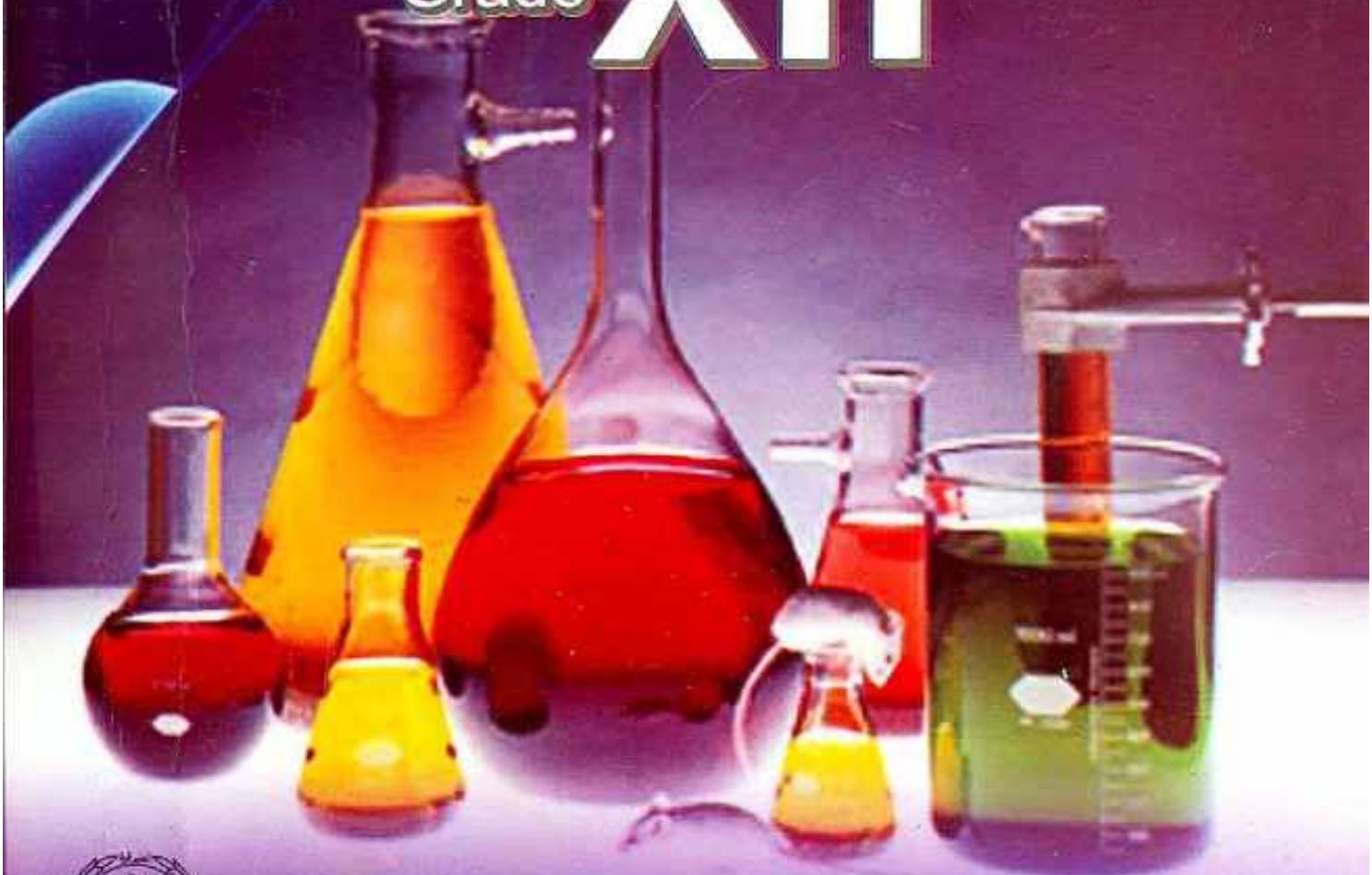
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

LEADING BOOKS
PUBLISHER

Textbook of CHEMISTRY

Grade XII



Khyber Pakhtunkhwa Textbook Board
Peshawar

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

رشوت اور بدعنوانی قومی معیشت کو کھوکھلا کر
دیتی ہے۔ قومی معیشت کو کھوکھلا ہونے
سے بچانے میں اپنا کردار ادا کرو۔

Wildlife adorens the environment

Scanned with CamScanner

Textbook of

CHEMISTRY

Grade – XII

Published by

Leading Books Publisher

Khyber Pakhtunkhwa Textbook Board
Peshawar

Scanned with CamScanner

All rights reserved with Leading Books Publisher, Peshawar.

Developed according to National Curriculum 2006 and approved by DCTE Abbottabad.
Vide No. dated:

Authors:

Mushtaq-ur-Rehman
Muhammad Amin

Supervision:

Syed Bashir Hussain Shah Director DCTE, Abbottabad.

Reviewers:

1) Professor Muhammad Sajjad Khan GPGC No.1 Abbottabad.
2) Muhammad Shakeel, Assistant Professor GPGC Mandian Abbotabad.
3) Mr. Faisal Khan, Subject Specialist Bandi Dhundan Abbottabad.
4) Mr. Abrar Ahmad, Subject Specialist DCTE Abbottabad.
5) Mr. Arif Jamil, Subject Specialist Textbook Board Peshawar.

Editor:

Salmana zaman SS KP Textbook Board , Peshawar.
Khyber Pakhtunkhwa Textbook Board Peshawar.

Printing Supervision:

Asmatullah khan Gandapur (Chairman)
Mr. Saeedur Rehman, Member (E&P)
Khyber Pakhtunkhwa Textbook Board Peshawar.

Academic Year **2020-21**
Website: www.kptbb.gov.pk
Email : membertbb@yahoo.com
Phone: 091-9217159-60

Scanned with CamScanner

Contents

UNIT Number	Name	Page No.
13	s AND p- BLOCK ELEMENTS	1
14	d AND f- BLOCK ELEMENTS	46
15	ORGANIC COMPOUNDS	83
16	HYDROCARBONS	106
17	ALKYL HALIDES	186
18	ALCOHOLS, PHENOLS AND ETHERS	220

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Contents

UNIT Number	Name	Page No.
19	CARBONYL COMPOUNDS I: ALDEHYDES & KETONES	258
20	CARBONYL COMPOUNDS 2:CARBOXYLIC ACIDS AND FUNCTIONAL DERIVATIVES	285
21	BIOCHEMISTRY	316
22	INDUSTRIAL CHEMISTRY	360
23	ENVIRONMENTAL CHEMISTRY	387
24	ANALYTICAL CHEMISTRY	420
	GLOSSARY	451

Scanned with CamScanner

UNIT 13

s and p- Block Elements

Learning Outcomes:

After Studying this unit Students will be able to:

- Recognize the demarcation of the Periodic Table into s-block, p-block , d-block and f-block.
- Describe how physical properties like atomic radius, ionization energy, electronegativity, electrical conductivity and melting and boiling points of elements change within a group and period in the Periodic Table.
- Describe reactions of 3rd period elements with water, oxygen and chlorine.
- Describe physical properties and acid-base behaviour of oxides, chlorides and hydroxides of period 3 elements.
- Describe reactions of oxides and chlorides of period 3 elements with water.
- Explain the trends in physical properties and oxidation states in group I,II, IV and VII of the Periodic Table.
- Describe reactions of Group I elements with water, oxygen and chlorine.
- Explain effect of heat on nitrates, carbonates and hydrogen carbonates of Group I elements.
- Describe reactions of Group II elements with water, oxygen and nitrogen.
- Discuss the trend in solubility of the hydroxides, sulphates and carbonates of Group II elements.
- Discuss the trends in thermal stability of the nitrates and carbonates of Group II elements.

Scanned with CamScanner

- Differentiate beryllium from other members of its group.
- Describe reactions of Group IV elements with water.
- Discuss the chlorides and oxides of group IV elements.
- Explain the relative behaviour of halogens as oxidizing agents and reducing agents.
- Compare the acidity of hydrogen halides.
- Distinguish between an oxide and a peroxide.
- Write representative equations for the formation of oxides and sulphides.
- Compare the outermost s and p orbital system of an element with its chemical properties.
- Perform flame tests and explain the appearances of colours in the flame.
- Analyze acidic and basic Ions using various tests.
- Describe how the food and beverage industry uses steel, tin, aluminium and glass for canning purposes.
- Explain how certain elements are mined and extracted from the earth.
- Relate the properties of the halogens to their important commercial uses.
- Explain that iodine deficiency leads to goitre.
- Explain the applications of bleaching powder.
- Explain fluoride toxicity and deficiency.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Introduction:

The elements of first and second group constitute the "s" block of the periodic table. The valency electrons in these elements occupy the "s" orbitals. The first group elements are called alkali metals while the second group elements are called alkaline earth metals.

Elements of Group IIIA, IVA, VA, VIA, VIIA and VIIIA (noble gases or zero group) are known as p-block elements. These elements have outer electronic configuration of np^{1-6}. s-block elements consist of only metals, but p-block elements include both metals and non-metals.

13.1 3rd Period (Na to Ar):

13.1.1 Physical and atomic properties of elements of 3rd period:

Physical and atomic properties of the period 3 elements from sodium to Argon include ionization energy, atomic radius, electronegativity, electrical conductivity, melting and boiling point.

13.1.1.1 Electronic structure:

In third period of the periodic table electrons are successively filled in 3s and 3p orbitals of atoms of elements (Na to Ar). The electronic configurations of these elements are given below where [Ne] represents the electronic configuration **of Neon.**

$_{11}Na$ [Ne] $3s^1$

$_{12}Mg$ [Ne] $3s^2$

$_{13}Al$ [Ne] $3s^2\ 3p^1$

$_{14}Si$ [Ne] $3s^2\ 3p^2$

$_{15}P$ [Ne] $3s^2\ 3p^3$

$_{16}S$ [Ne] $3s^2\ 3p^4$

$_{17}Cl$ [Ne] $3s^2\ 3p^5$

$_{18}Ar$ [Ne] $3s^2\ 3p^6$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.1.1.2 Trends in atomic radius:

The diagram shows how the atomic radius changes as you go across the third period.



The figure is based on

- Metallic radii for Na, Mg and Al
- covalent radii for Si, P, S and Cl
- The Van der Waals radius for Ar because it does not form any chemical bond.

It is fair to compare metallic and covalent radii because they are both measured in strictly bonded circumstances. It is not suitable to compare these with Van der Waals radius, though, the Van der Waals radius is larger than covalent radii.

13.1.1.3 Trends in first ionization energy:

The first ionization energy is the energy required to remove the most loosely held electron from one mole of gaseous atoms to produce monopositive ion.

$$X_{(g)} \longrightarrow X^{+}_{(g)} + 1e^{-}$$

The pattern of first ionization energy of elements of 3rd period is given is figure 13.1

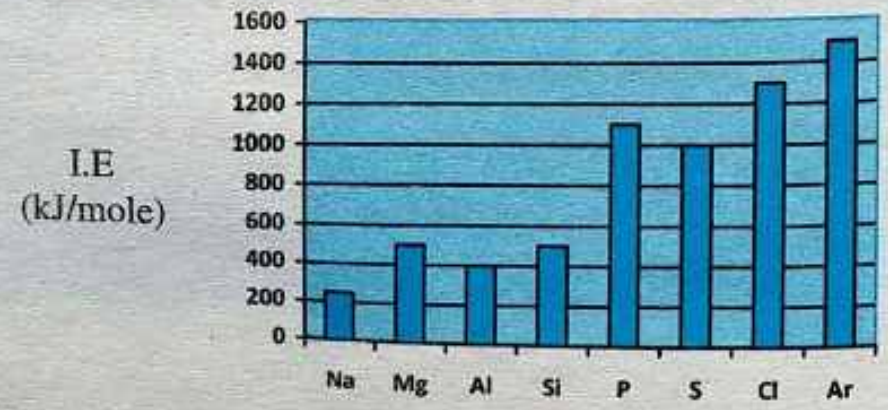


Fig. 13.1

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Notice that general trend is upward, but this is broken by fall between Mg and Al and between P and S.

Explaining the pattern:

First ionization energy depends on

- The charge on the nucleus.
- The distance of the outer electrons from the nucleus.
- The screening effect of inner electrons.
- Electronic configuration of the atom.

The I.E is generally increasing across the period 3 because the electrons are added in the same shell (3rd principal quantum number). So the secreening effect remains almost the same for the elements in third period.

The only major difference is the increase in nuclear charge and decrease in atomic radii from Na to Ar. As a result, the greater attraction between the nucleus and the valence electrons gradually increases the I.E.

13.1.1.4 Trends in electronegativity:

Electronegativity is a measure of the tendency of an atom to attract a shared pair of electrons towards itself.

The trend in electronegativity across third period is given as:

Elements:	Na	Mg	Al	Si	P	S	Cl	Ar
Electronegativity	0.93	1.31	1.81	2.02	2.19	2.58	3.16	-

Note that EN of Ar is not included. Electronegativity is related to the tendency of an atom to attract the shared pair of electrons. Since Argon does not form covalent bonds, you obviously cannot assign it an electronegativity value.

Moving from one elements to the next across the period, nuclear charge increases by one unit and one electron is added to the outer shell. As the positive charge on the nucleus rises, the atom has increasing electron attracting power and therefore an increasing electronegativity.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.1.1.5 Trends in electrical conductivity:

- Sodium, magnesium and aluminium are all good conductors of electricity. Conductivity increases as you go from sodium to aluminium.
- Silicon is semi conductor
- Phosphorous to Argon are non-conductors.

The metals conduct electricity because the delocalised electrons (in the electron sea) are free to move throughout the solid or liquid metals.

Silicon is semiconductor, while the rest do not conduct electricity because they are simple molecular substances. These have no mobile electron.

13.1.1.6 Trends in melting and boiling points:

The chart shows how melting and boiling points of element change across the period. The values are plotted in Kelvin instead of °C to avoid negative value.

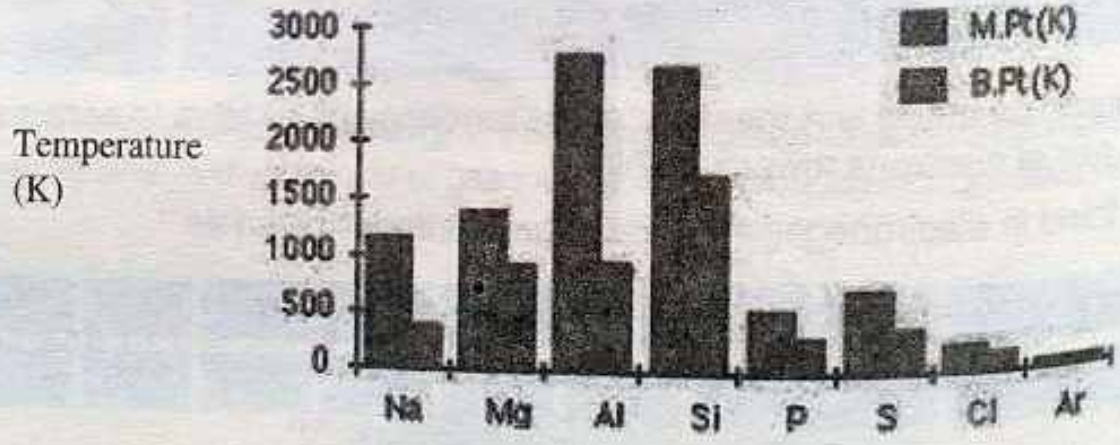


Fig. 13.2

13.1.2 Reactions of period 3 elements with water, oxygen and chlorine:

13.1.2.1 Reaction with water:

Sodium undergoes exothermic reaction with cold water producing hydrogen and a colourless solution of sodium hydroxide.

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

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Magnesium reacts slowly with cold water but burns in steam. A very clean coil of magnesium dropped into cold water eventually gets covered with small bubbles of hydrogen which floats it to the surface. Magnesium hydroxide is formed as very thin layer on the surface of magnesium which tends to stop further reaction:

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

Magnesium burns in steam with its typical white flame to produce white magnesium oxide and hydrogen.

$$Mg + H_2O \longrightarrow MgO + H_2$$

Aluminium powder when heated in steam produces hydrogen and aluminium oxide. The reaction is relatively slow because of the existing strong aluminium oxide layer on the metal and build up of even more oxide during reaction.

$$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2$$

Silicon will react with steam at red heat to produce silicon dioxide and hydrogen.

$$Si + 2H_2O \longrightarrow SiO_2 + 2H_2$$

Chlorine dissolves in water to some extent to give a green solution. A reversible reaction takes place to produce a mixture of hydrochloric acid and chloric (I) acid (hypochlorous acid).

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

In presence of sunlight, chloric (I) acid slowly decomposes to produce more hydrochloric acid, releasing oxygen gas.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$2HOCl \longrightarrow 2HCl + O_2$$

Net reaction $2Cl_2 + 2H_2O \longrightarrow 4HCl + O_2$

There is no reaction between Argon and water.

13.1.2.2 Reactions with oxygen

Sodium burns in oxygen with a yellow flame to produce a white solid mixture of sodium oxide and sodium peroxide.

For normal oxide:

$$4Na + O_2 \longrightarrow 2Na_2O$$

For peroxide

$$2Na + O_2 \longrightarrow Na_2O_2$$

Magnesium burns in oxygen with an intense flame to give white solid magnesium oxide.

$$2Mg + O_2 \longrightarrow 2MgO$$

Aluminium will burn in oxygen. If it is powdered, otherwise the strong oxide layer on Aluminium tends to inhibit the reaction. If you sprinkle aluminium powder into a Bunsen flame, white sparkles and white aluminium oxide is formed:

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

Silicon will burn in oxygen if heated strongly enough. Silicon dioxide is produced.

$$Si + O_2 \longrightarrow SiO_2$$

White phosphorus catches fire spontaneously in air, burning with white flame and producing clouds of white smoke. A mixture of phosphorus (III) oxide and phosphorus (V) oxide is formed.

For phosphorus (III) oxide

Scanned with CamScanner

$$P_4 + 3O_2 \longrightarrow P_4O_6$$

For phosphorus (v) oxide

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

Sulphur burns in air or oxygen on gentle heating with a pale blue flame. It produces colourless sulphur dioxide gas.

$$S + O_2 \longrightarrow SO_2$$

13.1.2.3 Reaction with Chlorine:

Sodium burns in chlorine with a bright orange flame. White, solid sodium chloride is produced.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

Magnesium burns with its usual intense white flame to give white magnesium chloride

$$Mg + Cl_2 \longrightarrow MgCl_2$$

Aluminium reacts with chlorine by passing dry chlorine over aluminium foil heated in a long tube. Aluminium burns in stream of chlorine to produce pale yellow aluminium chloride.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

If chlorine is passed over silicon powder heated in a tube, it reacts to produce a colourless liquid silicon tetrachloride.

$$Si + 2Cl_2 \longrightarrow SiCl_4$$

White phosphorus burns in chlorine to produce a mixture of two chlorides, phosphorus (III) chloride and phosphorus (v) chloride (phosphorus trichloride and phosphorus pentachloride).

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Phosphorus (III) chloride is colourless fuming liquid

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

Phosphorus (v) chloride is a straw coloured solid.

$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$

If a steam of chlorine is passed over some heated sulphur, it reacts to form an orange, foul smelling liquid disulphur dichloride S_2Cl_2

$$2S + Cl_2 \longrightarrow S_2Cl_2$$

It obviously does not make sense to talk about chlorine reacting with itself and Argon.

13.1.3 Physical properties of oxides:

This topic is related to physical properties of oxides of period (3) elements (sodium to chlorine) and their structures. Argon is obviously omitted because it does not form any oxide. The oxides and their physical properties are:

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
-	-	-	-	P_4O_6	SO_2	Cl_2O

The oxides in the top row are the oxides where period 3 elements are in their highest oxidation state. In these oxides, all the outer electrons in period 3 elements are being involved in bonding from just one in sodium to all seven outer electrons of chlorine in Cl_2O_7.

13.1.3.1 Structure

The trend in structure is from metallic oxides containing giant structures of ions on the left of the period via a giant covalent oxide (silicon dioxide) in the middle to molecular oxides on right.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.1.3.2 Melting and boiling points:

The giant structures (the metal oxides and silicon oxide) will have high melting and boiling points because a lot of energy is needed to break the strong bonds (ionic or covalent) operating in these lattices.

The oxides of phosphorus, sulphur and chlorine consist of individual molecules, some small and simple, others polymeric. The attractive forces between these molecules will be dispersion forces and dipole-dipole interactions. These vary in strength depending on the size, shape and polarity of various molecules but are always much weaker than the ionic or covalent bonds required in a giant structure. These oxides are gases, liquids or low-melting solids.

Formation of oxide	Melting points (°C)	Boiling points (°C)
Na_2O	1280	1950
MgO	2900	3600
Al_2O_3	2040	2977
S_iO_2	1610	2230
P_4O_{10}	340	360
P_4O_6	23.8	173.1
SO_3	– 17	45
SO_2	–72	–10
Cl_2O_7	–92	82
Cl_2O	–120.6	2

13.1.3.3 Electrical conductivity:

None of these oxides has any free or mobile electrons which means that none of them will conduct electricity when they are solid. The ionic oxides can, however, undergo electrolysis in molten state. They can conduct electricity because of the movement of ions towards the electrodes.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.1.3.4 Acid Base Behaviour of oxides:

Across the period from left to right there is a steady change in the structure of oxides from ionic through giant molecules to simple molecules. This change in the structure leads to profound difference in the way in which these oxides react with water, acids and alkalies. The ionic oxides contain O^{2-} ions in the crystal lattice. These O^{2-} ions in Na_2O react vigorously with H_2O to form an alkaline solution.

$$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)}$$

$$Na_2O_{(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)}$$

MgO is slightly soluble in water forming alkaline solution. It reacts with acids to form salt and water.

$$MgO_{(s)} + H_2O_{(l)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$$

$$MgO_{(s)} + 2HCl_{(aq)} \rightleftharpoons MgCl_{2(aq)} + H_2O_{(l)}$$

Al_2O_3 is amphoteric oxide. It does not react with water but it will react with both dilute acid (H^+) and dilute Alkali (OH^-).

$$Al_2O_{3(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)}$$

$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 2\,[Al(OH)_4]_{(aq)}$$

Aluminate ion

SiO_2 does not react with water, but it reacts with concentrated alkalies forming silicates ($S_iO_3^{-2}$)

$$SiO_2 + 2OH^-_{(aq)} \longrightarrow S_iO^{-2}_{3(aq)} + H_2O_{(l)}$$

NO_2 reacts with water to form a mixture of two acids HNO_2 and HNO_3.

Scanned with CamScanner

$$2NO_{2(g)} + H_2O_{(l)} \longrightarrow HNO_{2(aq)} + HNO_{3\,(aq)}$$

The oxides of phosphorus, Sulphur and chlorine except (ClO_2) react readily with water to form a strongly acidic solution.

$$P_4O_{10(s)} + 6H_2O_{(l)} \longrightarrow 4H_3PO_{4\,(aq)}$$

$$SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2SO_{4(aq)}$$

$$Cl_2O_{(g)} + H_2O_{(l)} \longrightarrow 2HClO_{(aq)}$$

Dichlorine oxide

$$Cl_2O_{7(l)} + H_2O_{(l)} \longrightarrow 2HClO_{4(aq)}$$

Perchloric Acid

13.1.3.5 Trends in Acid base Behaviours:

Properties of oxides of elements in period 3

Formula of oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10} (P_4O_6)	SO_3 (SO_2)	Cl_2O_7 (Cl_2O)
State of oxides	Solid	Solid	Solid	Solid	(Solid)	Liquid (gas)	Liquid (gas)
Electrical conductivity	good	good	good	v.poor	Nil	Nil	Nil
Structure of oxide	Giant structures				Simple Molecular structure		
Nature of oxide	Basic (alkaline)	Basic (weakly alkaline)	Amphoteric	Acidic	Acidic	Acidic	Acidic

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The above table shows that there is a change from strongly basic oxide on left side to strongly acidic oxide on right side while amphoteric oxides in the middle of third period.

13.1.3.6 Reactions of oxides with water, acids and bases:

The normal oxides of most metals e.g. Na_2O, CaO etc. combine with acids to form salts.

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

These usually dissolve in water to give soluble hydroxides.

$$Na_2 + H_2O \longrightarrow 2NaOH$$

Such oxides are called basic oxides.

Acidic oxides are oxides of non-metals e.g. CO_2, SO_2 etc. which react with bases to form salts and combine with water to form acids.

$$CO_2 + H_2O \longrightarrow Na_2CO_3 + H_2O$$
$$SO_2 + H_2O \longrightarrow H_2SO_3$$

Some oxides like BeO, Al_2O_3 etc. react with both acids and alkalies to form salts. These are called amphoteric oxides which are usually water insoluble.

13.1.4 Chlorides of the period 3 elements:-

Properties of Chloride of period 3 elements.

Formula of chlorides	NaCl	$MgCl_2$	Al_2Cl_6	$SiCl_4$	PCl_3	S_2Cl_2
State of chlorides (at 20C°)	solid	solid	solid	liquid	liquid	liquid
Melting point (C°)	801	708	192.4	–69	–93.6	–80
Boiling point of chlorides(C°)	1465	1418	423	57	74	136

Scanned with CamScanner

Electrical conductivity in liquid state	Good	good	Very poor	Nil	Nil	Nil
Structure of chloride	Giant structure		Molecular structure			
Effect of adding chloride to water	Solid dissolves readily		Chloride reacts with water producing fumes of HCl			

NaCl and $MgCl_2$ are gaint structures composed of oppositely charged ions which attract each other by strong electrostatic forces (ionic bonds). This means that the melting and boiling points of these compound would be high. But the molten substances will conduct electricity because the ions which they contain can move towards the electrodes of opposite charge.

All the other chlorides have simple molecular structure composed of small discrete molecules attracted to each other by relatively weak intermolecular forces. So, the melting & boiling points of these compounds are low and they will not conduct electricity in liquid state.

13.1.5 Hydroxides of period 3 elements:-

The word" Hydroxide" refers to anything which contains either a hydroxide ion (OH^-) or an –OH group covalently bounded to the element in question. Hydroxides containing OH^- ion are basic hydroxides e.g. NaOH, $Ca(OH)_2$. Aluminium hydroxide ($Al(OH)_3$) is amphoteric reacting both with acids and bases. The elements Si, P, S and Cl of period 3 form hydroxides in which –OH group is covalently bound to these elements e.g. $Si(OH)_4$, H_3PO_4, H_2SO_4 and $HClO_4$. These are all acids.

13.1.5.1 Sodium and magnesium hydroxides:-

These are white solids having soapy touch. Strong solutions of these hydroxides are very corrosive to skin. These are very hygroscopic.

Sodium hydroxide is only slightly soluble in alcohols. It is one of the most soluble substances in water evolving a considerable amount of heat due to the formation of a number of hydrates e.g. $NaOH.2H_2O$.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Sodium hydroxide (NaOH) is used in soap industry, petroleum refining and reclaiming of rubber.

Magnesium Hydroxide, $Mg(OH)_2$ is obtained as a white precipitate when caustic potash (KOH) solution is added to a soluble magnesium salt.

$$MgCl_2 + 2KOH \longrightarrow Mg(OH)_2 + 2KCl$$

Solubility of $Mg(OH)_2$ is enhanced tremendously by the addition of NH_4Cl.

$$2NH_4Cl \longrightarrow 2NH_4^+ + 2Cl^-$$
$$Mg(OH)_2 \longrightarrow 2OH^- + Mg^{2+}$$
$$2NH_4^+ + 2OH^- \longrightarrow 2NH_4OH$$

More $Mg(OH)_2$ therefore, dissolves to provide a further supply of OH^- in order to replace those fixed in the form of NH_4OH.

13.1.5.2 Aluminium Hydroxide:-

When an alkali is added to an aqueous solution of aluminium salt, Aluminium hydroxide $Al(OH)_3$ gets precipitated.

$$Al_2(SO_4)_3 + 6NH_4OH \longrightarrow 2Al(OH)_3 + 3(NH_4)_2SO_4$$

This hydroxide is soluble in acids and caustic alkalies forming aluminates in the later.

$$2Al(OH)_3 + 2NaOH \longrightarrow 2Na[Al(OH)_4]$$

The $Al(OH)_3$ can also be obtained by hydrolysis of $AlCl_3$ in excess water.

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The precipitated hydroxide has the capacity of absorbing various dyes forming colouring matter known as "lakes".

13.1.5.3 Other Hydroxides:-

Silicon hydroxide is a molecule with formula $Si(OH)_4$. It is produced by the following chemical reaction.

$$SiO_2 + 2H_2O \underset{}{\overset{800^\circ C}{\rightleftharpoons}} Si(OH)_4$$

This compound is unstable and rapidly polymerises.

13.2 Group I Elements

The element lithium (Li), sodium (Na), potassium (K) , rubidium (Rb), cesium (Cs) and francium (Fr) constitute sub-group IA of the periodic table. These are known as alkali metals since they form oxides and hydroxides which combine with water to produce alkaline solution. Only the first three of these are safe to keep in the school lab. The rest are violently reactive.

The characteristic feature of the sub-group IA is the s^1 arrangement in the outermost shell.

Element	Atomic No.	Electronic Configuration
Li	3	$1s^2, 2s^1$
Na	11	$1s^2, 2s^2, 2p^6, 3s^1$
K	19	$1s^2, 2s^2, 2p^6, 3s^2\ 3p^6, 4s^1$
Rb	37	$1s^2, 2s^2 2p^6, 3s^2\ 3p^6\ 3d^{10} 4s^2\ 4p^6\ 5s^1$
Cs	55	$1s^2, 2s^2\ 2p^6, 3s^2 3p^6 3d^{10}, 4s^2\ 4p^6 4d^{10}\ 5s^2$
		$5p^6\ 6s^1$
Fr	87	$[k_r]\ 5s^2\ \ 5p^6\ \ 5d^{10}\ 6s^2\ 6p^6\ 7s^1$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Like all metals, they are good conductors of heat and electricity. But they are softer than other metals. You can cut them with knife. They are lighter than other elements and having low melting point, boiling points and density.

13.2.1 Trends in Physical properties:-

The elements in a group behave in similar way, but they also show trends of variations in properties as given below:

13.2.1.1 Trends in Atomic radius:-

As we move from Lithium to Cesium an extra shell of electrons is added to next element. The addition of extra shells increases the atomic radius.

Elements:	Li	Na	K	Rb	Cs
Atomic radius (A°):	1.55	1.90	2.35	2.48	2.67

13.2.1.2 Trend in First ionization energy:-

The ionization energies of these elements are relatively low and first I.E of these elements decreases on moving from Li to Cs. Due to their low I.E, these metals have a greater tendency to lose the valence electron to change into M^+ ions.

Elements:	Li	Na	K	Rb	Cs
I.E (ev) :	5.4	5.1	4.3	4.2	3.9

13.2.1.3 Trends in Electronegativity:-

Since these metals are highly electropositive, their electronegativity values are very low.

As their electropositive character increases from Li to Cs, their electro negativities decrease in the same order.

Elements:	Li	Na	K	Rb	Cs
Electronegativities (Paulings):	1.0	0.9	0.8	0.8	0.7

Scanned with CamScanner

13.2.1.4 Trends in melting and boiling points:-

The forces binding the atoms in crystal lattices of these metals are relatively weak. Consequently these metals are soft and possess low melting and boiling points which decrease down the group.

Elements	Li	Na	K	Rb	Cs
B. pt (°C)	1330	892	760	688	670
M.pt (°C)	1085	97.8	63.7	38.9	28.7

13.2.1.5 Trends in Density:-

Density increase in moving from Li to Cs, Potassium is, however, lighter than sodium.

Elements	Li	Na	K	Rb	Cs
Density (g/cm3)	0.534	0.972	0.86	1.53	1.903

13.2.2 Trend in Chemical properties :-

13.2.2.1 Reaction with water :-

Group-I elements are very good reducing agents. They all react vigorously with water reducing it to hydrogen gas.

$$M_{(s)} \rightarrow M^{+}_{(aq)} + 1e^{-}$$

$$H_2O_{(l)} + 1e^{-} \rightarrow 1/2H_{2(g)} + OH^{-}_{(aq)}$$

$$M_{(s)} + H_2O_{(l)} \rightarrow MOH_{(aq)} + 1/2H_2$$

Excluding Lithium, which reacts slower than all the other elements of group-I. Sodium reacts vigorously, fizzing and skating about on the water surface. Potassium reacts even more vigorously. It cracks and pops as hydrogen explodes. Rb and Cs explode violently in contact with water.

The reactivity of Group-I elements with water closely follows the values of electrode potential.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Elements	Li	Na	K	Rb	Cs
Electrode potential (V)	−3.05	−2.71	−2.93	−2.98	−3.02

13.2.2.2 Reactions with Oxygen:-

These are all very reactive metals and have to be stored without contact with air to prevent their oxidation. Reactivity increases down the group.

Li, Na and K are stored in oil, Cs and Rb are normally stored in a sealed glass tubes to prevent air contact.

Alkali metals react with air or oxygen to form various types of oxides. Some of the reactions are given below.

$$4Li + O_2 \rightleftharpoons 2Li_2O$$

(Lithium oxide)

Sometimes "Li" reacts with nitrogen in the air to give Li_3N.

$$6Li + N_2 \longrightarrow 2\,Li_3N$$

$$4\,Na + O_2 \longrightarrow 2\,Na_2O \text{ (sodium oxide)}$$

For peroxide, the reaction is

$$2Na + O_2 \longrightarrow N\,a_2\,O_2 \text{ (sodium peroxide)}$$

$$2K + O_2 \longrightarrow K_2O_2 \text{ (potassium peroxide)}$$

For the super oxide, the reaction is

$$K + O_2 \longrightarrow KO_2 \text{ (potassium superoxide)}$$

Scanned with CamScanner

"Rb" and "Cs" catch fire in air and produce superoxide such as RbO_2 and CsO_2 respectively.

Reactions of oxides with water :-

Reaction with water

Oxides of alkali metal may react with water in the following manner.

$$\underset{\text{(normal oxide)}}{X_2O} + H_2O \longrightarrow \underset{\text{(Metal Hydroxide)}}{2XOH}$$

$$\underset{\text{(Peroxide)}}{X_2O_2} + 2H_2O \longrightarrow 2XOH + \underset{\text{(Hydrogen peroxide)}}{H_2O_2}$$

$$\underset{\text{(Super oxide)}}{2XO_2} + 2H_2O \longrightarrow 2XOH + H_2O_2 + O_2$$

Reactions of oxides with dilute acids:-

Normal oxides react with dilute acids forming salts and water. While per-oxides and superoxide also give other products.

$$\underset{\text{(Normal oxide)}}{X_2O} + 2HCl \longrightarrow \underset{\text{Salt}}{2XCl} + H_2O$$

$$\underset{\text{(Per oxide)}}{X_2O_2} + 2HCl \longrightarrow \underset{\text{Salt}}{2XCl} + H_2O_2$$

$$\underset{\text{(Superoxide)}}{2XO_2} + 2HCl \longrightarrow 2XCl + H_2O_2 + O_2$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.2.2.3 Reaction with Chlorine:-

Sodium burns with an intense orange flame in chlorine in exactly the same way as it does in pure oxygen. Other alkali metals behave similarly. The reactions give white solid chlorides of these metals.

$$2X + Cl_2 \longrightarrow 2XCl$$
$$2Na + Cl_2 \longrightarrow 2NaCl$$
$$2K + Cl_2 \longrightarrow 2KCl$$

13.2.2.4 Effect of heat on nitrates, carbonates and hydrogen carbonates explaining the trends in terms of the polarizing ability of the positive Ion :-

Compounds of Group-I A Elements are more stable to heat than the corresponding compounds of group-II elements with the exception of Lithium compounds.

Effect of heat on Nitrates:-

Most Nitrates tend to decompose on heating to produce metal oxide, nitrogen dioxide (brown fumes) and oxygen.

Lithium nitrate produces lithium oxide, nitrogen dioxide and oxygen

$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$

Nitrates of the other alkali metals decompose to corresponding nitrites.

$$2XNO_3 \longrightarrow 2XNO_2 + O_2$$

Effect of heat on Carbonates:

Lithium carbonate decomposes on heating to give litium oxide and carbon dioxide e.g.

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The rest of group-I carbonates do not decompose even at higher temperature.

Effect of heat on Hydrogen Carbonates:-

Hydrogen Carbonates of alkali metals are stable enough to be isolated as solids. However, they decompose on heating forming carbonates.

$$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

Thermal stability of hydrogen carbonates of group I and group II increases down the group. The reason is increasing size and decreasing charge density of the metal ions. The polarizing power of a cation increases with increasing charge on the ion and decreasing the radius of the ion.

Cation of greater polarizing power distorts the HCO_3^- ion more and facilitates its decomposition than a cation of larger size and lesser polarizing power. Due to the same reason, bicarbonates of group-I are more stable than those of group-II.

13.2.2.5 Flame Tests:-

The alkali metals give characteristic colours to the Bunsen flame because even the small amount of energy of the flame causes an excitation of the outermost electron which on dropping back to its original position gives out the energy so absorbed as visible light. These colours differ from one another as shown in the table.

Li	Na	K	Rb	Cs
red	yellow	Lilac	red	Blue/violet

13.3 Groups II - Elements:-

Name of elements in group-IIA

Alkaline earth metals do not exist free in nature. They exist in combined form. Magnesium and calcium are very abundant in the rocks of earth's crust.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The chief sources of Mg are sea water , underground brines, the mineral dolomite and magnesite ($MgCO_3$). Calcium compounds are obtained from sea shell e.g. $CaCO_3$ and gypsum ($CaSO_4 \cdot 2H_2O$) which is one of the important minerals of calcium. Other alkaline earth metals are much less common than magnesium and Calcium.

Elements of group IIA (alkaline earth metals) possess two electrons in the outermost s-orbital. They form dispositive ions by loss of both the electrons. The elements and their atomic numbers etc. are given in table below.

Element	Symbol	At. No.	Electronic configuation
Beryllium	Be	4	$1s^2, 2s^2$
Magnesium	Mg	12	$1s^2, 2s^2, 3s^2$
Calcium	Ca	20	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$
Strontium	Sr	38	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2$
Barium	Ba	56	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 5p^6, 6s^2$
Radium	Ra	88	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 4f^{14}, 5s^2, 5p^6, 5d^{10}, 6s^2, 6p^6, 7s^2$

All alkaline earth metals except Be are white in colour. They are quite reactive and tarnish in air.

The values of their densities, melting points and boiling points are higher than those of alkali metals.

13.3.1 Trends in physical properties:-

13.3.1.1 Trends in Atomic Radius:-

Due to the successive addition of extra shell of electrons to each element from Be to Ra, the atomic radius increases. While the atomic radii of these elements are smaller than those of alkali metals. These elements harder, have higher densities and higher melting points than the corresponding alkali metals.

Elements:	Be	Mg	Ca	Ba	Ra
Atomic Radii (A°):	1.12	1.60	1.97	2.15	2.22

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.3.1.2 Trends in First Ionization energy:-

The first Ionization energy of these elements decreases with increase of atomic radii from Be to Ba. However, the value of I.E of Ra is higher than I.E of Ba.

Elements	Be	Mg	Ca	Sr	Ba	Ra
Ionization Energies (ev)	9.3	7.6	6.1	5.7	5.2	5.3

13.3.1.3 Trends in Electronegativity:-

The electronegativity values of these elements are small and decrease from Be to Ba.

Elements	Be	Mg	Ca	Sr	Ba	Ra
Electronegativity	1.5	1.2	1.0	1.0	0.9	0.9

13.3.1.4 Trends in Melting and Boiling Points:-

Melting and boiling points do not show any regular trend. These are, however, higher than those of alkali metals.

Elements	Be	Mg	Ca	Sr	Ba	Ra
M.Pt (°C)	1289	651	851	771	727	700
B.pt (°C)	2500	1105	1494	1381	1850	1700

13.3.2 Trends in chemical properties:-

13.3.2.1 Trends in reactivity with water:-

These metals react slowly with water liberating hydrogen and forming hydroxides. The reaction becomes increasingly vigorous with an increase in atomic number. However, Beryllium does not react with water or steam at red heat. Mg burns in steam to produce white MgO and H_2 gas.

$$Mg_{(s)} + H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}$$

Group-II elements become more reactive towards water as we go down the group.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.3.2.2 Reaction with oxygen and Nitrogen:-

13.3.2.2.1 Formation of Simple oxide:-

All the metals of group II react with oxygen and form simple oxides. It is almost impossible to find any trend in the way the metal react with oxygen.

$$2Ca_{(s)} + O_{2(g)} \longrightarrow 2CaO_{(s)}$$

Be is reluctant to burn unless it is in the form of dust or powder. Be has very strong layer of BeO on its surface which prevents any more oxygen reaching the underlying beryllium to react with it.

13.3.2.2.2 Formation of Peroxide on heating with oxygen:-

Be, Mg and Ca do not form peroxide when heated with oxygen. But Sr and Ba react in oxygen to form peroxides SrO_2 and BaO_2 respectively. The reactions are.

$$Ba_{(s)} + O_{2(g)} \longrightarrow BaO_{2(s)}$$

$$Sr_{(s)} + O_{2(g)} \longrightarrow SrO_{2(s)}$$

13.3.2.2.3 Formation of Nitrides on heating in air:-

The nitrides of alkaline earth metal are Ionic and solid in nature except that of Be which is covalent and unpredictable.

The reaction of alkaline earth metals with air rather than oxygen is complicated by the fact that they all react with nitrogen to produce nitrides. In each case we get a mixture of metal oxide and nitride.

$$Mg_{(s)} + N_{2(g)} \xrightarrow{\Delta} Mg_3N_{2(s)}$$

$$Be_{(s)} + N_{2(g)} \xrightarrow{\Delta} Be_3N_{2(s)}$$

13.3.2.3 Trends in solubility of Hydroxides, Sulphates and Carbonates.

The solubility of Hydroxides in water increase from $Be(OH)_2$ to $Ba(OH)_2$ as indicated by increasing values of their solubility product.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$Be(OH)_2 = 1.6 \times 10^{-26}$ $Mg(OH)_2 = 8.6 \times 10^{-12}$

$Ca(OH)_2 = 1.3 \times 10^{-4}$ $Sr(OH)_2 = 3.2 \times 10^{-4}$

$Be(OH)_2 = 5.4 \times 10^{-3}$

The solubility of sulphates decreases as we go down the group. $CaSO_4$ is sufficiently soluble in water while Strontium and Barium sulphates are almost insoluble.

All carbonates of these elements are insoluble in neutral medium, while all dissolve in acids and decompose at red heat. The stability of carbonates increases down the group as is evident from the temperature at which they decompose.

$BeCO_3 < 100^{\circ}C$ $MgCO_3 = 540^{\circ}C$

$CaCO_3 = 900^{\circ}C$ $SrCO_3 = 1290^{\circ}C$

$Ba\ CO_3 = 1360^{\circ}C$

13.3.2.4 Trend in Thermal Stability of the Nitrates and Carbonates

Both carbonates and nitrates become more thermally stable as we go down the group. The ones at lower position have to be heated more strongly than those at the top before they decompose.

$$XCO_{3(s)} \xrightarrow{\Delta} XO_{(s)} + CO_{2(g)}$$

$$2X(NO_3)_{2(s)} \longrightarrow 2XO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

13.3.3 How Beryllium Differs from other members of its group:-

Beryllium differs from other alkaline earth metals in many respects. This is partly due to its small size and partly due to its high electro-negativity.

1- Be unlike other alkaline earth metal is not easily affected by dry air, and does not decompose even in boiling water.
2- Oxides, nitrides, sulphides, chlorides etc. of Group II elements are ionic, while those of Be are covalent.
3- Salts of Be do not impart any colour to the flame unlike its family members.
4- Beryllium oxide is insoluble in water unlike oxides of other members of its family.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.3.4 Why is Beryllium chloride Covalent and not Ionic

The polarizing power of Be^{+2} ion is high and polarizability of Cl^- ion is also high. So Be^{+2} essentially pulls the electron cloud from Cl^-, such that the electrons are effectively shared. This gives covalent character to $BeCl_2$.

13.3.5 Amphoteric Beryllium Hydroxide:-

Beryllium hydroxide can act both as an acid and as a base because it can neutralize both.

As a base: (neutralizing acid)

$$Be(OH)_2 + 2HCl \longrightarrow BeCl_2 + 2H_2O$$

As an Acid: (neutralizing base)

$$Be(OH)_2 + 2NaOH \longrightarrow \underset{\text{complex}}{Na_2[Be(OH)_4]}$$

13.4 Group-IV elements:-

The Group-IV A of the periodic table consists of five elements C,Si,Ge,Sn and Pb. This group is present in the middle of periodic table forming a link between more electropositive elements of groups IA to IIIA and more electronegative elements of group VA-VIIA. The elements of group IVA evidently exhibit an intermediate character.

13.4.1 Physical properties: -

13.4.1.1 Melting and boiling point:-

The decrease in melting point from silicon downwards is due to the presence of weak bonds which become weaker due to increase in atomic size. Moreover, Tin and Lead do not use all the four electrons for metallic bond. The extremely high boiling points of Carbon and Silicon are due to very stable arrangement of diamond type lattice.

Scanned with CamScanner

Elements	Melting point (°C)	Boiling Point (°C)
C	3600	4827
Si	1420	2355
Ge	937	2830
Sn	232	2560
Pb	328	1744

13.4.1.2 Trend from non-metal to metal :-

The change from non-metallic to metallic character with the increase of atomic number is best illustrated in this group e.g. C and Si are non-metals. Ge is metalloid and Sn and Pb exhibit metallic character.

13.4.1.3 Oxidation state:-

Oxidation state is defined as the apparent charge positive or negative on an atom of an element in a molecule or ion.

Carbon and Silicon show +4 oxidation state in carbonates and silicates. The remaining members can show +2 as well as +4 oxidation states. Since, the electronegativity of these elements is low, they do not have such a high tendency to form negative ions. However, carbon forms C^{-4} and C_2^{-2} ions in certain compounds.

Be_2C (C=–4, Be=+2), Na_2C_2 (C_2 = –2, Na = +1)

Oxidation state of group-IV elements may be positive or negative depending upon the nature of the compounds. The typical oxidation state shown by elements of group-IV is +4, found in compounds like CCl_4, $SiCl_4$ and SnO_2. However, down the group there are more and more examples where the oxidation state is +2, such as $SnCl_2$ and $PbCl_2$.

13.4.1.2 Inert pair effect in formation of ionic bond:-

All the elements in group-IV have valence electronic structure of ns^2, np^2, where 'n' varies from 2 (for carbon) to 6 (for lead). The oxidation state of +4 is found where all these outer electrons are involved in bonding. But

Scanned with CamScanner

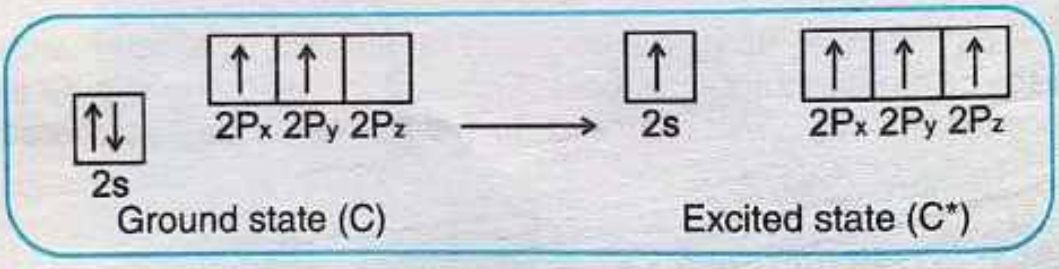
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

at the bottom of the group there is tendency for the s^2 pair not to be used in bonding. This is called inert pair effect which dominates in lead.

If the elements of group-IV form M(+2) ions they will lose the 'p' electrons, leaving the s^2 pair unused e.g. In the formation Pb^{+2} ions, Pb will lose the two '6p' electrons, but the '6s' electrons will be left unchanged (inert pair effect). Therefore, the compounds of Pb^{+2} are ionic in nature.

13.4.1.3 Inert pair effect and the formation of covalent bonds:-

Although the most stable electronic configuration of a carbon atom requires it to be divalent, but carbon is tetravalent in majority of compounds. In order to explain this apparent anomaly, it is assumed that electron from '2s' orbital is promoted to an empty '2p' orbital.



It is obvious from the electronic configuration (C*) that it can form four covalent bonds due to its C(+4) oxidation state.

While the other members of the same group show +2 as well as +4 oxidation state. Therefore, these members can form both ionic and covalent compounds depending upon the size of cation. The nature of compounds M^{+2} and M^{+4} cations can be predicted by Fajan's rule e.g. Sn^{+4} is smaller than Sn^{+2} so the compounds of Sn^{+4} are covalent, while those of Sn^{+2} are ionic.

13.4.2 Chemical properties

13.4.2.1 Chlorides of carbon, silicon and lead:-

All these elements give tetrachlorides (MCl_4) which are covalent and tetra-hedral due to sp^3 hybrid orbitals. MCl_4 are fuming liquids at room temperature. The stability of MCl_4 decreases from CCl_4 to $PbCl_4$. $PbCl_4$ decomposes to give $PbCl_2$ and Cl_2 gas.

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

Scanned with CamScanner

13.4.2.1.1 Structure and stability :-

At the top of group-IV A the most stable oxidation state shown by an element is +4. This oxidation state is shown by carbon and silicon in CCl_4 and $SiCl_4$. These have no tendency to form dichloride. However, the relative stability of +4 oxidation state falls down the group and +2 oxidation state becomes the most stable at lead.

13.4.2.1.2 Reaction with water :-

CCl_4 does not react with water. This is due to bulky nature of chlorine atoms around small carbon atom. As a result oxygen of water cannot penetrate to reach carbon atom. $SiCl_4$ to $PbCl_4$ react violently with water to produce their respective oxides and fumes of HCl.

$$SiCl_4 + 2H_2O \longrightarrow \underset{\text{White}}{SiO_2} + 4HCl$$

$$PbCl_4 + 2H_2O \longrightarrow \underset{\text{Brown}}{PbO_2} + 4HCl$$

$PbCl_2$ is ionic in nature and sparingly soluble in cold water but more soluble in hot water. The solubility in water involves break up of the ionic lattice and the hydration of Pb^{+2} and Cl^- ions:

$$PbCl_{2(s)} \xrightarrow{H_2O_{(l)}} Pb^{+2}_{(aq)} + 2Cl^-_{(aq)}$$

13.4.2.2 Oxides :-

The elements of group-IV form two types of oxides i.e. monoxide and dioxide in which these exist in +2 and +4 oxidation states.

Monoxides include CO, SnO and PbO while the dioxides include CO_2, SiO_2, SnO_2 and PbO_2. The oxides of carbon and silicon are non-metal oxides and are covalent in nature, whereas, oxides of tin and lead are metal oxides and are ionic in nature.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.4.2.2.1 Structure of Carbon dioxide and Silicon dioxide

Carbon dioxide and silicon dioxides are formed by the direct combination of these elements with oxygen. However, CO_2 is a gas whereas SiO_2 is a hard, high melting solid. The other oxides of group-IV are also solids. The fact that CO_2 is a gas suggests that it must consist of simple discrete molecules, with double bonds between carbon and oxygen atoms.

$$O = C = O$$

The molecule has linear shape and hence the carbon atom is supposed to be 'sp' hybridized in it. The two 'sp' hybrid orbitals of carbon atom form two sigma bonds with 'p' orbitals of each oxygen atom. Half filled 'p' orbitals on carbon atom which do not participate in hybridization process form two "π" bonds with two oxygen atoms.

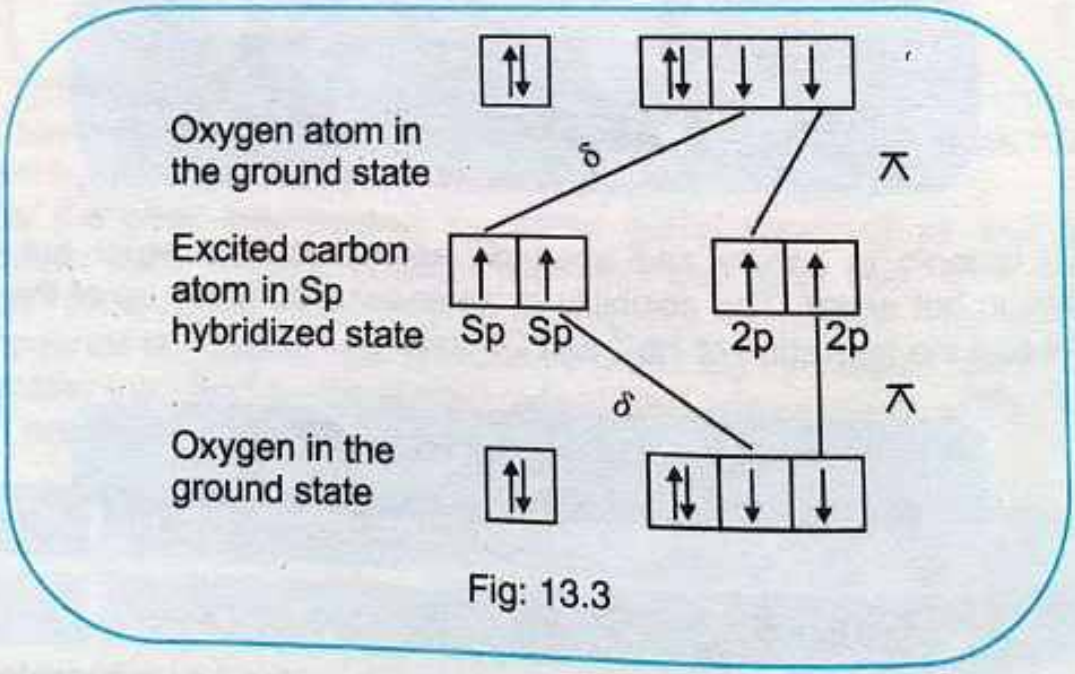


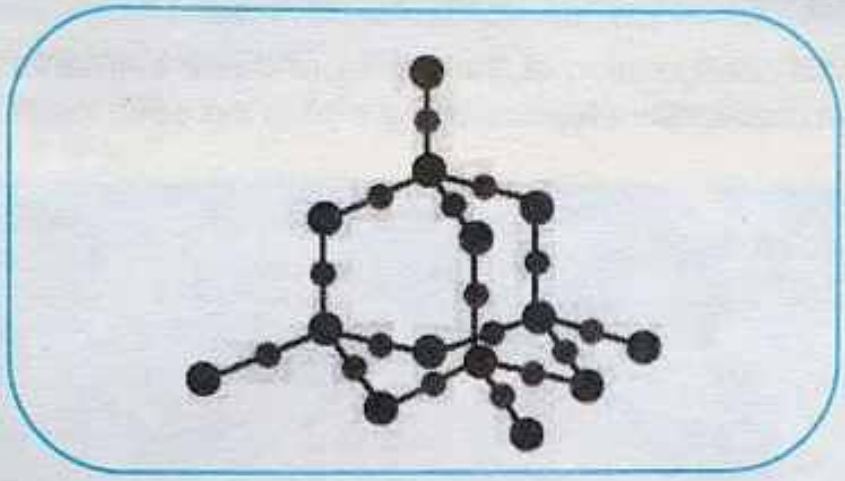
Fig: 13.3

Silicon atoms are bigger than carbon atoms, which means that silicon-oxygen bond will be long as compared to carbon-oxygen bond. The 'p' orbital on the silicon and the oxygen are not quite close enough together to allow enough side wise overlap to give us a stable "π" bond. Thus silicon-oxygen bond is a single sigma bond.

The SiO_2 molecule is a giant covalent structure in which each silicon atom is bonded to four oxygen atoms through single covalent bonds whereas each oxygen atom is bonded to two silicon atoms.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



The geometry of the SiO_2 is tetrahedral (diamond like)

13.4.2.2.2 Acid Base Behaviour of Group IV oxides

The acidity of group-IV oxides decreases as we move down the group. Thus CO_2 and SiO_2 are acidic and GeO_2, snO_2 and PbO_2 are amphoteric. Among the mono oxides of these elements CO is neutral while SnO and PbO are amphoteric. Acid base reactions of these oxides are given below.

Acidic

$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$SiO_2 + NaOH \rightarrow 2Na_2SiO_3 + H_2O$$

Amphoteric

$$SnO + NaOH + H_2O \rightarrow Na_2Sn(OH)_4 \text{ (Acidic)}$$
$$SnO + HCl \rightarrow SnCl_2 + H_2O \text{ (Basic)}$$

Amphoteric

$$PbO + 2HCl \rightarrow PbCl_2 + H_2O \text{ (Basic)}$$
$$PbO + NaOH + H_2O \rightarrow Na_2Pb(OH)_4 \text{ (Acidic)}$$

13.5 Group VII A Elements: halogens :-

Group VIIA comprises the elements fluorine, chlorine, bromine, iodine and astatine. The elements are collectively known as halogens due to their salt forming tendency. These are non-metals.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.5.1 Physical properties :-

The electronic configuration of the atoms of these elements is shown in table below, the charactistics feature being s^2p^5 in the outer most shell.

Elements	Atomic No	Complete electronic configuration	Valence shell configuration
F	9	2,7	$2s^2\ 2p^5$
Cl	17	2,8,7	$3s^2\ 3p^5$
Br	35	2,8,18,7	$4s^2\ 4p^5$
I	53	2,8,18,18,7	$5s^2\ 5p^5$

Halogens in the uncombined state exist as diatomic covalent molecules (F_2, Cl_2, etc). These discrete molecules are held together by weak Van der Waals forces which explain the volatile nature of these elements. These elements are also poisonous in nature.

13.5.1.1 Trends in Atomic Radius :-

Atomic radius of Group VII elements, in the periodic table increases down the group as shown in the fig 13.4.

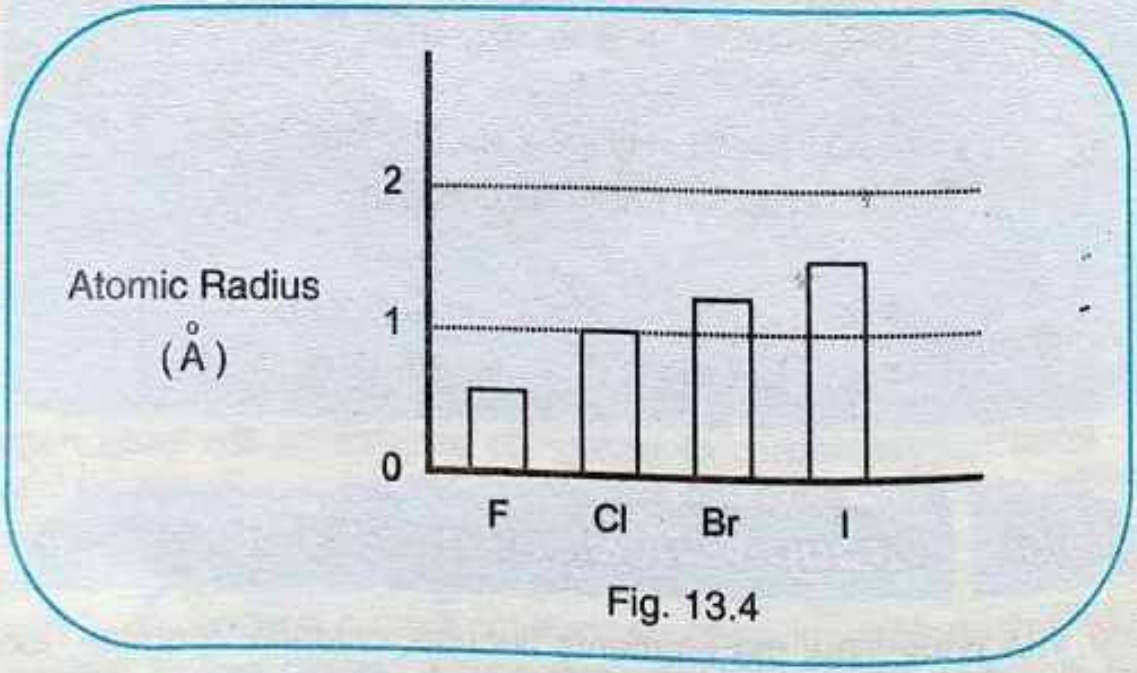


Fig. 13.4

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.5.1.2 Trends in Electronegativity :-

It is usually measured on Pauling scale, on which Flourine is the most electronegative element having E.N value of 4.0. These values decrease gradually from F to I.

Elements	F	Cl	Br	I
Electronegativity	4.0	3.0	2.8	2.5

13.5.1.3 Trends in Electron Affinity :-

The trend down the group is not regular. The electron affinity of halogens decreases down the group with the exception of fluorine (F).

The electron affinity is the measure of the attraction between the incoming electrons and the nucleus. The higher the attraction the higher the electron affinity.

Elements	F	Cl	Br	I
Electron affinity (ev)	–3.7	– 4.0	– 3.8	– 3.4

13.5.1.4 Trends in melting and boiling points :-

The melting and boiling points increase down the group in group VII A of the periodic table. This trend is given below.

Elements	F	Cl	Br	I
M.pt ($^{\circ}C$)	–219.6	– 101.0	– 7.2	+ 113.7
B.pt ($^{\circ}C$)	–188.2	– 34.7	+ 59	+ 184

13.5.1.5 Bond Enthalpies:-

Bond enthalpy is the amount of heat needed to break one mole of covalent bonds to form individual atoms. It begins with the original substance in a gaseous state and ending with gaseous atoms.

$$Cl - Cl_{(g)} \xrightarrow{\Delta} 2Cl_{(g)}$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.5.1.5.1 Bond Enthalpy in halogens:-

Bond enthalpy is the energy required to break a chemical bond. The exact bond enthalpy of a particular chemical bond depends upon the molecular environment in which the bond exists. Bond breaking is an endothermic process and bond enthalpy involved is given +ive sign.

The following table illustrates the Halogen-Halogen bond enthalpies.

Bond	Bond length (nm)	Bond enthalpy (kJ/mol)
F – F	0.142	158
Cl – Cl	0.199	242
Br – Br	0.228	193
I – I	0.267	151

The abnormal behaviour in F – F bond is due to its smaller size and high repulsion between nuclei of fluorine atoms.

13.5.1.5.2 Bond Enthalpies in Hydrogen Halides:-

As the halogen atoms get bigger down the group, the bonding pair electrons get more and more distant from the nucleus, so attraction becomes less and the bond becomes weaker. The bond enthalpy is important in the thermal stability of Hydrogen halides.

H – I is easily decomposed into its components by plunging a red hot wire into a test tube of the gas.H–Br may or may not decompose depending on the exact temperature of the wire.

H – F and H – Cl are very stable to heat and they do not decompose. Bond enthalpies of halides are given in table.

Stronger bond ↑ less easily decomposed

Bond	Bond enthalpies(kJ/moles)
H – F	568
H – Cl	432
H – Br	366
H – I	298

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.5.2 Strength of Halogens as oxidizing agents:-

When halogens combine with a metal or non-metal they normaly act as oxidizing agents. The element with which they react has +ive oxidation number in resultant compounds e.g. when halogens combine with a metal to form ionic compounds, they gain electron from metal to form –ive halide ions.

$$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2Na^{+}Cl^{-}{}_{(s)}$$

The halogen accepts electron during the above reaction and acts as oxidizing agent. Fluorine is the most reactive halogen and most powerful oxidizing agent.

The order of decreasing power as oxidizing agent is $F_2 > Cl_2 > Br_2 > I_2$

The electrode potential of halogens become less positive from F to I which reflects decreasing oxidizing power.

"F" and "Cl" are such powerful oxidizing agents that they can oxidize coloured dyes to colourless substances acting as oxidizing agents for bleaching.

When chlorine water is added to KI solution, the solution becomes brown. This is due to formation of Iodine.

$$2I^{-}{}_{(aq)} \longrightarrow I_{2(s)} + 2e^{-}$$

The "Cl_2" acts as oxidizing agent accepting electrons from "I_2" forming Cl^{-} Ions.

$$Cl_{2(g)} + 2e^{-} \longrightarrow 2Cl^{-}{}_{(aq)}$$

Chlorine can oxidize I^{-} to I_2 and Br^{-} to Br_2.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13.5.3 The Acidity of Hydrogen Halides:-

According to Bronsted and Lowery definition acid is a proton donor. HCl is an acid because it gives proton to other substances HCl, HBr and HI are strong acids, while HF is a weaker acid. HCl is soluble in water and produce H_3O^+ and Cl^- ions.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

This reaction shows that HCl completely dissociates in water and is a strong acid.

HBr and HI dissolve in water in exactly the same way as HCl. By contrast although HF dissolves freely in water yet it is a weak acid.

13.5.4 Halide Ions as Reducing Agents and Trends in Reducing Strength of Halide Ions:-

As reducing agents halide ions show the following trend in reducing strength:

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

Larger the size of the halide ion, the stronger, it is as reducing agent. For example, Br^- reduces sulphuric acid to SO_2. There is a decrease of oxidation state of sulphur from "+6" in H_2SO_4 to "+4" in SO_2.

$$H_2\overset{+6}{S}O_4 + 2H^+ + 2Br^- \rightarrow Br_2 + \overset{+4}{S}O_2 + 2H_2O$$

'I^-' is stronger reducing agent than "Br^-".

$$H_2\overset{+6}{S}O_4 + 8H^+ + 8I^- \rightarrow 4I_2 + H_2\overset{-2}{S} + 4H_2O$$

Scanned with CamScanner

SST

Society, Technology and Science

Bleaching powder is white amorphous powder which smells strongly like chlorine. Bleaching powder is frequently called "Bleach". It is oxidizing agent. This property is due to the hypochlorite ion, which takes up two electrons from the substance undergoing oxidation.

$$CaOCl_2 + H_2SO_4 \longrightarrow CaCl_2 + CaSO_4 + 2HClO$$

$$HClO \longrightarrow HCl + [O]$$

$$\text{Coloured matter } [O] \longrightarrow \text{Colourless product.}$$

The formation of nascent oxygen gives the oxidizing or bleaching properties. Bleaching powder is used for beaching cotton, linen and wood pulp. It is used as disinfectant and germicide. It is also used for manufacture of chloroform. Severe iodine deficiency results in impaired thyroid hormone synthesis or thyroid gland enlargement (goiter).

Iodine is chemical element. It is found in traces amounts in the human body, in which its only function is the synthesis of thyroid hormone.

Worldwide, the soil in large geographic areas is deficient in iodine. Twenty-nine percent of the world population, living in approximately 130 countries is estimated to live in the areas of deficiency. This occurs primarily in mountainous regions such as Himalayas, the European Alps and Andes.

