

(i) I.R spectroscopy provides information for the presence of different functional groups in the organic molecules.

(ii) I.R spectroscopy is also useful for identifying the impurities present in the sample to be analyzed.

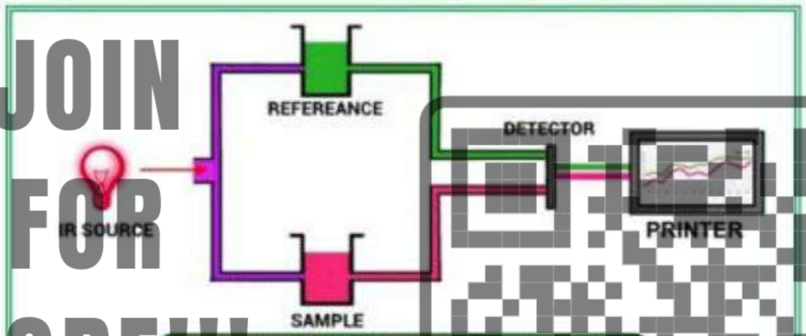


Fig 13.4:Block diagram of Infrared spectrophotometer

Ultra-violet/Visible (UV-Vis) Spectroscopy

"Ultra-violet-visible spectroscopy is used to determine the presence of double and triple bonds as well as conjugated system in the molecule".

The U.V region of electromagnetic spectrum extends from 200nm to 400nm and the visible region extends from 400nm to 800nm.

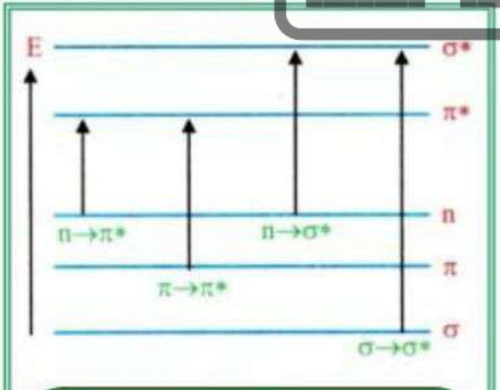


Fig 13.5:
Electron transition in organic compound due to interaction with U.V-visible radiations

When a molecule absorbs electromagnetic radiations of U.V- visible range (200nm-800nm) electronic transitions Occur. Its electrons are promoted from lower energy level to higher energy level. The transition of electrons may be of the following types.

(i) σ – σ* transition:

It requires very high energy which is beyond the range of U.V-visible radiations therefore carbon-carbon single bond do not absorb U.V- visible radiations and cannot be detected.

(ii) π – π* transition:

This transition occurs in the molecule that contain double or triple bonds or aromatic rings. The range of wavelength for the absorption of T-* transition is 180-320 nm.

(ii) n – π* transition:

This transition is associated with the molecules in which double or triple bond is connected with a hetero atom (N, 0, S) for example aldehyde and ketone, etc. The range of wavelength of n-* transition can vary depending upon the specific molecular system, however it is approximately 200- 500nm.

(iv) n – σ* transition:

This transition is concerned with the saturated molecule with hetero atoms like alkyl halide, alcohol etc. The range of n-g* transition roughly falls around 150-300nm.

Application of U.V-visible spectroscopy

(i) U.V spectroscopy can provide valuable information regarding the structure of a compound particularly in relation to the presence of double bond, triple bond, aromatic system and hetero atoms.

(ii) U.V spectroscopy is extensively used for determining the concentration of unknown compounds in a solution by using Beer-Lambert's law.

Nuclear Magnetic Resonance (NMR) Spectroscopy

The nucleus of certain elements like 'H (proton) exhibits random spin and behave like a tiny magnet due to their charged nature. When an external magnetic field is applied, the spin of nucleus aligned in two ways.

(ii) It can align in the same direction of the applied magnetic field and it is said to be low energy spin state.

(i) It can be in the opposite direction of the applied magnetic field and said to be high energy spin state.

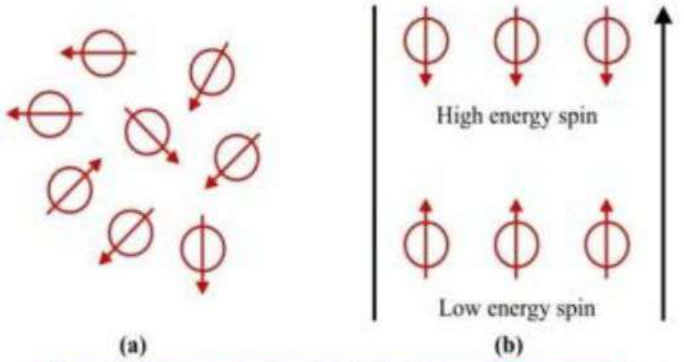


Fig 13.7: Spinning of proton (^1H) (a) in the absence of magnetic field (b) in the presence of magnetic field

When a sample of a compound is placed in a strong magnetic field and subjected to radio frequency radiation, the nuclei with specific spin state absorbs energy and flip into a high energy state, this absorption of energy is detected as signals in the NMR spectrum. The solvent used in NMR spectroscopy is usually D_20 or DMSO, since it does not interfere with NMR of the sample but with the conditions that compound is soluble in both solvents.