Poor nutrition enhances the toxicity of fluorides. As discussed below, nutrient deficiencies have been specifically linked to increased susceptibility to fluoride induced tooth damage, bone damage. Fluoride deficiency may lead to increased cavities, weak bones and teeth.

Halogens are commercially used in halogen lamps formation, glass etching, Tincture of iodine, water fluorination, fluorides in toothpaste, dry cleaning, refrigerants, agriculture fumigant.

Aluminium is used in coming because it is light, non-toxic, resistant to corrosion. Steel is wonderfully hydenic and durable alloy, which is the material of choice in industries as diverse as processing of milk and dairy products confectionary and cooked meat etc.

Scanned with CamScanner

KEY POINTS

Key Points:

- group IA and group IIA elements belong to s-block.
- group IIIA – VIIIA element belong to p-block.
- atomic radius of group II A increases down the group.
- atomic radius in third period decreases across the period but Ar does not follow the trend.
- electrical conductivity increases from Na to Al.
- phosphorus and sulphur do not react with water.
- Phosphorous react with oxygen and produces mixture of phosphorous (III) oxide and phosphorous (V) oxide.
- Oxides of Na and Mg are basic, while those of Al are amphoteric and oxides of rest of the elements in third period are acidic oxide.
- All the oxides of groups I A react with water to produce hydroxide, peroxide and superoxide.
- Most of the nitrates of group I elements decompose on heating and produce metal oxides, nitrogen dioxide and oxygen.
- Group I-A bicarbonates are solid which easily decompose on heating.
- The electronegativity of group II-A elements decrease from Be to Ba.
- Group II-A metals react slowly with water liberating hydrogen and forming hydroxides.
- All the metals of group II-A react with oxygen and form simple oxide.
- The solubility of hydroxide in water increase from $Be(OH)_2$ to $Ba(OH)_2$.

Scanned with CamScanner

EXERCISE

Exercise

Q.1 Choose the correct answer from the given choices in each case.

(i) Electronegativity of Be is approximately equal to that of

(a) Al (b) Mg

(c) B (d) Na

(ii) The word Alkali means

(a) Base (b) Basic salt

(c) Ashes (d) spirit

(iii) The elements which are most abundant in earth crust.

(a) Si & Al (b) Ca & Mg

(c) B & Ar (d) All

(iv) Carbonates of Li are not stable like that of sodium due to

(a) Low electronegativity

(b) Low electropositivity

(c) High charge density of Li^+

(d) All of the above

(v) Which one of the following is not an alkali metal?

(a) Fr (b) Cs

(c) Rb (d) Ra

(vi) Which one of the following metal sulphates is not soluble in water?

(a) Na_2SO_4 (b) K_2SO_4

(b) $BaSO_4$ (d) $ZnSO_4$

Scanned with CamScanner

(vii) Which one of following alkali metal forms only normal oxide with O_2?

(a) Li (b) K
(c) Na (d) Rb

(viii) Strongest reducing agent among the halogens is

(a) Cl_2 (b) F_2
(c) Br_2 (d) I_2

(ix) Which one of the following has lowest electron affinity?

(a) F (b) I
(c) Cl (d) Br

(x) Which is the highest melting halide?

(a) NaCl (b) NaBr
(c) NaF (d) NaI

(xi) The highest boiling point of HF amongst the hydrogen halides is due to

(a) Lowest electronegativity of F
(b) Highest electronegativity of F
(c) Lowest atomic weight of F
(d) Lowest atomic radius of F

(xii) The dry ice is

(a) Solid ice without water (b) Solid CO_2
(c) Solid SO_2 (d) Solid C_6H_6

(xiii) Which one of the following is acidic in nature?

(a) Al_2O_3 (b) CO_2
(c) CO (d) CaO

Scanned with CamScanner

(xiv) Third period element that initially reacts rapidly with oxygen to form a protective oxide coating that prevents further reaction is.
(a) Na (b) Al
(c) Si (d) Mg

(xv) The yellow flame shown by sodium in Bunsen flame is due to excitation of electron.
(a) 2p to 3s (b) 3p to 1s
(c) 4p to 4s (d) 5p to 4s

(xvi) When sodium is heated with excess of O_2, which of the following is formed?
(a) NaO (b) NaO_2
(c) Na_2O (d) None of these

(xvii) Which of the following has a greater affinity for oxygen?
(a) B (b) Na
(c) K (d) Mg

(xviii) Which of the following is the strongest base?
(a) $Si(OH)_4$ (b) $Be(OH)_2$
(c) $Mg(OH)_2$ (d) $Al(OH)_3$

(xix) The inert pair effect dominates in
(a) Pb (b) Sn
(c) C (d) Si

(xx) Those elements of group IV-A which have no tendency to form a dichloride are
(a) C and Si (b) P and Sn
(c) Ga and C (d) Sn and Si

Scanned with CamScanner

Q2- Short questions:

(i) Explain reaction of magnesium with H_2O

(ii) Why the NaCl does not conduct electricity in solid state?

(iii) Rubidium is below potassium in Group I-A. Predict how it will react with.
- (a) Water
- (b) Chlorine

And describe the products.

(iv) Why halogens are so reactive?

(v) What is flame test?

(vi) Write down any four characteristics of group II-A elements.

(vii) Explain the thermal stability of nitrates and carbonates of group II-A elements.

(viii) Why carbonates of group I-A elements are more thermally stable than those of group II-A?

(ix) Why Beryllium is differs from the members of its group?

(x) Explain the structure and stability of chlorides of group IV-A elements.

(xi) Why Fluorine is stronger oxidizing agent than chlorine?

(xii) Why $BeCl_2$ is covalent and not ionic?

(xiii) Explain the amphoteric nature of Be $(OH)_2$.

(xiv) Why the atomic radius of Argon is larger than all the member of third period?

(xv) Why fall in ionization energy occurs at Al and S in same period?

(xvi) Why the compounds of Sn^{4+} are covalent in nature while those of Sn^{2+} are ionic?

Q3 Long Questions

(i) Explain halide ions as reducing agents and discuss their trends in reducing strength.

(ii) Discuss the atomic and physical properties of halogens.

(iii) What is meant by bond enthalpy? Explain the bond enthalpies in halogens and hydrogen halides.

Scanned with CamScanner

(iv) Discuss physical properties of Group-IVA elements.
(v) Discuss oxides of carbon family and explain inert pair effect in formation of ionic and covalent bond.
(vi) Discuss in detail acid base behavior of Group IV-A oxides.
(vii) What are the trends in thermal stability of nitrates and carbonates of Group II-A elements?
(viii) Write down atomic and physical properties of group I-A and group II-A elements.
(ix) How peroxides, simple acids and nitrates of Group II-A elements are formed?
(x) Explain the reaction of Group II-A elements with oxygen.
(xi) Explain trends in reactivity of Group I-A elements with water.
(xii) Explain the properties of Hydroxide of third period elements.
(xiii) Explain the acid base behavior of oxides of third period elements.
(xiv) What is meant by inert pair effect? Explain inert pair effect in formation of ionic and covalent bond.

Scanned with CamScanner

UNIT 14

d and f -Block Elements

Learning Outcomes:

After Studying this unit Students will be able to:

- Describe electronic structures of elements and ions of d-block elements.
- Explain why the electronic configurations for chromium and copper differ from those assigned using the Aufbau principle.
- Describe important reactions and uses of Vanadium, Chromium, Manganese, Iron and Copper.
- Explain shapes, origin of colors, nomenclature of coordination compounds.
- Relate the coordination number of Atoms/ions to the crystal structure of the compound of which they are a part.
- Define an alloy and describe some properties of an alloy that are different from the metals that compose it.
- Describe the reactions of potassium dichromate with oxalic acid and Mohr's salt.
- Describe the reactions of potassium permanganate (VII) with ferrous sulphate, oxalic acid and Mohr's salt.
- Calculate the concentration of Iron (II) in solution with $KMnO_4$
- Explain the reaction of hexa aquacopper (II) ions with iodide and determine the concentration of copper (II) ions in the solution.
- To understand the important transition elements and their characteristics.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Introduction:

Transition elements are those elements which have partially filled d or f orbitals either in their atomic or in any common oxidation states. They are located between s and p block elements in the periodic table. The transition elements, for the sake of convenience, may be divided into two main categories.

a. The main transition elements or the 'd' block elements.
b. The 'f' block elements (Inner transition elements)

We will discuss the main transition elements only.

The main transition elements

These elements have partially filled (n-1) d orbitals in the ground state of their free atom or at least in one of their common ions. They are commonly known as d block elements and are further subdivided into four transition series.

i. The first transition series: This includes the elements from scandium(^{21}Sc) to copper (^{29}Cu).These elements have partially filled 3d orbitals.

ii. The second transition series: This includes nine elements starting from Yttrium (^{39}Y)to silver (^{47}Ag).These elements have partially filled 4d orbitals.

iii. The third transition series: This series includes the elements Lanthanum (^{57}La) and elements from Hafnium (^{72}Hf) to Gold (^{79}Au),all of which have partially filled 5d orbitals.

iv. The fourth transition series: This is incomplete transition series. It includes elements Actinium (^{89}Ac) and Rutherfordium

Scanned with CamScanner

(^{104}Rf) to Meitnerium (^{109}Mt).These elements have partially filled 6d 0rbitals.

Table 14.1 Transition elements series

I	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
II	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
III	La	Hf	Ta	W	Re	Os	Ir	Pt	Au
IV	Ac								

14.1 General Features

14.1.1 General Features of Transition Elements

1. They are all hard metals and have high melting and boiling points. This is due to high nuclear charge and small atomic radius.
2. They are good conductors of heat and electricity.
3. Most of these elements show variable valencies or oxidation states. This is due to fact that in addition to the outermost "s" electrons, transition elements can use (n–1) d electron, ((n–1)d and 'ns' electrons of comparable energy) in bond formation. So varying number of electrons can take part in bond formation leading to variable valencies.
4. Their compounds are mostly coloured in solid state and in solution. Colour is due to the incomplete "d" orbitals in which electronic transition is possible.
5. Some of these elements form paramagnetic compounds because of the presence of unpaired electrons.
6. They have the ability to form complexes because of the involvement of vacant d- orbitals.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

7 They form alloys with the d and f- block elements and also with the elements of other blocks.

14.1.2 Electronic structure

When we build up the electronic configurations of the atoms, we find that each transition metal series results from the belated filling of an inner subshell of electrons. Thus the first series (fourth period) corresponds to the filling of 3d subshell as shown in table 14.2. The "pre-transition" element calcium (Z=20) has an [Ar] $4s^2$ configuration. Scandium (Z=21), the first transition metal in this series, has the configuration [Ar] $3d^1$ $4s^2$. Addition of electrons to the 3d subshell continues until, at Zinc (Z=30), the 3d subshell is filled, with the 4s subshell still containing two electrons, as it did with calcium: [Ar] $3d^{10}$ $4s^2$. This transition from an empty 3d subshell to a filled one occurs with only two irregularities, one at Chromium (Z=24) and the other at Copper (Z=29).

The second, third and fourth transition metal series correspond to the filling of the 4d, 5d and 6d subshells respectively. The general valence shell electronic configuration of atoms of d-block elements may be written as

$$(n-1)d^{1-10}\ ns^{0,1,2}$$

In the lanthenides (^{58}Ce to ^{70}Yb) and Actinides (^{89}Ac to ^{103}Lw) series valence shell electron goes to "4f" and "5f" orbitals respectively.

The atomic and ionic radii of the first transition series (3-d block elements) decrease slightly from left to right in a period. This gradual decrease is due to the increase in nuclear charge, which results in greater attractive force between the nucleus and the outer electrons. Copper the

Scanned with CamScanner

last member of the transition series, shows a slight increase in atomic radius, which is the result of repulsion between the outer electrons. The atomic and ionic radii are given in table 14.2.The transition metals have high density because they possess greater mass to volume ratio.

Table 14.2 Electronic configuration and physical properties of transition metals

Elements	Atomic number	Electronic configuration	Atomic radius/nm	Ionic radius/nm	Density at 298K gm/cm3	E.N	Melting point °C	I.P kJ/mol
Sc	21	.....$3s^2,3p^6,3d^1,4s^2$	144	.81	2.99	1.2	1530	630
Ti	22	.....$3s^2,3p^6,3d^2,4s^2$	132	.76	4.54	1.3	1680	660
V	23	.....$3s^2,3p^6,3d^3,4s^2$	122	.74	6.11	1.45	1917	650
Cr	24	.....$3s^2,3p^6,3d^5,4s^1$	117	.69	7.19	1.55	1890	650
Mn	25	.....$3s^2,3p^6,3d^5,4s^2$	117	.66	7.42	1.6	1247	720
Fe	26	.....$3s^2,3p^6,3d^6,4s^2$	116	.64	7.87	1.65	1535	760
Co	27	.....$3s^2,3p^6,3d^7,4s^2$	116	.63	8.90	1.7	1490	760
Ni	28	.....$3s^2,3p^6,3d^8,4s^2$	115	.62	8.90	1.75	1452	740
Cu	29	.....$3s^2,3p^6,3d^{10},4s^1$	115	.66	8.94	1.75	1083	750

14.1.3 Binding Energy

Transition metals are generally tough having great mechanical strength due to strong metallic bonding. This is because, apart from s-electrons of the outermost shell, the unpaired electrons of underlying d-orbitals also participate in bonding.

In moving from left to right in any transition series, the number of unpaired electrons increases up to group VB and VIB, after that pairing takes place and the number of unpaired electrons goes on decreasing until it becomes zero at group IIB. Therefore, binding energy increases up to group VIB and then progressively decreases up to group IIB. For example in 3d series binding energy increases up to Vanadium and then decreases up to Zinc.

Scanned with CamScanner

14.1.4 Variable Oxidation states

Most of the transition metals show several oxidation states in their compounds. The cause of showing different oxidation states is that in addition to using electrons in the outermost sub-shell namely "ns", a variable number of inner (n–1)d electrons can also be used in bond formation.

The common oxidation states of each element include +2 or +3 or both. However +3 state is more common at the beginning of series and +2 state is more common at the end of series as shown in table 14.3.

Element Name and Symbol	Atomic Number	Common Oxidation States	Electron Configuration	
Scandium (Sc)	21	+3	Sc: [Ar] $4s^2 3d^1$	Sc: [Ar] $\underset{4s}{\uparrow\downarrow}$ $\underbrace{\uparrow \_ \_ \_ \_}_{3d}$
Titanium (Ti)	22	+4	Ti: [Ar] $4s^2 3d^2$	Ti: [Ar] $\underset{4s}{\uparrow\downarrow}$ $\underbrace{\uparrow \uparrow \_ \_ \_}_{3d}$
Vanadium (V)	23	+2, +3, +4, +5	V: [Ar] $4s^2 3d^3$	V: [Ar] $\underset{4s}{\uparrow\downarrow}$ $\underbrace{\uparrow \uparrow \uparrow \_ \_}_{3d}$
Chromium (Cr)	24	+2, +3, +6	Cr: [Ar] $4s^1 3d^5$	Cr: [Ar] $\underset{4s}{\uparrow}$ $\underbrace{\uparrow \uparrow \uparrow \uparrow \uparrow}_{3d}$
Manganese (Mn)	25	+2, +3, +4, +6, +7	Mn: [Ar] $4s^2 3d^5$	Mn: [Ar] $\underset{4s}{\uparrow\downarrow}$ $\underbrace{\uparrow \uparrow \uparrow \uparrow \uparrow}_{3d}$
Iron (Fe)	26	+2, +3	Fe: [Ar] $4s^2 3d^6$	Fe: [Ar] $\underset{4s}{\uparrow\downarrow}$ $\underbrace{\uparrow\downarrow \uparrow \uparrow \uparrow \uparrow}_{3d}$
Cobalt (Co)	27	+2, +3	Co: [Ar] $4s^2 3d^6$	Co: [Ar] $\underset{4s}{\uparrow\downarrow}$ $\underbrace{\uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \uparrow}_{3d}$
Nickel (Ni)	28	+2	Ni: [Ar] $4s^2 3d^7$	Ni: [Ar] $\underset{4s}{\uparrow\downarrow}$ $\underbrace{\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow}_{3d}$
Copper (Cu)	29	+2	Cu: [Ar] $4s^1 3d^{10}$	Cu: [Ar] $\underset{4s}{\uparrow}$ $\underbrace{\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow}_{3d}$
Zinc (Zn)	30	+2	Zn: [Ar] $4s^2 3d^{10}$	Zn: [Ar] $\underset{4s}{\uparrow\downarrow}$ $\underbrace{\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow}_{3d}$

Table 14.3

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The highest oxidation state from Sc^{+3} to Mn^{+7} corresponds to the involvement of all the electrons outside the Argon core. After this the increasing nuclear charge binds the d-electrons more tightly, so onward from Fe to Zn only the weakly held electrons of "4s" subshell are involved in oxidation state.

14.1.5 Catalytic properties

Most of the transition metals and their compounds are used as catalyst. Some common examples are Pt, Ni, Fe, Cr, V_2O_5 etc. Catalytic property of these elements is due either to the use of their d-orbital or the formation of interstitial compounds which absorb and activate the reacting substances.

Transition metals have variable oxidation states and hence are capable of forming intermediate compounds which help in the formation of desired product e.g. finely divided Iron is used as a catalyst in Haber Bosch process for the synthesis of ammonia. The application of V_2O_5, in the conversion of SO_2 to SO_3 for the manufacture of H_2SO_4 by contact process, the use of $TiCl_4$ in the polymerization of ethene to polythene polymer, the application of Ni, Pd or Pt in the catalytic hydrogenation of unsaturated hydrocarbons and the use of Cu in the oxidation of ethanol to acetaldehyde are examples of catalytic properties of transition elements.

14.1.6 Magnetic behaviour

Substances show two different types of behaviours when subjected to an external magnetic field. If a substance is weakly attracted by a strong magnetic field, it is called paramagnetic substance whereas a substance

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

weakly repelled by magnetic field is called diamagnetic substance.

Paramagnetic behaviour is due to the presence of one or more unpaired electrons in an atom, ion or molecule of the substance. The attraction is a result of interaction of magnetic field produced by spinning electron with the external field. In diamagnetic substances the electrons are paired up due to which magnetic field of oppositely spinning electrons cancel each other.

An extreme case of paramagnetism is called ferromagnetism as shown by Fe^{+3} and Mn^{+2} ions which have five unpaired electrons each.

14.1.7 Alloy Formation

Transition metals have another great characteristics that they easily mix with each other. This is because all the d-block metals have about the same atomic size. This allows them to replace one another easily in crystal lattice. When two or more metals mix or replace one another, we call the mixture an alloy.

Brass is a good example of alloy which is a mixture of copper and zinc. These elements and alloys are essential for the existence of life and also for of its progression through time. (Bronze age, Iron age etc.)

Some of the important alloys and their uses are shown in table 14.4.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Alloy	Composition	Uses
Brass	Cu= 60 – 80 % Zn = 20 – 40 %	Domestic utensils, cartridges, casting, condensers
Bronze	Cu = 75 – 90 % Sn = 10 – 25 %	Statues, coins, bells, blades, machine parts
Steel	Fe= 90 – 95 % C = 0.1 – 2 %	Cutlery, car bodies Bridge, utensils
Gold (18 carat)	Au = 70 – 75 % Cu = 20 – 25 %	Jewellery, Electrical devices. Tooth filling, statues.

Table 14.4

14.2 COORDINATION COMPOUNDS

14.2.1 Complex ion

Most transition elements can form complex ions, in which the metal ion is surrounded by groups of negative ions, or molecules for example if you add ammonia to a solution containing Cu(II) ions, a pale blue precipitate of Cu (II) hydroxide forms. It dissolves again if you add more ammonia, giving a deep blue solution, because a soluble complex ion forms.

In this complex, four ammonia molecules and two water molecules surround Cu^{+2} ion. Its formula is $[Cu(H_2O)_2(NH_3)_4]^{+2}$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

14.2.2 Nomenclature of coordination compounds

The coordination compounds are named according to the rules formulated by IUPAC. The rules are stated below:

1. The cation is named first, and then the anion, just like common salt as sodium chloride.

$[Cr(NH_3)_6](NO_3)_3$
Hexaamminechromium (III) nitrate

$K_2[PtCl_6]$
Potassium hexachloroplatinate (IV)

2. Nonionic complexes are given a one word name.

$[CO(NH_3)_3(NO_2)_3]$
Trinitrotriammine cobalt (III)

3. The names of neutral ligands are usually unchanged whereas names of negative ligands end in "o" and those of positive ligands end in "ium". Ligands of the same type are named in alphabetical order.

Cl^-	CH_3COO^-	$NH_2NH_3^+$	H_2O
chloro	acetato	hydrazinium	aqua

4. The ligands in a complex are named in order of negative, neutral and then positive without separation by hyphens.

$[Pt(NH_3)_4(NO_2)Cl]SO_4$ Chloronitrotetraammine platinum (IV) sulphate

5. The number of individual ligands is indicated by prefixes, mono, di, tri, tetra etc. The number of chelating ligands is named by prefixes bis, tris, tetrakis etc.

$[Co(NH_3)_4Cl_2]Cl$ Dichlorotetraamminecobalt (III) chloride

6. The oxidation state is indicated by a Roman numeral in parentheses after the name of central metal atom.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$Na_3 [Co (NO_2)_6]$	sodium hexanitrocobaltate (III)
$Na_3 [Fe (CN)_6]$	sodium hexacyanoferrate (III)

In cationic and neutral complexes the name of the metal remains the same. Whereas in anionic complexes the name of the metal is followed by ate e.g. Cr becomes Chromate, Fe, ferrate, Co Cobaltate, Cu Cuprate and Ag Argentate. Other examples are:

$K_3 [Fe(CN)_6]$	Potassium hexacyanoferrate (III)
$Na_2 [Fe (NO) (CN)_5]$	Sodium pentacyanonitrosylferrate (III)
$[Co (en)_2 Cl_2]$	Dichloro-Bis-ethylenediamine cobalt (II)

14.2.3 Shapes of complex ions

Coordination compounds have definite geometrical shapes because the bond formed between central metal atom and the ligands are directional in nature.

Hence, the ligands are arranged around central metal atom in a clear spatial geometry. This geometry depends on the number of ligands (coordination number) and type of hybridization taking place in central metal atom.

Complexes with coordination number four and six are very common. The former exists in two geometrical shapes, tetrahedral and square planar while those having coordination number six exist in octahedral shape.

Complexes having coordination number five are less common. These complexes exist in two main possible geometries i.e. trigonal bipyramidal and square pyramidal shapes.

Scanned with CamScanner

6-coordinated complex ions

These are complex ions in which the central metal ion is forming six co-ordinate covalent bonds or in simple words the central metal ion is attached to six ligands.

These ions have an ***octahedral*** shape. Four of the ligands are in one plane, while the fifth one lying above and the sixth one below the plane.

The diagram shows four fairly random examples of octahedral ions.

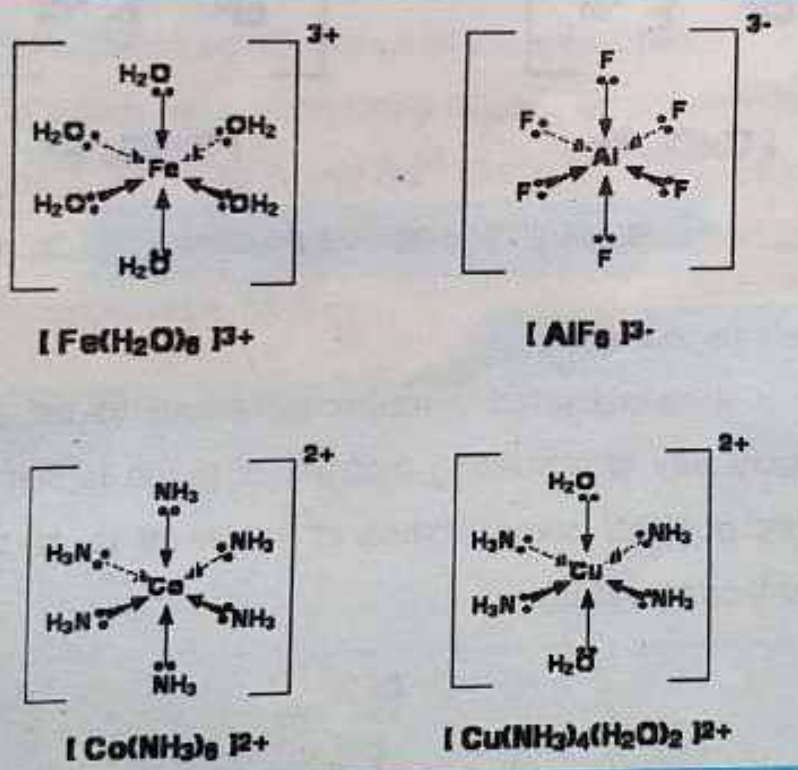


Fig 14.1 Different geometrical shapes of complexes

4-co-ordinated complex ions

These are far less common, and they can take up one of two different shapes.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Tetrahedral ions

The copper(II) and cobalt(II) ions have *four* chloride ions bonded to them rather than six, because the chloride ions are too big to fit any more around the central metal ion.

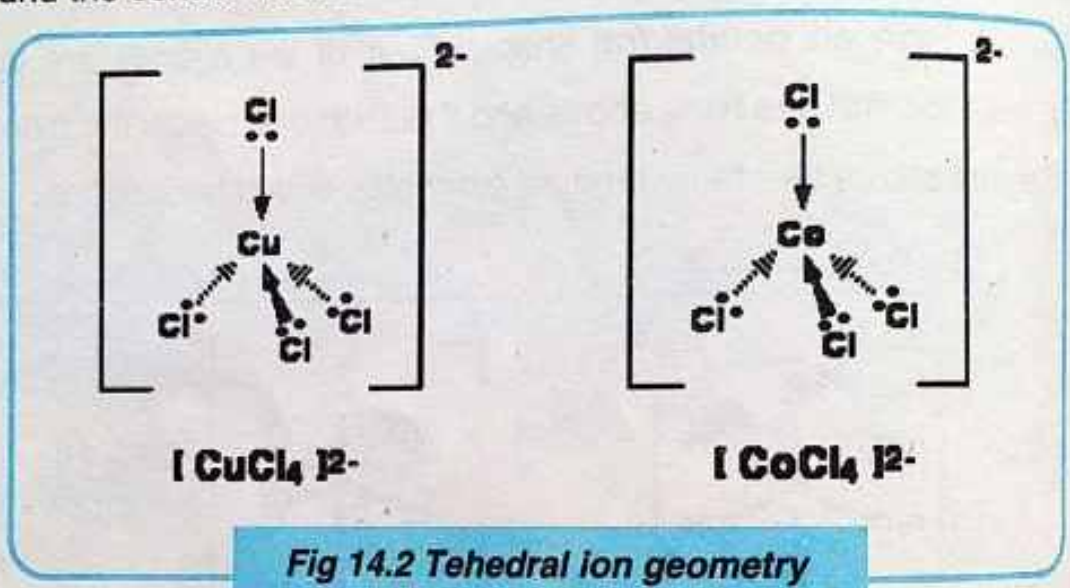


Fig 14.2 Tehedral ion geometry

A square planar complex

Occasionally a 4-co-ordinated complex turns out to be square planar. There's no easy way of predicting that this is going to happen. The only one you might possibly come across at this level is ***cisplatin*** which is used as an anti-cancer drug.

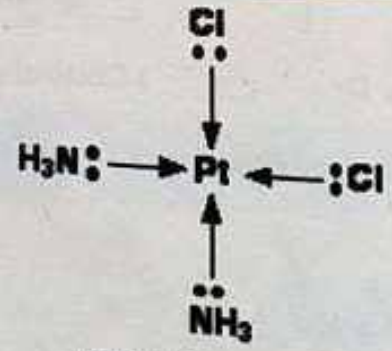


Fig 14.3 Square planar complex

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

14.2.4 Colours of complexes

Most of the compounds of the transition metals are coloured in solid or solution state. The colour of the transition metal ions is due the presence of unpaired electrons or incomplete d-orbitals. When light is allowed to fall on a substance, it absorbs from it the light of a particular colour whose wavelength is in the visible region (4000 – 7000 Å) and reflects the remaining light which has the colour complementary to that of the absorbed light. This complementary colour which is actually the colour of reflected light becomes the colour of the substance.

The ions which have completely filled or empty d-orbitals are colourless e.g. Cu^{+} ($3d^{10}$), Zn^{+2} ($3d^{10}$) and Sc^{+3} ($3d^{\circ}$), Ti^{+4} ($3d^{\circ}$) are colourless.

Colours of hydrated cations of the elements of first transition series is given in following table 14.5.

Ion	Outer configuration	No. of unpaired electrons	Colour
Sc^{3+}	$3d^0$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple
Ti^{4+}	$3d^0$	0	Colourless
Cr^{3+}	$3d^4$	4	Blue
Mn^{2+}	$3d^5$	5	Green
Fe^{3+}	$3d^5$	5	Yellow
Co^{2+}	$3d^6$	4	Blue
Ni^{2+}	$3d^8$	2	Green
Cu^{2+}	$3d^9$	1	Blue
Zn^{2+}	$3d^{10}$	0	Colourless

Table 14.5

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

14.3 Chemistry of some important Transition Elements

14.3.1 VANADIUM

I. INTRODUCTION

Vanadium, symbol V, silvery-white metallic element with an atomic number of 23. It was discovered in 1801 in Mexico by Andrés Manuel del Rio, but it was mistaken for a form of chromium. Vanadium was rediscovered in about 1830 by the Swedish chemist Nils Gabriel Sefström. The element was named after Vanadis, goddess of beauty and love in Scandinavian mythology.

14.3.1.1 Oxidation States

The oxidation state of an element is related to the number of electrons that an atom loses or gains or appears to use when joining with another atom in compounds. It also determines the ability of an atom to oxidize or to reduce other atoms or species. Almost all the transition metals have multiple potential oxidation states. Oxidation states of atoms depend upon unpaired electrons in d-orbitals.

Compounds of vanadium in +5, +4, +3 and +2 oxidation states are important. The compounds in the lower oxidation states are good reducing agents. They are also ionic in character and on account of incomplete electron shell they are also coloured. The compounds in the higher oxidation states are generally colourless due to the empty electron shell. When a colourless compound of V^{+5} ($3d^0\ 4s^0$) is reduced by suitable reducing agent, it first turns blue VO^{+2} ($3d^1 4s^0$), then green V^{+3} ($3d^2 4s^0$) and finally violet V^{+2} ($3d^3 4s^0$). Vanadium also shows +1,0,–1 oxidation

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

states in the compounds $[V(dipy)_3]^{+1}$, $V(CO)_6$ and $[V(CO)_6]^{-1}$ respectively.

14.3.1.2 As Catalyst in Contact process

The contact process is the common method of producing sulfuric acid in high concentrations needed for industrial processes. Platinum was formerly employed as a catalyst for the reaction, but as it is susceptible to poisoning by arsenic impurities in the sulfur feedstock, vanadium oxide (V_2O_5) is now preferred.

(V_2O_5) is used as catalyst in various oxidation reactions involving the use of O_2 as the oxidizing agent e.g. conversion of SO_2 to SO_3 in the manufacture of H_2SO_4.

$$2SO_{2(g)} + O_{2(g)} \overset{V_2O_5}{\rightleftharpoons} 2SO_{3(g)}$$

V_2O_5 is also used in the oxidation of alcohols and hydrogenation of olefins.

14.3.2 Chromium

Introduction to Chromium

Chromium, symbol Cr, atomic number 24 is a shiny metallic element. Being brilliant, hard, and corrosion-resistant, chromium makes a durable and attractive coating for other metals and is an important component of stainless steel.

The element was discovered in 1797 by the French chemist Louis Nicolas Vauquelin, who named it chromium (Greek *chroma*, "color") because it forms a large number of coloured compounds.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Chromium is a common element; overall it ranks about 21st in natural abundance among the elements in earth crust. Chromium has an atomic weight of 51.996; the element melts at 1907°C (3465°F), boils at 2672°C (4842°F), and has a specific gravity of 7.2.

Chromium is not found native. Its most common minerals are chromite or chrome iron stone ($FeO.Cr_2O_3$). It is also found as chrome ochre (Cr_2O_3) and crocite ($PbCrO_4$). Large quantities of chrome iron stone are found in Rhodesia, Transvaal, Turkey, Russia, India and Pakistan.

14.3.2.1 Oxidation States

The important and stable compounds of chromium are those in which chromium has +6, +3 and +2 oxidation states. The element in +3 oxidation state is most stable and hence Cr(+2) compounds are strong reducing agents while those of Cr(+6) are strong oxidizing agents.

With the increase in oxidation state of the element,

(a) The acidic character of oxides increases with increasing oxidation state.

Oxides:	CrO	Cr_2O_3	CrO_3
Oxidation state of Cr	+2	+3	+6
Nature	Basic	Amphoteric	Acidic

(b) Similarly the covalent character of the compounds also increases. Thus Cr(+2) compounds are ionic, Cr(+3) compounds ionize to some extent while those of Cr(+6) are covalent.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The compounds in which chromium shows +6 oxidation state are chromium trioxide (CrO_3), potassium chromate (K_2CrO_4) and Potassium dichromate ($K_2Cr_2O_7$).

Cr(+3) compounds are also called chromic compounds. These may be considered derived from chromic oxide, Cr_2O_3. These are formed either by oxidation of Cr(+2) or by reduction Cr(+6) compounds such as chromate or dichromate. Examples of chromic compounds are chromic chloride ($CrCl_3$), chromic sulphate ($Cr_2(SO_4)_3.18H_2O$).

Cr(+2) compounds are called chromous salts. These salts are unstable and tend to oxidize on exposure to air into corresponding Cr(+3) compound. Some of chromous salts are, $CrCl_2$, CrS, $CrSO_4.7H_2O$, $CrCO_3$ etc.

14.3.2.2 The Chromate - Dichromate Equilibrium

When solid potassium chromate, K_2CrO_4 is dissolved in water it forms a yellow solution. When solid potassium dichromate, $K_2Cr_2O_7$ is dissolved in water the resulting solution is orange. The colors come from the negative ions: $CrO_4^{2-}(aq)$ and $Cr_2O_7^{2-}(aq)$. However, in solution these ions are actually in equilibrium as indicated by the equation:



Figure 14.4

$$2\,CrO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \rightleftharpoons Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)}$$

This is dynamic equilibrium and sensitive to the acidity and basicity of solution. According to Le-Chatelier's principle, the addition of acid to the

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

reactant shifts the equilibrium towards right and yields more dichromate (orange). On the other hand, the addition of base promotes the conversion of dichromate to chromate.

$$\underset{\text{yellow}}{CrO_4^{-2}} \rightleftharpoons \underset{\text{orange}}{Cr_2O_7^{-2}}$$

14.3.2.3 Reduction of Chromate (VI) ions with Zn and an Acid :-

Dichromate VI ions (for example, in Potassium dichromate (VI) solution) can be reduced to Chromium (III) ions Chromium (II) ions using Zinc and either dilute Sulphuric acid or Hydrochloric acid. The equations for the two stages of the reaction are:

For the reduction from +6 to +3

$$Cr_2O_7^{2-} + 14H^+ + 3Zn \longrightarrow 2Cr^{3+} + 7H_2O + 3Zn^{2+}$$

For reduction from +3 to +2

$$2Cr^{3+} + Zn \longrightarrow 2Cr^{2+} + Zn^{2+}$$

14.3.2.4 Potassium Dichromate(VI) as an oxidizing agent in organic chemistry:

Potassium dichromate (VI) solution acidified with dilute sulphuric acid is commonly used as an oxidising agent in organic chemistry.

For example

It oxidise secondary alcohols to ketones

$$\underset{\text{Secondary alcohol}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-H} + [O] \xrightarrow[\text{Con. } H_2SO_4]{K_2Cr_2O_7} \underset{\text{Ketone}}{CH_3-\overset{\overset{O}{||}}{C}-CH_3} + H_2O$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

In case of primary alcohol

$$CH_3CH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} H-\overset{\overset{O}{\|}}{C}-H + H_2O$$

Primary alcohol — Formaldehyde

Formaldehyde is further oxidized to formic acid, under the above condition.

$$H-\overset{\overset{O}{\|}}{C}-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} H-\overset{\overset{O}{\|}}{C}-OH$$

Formaldelyde — Formic Acid

Tertiary alcohols are not oxidized by potassium dichromate.

14.3.2.5 Potassium Dichromate as an oxidizing agent in titrations:

In redox titration a standard solution of potassium dichromate ($K_2Cr_2O_7$) is used to determine the unknown concentration of a solution of Fe^{+2}.

Dichromate ion reduces to chromium(III) ions.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$$

Fe(II) is oxidized to Fe(III)

$$6Fe^{+2} \rightarrow 6Fe^{+3} + 6e^-$$

Therefore, 1 mole of $Cr_2O_7^{-2}$ (the oxidizing agent) reacts with 6 moles of Fe^{2+} (the reducing agent) to form 6 moles of Fe^{3+} and 2 moles of Cr^{3+}.

Thus, in net ionic form:

$$\underset{\text{orange}}{Cr_2O_7^{-2}} + 6Fe^{2+} + 14H^+ \rightarrow 6Fe^{+3} + \underset{\text{green}}{2Cr^{+3}} + 7H_2O$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The molecular form of the equation can be written as:

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + 7H_2O$$

The 1:6 mole ratio with respect to the amounts of $Cr_2O_7^{-2}$ and Fe^{2+} is consumed.

14.3.3 Manganese:

Manganese, symbol Mn, is silvery white, brittle metallic element used principally in making alloys. Manganese is one of the transition elements of the periodic table. The atomic number of manganese is 25.

Manganese was first isolated in 1774 by the Swedish chemist Johan Gottlieb Gahn. Manganese metal corrodes in moist air and dissolves in acid. The element melts at 1245°C (2271°F), boils at 2061°C (3742°F), and has a specific gravity of 7.4. Its atomic weight is 54.938.

Manganese does not occur in the free state, except in meteors, but is widely distributed over the world in the form of ores, such as pyrolusite, rhodochrosite, franklinite, psilomelane, and manganite. The principal ore is pyrolusite. The element's name comes from the Latin word *magnes*, "magnet" and was chosen because pyrolusite is magnetic. Manganese ranks about 12th in abundance among elements in Earth's crust. Ukraine, Georgia, and South Africa are important producers of manganese.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

14.3.3.1 Oxidation State of Manganese:

In accordance with electronic configuration of manganese ($3d^5 4S^2$). It shows a maximum oxidation state of +7. In addition to this state it also shows lower oxidation state such as +6, +4, +3 and +2.

Manganese compounds where 'Mn' is in oxidation state +7, which are restricted to the unstable oxide Mn_2O_7 and compounds of intensely purple permanganate ion (MnO_4^{-1}) are powerful oxidizing agents.

Mn^{+6} is present in MnO_3 in the salt of Manganic acid (H_2MnO_4). The free acid is unknown. Its salts are called manganates e.g. K_2MnO_4. The compounds having Mn^{+4} are very limited in number. The most familiar compound of Mn^{+4} is MnO_2. The compound of Mn^{+3} is called manganic compound. In aqueous solution Mn^{+3} ion is quite unstable since it is easily reduced to Mn^{+2} ions e.g.

$$H_2Mn_2O_4, Mn_2(SO_4)_3$$

$$Mn^{+3} + 1e^- \rightarrow Mn^{+2}$$

Mn^{+2} is the most stable oxidation state of Mn in neutral or acidic solution. Mn^{+2} ion exist as pale pink hexaaqua $[(Mn(H_2O)_6]^{+2}$ which is quite stable to oxidation. The stability of Mn^{+2} is due to half filled 3d-orbital. The compounds of Mn^{+2} are called manganous compounds such as

MnO, $MnCO_3$, $MnSO_4$, $MnCl_2$.

14.3.3.2 Potassium permanganate (VII) as an oxidizing agent in organic chemistry:

Alkenes react with potassium permanganate(VII) solution in the cold. The colour change depends on whether potassium manganate(VII) is used under acidic or alkaline conditions.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Manganate(VII) ion is strong oxidising agent, and in the first instance oxidise ethene to ethane-1,2-diol (old name: ethylene glycol).

Under acidic conditions, the permanganate (VII) ions are reduced to manganese(II) ions.

$$5CH_2{=}CH_2 + 2H_2O + 2MnO_4^- + 6H^+ \longrightarrow 5\underset{\underset{OH}{|}}{CH_2}\text{-}\underset{\underset{OH}{|}}{CH_2} + 2Mn^{2+}$$

Under alkaline conditions, the permanganate(VII) ions are first reduced to green manganate(VI) ions . . .

$$CH_2{=}CH_2 + 2MnO_4^- + 2OH^- \longrightarrow \underset{\underset{OH}{|}}{CH_2}\text{-}\underset{\underset{OH}{|}}{CH_2} + 2MnO_4^{2-}$$

dark green solution

. . . and then further to dark brown solid manganese(IV) oxide (manganese dioxide).

$$3CH_2{=}CH_2 + 2MnO_4^- + 4H_2O \longrightarrow 3\underset{\underset{OH}{|}}{CH_2}\text{-}\underset{\underset{OH}{|}}{CH_2} + 2MnO_2 + 2OH^-$$

dark brown precipitate

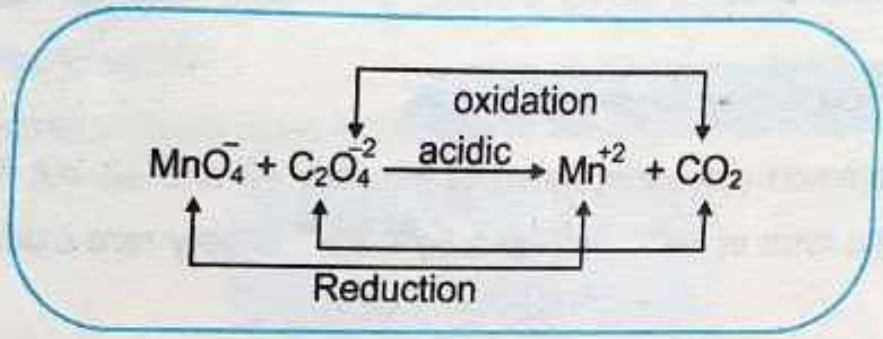
14.3.3.3 Potassium permanganate (VII) as an oxidizing agent in titrations:

$KMnO_4$ is a strong oxidizing agent with intense dark purple colour. During reduction the purple permanganate ion changes into colourless Mn^{+2} ion.

Scanned with CamScanner

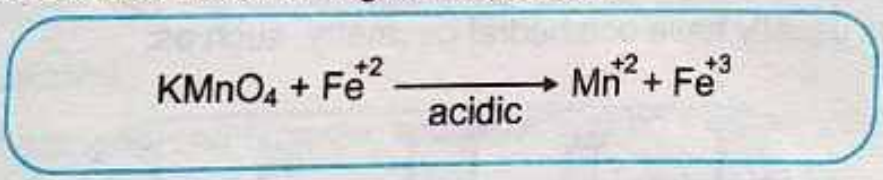
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The solution turns from dark purple to faint pink colour at equivalence point. The reduction of permanganate requires strong acidic conditions. For example oxalate ion reduces permanganate ion in acidic conditions.



No additional indicator is used in this titration because $KMnO_4$ acts itself as an indicator.

$KMnO_4$ solution is also used to find the concentration of Fe(II) ions in a solution. The redox reaction is given as under.



14.3.4 Iron:

Iron is a transition metal with a symbol (Fe) and Atomic number 26. It has two relatively stable oxidation states in its compounds (+2 and +3). It also forms a variety of complex ions such as $[Fe(H_2O)_6]^{+2}$, $[Fe((H_2O)_6]^{+3}$. It has characteristically coloured compounds e.g. Iron (II) salts (pale green), Iron (III) salts (yellow or brown). Iron is used to catalyse the synthesis of ammonia through Haber's process.

Iron rarely occurs in free state since it is highly reactive. Its important ores are red haematite (Fe_2O_3), Brown haematite or limonite ($2FeO_2O_3.3H_2O$), magnetite Fe_3O_4 etc. Iron ore is processed for the

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

following three varieties of Iron which differ from each other mainly in their carbon content i.e. cast iron or pig iron (2–3%), wrought or malleable Iron (0.1–0.25%) steel (0.25–2%).

14.3.4.1 Oxidation States of Iron

Most common oxidation states of iron are +2 and +3 but it can also exists in the form of Fe^{4+}, Fe^{5+} and Fe^{6+}. Fe^{6+} is very rare oxidation state of iron.

Iron in the +2 oxidation state is known as the Ferrous ion. This ion is pale green in colour and is very easily oxidized to ferric ion. Even traces of dissolved oxygen in solution will accomplish this oxidation. Solution of Ferrous ion is sometimes used as reducing agent. Complexes of the ferrous ions usually have octahedral geometry, such as;

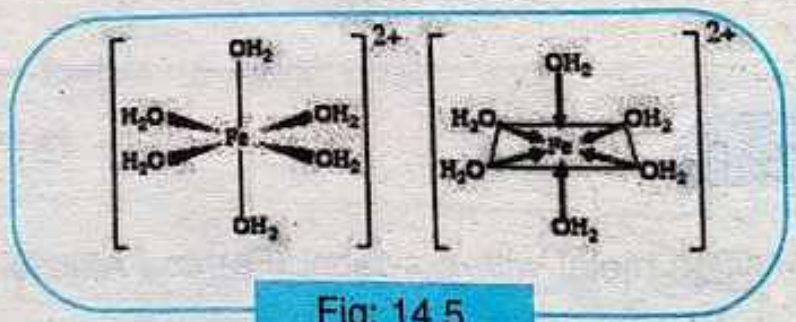


Fig: 14.5

When ferrocynide added to solution containing Ferric ions, a precipitate known as prussian blue $Fe_4[Fe(CN)_6]_3$ is formed. This compound is used in making blueprint and as a bluing agent in laundry.

Iron in +3 oxidation state is known as Ferric ion. Most solutions containing ferric ions are usually yellow or yellow-brown due to formation of $[Fe(H_2O)_5(OH)]^{2+}$.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

14.3.4.2 Iron as catalyst in Haber's Process

In the Haber process hydrogen reacts with nitrogen to produce ammonia. Without catalyst the process would proceed too slowly to be economically viable.

The reaction takes place according to the following steps:

$$N_2 + H_2 \rightarrow N_2H_2$$
$$N_2H_2 + H_2 \rightarrow N_2H_4$$
$$N_2H_4 + H_2 \rightarrow 2NH_3$$

However breaking open the nitrogen triple bond to form N_2H_2 is very difficult and resulting compound is highly unstable and is likely to dissociate almost as soon as it forms. The formation of N_2H_2 is highly endothermic. So the above reactions do not proceed easily without the use of catalyst.

The hydrogen and Nitrogen are adsorbed on metallic iron surface. The hydrogen almost immediately splits into its component atoms by sharing or exchange of electrons with the catalyst surface

$$N_{2(g)} \rightleftharpoons N_{2(ad)}$$
$$H_{2(g)} \rightleftharpoons 2H_{(ad)}$$

The nitrogen molecules split into their component atoms and they lock into the surface of the iron catalyst. This is the slowest step and so limits the rate of the entire process.

$$N_{2(ad)} \rightleftharpoons 2N_{(ad)}$$

The hydrogen atoms migrate across the surface of the catalyst and react with nitrogen and produce ammonia molecules that are still bound to the surface.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$N_{(ad)} + H_{(ad)} \rightarrow NH_{(ad)}$$
$$NH_{(ad)} + H_{(ad)} \rightarrow NH_{2(ad)}$$
$$NH_{2(ad)} + H_{(ad)} \rightarrow NH_{3(ad)}$$

The assembled ammonia molecules are desorbed from surface in the form of gas

$$NH_{3(ad)} \rightleftharpoons NH_{3(g)}$$

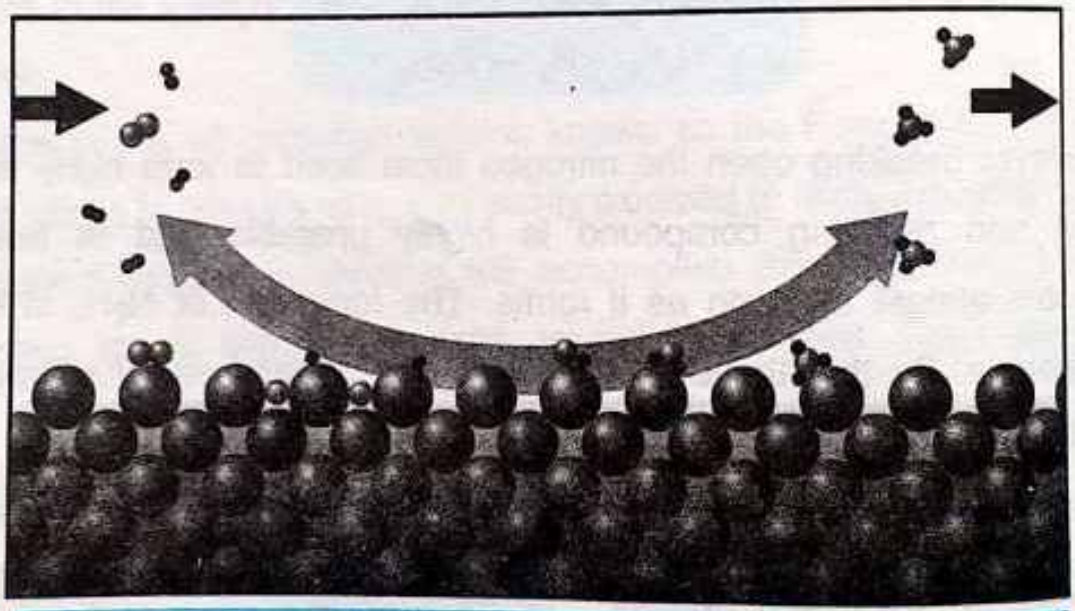


Fig: 14.6 Catalytic action of iron surface in Haber Process

14.3.4.3 Iron ions in the reaction between persulphate ions and iodide ions

The reaction between persulphate ions (peroxodisulphate ions), $S_2O_8^{2-}$ and iodide ions in solution can be catalysed using either iron(II) or iron(III) ions.

The overall equation for the reaction is:

$$\underset{\text{(Powerful oxidant)}}{S_2O_8^{2-}} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

Scanned with CamScanner

For the sake of argument, we'll take the catalyst to be iron(II) ions. The reaction happens in two stages.

$$S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{2-} + 2Fe^{3+}$$

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

If you use iron(III) ions, the second step of these reactions happens first.

14.3.4.4 Reaction of Hexaaqua iron (II), Hexaaqua iron (III) with water and Ammonia

Many hexaaqua complex ions can undergo acid base reaction with water to produce a solution of pH less than seven. These are not redox reaction because during the reaction no change in the oxidation state of central metal occurs e.g.

In Iron (II) case

$$[Fe(H_2O)_6]^{+2}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Fe(H_2O)_5(OH)]^{+1} + H_3O^+$$

In Iron (III) case

$$[Fe(H_2O)_6]^{+3} + H_2O_{(l)} \rightleftharpoons [Fe(H_2O)_5(OH)]^{+2} + H_3O^+$$

Fe^{+3} (Ferric) give a more acidic solution than Fe^{+2} (ferrous) ions.

In case of Alkaline solution OH^- ions remove H_3O^+ ions and equilibrium shifts more towards forward direction and more H^+ are lost from the complex in stages until a precipitate is formed.

$$[Fe(H_2O)_6]^{+3}_{(aq)} + 3OH^- \rightleftharpoons [Fe(H_2O)_3(OH)_3]^{0}_{(ppt)} + 3H_2O_{(l)}$$

In case of Fe (II) complex the reaction in alkaline medium does not proceed because it is energetically unfavourable.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Ammonia can act both as a base and a ligand. Here it simply acts as a base, removing H^+ from the aqua complex.

In Iron (II) case

$$[Fe(H_2O)_6]^{+2} + 2NH_3 \longrightarrow [Fe(H_2O)_4(OH)_2] + 2NH_4^+$$

orange

In Fe (III) case

$$[Fe(H_2O)_6]^{+3} + 3NH_3 \longrightarrow [Fe(H_2O)_3(OH)_3] + 3NH_4^+$$

Brown

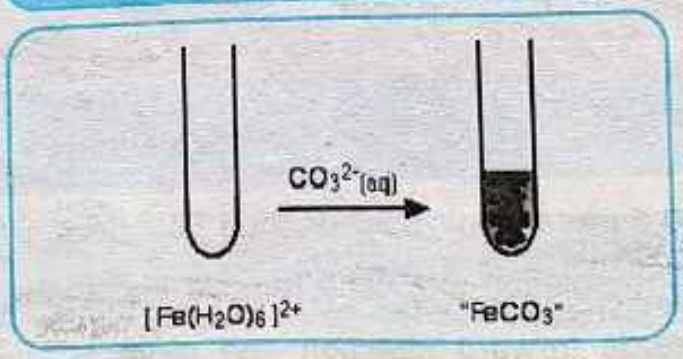
14.3.4.5 Reactions of the iron ions with carbonate ions

There is an important difference between the behaviour of iron(II) and iron(III) ions.

Iron(II) ions and carbonate ions

You simply get a precipitate of what you can think of as iron(II) carbonate.

$$Fe^{2+}_{(aq)} + CO^{2-}_{3(aq)} \rightarrow FeCO_{3(s)}$$



Iron(III) ions and carbonate ions

The hexa aquairon(III) ion is sufficiently acidic to react with the weakly basic carbonate ion.

If you add sodium carbonate solution to a solution of hexa aquairon(III) ions, you get exactly the same precipitate as if you added sodium hydroxide solution or ammonia solution.

Scanned with CamScanner

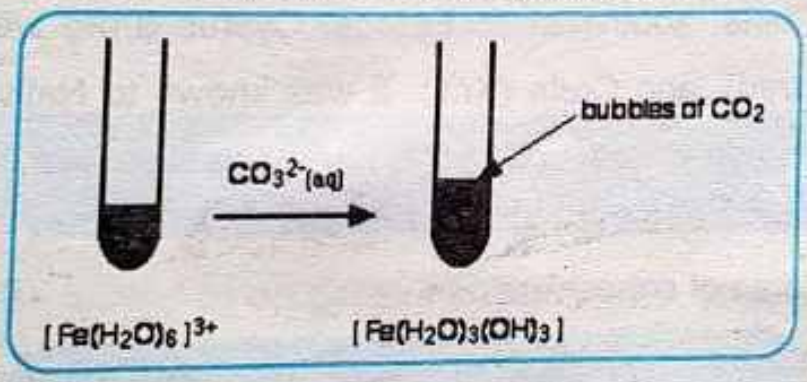
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

This time, it is the carbonate ions which remove hydrogen ions from the hexa aqua ion and produce the neutral complex.

Depending on the proportions of carbonate ions to hexa aqua ions, you will get either hydrogen carbonate ions formed or carbon dioxide gas from the reaction between the hydrogen ions and carbonate ions. The more usually quoted equation shows the formation of carbon dioxide.

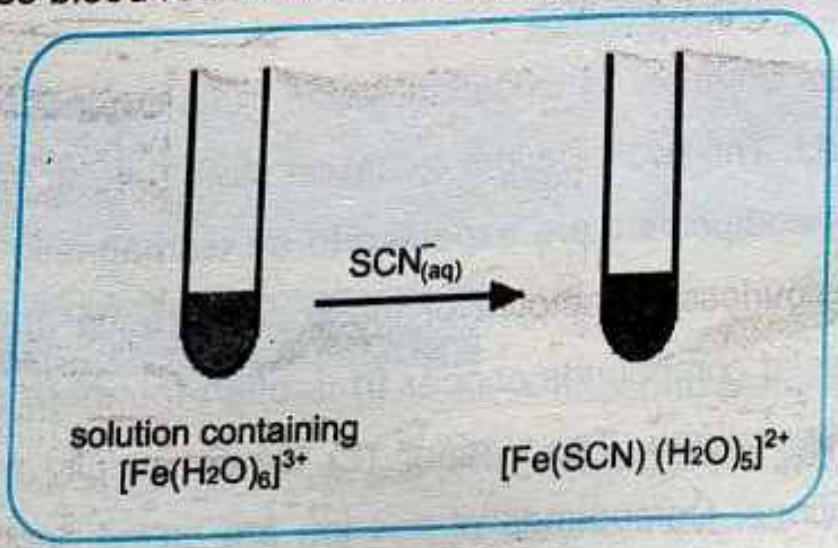
$$2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2[Fe(H_2O)_3(OH)_3] + 3CO_2 + 3H_2O$$

Apart from the carbon dioxide, there is nothing new in this reaction:



Testing for iron (III) ions with thiocyanate ions

This provides an extremely sensitive test for iron(III) ions in solution. If you add thiocyanate ions, SCN^-, (from, say, sodium or potassium or ammonium thiocyanate solution) to a solution containing iron(III) ions, you get an intense blood red solution containing the ion $[Fe(SCN)(H_2O)_5]^{2+}$.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

14.3.5 Copper:

INTRODUCTION

Copper, symbol Cu, is brownish-red metallic element that is one of the most widely used metals. Copper is one of the transition elements of the periodic table. The atomic number of copper is 29.

Copper was known to prehistoric people and was probably the first metal from which useful articles were made. Copper objects have been found among the remains of many ancient civilizations, including those of Egypt, Asia Minor, China, southeastern Europe, Cyprus (from which the word *copper* is derived), and Crete (Kríti). It was known to Native Americans, however these ores were found by the European explorers. It is also found in the pure state.

The principle ores of copper are

(i)	Malachite	$CuCO_3Cu(OH)_2$
(ii)	Azurite	$2CuCO_3Cu(OH)_2$
(iii)	Chalcocite	Cu_2S
(iv)	Copper pyrite	$CuFeS_2$

14.3.5.1 Oxidation States:

Copper exhibits a variety of oxidation states in its compounds which are mostly coloured. The two principal oxidation states of copper are +1 and +2. Copper (I) compounds are expected to be diamagnetic in nature and are usually colourless. Examples of these compounds are Cu_2O, CuCl, CuBr etc. In solid compounds copper (I) is often the more stable state at moderate temperatures. The copper (II) ion is usually more stable in aqueous solutions. Compounds of this ion are called cupric compounds

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

and are usually coloured. Examples are CuO, CuF_2, $CuCl_2$, $CuCO_3$, $CuSO_4$ etc.

Copper(III) is most characteristically found in oxides. A simple example is potassium cuprate, $KCuO_2$, a blue-black solid. The best studied copper(III) compounds are the cuprate superconductors. Yttrium barium copper oxide ($YBa_2Cu_3O_7$) consists of both Cu(II) and Cu(III) centres. Like oxide, fluoride is a highly basic anion and is known to stabilize metal ions in high oxidation states. Indeed, both copper(III) and even copper(IV) fluorides are known, K_3CuF_6 and Cs_2CuF_6, respectively.

14.3.5.2 Reactions of Hexaaqua copper (II) ions with Hydroxide ions, ammonia and carbonate ions

The simplest ion formed by copper in a solution is the typical blue Hexaaqua copper (II) ion. This complex ion performs the following reactions.

(a) Reaction with Hydroxide ions:

Hydroxide ions (from NaOH solution) remove H^+ ions from water ligands attached to the copper ion. It results in neutral complex which is insoluble in water and precipitation occurs. The chemical reaction is

$$\underset{\text{blue(sol)}}{[Cu(H_2O)_6]^{+2}} + 2OH^- \rightarrow \underset{\text{blue ppt}}{[Cu(H_2O)_4(OH)_2]} + 2H_2O$$

(b) Reaction with Ammonia:

When a small amount of ammonia is added to solution of hexaaqua copper (II) ions, it pulls out the H^+ ions from the complex ion exactly like above.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$[Cu(H_2O)_6]^{+2} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$$

blue — blue ppt

The precipitate dissolves in the presence of excess ammonia.

$$[Cu(H_2O)_4(OH)_2] + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{+2} + 2OH^- + 2H_2O$$

blue ppt

(c) Reaction with carbonates:

The Hexaaqua copper (II) ions are not strongly acidic enough to release CO_2 from carbonates. In these cases precipitation of metal carbonate takes place which is represented by the following reaction.

$$Cu^{+2}_{(aq)} + CO^{-2}_{3(aq)} \rightarrow CuCO_{3(s)}$$

SST

Society, Technology and Science

Transition metals and their compounds when dissolved mostly form coloured solutions. Different metals are known for their specific colour used as paints such as cobalt (II) nitrate (red), $K_2Cr_2O_7$ (orange), $KCrO_4$ (yellow), Nickle (II) Chloride (green) $KMnO_4$ (purple), while titanium oxide is an important ingredient in white paint.

Scanned with CamScanner

EY POINTS

Key Points:

- Transition elements are those elements which have partially filled d or f orbitals either in their atomic state or in any common oxidation state.
- The oxidation state of an element is related to the number of electrons that an atom loses, gains, or appears to use when joining with another atom in compounds.
- Those substances which are attracted in magnetic field are called paramagnetic substances and the phenomenon is known as paramagnetism.
- Transition metal atoms have similarity in their structure hence they are able to replace one another in the metallic lattice and form alloys.
- Coordination compounds have definite geometrical shapes because the bond formed between central metal atom and the ligands are directional in nature.
- Ionic and covalent compounds of transition metals are mostly coloured.
- All forms of Cr(VI) are powerful oxidizing agents, and oxidize any CH bonds on a carbon with an oxygen as far as possible without breaking any carbon-carbon bonds
- Fe (II) compounds are octahedral in geometry.
- Per manganate (VII) ions are strong oxidizing agents which oxidize ethane to ethyl alcohol.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

EXERCISE

Exercise

1. Select the most appropriate choice given at the end of each question?

1. The Transition metals Copper and.....are best electrical conductors.
   (a) Iron (b) Vanadium (c) Chromium (d) Manganese
2. Transition elements usually exhibit.....valencies.
   (a) variable (b) Normal (c) permanent (d) unchangeable
3. The coordination compound $[(Cu(Cl_4)]^{-2}$ exists in .....shape.
   (a) tetrahedral (b) octahedral (c) square planner (d) rhombic
4. The oxidation state of Chromium in CrO_2Cl_2 is.....
   (a) 2 (b) 3 (c) 4 (d) 6
5. A compound Potassium dichromate is used in dying and.....industry.
   (a) Tanning (b) Cement (c) Paper (d) Glass
6. Acidified Potassium permanganate acts as an..... agent.
   (a) Oxidizing (b) reducing (c) bleaching (d) colouring
7. The paramagnetic nature of a substance depends on:
   (a) The number of electron in the outermost orbit.
   (b) The number of electron that are easily ejected.
   (c) The number of unpaired electrons.
   (d) The number of lone pair of electrons.
8. V_2O_5 is used as catalyst in the:
   (a) Manufacture of Ammonia.

Scanned with CamScanner

(b) oxidation of Ammonia to Nitric Acid.

(c) polymerization of ethane to polythene.

(d) Manufacture of Sulphuric Acid

9. Select element which is not ferromagnetic.

(a) Fe (b) Co (c) Sb (d) Ni

10. The coordination number of iron in $[(Fe(CN)_6)]^{-4}$ is :

(a) 2 (b) 3 (c) 4 (d) 6

11. Select ligand which is bidentate:

(a) H_2O (b) NH_3 (c) CO (d) $C_2O_4^{-2}$

12. Cu^{+2} salt solution is blue in colour due to transition of electron from:

(a) s to p orbital (b) d to d orbital

(c) p to d orbital (d) p to p orbital

13. Potassium dichromate acts as a strong:

(a) Oxidizing agent (b) Reducing agent

(c) Bleaching agent (d) Dehydrating agent.

14. When solid potassium chromate, K_2CrO_4 is dissolved in water it forms a .....solution.

(a) yellow (b) pink (c) red (d) violet

15. Which ions are used as catalyst in the reaction between persulphate ions and iodide ions?

(a) Lead (b) Iron (c) copper (d) chromium.

Short questions

1. **Answer the following questions:**

(I) What is meant by the term "transition elements"?

(II) Write down the electronic configuration of first transition series?

Scanned with CamScanner

(III) Comment on the electronic configuration of chromium and copper?

(IV) Explain the catalytic behavior of transition elements?

(V) How coordination compounds are formed by transition elements?

(VI) Write a short note on the variable oxidation state.

(VII) What is the oxidation state of Fe in $FeCl_3$?

(VIII) What is the oxidation state of chromium in $[Cr(H_2O)_6]^{3+}$?

Long questions

1. What are the general characteristics of transition elements?
2. Explain the nomenclature of coordination compounds?
3. Explain the role of iron and Vanadium as catalysts?
4. Discuss Chromium and Manganese compounds as oxidizing agen
5. What are complex ions? Explain their shape and colours?
6. Give Reasons.
   i) Fe is a catalyst in Haber process while not in the preparation of sulphuric acid.
   ii) Why Iron has variable valancies.
   iii) The oxidation state of neutral compound is zero?
   iv) Existence of paramagnetism and ferromagnetism.

Scanned with CamScanner

UNIT 15

ORGANIC COMPOUNDS

Learning Outcomes:

After Studying this unit Students will be able to:

- Define organic chemistry and organic compounds.
- Explain why there is such a diversity and magnitude of organic compounds.
- Classify organic compounds on structural basis.
- Explain the use of coal as a source of aromatic and aliphatic hydrocarbons.
- Explain the use of plants as a source of organic compounds.
- Explain that organic compounds are also synthesized in the laboratory.
- Define functional group and homologous series and classify organic compounds on the basis of functional group.
- Make distinction among different organic compounds on the basis of their formula.
- Understand that organic compounds are obtained from plants and animals as well as partially or totally synthesized in the laboratory.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

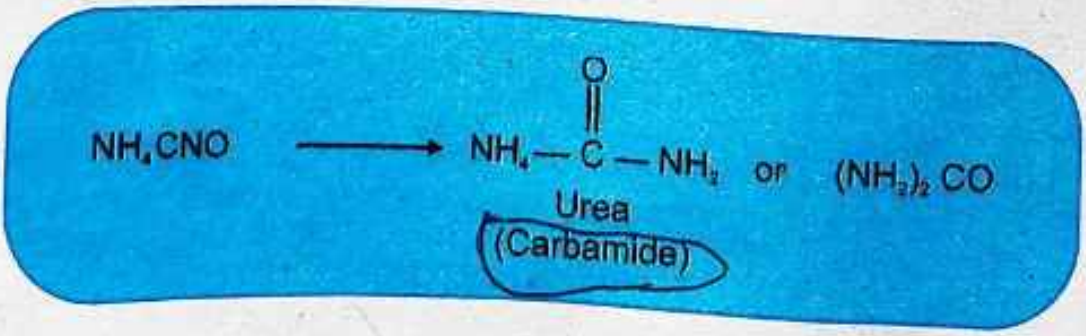
Introduction:

Organic chemistry is a branch of chemistry that deals with the scientific study of the structure, properties, composition, reactions and preparations of carbon based compounds i.e. hydrocarbons and their derivatives. An organic compound is any member of a large class of chemical compounds whose molecules contain carbon. Methane (CH_4) is one of the simplest organic compounds. These compounds may also contain any number of other elements, including hydrogen, nitrogen, oxygen, halogens, sulphur, phosphorous, silicon as well as metal atoms (organo-metallic compounds).