The graph of ^1H NMR consists of following parameters.

(i) X-axis represents chemical shift which shows position of proton signals relative to TMS (tetramethylsilane).

(i) y-axis represents absorption which shows shift. the intensity of NMR-signals.

(iii) Peaks represent splitting pattern (singlet, doublet, triplet, quartet) due to neighboring protons.

To understand ^1H NMR spectrum let us consider the example of ethanol. H NMR spectrum of ethanol has three types of protons.

- Methyl (CH_3) protons appear as triplet at around 1.1 to 1.3 ppm.
- Methylene protons (CH_2) appear as a quartet around 3.5 to 4 ppm.
- The hydroxyl proton appears as a broad singlet around 4 to 5 ppm.

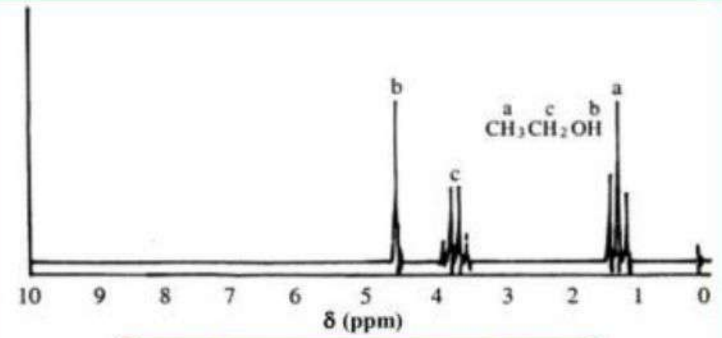


Fig 13.8: ^1H NMR spectrum of ethanol (C_2H_5OH)

Applications of NMR Spectroscopy

NMR spectroscopy is a powerful analytical technique, it provides valuable information about the chemical structure of organic compounds.

Each organic compound exhibits a unique NMR spectrum acting as a "fingerprint" that allows chemists to identify them. This technique is successfully applied in drug analysis, material science, forensic analysis and many other fields.

Atomic Absorption and Emission Spectroscopy

Atomic absorption and emission spectroscopy are established techniques used to identify elements in various samples including metal compounds. Within an atom, electrons are distributed in different energy levels, when atom receive energy from an external source like heat or an electric discharge, electrons can be promoted to higher energy level. These excited electrons than undergo transition involving the absorption or emission of electromagnetic radiations.

Atomic absorption spectroscopy

In atomic absorption spectroscopy, the sample is exposed to a wide range of light, the atom selectively absorbs specific wavelength of light that align with the energy needed to elevate electrons to higher energy level. The absorbed wavelengths of light appear as dark lines in a unique pattern specific for that element. By examining the absorbed wavelength, a chemist can identify the presence of specific element in the given sample.

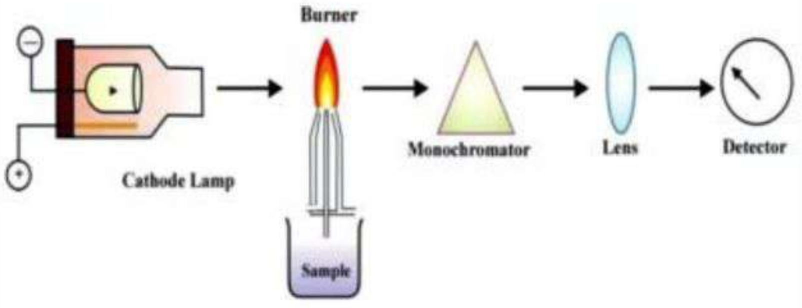


Fig 13.9: Atomic absorption spectrophotometer

In atomic emission spectroscopy the electron in an atom is first excited by providing energy from external source such as heat or electrical energy. When the excited electrons return to their ground state, they emit excess energy in the form of light of specific wavelengths.

This emitted light commonly found U.V visible or rarely in IR range. This emitted light appears as a series of bright lines against a dark background. Since each element has its distinct set of bright lines, chemist can identify the element based on this information.

Mass Spectrometry

"Mass spectrometry is technique used to determine the mass to charge ratio (m/z) of ions in a sample".

It provides information about the mass of different fragments of the molecule and play an important role in the structure elucidation of molecule.

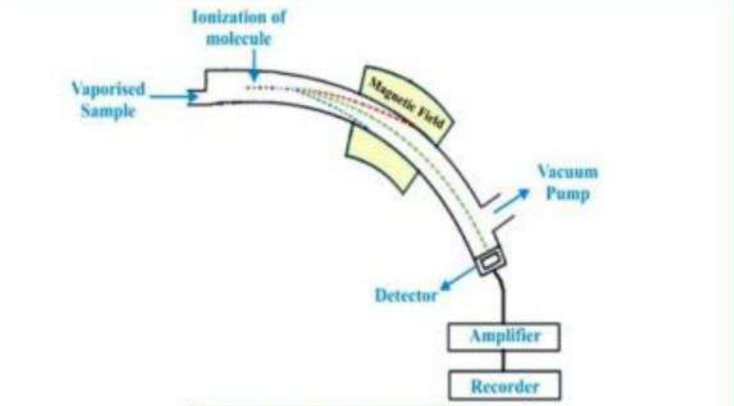


Fig 13.13: Mass spectrometer

Applications of mass spectroscopy

(i) It is used to determine the molecular mass of unknown compounds on the basis of mass to charge ratio.