In past all the known compounds were classified according to their source from which they were obtained. Compounds obtained from living organisms (plants and animals), like sugar (plant source) and urea (animal source), were named as "organic" compounds as word "organic" means "life or living". On the other hand, the compounds obtained from mineral sources were named as "inorganic" compounds as the word "inorganic" means "lifeless" as they came from non-living source.

At that time it was believed that organic compounds can only be obtained from living organisms as they possess a super-natural force called vital force". This theory is called "vital force theory". According to this theory the vital force is possessed only by living organisms and such compounds cannot be obtained or synthesized in the laboratory from other compounds but can be made only by living organisms. Thus according to old concept, those compounds which were obtained from living organisms (plants and animals) were called organic compounds and the study of such compounds was named organic chemistry by Berzelius in 1807.

However, in 1828, a German chemist, Friedrick Wohler synthesized in the laboratory an organic compound, Urea, by heating an inorganic compound Ammonium cyanate.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Urea had long been considered to be an "Organic" compound being a constituent of urine, where it is formed from the breakdown of protein.

Wohler's experiments were followed by many other scientists, where increasingly complex organic substances were synthesized from inorganic ones without the involvement of any living organism and thus vital force theory was rejected.

When the composition of all the organic compounds was studied, they were found to contain carbon as a major element alongwith other elements like hydrogen, oxygen, nitrogen etc.

Thus organic compounds are the compounds containing carbon which are obtained from living things (plants and animals) as well as synthesized in the laboratory, while study of the chemistry of these carbon containing compounds is called organic chemistry.

Almost all the organic compounds contain carbon along with hydrogen. Such compounds are called hydrocarbons and the rest which also contain oxygen, nitrogen, halogens etc are considered to be their derivatives.

However, there is an exception to the above generalization. There are some compounds like carbon containing alloys (including steel), metal carbonates, bicarbonates, carbonyls, simple oxides of carbon (CO, CO_2), cyanides ($NaCN$), cyanates ($KOCN$, NH_4OCN), sulfides (CS_2) as well as the allotropes of carbon (diamond and graphite), which although contain carbon but are not organic compounds. They are inorganic in nature either by their source or properties or nature of bonding.

15.1 Sources:

Major sources of organic compounds are coal, natural gas and petroleum (fossil fuel).

15.1.1 Fossil Remains:

Fossil fuels are formed by the anaerobic decomposition of buried plants and animals.

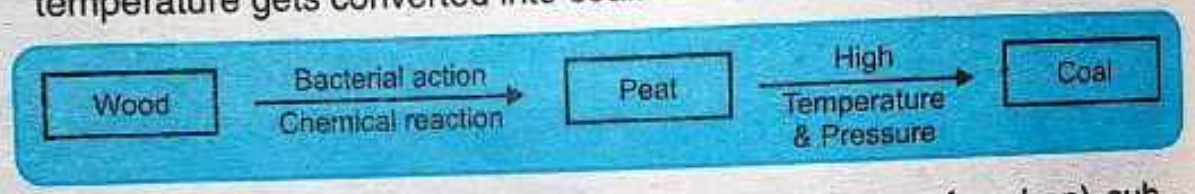
a. Coal:

Coal is an important solid fossil fuel of black or brownish–black colour normally occuring in rock strata in layers called coal beds.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Coal is mainly composed of carbon along with other elements like hydrogen, oxygen, sulphur and nitrogen. Coal is formed in nature from the decay of plant matter buried under the soil millions of years ago. Due to different bacterial and chemical reactions, it is first converted into a coal precursor called peat which under high pressure and temperature gets converted into coal.



Coal exists in different forms like lignite (low %age of carbon) sub-bituminous coal, bituminous coal and anthracite (highest rank coal due to presence of high percentage of carbon more than 91.5 %).

Coal is suitable fuel for power generation to minimize the use of petroleum and natural gas for heating homes. Coal is mainly used as a fuel to produce electricity and heat through combustion. It is the largest source of energy for the generation of electricity world wide. Coal is a major source of a large number of organic compounds, especially aromatic compounds.

2. Petroleum:

The word petroleum is derived from latin words: "petra" means "rock" and "oleum" means "oil". Thus the word petroleum means "rock oil" as it is present in underground porous rocks. It is also sometimes called "mineral oil" or "crude oil" or "liquid gold" Petroleum exists as a viscous liquid having dark brown colour with a strong unpleasant smell.

Composition: Petroleum is a mixture of hydrocarbons. The hydrocarbons in petroleum are mostly alkanes, cycloalkanes and aromatic hydrocarbons, while some other organic compounds in trace amounts are found which contain nitrogen, oxygen, sulphur as well as trace amounts of metals such as nickel, copper and vanadium.

3. Natural Gas:

Natural gas is a gaseous form of fossil fuel which is a mixture of low boiling hydrocarbons, methane, ethane, propane and butane.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Natural gas, a source of organic compounds, is also formed by the dead decay of animal matter and is usually found above the underground deposits of petroleum.

In strict sense, petroleum includes only crude oil but in common usage, it includes both crude oil and natural gas. Under normal pressure and temperature the lighter hydrocarbons methane, ethane, propane and butane occur as gases while the heavier ones from butane onwards are in the form of liquids. Usually natural gas and petroleum deposits, are found in association with each other.

15.1.2 Plants and Natural Products Chemistry:

Plants and animals are the major sources of organic compounds. Those compounds which are produced by plants and animals are called natural compounds or natural products and the study of the chemistry of such compounds is called natural product chemistry. Plants have always been a rich source of a large number of organic compounds. Natural products may be extracted from tissues of plants. These compounds may be of medicinal importance and can be used in pharmaceutical drug discovery and drug design. Even today a large number of organic compounds are isolated from plants. Still the number of plants that have been extensively studied is very few and the vast majority has not been studied at all. Clinically, useful drugs which have been recently isolated from plants include the anticancer agent palliate (Taxol) from the yew tree, and the anti malarial agent artemisinin from Artemisia annual.

15.1.3 Partial and Total Synthesis:

According to modern concept, organic compounds can be isolated from living organisms as well as synthesized in the laboratory. The study of processes or chemical reactions by which organic compounds can be synthesized in the laboratory from a living or non living source is called synthetic organic chemistry and the compounds are called synthetic organic compounds or simply synthetic compounds.

Organic compounds can be synthesized either through partial synthesis, or through total synthesis. Mostly, organic reactions occur in many steps. Sometimes, an intermediate product of a reaction is used to synthesize a targeted product. This process is known as partial synthesis. Sometimes

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

the starting material converts through many steps into targeted product. Such process is known as total synthesis. In other words, total synthesis is the process of finding new synthesis routes for a given compound. The first demonstration of total synthesis was Friedrich Wholer's synthesis of urea in 1828 and this process was commercialized for the first time by Gustaf Kompa from the synthesis of camphor (an organic compound) in 1903.

Partial and total synthesis are used to synthesize a large number of organic compounds.

15.1.4 Products of Biotechnology:

Biotechnology is a field of applied biology that involves the use of living organisms and bioprocesses in engineering, technology, medicine and other fields requiring bio-products. Most of products of biotechnology are organic compounds. One application of biotechnology is the direct use of organisms for the manufacturing of organic products. For example beer and milk products.

Chemicals which have been made using biotechnology include benzylpenicilin (an antibiotic), ethanol, ethylene glycol, insulin (a hormone), polyhydroxybutyrate (a biodegradable thermoplastic), rennin (an enzyme) and Chemosensory protein (CSP) etc.

15.2 Coal as a Source of Organic Compounds:

Coal is a rich source of organic compounds. It can be converted into many organic compounds by the following ways.

15.2.1 Destructive Distillation of Coal:

When coal is heated in the absence of air, it does not burn but produces many by-products. This process of heating coal in the absence of air is called destructive distillation of coal. The main products obtained by the destructive distillation of coal are:

i. Coke
ii. Coal Tar
iii. Ammoniacal Liquor
iv. Coal gas

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

i. Coke:

Coke is a fuel which is used in homes and factories but it is mainly used in industries as reducing agent for the extraction of metals from their ores.

ii. Coal Tar

One of the products of coal is Coal tar, which is a mixture of organic compounds. These can be separated by fractional distillation. The compounds, so obtained can be used for making soap, fats, dyes, plastics, perfume, drugs, pesticides, explosives. On fractional distillation, coal tar gives important organic compounds like benzene, toluene, xylene, phenol, cresol, naphthalene, anthracene etc.

iii. Ammoniacal liquor:

The other by product is ammonia solution called ammoniacal liquor which is used for making fertilizers like ammonium sulphate, ammonium super phosphate etc.

iv. Coal gas:

The coal gas, also called town gas, is a mixture of hydrogen, carbon monoxide, which is combustible, making the coal gas an excellent fuel.

15.2.2 Conversion of Coal to Petroleum:

Coal gas, obtained from the distructive distillation of coal can be converted into petroleum by a process known as Fischer–Tropsch (FT) process. The Fischer–Tropsch synthesis or process is a set of chemical reactions that convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons mainly alkanes.

$$(2n+1)H_2 + nCO \longrightarrow C_nH_{2n+2} + nH_2O$$

The conversion of CO to alkanes in presence of hydrogen involves hydrogenolysis of C – O bond and the formation of C – C bond. This process takes place in presence of transition metal catalysts (cobalt, iron, ruthenium and nickel) at a temperature range 150 – 300°C.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Fischer –Tropsch (FT) plants associated with coal (source of carbon) convert it into gaseous reactants i.e CO and H_2. This conversion is called gasification. Coal based FT plants can produce a petroleum substitute that is used as synthetic fuel and as synthetic lubricating oil.

15.3 Characteristics of Organic Compounds:

The Following are some of the important characteristic features of organic compounds.

1. Unique Properties of Carbon:

Carbon has the property of self linkage. It can link with hundreds and thousands of other carbon atoms to form long C – C chains or rings. This self–linkage of carbon atoms to form chains and ring compounds is called catenation. Carbon can also form stable single and multiple bonds with each other and other atoms like hydrogen, oxygen, nitrogen, halogens, sulphur etc.

2. Isomerism:

When two or more organic compounds have the same molecular formula but different structures, these are called isomers and this phenomenon is called isomerism.

3. Non –Ionic Character:

Majority of organic compounds mainly involve covalent bond between C—C and C—H, therefore, they are generally non–polar and have non–ionic characters.

4. Solubility:

Solubility depends upon the forces of attraction between the solute and solvent molecules. When these forces are stronger than the intermolecular forces of solute-solute and solvent-solvent, then solute dissolves easily. But the organic compounds are formed by covalent bonds i.e. non-ionic and almost non-polar, so most of the organic compounds are insoluble in water, while some are partially soluble but

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

they are readily soluble in non–polar solvents like ether, benzene carbon tetrachloride etc.

5. Rates of Organic Reactions:

Bonds between atoms in organic molecules are formed by mutual sharing of electrons and reaction needs the breakage of these bonds. The organic reactions are slow because these involve breaking of certain bonds and formation of new bonds.

6. Similar Structural features and behaviour:

Mostly organic compounds have similar structural features and similar physical and chemical properties. Therefore they show similar beahaviour to various reactants. This similarity in behaviour has reduced the study of millions of organic compounds to a few homologous series.

15.4 Uses of Organic Compounds:

Life is a practical version of chemistry, especially organic chemistry. No field of science is so closely related to our daily life as is organic chemistry. The importance of organic compounds and products can hardly be overemphasized. Most of the things that we come across in our daily life are organic substances like, the food we eat (carbohydrates, proteins, vitamins, fats etc) and the clothes we wear (cotton, silk, nylon) are organic compounds. We have become dependent upon organic compounds for our food, medicines and clothing.

Similarly, the chemists have learnt to synthesize paper, rubber, ink, plastics, leather, fibres, fertilizers, shoe polishes, pesticides, cosmetics, paints, dyes, preservatives, detergents and medicines etc, that we use in our daily life. In fact, our own body is made of thousands of complex organic molecules like proteins, nucleic acids, enzymes, fats, lipids etc. that are called life molecules.

Almost all the chemical reactions that takes place in living systems, including our own body, are organic in nature.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The fuels like petroleum products, petrol, diesel oil, compressed natural gas (CNG), coal as well as natural gas (suigas) etc, are also mixtures of organic compounds that run our cars and industries.

SST

Society, Technology and Science

Just about every substance you pull out of plants or animals is made of mostly carbon atoms except water. The chemist uses plant and animal compounds to make new compounds not found in nature. Many farmers in USA grow Maize for enthanol rather than food. There are over hundred chemical substances, that have been derived from plants for use as medicines e.g. Quinine (Antimalaria) Asprine (Cardiac diseases, pain killer), Borneol (Anitinflametery), Benzyl benzoate (scabicide) and Galantamine hydrobromide (Alzheimer's disease)

15.5 New Allotrope of Carbon: Bucky Ball

Bucky ball is a member of a class of structures called carbon fullerenes. Fullerenes are molecules composed entirely of carbon in the form of a hollow sphere, ellipsoid or tube. Spherical fullerenes are known as bucky balls. Fullerenes are solid allotrope of the element carbon. The discovery of fullerenes significantly expanded the number of known allotropes of carbon, which were until recently limited to graphite, diamond and amorphous carbon like soot & coal. Bucky balls and other fullerenes are similar in structure to graphite, which consists of hexagonal rings made of carbon, but also pentagonal (or sometimes heptagonal rings). The first fullerene was discovered in **1985** by Herold Kroto, James Heath, Sean O'Brion , Robert Curl and Richard Smalley for which they were awarded Nobel prize in 1996. It was named Buckminster fullerene (or Bucky ball) that contained 60 carbons (C_{60}). The name is a tribute to Richard Buckminster Fuller, a known architecture, who popularized

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

geodesic domes and the shape of C_{60} bucky ball is similar to that sort of dome.

In Bucky balls, the smallest member is C_{20} which is made of 20 carbon atoms while the most common one is C_{60}.

The existence of fullerenes is very rare in nature. Negligible amounts of $C_{60}, C_{70}, C_{76}, C_{84}$ are found in nature. In 2010, fullerenes were also discovered in outer space.

15.6 Functional Groups and Homologous Series:

There are millions of organic compounds known so far and thousands are discovered and synthesized every year. As mentioned this diversity and such a large number of organic compounds is due to some peculiar behaviour of carbon. It is difficult to study the chemistry of each individual compound. Therefore, the organic compounds are classified into different groups, in order to make their study easy. One such classification is on the basis of structure of organic molecules and the other on the basis of functional groups.

a. Classification on the basis of Structure: (old classification)

This classification of organic compounds is based on the arrangement of carbon atoms in molecules. According to this classification organic compounds are broadly divided into the following groups.

i. Open Chain or Acyclic organic Compounds:

In these compounds carbon atoms are linked to each other in open chains, which may be a straight chain or a branched chain.

$CH_3 - CH_2 - CH_2 - CH_3$

Butane (a straight chain compound)

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

iso-butane (a branched compound)

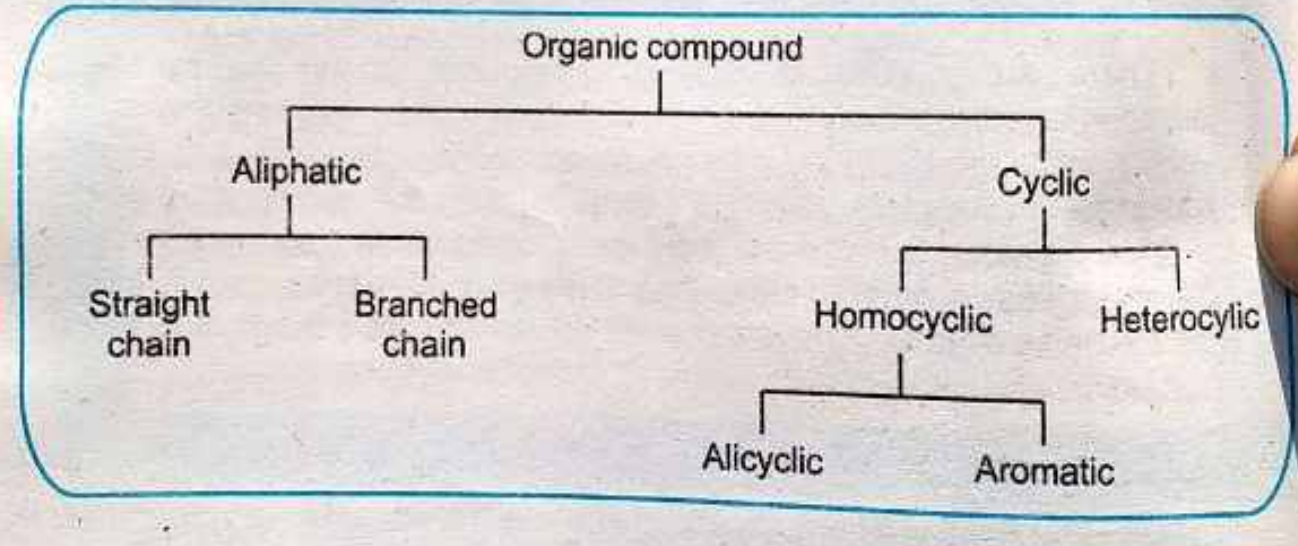
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

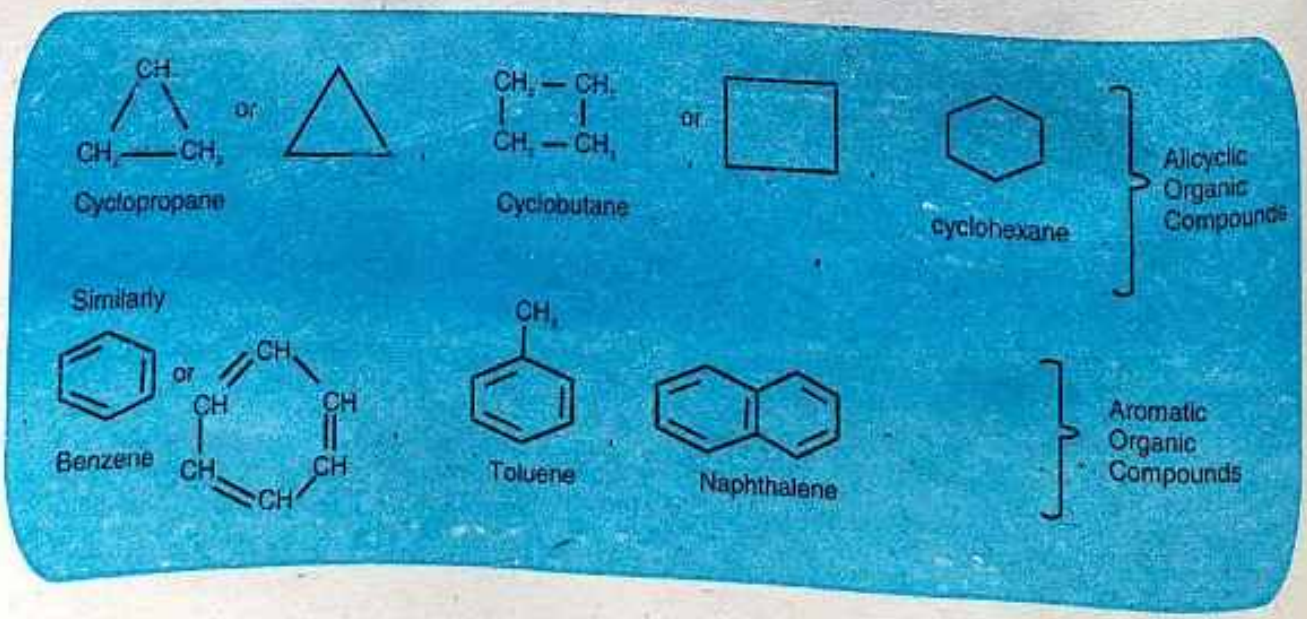
ii. Closed chain or cyclic organic Compounds:

In closed chain compounds carbon atoms are arranged in closed chain forms. They may be homocyclic or heterocyclic organic compounds.

Homocyclic, which are also known as carbocyclic organic compounds, are those in which cycle or ring is made only of carbon atoms. They are further divided into alicyclic having properties similar to open chain compounds and aromatic in which benzene ring is present.



On the other hand, heterocyclic organic compounds are those cyclic compounds in which the ring contains at least one atom other than carbon.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



b. Classification on the basis of Functional group:

An atom or a group of atoms that gives certain characteristic properties to an organic compound is called a functional group.

It is called a functional group because it is the chemically active or functional part of a molecule. Each functional group represents a different class of organic compounds.

Organic compounds are divided into:

i. Hydrocarbons ii. Derivatives of hydrocarbons.

i. Hydrocarbons:

Hydrocarbons are those organic compounds which are made up of carbon and hydrogen only. They may be aliphatic or open chain hydrocarbons and cyclic or closed chain hydrocarbons.

In open chain hydrocarbons, carbon and hydrogen atoms are arranged in open chain forms. They are further subdivided into alkanes (saturated hydrocarbons) in which all the four valencies of carbon are fully satisfied through single bonds. Unsaturated hydrocarbons are those in which at least one double bond (=) or a triple bond (≡) is present between adjacent carbon atoms. The former is called alkene and the later is called alkyne.

The cyclic or closed chain hydrocarbons are either alicyclic or aromatic hydrocarbons.

ii.

The derivatives of hydrocarbons are organic compounds obtained by replacing alteast one hydrogen from hydrocarbons especially saturated hydrocarbons and aromatic hydrocarbons. i.e benzene ring. They are alkyl halides, alcohols and phenol, ethers, ketones, aldehyde, carboxylic acids and their derivatives.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Different classes of organic compounds, their functional groups and general formulae are summarized in the following table alongwith examples.

Table: 15.1 Classification of organic compounds based on Functional groups.

Class of Compounds	Functional group	Name of Functional group	General Formula	Example
Alkane	$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$	Single bond	C_nH_{2n+2} $n = 1,2,3.....$ shows member of carbon atoms	CH_4, CH_3-CH_3 Methane, Ethane or C_2H_6
Alkene	$>C=C<$	Double bond	C_nH_{2n}	C_2H_4 or $CH_2=CH_2$ Etheine
Alkyne	$-C\equiv C-$	Triple bond	C_nH_{2n-2}	$HC\equiv CH$ or C_2H_2 (ethyne)
Alkyl halide	$-X$ (F, Cℓ, Br, I)	Halo (Flouro, Chloro, Bromo)	$R-X$ or $C_nH_{2n+1}X$	$CH_3-C\ell$ Methyl chloride C_2H_5-I Ethyl Iodide
Alcohol or alkanol	$-OH$	Hydroxyl	$R-OH$ or $C_nH_{2n+1}OH$	CH_3-OH Methylalcohol (Methanol)

Scanned with CamScanner

Amine	$-NH_2$	Amino	$R-NH_2$ or $C_nH_{2n+1}NH_2$	CH_3-NH_2 Methylamine
Ether	$-O-$	Oxygen	$R-O-R$ or $(C_nH_{2n+1})_2O$	CH_3-O-CH_3 Dimethylether
Ketone	$-\overset{\overset{O}{\|\|}}{C}-$	Carbonyl (Keto group)	$(C_nH_{2n+1})_2CO$	$CH_3-\overset{\overset{O}{\|\|}}{C}-CH_3$ Dimethyl ketone (acetone)
Aldehyde	$-\overset{\overset{O}{\|\|}}{C}-H$ or $-CHO$	Formyl	$R-\overset{\overset{O}{\|\|}}{C}-H$ or $C_nH_{2n+1}CHO$	$CH_3-\overset{\overset{O}{\|\|}}{C}-H$ (acetaldehyde)
Carboxylic acid	$-\overset{\overset{O}{\|\|}}{C}-OH$ or $-COOH$	Carboxyl	$R-\overset{\overset{O}{\|\|}}{C}-OH$ or $C_nH_{2n+1}COOH$	$CH_3-\overset{\overset{O}{\|\|}}{C}-OH$ (acetic acid)
Acid halide	$-\overset{\overset{O}{\|\|}}{C}-X$ or $-COX$	Acyl	$R-\overset{\overset{O}{\|\|}}{C}-X$ or $C_nH_{2n+1}COX$	$CH_3-\overset{\overset{O}{\|\|}}{C}-C\ell$ (acetyl chloride)
Acid amide	$-\overset{\overset{O}{\|\|}}{C}-NH_2$ or $-CONH_2$	Amide	$R-\overset{\overset{O}{\|\|}}{C}-NH_2$ or $(C_nH_{2n+1}CONH_2)$	$CH_3-\overset{\overset{O}{\|\|}}{C}-NH_2$ (Acetamide)

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Ester	$-\overset{\overset{O}{\|\|}}{C}-OR'$ or $-COOR$	Ester	$R-\overset{\overset{O}{\|\|}}{C}-O-R$ or $(C_nH_{2n+1}COOC_nH_{2n+1})$	$CH_3-\overset{\overset{O}{\|\|}}{C}-OCH_3$ (Methyl acetate)
Alkyl cyanide or Nitrile	$-C\equiv N$	Cyano	$R-CN$ or $C_nH_{2n+1}CN$	CH_3CN Methyl cyanide

Homologous Series:

A series of organic compounds in which all members possess similar structural features and similar chemical characteristics, but each member is different from the next member by a methylene $(-CH_2-)$ group is called homologous series. All the members that differ from each other by metheylene are called homologues. Each class of organic compounds has its own homologous series which can be represented by a general formula. For example, alkanes (saturated hydrocarbons) form a series of compounds. It can be represented by a general formula C_nH_{2n-2} where 'n' shows the number of carbon atoms in the corresponding alkane.

Table 15.2 Alkane Homologoues Series

No. of C atoms	Molecular formula (C_nH_{2n+2})	Name with suffix (-ane)	Structural formula
1	CH_4	Methane	CH_4
2	C_2H_6	Ethane	CH_3CH_3

Scanned with CamScanner

3	C_3H_8	Propane	$CH_3CH_2CH_3$
4	C_4H_{10}	Butane	$CH_3CH_2CH_2CH_3$
5	C_5H_{12}	Pentane	$CH_3CH_2CH_2CH_2CH_3$
6	C_6H_{14}	Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$
7	C_7H_{16}	Heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
8	C_8H_{18}	Octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
9	C_9H_{20}	Nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
10	$C_{10}H_{22}$	Decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

As it is clear from alkane homologous series that each member is different from the adjacent member by CH_2. Similarly this series can be expanded beyond C_{10} to higher alkanes. Similar homologous series can be developed for alkenes, alkynes, alcohols, ethers, amines, carboxylic acids, carbonyl compounds etc.

Characteristics of homologous Series:

- As mentioned, each class of organic compounds has its own homologous series having general formula.
- All the members of homologous series have similar chemical properties and same general methods of preparation similar structural features and same functional group.
- The physical properties like melting point, boiling points, densities etc increases down the series due to increase in their molecular masses.

Scanned with CamScanner

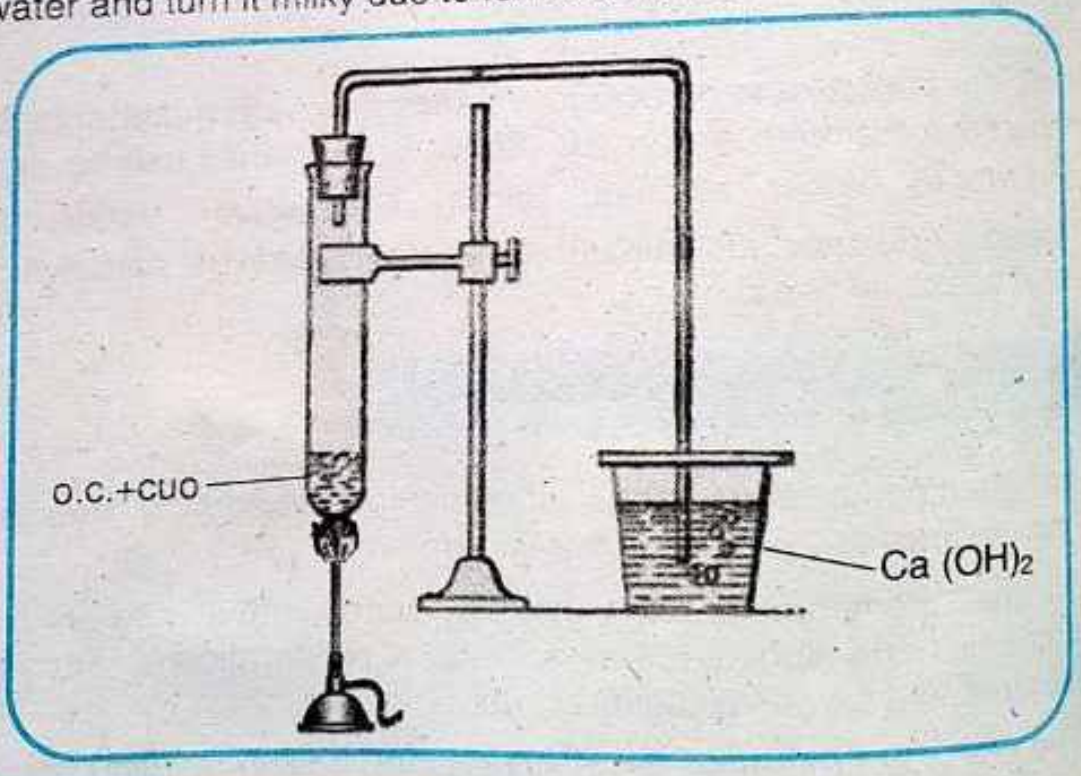
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

15.7 Detection of elements in Organic Compounds:

The main elements present in organic compounds are carbon and hydrogen as well as oxygen, nitrogen, sulphur and halogens. Following methods can be used to detect these elements, in the organic compound.

Detection of Carbon:

As carbon is always present in all the organic compounds, there is no need to test for it. The test is performed only to establish whether a given compound is organic or not. The organic substance is mixed with dry copper oxide in 1:3 ratio and heated in a test tube fitted with a delivery tube. The other end of which is dipped into lime water, $Ca(OH)_2$. Carbon converts to carbon dioxide which reacts with lime water and turn it milky due to formation of calium carbonate.



Detection of Hydrogen:

If hydrogen is present in the compound, it oxidizes to water vapours which condenses in small droplets on the cooler end of the test tube. The water formation is further confirmed by passing the issuing gases (water vapours) from anhydrous copper sulphate (white) that

Scanned with CamScanner

is turned blue as copper sulphate converts to hydrated form ($CuSO_4 5H_2O$).

Detection of Nitrogen, Sulphur and Halogens:

Nitrogen, sulphur and halogens can be detected in organic compounds by extract sodium test or lassaign's test. For this, sodium extract or lassaign's solution is prepared first. The substance is heated strongly with sodium metal in a fusion tube till the tube becomes red hot which is dipped in water in a china dish and filtered after boiling the contents of china dish. The filtrate is called lassaign's solution or sodium extract.

Detection of Nitrogen:

Take a part of lassaign's solution in a test tube and add to it few drops of sodium hydroxide and then few millilitres of freshly prepared ferrous sulphate ($FeSO_4$) solution and boil it. After cooling, add few drops of ferric chloride ($FeCl_3$) solution and excess of concentrated acid (HCl or H_2SO_4). The formation of Prussian blue or green colouration confirms the presence of nitrogen.

Detection of Sulphur:

To another portion of sodium extract add some acetic acid first and then lead acetate solution. Black precipitate of lead sulphide will be formed which confirms the presence of sulphur.

Detection of Halogens:

Boil a portion of sodium extract with concentrated nitric acid and then add to it silver nitrate solution. The formation of white precipitate soluble in ammonium hydroxide solution indicates chlorine, pale yellow precipitate slightly soluble in NH_4OH indicates bromine and deep yellow precipitate insoluble in ammonia solution shows the presence of iodine in the organic compound.

Scanned with CamScanner

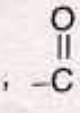
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Detection of Oxygen:

Oxygen can not be detected by any direct method but for its detection following indirect methods can be employed.

i. The substance is heated alone in a dry test tube usually in nitrogen atmosphere. Formation of water droplets on the cooler part of the test tube obviously show the presence of oxygen.

ii. Different tests are applied for oxygen containing functional groups like alcohol, (OH) carbonyl compounds like


(Ketone), 
(aldehyde) and carboxylic acids (COOH). If any one is detected, the presence of oxygen is confirmed.

iii. The most important test for presence of oxygen is combustion analysis in which the percentages of C and H are determined. If their sum is less than 100 then the remaining percentage is that of oxygen.

Scanned with CamScanner

KEY POINTS

Key Points:

- Generally all the compounds were classified on the basis of their origin. The compounds that were having living source (plants and animals) were called organic and those coming from non living sources (minerals) were called inorganic.
- According to vital force theory, organic compounds can only be obtained from organism and could not be synthesized in the laboratory from inorganic sources.
- The study of the chemistry of the carbon containing compounds (organic compounds) is called organic chemistry.
- The Major sources of organic compounds are plants and animals as well as fossil fuels.
- The abundance of organic compounds is due to unique behaviour of carbon as well as due to some special characteristics of these compounds themselves.
- Organic chemistry have applications in almost all fields and the importance of organic compounds can hardly be over emphasized.
- The discovery of fullerenes (bucky balls) have significantly expanded the number of known allotropes of carbon.
- Functional group is the active part of organic compounds which greatly effect the chemistry of organic compounds.
- Organic compounds can be classified on the basis of structure as well as on the basis of functional group.
- Each class of organic compounds have their own homologous series that can be represented by a general formula.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

EXERCISE

Exercise

Q.1 Multiple Choice questions. Choose the correct answer from the given choices in each case.

i. The first organic compound prepared in the laboratory was.
a. Peat b. Urea c. Sugar d. Alcohol

ii. All the substances are organic except.
a. Graphite b. Urea c. Methane d. Acetic acid

iii. The final stage of conversion of decaying plants into coal is
a. Anthracite b. Lignite c. Peat d. Bituminous

iv. Petroleum is mainly a mixture of
a. Heterocyclic compounds b. Aromatic Hydrocarbons
c. Saturated hydrocarbons d. Unsaturated hydrocarbons

v. The major component of natural gas is
a. Butane b. Ethane c. Propane d. Methane

vi. All of the following fractions are obtained by destructive distillation of coal except.
a. Coal tar b. Refinery Gas c. Coal gas d. Coke

vii. Coal can be converted to petroleum by
a. Haber process b. destructive distillation
c. Fischer –Tropsch process d. Fractional distillation

viii. Pyridine belongs to which class of organic compounds.
a. Heterocyclic b. Hydrocarbon c. Alicyclic d. Homocyclic

ix. Which of the following represents the functional group of amides.
a. –COOR b. $-NH_2$ c. $-C \equiv N$ d. $-CONH_2$

x. Which of the following elements can not be detected in a given organic compound directly.
a. Chlorine b. Phosphorous c. Nitrogen d. Oxygen

Scanned with CamScanner

Q. 2 Briefly answer the following questions.

i. What is meant by organic compounds and organic chemistry?

ii. Why dil.HNO_3 is added to the sodium extract before detection of halogens in organic compound.

iii. Explain the significance of Wohler's work in the development of organic chemistry.

iv. Although bucky ball is an allotropic form of carbon, but it is included in organic chemistry.

v. What are those compounds which although contain carbon but are not considered organic?

vi. Differentiate between partial and total synthesis?

vii. How coal can be converted into petroleum?

viii. Discuss the reasons for the presence of large number of organic compounds?

ix. Differentiate between acyclic and cyclic organic compounds.

Q.3 What are fossil fuels? Discuss different types of fossil fuels.

Q.4 Elaborate the detection of various elements in organic compound.

Q.5 What are the different fraction obtained by the destructive distillation of coal. Give their importance.

Q.6 Explain some of the important characteristics of organic compounds.

Q.7 Define functional group. How organic compounds are classified on the basis of functional group.

Q.8 Give old classification of organic compounds based on arrangement of carbon atoms in the molecule.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

UNIT 16

HYDROCARBONS

Learning Outcomes:

After carefully studying this unit and working the exercise, the student will be able to:

- Classify hydrocarbons as aliphatic and aromatic.
- Deseribe nomenclature of alkanes and cycloalkanes.
- Explain the shapes of alkanes and cycloalkanes exemplified by ethane and cyclopropane.
- Explain unreactive nature of alkanes towards polar reagents.
- Define homolytic and heterolytic fission, free radical initiation, propagation and termination.
- Describe the mechanism of free radical substitution in alkanes exemplified by methane and ethane.
- Identify organic redox reactions.
- Explain what is meant by a chiral centre and show that such a centre gives rise to optical isomerism.
- Identify chiral centres in given structural formula of a molecule.
- Explain the nomenclature of alkenes.
- Explain the shape of ethene molecule in terms of sigma and pi C–C bonds.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

- Describe the structure and reactivity of alkenes as exemplified by ethane.
- Define and explain with suitable examples the terms isomerism, stereoisomerism and structural isomerism.
- Explain dehydration of alcohols and dehydrohalogenation of RX for the preparation of ethene.
- Describe the chemistry of alkenes by the following reactions of ethane Hydrogenation, Hydrohalogenation, hydration, Halogenation, Halohydration, Epoxidation, ozonolysis, polymerization.
- Explain the concept of conjugation in alkenes, having alternate double bonds.
- Use the IUPAC Naming system for alkenes.
- Explain the shape of benzene molecule (MOT).
- Define resonance, resonance energy and relative stability.
- Compare the reactivity of benzene with alkanes and alkenes.
- Describe what is meant by term delocalized electrons in the context of benzene ring.
- Describe addition reactions of benzene and toluene.
- Describe the mechanism of electronphilic substitution in benzene.
- Discuss the chemistry of benzene and toluene by nitration, sulphanation, halogenations, Friedel –Craft's alkylation and acylation.
- Apply the knowledge of positions of substituents in the electrophilic substitution of benzene.
- Use the IUPAC naming system of alkynes.
- Compare the reactivity of alkynes with alkenes, alkenes and arenes.
- Discuss the shape of alkynes in terms of sigma and pi C–C bonds.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

- Describe the preparation of alkynes, using elimination reactions.
- Describe acidity of alkynes.
- Discuss the chemistry of alkynes by hydrogenation, hydrohalogenation, hydration, bromination, ozonlysis and reaction with metals.
- Describe and differentiate between substitution and addition reactions.
- Explain isomerism in alkanes, alkenes, alkynes and substituted benzene.
- Identify and link uses of various hydrocarbons in daily life and also their significance as fuels for the future energy needs of Pakistan.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Introduction:

Hydrocarbons are the organic compounds which contain carbon and hydrogen only. For example methane (CH_4), benzene (C_6H_6) etc. These compounds are thought to serve as basis for all other organic compounds. That is, all other organic compounds are the derivatives of hydrocarbons where one or more hydrogen atoms have been replaced by another atom or group of atoms. Petroleum, natural gas and coal are the main natural sources of hydrocarbons. These sources are frequently found in under ground deposits. The significance of hydrocarbons can be realized by their uses in daily life and in industries and power generation as fuel and as raw materials for synthesis of many other organic compounds. If the fossil fuels are simply bound to produce heat, which is then used to produce power and heat up our homes, we need not be concerned with the molecular make up of these substances. But to appreciate the treatments these gas, liquid and solid materials receive and the roles, the products from these play, you must know about their molecular make up and their chemical reactions.

16.1 Types of Hydrocarbons:

Hydrocarbons are divided into two major categories i.e.

(A) Aliphatic hydrocarbons (B) Aromatic hydrocarbons.

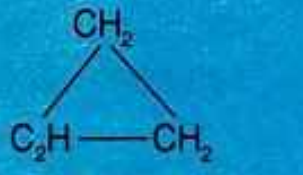
A. Aliphatic Hydrocarbons:

These include the open chain (acyclic) compounds and those cyclic compounds which resemble the open chain compounds in their chemical properties e.g.

$CH_3 - CH_2 - CH_3$

n-propane

(Acyclic compound)



Cyclopropane

(Cyclic compound)

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

i. Open chain or acyclic hydrocarbons:

In these hydrocarbons, the carbon atoms are linked together in the form of chains which may either be:

i. Straight Chain:

In this case no carbon atom is linked directly to more than two carbons atoms.

$$CH_3 - CH_2 - CH_2 - CH_3$$

Butane

ii. Branched Chain:

In this case, at least one carbon atom is linked directly to three or four carbon atoms. For example.

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

Isobutane

Both straight and branched hydrocarbon may be:

a. Saturated hydrocarbons:

These are also called alkanes and in these compounds all the carbon atoms are bonded to each other by single bonds and hence each carbon is bonded to four other atoms. They are called saturated because their valencies are fully satisfied e.g.

$$CH_3 - CH_2 - CH_2 - CH_3$$

Butane

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

They can be represented by the general formula C_nH_{2n+2}, where n is the number of carbon atoms.

b. Unsaturated hydrocarbons:

In these hydrocarbons, the chain contains carbon–carbon multiple bonds.

$CH_3-CH=CH_2$	$CH_3-C\equiv C-CH_3$
Propene	Butyne

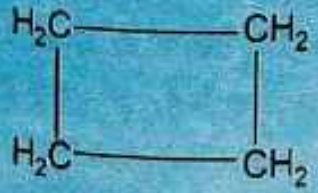
Unsaturated hydrocarbons, having carbon–carbon double bond are called alkenes, represented by general formula C_nH_{2n}, while those having carbon–carbon triple bond are called alkynes, represented by general formula C_nH_{2n-2}

ii. Closed Chain or Cyclic Hydrocarbons:

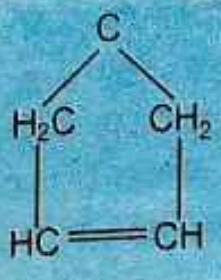
In these hydrocarbons the carbon atoms are bonded together in such a way that they form a ring or cyclic structure. Like open chain hydrocarbons, they may also be classified as

i. Saturated
ii. Unsaturated

For example,



Cyclobutane (saturated)



Cyclopentene (unsaturated)



Cyclohexyne (Unsaturated)

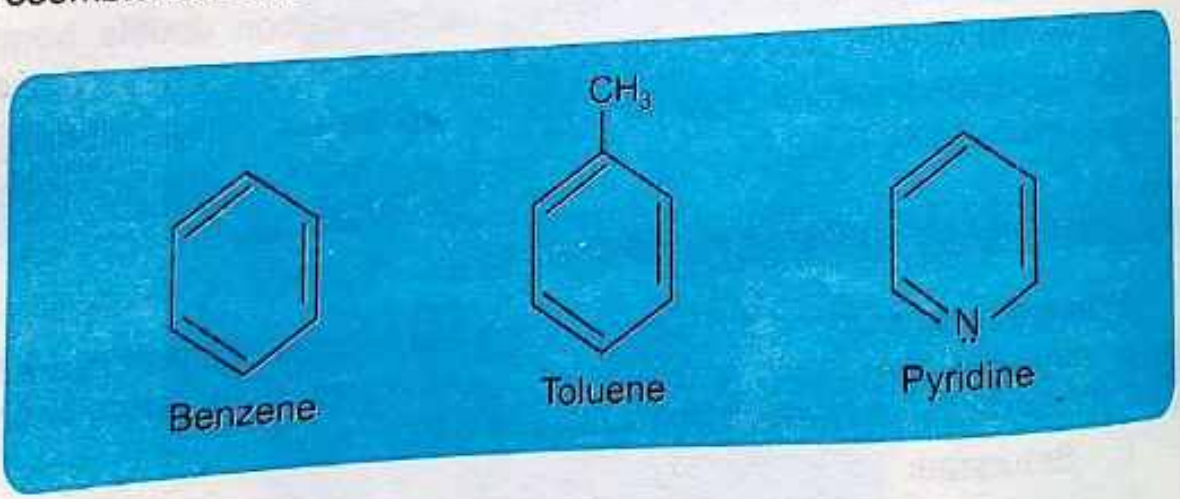
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Saturated cyclic hydrocarbon are called cycloalkanes, unsaturated are called cycloalkenes and cycloalkynes.

B. Aromatic Hydrocarbons:

Benzene (C_6H_6) is the parent member of this class and hence aromatic is the term used for benzene and all those compounds that resemble benzene in their chemical properties e.g.



16.2 Alkanes and Cycloalkanes:

Alkanes are open chain saturated hydrocarbons, which can be represented by the general formula C_nH_{2n+2} (where "n" is the number of carbon atoms), while cycloalkanes are cyclic saturated hydrocarbons represented by the general formula C_nH_{2n} (n is the number of carbon atoms; and $n \geq 3$). It is to be noted that cyclo alkanes are two H – atoms less than the corresponding alkanes, in their formula.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

16.2.1 Nomenclature:

The systematic process of naming a compound is called nomenclature. At the beginning of organic chemistry, each new compound was given an individual name, which was based on its source, some property or other trivial reason. For example, the compound "HCOOH" was given the name formic acid because it was obtained from red ants. (Latin, formica = ants). Similarly the compound "CH_3COOH" was named as acetic acid (Greek, Acetum = vinegar). These names, which are based on the source of the compounds are called common names or trivial names.

With the increase in the number of organic compounds it became impossible to give names to such a large number of organic compounds. Moreover trivial names do not give any information about the structure of the compounds. Need was, therefore, felt to name organic compounds in a systematic way. Thus, the "International Union of pure and Applied chemistry" (IUPAC) in 1957, set rules for giving systematic names to organic compounds on the basis of structure. This is known as the IUPAC system of nomenclature.

Alkanes:

Alkanes are named by the following two systems.

(A) Common System (B) IUPAC System.

A. Common System:

The first four members of the series (C_1 to C_4) are named as methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}) while the rest are named by using the Greek prefixes that indicate number of carbon atoms in the molecule. Thus the prefix penta (5) is used for the compound having five carbon atoms, hexa (6) for six, hepta (7) for seven, octa (8) for eight, nona (9) for nine and deca (10) for ten carbon atoms (see table 16.1) the prefix is followed by the ending "ane".

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

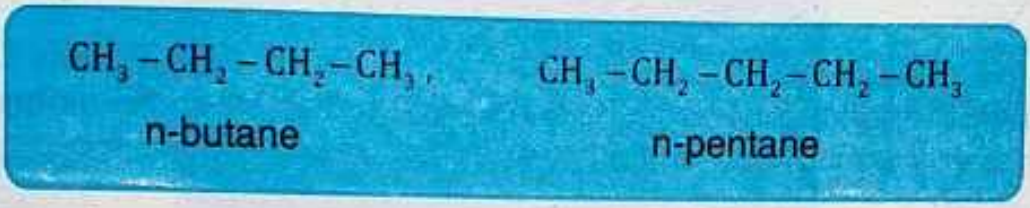
Table 16.1 Name and formulae of first 10 alkanes

No. of Carbon Atoms	Name	Molecular Formula	Structural Formula
1	Methane	CH_4	CH_4
2	Ethane	C_2H_6	CH_3CH_3
3	Propane	C_3H_8	$CH_3CH_2CH_3$
4	Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$
5	Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$
6	Hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$
7	Heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
8	Octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
9	Nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
10	Decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

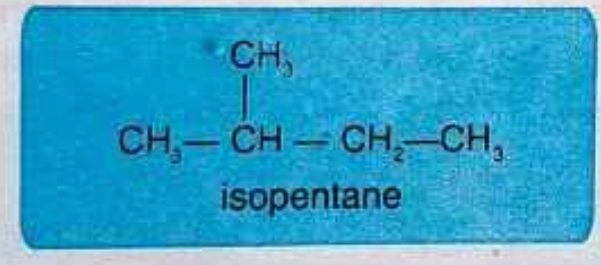
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

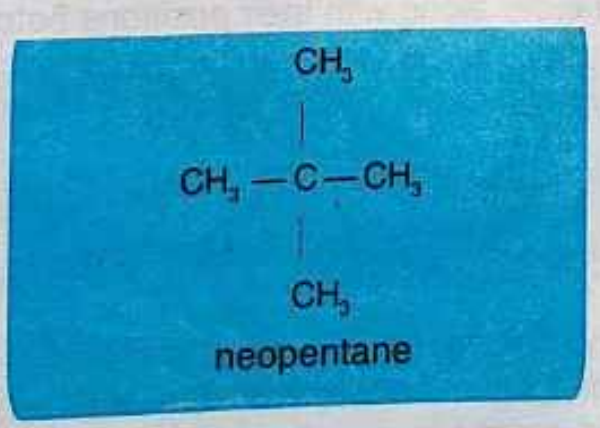
i. The prefix n – is used for those alkanes in which all the carbon atoms are in one continuous chain (straight chain or normal alkanes)



ii. The prefix iso is used for those alkanes which have a methyl group $(-CH_3)$ attached to the second last carbon atom of the continuous chain.



iii. The prefix neo is used for those alkanes which have two methyl groups attached to the second last carbon atom of the continuous chain.



B. IUPAC System:

In this system the parent names of the alkanes are retained such as methane, ethane, propane, butane, pentane, hexane and so on while the branching (if any) is treated as substitutuent, attached to the main continuous carbon chain.

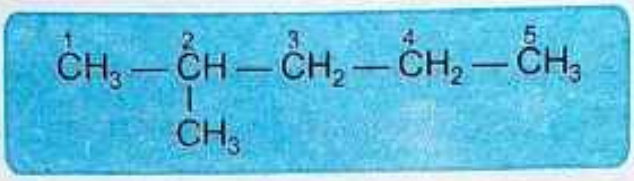
Rules for naming alkanes are:

Scanned with CamScanner

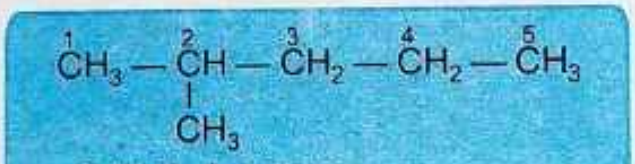
1. Select the longest continuous chains of carbon atoms and consider it as a parent compound.



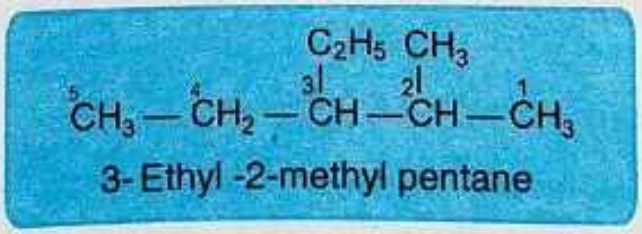
2. Number the longest chain from one end or the other, so as to give the carbon carrying the substituent (alkyl group), the lowest possible number.



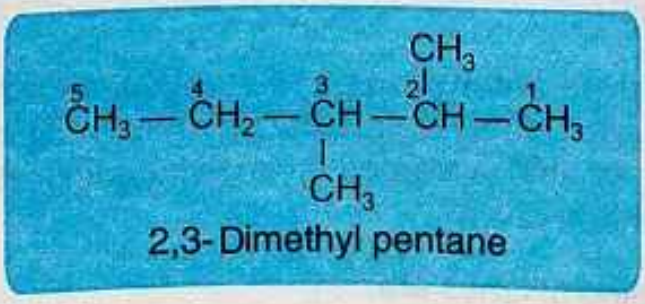
3. Name the substitutuant along with its position by indicating the number of the carbon atom to which it is attached, before the parent name.



4. When two or more different substituents are attached, they are named in alphabetical order along with their positions before the parent name.



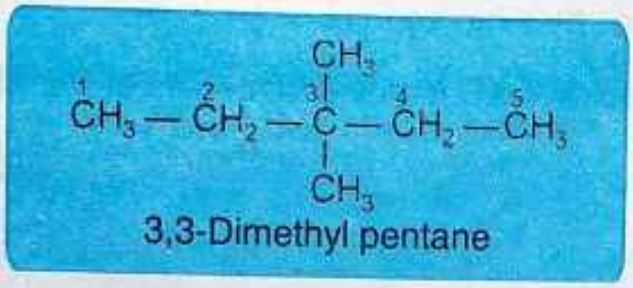
5. When the same substituent is present more than once, a prefix di, tri, tetra etc is used before the substitutent name and position of each substituent is indicated by a separate number.



Scanned with CamScanner

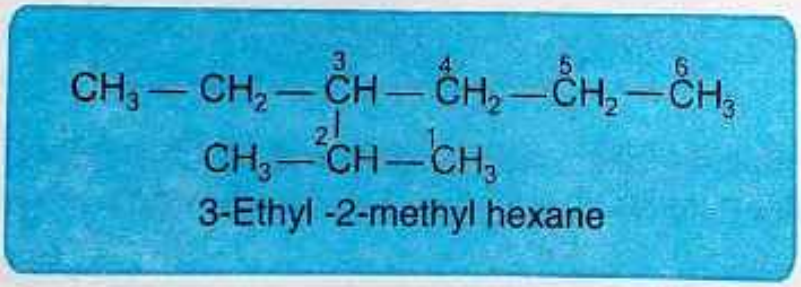
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

6. When two substitutents (same or different) are attached to the same carbon atom, the number of that carbon atom is repeated.



3,3-Dimethyl pentane

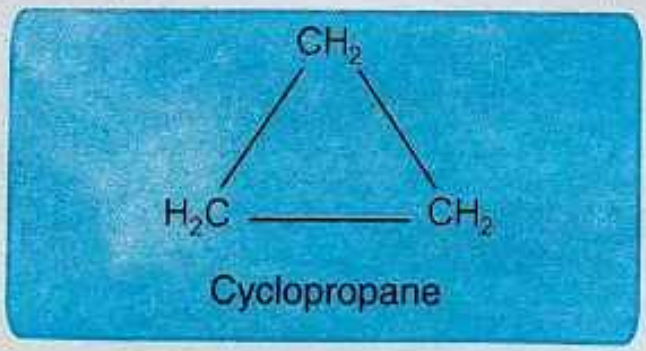
7. When there are more than one longest chains, select the chain which carries more substituents.



3-Ethyl -2-methyl hexane

Cycloalkanes:

1. Cycloalkanes are named by placing the prefix "cyclo –" to the name of alkane having the same number of carbon atoms as in the ring.



Cyclopropane

For convenience, cyloalkanes are represented by geometric figures. Each corner represents a $-CH_2$ group.

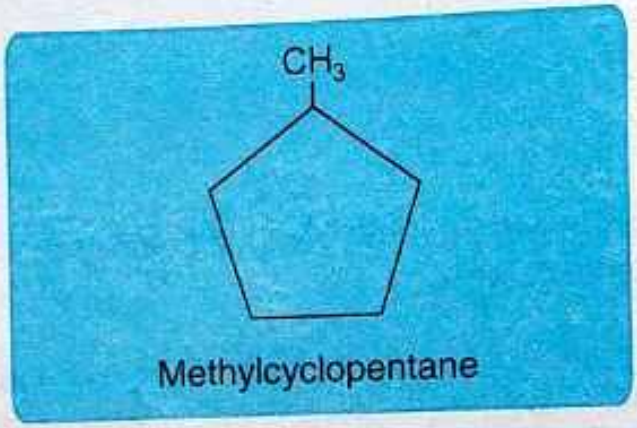
- Cyclopropane is represented by a friangle (△)

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

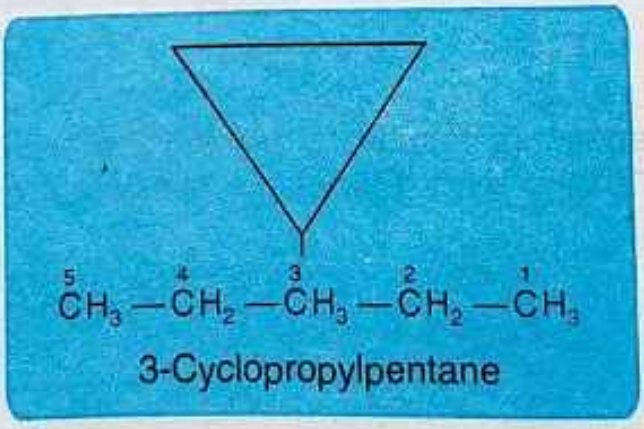
- Cyclopentane by a pentagon ( )
- Cyclohexane by a hexagon ( )

2. Substituted cycloalkanes are named as alkylcycloalkanes e.g.



Methylcyclopentane

3. The ring is taken as substitutuants, if the side chain contains greater number of carbon atoms than the ring.



3-Cyclopropylpentane

16.2.2 Physical Properties:

(A) Alkanes:

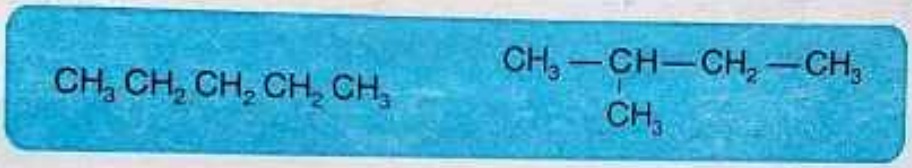
1. First four members $(C_1 - C_4)$ of the alkane series methane, ethane, propane and butane are colourless gases. Next thirteen members $(C_5 - C_{17})$ are colourless liquids. Higher alkanes are wax like (soft) solids.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

2. Alkanes, being non polar, are soluble in nonpolar solvents like CCl_4 and C_6H_6 but they are insoluble in polar solvents such as water.

3. The boiling points of normal alkanes increase with the increase in molecular weight. Moreover, straight chain alkanes have higher boiling points than the isomeric branched alkanes.



4. The melting points of alkanes also increase with increasing molecular weight. However, there is no regularity in the change in melting point with the number of carbon atoms in a molecule.

5. The specific gravities of alkanes, in general , increase with increasing molecular weight.

6. Viscosity also increases with increase in the number of carbon atoms in the molecule.

Table 16.2 Boiling and Melting points of some alkanes:

Alkane	Formula	Boiling Point (°C)	Melting Point (°C)
Methane	CH_4	–161.5	–182.5
Ethane	$CH_3 - CH_3$	–88.6	–172
Propane	$CH_3 - CH_2 - CH_3$	–42.1	– 188
Butane	$CH_3(CH_2)_2 CH_3$	0.00	– 138
Pentane	$CH_3(CH_2)_3 CH_3$	36.0	– 130
Hexane	$CH_3(CH_2)_4 CH_3$	68.7	–95.3

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

(B) Cycloalkanes:

1. First two members i.e. Cyclopropane and cyclobutane are gases at room temperature and atmospheric pressure, while remaining cycloalkanes are liquids.
2. They are insoluble in water but dissolve in ethanol and ether.
3. Their melting and boiling points show a gradual increase with the increases the molecular weight.

Table 16.3 Boiling and Melting points of some cycloalkanes:

Cycloalkane	Boiling Points (°C)	Melting Points (°C)
Cyclopropane	– 33	– 127
Cyclobutane	+ 13	–50
Cydopentane	+ 49.2	–94
Cyclohexane	+ 81	6.7

16.2.3 Structure:

(A) Let us consider ethane $(CH_3 - CH_3)$ for illustrating the orbital structure of alkanes. In ethane, each carbon atom is bonded to four other atoms, so it uses sp^3 hybrid orbitals to form these bonds. There are six C–H covalent bonds and one C–C covalent bond. Each of the C–H bonds, is the result of linear overlap of an sp^3 hybrid orbital of carbon and an 's' orbital of hydrogen. The C–C bond is formed due to the overlap of sp^3 orbitals, one from each carbon atom (Fig.16.1). All the C–H and C–C bonds are sigma (δ) bonds. All the bond angles are 109.5° (tetrahedral geometry). The C–C bond length is 1.54°A and each C–H bond length is 1.09°A.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

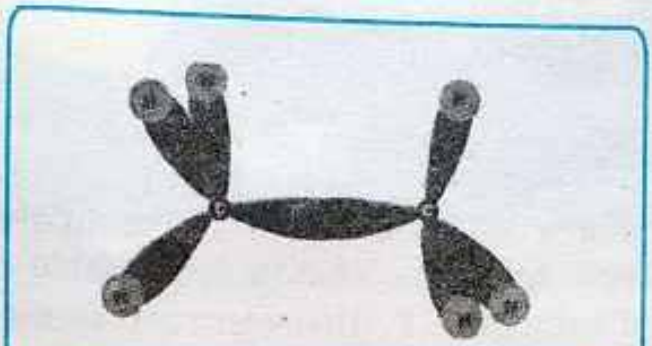
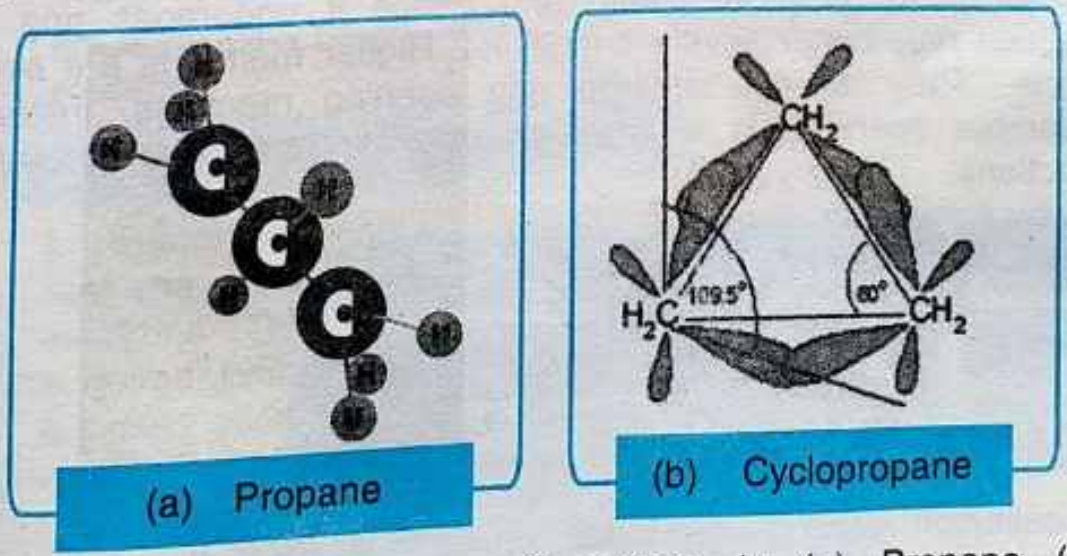


Fig. 16.1 Structure of ethane

(B) In cyclopropane (C_3H_6), each carbon atom, like alkanes, is bonded to four other atoms, so it uses sp^3 hybrid orbitals to form these bonds. However, in this case, the $sp^3 - sp^3$ overlap of C – C bond is not maximum as in the case of alkanes. This is due to the fact that in cyclopropane the C – C – C bond angle is 60° and not 109.5° (true tetrahadred angle) due to which orbitals do not overlap exactly along their axes (Fig. 16.2). Thus the small bond angles of cyclopropane indicate that the overlap of sp^3 orbitals of carbon is less than the overlap of sp^3 - orbitals of carbon in alkanes (e.g. propane).

In cylopropane the three carbon atoms occupy the corners of an equilateral triangle, which results in the C – C – C bond angles to be of 60°. This compression (deviation) from the normal tetrahedral angle of 109·5° to 60° is called the "Angle Strain".



(a) Propane (b) Cyclopropane

Fig 16.2 Overlap between sp^3 orbitals in (a) Propane (b) Cyclopropane: Maximum overlap occurs in propane.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

16.2.4 Relative Stability and Reactivity:

(A) Alkanes:

The carbon atoms in alkanes are fully saturated due to which alkanes are quite inert. Moveover, due to comparable electronegativities of carbon (2.5) and hydrogen (2.1) the electrons in the C–H bonds are practically shared equally between them, and the bond is almost non polar. Consequently polar reagents do not react with alkanes under normal conditions. Furthermore the C–H and C–C bonds are strong bonds and hence alkanes are relatively stable to common reagents such as acids, alkalies and oxidizing agents at room temperature. That is why they are also called paraffins (latin Parum = Little, affins = affinity or reactivity.

(B) Cycloalkanes:

Cycloalkanes resemble alkanes in their chemical behaviour except for cyclopropane and cyclobutane. The strength of bond and hence the stability, depends on the extent of overlap of orbitals. In the case of cyclopropane and cyclobutane, the extent of overlap of orbitals is not maximum due to greater angle strains and are unstable Cyclopropane undergoes ring opening reactions with H_2/Ni and HBr to give open –chain addition products. Cyclobutane, having less angle strain than that of cyclopropane, is more stable and hence it undergoes ring opening reaction only under severe conditions. Higher members are even more stable. They do not undergo ring opening reactions. Instead, they resemble open chain alkanes in reactivity and undergo substitution reactions.

16.2.5 Rreaction of alkanes:

16.2.5.1 Radical Substitution Reactions:

16.2.5.1.1 Substitution reactions:

Substitution reactions are those reactions in which an atom or group of atoms, directly attached to the carbon in the substrate molecule is replaced by another atom or group of atoms. (The term substrate is used for the reactant molecule, undergoing chemical change).

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

For example,

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow{h\nu} \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$

A hydrogen atom of the methane molecule is replaced by a chlorine atom.

A substitution reaction may be initiated by nucleophile, electrophile or free radical.

1. Homolytic and heterolytic bond fission

Bond breaking (fission) is an endothermic process. If sufficient amount of energy is available, a covalent bond (δ – bond) can undergo fission in two ways.

a. Homolytic fission or Homolysis:

In Homolysis when a chemical bond breaks in such a way that each of the two bonded atoms acquires one of the bonding electrons.

$$A-A \rightarrow A^{\bullet} + A^{\bullet}$$

The products $A^{\bullet}$ and $A^{\bullet}$ are called the free radicals, which are electrically neutral species and have one unpaired electron.

b. Heterolytic fission or Heterolysis:

In Heterolysis when a chemical bond breaks in such a way that one of the bonded atoms acquires both of the bonded electrons. The atom with high electronegativity, usually, acquires both the bonding electrons. The arrow in the following general example indicates that the sigma electrons are leaving A and becoming a property of the B.

$$A-B \rightarrow A^{+} + B^{-}$$

The product in this case are the ions.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

2. Electrophile: (Electron loving)

A reagent which can accept an electron pair in a reaction is called an electrophile. An electrophile may be positive ion or neutral molecule with an electron–deficient centre. Examples are;

$H^+, C\ell^+, Br^+, I^+, NO_2^+, R_3C^+, \overset{+}{S}O_3H, A\ell C\ell_3, BF_3$ etc

3. Nucleophile (Nucleus –Loving):

A reagent which can donate an electron –pair in a reaction, is called a nucleophite. A nucleophile may be negative ion or neutral molecule with lone pair of electrons. Examples are,

$C\ell^-, Br^-, I^-, \overline{C}N, \overline{O}H, R-\ddot{N}H_2, \ddot{N}H_3, H_2\ddot{O}:, R\ddot{O}H$ etc

16.2.5.1.2 Mechanism of Free Radical Substitution Reactions:

The step wise description of a chemical reaction, showing the breaking of older bonds and making of new bonds in the substrate leading to the formation of the final product, through transitory intermediates (if any) is called mechanism of the reaction.

Substitution reactions, which are initiated by a free radical are called the free radical substitution reactions. One of the examples of such reactions is the chlorination of methane and ethane in the presence of ultraviolet (u.v.) light.

$$\underset{\text{Methane}}{CH_4} + C\ell_2 \xrightarrow{\text{U.V. Light}} \underset{\text{Methyl Chloride}}{CH_3C\ell} + HC\ell$$

The mechanism involve the following steps:

Step 1. Initiation: A chlorine molecule undergoes homolytic fission in the presence of u.v. light to give chlorine free radicals.

$$C\ell_2 \xrightarrow{U.V} 2C\ell^\bullet$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Step 2. Propagation: (a) A chlorine free radical attacks the methane molecule to give methyl free radicals and $HC\ell$.

$$C\ell^{\bullet} + CH_4 \longrightarrow \dot{C}H_3 + HC\ell$$

Methyl free radical

(b) The methyl free radical ($\dot{C}H_3$), thus produced attacks a chlorine molecule to form methyl chloride and chlorine free radical.

$$\dot{C}H_3 + C\ell - C\ell \longrightarrow CH_3 - C\ell + \dot{C}\ell$$

Methyl chloride

These propagation steps are repeated again and again.

Step 3. Termination: The above chain reaction comes to an end, when any two free radicals combine to form stable products.

$$\dot{C}\ell + \dot{C}\ell \longrightarrow C\ell - C\ell$$
$$\dot{C}H_3 + \dot{C}\ell \longrightarrow CH_3 - C\ell$$
$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3$$

In actual practice the above reaction does not stop at $CH_3 - C\ell$ stage. The remaining three hydrogen atoms of methyl chloride can be successively replaced by chlorine atoms.

$$CH_3 - Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

Methylene chloride
(Dichlomethane)

$$CH_2 - Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$

Chloroform
(Trichloro methane)

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$
Carbon tetrachloride

Thus a mixture of all the four substitution products (CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4) is obtained. The extent of their concentration in the mixture depends on the relative amounts of chlorine and methane. If $C\ell_2$ is taken in excess, the reaction goes to the final substitution product and carbon tetrachloride is the major product. On the contrary, when $C\ell_2$ is limited (or CH_4 is taken in excess), the major product of the reaction is $CH_3C\ell$.

16.2.5.2 Oxidation of Organic Compounds (Combustion):

Alkanes like all other hydrocarbons, burn in air to produce carbon dioxide and water. The reaction is highly exothermic and large quantity of heat is evolved. For example,

$$CH_4 + 2O_2 \xrightarrow[\text{Ignition}]{\text{Flame or}} CO_2 + 2H_2O + 890.95\ kJ/mol$$
Methane

$$2CH_3CH_3 + 7O_2 \xrightarrow{\text{Flame}} 4CO_2 + 6H_2O + 1559\ kJ/mol$$
Ethane

The reaction is of high significance, as it provides basis for their use as fuels to get heat and power. When there is an insufficient supply of oxygen, alkanes on combustion, form carbon monoxide and water or carbon soot and water.

$$2CH_4 + 3O_2 \xrightarrow{\text{Flame}} 2CO + 4H_2O + Heat$$
(Limited)

$$CH_4 + O_2 \longrightarrow C + 2H_2O + Heat$$
(Very limited)

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

16.3 Alkenes:

Alkenes are the unsaturated hydrocarbons which contain a carbon–carbon double bond. They can be represented by the general formula C_nH_{2n}. They are also known as olefins because their lower members form oily products on treatment with chlorine or bromine.

16.3.1 Nomenclature:

There are two systems for naming alkenes.

(A) Common System (B) IUPAC System

(A) Common System:

1. The common names of fist four members are derived from those of the corresponding alkanes by replacing the ending "ane" with "–ylene".

$CH_2 = CH_2$
Ethylene

2. Greek letters, α, β, γ etc are used to distinguish isomers having double bonds at different positions.

$\overset{\alpha}{C}H_2 = \overset{\beta}{C}H - \overset{\gamma}{C}H_2 - \overset{\delta}{C}H_3$, $\overset{\alpha}{C}H_3 - \overset{\beta}{C}H = \overset{\gamma}{C}H - \overset{\delta}{C}H_3$

α–Butylene β–Butylene

(B) IUPAC System:

The IUPAC rules for naming alkenes are same as those for alkanes except the following.

1. The longest continuous carbon chain must include the double bond.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

2. The name given to the longest chain will act as parent name, whereby the ending "ane" of the corresponding alkane is replaced by "ene".

3. Number the chain from that end that will confer upon atom holding the $-C=C-$ the smallest possible number.

4. Since double bond appears between two carbon atoms, therefore its position is indicated by the number of that carbon atom, bearing lower number and this number is written before -ene.

5. If there are more than one double bonds in the molecule, these are indicated by the prefixes di, tri, tetra etc before –ene.

For example:

i. $CH_2 = CH_2$
Ethene

ii. $CH_3 - CH = CH_2$
Propene

iii. $\overset{4}{C}H_3 - \overset{3}{C}H_2 - \overset{2}{C}H = \overset{1}{C}H_2$
1–Butene
OR
But-1-ene

iv. $\overset{1}{C}H_3 - \overset{2}{C}H = \overset{3}{C}H - \overset{4}{C}H_3$
2–Butene
OR
But-2-ene

v. $\overset{5}{C}H_3 - \overset{4}{C}H(CH_3) - \overset{3}{C}H_2 - \overset{2}{C}H = \overset{1}{C}H_2$
4–Methyl–1– pentene
(or 4–Methyl–Pent–1–ene)

vi. $\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H = \overset{4}{C}H - \overset{5}{C}H_3$
1,3–Pentadiene
OR
Pent -2,3-diene

16.3.2 Relative Stability of Alkenes:

Various alkenes differ in stability. The extent of stability of alkenes depends upon the following factors.

i. Position of the double bond in the molecule.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

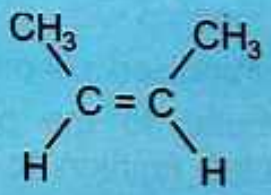
ii. Number and nature of substituents, attached.

iii. Relative positions of the substituents on the doubly bonded carbon atoms.

Measurment and comparison of the heats of hydrogenation of different alkenes, give us a clue about the relative stability of these alkenes. The stabilities of alkenes, which give the same products on combustion can be compared as follows.

$$CH_3-CH_2-CH=CH_2 + 6O_2 \longrightarrow 4CO_2 + 4H_2O + 2719\ kJ/mol$$

1-Butene



$$+ 6O_2 \longrightarrow 4CO_2 + 4H_2O + 2712\ kJ/mol$$

cis-2-Butene



$$+ 6O_2 \longrightarrow 4CO_2 + 4H_2O + 2707\ kJ/mol$$

trans-2-Butene

$$(CH_3)_2C=CH_2 + 6O_2 \longrightarrow 4CO_2 + 4H_2O + 2703\ kJ/mol$$

Isobutylene

Comparison of the heats of combustion of butenes show that 1-butene evolves the largest amount of heat of combustion. In other words, 1-butene possess the highest energy and is thus the least stable of the butenes. Similarly isobutylene is the most stable of the four isomers.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

However, it has been observed that the stabilizing effect increases with increasing the number of substitutions in the molecules. In general, the greater the number of alkyl groups attached to the double bonded carbons, the greater is the stability of alkene.

16.3.3 Structure of Alkenes:

Consider ethene $(CH_2 = CH_2)$ to illustrate the structure of alkenes. In ethene, each carbon atom has three sp^2– hybridized orbitals which are coplanar. One of the sp^2 hybrid orbitals of one carbon atom overlaps linearly with that of another carbon atom to form a sigma (δ) bond. The other two sp^2 hybrid orbitals of each carbon atom overlap with "s" orbitals of hydrogen atoms to form sigma bonds. The unhybridized p–orbitals of the two carbon atoms, which remain perpendicular to the plane of hybridized orbitals, overlap in a side wise (parallel) fashion to form a pi(π) bond between the two carbon atoms. (Fig.16.3).

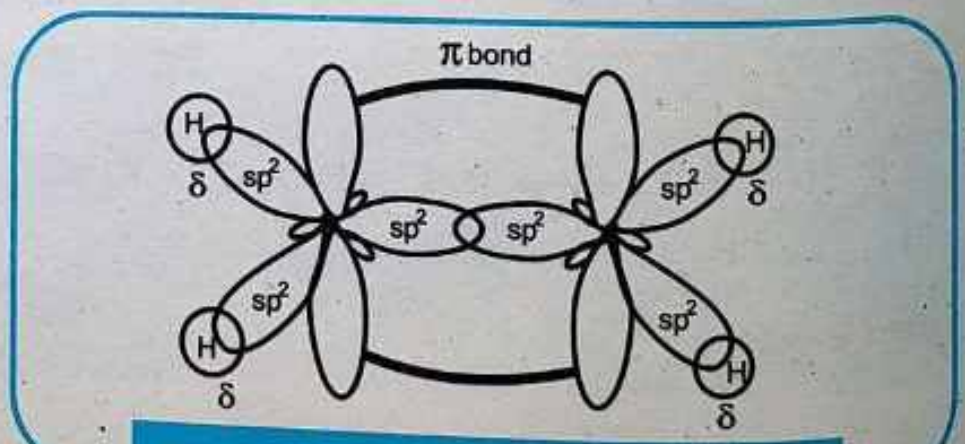


Fig. 16.3 Structure of ethene molecule

The overall structure of ethene is planar in which H–C–C and H–C–H bond angles are approximately equal to 120°. The carbon-carbon double bond length is 1.34A° and the C–H bond lengths are 1.09A° each.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

16.3.4 Preparation of Alkenes:

Alkenes can be prepared by the following methods.

16.3.4.1 By Dehydration of Alcohols:

When an alcohol is heated at 170°C, in the presence of sulphuric acid, a water molecule is eliminated, resulting in the formation of an alkene.



Ethyl alcohol — Ethene

16.3.4.2 By Dehydrohalogenation of Alkyl Halides:

When an alkyl halide is heated with alcoholic solution of KOH or NaOH, a molecule of hydrogen halide (HX) is eliminated which results in the formation of an alkene.



Ethyl bomide — Ethene

16.3.5 Reactivity of Alkenes:

Alkenes are more reactive than alkanes due the presence of π-bond in the alkene molecules. The electron density of pi (π) bond lies above and below the bond axis. It is therefore, more exposed and easily accessible to an external electrophilic (electron seeking) reagent, commonly known as electrophile. Secondly, the overlap of atomic orbitals forming the π bond is not as effective as that in δ – bonds. Thus π bond is weaker than a sigma bond and more easily broken. It is, therefore, favourable for alkenes to add an electrophile

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

across the double bond by breaking the weak π bond and to produce a saturated compound. Such reactions in which unsaturated hydrocarbons (alkenes) are converted into saturated compounds, are called addition reactions.

16.3.6 Reactions of Alkenes:

16.3.6.1 Hydrogenation (Addition of Hydrogen):

Alkenes readily react with hydrogen to form alkanes in the presence of catalyst such as nickel, platinum or palladium at a temperature of 200 – 250°C, under pressure (1–1.5 atm). This is called catalytic hydrogenation.

$$\underset{\text{Ethene}}{H_2C=CH_2} + H_2 \xrightarrow[\text{or Pt or Pd/25°C}]{\text{Ni/200–250°C}} \underset{\text{Ethane}}{CH_3-CH_3}$$

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2 \xrightarrow[\text{Pt or Pd or/25°C}]{\text{Ni 200–250°C}} \underset{\text{Propane}}{CH_3-CH_2-CH_3}$$

The hydrogenation of alkenes is industrially used for the conversion of vegetable oils into ghee.

$$\text{Vegetable oil} + H_2 \xrightarrow[200–250°C]{\text{Ni}} \text{vegetable ghee.}$$

16.3.6.2 Hydrohalogenation (Addition of halogen acids, HX):

Alkenes react with halogen acids (HCℓ, HBr, or HI) to form alkyl halides.

Scanned with CamScanner

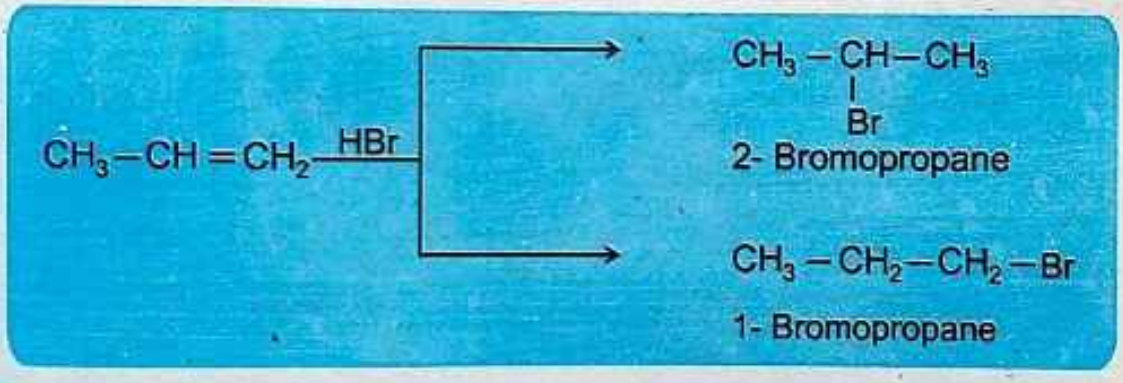
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$CH_2 = CH_2 + HBr \longrightarrow CH_3 - CH_2\,Br$$

Ethene — Ethyl bromide

Mechanism:

The order of reactivity of halogen acids is HI > HBr > HCl > HF. When the alkene is symmetrical (as in the case of ethene), the product formed is the same, no matter which way H – X becomes attached to the alkene. But if the alkene is unsymmetrical, two different isomeric products are possible. For example, propene can react with H – Br in the following two ways.



However, experimentally it has been found that 2 – Bromopropane is the major product. In fact this is in accordance with the Markovnikov's rule.

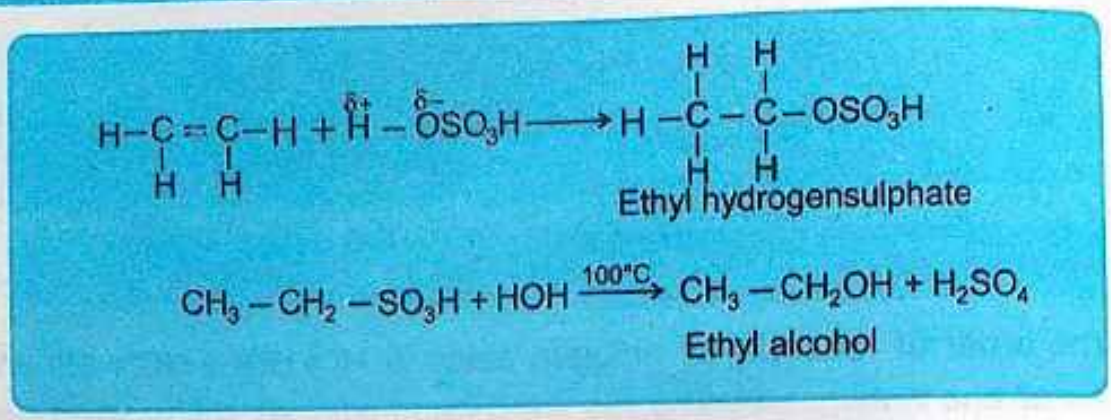
Markovnikov's Rule: It states that when an unsymmetrical (or Polar) reagent is added to an unsymmetrical alkene, the positive part of the reagent attaches itself to that carbon atom involved in the double bond, holding greater number of hydrogen atoms.

16.3.6.3 Hydration (Addition of Water):

Alkenes react with sulphuric acid to produce alkyl hydrogen sulphates, which on hydrolysis yield alcohols, at 100°C.

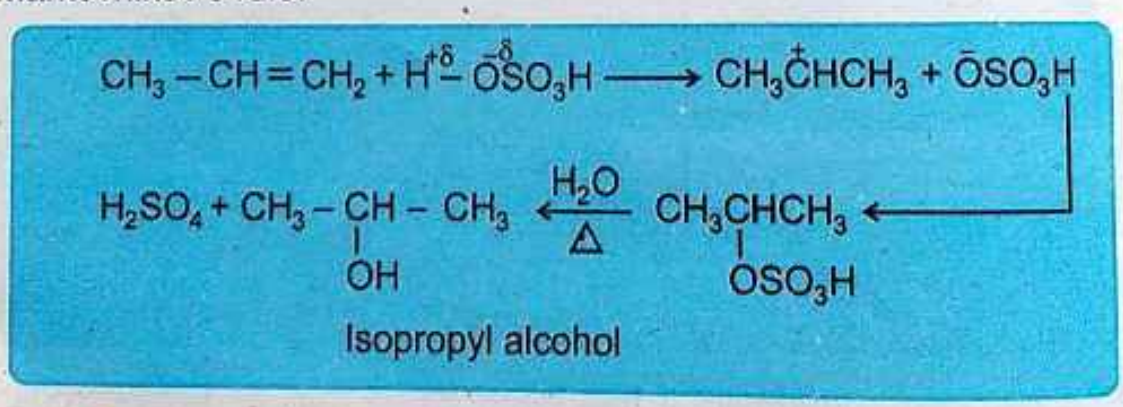
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



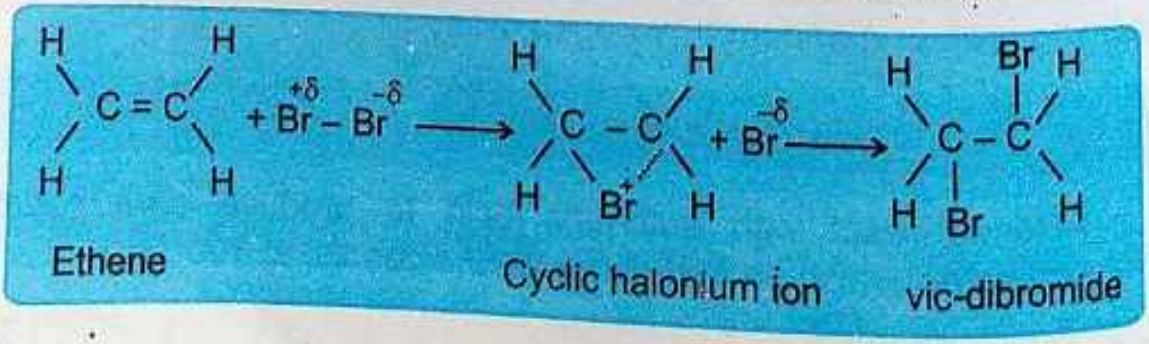
The overall result of the above reaction appears to be the addition of H_2O (hydration) to the double bond.

In case of unsymmetrical alkenes, the reaction follows the Markovnikov's rule.



16.3.6.4 Halogenation (Addition of Halogens):

Alkenes react with halogens ($C\ell_2$ or Br_2) in the presence of an inert solvent (CCl_4) to form dihaloalkanes (vicinal dihalides).



The bromination of alkenes provides a useful test for the presence of a double bond in the molecules. The colour of bromine rapidly discharges

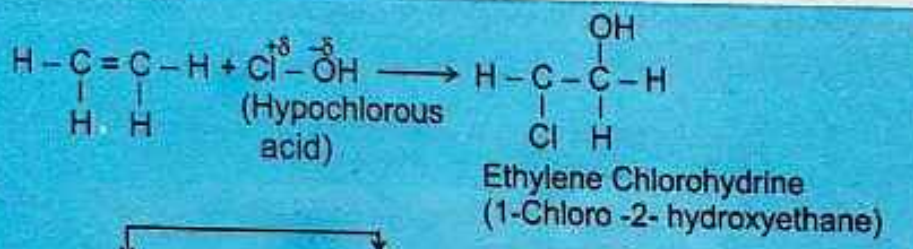
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

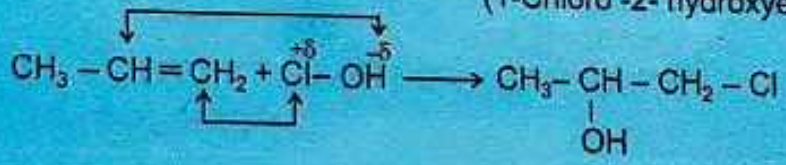
as the colorless dibromo compound is formed. The order of reactivity of various halogens with alkenes is $F_2 > Cl_2 > Br_2 > I_2$.

16.3.6.5 Halohydration: (Addition of Hypohalous acids, X – OH)

Alkenes react with hypohalous acids $(X-OH)$ to form halohydrins. Halohydrins are the organic compounds having hydroxyl group and halogen at the adjacent carbon atoms. The Markovinkov's rule is followed in case of unsymmetrical alkenes.



Ethylene Chlorohydrine
(1-Chloro -2- hydroxyethane)

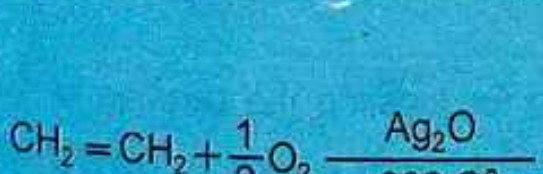


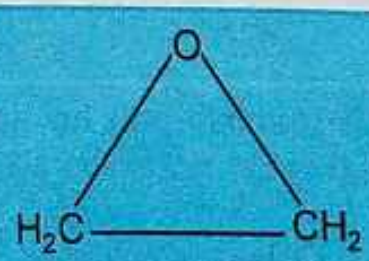
Propene

1-Chloro-2-hydroxypropane.

16.3.6.6 Epoxidation (Addition of O_2):

Alkenes react with oxygen in the presence of silver (Ag) catalyst at temperature 300C° to form epoxides.



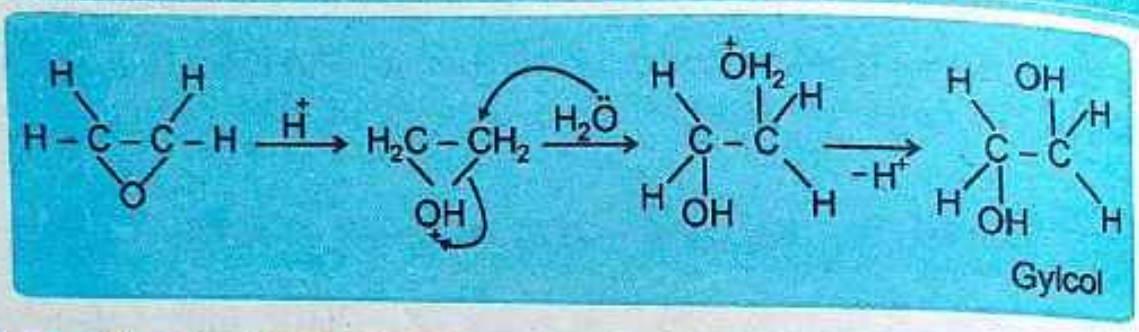


Ethylene oxide
(Epoxide)

The epoxides are very important compounds. They on acid hydrolysis produce glycols.

Scanned with CamScanner

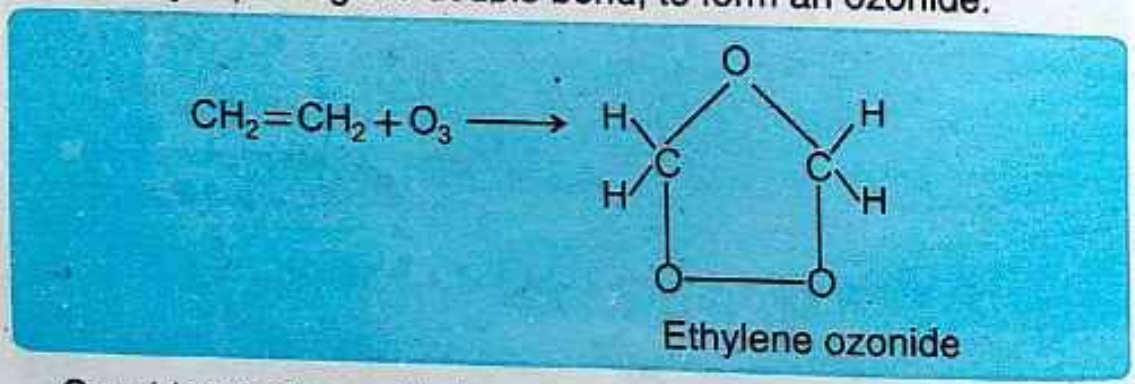
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



Gylcol

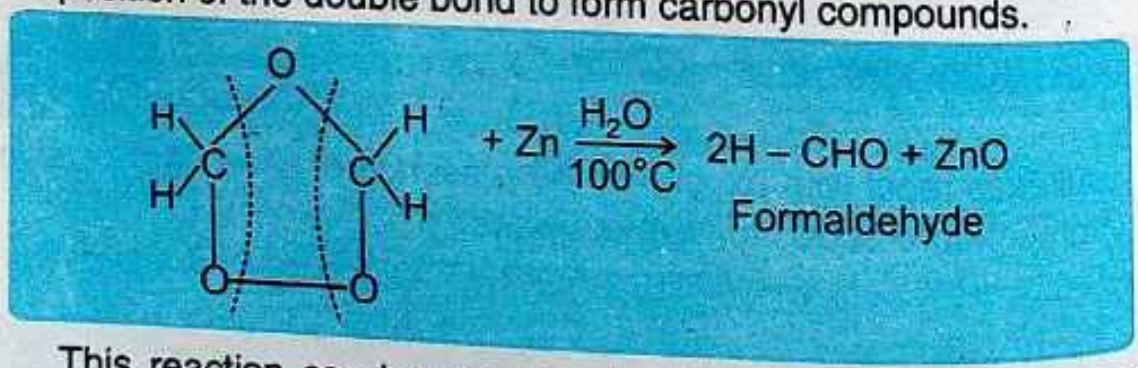
16.3.6.7 Ozonolysis:

When ozone (O_3) is passed through an alkene in an inert solvent, it adds by rupturing the double bond, to form an ozonide.



Ethylene ozonide

Ozonides, being explosive compounds, cannot be isolated. They on warming with Zn and water (hydrolyzed) undergo cleavage at the position of the double bond to form carbonyl compounds.



Formaldehyde

This reaction can be used for locating the position of the double bond in the unknown alkenes.

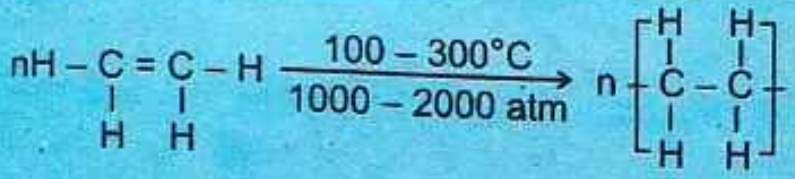
16.3.6.8 Polymerization:

The process by which simple molecules (molecules of low molecular weight) chemically join together to form large molecules with high molecular weight, is called polymerization. The simple molecules that undergo the process are called monomers and the bigger molecule is called the polymer. Simple alkenes when subjected to high

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

temperature (100 – 300°C) and pressure (1000 – 2000 atm) in the presence of a catalyst, form long chain addition polymers, (Molecular weight approximately 20,000 or more).

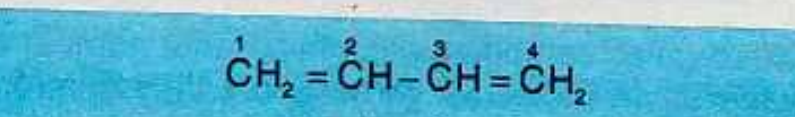


Polyethene

Polyethylene is commercially known as "polyethene" and is used as plastic material in the industries. It is used in the manufacture of buckets, dustbins, carpet backing, packing materials and cable insulation.

16.3.7 Conjugation in Alkenes:

Conjugated compounds are those compounds in which the carbon atoms are linked alternatively by single and double bonds. For example, 1,3 –butadiene.



1,3-butadiene

All the four carbon atoms in this compound are sp^2 hybridized. The C–C and C–H sigma bonds are the result of the overlap of sp^2 hybrid orbitals with each other and with "s" orbitals of the hydrogen atoms. All the carbon and hydrogen atoms lie in the same plane.

Each of the four carbon atom also possess an unhybridized p – orbital, which are perpendicular to the plane of δ – bonds. The p – orbitals of the second and third carbon atoms can overlap on either side. Thus all four p – orbitals overlap to form a large π molecular orbital (MO) (Fig 16.4). Each pair of π electrons is thus attracted not by two, but all four carbons. We can say that the π electrons are delocalized. The delocalization of π electrons is responsible for greater stability of 1,3 – butadiene. The C – C single bonds in 1,3 – butadiene are shorter (1.48 Å) than the normal

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

(1.54 Å) C – C single bonds, while the C – C double bonds are longer (1.37 Å) than normal (1.33 Å) isolated C – C double bonds.

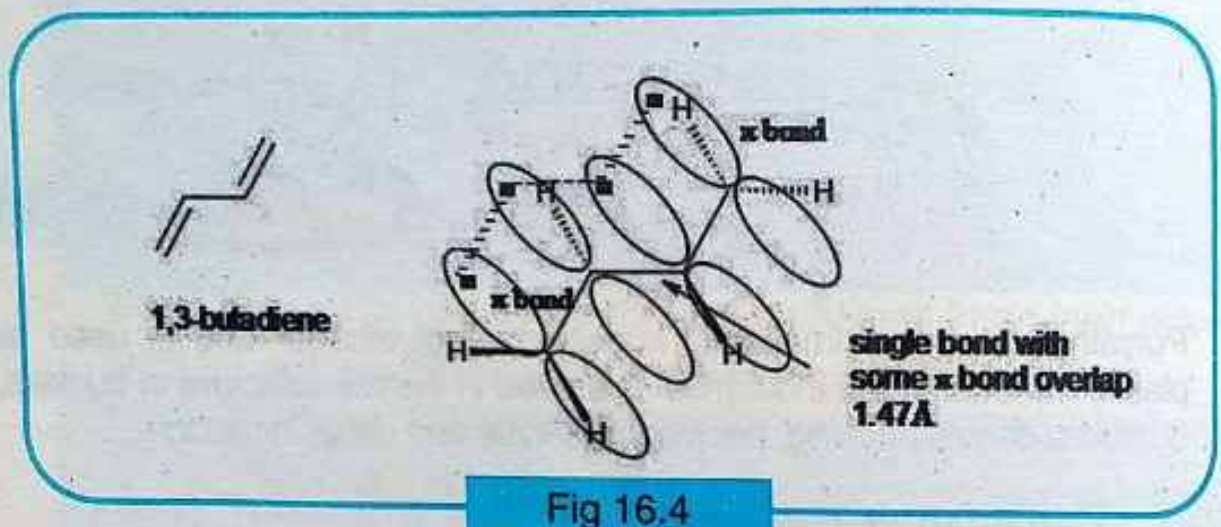


Fig 16.4

16.4 Isomerism:

Many of the organic compounds contain equal number of like atoms and thus have the same molecular formula but they different from each other in their structure, physical and chemical properties. Such compounds are called isomers and this phenomenon is called isomerism.

16.4.1 Types of isomerism

There are two main types of isomerism.

1. Structural isomerism
2. Stereoisomerism

16.4.1.1 Chiral Centres:

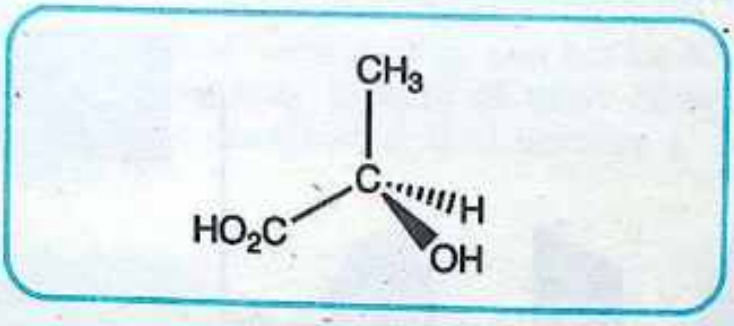
A structural feature within a molecule that is responsible for its chirality is called chiral centre, of the molecule.

16.4.1.2 Carbon based Chiral Centres:

A carbon atom which is bonded to four different groups is called a chiral carbon atom or asymmetric carbon atom. For example,

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



The chirality of lactic acid (described in optical isomerism) is due to the presence of a chiral carbon atom in the molecule. However, a chiral atom is not necessary condition for chiralty. A molecule may not have a chiral atom but still be chiral. On the other hand a molecule may have more than one chiral atoms but still be achiral.

16.4.1.3 Optical Activity:

Ordinary light is an electromagnetic radiation composed of waves vibrating in many different planes. The oscillating waves are of different wave lengths in all possible planes perpendicular to the direction of propagation. It becomes monochromatic (light of a single wave length) when it is passed through a monochromator but it still has waves in all the planes. When it is passed through a polarizer such as Nicol prism (made of calcite, $CaCO_3$), the light is found to vibrate only in one plane, and is said to be plane –polarized or simply polarized light. (Fig 16.5).

Solutions of some organic compounds have the ability to rotate the plane of polarized light. These compounds are said to be optically active, and this property of a compound is called optical activity. Optical activity of a compound is measured by an instrument called polarimeter.

An optically active compound can exist in two isomeric forms, which rotate the plane of polarized light in opposite directions. These are called optical isomers. The isomer which rotates the plane of polarized light to the right (clockwise direction) is said to be dextrorotatory isomer or (+) isomer and the isomer which rotates the plane of polarized light to the left (anticlockwise direction) is said to be levorotatory isomer or (–) isomer.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

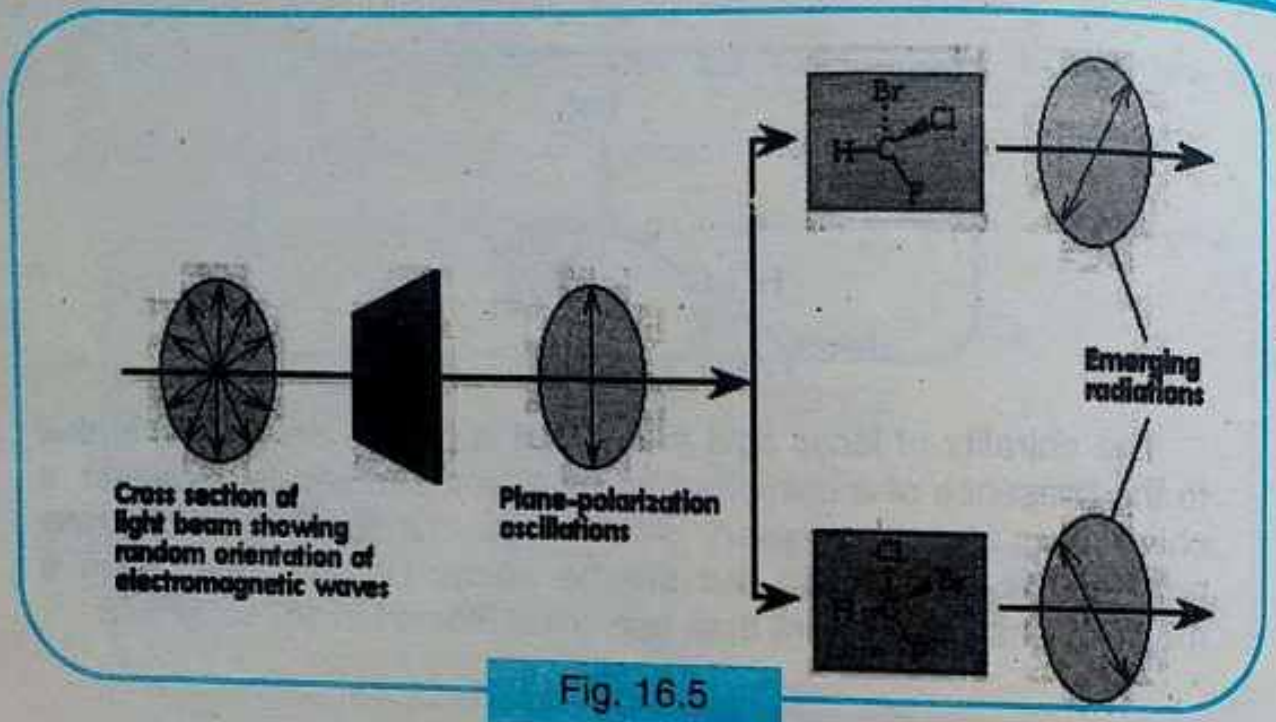
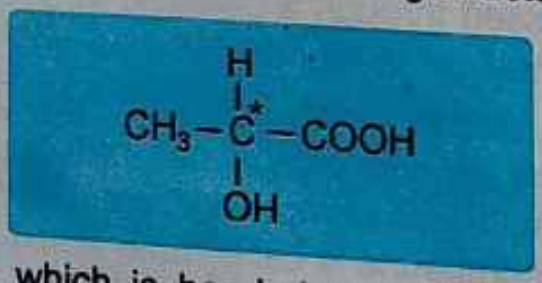


Fig. 16.5

16.4.1.4 Optical Isomerism:

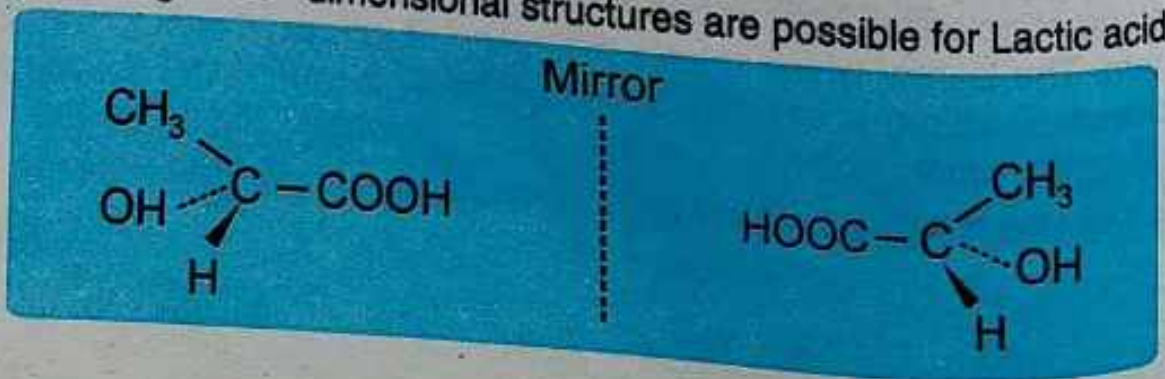
Optical isomerism is a type of Isomerism in which the isomers differ in their interaction towards plane polarized light.

Lactic acid (2–Hydroxy Propanoic acid) is an example of a compound which shows optical isomerism. It contains one asymmetric carbon atom, shown by asteric in the following structure.



A carbon atom which is bonded to four different groups is called Asymmetric or chiral carbon atom.

The following three –dimensional structures are possible for Lactic acid.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

These structures are not identical because they can not be superimposed on each other. They are the mirror images of each other. Such non superimposable mirror images constitute optical isomers and are called enantiomers of each other.

16.4.2 Stereoisomerism:

When isomerism is caused by different arrangement of atoms or groups in space, the phenomenon is called stereoisomerism. Thus the stereoisomers have the same structural formula (and of course the same molecular formula) but differ in the arrangement of atoms or groups in space. In other words, the isomers have different configuration (Three dimensional arrangement of atoms is space is called configuration).

Stereoisomerism is of two types.

i. Geometric or cis –trans isomerism.

ii. Optical isomerism.

Geometrical Isomerism (or cis –trans Isomerism):

The type of isomerism, where isomers possess the same structural formula containing double bond and differ only in respect of arrangement of atoms or groups about the double bond.

These isomers occur when there is restriction to the rotation somewhere in the molecule. For example, 2 – butene can be written in two isomeric form.



These are two different compounds, as they have different boiling points. These two compounds are referred to as the geometric isomer. The isomers in which the two similar groups are on the same side of the double bond is called the cis isomer, while trans isomer has got

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

them on the opposite sides of the double bond. Consequently this type of isomerism is also called cis –trans isomerism.

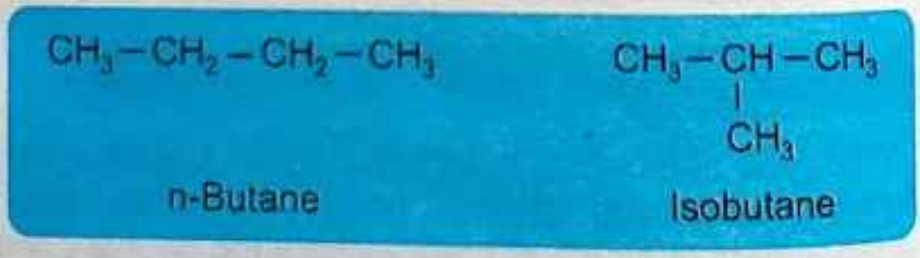
Geometric isomerism in alkenes is possible only when each double bonded carbon atom is attached to two different atoms or groups, thus propene does not have geometric isomers.

16.4.3 Structural Isomerism:

In this type of isomerism, the isomers (compounds) have the same molecular formula but different structural formula i.e. the arrangement of atoms is different in different isomers without any reference to space. Structural isomerism is of five types.

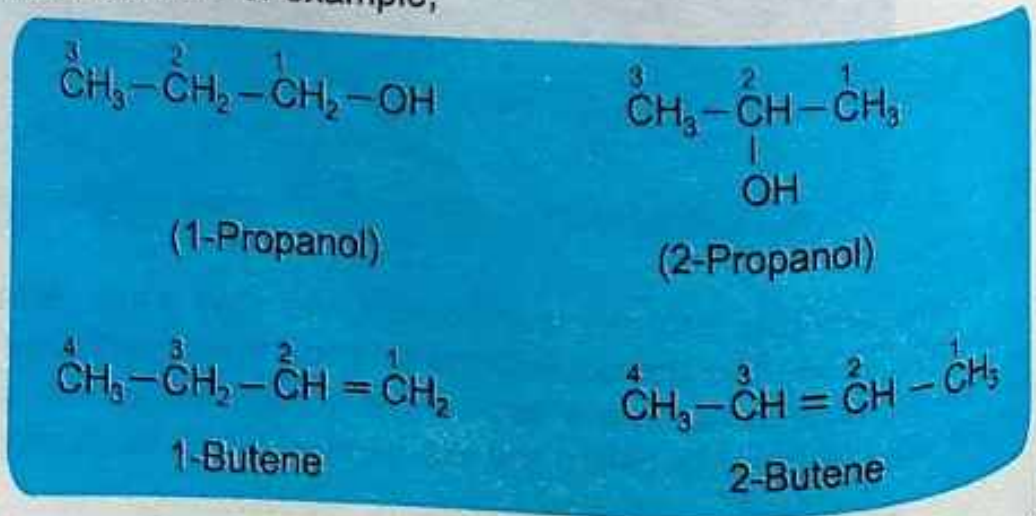
i. Chain Isomerism (Skeletal Isomerism):

Compounds which have same molecular formula but different carbon chains or skeletons are said to be chain isomers and the phenomenon is called chain isomerism. For example;



ii. Position Isomerism:

Position isomers have the same molecular formula but differ in the position of a functional group or the position of double or triple bound. For example;



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

iii. Functional group isomerism:

Functional group isomerism involves compounds, having the same molecular formula but different functional groups. For example,

CH_3-CH_2-OH	CH_3-O-CH_3
Ethyl alcohol	Dimethyl ether
CH_3-CH_2-CHO	$CH_3-CO-CH_3$
Propionaldehyde	Acetone

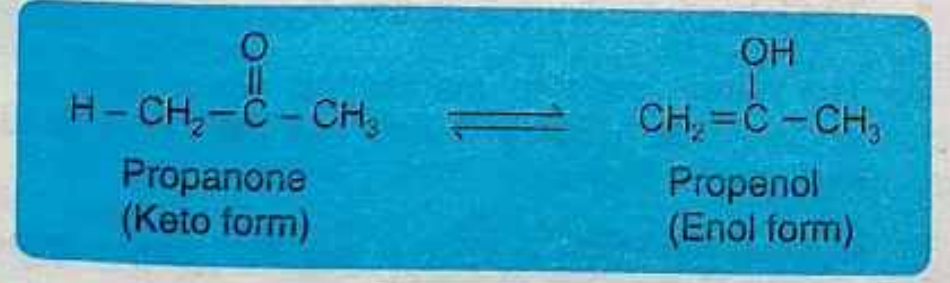
iv. Metamerism:

This type of isomerism is exhibited due to the unequal distribution of carbon atoms or (alkyl groups) on either side of the functional group. Isomers belong to the same homologous series. For example,

$CH_3-CH_2-O-CH_2-CH_3$	$CH_3-O-CH_2-CH_2-CH_3$
Diethyl ether	Methylpropyl ether

v. Tautomerism:

It is a special type of functional group isomerism, in which the isomers are in dynamic equilibrium with each other. For example



Propanone (Keto form) ⇌ Propenol (Enol form)

16.5 Alkynes:

Alkynes are unsaturated hydrocarbons which contain a carbon – carbon triple bond. They can be represented by the general formula

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

C_nH_{2n-2}. The first and most important member of this series is acetylene ($CH \equiv CH$) and hence these are generally called acetylenes.

16.5.1 Nomenclature:

There are two systems for naming alkynes.

(A) Common System:

1. The first member of the alkyne series is named as acetylene.

$$H-C \equiv C-H$$
Acetylene

2. The higher alkynes are regarded as the alkyl derivatives of acetylene. For example,

$CH_3-C \equiv CH$ — Methyl acetylene

$CH_3-C \equiv C-CH_3$ — Dimethyl acetylene

(B) IUPAC System:

The IUPAC rules for naming akynes are the same as those for alkanes, except the following.

1. The longest continuous carbon chain must include the triple bond.
2. The name given to the longest chain acts as parent name, whereby the ending "–ane" of the corresponding alkane is replaced by "–yne".
3. Number the chain in such a way that triply bonded carbon atom ($-C \equiv C-$) gets the smallest number.
4. The position of the triple bond is indicated by the number of that triply bonded carbon atom which bears lower number and this number is written before "–yne".

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

5. For more than one triple bonds in the molecule, the prefix di, tri, tetra etc are used before "–yne".

The following examples will illustrate the above rules.

i. $CH \equiv CH$
Ethyne

ii. $CH_3 - C \equiv CH$
Propyne

iii. $\overset{4}{C}H_3 - \overset{3}{C}H_2 - \overset{2}{C} \equiv \overset{1}{C}H$
1-butyne

iv. $\overset{1}{C}H_3 - \overset{2}{C} \equiv \overset{3}{C} - \overset{4}{C}H$
2-butyne

16.5.2 Relative Stabilities of alkynes:

Like alkenes, the alkynes also exhibit stability to varying degree. The stability of alkynes, also depends on the following factors.

i. Position of the triple bond in the molecule.

ii. Number and nature of the substitutuents, attached.

The stabilities of various isomers of an alkyne (having same molecular mass), can be compared, by measuring their heats of hydrogenation or heats of combustion.

16.5.3 Structure:

In acetylene each carbon atom has two sp hybrid orbitals which lie on the same line .Each carbon atom also has two unhybridized p–orbitals, which are perpendicular to each other and to the plane of sp–hybrid orbitals. One sp–hybrid orbital of one carbon atom linearly overlaps with the sp hybrid orbital of the other carbon atom to form δ–bond between the two carbon atoms. The other sp–hybrid orbitals of both the carbon atoms overlaps with the "s" orbitals of the two hydrogen atoms to form two C–H δ bonds.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The two p –orbitals (unhybridized) of both the carbon atoms approach each other in a sidewise manner $(p_y - p_y$ and $p_z - p_z)$ to form two pi(π) bonds. (Fig 16.6)

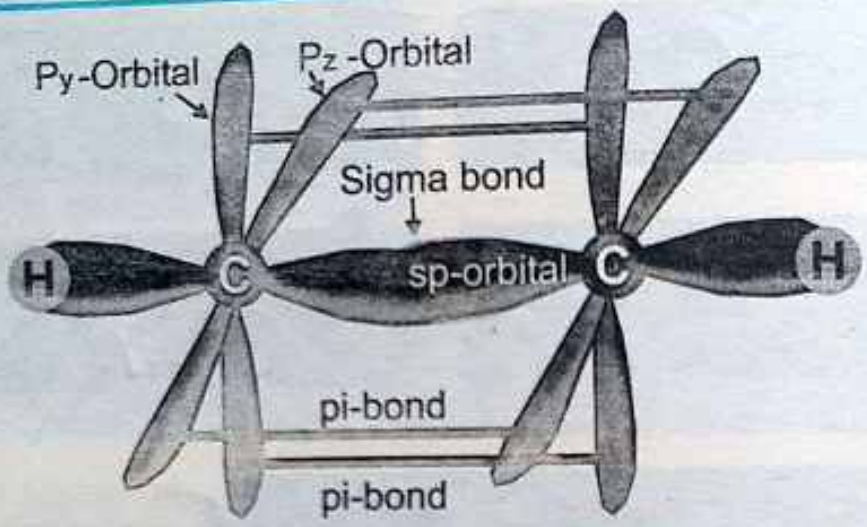


Fig: 16.6 Structure of acetylene

Thus the carbon –carbon triple bond is made up of one sigma (δ) and two pi(π) bonds. The acetylene molecules has linear geometry with C–C–H bond angle of 180°. The carbon –carbon triple bond length is 1.19Å and that of C–H bond is 1.09Å

16.5.4 Physical Properties:

1. The first three members (ethyne, propyne and butynes) are gases, next eight $(C_5 - C_{17})$ are liquids and higher alkynes are solids at room temperature and pressure.
2. With the exception of acetylene which has garlic like odour, all other alkynes are odourless and colourless.
3. They are soluble in organic solvents such as acetone, benzene, ethanol etc but only slightly soluble in water.
4. The boiling points of alkynes are slightly higher than the corresponding alkenes, and increase regularly with increase in the number of carbon atoms in the alkynes. However, their melting points do not follow a

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

regular sequence. Instead, they change irregularly with increase in the number of carbon atoms (Table 16.4).

5. They are slightly more denser than the corresponding alkanes and alkenes.

Table 16.4 Boiling and melting points of some alkynes.

Name	Formula	M.P (°C)	B.P (°C)
Acetylene	$CH \equiv CH$	–82	–75
Propyne	$CH_3 - CH \equiv CH$	–102	–23
1– Butyne	$CH \equiv C - CH_2 - CH_3$	–122	09
1Pentyne	$CH_3 - CH_2 - CH_2 - C \equiv CH$	–98	40

16.5.5 Preparation of Alkynes by Elimination Reactions:

Elimination reactions involve the removal of atoms or groups from two adjacent carbon atoms. These reactions result in the formation of unsaturated compounds. Alkyne can be prepared by the following elimination reactions.

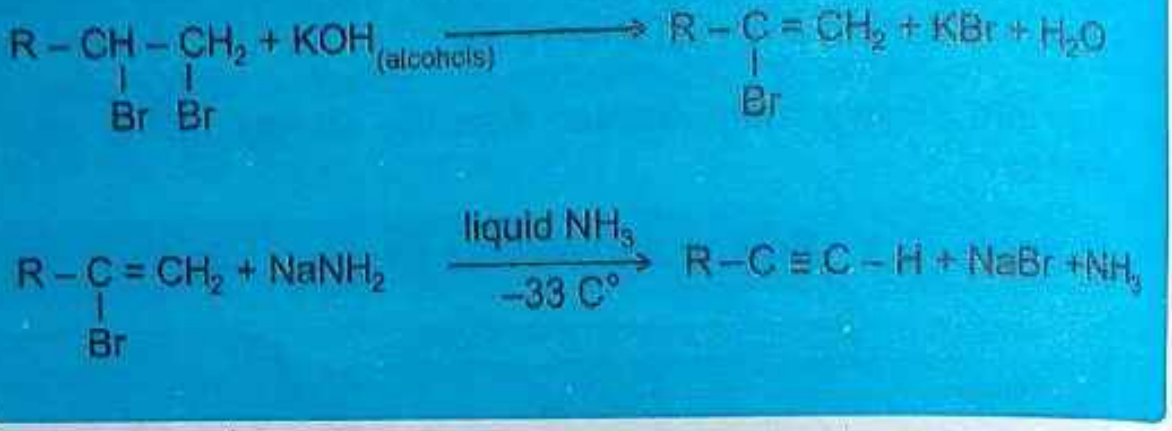
1. By the dehydrohalogenation of Vicinal Dihalides:

Compounds having two halogen atoms on adjacent carbon atoms are called vicinal dihalides.

These compounds, when treated with alcoholic KOH followed by sodium amide ($NaNH_2$) in liquid ammonia form alkynes. It is a two step reaction. The elimination product of the first step (vinyl halide), being unreactive, is treated with stronger base ($NaNH_2$) to remove another HX molecule.

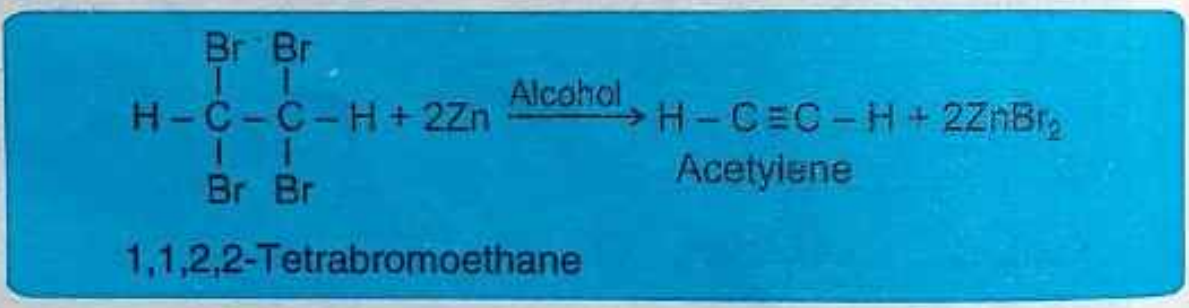
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



2. By the dehalogenation of Tetrahalides:

When tetrahalides are heated with zinc dust in alcohol, alkynes are formed.



16.5.6 Reactivity of Alkynes:

Alkynes are unsaturated hydrocarbons like alkenes. Thus they resemble alkenes in most of their reactions. For example, alkyne add hydrogen, halogens, and halogen acids much like the addition of these reagents to alkenes. However, unlike alkenes which add one molecules of these reagents, alkynes add two molecules in a step-wise manner.

It is to be noted that a carbon–carbon triple bond (alkynes), in general, is less reactive than a carbon–carbon double bond (alkenes) towards electrophillic reagents. This is due to the following two reasons.

i. In alkynes, there are two π-bonds, the four lobes of which merge to form a single electron cloud. This cloud is cylindrically symmetrical about the internuclear axis and occupies a big volume. (Fig 16.7). Thus electron –density per unit volume becomes low.

Due to decrease in the electron density, π–electrons are not easily available to an electrophile. Hence alkynes are less reactive towards electrophilic addition reactions.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

ii. The carbon atom in alkynes are sp – hybridized while in alkenes are sp^2 hybridized. Greater the s – character of an orbital, the more highly the electrons in that orbital are held by the nucleus. Thus π electrons in alkynes (50% s – character) are more strongly held by the carbon atom than in case of alkenes (33% s – character) and are less easily available for reactions with electrophile. This makes alkynes less reactive than alkenes in electrophilic reactions.



Fig. 16.7

16.5.7 Acidity of Terminal Alkynes:

Alkynes in which the triple bond is at the end of the chain, are refered to as terminal or 1 – alkynes.

$H-C\equiv C-H$ Acetylene

$R-CH_2-C\equiv CH$ terminal alkyne

Terminal alkynes and acetylene are acidic in nature. They readily donate proton to a strong base. Thus if acetylene or a terminal alkyne is treated with a solution of sodium amide ($NaNH_2$) in liquid ammonia, sodium acetylide is obtained.

$$H-C\equiv C-H + NaNH_2 \xrightarrow{\text{Liq. } NH_3} H-C\equiv CNa + NH_3$$

Acetylene — Sodium acetylide

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$R-C\equiv C-H + Na\,NH_2 \xrightarrow{Liq.\ NH_3} R-C\equiv CNa + NH_3$$

1–Alkyne → Sodium alkynide

In ethyne and other terminal alkynes, the hydrogen atom is bonded to the carbon atom with sp-s overlap. An sp hybrid orbital has 50% s character in it and renders the carbon atom more electronegative than sp^2 and sp^3 hybridized carbons. As a result, the sp hybridized carbon atom of a terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic.

$$R-C\equiv \overset{-\delta}{C}-\overset{+\delta}{H}$$

Because of acidic nature, acetylene and 1–alkynes react with ammoniacal solutions of cuprous chloride and silver nitrate to form acetylides and alkynides of these metals.

$$CH\equiv CH + Cu_2Cl_2 + 2\,NH_4OH \longrightarrow Cu\overset{+}{C}\equiv C\overset{-}{C}Cu^{+} + 2\,NH_4Cl + 2H_2O$$

Copper acetylide (red ppt.)

$$HC\equiv CH + 2\,Ag(NO_3)_2 + 2NH_4OH \longrightarrow Ag\overset{+}{C}\equiv C\overset{-}{C}Ag^{+} + 2\,NH_4NO_3 + 2H_2O$$

Silver acetylide (White ppt)

Copper and silver acetylides are highly explosive in dry condition. They can however, be decomposed by acids such as HNO_3 to regenerate acetylene.

Since other alkynes (non–terminal) do not form acetylides (alkynides), this reaction can be used as a test to distinguish 1–alkynes from non –terminal alkynes.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

16.5.8 Addition Reactions of Alkynes:

1. Hydrogenation (Addition of Hydrogen):

Two molecules of hydrogen are added to alkynes stepwise, initially forming the corresponding alkenes and finally alkanes. This reaction takes place in the presence of catalysts such as Pt, Pd or Ni.

$$H-C\equiv C-H+H_2 \xrightarrow[Pt/\,Pd]{230-250^\circ C,\ Ni} CH_2=CH_2$$

Ethyne — Ethene

$$CH_2=CH_2+H_2 \xrightarrow[Pt/Pd]{230-250^\circ C,\ Ni} CH_3-CH_3$$

Ethane

The reaction can be stopped at the alkene stage by poisoning Pd catalyst with $BaSO_4$ + quinoline (Lindlar's catalyst).

2. Reduction by Dissolving Metal (Salt Formation):

1–alkynes and acetylene, react with metals in liquid ammonia such as sodium, to form salts called alkynides or acetylides, however non-terminal alkynes give trans alkenes under this condition.

$$H-C\equiv C-H+Na \xrightarrow{liq\ NH_3} H-C\equiv CNa+1/2H_2$$

Acetylene — Sodium acetylide

$$R-C\equiv C-R+Na \xrightarrow{liq\ NH_3} \begin{matrix} R \\ H \end{matrix}\!\!>\!C=\!<\!\!\begin{matrix} H \\ R \end{matrix}$$

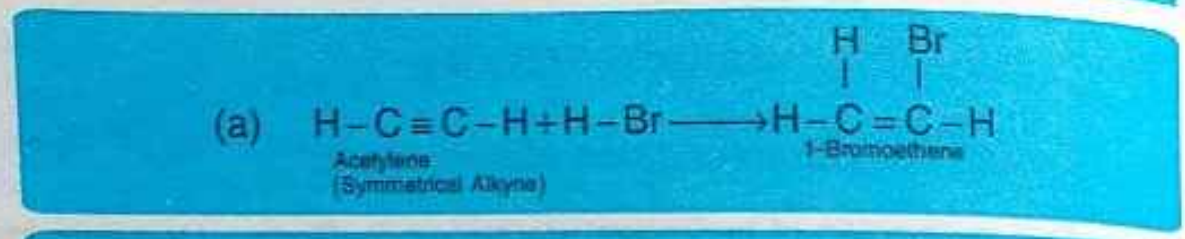
3. Hydrohalogenation (Addition of Halogen Acids):

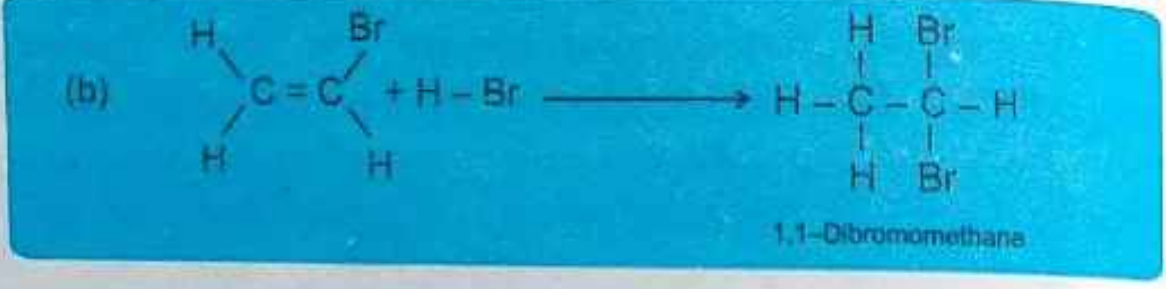
Two molecules of halogen acids are added to alkynes in two steps. In case of symmetric alkyne, the second step follows the Markovnikov's rule. However addition of halogen acids, HX to unsymmetrical alkynes follows Markovnikov's rule in both the steps.

For symmetrical alkyne:

Scanned with CamScanner

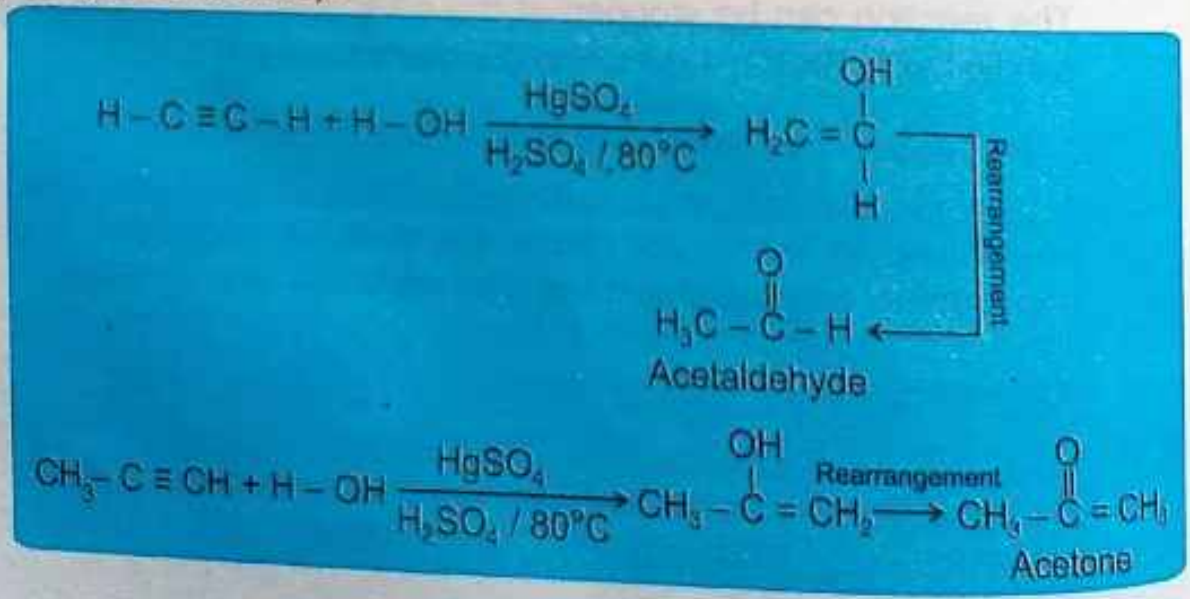
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)





4. Hydration (Addition of Water):

Alkynes react with water in the presence of mercuric sulphate ($HgSO_4$) and sulphuric acid (H_2SO_4) to form a carbonyl compound (aldehyde or ketone).

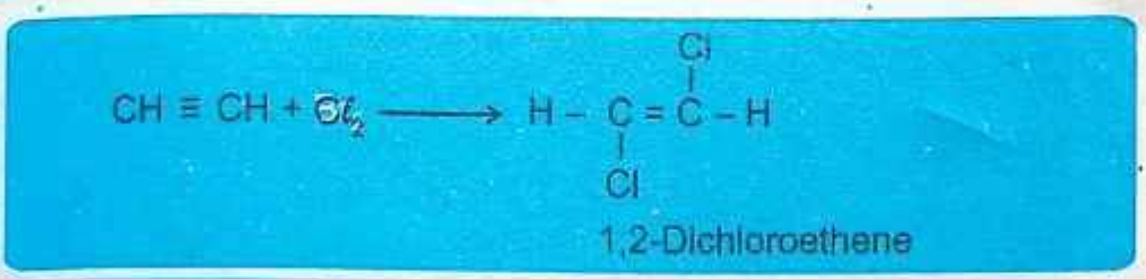


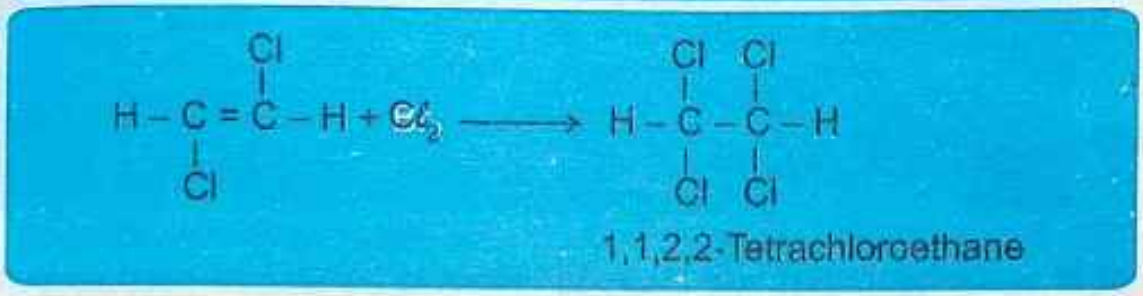
5. Halogenation (Chlorination):

Bromine adds to alkynes in two steps, forming dihalides (dihaloalkene) and then tetra halides (tetrahaloalkanes).