(i) It is used for the identification and purification of drugs and other pharmaceutical products.

Short Questions

1. What types of nuclei are detected in proton NMR spectroscopy?

Proton NMR (^{1}H NMR) spectroscopy specifically detects the nuclei of hydrogen atoms (protons). This is because the technique relies on the magnetic properties of the proton and its interaction with an applied magnetic field. Other nuclei with magnetic moments, like ^{13}C (carbon-13) or ^{19}F (fluorine-19), can be detected using different NMR spectroscopy techniques with appropriate frequencies.

2. Name the components which represents x-axis and y-axis of a proton NMR spectrum.

In a proton NMR spectrum:

- **X-axis (chemical shift, δ):** This axis represents the resonance frequency of the protons relative to a reference standard (usually tetramethylsilane, TMS). The chemical shift is measured in ppm (parts per million) and reflects the electronic environment surrounding each proton. Protons in different chemical environments experience slightly different magnetic fields due to shielding effects from neighboring electrons, leading to variations in their resonance frequencies.
- **Y-axis (intensity):** This axis represents the integrated signal intensity, which is proportional to the number of protons giving rise to that particular resonance peak. The integration allows you to determine the relative abundance of protons in different environments within the molecule.

3. Differentiate between atomic absorption and emission spectroscopy.

- **Atomic Absorption Spectroscopy (AAS):**
  - In AAS, the sample is vaporized using high temperatures.
  - Ground state atoms in the vapor absorb specific wavelengths of light from a source element (same element being analyzed).
  - The amount of light absorbed is measured and is related to the concentration of the element in the sample.
  - AAS is a quantitative technique used to determine the concentration of specific elements in a sample.
- **Emission Spectroscopy:**

  - In emission spectroscopy, the sample is excited using an energy source (heat, electricity, etc.).
  - Excited atoms in the sample emit light at specific wavelengths as they return to their ground state.
  - The emitted light is analyzed by a spectrometer to identify the elements present based on their characteristic emission wavelengths.
  - Emission spectroscopy is a qualitative technique used to identify the elements present in a sample and can sometimes offer semi-quantitative information.

4. What the purpose of U.V-visible spectroscopy? What is its applications in chemistry and biology?

- **Purpose:** U.V.-visible spectroscopy measures the absorbance or reflectance of ultraviolet (UV) and visible light by a sample. It allows us to study how molecules interact with light at these specific wavelengths.
- **Applications in Chemistry and Biology:**
  - **Chemical analysis:** Identify unknown compounds by comparing their absorption spectra with reference data.
  - **Concentration determination:** Quantify the concentration of colored solutions using Beer-Lambert Law.
  - **Monitoring reactions:** Track the progress of reactions that involve changes in colored components.
  - **Biomolecular studies:** Analyze the structure and interactions of biomolecules like proteins and nucleic acids, which absorb UV light due to aromatic amino acids and conjugated double bonds.

Descriptive Questions

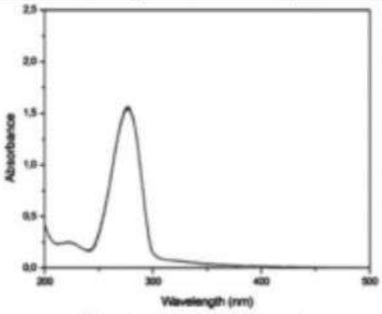
1. What information about the structure of a molecule we can get from mass spectroscopy? Give the applications of mass spectroscopy.

Notes

2. What is proton NMR spectroscopy? How does it work? Give its applications.

Notes

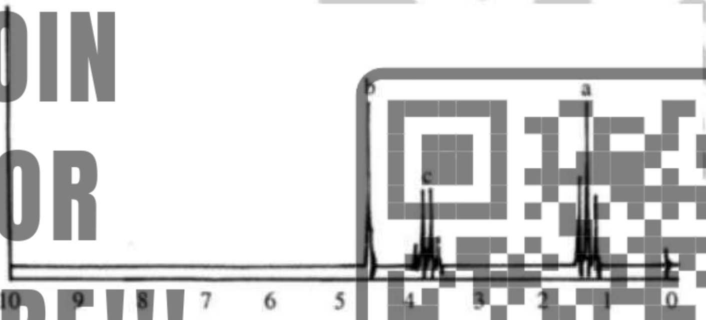
3. Explain max With the help of U.V-visible spectrum of ethanol (C_2H_5OH).



Spectrum of ethanol

Notes

4. Explain the graph of proton NMR of ethanol (C_2H_5OH) proton peaks of OH, CH_2 and CH_3



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