Scanned with CamScanner

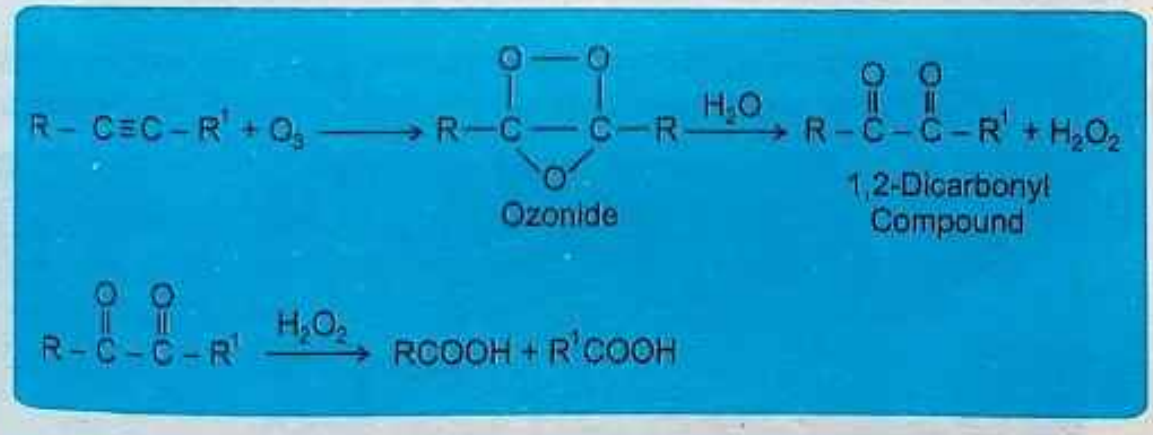
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)





6. Ozonolysis (addition of ozone, O_3):

Alkynes react with ozone (O_3) to form ozonides. The ozonides may be decomposed with water to give ketones, which are finally oxidized to acids by H_2O_2 produced in the reaction, resulting in formation of carboxylic acid.

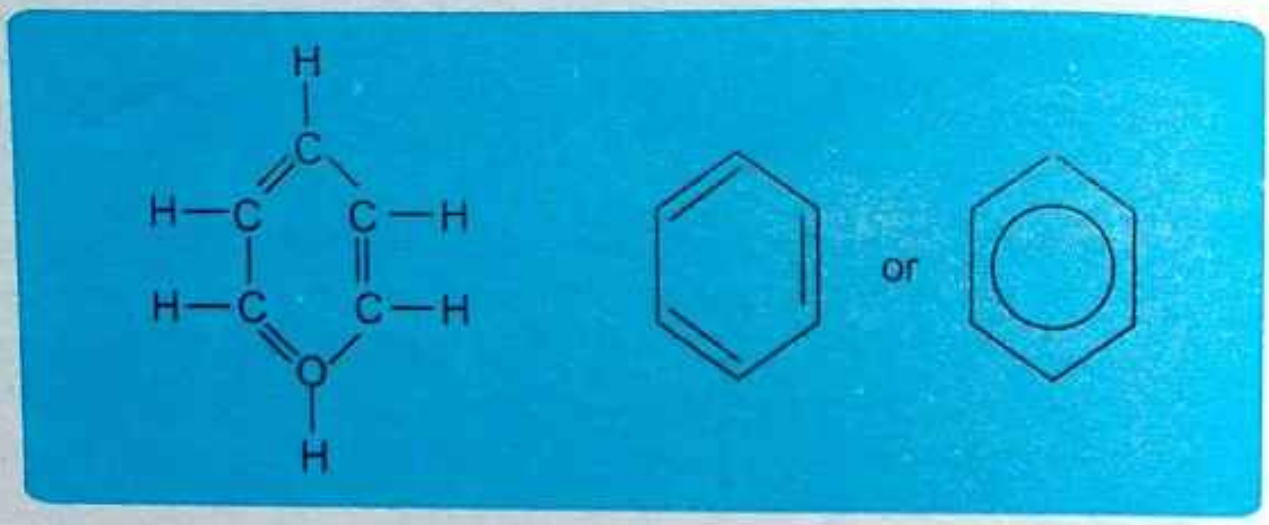


16.6 Benzene and Subtituted Benzenes:

Benzene is an aromatic hydrocarbon. Its molecular formula is C_6H_6. The following ring structure is usually written for benzene, where each corner represents a carbon atom.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



It is understood that one hydrogen atom is bonded to each carbon atom. Mono substituted, disubstituted and polysubstituted benzene derivatives are formed by the replacement of one, two or more hydrogen atoms respectively.

16.6.1 Nomenclature:

Benzene and its substituted compounds are named by common names which are also accepted by the IUPAC System.

1. a. Mono substituted benzene derivatives are named by putting the name of the substituent before the word benzene. For example,

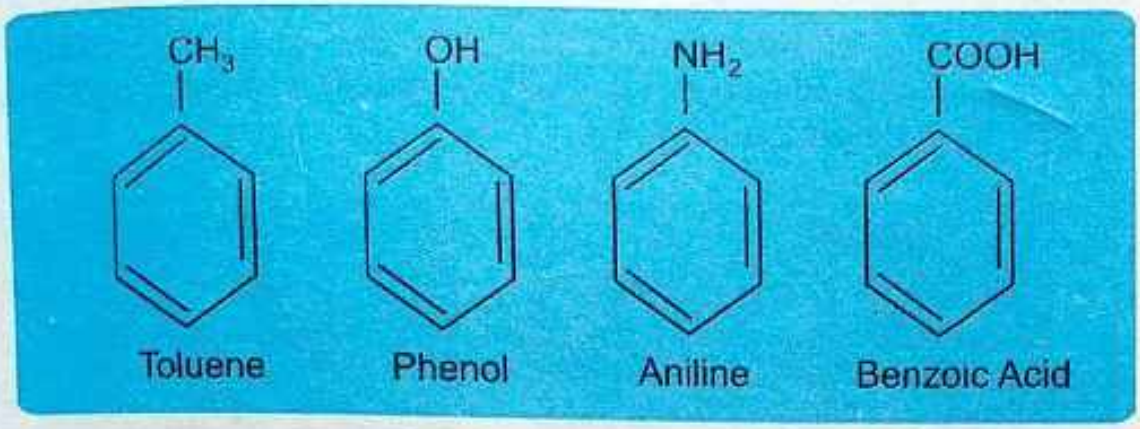


Bromobenzene

b. Some Mono substituted benzene derivatives have been given "Special names". They must be remembered as such. For examples,

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

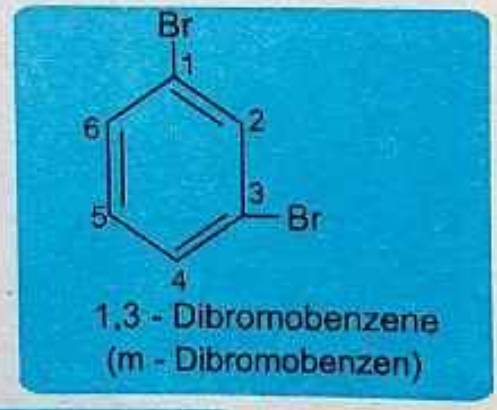


2. In disubstituted benzene derivates, the relative substitutions are mentioned by using numbers (1,2)(1,3)(1,4) or by using the prefixes ortho (0–), meta (m–) and para (p–).

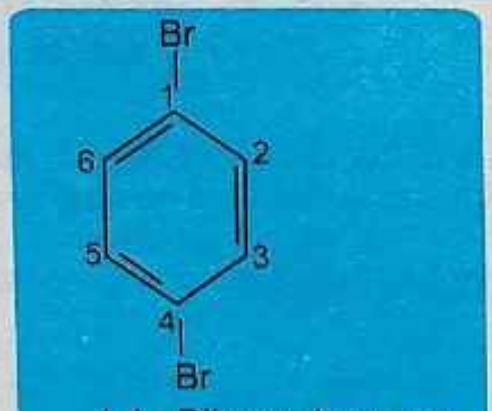
   a. For similar substituents, the prefix di is also used before the name of the substituents. For example



1,2 - Dibromobenzene
(o - Dibromobenzen)



1,3 - Dibromobenzene
(m - Dibromobenzen)



1,4 - Dibromobenzene
(p - Dibromobenzen)

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

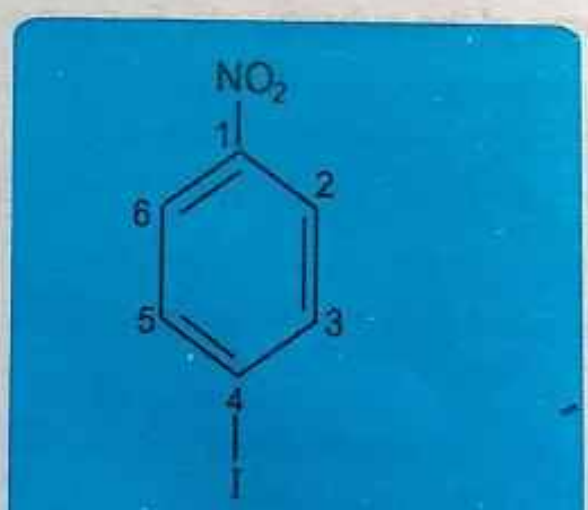
b. If the substituents are different, they are named in alphabatical order the last named substituent is understood to be at position 1. e.g;



2 - Bromonitrobenzene
(o - Bromonitrobenzene)



3 - Chloroiodobenzene
(m - Chloroiodobenzene)

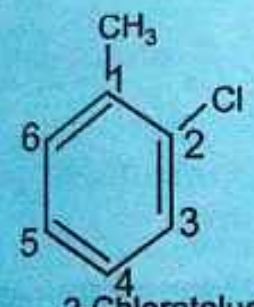


4 - Iodonitrobenzene
(p - Iodonitrobenzene)

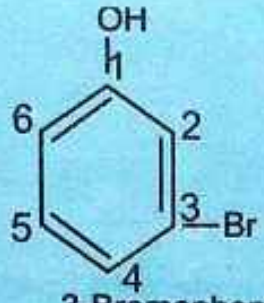
c. If one of the substiuent is such that it gives special name to the molecule then the special name is used as the parent name. The other substituent, alongwith its position, is mentioned before the parent name. For example,

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



2-Chlorotoluene
(o-Chlrorotoluene)

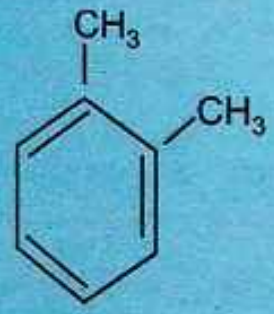


3-Bromophenol
(m-Bromophenol)



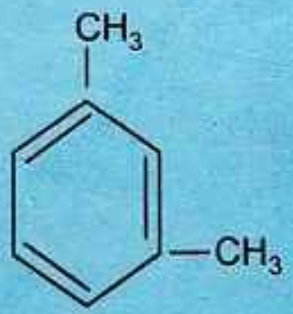
4-Nitroaniline
(p-Nitroaniline)

d. Some disubstituted benzene derivatives are given special names. For example,



o-xylene

or
1,2-Dimethyl
benzene

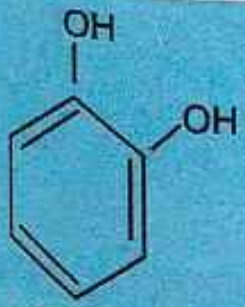


m-xylene

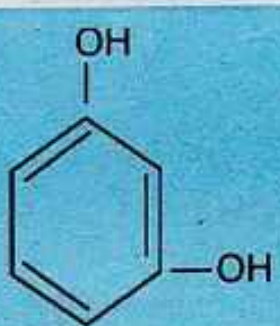
or
1,3-Dimethyl
benzene



p-xylene
or 1,4-Dimethyl
benzene



Catechol



Resorcinol



Hydroquinone
(Quinol)

Scanned with CamScanner

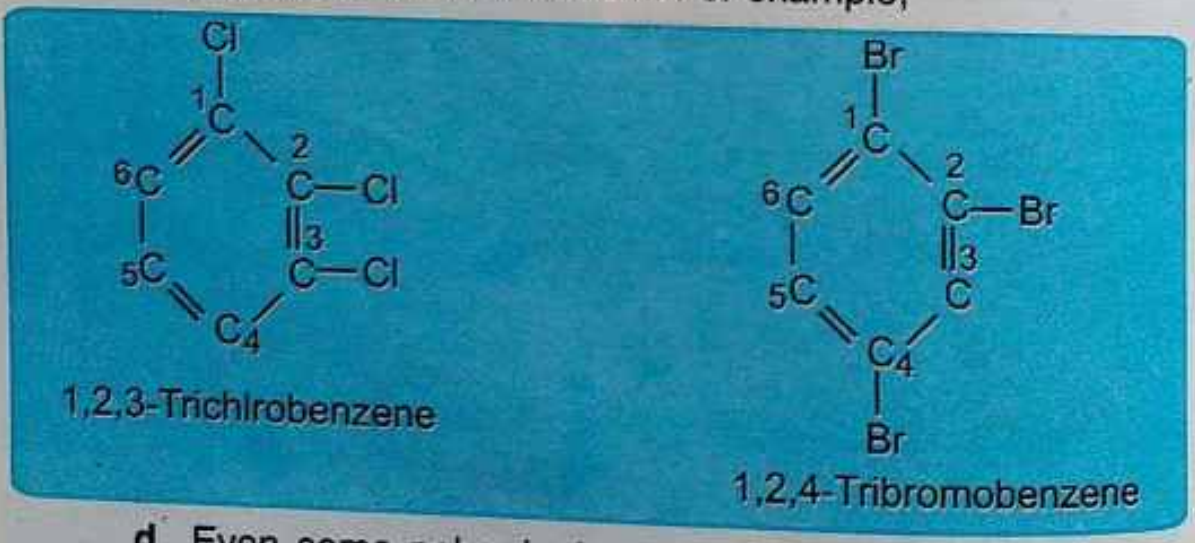
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

3. Polysubstituted benzene derivatives, are invariably assigned systematic names.

   a. For similar atoms / groups the prefix tri, tetra etc are used before the substitutents.

   b. If the groups attached, are different, they are named in alphabetical order. The last one in the order will be understood to be at position number one.

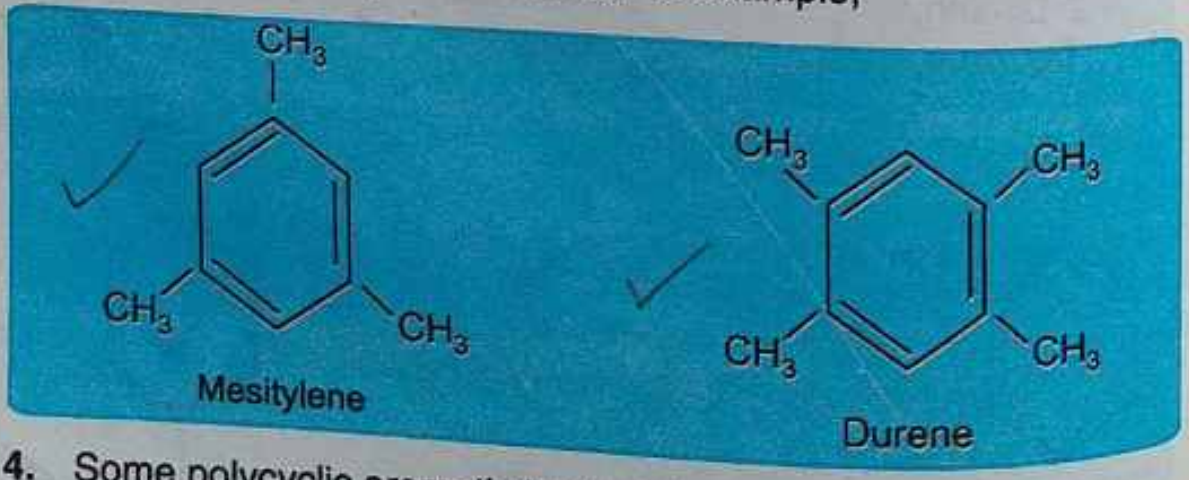
   c. To indicate the position of the substituents, the ring is numbered in such a way that all the numbers used in the name, give the lowest sum. For example,



1,2,3-Trichlrobenzene

1,2,4-Tribromobenzene

   d. Even some polysubstituted benzene derivatives have been assigned special names. For example,



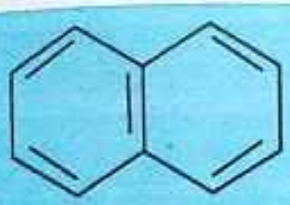
Mesitylene

Durene

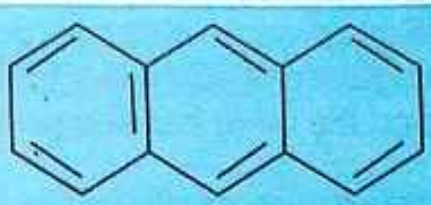
4. Some polycyclic aromatic hydrocarbons are:

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



Naphthalene



Anthracene

16.6.2 Physical Properties of Benzene:

At room temperature and atmospheric pressure, benzene is a colourless liquid. It has a peculiar smell and burning taste. The specific gravity of benzene is 0.8788. Benzene melts at 5.5°C and boils at 80·2°C. It is highly inflammable. Benzene is insoluble in water but soluble in ether, alcohol and petrol. It is used as solvent for many fats and resins.

16.6.3 Structure:

Molecular Orbital Aspects:

The structure of benzene can best be described in terms of the modern Molecular Orbital Theory (MOT). Each carbon atom of the ring is linked to others by sp^2 hybrid orbitals and with s orbitals of the six hydrogen atoms, forming six C – C and six C – H sigma bonds. (fig 16.8)

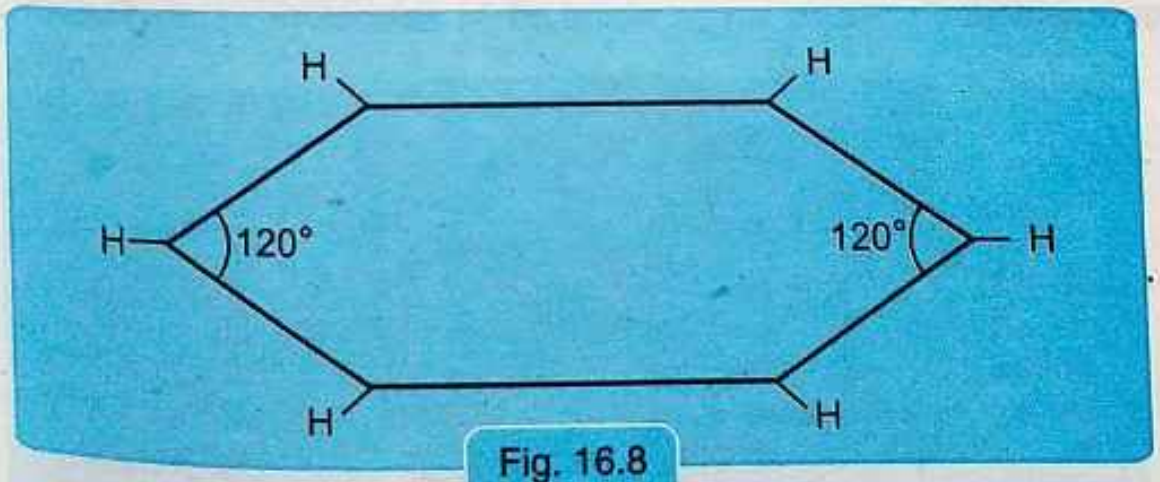


Fig. 16.8

Since the δ – bond results from the overlap of planar sp^2 hybrid orbitals, all carbon and hydrogen atoms in benzene lie in the same plane. All δ – bonds in benzene lie in one plane and all the bond angles are 120°.

Each carbon atom also possesses an unhybridized p orbital (containing one electron), which are perpendicular to the plane of δ bonds. The lateral

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

(side wise) overlap of these p orbitals produces a π molecular orbital containing six electrons. (fig 16.9). one half of this π molecular orbital lies above and the other half lies below the plane of the δ bonds.

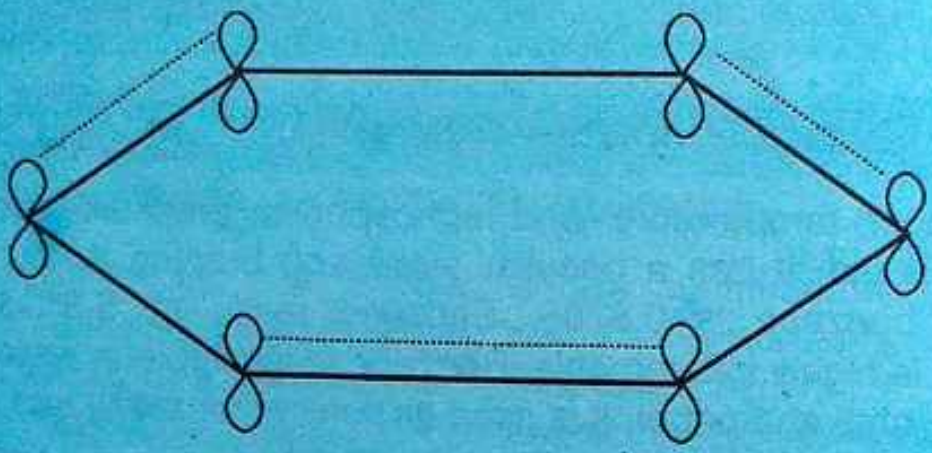
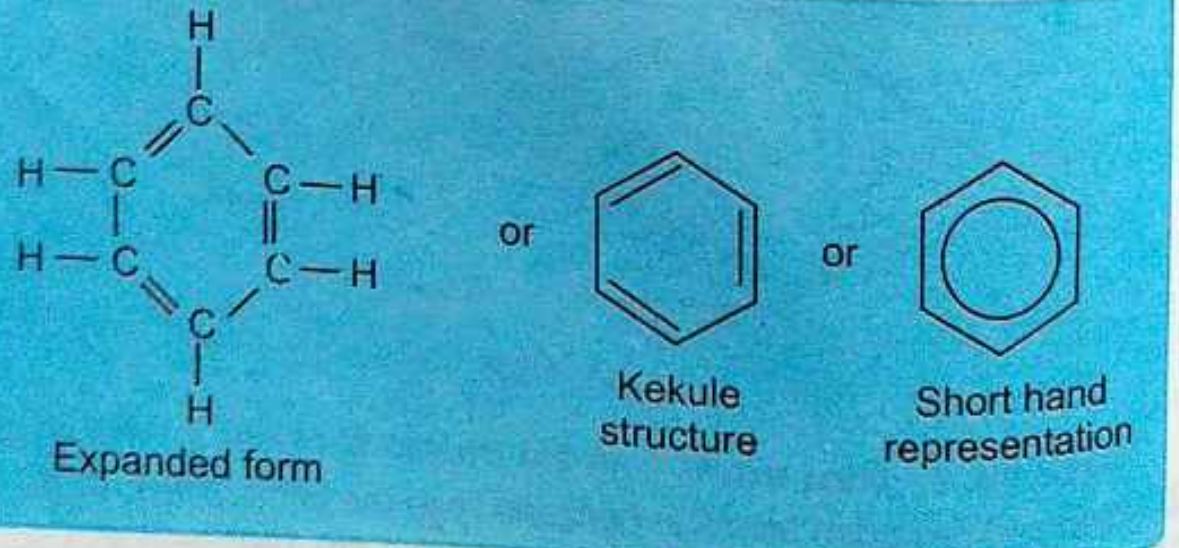


Fig. 16.9 Unhybridized p-p orbitals overlap to form π bonds

The six electrons of the p orbitals are associated with all the six carbon atoms and are said to be delocalized. Hence a stronger π bond and a more stable molecule of benzene is formed. It is this extensive π-electron delocalization which is responsible for the special chemical behavior of benzene. There are three ways in which benzene can be represented.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

16.6.4 Resonance, Resonance Energy and Stabilization:

Resonance:

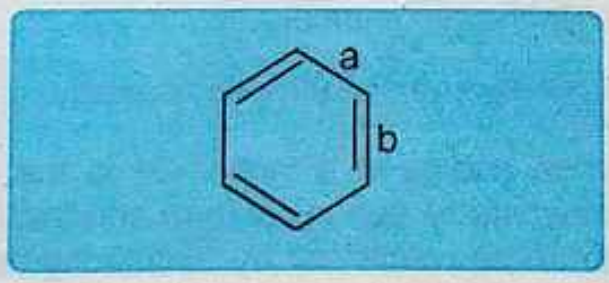
Generally, if the properties of compound are known, we can predict/draw its Lewis structure or if the lewis structure of a compound is known, we can guess its chemical properties. For example a compound with structure $CH_3-\overset{b}{C}H=\overset{a}{C}H-CH_2-OH$ should have the following properties.

i. It will react with carboxylic acids to form esters, by virtue of the presence of –OH group.

ii. It will add molecule of H_2 or Br_2 by virtue of the presence of double bond.

iii. The bond length of bonds "a" and "b" will be 1.54°A and 1.33°A respectively.

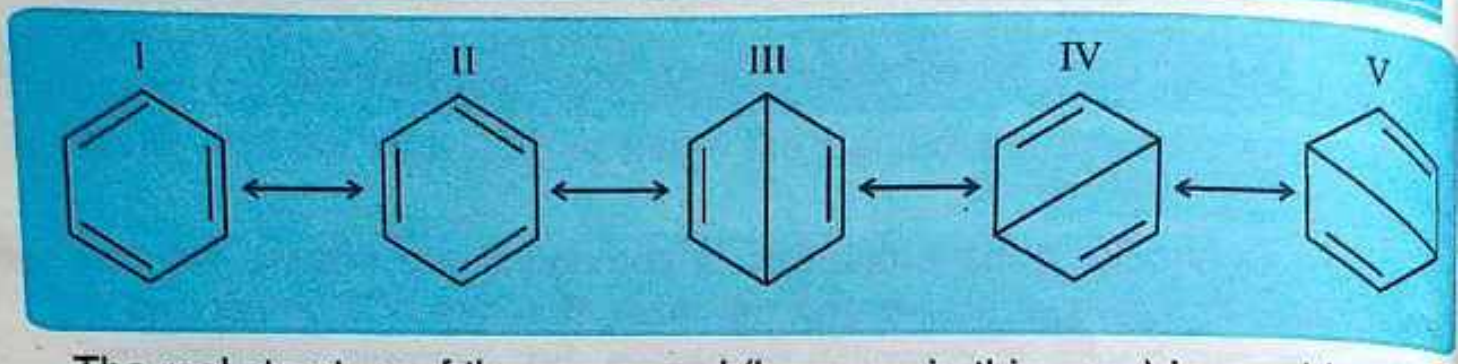
But this is not true for a compound, having a delocalized π electron system. For example, the following structure (which is in fact 1,3,5 –cyclohexatriene) commonly known as benzene is expected to add readily three molecules of Br_2 but in actual practice it does not do so.



Similarly the bond lengths of bonds "a" and "b" are not equal to 1.54A° and 1.33A°. Thus it can be said that the above structure is not the actual structure of benzene. In such a case we write more than one structures to represent the actual structure of the molecule. These structures together may explain the properties of the compound but none of them is the real structure of the compound. Thus for benzene the following structures (including the one written above) are suggested to better explain the behaviour of benzene.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



The real structure of the compound (benzene in this case) is considered to be a weighted average of all the contributing structures.

"The representation of a real structure as a weighted average of two or more contributing structures is called resonance".

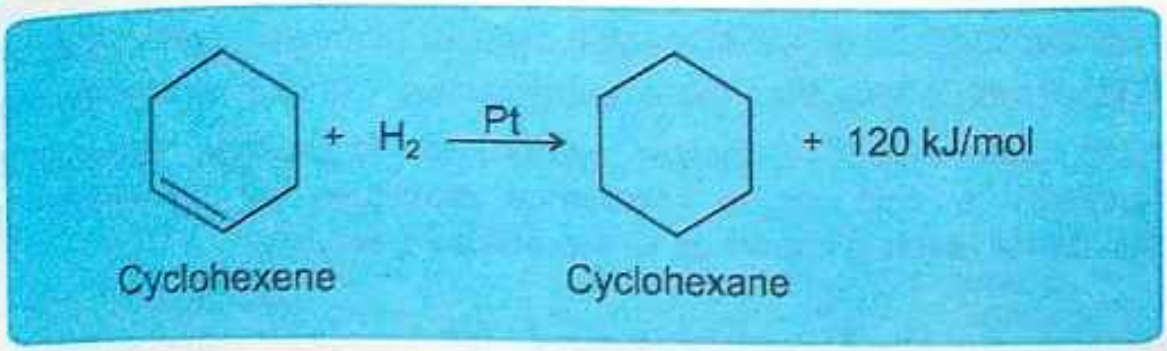
The contributing structures are called canonical forms and the real structure (which is actually not known) is called the resonance hybrid. It should be noted that all the canonical (contributing) forms do not have equal contribution and thus they are not of equal importance. For example, the contribution of structure I and II to the actual structure has been calculated to be 39% each, where as that of structures III, IV and V is 7.3% each. It should further be noted that the resonance concept of describing a molecule (as shown above in the case of benzene) does not mean that the structure rapidly shifts between the canonical forms, neither it means that some molecules are like one canonical form and other like another form. In fact, all the molecules of a substance have the same structure all the time, in which the electrons are delocalized over the whole system involved in the resonance.

Resonance Energy and stability of benzene:

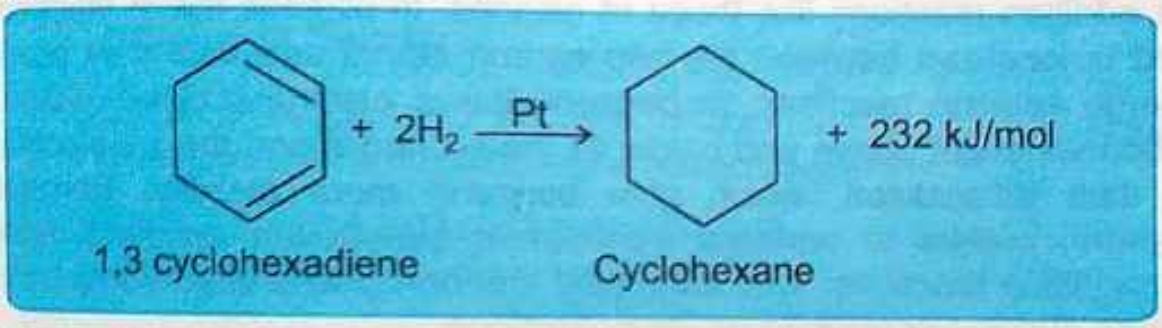
"The resonance energy of a molecules is the difference between the energy of the most stable canonical form and that of the actual molecule". For benzene it can be calculated by measuring its heat of hydrogenation and comparing it with that of the most stable canonical from. Hydrogenation of cyclohexene (having one double bond) evolves 120 kJ/mole heat energy to form cyclohexane.

Scanned with CamScanner

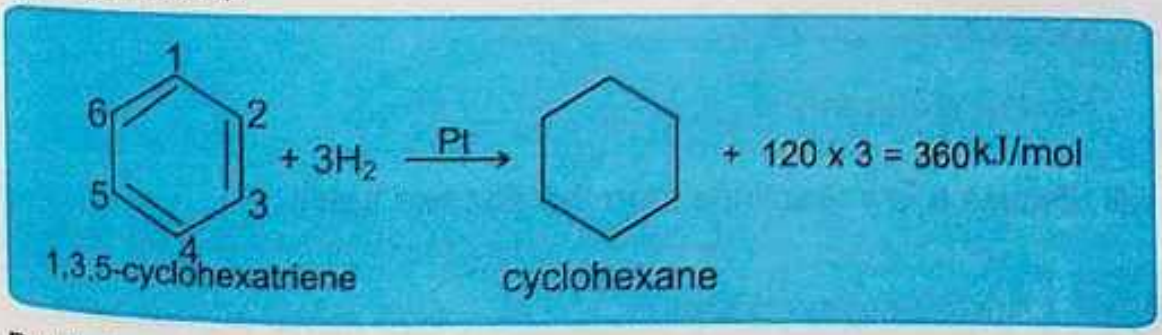
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



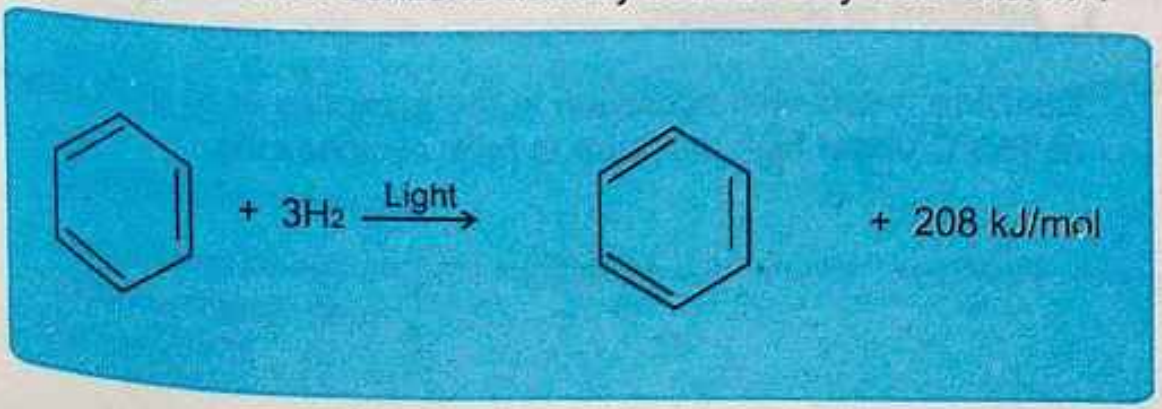
Hydrogenation of 1,3–cyclohexadiene (having two double bonds) evolves 232 kJ/mol to from cyclohexane, which is almost double of the value 120 kJ for cyclohexene.



The molecule 1,3,5–cyclohexatriene (kekule structure) normally written for benzene and having three double bonds, should release energy three times that of cyclohexane (i.e. $120 \times 3 = 360$ kJ/mol, on hydrogenation).



But hydrogenation of benzene actually evolves only 208·0kJ/mol



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Thus the measured (experimental) heat of hydrogenation of benzene (208 kJ/mol) is less than the expected value (360 kJ/mol) of the most stable canonical form by an amount of 152 kJ/mol. Benzene is, therefore, is said to be resonance stabilized by an amount of 152 kJ/mol which is known as its resonance energy.

16.6.5 Reactivity and Reactions:

Due to unusual stability (resonance stabilized), benzene does not give addition reactions like those of alkenes. In alkenes the π electronic cloud is localized between the two carbon atoms and thus they readily undergo addition reactions. In benzene the π electronic cloud makes a continuous sheet above and below all the six nuclei and the π-electrons are thus delocalized, which give benzene more stability. Benzene, therefore, prefers to undergo electrophilic substitution reactions rather than addition reactions. It is, thus, said that benzene is less reactive than alkenes during electrophilic addition reactions.

The main types of reactions of benzene are:

A. Addition Reactions.

B. Electrophilic Substitution Reactions.

C. Oxidation Reactions.

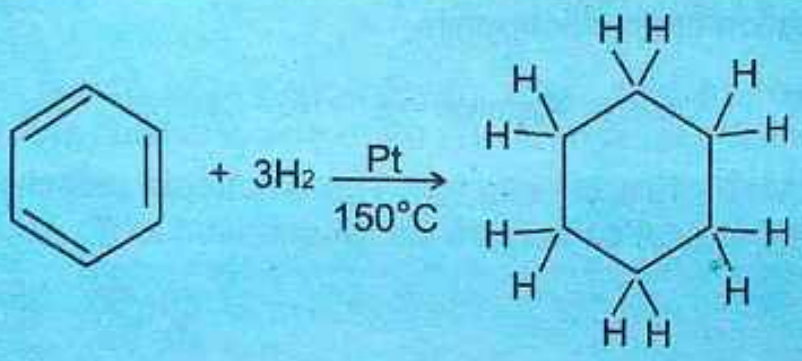
We will discuss a few reactions from the first two types.

16.6.5.1 Addition Reactions:

1. Addition of Hydrogen:

Benzene reacts with hydrogen in the presence of Ni or Pt catalyst at 150°C, under high pressure to form cyclohexane.

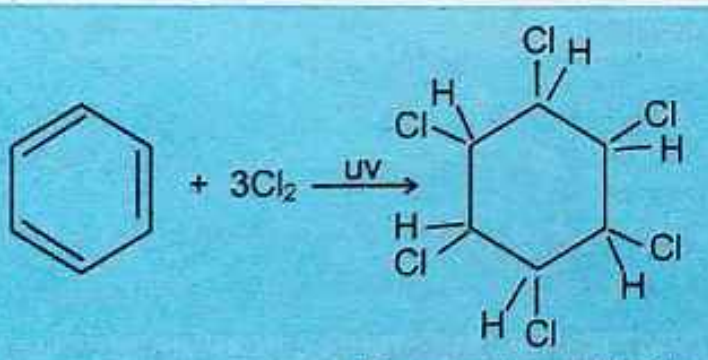
Scanned with CamScanner



Cyclohexane

2. Addition of Halogens:

Benzene reacts with chlorine or bromine in the presence of ultraviolet light to form benzene hexachloride:



Benzenehexachloride
(1,2,3,4,5,6 hexachlorocyclo hexane)

16.6.5.2 Electrophillic Aromatic Substitution Reactions:

Reactions in which hydrogen atom of the aromatic ring is replaced by electrophiles are called electrophilic aromatic substitution reactions. Benzene ring with its delocalized π electrons is an electron rich system. It is attacked by electrophiles (electron–loving species), giving substituted products.

General Mechanism:

Mechanism of electrophilic aromatic substitution reaction involves the following three steps.

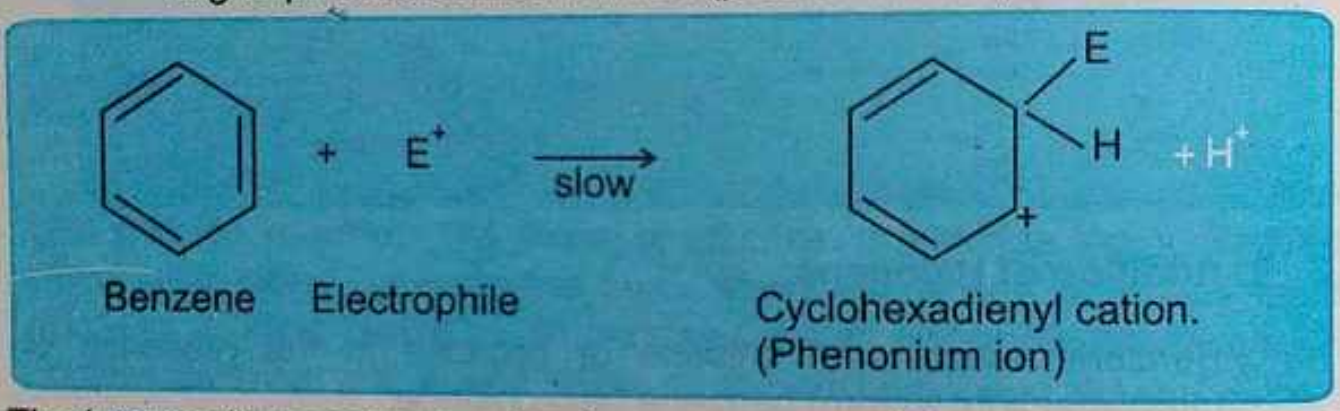
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

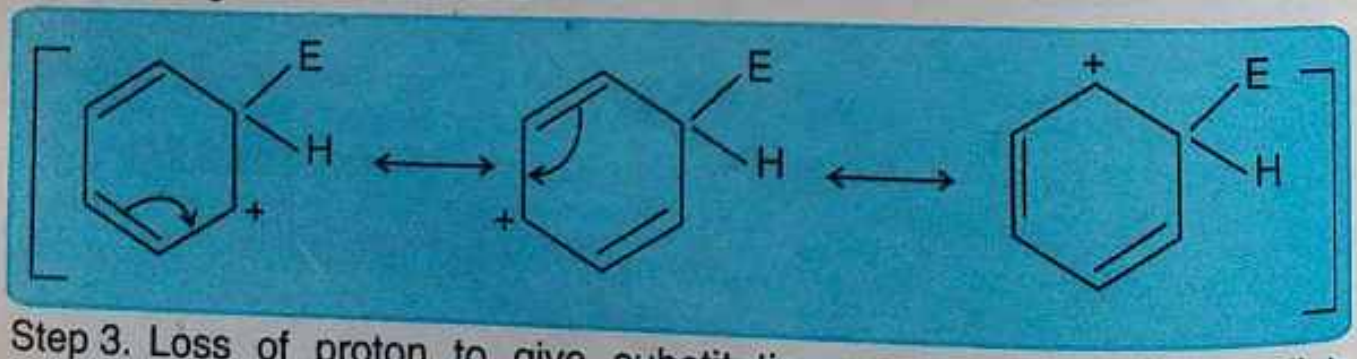
Step 1. Formation of an electrophile

$$E-Nu+catalyst \rightarrow E^{+} + Nu-Catalyst$$

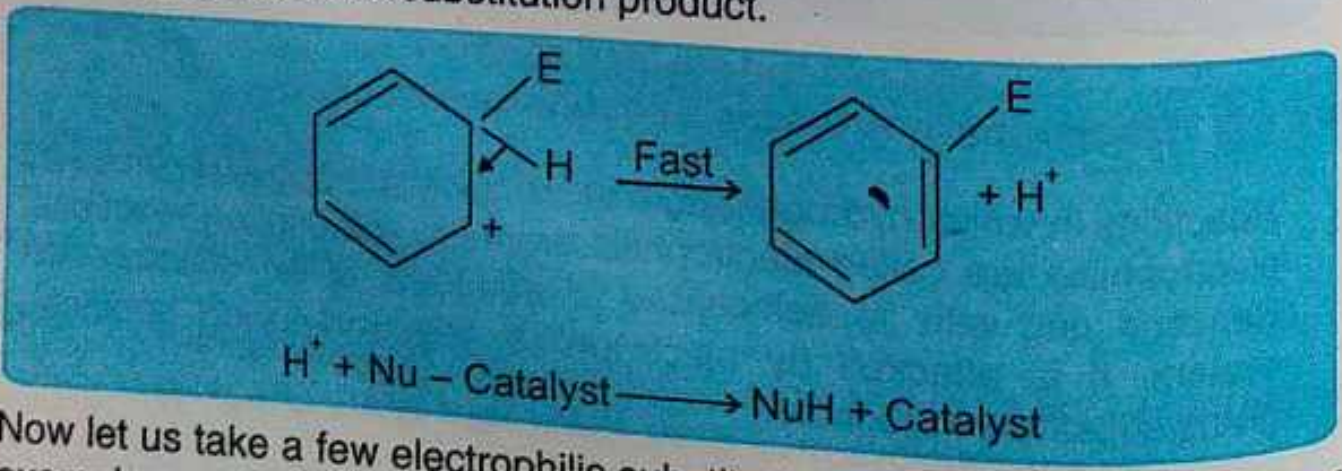
Step 2. Formation of carbonium ion: The electropile attacks the aromatic ring to produce carbonium ion (phenonium ion).



The intermediate carbonium ion is resonance stabilized and is a hybrid of the following three structures.



Step 3. Loss of proton to give substitution product. The intermediate carbonium ion is non aromatic species and is unstable. It loses a proton to form a stable aromatic substitution product.



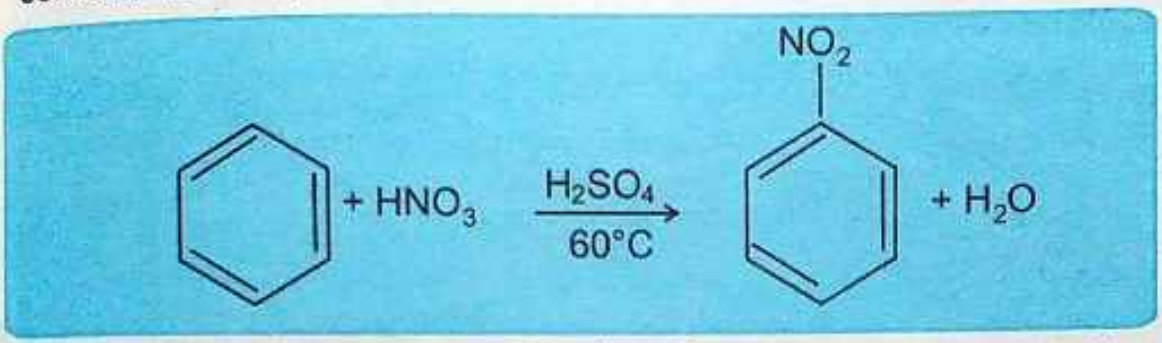
Now let us take a few electrophilic substitution reactions of benzene as an example.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

1. Nitration:

Benzene reacts with concentrated nitric acid in the presence of concentrated sulphuric acid at 60°C to form nitrobenzene.

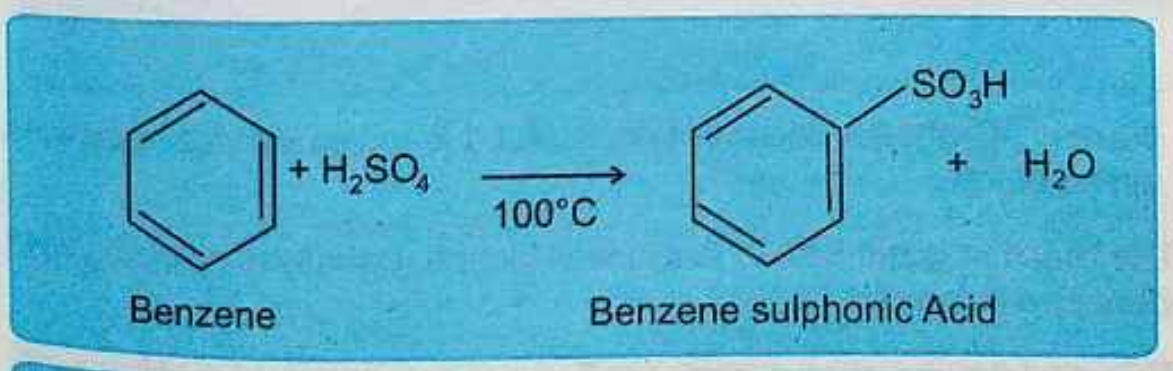


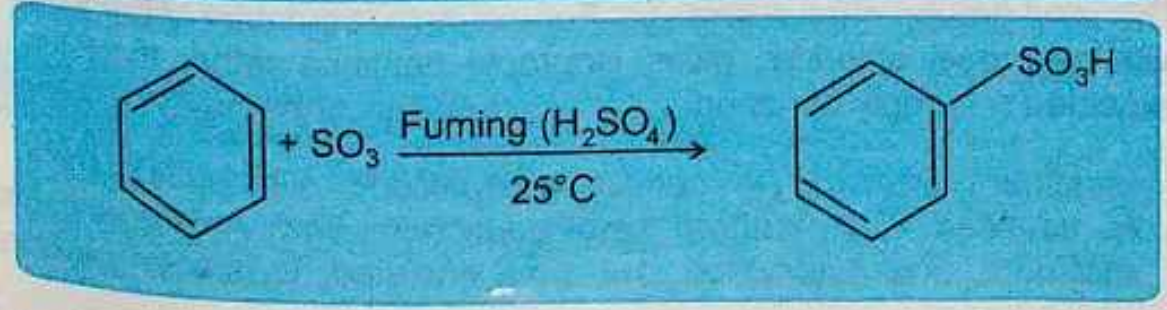
In this case the electrophile $\left(NO_2^+\right)$ is produced by reaction of H_2SO_4 and HNO_3.



2. Sulphonation:

Benzene reacts with concentrated H_2SO_4 at 120°C or fuming H_2SO_4 at room temperature, to give benzene sulphonic acid. Fuming sulphuric acid is concentrated sulphuric acid in which SO_3 has been dissolved.



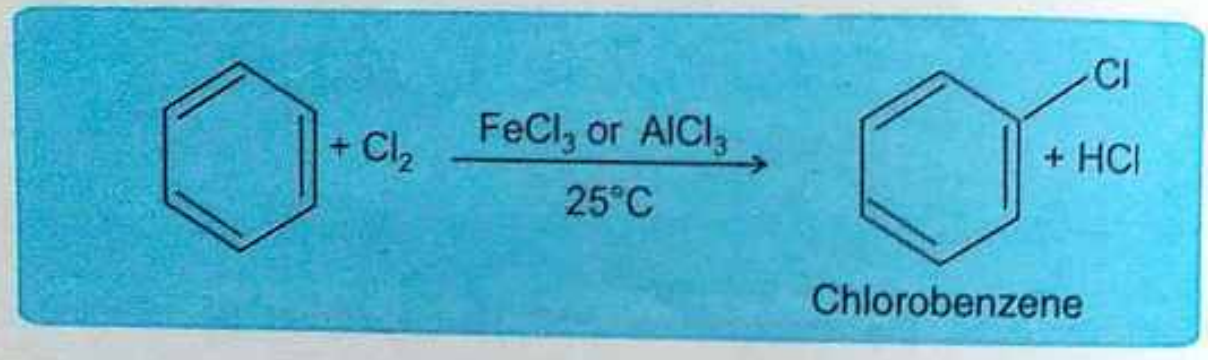


Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

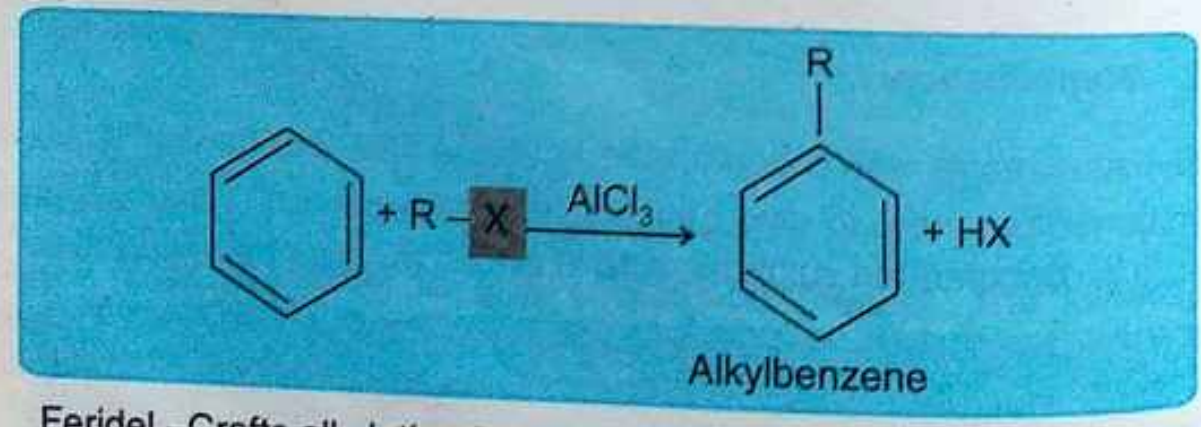
3. Halogenation:

Benzene is halogenated on treatment with molecular halogen in the presence of $FeCl_3$ or $AlCl_3$ (Lewis catalyst) at room temperature to form halobenzene.



4. Friedel –Craft's Alkylation:

Benzene reacts with alkyl halides in the presence of $AlCl_3$ to form alkyl benzenes.



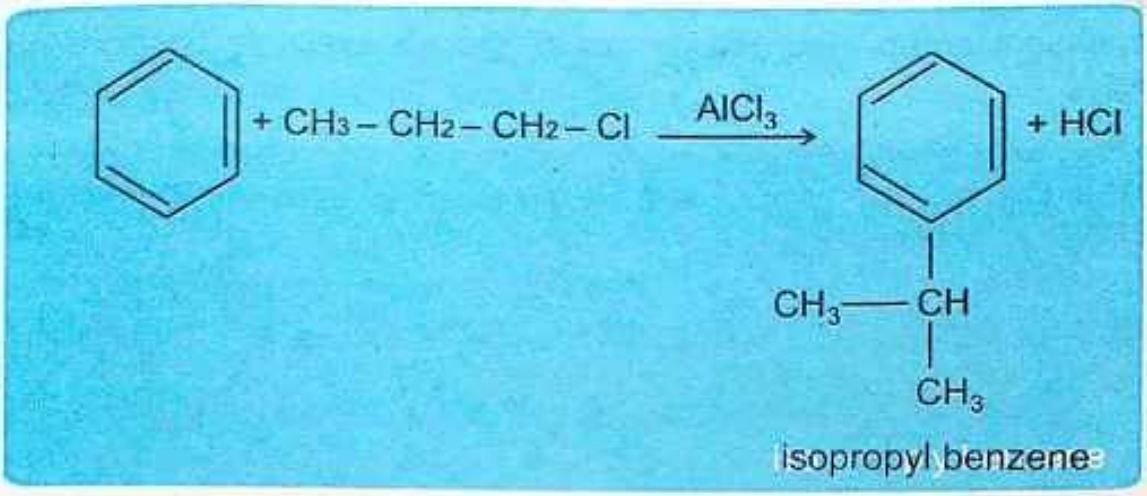
Feridel –Crafts alkylation is less useful due to two serious objections, given below.

i. The reaction is not limited to monoalkylation. Usually di or tri alkylated benzene is formed.

ii. The alkyl groups often rearrange. For example, treatment of benzene with n – propyl chloride, gives isopropyl benzene rather than the expected n –proply benzene.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

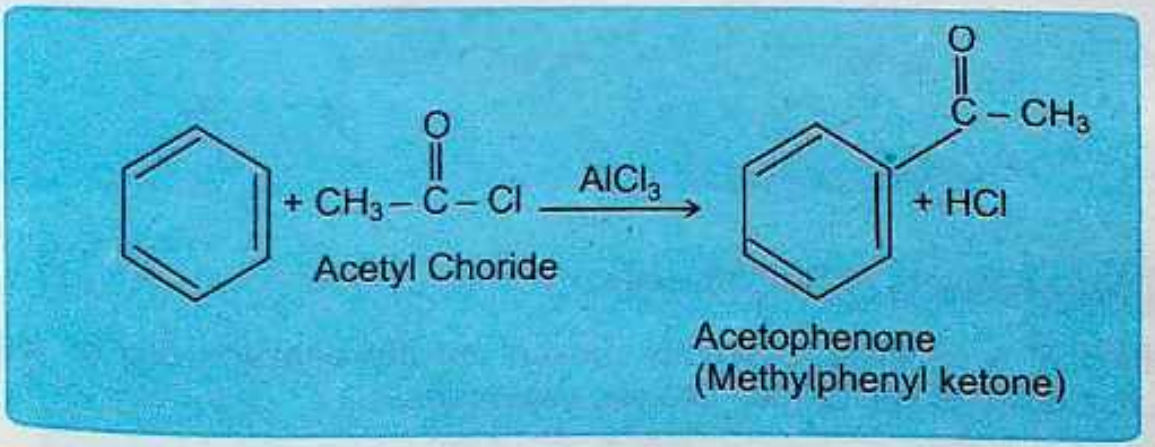


This is because the reaction involves formation of carbonium ion which can undergo rearrangement before attacking the benzene ring.

Thus the possibility of rearrangement brings uncertainty about the actual products, formed.

5. Fridel –Crafts Acylation: (Substitution of acyl $(-\overset{O}{\overset{\|}{C}}-R)$ group).

Benzene reacts with acid halides (or anhydrides) in the presence of a Lewis acid catalyst $(Al\ Cl_3)$ to give aromatic ketones. For example,



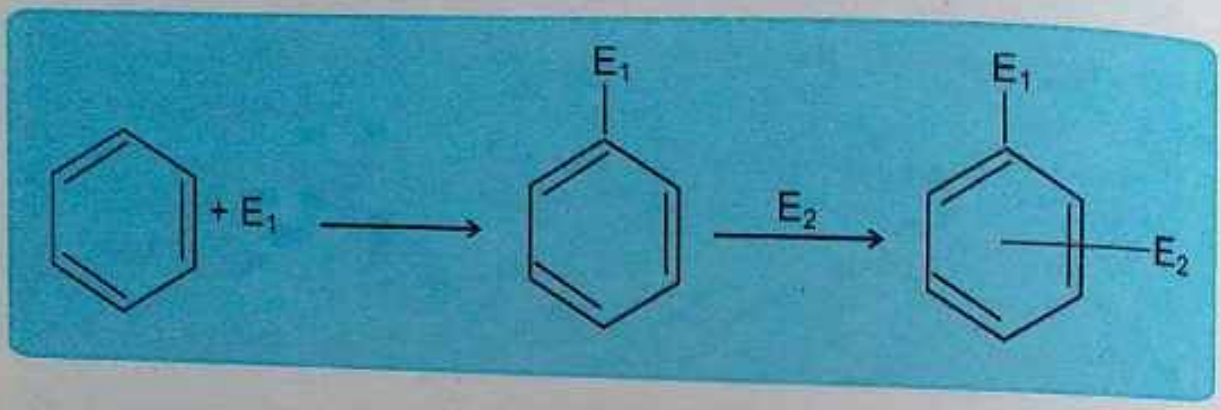
16.6.5.3 Substituent Effects:

An electrophilic Substitution reaction of benzene results in the formation of only one monosubstituted product. It is because all the hydrogen atoms of benzene ring are equivalent and therefore the

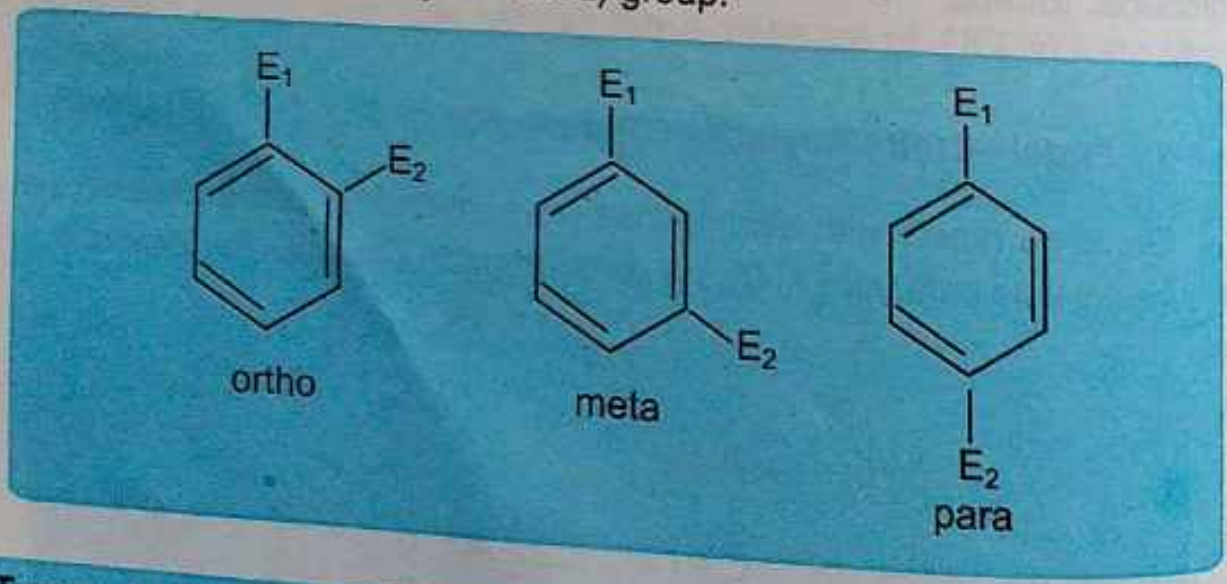
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

substituent group may occupy any of the six available positions on the ring.



However, a second substituent, can occupy any of the remaining five positions to yield three isomeric disubstituted benzenes depending on whether the second group occupies ortho, meta or para position with respect to the first (already attached) group.



Types of effects of Substituents:

Effect of a substituent already present on the benzene ring on further substitution can be divided into two categories.

(A) Directive or orientation Effect.

(B) Effect on reactivity of benzene ring.

Scanned with CamScanner

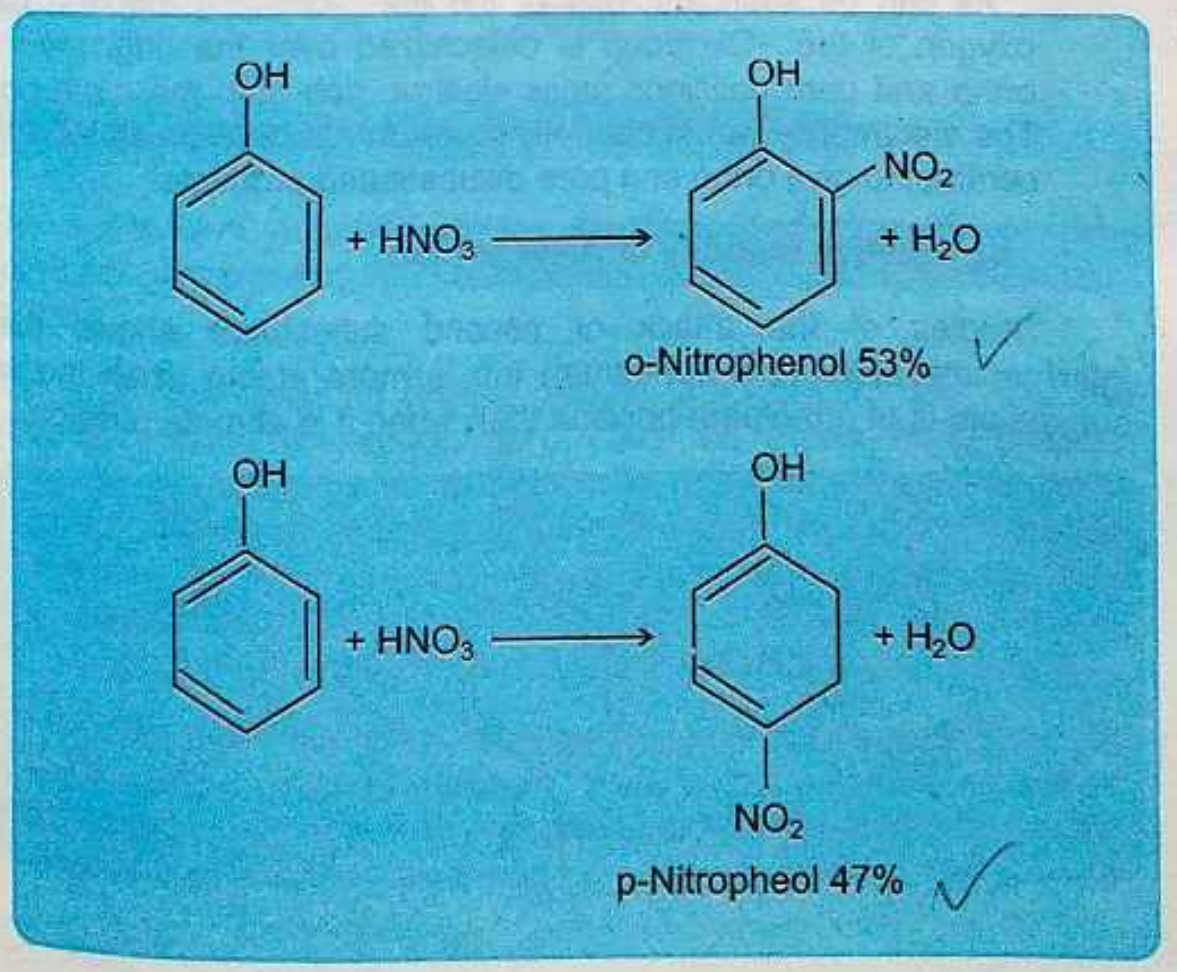
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

(A) Directive or Orientation Effect:

The first substitutent (X) may direct the incoming substituent (Y) to ortho, meta or para position, depending on the nature of the first substituent. This is called the directive or orientation effect. It has been experimentally observed that some groups, when attached to the benzene ring, direct the second incoming substituent to either ortho and para positions or to the meta position. Thus the substituents (groups) can be divided into two classes.

i. Ortho/Para Directing/substituents

Substituents which direct the second substituent to the ortho and para positions simultaneously are called the ortho/para directing substituents. For example, when phenol is nitrated, the reaction yields only the o-Nitrophenol and p-Nitrophenol (in the ratio 53% : 47%) and no meta isomer is produced.



Scanned with CamScanner

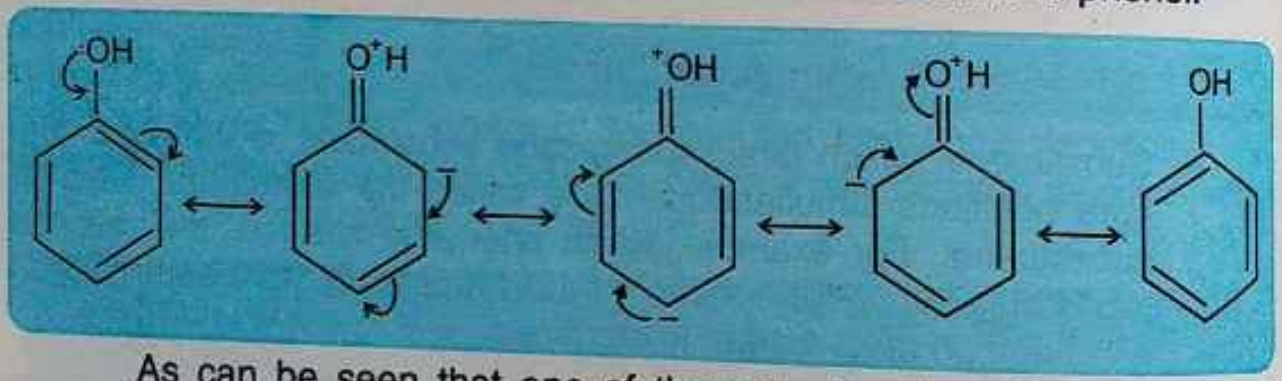
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Thus the substituent –OH which has directed the second substituent $-NO_2$ to ortho and para positions, is designated as ortho/para directing. Some common ortho/para directing groups are –Cl, –Br, –I, –OH, $-NH_2$ – CH_3, $-C_2H_5$ (Table 16.5).

The ortho/para directing effect can be explained in terms of (a) charge distribution and (b) Relative stability of arenium ion.

a. Charge Distribution:

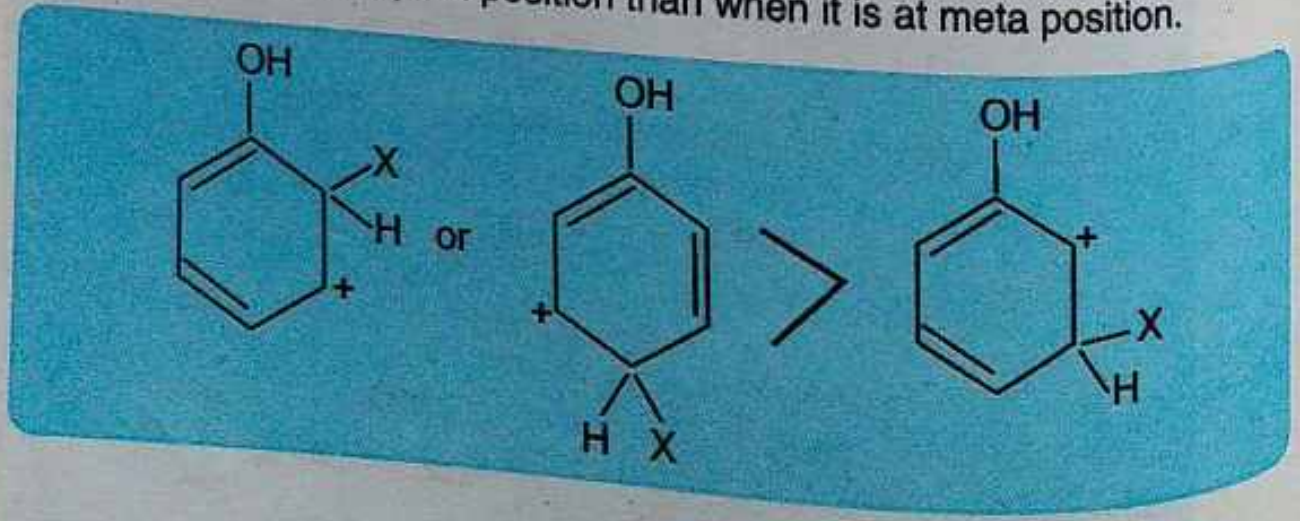
Consider, for example, the various resonance forms of phenol.



As can be seen that one of the non –bonding electron pairs of oxygen of the –OH group is delocalized over the ring, making the ortho and para positions more electron rich than the meta position. The electrophile would naturally prefer to attack at these electron rich centres, to give ortho and para disubstituted products.

b. Relative Stability of Arenium ion:

Studies of the attack of second substituent shows that the intermediate arenium (Phenonium) ion is more stable when the second substituent is at ortho/para position than when it is at meta position.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

II. Meta Directing Substituents:

The substituents which direct the second incoming substituent to meta position, are called meta–directing substituents. For example, nitration of nitrobenzene gives mainly meta dinitrobenzene (94%).

Thus the substituent $-NO_2$ group, which has directed the second $-NO_2$ group to the meta –position, is meta–Directing. Some common meta directing groups are. $-NO_2$, –CN, –CHO, –COOH etc. (Table 16.5)

The meta –directing effect of a group may also be due to the following two reasons.

(a) Meta position of the ring has relatively more electronic density than ortho and para positions.

(b) Secondly, the arenium ion (Phenonium ion) with the second substituent at meta position is more stable than when the second subtituent is at ortho or para position.

(B) Effect of Substituent on the reactivity of the Ring

The substituent attached to the benzene ring also affects the reactivity of benzene ring in comparison with the unsubstituted benzene.

The ortho/para directing groups release electrons to the ring by resonance making it electron rich. Thus the attack of a second electrophile would be faster as compared to the benzene ring itself. That is the ortho/para directing species increase the reactivity of the benzene ring. They are ring activators and are referred to as activating groups. Halogens are the exceptions to this. It has been observed that halogens, though ortho/para directing, are ring deactivators.

On the other hand, the meta–directing groups withdraw electrons from the ring making it electron deficient. Thus in the presence of meta–directing species, the attack of a second electrophile would be slower as compared to the benzene ring i.e. the meta–directing species

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

decreases the reactivity of the benzene ring. These are ring deactivators and are referred to as deactivating groups. (Tabel 16.5).

Table 16.5 Orientation and activity effect of some Common Groups.

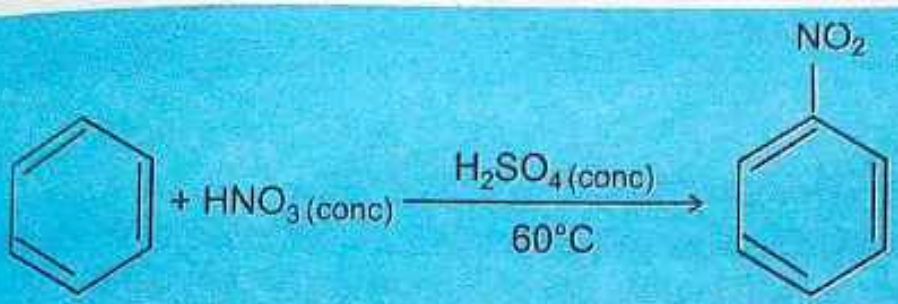
Ortho/Para directing		Meta directing	
Ring Deactivators	Ring Activators	Ring Deactivators	
–F	–OR	$-NO_2$	–COR
–Cl	$-C_6H_5$	–CHO	$-\overset{+}{N}H_3$
–Br	–NHR	–COOH	–COOR
–I	$-NR_2$	–CN	$-\overset{+}{N}R_3$
	$-CH_3$	$-SO_3H$	
	–OH		
	$-NH_2$		

16.6.5.4 Making Polysubstituted Benzenes:

Polysubstituted benzenes are the derivatives of benzene in which two or more hydrogen atoms have been substituted by other atoms or group of atoms. These can be made under different conditions. The position of second, third etc substituents on the ring, relative to the first, depends on the nature of the first and successive substitutions already attached to the ring. Moreover, the reactivity of the ring also increases or decreases by the presence of preceding substituents attached to the ring. For example, using nitrating mixture (conc HNO_3 + conc H_2SO_4), benzene can be nitrated at 60°C, to form nitrobenzene.

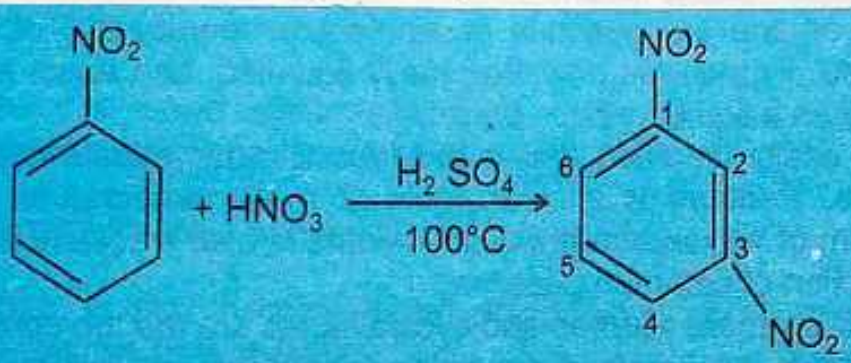
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



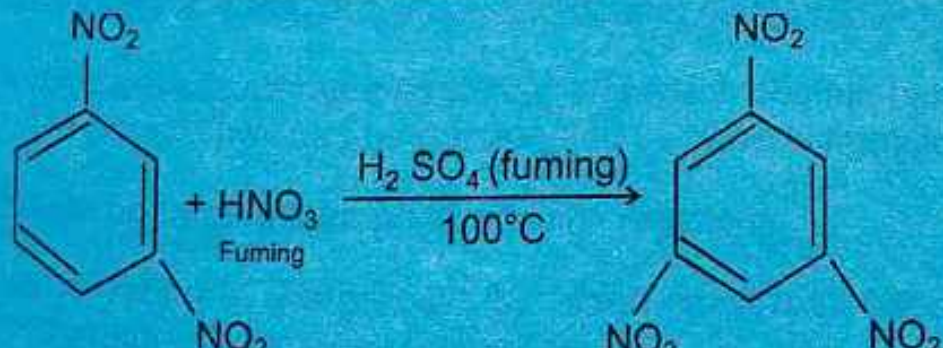
Nitrobenzene

Nitro group being deactivator, deactivates the benzene ring and further substitution becomes, difficult. Dinitrobenzene in obtained only if the reaction is carried out at higher temperature.



1,3-Dinitrobenzene

The second $-NO_2$ group further deactivates the ring. Thus trinitrobenzene is obtained only by using a mixture of fuming nitric acid and sulphuric acids.



1,3,5 - Trinitrobenzene

Similarly 2,4,6 –Trinitrotoluene (TNT) may be prepared by the nitration of toluene. TNT is widely used as a powerful explosive.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Society, Technology and Science

Hydrocarbons are a primary energy source for current civilizations. The predominant use of hydrocarbons is as a combustible fuel source. In their solid form, hydrocarbons take the form of asphalt used in road construction. Mixtures of volatile hydrocarbons are now used in preference to the chlorofluorocarbons as a propellant for aerosol sprays, due to negative impact of CFC's on ozone layer.

Methane and ethane are gaseous at ambient temperatures and cannot be readily liquefied. Propane is however easily liquefied, and exists in "propane bottles" mostly as a liquid.

Butane is so easily liquefied that it provides a safe, volatile fuel for small pocket lighters. Pentane is a clear liquid at room temperature, commonly used as solvent of waxes and greases. Hexane is also a solvent as well as a significant fraction of common gasoline.

The 6C to 10C alkanes, alkenes and cycloalkanes are the top components of gasoline, naphtha, jet fuel and specialized industrial solvent mixtures. The long chain hydrocarbons obtained from crude oil are used as lubricants, roofing compounds, pavement composition, wood preservatives, etc.

Scanned with CamScanner

EY POINTS

Key Points:

- Aliphatic hydrocarbons include the open chain (acyclic) and those cyclic compound which resemble the open chain in their chemical properties (Alicyclic).
- Aromatic hydrocarbons include benzene and those compounds which resemble benzene.
- Acyclic hydrocarbons contain saturated and unsaturated open chain hydrocarbons.
- Alkanes are open chain saturated hydrocarbons, which can be represented by general formula $C_n H_{2n+2}$.
- The general formula of cycloalkanes is $C_n H_{2n}$.
- Homolysis is the chemical bond dissociation of a neutral molecule generating two free radicals.
- Heterolysis is chemical bond cleavage of a neutral molecule generating cation and anion.
- Electrophile is a reagent which can accept electron pair in a reaction.
- Nucleophile is a reagent which can donate electron pair in a reaction.
- Alkenes are unsaturated hydrocarbons which contain carbon–carbon double bond. They can be represented by general formula $C_n H_{2n}$.
- Alkenes undergo electrophilic addition reactions.
- Polymerization is the process by which small molecules chemically join together to form large molecules.
- In conjugated compounds carbon atoms are linked alternatively by single and double bonds.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

- Compounds having the same molecular formula but different structural formula are known as 'isomers' and this phenomenon is called "Isomerism".
- Tautomerism is a special type of functional group isomerism, in which isomers are in equilibrium with each other.
- Stereoisomerism is caused by different arrangements of atoms or groups in space.
- Carbon atom which is bonded to four different group is called chiral carbon.
- Alkynes contain carbon—carbon triple bond. They can be represented by general formula $C_n H_{2n-2}$.
- Benzene is aromatic hydrocarbon. Its molecular formula is C_6H_6.
- The representation of a real structure as a weighted average of two or more contributing structure is called resonance.
- The contributing structures are called canonical forms and real structure is called resonance hybrid.
- Electrophilic aromatic substitution reactions are those in which hydrogen is replaced by an electrophile.
- Carbonium ion is a positively charge organic ion in which most of positive charge is localized on carbon atom.
- Substituents which direct the second substituent to ortho and para position simultaneously are called ortho/para directing.
- The substituents which direct the second incoming substituent to meta position are called meta-directing.

Scanned with CamScanner

EXERCISE

Exercise

Q1. Select the correct option.

(i) Which one of the following deactivates benzene ring and is o/p-directing?

(a) $-NH_2$ (b) $-OH$ (c) $-OCH_3$ (d) $-Cl$

(ii) Which one of the following compounds is expected to exhibit geometrical isomerism.

(a) 1-butene (b) 2-butene (c) 2-methyl propane

(d) 2-butyne

(iii) The overlapping of orbitals in benzene is of the type of

(a) $sp - sp$ (b) $sp^2 - sp^2$

(c) $sp^3 - sp^3$ (d) $s - s$

(iv) When acetylene is treated with HBr, we get.

(a) Methyl bromide (b) Methyl chloride

(c) Ethyl bromide (d) Ethylene bromide

(v) The general formula of cycloalkanes is

(a) C_nH_{2n+2} (b) C_nH_{2n}

(c) C_nH_{2n+1} (d) C_nH_{2n-2}

(vi) How many isomers are possible for C_2H_6O

(a) 2 (b) 4 (c) 8 (d) 5

(vii) Dehydrohalogenation of alkylhalide is carried out in presence of _____.

(a) Zn dust (b) H_2SO_4 (c) Alcoholic KOH

(d) aqueous KOH

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

(viii) The marsh gas mainly consists of _____.

(a) C_2H_4 (b) CH_4 (c) H_2S (d) SO_2

(ix) Ethene and Ethyne can be distinguished by

(a) Anh. $AlCl_3$ (b) Br_2 in CCl_4

(c) Cold. H_2SO_4 (d) $AgNO_3$ in NH_4OH

(x) The homolytic fission of C–C bond in ethane give an intermediate in which "C" is _____ hybiridized.

(a) sp^3 (b) sp^2 (c) sp (d) sp^2d

(xi) Which one of the following compound has planar structure?

(a) Alkane (b) Alkene (c) Alkyne (d) Cycloalkane

(xii) When carbon undergoes sp^2 hybridization then H–C–H bond angles are:

(a) 120° (b) 180° (c) 109.5° (d) 107.5°

(xiii) In the following reaction $C_6H_6 + Cl_2 \xrightarrow{AlCl_3} C_6H_5Cl + HCl$, what type of reaction has taken?

(a) Electrophilic substitution (b) Electrophilic addition

(c) Friedel-craft's alkylation (d) Non of these

(xiv) Nitrobenzene reacts with chlorine in presence of $AlCl_3$. The product obtained is.

(a) o-chloro nitrobenzene (b) m-chloronitrobenzene

(c) p-chloro nitrobenzene (d) All of them

2. Write short answers of the following questions.

(i) What is the difference between aliphatic and aromatic hydrocarbons?

Scanned with CamScanner

(ii) What is meant by resonance?

(iii) How do you detect the unsaturation in Alkenes?

(iv) Why benzene is less reactive than ethene but more reactive than ethane?

(v) Why halogens are deactivating groups although they are ortho/para directing?

(vi) Why ethyne is less reactive towards electrophilic addition reaction than ethene.

(vii) What is meant by chirality?

(viii) Why there are no geometrical isomers of but-1-ene (1-butene)?

(ix) Why cyclopropane is more reactive than propane?

(x) Differentiate between Homolytic and heterolytic fission.

(xi) Write down the resonance structure of benzene.

(xii) Write down the two reasons of meta-directing effect.

(xiii) How can you distinguish 1-alkyne from other non-terminal alkynes?

(xvi) Why Lindlar's catalyst is used in hydrogenation of alkynes?

(xv) What is the main difference between tautomerism and metamerism?

Q.3 Long questions:

(i) Describe the mechanism of chlorination of methane in detail.

(ii) (a) Explain the structure and reactivity of cycloalkanes.

(b) Mention at least four physical properties of alkynes.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

(iii) (a) What are hydrocarbons? How will you classify them? Give an example of each class.

(b) Write down the physical properties of alkanes and cyclo alkanes.

(iv) (a) Give methods of preparation of ethene from

(a) An alcohol (b) An alkylhalide

(b) Explain the relative stabilities of different alkenes.

(c) Starting from alkene how would you prepare the following compounds.

(a) Vicinal dihalide (b) Alcohol

(c) Ozonide (d) Epoxide

(v) (a) Describe any two methods of preparation of alkynes.

(b) Mention at least four physical properties of alkynes

(vi) (a) Describe the structure of benzene on the basis of MOT.

(a) How would you prepare the following compounds from Benzene?

(a) Acetophenone (b) Toluene

(b) Trinitrobenzene (d) Benzenesulphonic acid

(vii) (a) Describe mechanism of electrophilic substitution reaction in benzene.

(b) Explain the directive and activitating effect in mono substituted benzene.

(viii) Write notes on the following.

(a) Conjugation in alkenes

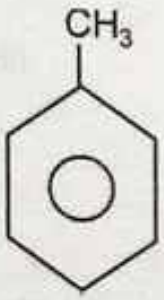
Scanned with CamScanner

(b) Polymerization

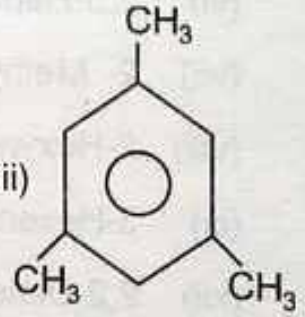
(c) Resonance

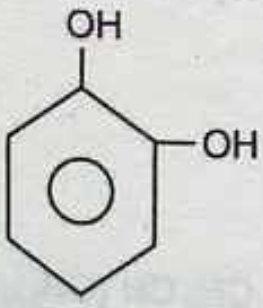
(d) Structure of alkyne

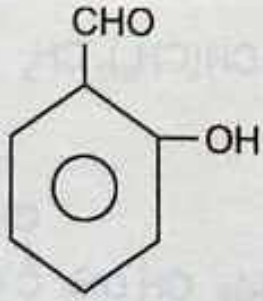
Q.4 Names the following compounds.

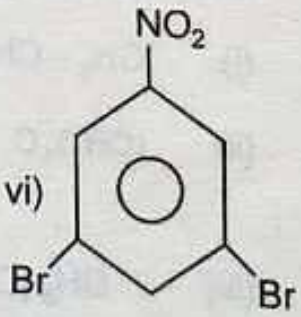
i) 

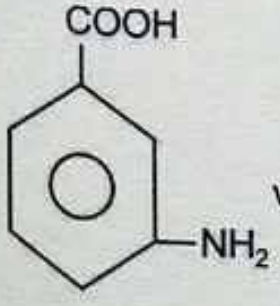
ii) 

iii) 

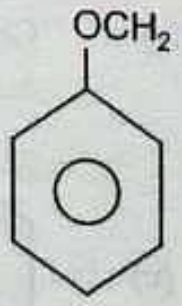
iv) 

v) 

vi) 

vii) 

viii) 

ix) 

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Q.5 **Draw the structural formula of the following compounds.**

(i) Anthracene

(ii) Naphthalene

(iii) 3- Phenyl pentane

(iv) Isobutylene

(v) 2,3,4-Trimethyl hexane

(vi) 2,5-Heptadiene

(vii) 2- Methyl-2-pentene

(viii) 2-Hexyne

(ix) 3-Hexen -1-yne

(xii) 2,2-Dimethyl butane

Q.6 **Give IUPAC names to the following Hydrocarbons.**

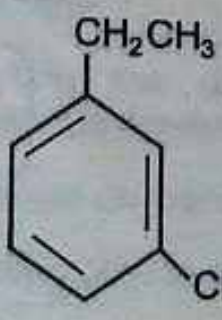
(i) $CH_3-CH=CH(CH_2)_2CH_3$

(ii) $(CH_3)_4C$

(iii) $CH_3(CH_2)_2\underset{\displaystyle C_2H_5}{\underset{|}{CH}}CH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH_2 . CH_2CH(CH_3)_2$

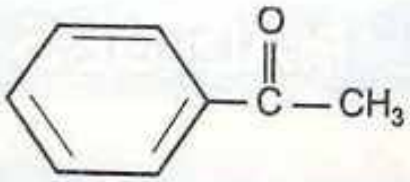
(iv) $CH_3-C\equiv C-CH(CH_3)_2$

(v)

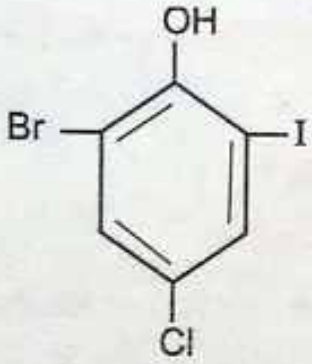


Scanned with CamScanner

(vi)



(vii)



(viii) $(C_6H_5)_3\,CH$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

UNIT 17

ALKYL HALIDES

Learning Outcomes:

After studying this unit and working the exercise the student will be able to,

- Name alkyl halides using IUPAC system.
- Discuses the structure and reactivity of RX.
- Describe the preparation of RX by the reaction of alcohols with HX, $SOC\ell_2$ and PX_3 and by radical halogenation of alkanes.
- Describe the mechanism and types of nucleophilic substitution reactions.
- Describe the mechanism and types of elimination reactions.
- Discuss chemistry of Grignard reagents by the addition of aldehydes, ketones, esters and carbon dioxide.
- Discuss nomenclature, structure and basicity of amines.
- Describe the preparation of amines by alkylation of ammonia with RX and reduction of nitriles, nitro and amide functional groups.
- Describe the chemistry of amines by alkylation of amines with RX, reactions with aldehydes, ketones preparation of amines and diazonium salts.
- Describe isomerism of alkyl halides and amines.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

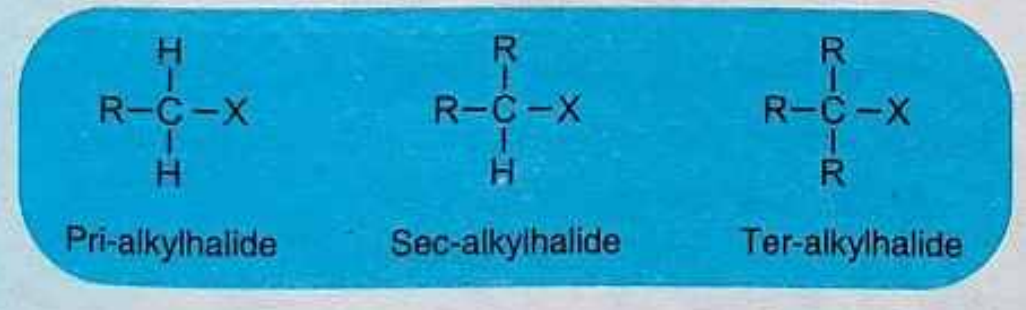
17.1 Alkyl Halides:

Monohaloalkanes are usually called alkylhalides. Alkyl halides are the compounds of carbon, hydrogen and halogen. The functional group of these compounds is halogen. These are the derivatives of alkanes in which one hydrogen atom is replaced by a halogen atom.

$$R-X$$

They are represented by $R-X$, where R is an alkyl group and "X" is functional group. The general formula of alkylahlides is $C_nH_{2n+1}X$ where n represents the number of carbon atoms.

Alkyl halides are classified as primary, secondary and tertiary alkylhalides depending upon whether the halogen atom is directly bonded to a primary, secondary or tertiary carbon atom in the molecule. For example.



Alkyl halides are the most suitable organic compounds used to incorporate alkyl groups into other molecules.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

17.1.1 Nomenclature of Alkyhalides:

Common System: According to this system the names of alkylhalides are two word names. In this two word names, the alkyl group of alkylhalide is named first followed by the name of halogen group as halide.

$CH_3-C\ell$ (Methylchloride) CH_3-CH_2-I (Ethyliodide)

In case of primary, secondary and tertiary alkyl halides, the words pri, sec, and ter are written before the names of alkyl halides.

IUPAC System:

Rules:

1. Selection of the longest continuous chain of carbon atom containing the halogen atom.
2. Derivation of the basic name by writing the word halo before the name of alkane from which the alkylhalide has been derived. The basic name becomes as a Haloalkane.
3. Numbering of the carbon atoms of the selected chain from the end nearer to halogen group.
4. Naming all the other substituents and indication of their positions by appropriate numbers.

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

1-Chloro - 2 - methyl propane

17.1.2 Physical Properties of Alkyl halides:

Lower alkyl halides $CH_3C\ell$; $C_2H_5C\ell$ and CH_3F are gases at room temperature. Alkyl halides upto C_{18} are colorless liquids while those beyond

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

C_{18} are colourless solids. They are usually insoluble in water due to their inability to form hydrogen bonding with water. They are soluble in organic solvents. Alkyl chlorides and alkylflourides are lighter than water while alkyl iodides and alkyl bromides are denser than water. They have higher boiling points than the corresponding alkanes. For a given alkyl group the boiling points of alkyl halides increase with increasing size of the halogen atom while for a given halogen atom the boiling points of alkylhalides increase with the increasing size of the alkyl group.

Table 7.1: Boiling Points of Alkyl halides:

Name	Structure	Boiling Point °C
Methyl chloride	$CH_3-C\ell$	−24
Methyl bromide	CH_3-Br	5
Methyl iodide	CH_3-I	40
Ethyl chloride	$CH_3-CH_2-C\ell$	13
Ethyl bromide	CH_3-CH_2-Br	38
Ethyl iodide	CH_3-CH_2-I	72

17.1.3 Structure of Alkyl Halides:

To understand the structure of alkyl halides, let us consider methyl chloride $(CH_3C\ell)$. In this molecules all the bonds of carbon are single, therefore, carbon atom is sp^3 – hybridized. During the process of bond formation, one sp^3 orbital of carbon atom overlaps with the half filled p–orbital of chlorine atom and forms a single "δ" covalent bond. In the meantime the remaining three sp^3 orbitals of this carbon atom overlap with three half filled s-orbitals of hydrogen atoms and forms single

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

"δ" covalent bonds. The H–C–H and H–C–X bond angles are approximately equal to 109.5 °.

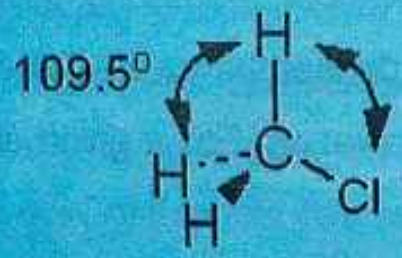


Fig: 17.1

17.1.4 Preparation of Alkyl Halides:

Alkyl halides can be prepared by different methods. Some of these are given as under.

17.1.4.1 Reaction of halogen acids with alcohols

Alcohols readily react with HBr and HI to form alkylbromides and alkyliodides. HCl is least reactive towards alcohols, therefore, anhydrous $ZnCl_2$ is used as catalyst while treating alcohol with HCl to produce alkyl chlorides ($ZnCl_2$/HCl is called Lucas reagent).

$$\underset{\text{Alcohol}}{R-OH} + \underset{\text{Halogen acid}}{H-X} \longrightarrow \underset{\text{Alkylhalide}}{R-X} + H_2O$$

$$\underset{\text{Ethylalcohol}}{CH_3-CH_2-OH} + H-Br \longrightarrow \underset{\text{Ethylbromide}}{CH_3-CH_2-Br} + H_2O$$

$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} + H-I \longrightarrow \underset{\text{Ethylcheride}}{CH_3-CH_2-I} + H_2O$$

Ethyliodide

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$CH_3-CH_2-OH+H-C\ell \xrightarrow{Anh.(ZnC\ell_2)} CH_3-CH_2-C\ell+H_2O$$

Ethyl alcohol — Ethylchloride

17.1.4.2 (a) By the action of Phosphorous Halides on Alcohols:

Alcohols react with phosphorous trihalides $(PC\ell_3, PBr_3)$ and form the corresponding alkyl halides.

$$3R-OH+PX_3 \longrightarrow 3R-X+H_3PO_3$$

Alcohol — Alkylhalide

$$3CH_3-OH+PCl_3 \longrightarrow 3CH_3-Cl+H_3PO_3$$

Methylalcohol — Methylchloride

$$3CH_3-CH_2-OH+PI_3 \longrightarrow 3CH_3-CH_2-I+H_3PO_3$$

Ethylalcohol — Ethyliodide

$$3CH_3-CH_2-OH+PBr_3 \longrightarrow 3CH_3-CH_2-Br+H_3PO_3$$

Ethylalcohol — Ethylbromide

Phosphorous trihalides are produced in situ by the action of red phosphorous on halogen.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

(b) By The Action of Thionylchloride on Alcohols:

Alcohols react with thionylchloride $(SOCl_2)$ in the presence of pyridine to yield the corresponding alkyl halides. Pyridine being a base absorbs $HC\ell$ just after its production in the reaction mixture.

$$R-OH + SOCl_2 \xrightarrow[-HCl]{\text{Pyridine}} R-Cl + SO_2$$

Alcohol — Thiony chloride — Alkyl halide

$$CH_3-OH + SOCl_2 \xrightarrow[-HCl]{\text{Pyridine}} CH_3-Cl + SO_2$$

Methyl alcohol — Methyl chloride

$$CH_3-CH_2-OH + SOCl_2 \xrightarrow[-HCl]{\text{Pyridine}} CH_3-CH_2-Cl$$

Ethyl alcohol — Ethyl chloride

17.1.4.3 By Free Radical Halogenations of Alkanes:

Alkanes react with halogens in the presence of ultraviolet (uv) light or at high temperature of about 400°C to yield alkyl halides. In this process one or more hydrogen atoms of alkanes are replaced by halogens giving a mixture of different alkyl halides. That is why it is not a good method for preparation of pure alkylhalides.

$$R-H + C\ell_2 \xrightarrow[400°C]{uv} R-C\ell + HC\ell$$

This reaction occurs through free radical mechanism.

17.1.5 Reactivity of Alkyl halides:

The bond between carbon and halogen of alkyl halides is reactive due to its polar nature $(C^{+\delta}-X^{-\delta})$. The polarity is due to higher electronegativity of halogen than carbon atom. Due to this polarity the

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

carbon atom of alkyl halide is a good and attractive target for the attack of a nucleophile. That is why allyl halides are considered as a reactive group of organic compounds. These are widely used for the synthesis of a large variety of organic compounds.

The strength of carbon –halogen bond $(C-X)$ decreases down the group from fluorine to iodine. This can be explained on the basis of their bond energies that are given in the table.

C–X Bond	Bond Energy $(kJ.mol^{-1})$
C–F	467
C–Cl	346
C–Br	290
C–I	228

This shows that iodo compounds are most reactive while floro compounds are least reactive. Therefore, the order of reactivity of alkyl halides is $R-I > R-Br > R-C\ell > R-F$.

17.1.6 Nucleophilic Substitution Reactions:

17.1.6.1 General introduction: Alkyl halides undergo nucleophilic substitution reaction in which a stronger attacking nucleophile replaces the halogen of alkyl halide as halide ion $(\bar{X})$. A general example of such a reaction is given as

$$\underset{\text{Substrate}}{CH_3-X} + \underset{\substack{\text{Attacking}\\ \text{Nucleophile}}}{\ddot{\bar{N}}u} \longrightarrow \underset{\text{Product}}{CH_3-Nu} + \underset{\substack{\text{Leaving group}\\ \text{or}\\ \text{Nucleofuge}}}{\bar{X}}$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

17.1.6.2 Important Concepts

17.1.6.2.1 Carbocations and their Stability:

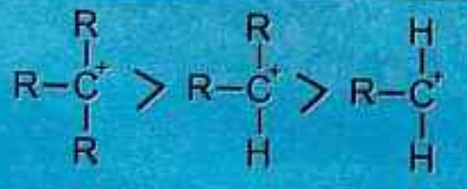
When halogen atom detaches from the carbon atom of an alkyl halide as halide ion $(\overline{X})$, the substrate is converted into a positively charged ion. This ion in which carbon atom bears positive charge is known as carbocation or carbonium ion.

$$(R)_3C-Br \rightarrow (R)_3C^+ + Br^- \quad \Delta H = 149 kcal/mol$$

$$(R)_2CH-Br \rightarrow (R)_2CH^+ + Br^- \quad \Delta H = 163 kcal/mol$$

$$RCH_2-Br \rightarrow R-CH^+ + Br^- \quad \Delta H = 182 kcal/mol$$

There are three types of carbocations. Primary alkyl halides produce primary carbocations while secondary and tertiary alkyl halides yield secondary and tertiary carbocations.



Tertiary carbocations are more stable than secondary and secondary are more stable than primary ones. This stabilization comes from the stabilization of the positive charge of carbocation by the electron donating alkyl groups directly attached. Greater the number of alkyl groups, greater is the stability of the carbocation.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

17.1.6.2.2 Nucleophile and Base:

Nucleophile means nucleus lover. It is a species which donates a pair of electrons in a chemical reaction.

It attacks the regions of low electron density e.g. positive centre in the molecule of substrates. They may be negative ions or neutral species with lone pair of electrons.

A nucleophile is generally represented by $N\bar{u}$. Any species neutral or negatively charged with a lone pair of electrons can act both as a base and a nucleophile. But a base is a species which has affinity for proton whereas a nucleophile has the ability to form bond with carbon atom. A base attacks a hydrogen atom in the elimination reaction while a nucleophile attacks carbon atom in the substitution reactions.

Mechanisms of Nucleophilic substitution Reactions or (SN Reaction):

Alkyl halides undergo nucleophilic substitution (SN) reactions by two different types of mechanisms. The type of mechanism depends upon the nature of alky halides. Tertiary alkyl halides undergo unimolecular nucleophilic substitution (SN^1) while primary alkyl halides undergo bimolecular nucleophilic substitution (SN^2).

17.1.6.2.3 Substrate and leaving group:

The molecule which undergoes nucleophilic substitution reaction is called substrate. In this case alkyl halides are substrates.

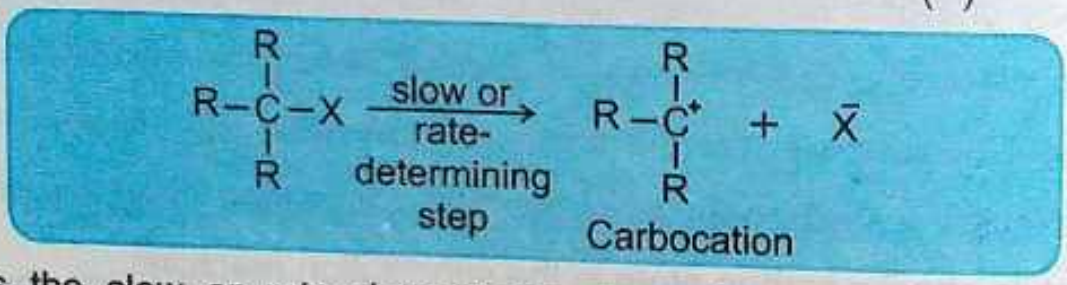
The group or species which leaves the substrate or which is being replaced by the incoming entering group is called leaving group. It is also called nucleofuge. In this reaction halogen leaves the substrate as halide ion $(\bar{X})$.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

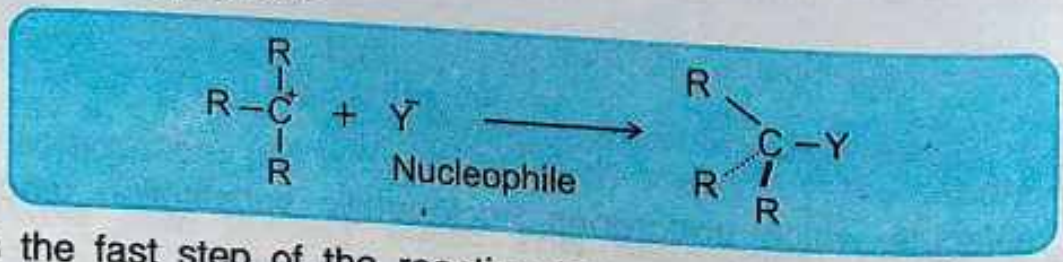
17.1.6.3 SN^1 –Mechanism:

SN^1 stands for unimolecular nucleophilic substitution reaction. SN^1 reactions are defined as those nucleophilic substitution reactions in which only one molecule is involved in the rate determing or slow step of the reaction. These reactions are generally followed by tertiary alkyl halides in polar solvents. These reactions complete in two steps. In first step, the substrate undergoes ionization and yields a carbocation. The halogen atom completely detaches from the substrate as halide ion $(\bar{X})$.



This is the slow or rate determining step of the reaction because it involves dissociation of substrate. Since only one molecule (substrate) is involved in this rate determining step this reaction is called unimolecular nucleophilic substitution reaction (SN^1).

In the second step the entering nucleophile attacks the carbocation to produce the end product.



This is the fast step of the reaction because it involves the ions. The kinetic studies have shown that reactions proceeding through SN^1 – mechanism follow the first order kinetics. The rate of reaction depends only upon the concentration of substrate. The rate equation is

$$\text{Rate} = K[(R)_3C-X]$$

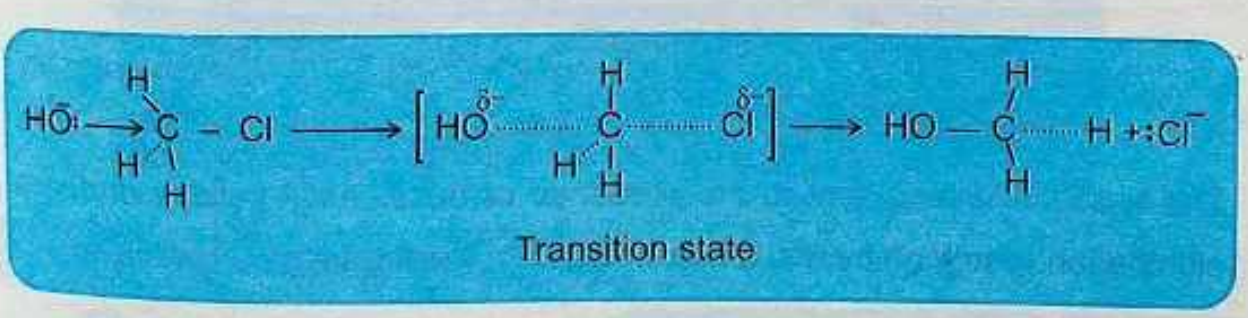
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

17.1.6. 4 SN^2 –Mechanism:

SN^2 stands for bimolecular nucleophilic substitution reaction. SN^2 reactions are defined as those nucleophilic substitution reactions in which two species are involved in the rate determing or slow step of the reaction. This mechanism is generally followed by primary alkyl halides in non – polar solvents. These reactions are completed in one step only.

The attacking nucleophile attacks the electrophilic carbon atom of the substrate before the leaving group departs. The entering group can attack only from the back side because the front side is blocked by the halogen atom. As the reaction proceeds the bond between the entering group and substrate starts to form and the bond between the leaving group and substrate weakens. A transition state is formed in which both the entering and leaving groups are partially bonded to the carbon atom of the substrate. In other words, the extent of bond formation on one side is equal to the extent of bond breaking on the other side.



Transition state

Finally, the bond between the leaving group and substrate is completely broken while the bond between the entering group and substrate is formed completely.

Primary alkyl halides undergo SN^2 and tertiary alkyl halides undergo SN^1 mechanism. The type of mechanism followed by the secondary alkyl

Scanned with CamScanner

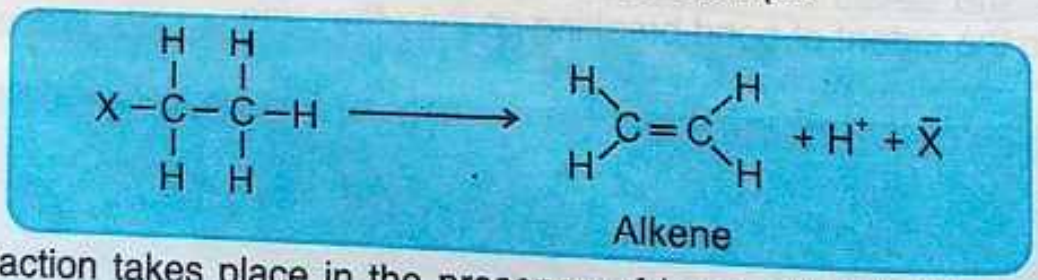
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

halides is governed by the nature of the solvent. If polar solvent is present, they follow SN^1 mechanism while in non polar solvents they follow SN^2 mechanism.

17.1.7 Elimination Reactions:

17.1.7.1 Overview:

Elimination reactions are those reactions which involve the elimination or removal of atoms or group of atoms from two adjacent carbon atoms in the substrate molecule to form a multiple bond. These are the reverse of addition reactions. During elimination reactions two strong sigma (δ) bonds are broken down and a new weaker $\text{Pi}(\pi)$ bond is formed. The saturated compounds are converted to unsaturated compounds. In the molecules of alkyl halides, during elimination, a hydrogen and halogen are removed from adjacent carbon atoms resulting in the conversion of alkyl halide to alkene. For example



Alkene

The reaction takes place in the presence of base. Alkyl halides undergo elimination reactions by two different types of mechanisms. These are:

17.1.7.2 E^1 – Mechanism:

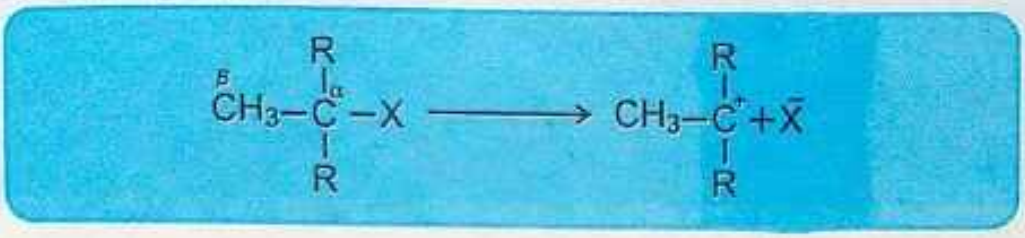
E^1 stands for unimolecular elimination reactions. In these reactions only one molecule e.g. substrate is involved in the rate determining or slow step. These reactions, therefore, follows first order kinetics. These

Scanned with CamScanner

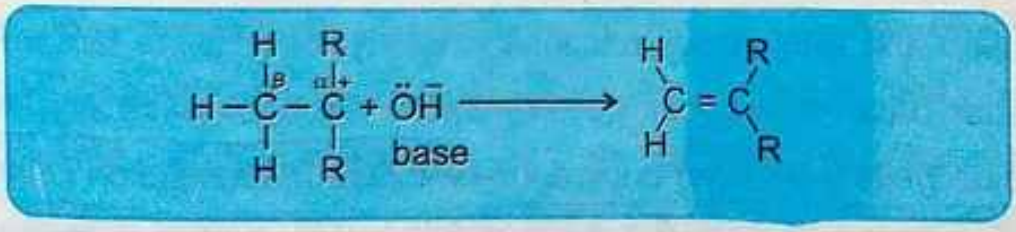
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

reactions are usually followed by tertiary alkyl halides which are completed in two steps, like SN^1 reactions.

In the first step, substrate ionizes and forms a tertiary carbocation. Halogen leaves as halides ion $(\bar{X})$.



This step involves the breaking of bond, therefore, it is the slow step or rate determining step of the reaction. In the second step, the base removes a hydrogen atom from the β–carbon atom of the carbocation as proton. This results in the formation of a double bond between α and β carbon atoms. The end product is an alkene



The rate equation for E^1 reactions is

$$\text{Rate} = k[R-X]$$

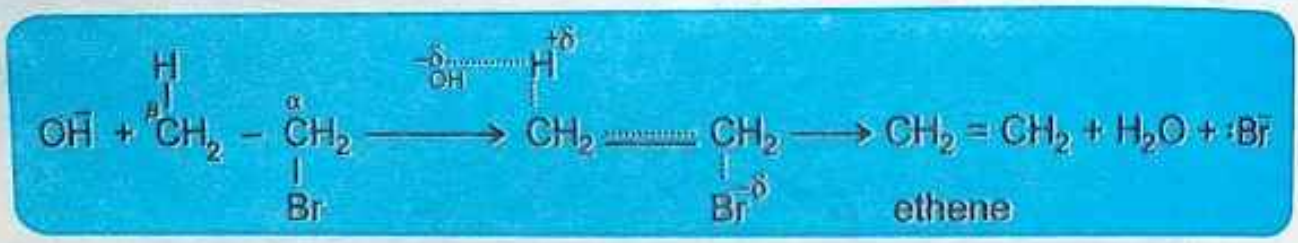
17.1.7.3 E^2 –Mechanism:

E^2 stands for bimolecular elimination reaction. Two species i.e. substrate and base are involved in the rate determining step of these reactions. These reactions follow second order kinetics therefore, their molecularity is two. E^2 reactions are generally followed by primary alkyl halides and are completed in one step like SN^2 reactions.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The removal of proton from the β–carbon atom by a base and the removal of halide ion $(\overline{X})$ from the α–carbon atom of the substrate takes place simultaneously. For example



The rate equation of E^2 reactions is

$$\text{Rate} = k[\text{Substrate}][\text{Base}]$$

17.1.8 Substitution Versus Elimination:

As all the bases are also nucleophiles, the competition between substitution and elimination reactions is determined by the fact whether it is a better base or a better nucleophile. A stronger base will favour in elimination while a stronger nucleophile will favour substitution in the same substrate. For example 2–bromopropane on reaction with ethoxide undergoes elimination and produces alkene as the major product because ethoxide is a strong base. On the other hand the same 2–bromopropane on reaction with an anion of the corresponding thioalcohol ($C_2H_5S^-$) undergoes substitution reaction because $C_2H_5S^-$ is more nucleophilic and less basic than $C_2H_5O^-$.

Crowding within the molecule of substrate also generally favours elimination over substitution reaction. This is due to the greater steric hindrance when the nucleophile approaches towards α carbon atom of the substrate. The greater number of alkyl groups on the substrate favours

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

elimination over substitution because these alkyl group stabilize alkene more than the substitution product.

17.2 Organometallic Compounds (Grignard Reagents):

All those organic compounds which contain at least one carbon–metal bond in their structures are known as organometallic compounds.

$$R\text{–}M$$

Where $M = Mg, Li, Pb, Zn$ etc.

They are named simply by adding the name of the metal to the organic group bonded directly to the metal. For example,

$CH_3 - MgI$	$(CH_3)_4 Pb$
Methylmagnessium iodide	Tetramethyllead

Alkyl or aryl magnesium halides are commonly known as Grignard reagents. They were discovered, prepared and studied by victor Grignard, therefore, they were named after him as Grignard reagents. They are highly reactive organic compounds. They are used in the synthesis of a large number of alkanes, alkynes, alcohols, aldehydes, ketones, carboxylic acids etc. Due to this great achievement Grignard was awarded with Noble Prize in 1912. The general formula of Grignard reagents is R–MgX where R represent Alkyl group and X represent Halogen atom (Cl, Br, I).

Examples are

$$CH_3 — Mg — Br$$
$$CH_3 — CH_2 — Mg — Cl$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

17.2.1 Preparation of Grignard Reagents:

Grignard reagents are prepared in the laboratory by the action of alkyl or aryl halides on freshly prepared magnesium metal in the presence of anhydrous or dry ether.

$$R-X+Mg \xrightarrow{\text{Ether}} R-MgX$$

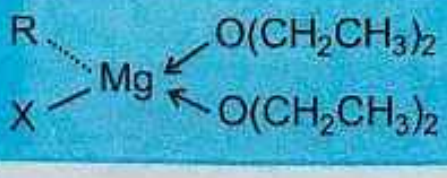
This reaction takes place in two steps. In the first step alkyl halide reacts with magnesium and yields alkyl radical and an $\dot{M}gX$ type of species.

$$\underset{\text{Alkylhalide}}{R-X} + Mg \xrightarrow{\text{1st Step}} \underset{\text{Alkyl Radical}}{\dot{R}} + \dot{M}gX$$

In the second step, $\dot{R}$ combines with $\dot{M}gX$ and yields the Grignard reagent

$$\dot{R} + \dot{M}gX \xrightarrow{\text{2nd Step}} \underset{\text{Grignard Reagent}}{R-MgX}$$

Diethyl ether used in the preparation of Grignard reagent plays two important roles. At one hand it provides a medium (Solvent) for the reaction, at the other hand it dissolves the Grignard reagent by the process of solvation.



Grignard reagent cannot be isolated, therefore, its ethereal solution is directly used in the synthetic reactions. The ease of formation of Grignard

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

reagent depends upon the nature of both alky or aryl group and the nature of halogen group. Increasing size of the alkyl group makes the formation of Grignard reagent difficult. For the same alkyl group, the ease of formation follows the order for halogens as $I > Br > C\ell$. Alkyl or aryl magnesium fluorides are not known. Alkyl bromides are the most suitable for preparation of Grignard reagents because alkyliodides are expensive.

17.2.2 Reactivity of Grignard Reagents:

The carbon magnesium bond of Grignard reagent is polar in nature. This is due to higher electronegativity of carbon than magnesium. So the electronic density is lying close to carbon than magnesium. As a result of this electronegativity difference, the carbon atom has a partial negative while magnesium has a partial positive charge.

$$R^{-\delta} - Mg^{+\delta}X$$

The alkyl group being an electron rich centre, acts as carbanion or nucleophile. It would attack polarized molecules at the point of low electronic density. Therefore, the characteristic reactions of Grignard's reagents are nucleophilic substitution and nucleophilic addition reactions.

17.2.3 Reactions of Grignard Reagents:

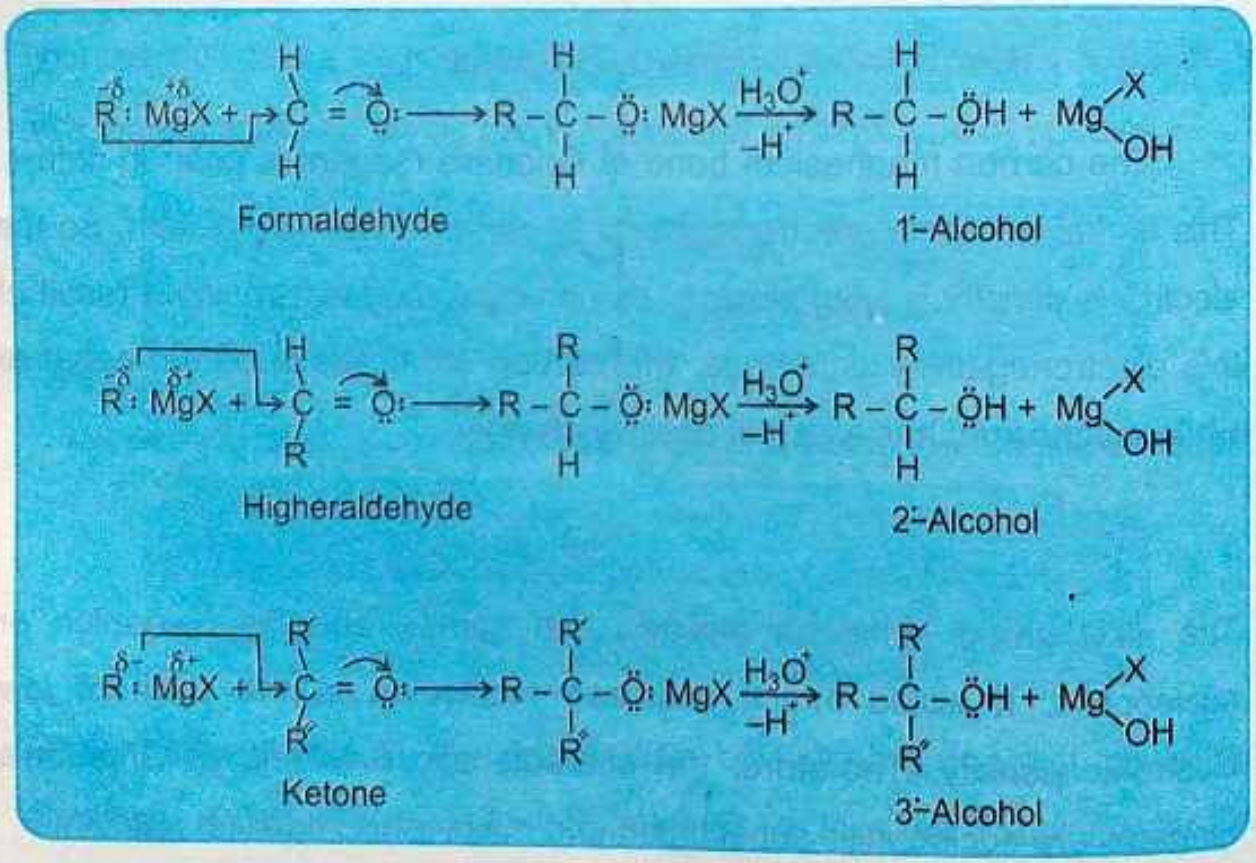
Grignard reagents are highly reactive compounds. Therefore, they react with many organic and inorganic compounds to produce a large number of valuable products. Some of these reactions are as follows.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

17.2.3.1 Reactions With Aldehydes and Ketones:

Grignard reagents react with aldehydes and ketones to yield addition products. Addition products upon their acid hydrolysis yield alcohols. Formaldehydes produce primary alcohol, higher aldehydes produce secondary, while ketones produce tertiary alcohols on treatment with Grignard reagents.



17.2.3.2 Reactions with Esters:

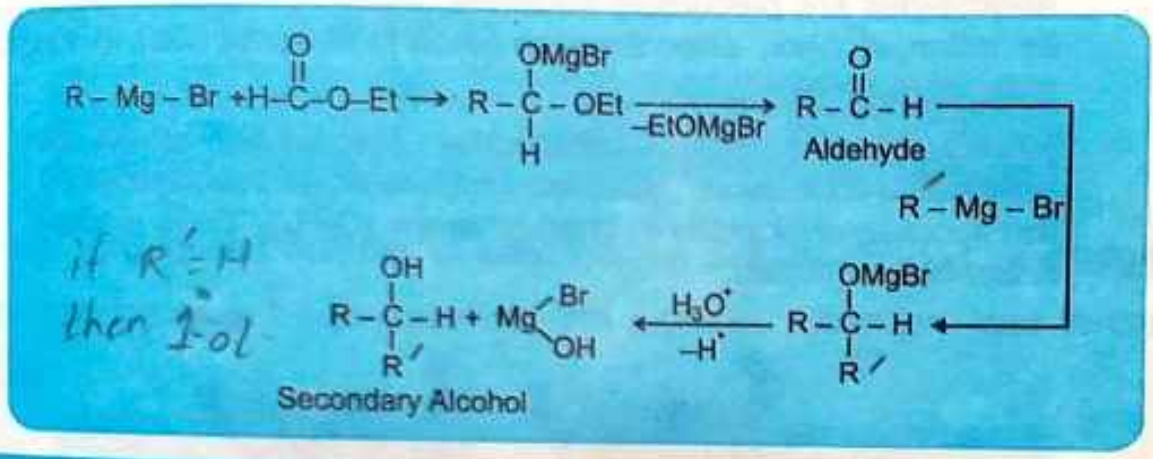
Grignard reagents react with esters to yield carbonyl compounds. These carbonyl compounds react with more of the Grignard reagent in the same reaction mixture and yield alcohols as the final products.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

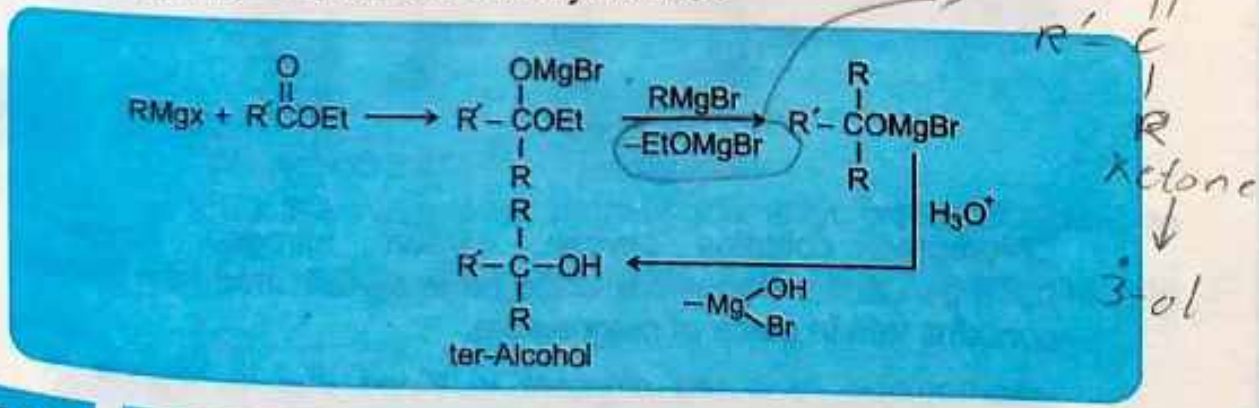
a. Reaction With Ethyl formate:

Ethyl formate reacts with Grignard reagent yielding an addition product. Addition product undergoes elimination and forms aldehyde. This aldehyde further reacts with another molecule of the Grignard reagent and yields secondary alcohol.



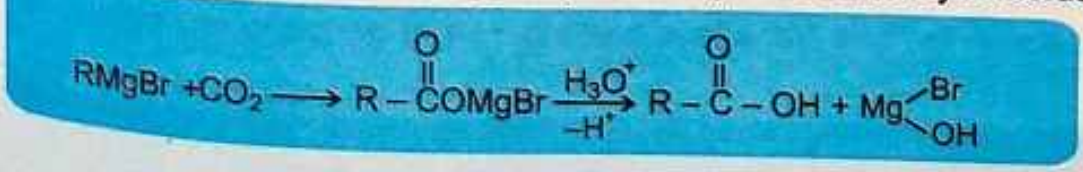
b. Reaction With Ethyl acetate:

Ethyl acetate reacts in the same way as ethyl formate but the end product of this reaction is a tertiary alcohol.



17.2.3.3 Reaction With CO_2:

Grignard reagents react with CO_2 forming an addition product. Addition product undergoes acid hydrolysis and yields carboxylic acids.



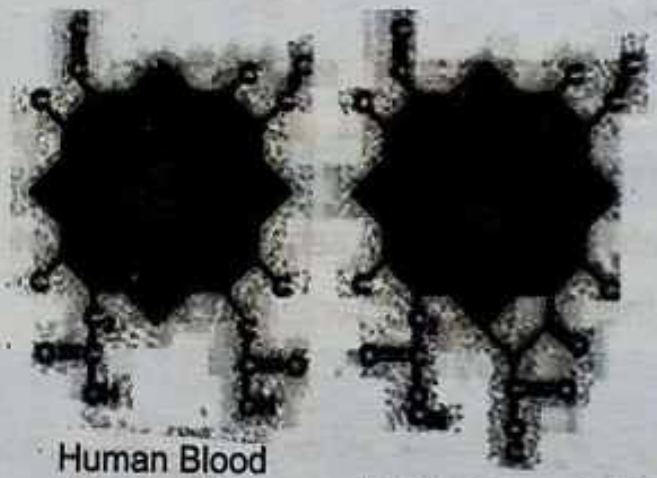
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Society, Technology and Science

Alkylhalides are precursors for many organic compounds such as as teflon, alcohol, phenobareton (used in sleeping pills), Grignard reagent, Amines etc.

Several organometallic compounds are under study as candidates for diverse therapies. Much work as investigated by the success of cisplatin in chemotherapy $(C_2H_5)_2$ Ti Cl_2 display anticancer activities.



Human Blood Hemoglobin

Plant Chlorophyll

Chlorophyll contains oxygen, carbon, nitrogen, oxygen, hydrogen and magnesium while haemoglobin from the blood contains iron in place of magnesium.

Heamoglobin is a red pigment in blood that is capable of transporting oxygen.

Chlorophyll is the green pigment in plants and certain organism that is capable of trapping energy from the sun to enhance the process of photosynthesis.

Scanned with CamScanner

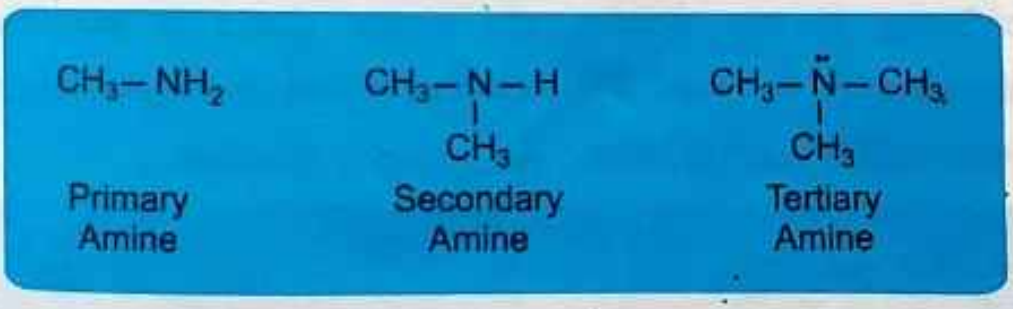
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

17.3 Amines:

Amines are important nitrogen containing organic compounds. These are the derivatives of NH_3 in which one or more hydrogen atoms have been replaced by one or more similar or different alkyl groups. The functional group of amines may be

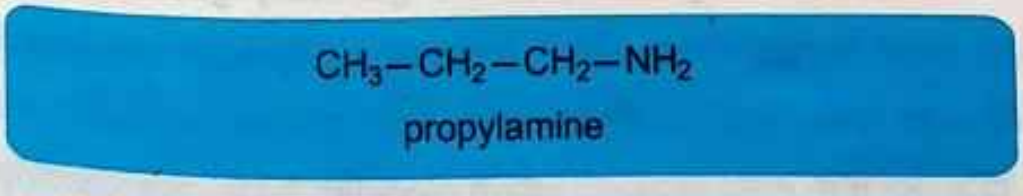


On the basis of the number of alkyl groups directly bonded to nitrogen atom, amines have been classified into primary, secondary and tertiary amines.



17.3.1 Nomenclature of Amines:

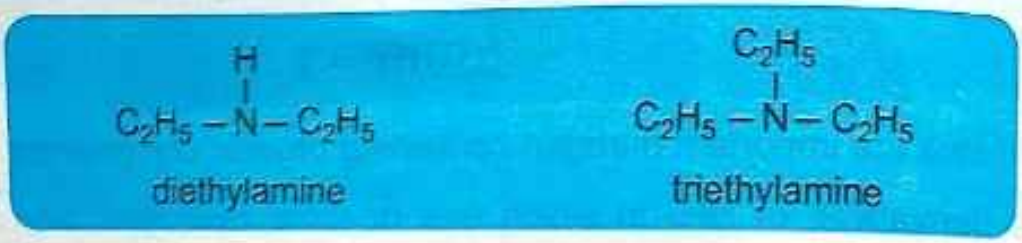
- Primary amines are named by naming the alkyl group attached to nitrogen first followed by the word amine. Names are written as one word.



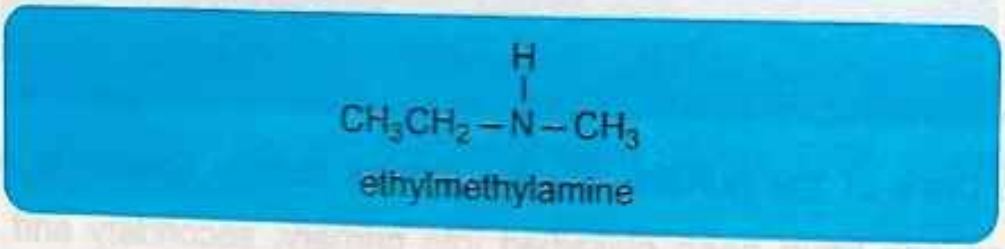
- In case of secondary and tertiary amines when two or three identical alkyl groups are attached to nitrogen the prefix "di" and "tri" are added to the name of amine.

Scanned with CamScanner

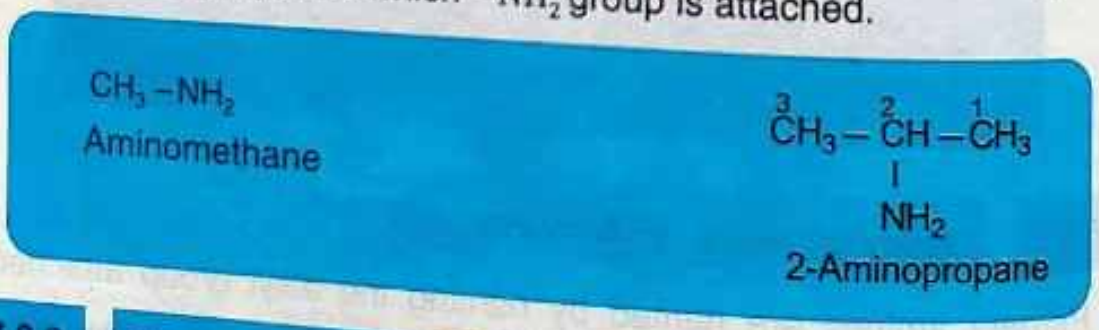
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



- If different alkyl groups are attached to the nitrogen, then they are named separately in alphabetical order.



- In case of complicated amines, IUPAC system is used for naming. According to this system, the amino group is considered as substituent in the chain is represented by the lowest possible number of that carbon atom to which $-NH_2$ group is attached.

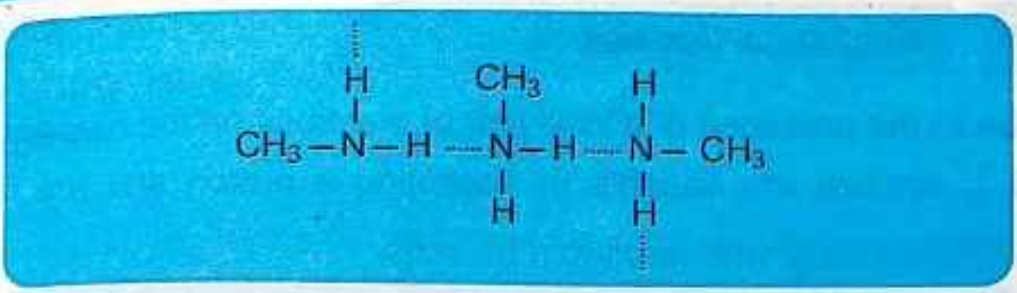


17.3.2 Physical Properties of Amines:

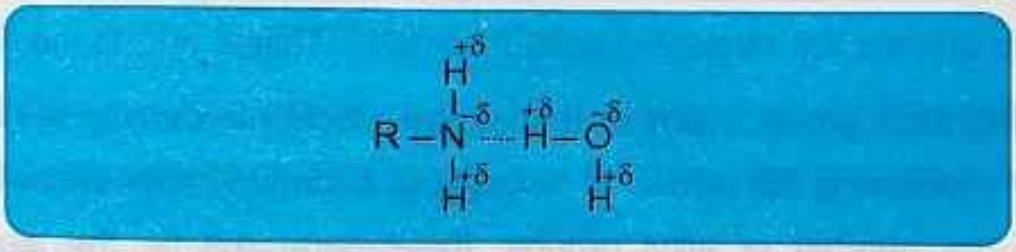
Low molecular weight amines are generally gases or low boiling liquids at room temperature. They possess a characteristic ammonia like smell. Amines have higher boiling points than alkanes of similar molecular weight due to the presence of intermolecular hydrogen bondings. The molecules of primary and secondary amines have high boiling points because they are able to form hydrogen bondings among their molecules.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

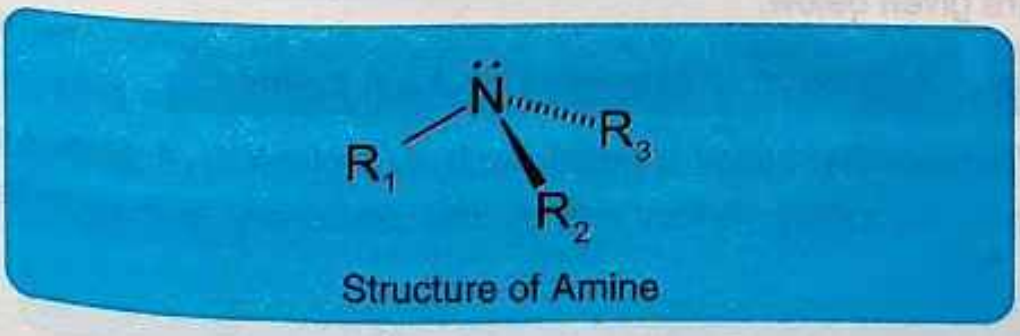


Molecules of tertiary amines cannot form hydrogen bondings among themselves, thus having lower boiling points than primary and secondary amines of the same molecular weight. However, all the primary, secondary and tertiary amines can form hydrogen bondings with water and are soluble in water.



17.3.3 Structure of Amines:

Amines are derivatives of Ammonia (NH_3) molecule where one or more H atoms have been replaced by alkyl groups (R). Since NH_3 molecule has a trigonal pyramidal shape, the resulting amines also have the same geometry. In these amines R–N–H or R–N–R angles is close to tetrahederal angle.



Structure of Amine

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

17.3.4 Basicity of Amines:

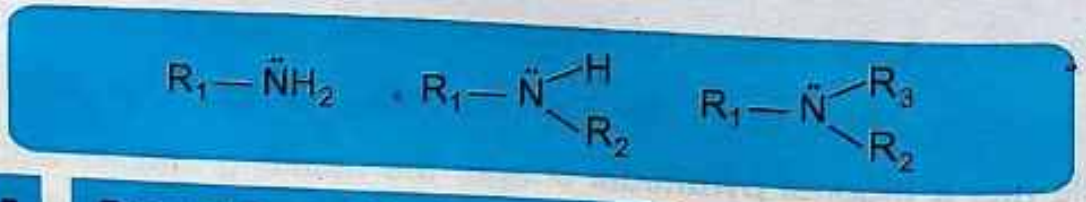
Due to the presence of a lone pair of electrons on the nitrogen atoms $(R-\ddot{N}H_2)$, amines are capable of accepting a proton and are basic in nature. Amines react with acids to form salts.

$$R-\ddot{N}H_2 + HX \xrightarrow[H_2O]{} R - \overset{+}{N}H_3\bar{X}$$
amine salt

Amines are weak bases and, therefore, partially ionize in aqueous solution with the following equilibrium.

$$R\ddot{N}H_2 + H_2O \rightleftharpoons R\overset{+}{N}H_3 + \bar{O}H$$

Aliphatic amines are stronger bases than NH_3. This is due to the electron –donating alkyl group which increases the electronic density of nitrogen thereby increasing its power of accepting a proton from an acid. The greater the number of alkyl groups, the greater will be the electronic density on nitrogen and, therefore, greater will be the power of nitrogen to accept proton and vice versa.



17.3.5 Preparation of Amines:

Amines can be prepared by a number of different methods. Some of these are given below.

17.3.5.1 Alkylation of Ammonia by Alkyl halides:

When an alkyl halide is heated with alcoholic NH_3, it yields a mixture of primary, secondary, tertiary amines and quaternary ammonium Salt.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

During this reaction the hydrogen atoms of NH_3 are replaced by alkyl groups of alkyl halide, therefore, this reaction is also known as alkylation of ammonia.

$$\underset{\text{Methylbromide}}{CH_3-Br} + NH_3 \longrightarrow \underset{\text{Methylamine}}{CH_3-NH_2} + HBr$$

$$CH_3-NH_2 + Br-CH_3 \longrightarrow \underset{\text{Dimethylamine}}{CH_3-NH-CH_3} + HBr$$

17.3.5.2 Reduction of Nitrogen Containing Functional Groups:

17.3.5.2.1 Reduction of Nitroalkanes:

Primary amines are prepared by the reduction of nitroalkanes with H_2 in the presence of "Pt/Pd" or "Ni" catalyst. They can also be reduced by lithium aluminum hydride in ether.

$$\underset{\text{Nitromethane}}{CH_3-NO_2} + 3H_2 \xrightarrow{Pt/Pd} \underset{\text{Methylamine}}{CH_3-NH_2} + 2H_2O$$

$$\underset{\text{Nitroethane}}{CH_3-CH_2-NO_2} + 6[H] \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Ethylamine}}{CH_3-CH_2-NH_2} + 2H_2O$$

17.3.5.2.2 Reduction of Nitriles:

When nitriles or alkyl cyanides are reduced they yield the corresponding primary amines. This reduction can be brought about by H_2 in the presence of Ni catalyst or by lithium aluminum hydride in ether.

$$\underset{\text{Methylcyanide}}{CH_3-C\equiv N} + 2H_2 \xrightarrow{Ni} \underset{\text{Ethylamine}}{CH_3-CH_2-NH_2}$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$CH_3-C\equiv N+4[H]\xrightarrow[\text{Ether}]{LiAlH_4}CH_3-CH_2-NH_2$$

Ethylamine

$$CH_3-CH_2-C\equiv N+4[H]\xrightarrow[\text{Ether}]{LiAlH_4}CH_3-CH_2-CH_2-NH_2$$

Ethylcynide Propylamine

17.3.5.2.3 Reduction of Amides:

Primary amines are obtained when simple amides are reduced by lithium aluminum hydride in ether.

$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2+4\,[H]\xrightarrow[\text{ether}]{LiAlH_4}CH_3-CH_2-NH_2+H_2O$$

17.3.6 Reactivity of Amines:

The chemistry of amines is mainly due to the lone pair of electron on nitrogen atom. This lone pair of electrons is available to the electron deficient reagents called electrophiles. On the basis of this lone pair of electrons amines act as nuclcophilic reagents.

17.6.7 Reactions of Amines:

17.6.7.1 Overview

Amines are important and reactive organic compounds. These react with a number of different substances to produce valuable organic compounds. Some of their reactions are:

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

17.6.7.2 Alkylation of Amines By Alkyl halides:

When amines, specially primary amines are treated with alkyl halide, they produce a mixture of secondary, tertiary amines and quaternary ammonium salt. In this process the hydrogen atoms in the amine are successively replaced by the alkyl groups of alkyl halide.

$$R-NH_2 + X-R \longrightarrow R-NH-R + HX$$

Primary amine Secondary amine

$$CH_3-NH_2 + I-CH_3 \longrightarrow CH_3-NH-CH_3 + HI$$

Methylamine Dimethylamine

$$CH_3-NH-CH_3 + I-CH_3 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}}-CH_3 + HI$$

Trimethyl amine

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}}-CH_3 + I-CH_3 \longrightarrow \left[CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{\overset{\displaystyle |}{N}}}}-CH_3\right]^{+} \bar{I}$$

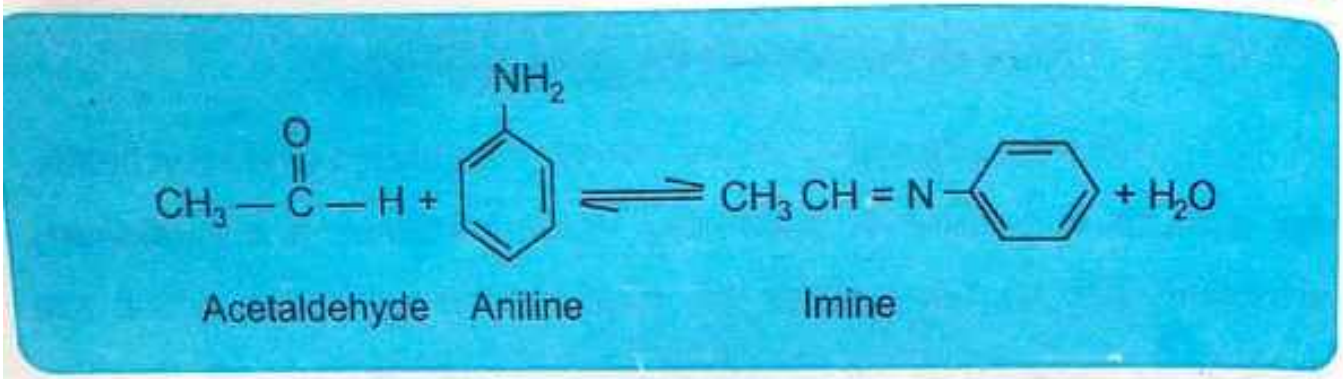
Quartenary methyl ammomium iodide

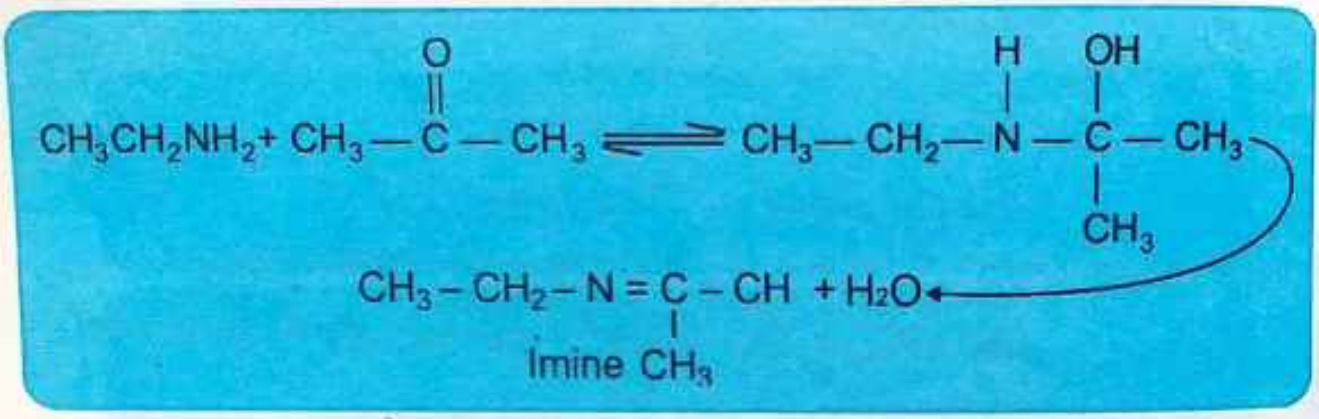
17.6.7.3 Reaction of Amines with Aldehydes and Ketones:

Primary amines react with aldehydes and ketones yielding condensation products called imines. These imines are also known as schiff's bases.

Scanned with CamScanner

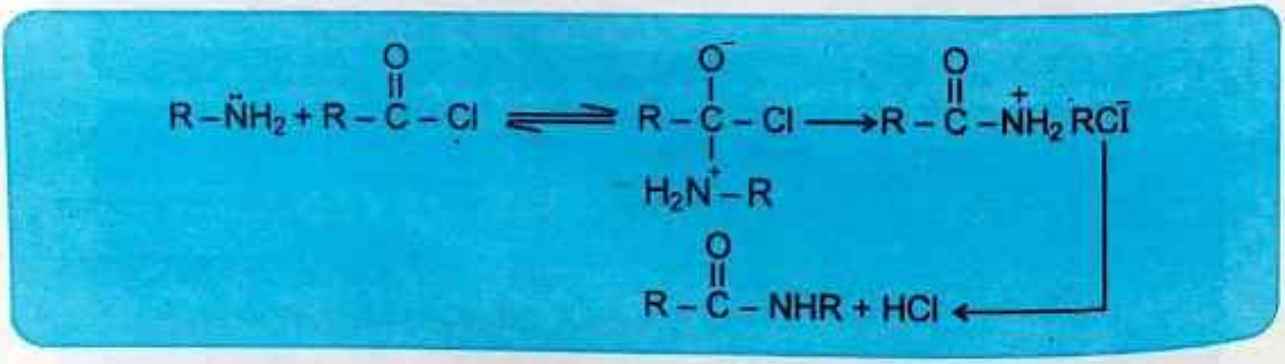
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



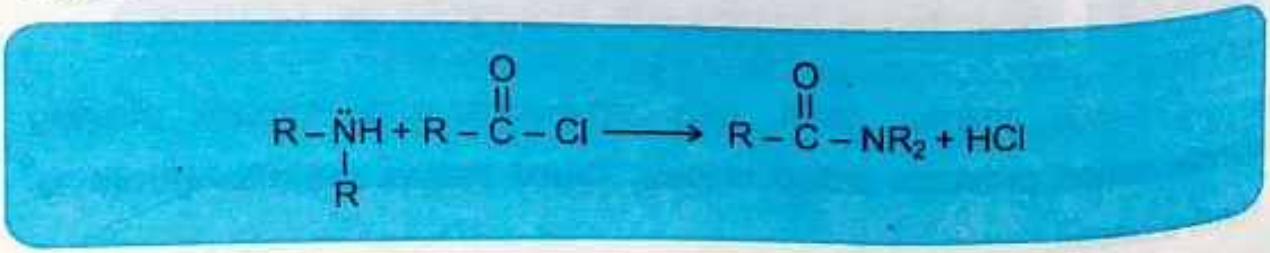


17.6.7.4 Preparation of Amides:

Primary amines react with acid chloride or acid anhydride to produce N – substituted amides.



Secondary amines react with acid chlorides to produce N, N –disubtituted amides.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

As tertiary amines have no hydrogen atom directly attached to the nitrogen, therefore, they don't react with acid chlorides to produce amides.

17.6.7.5 Preparation of Diazonium Salts:

When primary aliphatic amines are treated with nitrous acid they yield highly unstable salts known as diazonium salts. This reaction is termed as diazotization reaction. Nitrous acid being an unstable acid is prepared in situ by the reaction of $NaNO_2$ and dil HCl.

$$CH_3-CH_2-CH_2-NH_2 + NaNO_2 + 2HCl \rightarrow \underbrace{\left[CH_3-CH_2-CH_2-N^+\equiv N\right]\bar{Cl}}_{\text{Diazonium salt}} + 2H_2O + NaCl$$

Diazonium salt prepared from aliphatic amines are less important synthetically however the process could be useful analytically. Diazonium salts of aromatic primary amines are of considerable synthetic importance because they serve as intermediates in a variety of synthetic organic reactions, in which the diazonium group $-\overset{+}{N}\equiv N$, is replaced as N_2 by various other functional groups. Aryl bromides, Arylchlorides phenol, Aryl cyanide, benzene are best prepared from diazonium salts.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Key Points:

- General formula of alkyl halide is R–X.
- Each carbon atom in alkyl halide is sp^3 hybridized.
- The molecule which undergoes substitution reaction is called 'substrate'.
- The group or species which leaves the substrate is called "leaving group".
- The end product of substitution is known as reaction product.
- SN^1 Mechanism is defined as that nucleophilic substitution reaction in which only one molecule is involved in rate determing or slow step.
- Those nucleophilic substitution reactions where two species are involved in the rate determing or slow step.
- The primary alkyl halides undergo SN^2 mechanism while tertiary alkyl halides undergo SN^1 Mechanism.
- In polar solvent secondary alkylhalides follow SN^1-mechanism while in non-polar solvents follow SN^2-mechanism.
- During elimination reaction two strong sigma bonds are broken and a new weaker pi bond is formed.
- E^1 stands for unimolecular elimination while E^2 stands for bimolecular elimination reaction.
- Those organic compound which contain at least one carbon—metal bond in their structure are known as organo–metallic compounds.
- Amines are derivatives of NH_3 in which one or more hydrogen atom have been replaced by one or more similar or different alkyl group.
- The functional group of amines may be $-NH_2$, $-\underset{|}{N}H$, or $-\underset{|}{\overset{|}{N}}$
- Due to presence of lone pair of electrons on nitrogen atoms ($R–NH_2$) amines are basic in nature.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

EXERCISE

Exercise

Q1. Choose the correct option.

1. The reaction of CH_3MgI with acetone followed by hydrolysis gives.
   (a) ter-butanol (b) sec-butanol
   (c) n-butanol (d) none of these
2. Which one of the following halide is most reactive towards nucleophilic substitution reaction?
   (a) C_2H_5Br (b) C_2H_5I
   (c) C_2H_5F (d) C_2H_5Cl
3. All electron deficient species are classified as.
   (a) Nucleophiles (b) Electrophiles
   (c) Bases (d) All of these
4. $R–CH_2–X$ is an example of
   (a) Primary alkyl halide (b) Secondary alkyl halide
   (c) Isopropyl halide (d) Both (a) and (b)
5. The carbon atom carrying positive charge and attached to three other atoms or groups is called.
   (a) Carbonium ion (b) Carbon ion
   (c) Oxonium ion (d) Carbanion
6. Grignard reagent can be represented by general formula
   (a) R–Mg– N (b) R–Mg–O
   (c) R–Mg–OH (d) R–Mg–X

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

7. The end product of reaction of Grignard reagent with Ethyl acetate is

   (a) primary alcohol (b) secondary alcohol
   (c) tertiary alcohol (d) none of these

8. An electron pair donor is classified as

   (a) Lewis acid (b) Lewis base
   (c) Bronsted acid (d) Bronsted base

9. In primary alkyl halides the carbon atom to which the halo group is attached is in turn bonded directly to

   (a) one other carbon (b) two other carbons
   (c) three other carbons (d) four other carbons

Q II Short questions.

1. What is the importance of Grignard reagent?
2. Compare nucleophilic substitution reaction and electrophilic substitution reaction.
3. Why tertiary carbocation is more stable?
4. In reaction between chloroethane and aqueous sodium hydroxide identify the attacking nucleophile and atom in the chloro-ethane molecule being attacked.
5. What is the importance of diazonium salt?
6. Define the following terms.

   (a) substrates (b) leaving group
   (c) carbocation

Scanned with CamScanner

QIII. Long questions

1. Discuss various methods of preparation of alkyl halides.
2. Explain elimination reaction in alkyl halides.
3. Discuss the mechanism of SN^1 and SN^2 reactions.
4. (a) How can you prepare Grignard reagent.
   (b) Discuss the reaction of Grignard reagent with.
   (i) aldehydes (ii) ketones
   (iii) esters (iv) carbon dioxide
5. How amines are prepared? Discuss its structure and acidity.
6. Write down different reactions of amines.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

UNIT 18

ALCOHOLS, PHENOLS AND ETHERS

Learning Outcomes:

After carefully studying this unit and working the exercise, students will be able to.

- Explain nomenclature, structure and acidity of alcohols as exemplified by ethanol.
- Describe the preparation of alcohols by reduction of aldehydes, ketones, carboxylic acids and esters.
- Explain reactivity of alcohols.
- Describe the chemistry of alcohols by preparation of ethers and esters, oxidative cleavage of 1, 2 –diols.
- Discuss thiols (RSH).
- Explain the nomenclature, structure and acidity of phenols.
- Describe the preparation of phenol from benzene sulphonic acid, chlorobenzene, acidic oxidation of cumene and hydrolysis of diazonium salts.
- Discuss the reactivity of phenol and their chemistry by electrophilic aromatic substitution, reaction with sodium metal and oxidation.
- Differentiate between alcohol and phenol.
- Describe isomerism in alcohols and phenols.
- Identify ethers from their formula.

Scanned with CamScanner

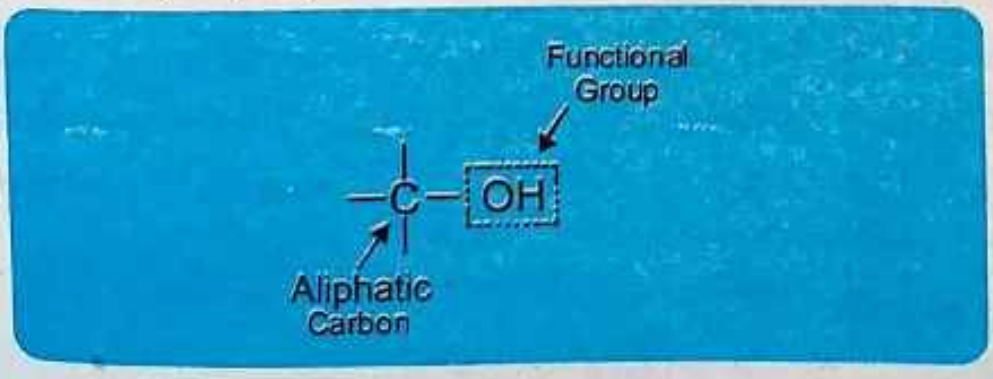
18.1 ALCOHOLS

Introduction:

Alcohols, phenols and ethers are derivatives of water. In alcohol one H of H_2O has been replaced by an alkyl group. In phenol one H is replaced by an aromatic ring, whereas in ether both H have been replaced by two alkyl groups.

R – OH	Ar – OH	R – $\ddot{O}$ – R
Alchol	Phenol	Ether

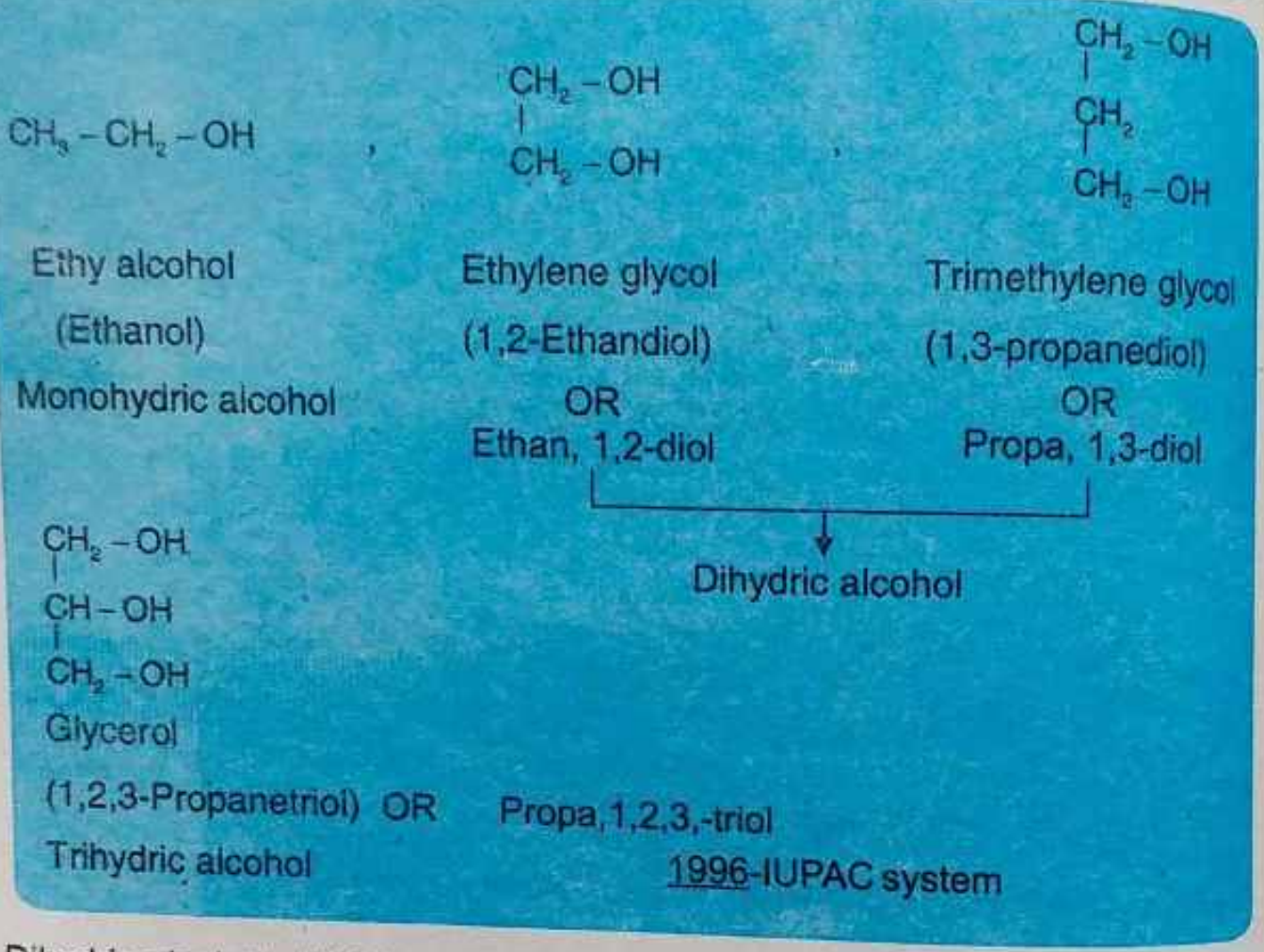
Alcohols are organic compounds, in which a hydroxyl group (–OH) is attached to an aliphatic carbon atom. Hydroxyl group is the functional group of alcohols. The general formula of alcohols is R – OH or $C_nH_{2n+1}OH$ e.g methyl alcohol (CH_3OH)



Alcohols may be monohydric, dihydric, trihydric or polyhydric, depending upon the number of –OH groups in a molecule

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



Dihydric alcohols (diols) are usually called glycols because of their sweet taste. (Greek glycys= Sweet).

- Monohydric alcohols may be primary, secondary or tertiary. When the hydroxyl group is attached to the primary carbon atom, it is classified as primary alcohol but when the hydroxyl group is attached to the secondary or tertiary carbon atom, the alcohol is accordingly classified as secondary or tertiary alcohol.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

18. 1.1 Nomenclature

Alcohols are named by the following two systems.

a. Common System. b. IUPAC System.

a. Common System:

In this system, alcohols (R – OH) are named "Alkyl Alcohols". That is alkyl group (R) of the alcohol is named first, which is followed by the word alcohol. For example,

$CH_3 - OH$
Methyl alcohol

$CH_3 - CH_2 - OH$
Ethyl alcohol

$CH_3 - CH_2 - CH_2 - OH$
n –Propyl alcohol

$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - OH$
Isopropyl alcohol

For higher members in the series, it becomes necessary to indicate, whether a particular alcohol is primary (pri.), secondary (sec.) or tertiary (ter.) For example,

$CH_3 - CH_2 - CH_2 - CH_2 - OH$
n –Butyl alcohol

$CH_3 - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$
sec –Butyl alcohol

$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - OH$
ter –Butyl alcohol

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

b. IUPAC System:

In this system alcohols are named as "alkanols". That is, the final "e" of the corresponding alkane is replaced by "-ol".

The IUPAC rules are:

1. Select the longest continuous carbon chain containing the –OH group.
2. Name this chain as "alkanol". That is, drop the ending "e" of the corresponding alkane and add "ol" as suffix. This will serve as the parent name or stem name of the alcohol.
3. Number the chain from one end or the other, so as to give the carbon carrying the –OH group, the lowest possible number.
4. Mention the position of the hydroxyl group by putting its number before the parent name or before the "-ol".
5. Indicate the positions of the other substituents (if any) using the numbers of the carbon atoms, to which they are attached.
6. The substituents, along with their positions, are named in alphabetical order before the parent name.
7. If the number of carbon atoms carrying the hydroxyl group is the same from either side, then number the chain from the end which is heavily substituted.
8. In case of dihydric, trihydric and polyhydric alcohols, the prefix di, tri, tetra etc is used before "–ol", alongwith the numbers of the carbon atoms to which these hydroxyl groups are attached.
9. If more than one hydroxyl groups are attached to the same carbon atom, the number of that carbon atom is repeated.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The following examples will illustrate the above rules.

1. $CH_3 - OH$

Methanol

2. $CH_3 - CH_2 - OH$

Ethanol

3. $^3CH_3 - ^2CH_2 - ^1CH_2 - OH$

1 –Propanol

4. $^3CH_3 - ^2\underset{\displaystyle OH}{\underset{|}{CH}} - ^1CH_3$

2 –Propanol

Prop-2-ol

5. $^1CH_3 - ^2\underset{\displaystyle OH}{\underset{|}{CH}} - ^3CH_2 - ^4CH_3$

2 –Butanol (or But -2- ol)

6. $^1CH_3 - ^2\underset{\displaystyle OH}{\underset{|}{CH}} - ^3\underset{\displaystyle CH_2 - CH_3}{\underset{|}{CH}} - ^4\underset{\displaystyle OH_3}{\underset{|}{CH}} - ^5CH_3$

3 –Ethyl -4 –methyl -2 –pentanol

(or 3 –Ethyl -4 –methyl–pent -2–ol)

7. $^1CH_3 - ^2\underset{\displaystyle CH_3}{\underset{|}{C}} - ^3\underset{\displaystyle OH}{\underset{|}{CH}} - ^4\underset{\displaystyle H}{\underset{|}{C}} - ^5CH_3$ (with CH_3 on ^4C)

2, 2, 4 –Trimethyl pent -3 -ol.

8. $^1CH_3 - ^2\underset{\displaystyle OH}{\underset{|}{CH}} - ^3\underset{\displaystyle OH}{\underset{|}{CH}} - ^4\underset{\displaystyle Cl}{\underset{|}{CH}} - ^5CH_3$

4 –Chloropenta -2,3-diol.

or (4-chloro-2,3-penta diol)

9. $^1CH_2 - OH$

$^2CH_2 - OH$

Ethane -1,2 –diol

or (1,2-Ethanediol)

10. $^1\underset{\displaystyle OH}{\underset{|}{CH_2}} - ^2\underset{\displaystyle OH}{\underset{|}{CH}} - ^3\underset{\displaystyle OH}{\underset{|}{CH_2}}$

Propa -1,2,3 –triol

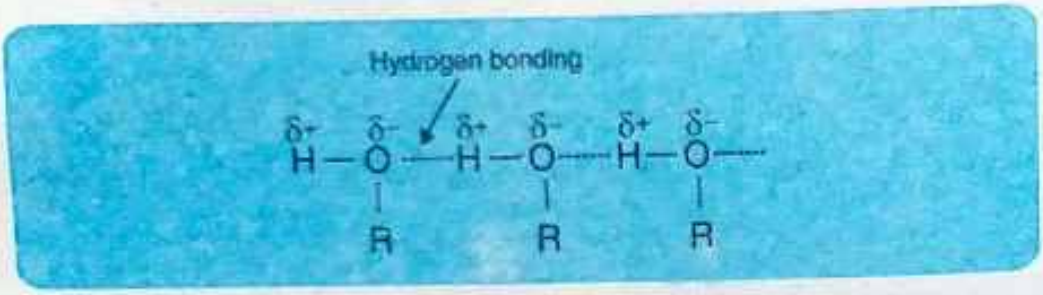
or (1,2,3-Propan triol)

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

18. 1.2 Physical Properties

Lower alcohols are colourless, toxic liquids. They have characteristic sweet smell. The boiling points of alcohols are much higher than those of corresponding alkanes. It is due to hydrogen bonding among the alcohol molecules.



Boiling points of alcohols increase regularly with the increase in the number of carbon atoms.

Table 18.1 Boiling point of some alcohols.

Name	Structure and Name	Boiling Points (°C)
Methanol	CH_3-OH	64.5
Ethanol	CH_3-CH_2-OH	78.3
1 –Propanol	$CH_3-CH_2-CH_2-OH$	97.0
1 –Protanol	$CH_3-CH_2-CH_2-CH_2-OH$	118.0
1 –Pentanol	$CH_3-CH_2-CH_2-CH_2-CH_2-OH$	138.0

However, among the isomeric alcohols, as the branching increases, the boiling points decrease.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

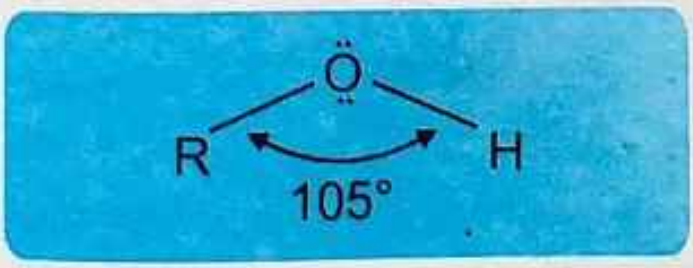
For Example:

$CH_3-CH_2-CH_2-CH_2-OH$	$CH_3-\underset{\displaystyle OH}{\underset{\vert}{CH}}-CH_2-CH_3$	$CH_3-\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle CH_3}{\underset{\vert}{C}}}}-OH$
1-Butanol OR (But, 1-ol) (BP 118°C)	2-Butanol OR (But, 2-ol) (BP 99°C)	2-Methyl-2-Propanol (2-Methyl Prop,2-ol) (BP 83°C)

Lower alcohols $(C_1 - C_3)$ are completely soluble in water in any proportion. However the solubility of higher alcohols in water falls rapidly.

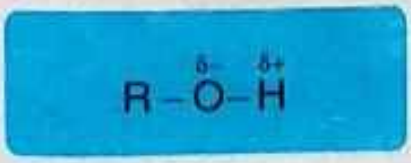
18.1.3 Structure of Alcohols

Alcohol are alkyl derivatives of water molecules. Water molecule has an angular structure with H–O–H bond angle slightly smaller than tetrahedral angle (109.5°). Alcohols molecule have a similar geometry where R–O–H angle is 105°.



18.1.4 Acidity of Alcohols

Alcohols are acidic in nature. It is because the O–H bond in alcohols is polar due to difference in electronegativities of the two atoms.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

This allows the release of hydrogen atom as proton (H^+). Due to this acidic behaviour, alcohols react with sodium or potassium to form alkoxide with the liberation of hydrogen gas.

$$\underset{\text{Alcohol}}{2ROH} + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2RO^- Na^+} + H_2 \uparrow$$

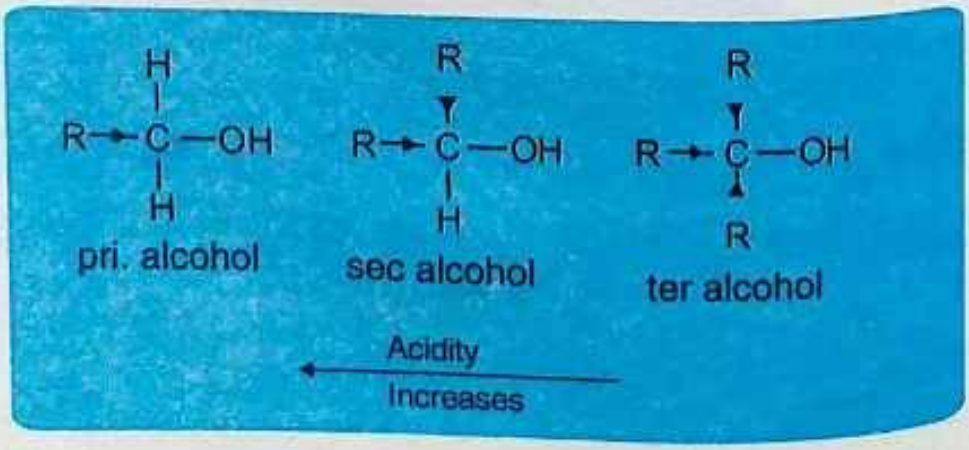
$$\underset{\text{Ethanol}}{2CH_3CH_2OH} + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{CH_3CH_2ONa} + H_2 \uparrow$$

However, alcohols are very weakly acidic with Ka value 10^{-16} to 10^{-18}

$$\underset{\text{Water}}{H-OH} \longrightarrow H^+ + OH^-, (Ka = 1\times10^{-14})$$

$$\underset{\text{Alcohol}}{R-OH} \longrightarrow RO^- + H^+, (Ka = 1\times10^{-16} - 1\times10^{-18})$$

The alkyl group in alcohols releases electrons (electron donating group) towards the oxygen atom, increasing its partial negative charge and hence the release of proton becomes difficult. That is why the alcohols are less acidic than water. Tertiary alcohols are less acidic than secondary alcohols and secondary alcohols are less acidic than primary alcohols.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

It is to be noted that alcohols are not acidic enough to react with aqueous NaOH or KOH.

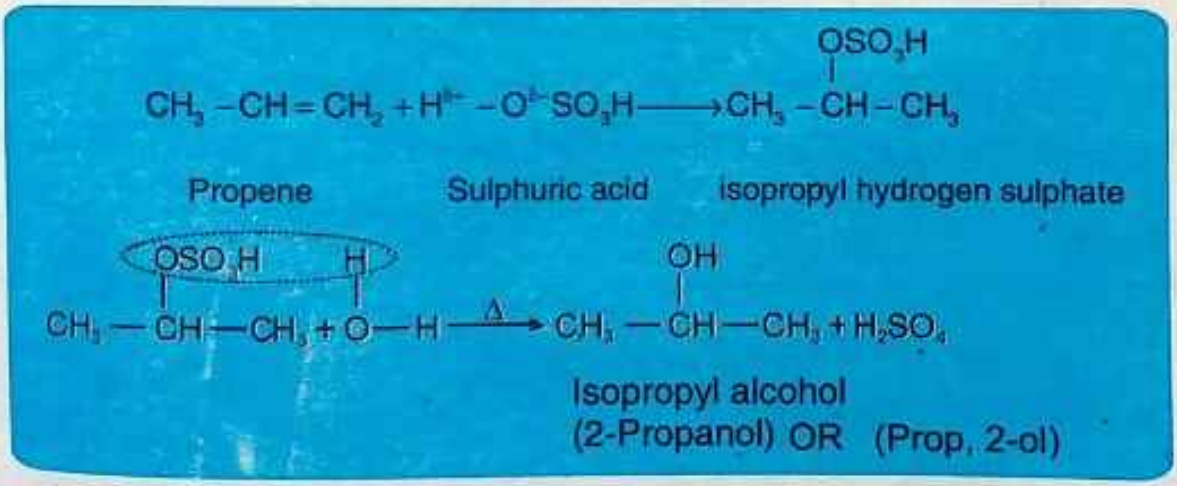
$$R-OH + NaOH \longrightarrow \text{No Reaction}$$

18. 1.5 Preparations of Alcohols

Alcohols can be prepared by the following methods.

18.1.5.1 Hydration of Alkenes:

Alkenes react with cold concentrated sulphuric acid to produce alkyl hydrogen sulphates, which on hydrolysis yield alcohols. Unsymmetrical alkenes follow the Markovnikov's rule.



18.1.5.2 Hydrolysis of Alkyl halides:

Alcohols can be prepared by the hydrolysis of alkyl halides by means of water or an aqueous alkali.

$$CH_3I + KOH \xrightarrow[H_2O]{\Delta} CH_3-OH + KI$$

Methyl iodide — Methyl alcohol

$$CH_3-CH_2-Br + KOH \xrightarrow[H_2O]{\Delta} CH_3-CH_2-OH + KBr$$

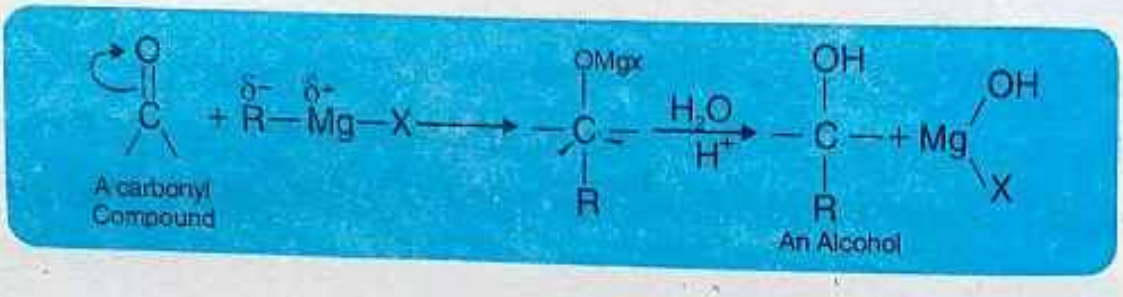
Ethyl bromide — Ethyl alcohol

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

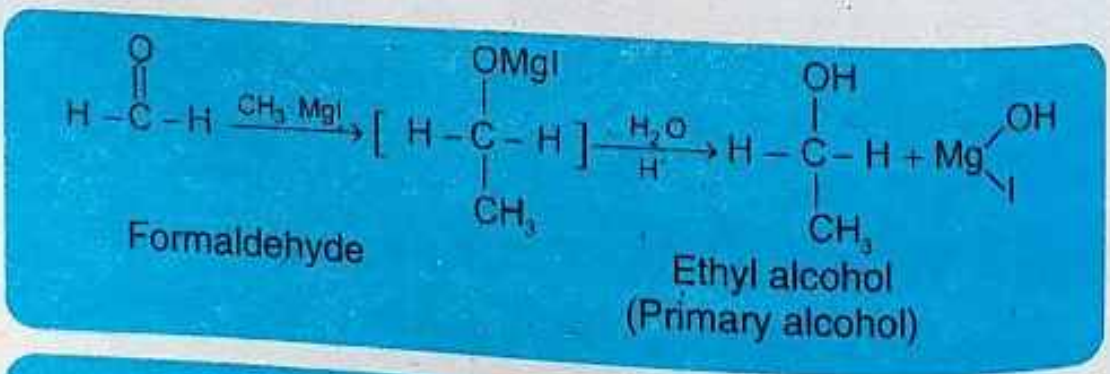
18.1.5.3 Reaction of RMgX with Aldehydes and Ketones (Grignard Synthesis):

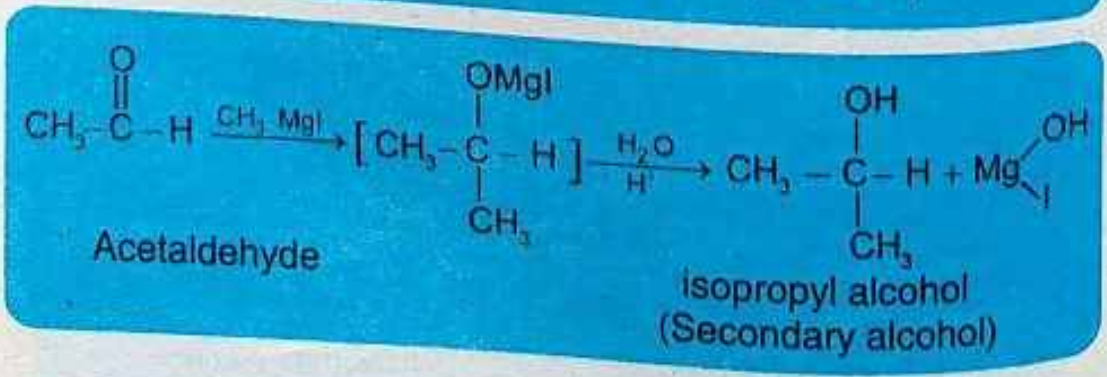
Grignard reagent (R – Mg – X) adds to the carbon –Oxygen double bond (–C(=O)–) of the carbonyl compound to form an addition compound which on acid hydrolysis gives alcohol.



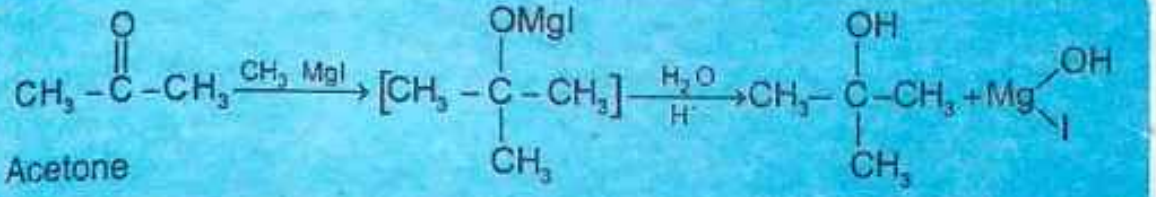
Formaldehyde reacts with Grignard reagents to produce primary alcohols. Other aldehydes give secondary alcohols. Ketones on reaction with Grignard reagent produce tertiary alcohols.

For Example:



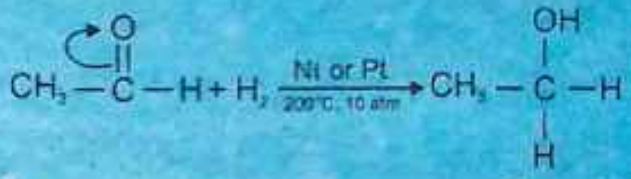


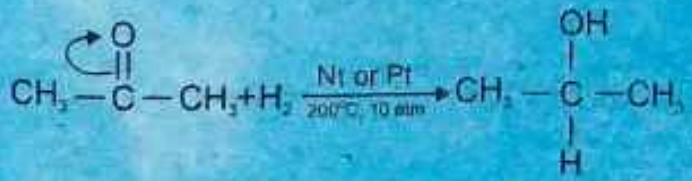
Scanned with CamScanner



18.1.5.4 Reduction of Aldehydes and ketones:

Carbonyl compounds can easily be reduced to alcohols under different conditions. Aldehydes produce primary alcohols while ketones produce secondary alcohols. Reduction (Hydrogenation) is carried out in the presence of metal catalyst such as Ni, Pt or Pd at elevated temperatures (200°C) and pressure (10 atmosphere)





18.1.5.5 Reaction of R –Mg –X with Esters:

Formate esters on reaction with Grignard reagent produce secondary alcohols while other esters form tertiary alcohols.

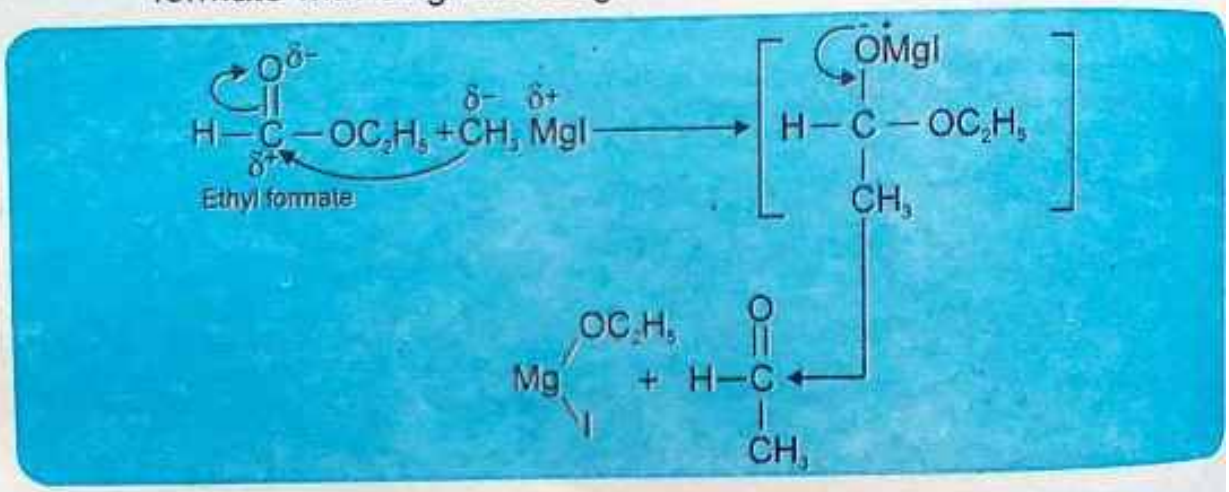
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

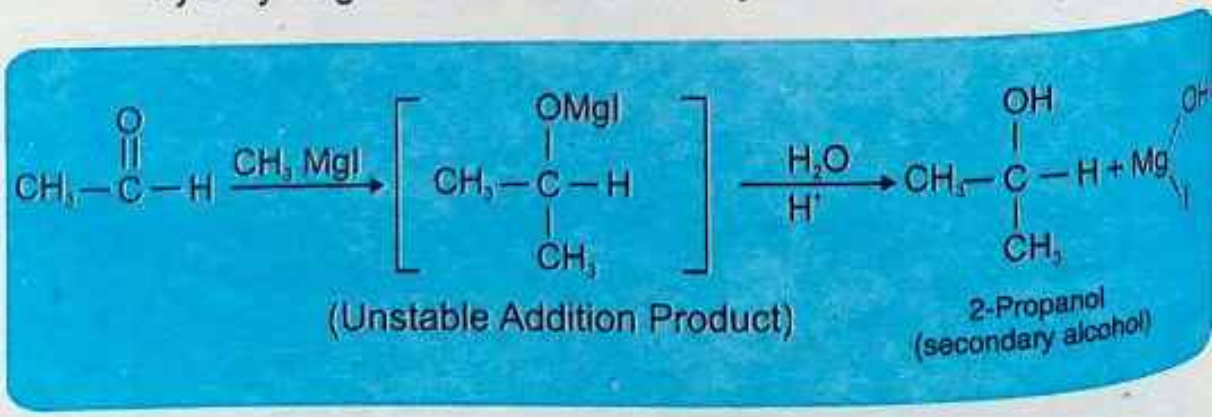
a. Reaction of R- Mg –X with Ethyl Formate:

In this case, a secondary alcohol is formed which involves two steps.

Step 1: An aldehyde is first formed by the reaction of ethyl formate with Grignard reagent.



Step 2: The aldehyde then reacts with another molecule of the Grignard reagent to form an unstable addition product which on hydrolysis gives rise to a secondary alcohol.



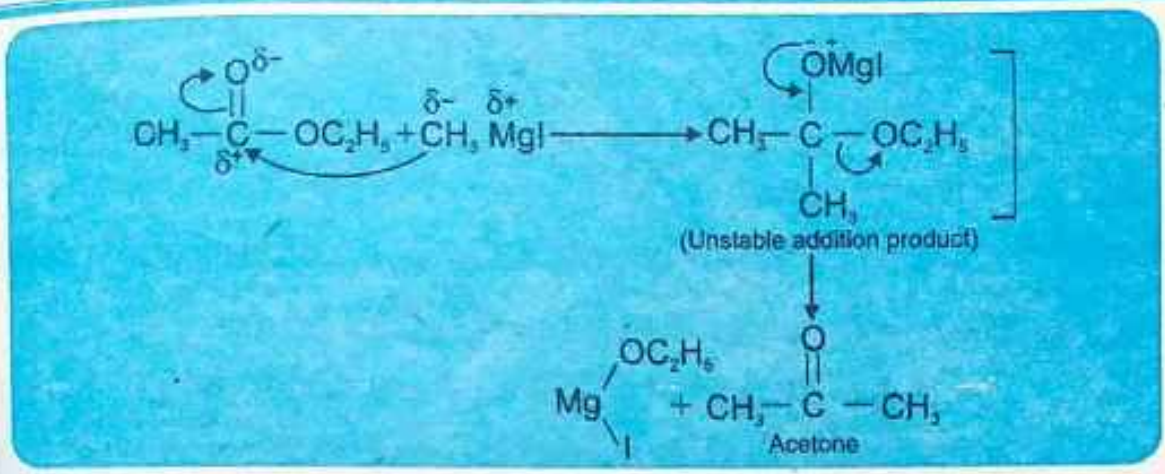
b. Reaction of R –Mg –X with Ethyl Acetate:

In this case a tertiary alcohol is formed which also involves two steps.

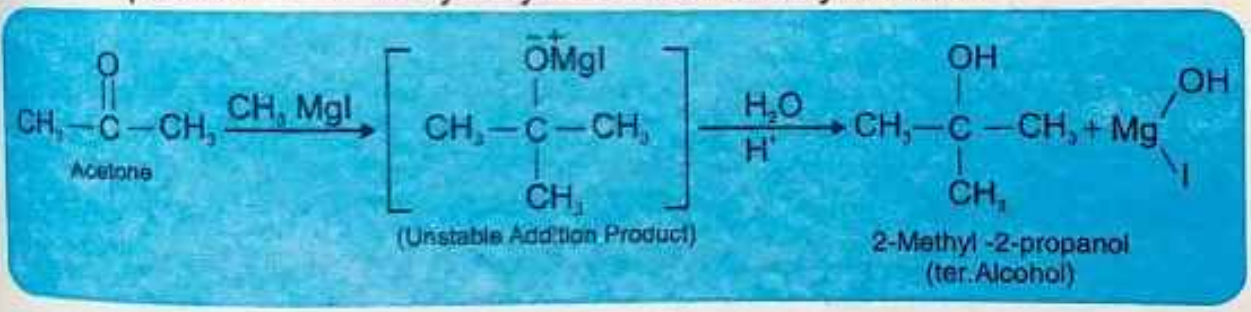
Step 1: A ketone is first formed by the reaction of ethyl acetate with Grignard reagent.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

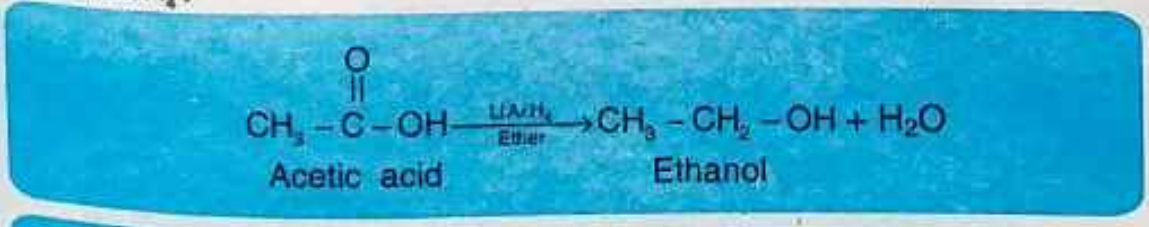


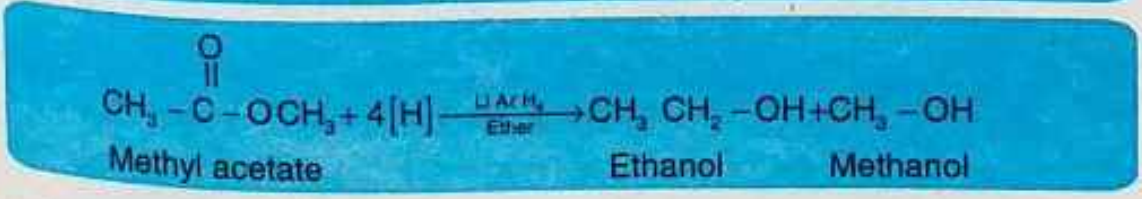
Step 2: The Ketone (in this case the acetone) then reacts with another Grignard reagent molecule to give an unstable addition product which on hydrolysis forms a tertiary alcohol.



18.1.5.6 Reduction of Carboxylic Acids and Esters:

Both carboxylic acids and esters can be reduced to Primary alcohols with $LiAlH_4$.





Carboxylic acids cannot be reduced with H_2/Ni or $Na + C_2H_5 - OH$.

Scanned with CamScanner

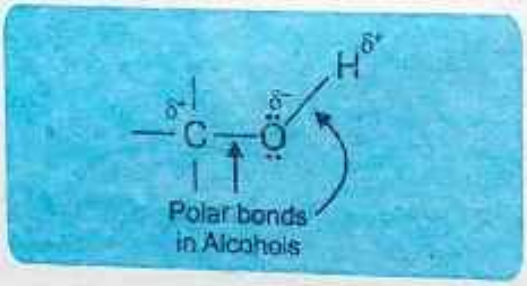
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

18. 1.6 Reactivity:

Alcohols are reactive compounds. They readily react with polar or ionic reagents. This reactivity can be attributed to:

i. Polarity of C – O and O – H bonds since oxygen is highly electronegative.

ii. The oxygen atom of alcohols has two unshared pairs of electrons and hence is an electron rich centre.



Generally, the reactions of alcohols $\left(-\overset{|}{\underset{|}{C}}-\ddot{O}-H\right)$ involve the fission of either the O – H bond or the C – O bond. Cleavages of either of the two bonds may involve a substitution reaction or an elimination reaction.

18. 1.7 Reactions of Alcohols:

18.1.7.1 Reaction with Halogen acids (HX):

Alcohols react with halogen acids (HX) to form the corresponding alkyl halides.

$$\underset{\text{Alcohol}}{R-OH} + HX \longrightarrow \underset{\text{Alkyl halide}}{R-X} + H_2O$$

$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} + HBr \longrightarrow \underset{\text{Ethyl bromide}}{CH_3-CH_2-Br} + H_2O$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The order of reactivity of different hydrogen halides with a particular alcohol is:

$$HI > HBr > HCl$$

HCl reacts only in the presence of a catalyst (anhydrous $ZnCl_2$), while HBr and HI require no catalyst. The order of reactivity of various alcohols with a particular hydrogen halide is:

Tertiary alcohol > Secondary alcohol> Primary alcohol.

Lucas Test: This test is used to distinguish between primary, secondary and tertiary alcohols. In this test alcohols are treated with a solution of HCl and $ZnCl_2$ (Lucas reagent) to form alkyl halides (R – X), $ZnCl_2$ acts as a catalyst.

$$\underset{\text{Alcohol}}{R-OH} + HCl \xrightarrow{ZnCl_2} \underset{\text{Alkyl halides}}{R-Cl} + H_2O$$

The three types of alcohols undergo this reaction at different rates. Tertiary alcohols react with Lucas reagent immediately. Secondary alcohols react some what slower. Primary alcohols react even more slowly.

18.1.7.2 *Reaction with thionyl Chloride ($SOCl_2$) and Phosphorous Trihalides (PX_3):*

Alcohols react with thionyl chloride ($SOCl_2$) to form alkyl chlorides.

$$\underset{\text{Ethyl Alcohol}}{CH_3CH_2-OH} + SOCl_2 \longrightarrow \underset{\text{Ethyl Chloride}}{CH_3-CH_2-Cl} + SO_2 + HCl$$

Phosphorous Trihalides (PX_3) also form alkyl halides with alcohols.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$3CH_3-CH_2-OH + PBr_3 \longrightarrow 3CH_3-CH_2-Br + H_3PO_3$$

Ethyl alcohol — Ethyl bromide

$$3CH_3-OH + PI_3 \longrightarrow 3CH_3-I + H_3PO_3$$

Methyl alcohol — Methyl iodide

18.1.7.3 Dehydration:

Alcohols, when treated with concentrated sulphuric acid at 170°C undergo dehydration to form alkenes. In case of ethyl alcohol, ethylene is formed.

$$CH_3-CH_2-OH \xrightarrow[170^\circ C]{Conc.\ H_2SO_4} CH_2=CH_2 + H_2O$$

Ethyl alchol — Ethylene

The order of rate of dehydration of different alcohols is tertiary alcohols> secondary alcohols> Primary alcohols.

18.1.7.4 Reaction With Carboxylic Acids (Esterification):

Alcohols react with carboxylic acids to form esters. Concentrated H_2SO_4 is used as catalyst.

$$CH_3-CH_2O\boxed{H+HO}-\overset{\overset{O}{\|}}{C}-CH_3 \underset{}{\overset{Conc.\ H_2SO_4}{\rightleftharpoons}} CH_3CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O$$

Ethyl alcohol — Acetic acid — Ethyl acetate

The reaction is reversible. The equilibrium can be shifted in the forward direction by removing water as soon as it is formed.

Scanned with CamScanner

18.1.7.5 Oxidation:

Using strong oxidizing conditions such as "$Na_2Cr_2O_7 + H_2SO_4$" or "$KMnO_4 + H_2SO_4$", alcohols can be oxidized to carbonyl compounds, and finally to acids.

Primary alcohols are first oxidized to aldehydes and then to acids.

$$CH_3CH_2OH \xrightarrow[Na_2Cr_2O_7/H^+]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[Na_2Cr_2O_7/H^+]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Secondary alcohols are first oxidized to corresponding ketones, whose further oxidation to carboxylic acids needs even more drastic conditions.

$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[Na_2Cr_2O_7/H^+]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$$

Isopropyl alcohol — Acetone

Tertiary alcohols are stable to oxidation under normal conditions.

$$CH_3-\underset{\underset{CH_3}{|}}{\underset{OH}{\underset{|}{C}}}-CH_3 \xrightarrow[Na_2Cr_2O_7/H^+]{[O]} \text{No Reaction}$$

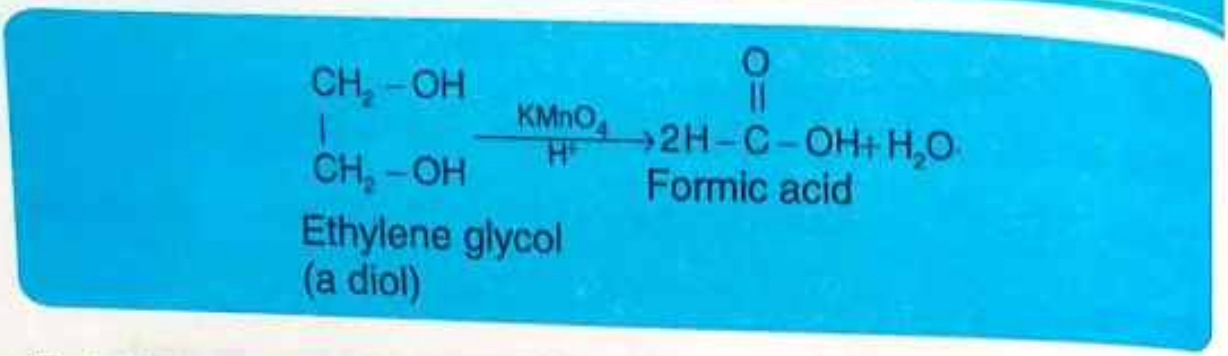
Ter-Butyl alchol

18.1.7.6 Cleavage of 1, 2 diols (Glycols):

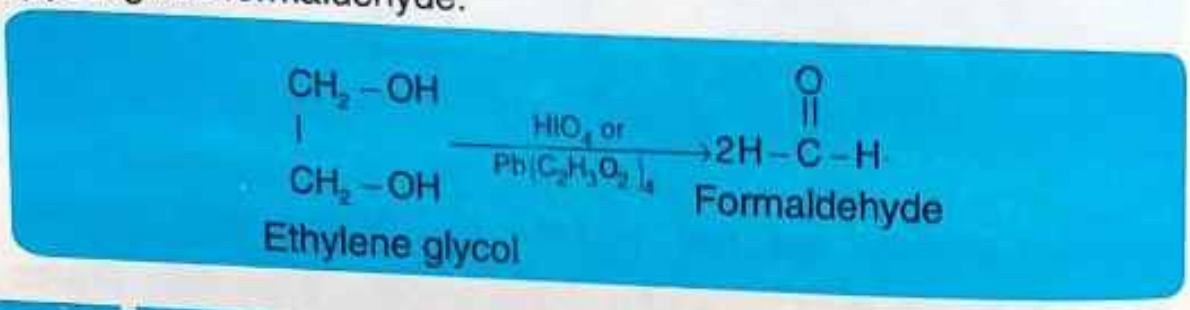
1, 2 –diols (glycols), for example, ethylene glycol when treated with acidic $KMnO_4$ or $K_2Cr_2O_7$, results in the formation of formic acid by cleavage of C – C bond.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



But when treated with periodic acid or lead tetra acetate, ethylene glycol gives formaldehyde.



18.1.8 The Sulphur Analogues (Thiols, RSH):

Both oxygen and sulphur belong to the same group VI of the periodic table. Thus, there are sulphur analogies of alcohols and ethers.

R – OH	R – SH	R – O – R	R – S – R
Alcohol	Thiol	Ether	Thioether

The Sulphur analogues of alcohols are called Thiols or alkyl hydrogen sulphides or Mercaptans. The functional group of thiols is –SH. It is called sulphydryl or Marcapto or thiol group. These compounds react with mercuric ions to form insoluble salts, and hence the name Mercaptans (Latin, mercurium captans = mercury catching). Methanthiol (CH_3SH) is a gas. Ethanthiol (C_2H_5SH) and higher members are colourless, volatile liquids at STP. Lower members have strong repulsive odours. For example, methanthiol and ethanthiol are added to natural gas in minute

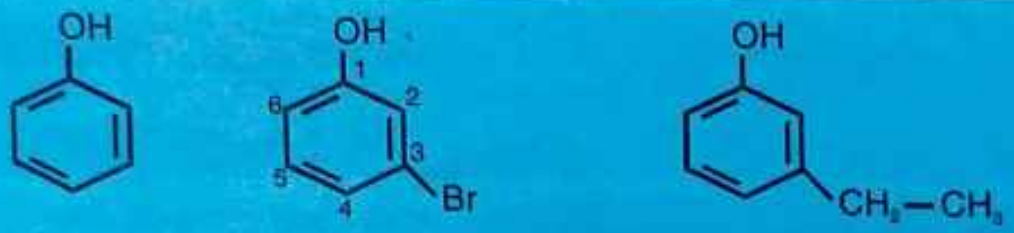
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

amounts to make gas leakage detectable by smell. Thiols have lower boiling points than the corresponding alcohols, due to lack of hydrogen bonding. They are insoluble in water but soluble in ethanol and ether.

18.2 Phenols

Introduction: Phenols are organic compounds in which –OH group is attached directly to an aromatic ring. Just like alcohols, they may also be monohydric, dihydric or polyhydric, depending upon the number of –OH groups attached per molecule. The word "phenol" is also used as the name of a specific compound "hydroxyl benzene". Some examples are.

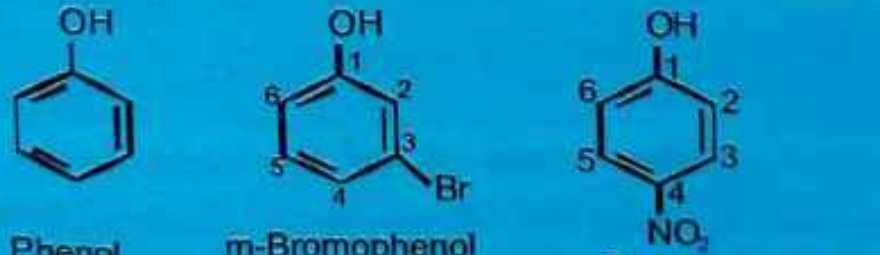


Phenol | m - Bromophenol | m - Ethylphenol

18.2.1 Nomenclature:

Phenols are usually named as derivatives of the parent phenol (C_6H_5OH).

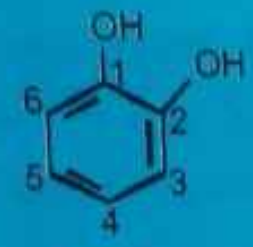
Examples are:



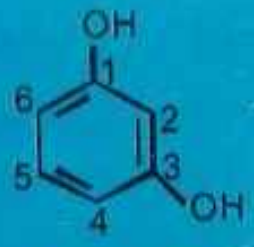
Phenol | m-Bromophenol (3-Bromophenol) | p - Nitrophenol (4 - Nitrophenol)

Scanned with CamScanner

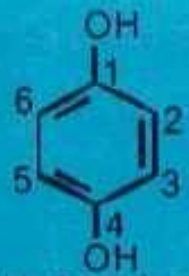
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



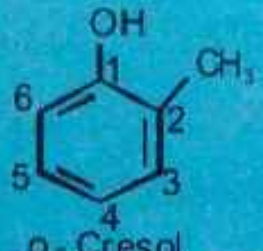
Catechol
(1,2-dihydroxy benzene)



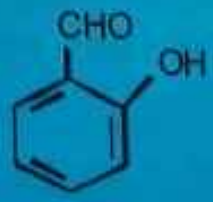
Resoroinol
(1,3-dihydroxy benzene)



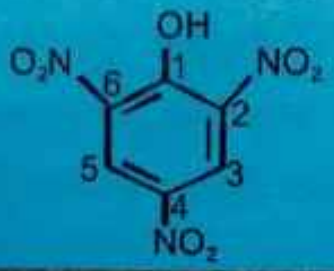
Hydroquinone
(1,4-dihydroxy benzene)



o - Cresol
(o - Methyl phenol)



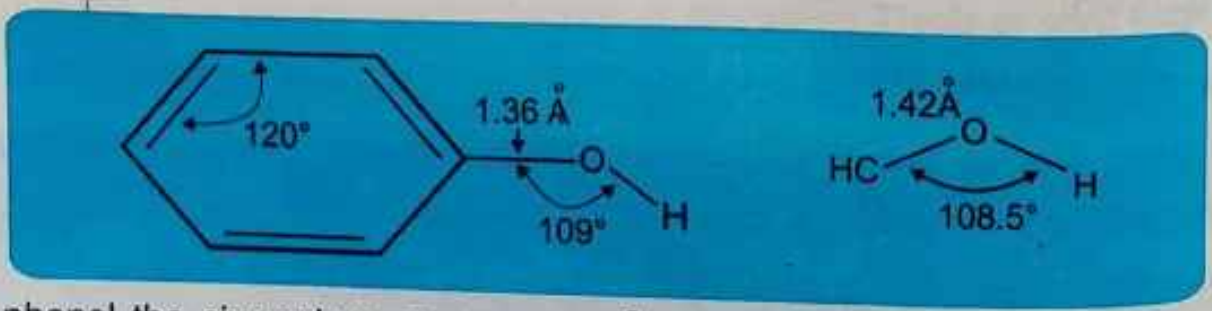
Salicylaldehyde
(o-Hydroxybenzaldehyde)



Picric acid
(2, 4, 6-Trinitrophenol)

18. 2.2 Structure of phenol:

In phenol molecule hydroxyl group (–OH) is attached to a benzene ring. The molecule is planar, with a C–O–H bond angle of 109°, almost the same as tetrahedral angle and not much different from the 108.5° C–O–H angle of methanol.



In phenol the six carbon atoms are sp^2 hybridized forming a hexagonal ring with internal angles of 120°. Since the bonds formed by sp^2 hybridized carbon, are shorter than those formed by sp^3 hybridized carbon, therefore

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

the C–O bond length is slightly less than the C–O bond length in methanol.

18. 2.3 Physcisl Properties:

1. Phenols are colourless liquids or low melting crystalline solids at room temperature and pressure.
2. They have a characteristic odour.
3. The vapours of phenol itself is highly toxic.
4. The boiling points of phenols are slightly higher than the aliphatic alcohols of comparable molecular weights, due to the presence of stronger hydrogen bonding in phenols than in alcohols.
5. Due to stronger hydrogen bonding, phenols are more soluble in water than alcohols of comparable molecular mass. Above 65°C both phenols and water are miscible in all proportions.
6. The liquid phenol, containing 5% of water is known as carbolic acid and is used as disinfectant and germicide.

18. 2.4 Acidity of Phenols:

Phenols are much more acidic than alcohols but are less acidic than carboxylic acids or even water and carbonic acid. This is clear from the pKa values of these compounds.

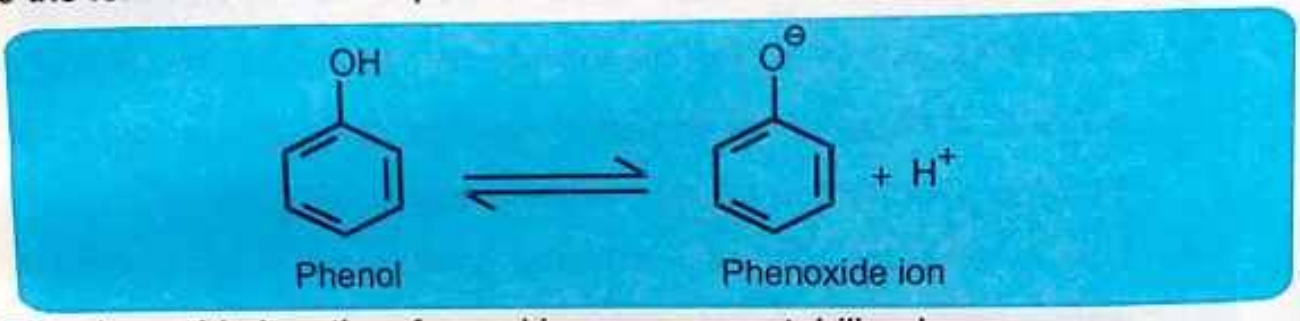
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

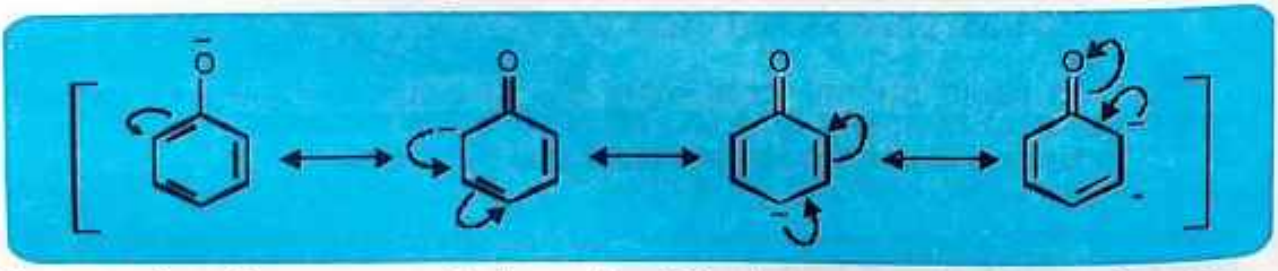
Table 18.2 ka & pka values of some compounds.

Compound	Formula	ka (approx)	pka
Phenol	Ar – OH	10^{-10}	10
Alcohols	R – OH	$10^{-16} - 10^{-18}$	16 – 18
Carboxylic acids	R – COOH	10^{-5}	5
Water	H – OH	10^{-7}	7

The acidic nature of phenols, as compared to alcohols, can be attributed to the formation of stable phenoxide ions after loss of proton.

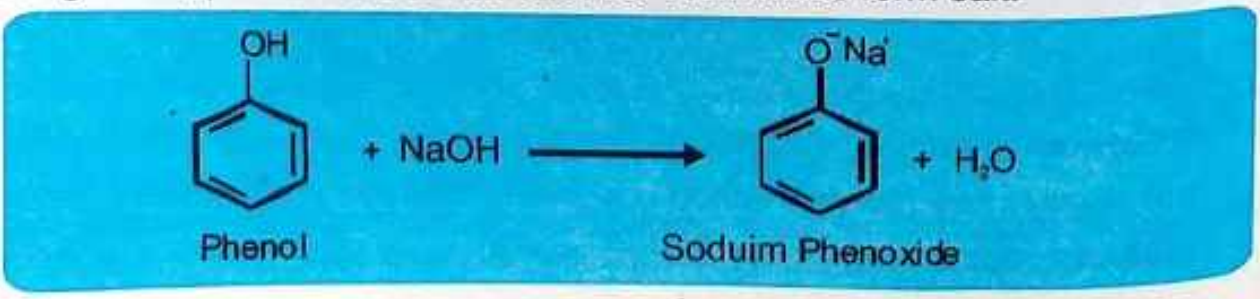


The phenoxide ion, thus formed is resonance stabilized.



The negative charge spreads throughout the benzene ring and is thereby dispersed. This delocalization of the charge accounts for the stability of the phenoxide ion.

Being acidic, phenol reacts with NaOH or Na metal to form salt.



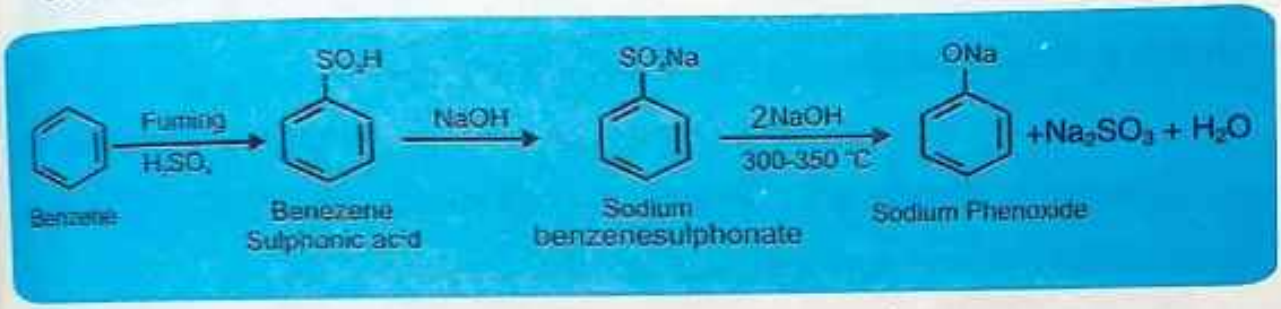
Scanned with CamScanner

18. 2.5 Preparation of Phenols:

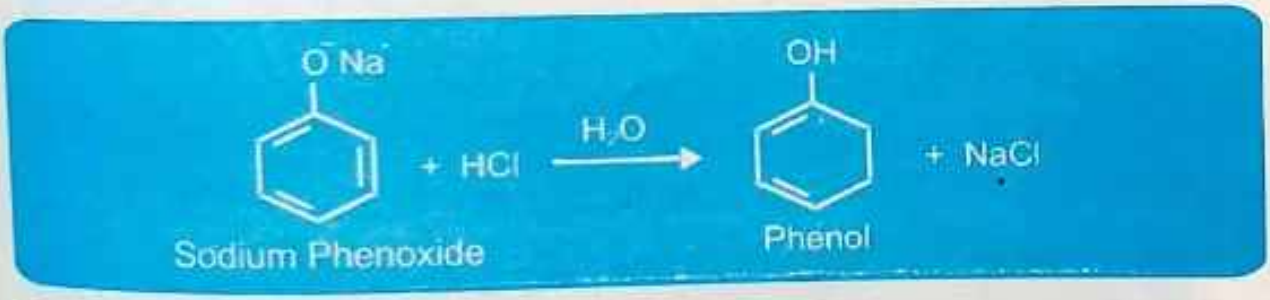
Phenols can be prepared by the following methods.

18.2.5.1 From Benzene Sulphonic Acid:

This method involves the fusion of sodium–benzene sulphonate with solid NaOH at 300 – 350°C.

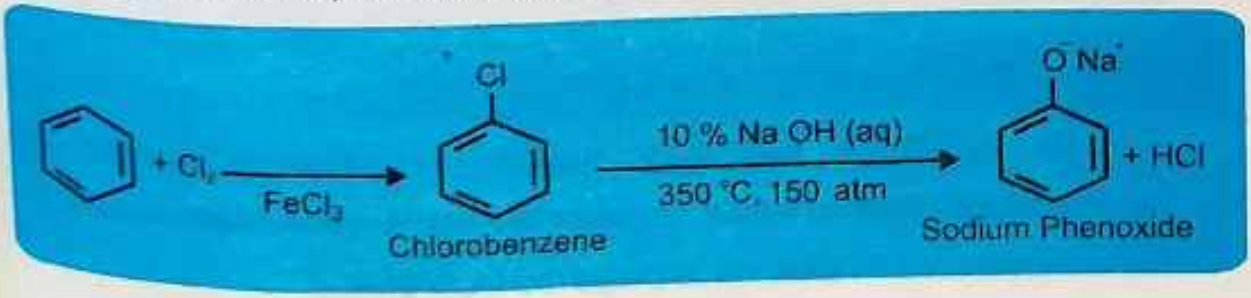


The resultant sodium phenoxide is then treated with dilute HCℓ to form phenol.



18.2.5.2 From Chlorobenzene:(Dow Process):

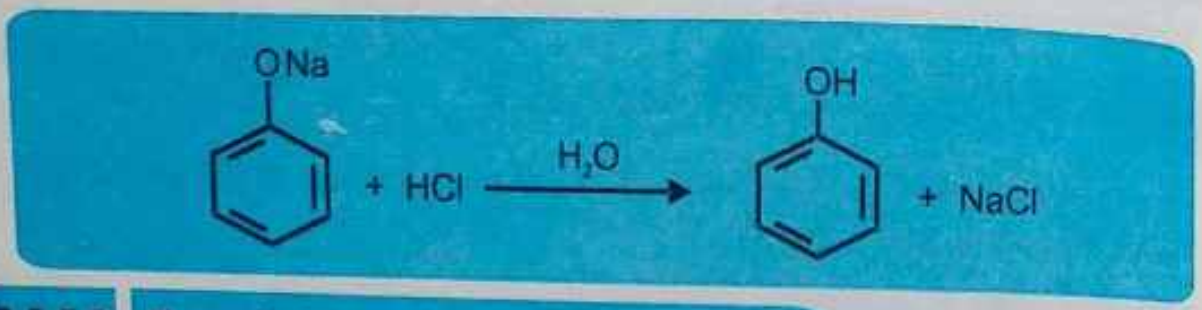
In this method, chlorobenzene is hydrolysed with aqueous NaOHat high temperature and pressure. This process was developed by Dow Chemical Company of USA in 1928.



Scanned with CamScanner

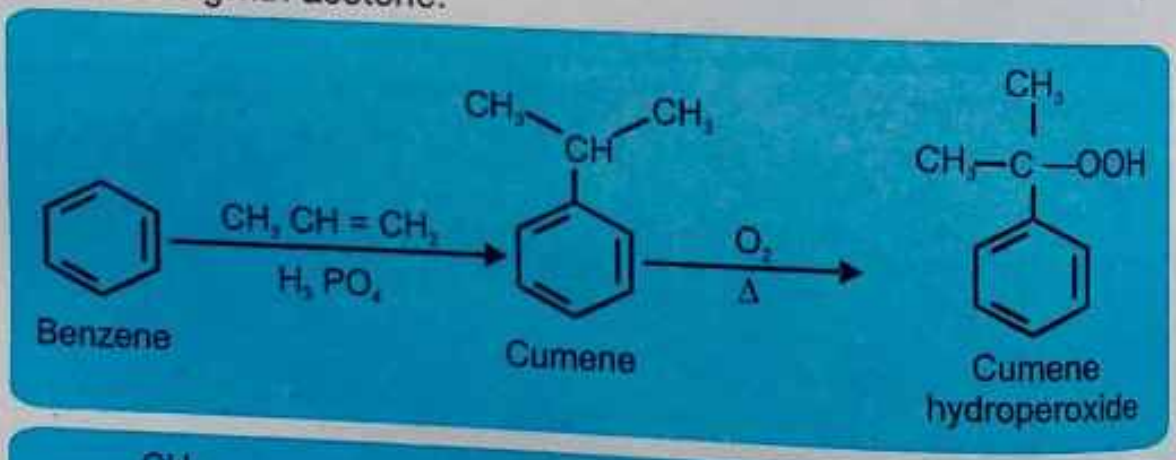
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

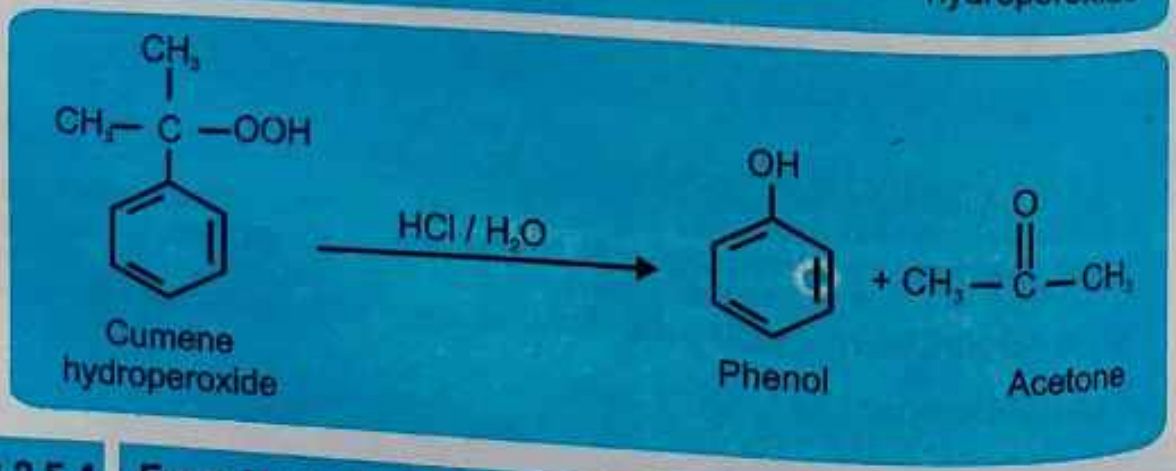
The resultant sodium phenoxide is then treated with dilute HCl to form phenol.



18.2.5.3 From Acidic oxidation of Cumene:

This method involves air oxidation of cumene (isopropyl benzene) to cumene hydroperoxide, which on treatment with dilute HCl forms phenol alongwith acetone.



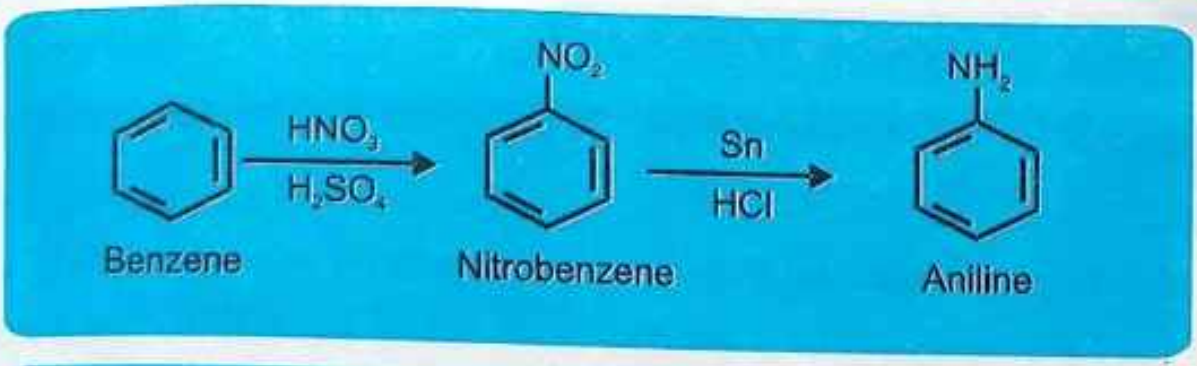


18.2.5.4 From Hydrolysis of Diazonium Salts:

This is a simple laboratory method in which a solution of benzenediazonium chloride is warmed on a water bath at 50°C. Benzenediazonium chloride is prepared from aniline.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)





Phenol is recovered by steam distillation and extracted with diethyl ether.

18. 2.6 Reactivity of Phenol:

Generally phenols exhibit two types of reactions. (1) reactions due to hydroxyl group and (2) reactions due to the aromatic ring.

In the first type of reactions, usually the O – H bond is broken to form salts, ethers, esters etc. In the second type of reactions, the benzene ring of phenol undergoes electrophilic substitution reactions which are characteristic of most of the aromatic compounds.

The presence of hydroxyl group on the benzene ring in phenol increases electron density of the ring at ortho and para positions by giving its electron pair to the ring and hence increases the reactivity of the ring relative to benzene itself, for electrophillic substitution reactions.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

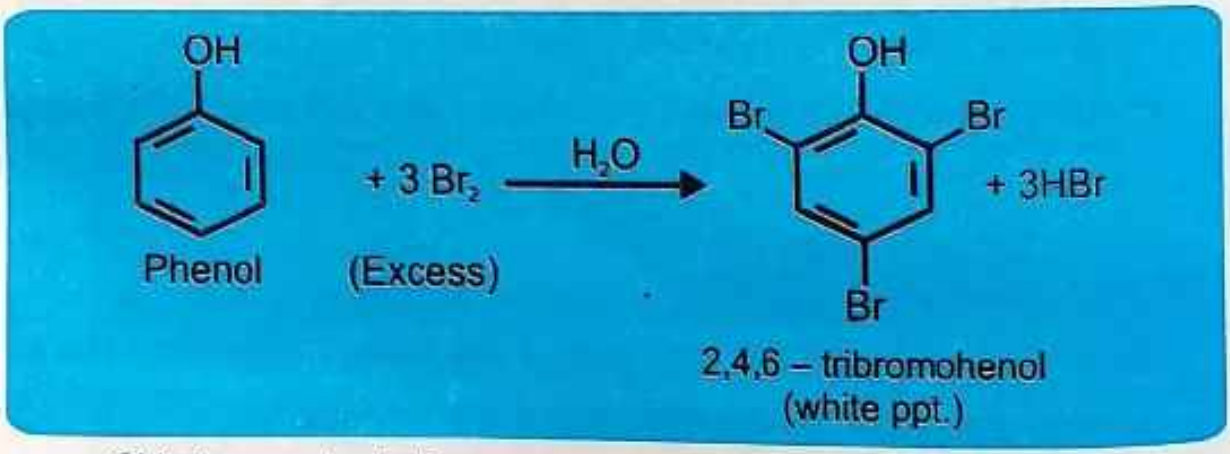
18. 2.7 Reactions of Phenols:

18.2.7.1 Electrophilic Aromatic Substitutions: (Reactions due to Benzene ring)

In these reactions an electrophile is introduced into the aromatic ring and the hydroxyl group remains intact. Some electrophilic substitution reactions are given below.

i. ***Halogenations:***

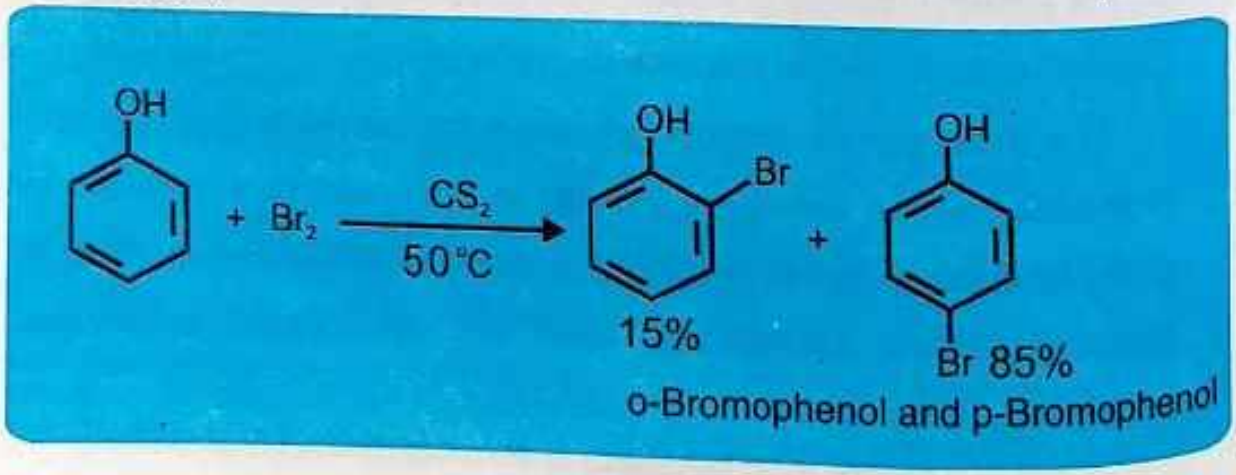
Phenol reacts with bromine water (aqueous bromine) to give a precipitate of 2,4,6 tribromophenol.



Phenol

2,4,6 – tribromohenol
(white ppt.)

Chlorine reacts in the same way. In the presence of a non–polar solvent like CCl_4 or CS_2, a mixture of ortho and para–bromophenols is formed.



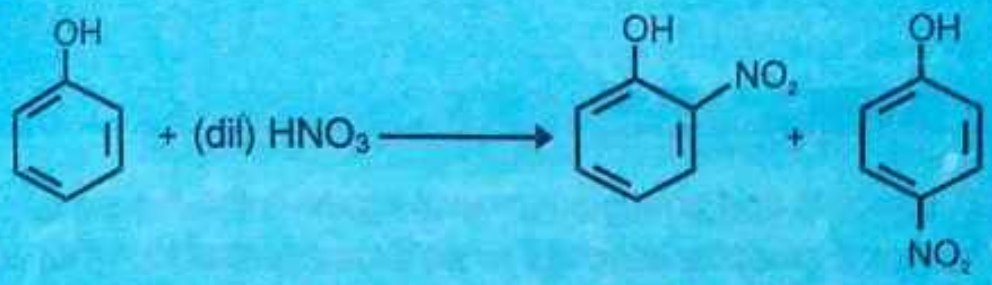
o-Bromophenol and p-Bromophenol

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

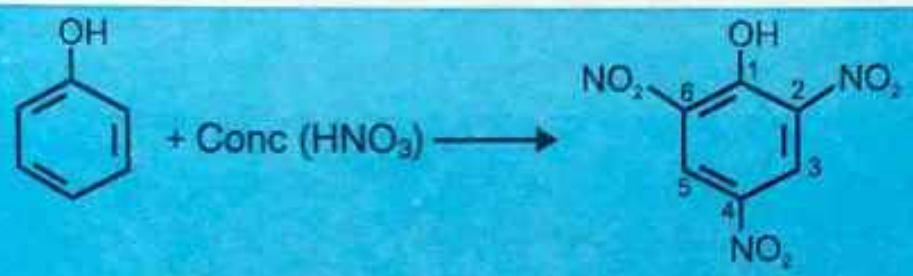
ii. ***Nitration:***

With dilute HNO_3, phenol reacts to form ortho and para nitrophenol.



o- and p- Nitrophenol

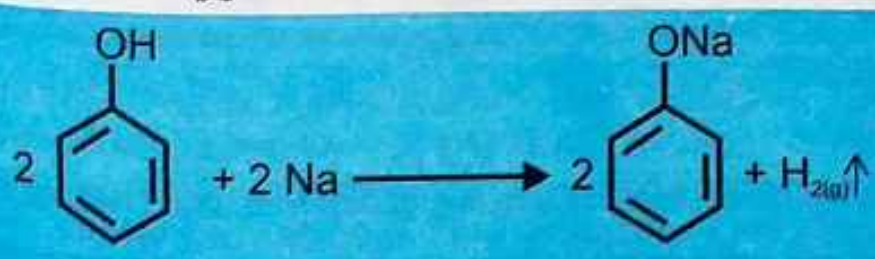
With concentrated HNO_3, picric acid (2,4,6 –trinitrophenol) is formed.



Picric acid
(2,4,6 –Trinitrophenol)

18.2.7.2 Reaction with Sodium Metal:

Phenol, being acidic in nature, reacts with sodium metal to form salt with the release of H_2 gas



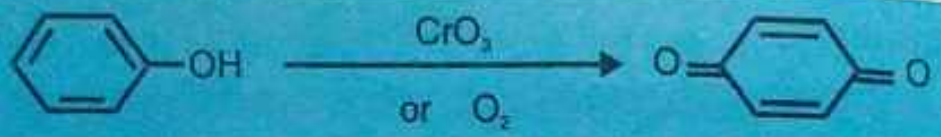
Phenol Soduim Phenoxide

18.2.7.3 Oxidation:

Phenol undergoes oxidation with air or chromic acid to form p–benzoquinone.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

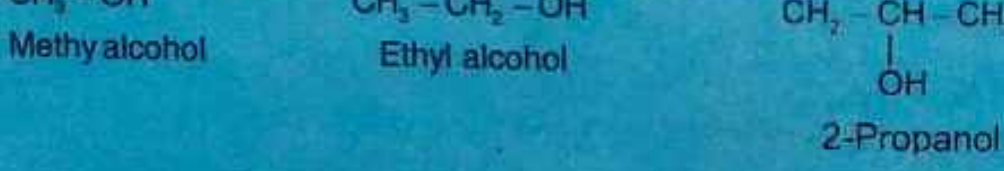


p – Benzoquinone

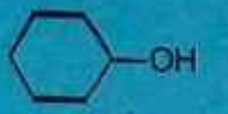
18.2.8 Difference Between Alcohol and Phenol:

In both alcohols and phenols hydroxyl group is the functional group. In phenols hydroxyl group is attached to an aromatic carbon while in alcohol the hydroxyl group is attached to carbon atom other than aromatic carbon.

For Example,



2-Propanol



Cyclopentanol

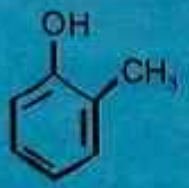


Cyclohexanol

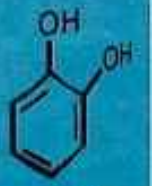
are alcohols; and



Phenol



Cresol

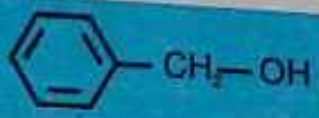


Catechol

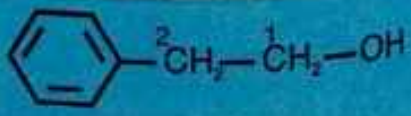
are phenols

Compounds which contain a hydroxyl group in a side chain attached to an aromatic ring are not phenols. They are called aromatic alcohols.

For example:



Benzyl alcohol
(an alcohol)



2 – Phenyl ethanol)
(an alcohol)

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Society, Technology and Science

The common home disinfectant is chlorine bleach (a 5% solution of sodium hypochlorite), which is effective against most common pathogens, such as tuberculosis , hepatitis B and C, fungi etc.

The negative effect of disinfectant is that it is caustic to the skin, lungs, and eyes (especially at higher concentrations), it degrades in the presence of organic substances, it has a strong odor and extreme caution must be taken not to combine it with ammonia or any acid (such as vinegar), as this can cause noxious gases to be formed.

To use chlorine bleach effectively, the surface of item to be disinfected must be clean. In the bathroom special caution must be taken to wipe up urine first, before applying chlorine, to avoid reaction with the ammonia in urine, causing toxic gaseous by-products. Extreme caution must be taken to avoid contact with eyes and mucous membranes. Protective goggles and good ventilation are mandatory when applying concentrated bleach.

All disinfectants kill bacteria (called bactericidal). Some also kill fungi (fungicidal), bacterial spores (sporicidal) and/or viruses (virucidal).

The term biocide is a broad term for a substance that kills, inactivates or otherwise controls living organisms. It includes antiseptics and disinfectants, which combat micro-organisms, and also includes pesticides.

Antiseptics are antimicrobial substances that are applied to living tissue/ skin to reduce the possibility of infection, sepsis, or putrefaction. Antiseptics are generally distinguished from antibiotics by the latter's ability to be transported through the lymphatic system to destroy bacteria within the body, and from disinfectants, which destroy microorganisms found on non-living objects.

The first person to demonstrate ether's use as anesthetic was Dr. Morton in 1846.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

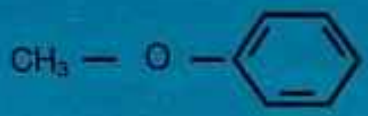
18.3 ETHERS:

Introduction:

Ethers are a class of compounds in which the oxygen atom is linked to two alkyl groups or two aryl groups or one alkyl and one aryl group. They can be represented by the general formula R – O – R′ where R and R′ may be the same or different. Thus the functional group of ethers is C – O – C. Examples of ethers are:

$CH_3 - O - CH_3$, Dimethyl ether (Methyl ether)

$CH_3 - CH_2 - O - CH_2 - CH_3$ Diethyl ether (Ethyl ether)



Methyl Phenyl ether

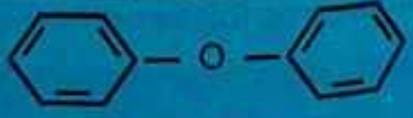
18. 3.1 Nomenclature:

(A) Common System:

The two alkyl or aryl groups that are attached to the oxygen atom are named in alphabetical order and the word ether is added. If the two groups are the same, the prefix "di" is used.

For example:

$CH_3 - CH_2 - O - CH_2 - CH_3$ Diethyl ether



Diphenyl ether or (Phenyl ether)

$CH_3 - O - C_2H_5$ Ethyl methyl ether

$CH_3 - O - C_6H_5$ Methyl phenyl ether

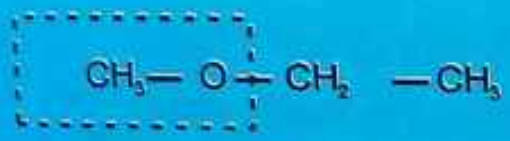
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

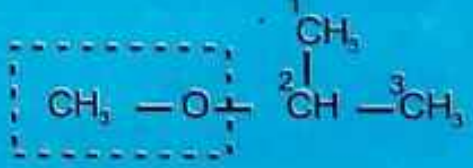
(B) IUPAC System:

In this system, ethers are generally named as alkoxy derivatives of hydrocarbons. The larger alkyl group is taken for parent name and the smaller alkyl group along with oxygen atom is named as alkoxy before the parent name.

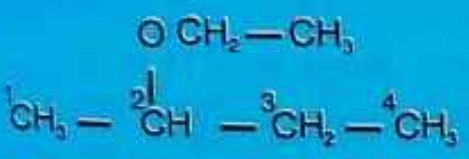
For example:



Methoxyethane



2-Methoxy propane



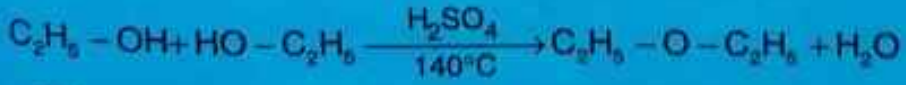
2-Ethyoxy butane

18.3.2 Preparation:

Ethers can be prepared by the following methods.

1. ***Dehydration of alcohols*:**

Symmetrical ethers (ethers with identical groups) are prepared by heating an excess of alcohol with concentrated H_2SO_4 at 140°C.



Ethanol — Diethylether

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The reaction conditions (Temp. = 140°C) must be well controlled otherwise at temperature higher than this the formation of alkenes is favoured.

2. *Williamson's Synthesis:*

In this methods, sodium alkoxide is treated with an alkyl halide.

$$ROH + Na \rightarrow RONa + H_2$$

Soduim alkoxide

$$CH_3 - O^-Na^+ + C_2H_5 - Br \rightarrow CH_3 - O - C_2H_5 + NaBr$$

Sodium methoxide Bromoethane Ethyl methylether

18. 3.3 Physical Properties:

1. Dimethyl ether and ethyl methyl ether are gases at STP, while others are colourless volatile liquids with pleasant odours.
2. Ethers are highly inflammable.
3. They have much lower boiling points than those of alcohols of comparable molecular weights.
4. Low molecular weight ethers are soluble in water as they form hydrogen bonding with water.
5. Ethers are generally less denser than water.
6. They are readily soluble in organic solvents.

18. 3.4 Chemical Reactivity:

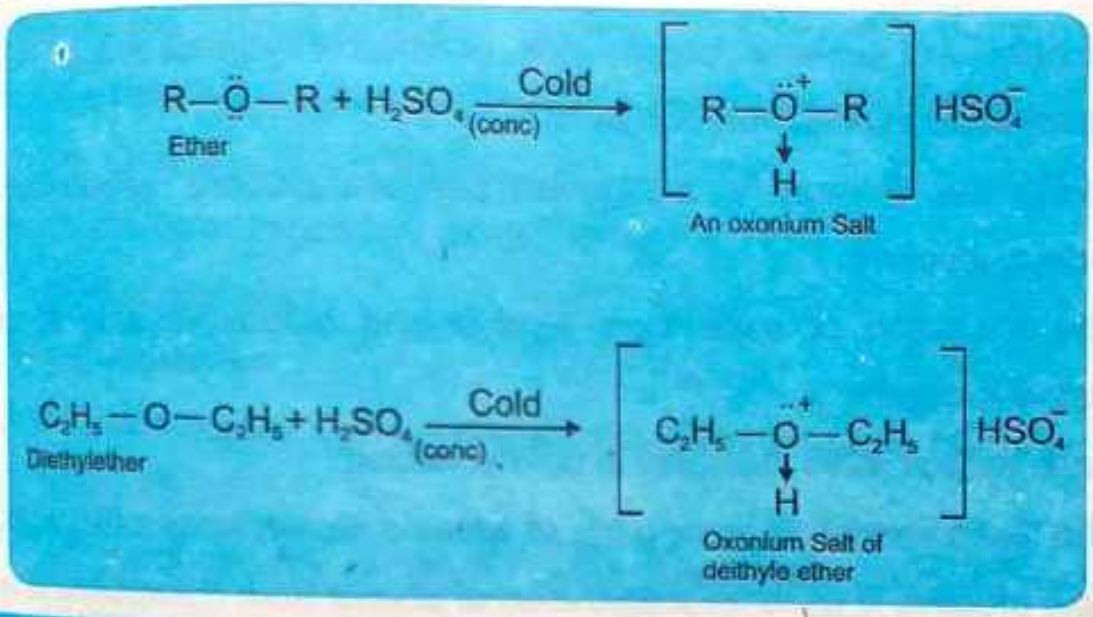
Ethers are quite stable compounds. They do not react with bases, active metals, oxidising agents and reducing agents. They are also stable to dilute acids. However, they form oxonium salts with strong concentrated acids.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

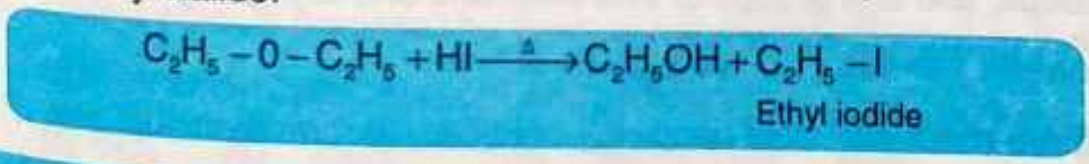
1. Formation of Oxonium Salts:

Ethers react with cold concentrated HCl or H_2SO_4 to form oxonium salts. Ethers donate a pair of electrons to hydrogen ion to form these salts.



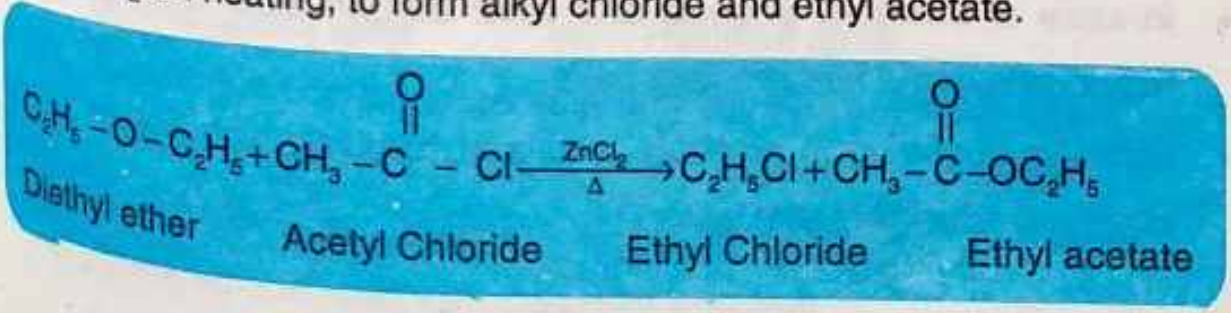
2. Reaction with halogen acids (HX):

Ethers react with hot concentrated HI or HBr to form an alcohol and alkyl halide.



3. Reaction with Acetyl Chloride:

Ethers react with acetyl chloride in the presence of anhydrous $ZnCl_2$, on heating, to form alkyl chloride and ethyl acetate.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Key Points:

- Alcohols are aliphatic compounds, in which a hydroxyl group (–OH) is attached to aliphatic carbon atom.
- Lucas test is used to distinguish between primary, secondary and tertiary alcohols.
- The formation of ester from alcohol and carboxylic acid is called 'esterification'.
- Each carbon atom in phenol is sp^2 hybridized.
- The liquid phenol containing 5% of water is known as carbolic acid.
- Dow process is used for preparation of phenol from chlorobenzene and aquous NaOH at high pressure and temperature.
- Ethers are class of compounds in which, with oxygen atom two alkyl groups, two aryl groups or one alkyl and one aryl group are attached.
- General formula of ether is R–O–R.
- Ethers react with cold conc.HCl or H_2SO_4 to form oxomium salt.
- In Williamson's synthesis, sodium alkoxide is treated with an alkyl halide to produce ether.
- In case of alcohols, phenols and ether oxygen atom undergoes sp^3 hybridization and has two lone pairs.
- Hydrogen bonding in alcohols results in relatively high boiling points and good miscibility with water.

Scanned with CamScanner

Exercise

Q1. Choose the correct option.

1. The reaction of alcohol with sodium produces
   (a) Ethane (b) Ethene (c) Alkoxide (d) Aldehyde
2. Oxidation of secondary alcohol gives
   (a) Organic acid (b) Ether
   (b) Aldehyde (d) Ketone
3. The compound 'x' when heated with dry silver oxide forms an ether identify 'x'
   (a) Alcohol (b) Phenol (c) Alkyl halide (d) Ether
4. Phenol on hydrogenation with H_2 in presence of Ni catalyst gives
   (a) Benzene (b) Toluene
   (c) Cyclohexanol (d) Aldehyde
5. Diethyl ether is prepared by passing vapours of ethanol over a catalyst under high pressure and temperature. The catalyst is
   (a) SiO_2 (b) CuO (c) Ag_2O (d) Al_2O_3
6. Denatured alcohal is known as
   (a) Absolute alcohal (b) Wood spirit
   (b) Methylated spirit (d) Rectified spirit
7. A compound "x" is formed when the vapours of phenol are passed over red hot zinc dust. The compound "x" is called
   (a) Toluene (b) xylene (c) Benzene (d) Benzol
8. Ethoxyethane react with Con.H_2SO_4 to give
   (a) Oxonium ion (b) Oxoanion
   (c) Alkyl free radical (d) Zwitter ion

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

9. The secondary alcohols undergo nucleophilic substituion reaction by

(a) SN^1 (b) SN^2

(c) Both SN^1 and SN^2 (d) Neither SN^1 and SN^2

10. The appearance of cloudiness in the Lucas test for alcohol is due to formation of:

(a) Alkyle chloride (b) Acid chlorides

(c) Aldehydes (d) Ketones

Q II. Short questions:

1. What is the functional group of alcohols?
2. Indicate some physical properties of alcohol.
3. What is Lucas test?
4. Why phenol is more acidic than alcohols?
5. What is meant by primary, secondary and tertiary alcohols?
6. Why alcohol is easily protonated unlike phenol?
7. Differentiate between alcohol and phenol.
8. Enlist the physical properties of ether.

Q III. Long questions:

1. (a) Describe the method for preparation of diethyl ether from alcohol and sodium methoxide.
   (b) Write two chemical reactions of diethyl ether.
2. (a) What are phenols? Give method of preparation of phenol.
   (b) Discuss the acidic behaviour of phenol.
3. Give detail description of chemical properties of phenol.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

4. Discuss the structure of alcohol.

5. (a) How alcohol can be prepared from Grignard reagents.

(b) Mention the reaction for the formation of following compound from an alcohol.

(a) Ethene
(b) Ethlyacetate
(c) Acetone
(d) Formaldehyde

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

UNIT 19

Carbonyl Compounds I: Aldehydes and Ketones

Learning Outcomes:

After Studying this unit Students will be able to:

- Explain nomenclature and structure of Aldehydes and ketones.
- Discuss the preparation of aldehydes and ketones.
- Describe the reactivity of aldehydes and ketones and their comparison.
- Describe acid and base catalysed nucleophillic addition reactions of aldehydes and ketones.
- Discuss the chemistry of aldehydes and ketones by their reduction to hydrocarbons. Alcohols by using carbon nucleophiles, nitrogen nucleophiles and oxygen nuclcophiles.
- Describe oxidation reactions of aldehydes and ketones.
- Identify aldehydes and ketones in the laboratory tests.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Introduction:

Some important classes of organic compounds like aldehydes, ketones, carboxylic acid, esters, amides, acid halides, acid anhydrides etc contain a functional group called carbonyl group are called carbonyl compounds. Many of these compounds are important commercially and in biological processes. A carbonyl group is a functional group composed of a carbon atom doubly bonded to an oxygen atom.

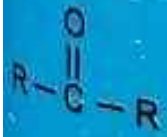


Aldehydes and ketones are two different classes of organic compounds containing a carbonyl group. Aldehydes have at least one hydrogen atom attached to the carbonyl carbon. The other group may be an alkyl group (or H atom in case of formaldehyde). Thus the functional group of aldehyde is



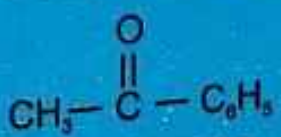
called formyl group.

In ketones the carbonyl carbon atom is connected to two other carbon atoms. The ketone functional group is called keto group and is represented as –CO–. The two groups attached to it may be both alkyl groups (same or different) an alkyl and aryl group or both aryl groups.

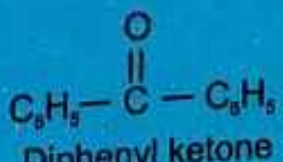




Dimethyl ketone



Acetophenone



Diphenyl ketone

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

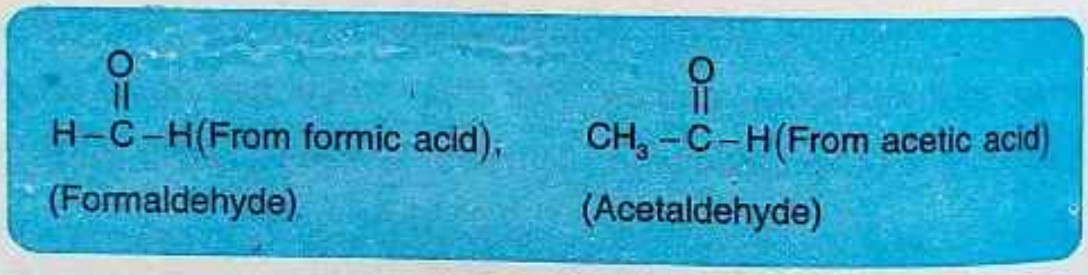
19.1 Nomenclature:

Two types of naming systems are used for naming aldehydes and ketones. Common naming system and IUPAC system.

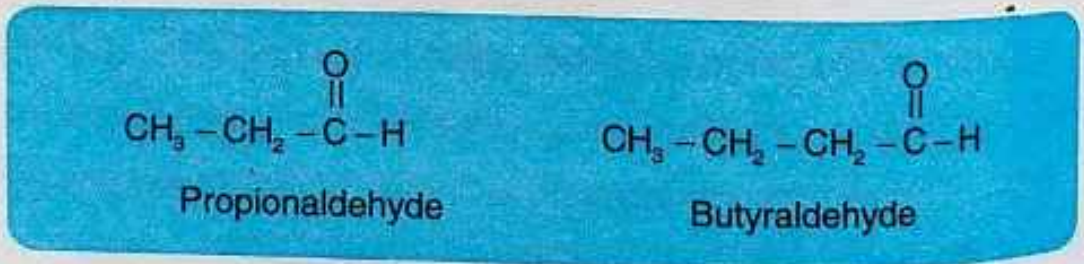
19.1.1 Nomenclature of Aldehydes:

1. Common Naming System:

Common names of Aldehydes are derived from the common names of carboxylic acids containing the same number of carbon atoms. While naming aldehydes in this system, the ending "ic acid" in the common name of corresponding carboxylic acid is replaced by the word "aldehyde".



Similarly

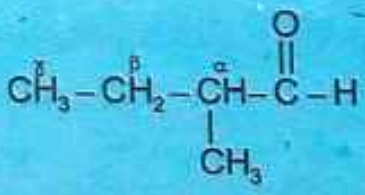




Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The positions of other groups on the chain are indicated by Greek letters ($\alpha, \beta, \gamma, \delta$ etc). Lettering starts from the carbon atom adjacent to formyl group.



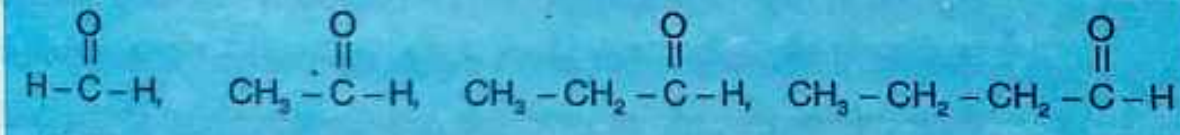
α – Methyl butyraldehyde

2. IUPAC Naming System:

In this system, following rules are used for naming aldehydes.

a. Chain Selection:

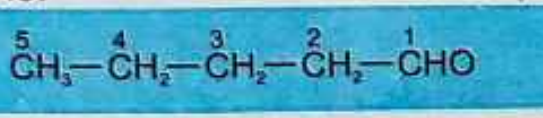
Locate the longest chain of carbon atoms containing formyl group to get the stem name. In IUPAC system, the ending "-e" of the corresponding alkane is replaced by "al".



Methanal Ethanal Propanal Butanal

b. Numbering of the Selected Chain:

Carbon atoms of the selected chain are numbered from the carbon of formyl group (–CHO) because it is always at the terminal position It is not necessary to mention the position of aldehydic group during naming as it always one.

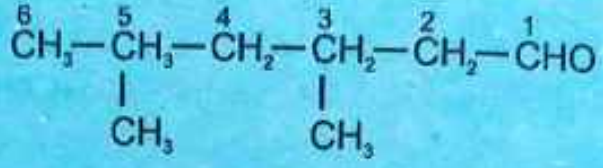


c. Branch Rules:

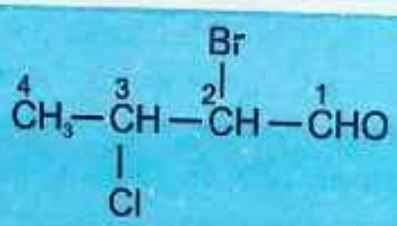
The rules for naming branches are same as in case of alkanes.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



3,5 – Dimethylhexanal

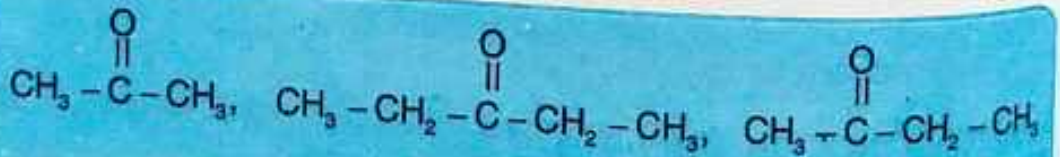


2-Bromo-3-chlorobutanal

19.1.2 Nomenclature of Ketones:

a. Common System

In this system ketones are named by writing first the name for the alkyl groups attached to the carbonyl carbon followed by the word "Ketone". For similar groups prefix "di" is used before their name. In case of different groups attached to the carbonyl carbon, alphabetical order is followed for writing their names.



Dimethyl ketone | Diethyl ketone | Ethyl methyl ketone

If the two alkyl groups attached to carbonyl carbon are the same the ketone is called symmetrical and if different, it is called unsymmetrical ketone.

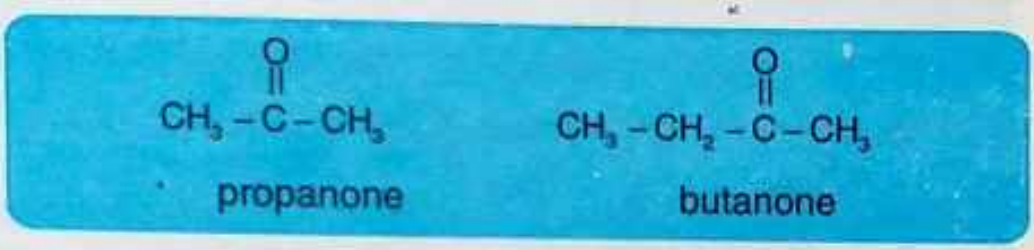
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

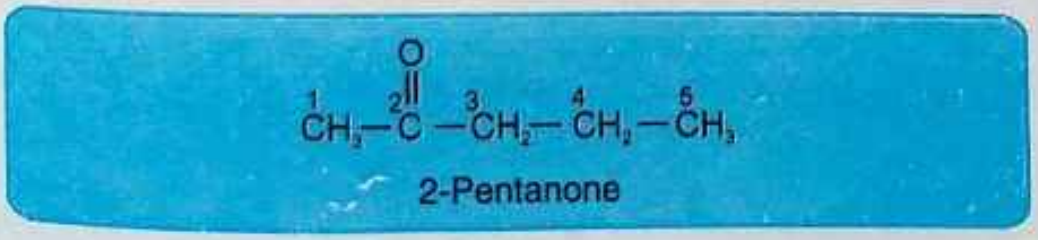
b. IUPAC System:

While naming ketones in IUPAC system following steps are taken

i. **Chain Selection:** Select the longest chain as stem name for ketone, which is then named by replacing the ending "-e" of corresponding alkane by "-one". No numbering is necessary for propanone and butanone.



ii. **Numbering the Chain:** The carbons of the selected chain are numbered to mention the position of the carbonyl carbon before stem name because in ketones carbonyl group may occur at various positions on the carbon chain. Numbering is done from that end at which the carbonyl carbon has the lowest possible number.

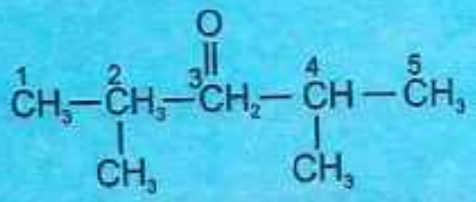


c. Branch Rules:

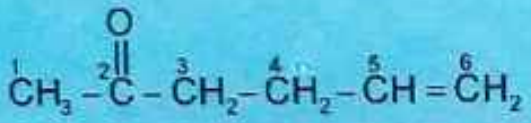
If one or more branches are attached to the selected chain then the same rules are obeyed as mentioned for IUPAC names of alkanes.

Scanned with CamScanner

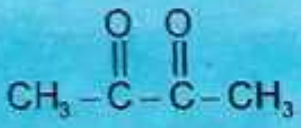
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



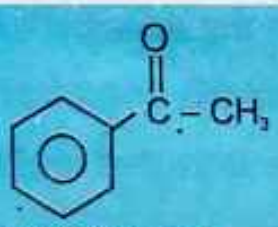
2,4-Dimethylpentan-3-one
(2,4-Dimethyl-3-pentanone)



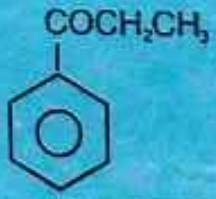
5-Hexen - 2-one



Butan-2, 3-dione



Phenylethanone
(Acetophenone)



Phenyl propanone
(Propiophenone)

19.2 Physical Properties:

1. Lower aldehydes like formaldehyde and acetaldehyde have very sharp pungent odour whereas higher members of aldehydes,

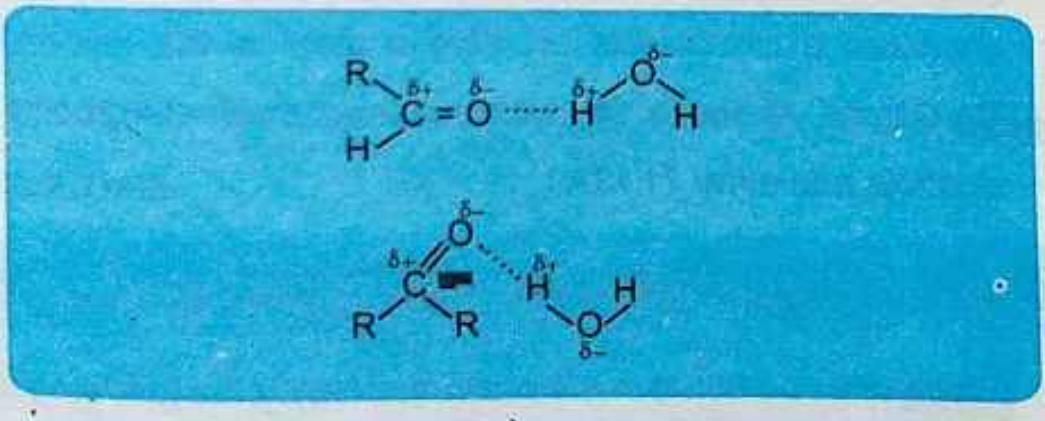
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

aromatic aldehydes as well as most of the ketones have pleasant smell.

2. Formaldehyde is a gas at room temperature while aldehydes are colourless liquids. Acetone, the simplest ketone, is a liquids at room temperature with pleasant odour. All the other members of ketone series are also colourless liquids with characteristic odour.

3. Low molecular weight aldehydes and ketones (up to C_4) are water soluble. Water solubility decreases as the size of the molecules increases. Higher members of aldehydes and ketones (C_5 onward) are usually insoluble in water, while formaldehyde is highly soluble in water. Carbonyl compounds cannot form hydrogen bonds with themselves as there is no hydrogen on the carbonyl oxygen. However, their solubility in water is due to hydrogen bond formation of carbonyl oxygen with water molecules



4. Aldehydes and ketones are polar compounds due to high dipole moment of their C = O bond. As a result they have high boiling points than the corresponding alkanes and non-polar compounds like ethers but lower than alcohols. The boiling point of methanal is −21°C whereas ethanal boils at 21°C, close to room temperature.

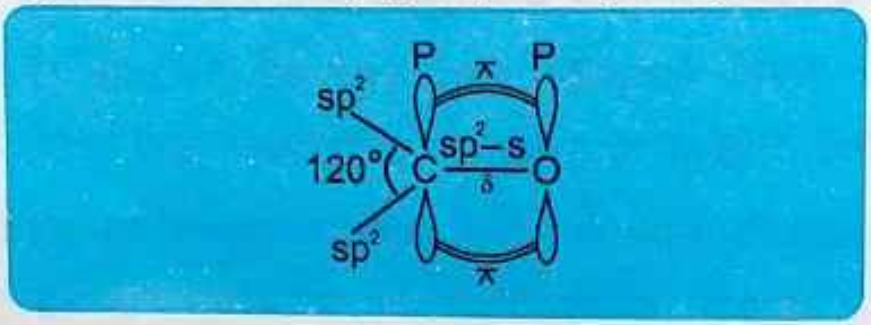
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Acetone has boiling point of 56°C. The boiling point of aldehydes and ketones increase with the increase in the molecular weights.

19.3 Structure:

The carbon and oxygen in the carbonyl group, present in aldehydes and ketones, consists of a sigma bond and a pi bond. Both carbon as well as oxygen of the carbonyl group are sp^2 – hybridized.



The three atoms attached to carbonyl carbon lie in a plane with bond angles of approximately 120°. The pi bond is formed by the overlap of a p–orbital of carbon with p–orbital of oxygen atom. There are two unshared electron pairs on oxygen atom of the carbonyl group. The C = O bond distance is 1.23 Å, shorter than C – O bond distance in alcohols and ether (1.43 Å).

19.4 Preparation of aldehydes and Ketones:

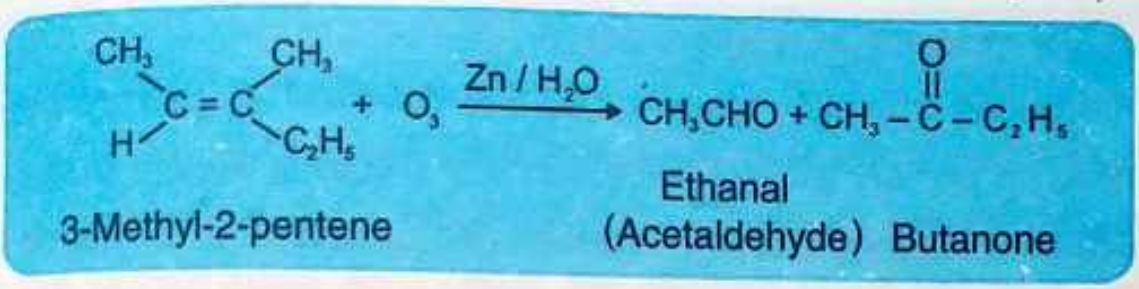
Aldehydes and ketones may be prepared by the following methods.

19.4.1 Ozonolysis of Alkenes:

Ozone, an allotropic form of oxygen, reacts vigorously with alkenes to form an unstable intermediate compound called ozonide. The ozonide is reduced directly to aldehydes and ketones by zinc and water. This reaction is called ozonolysis.

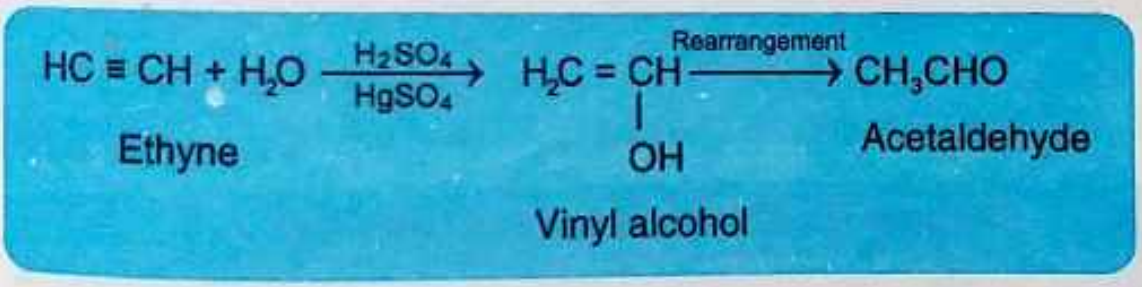
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

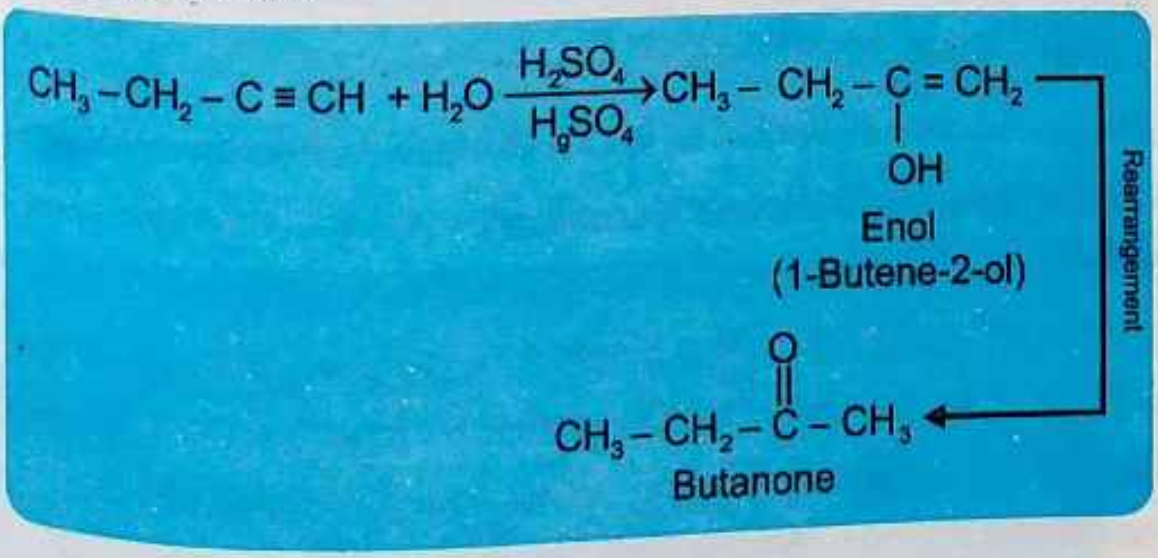


19.4.2 Hydration of Alkynes:

Water adds to alkynes in the presence of mercuric sulphate and sulphuric acid to form an unstable intermediate, unsaturated alcohol (enol). The enol intermediate then undergoes rearrangement to form aldehyde or ketone depending on the starting alkyne used.



In case of unsymmetric alkynes H_2O addition takes place according to Markovinkoff's rule.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

19.4.3 Oxidation of Alcohols:

Aldehydes are also prepared by the oxidation of primary alcohols. When a primary alcohol is treated with oxidizing agents like acidified potassium dichromate or potassium permanganate it is oxidized to an aldehyde.

$$RCH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} R - CHO + H_2O$$

Primary alcohol Aldehyde

While oxidation of secondary alcohols gives ketones

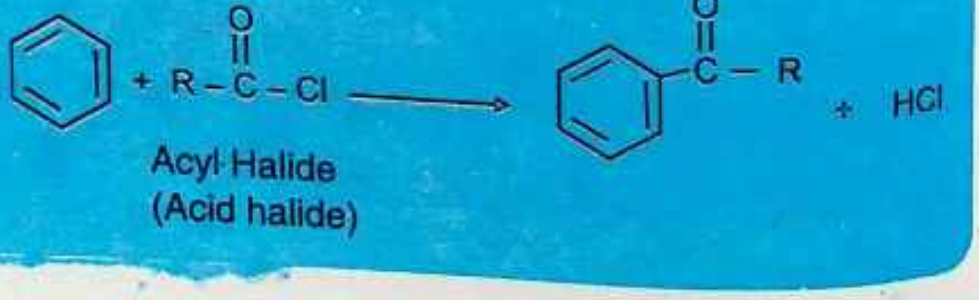
$$R - \underset{\displaystyle R}{\overset{\displaystyle |}{CH}} - OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} R-\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}-R + H_2O$$

Ketone

19.4.4 Friedel –Crafts Acylation of Aromatics:

The introduction of acyl group $(R-\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}-)$ into the aromatic ring (benzene ring) in the presence of acyl halide and anhydrous $AlCl_3$ catalyst is called Friedel –Crafts acylation or simply acylation.

When benzene is treated in the presence of Lewis acid, $AlCl_3$, with acid halide, an aromatic ketone is produced.



Acyl Halide
(Acid halide)

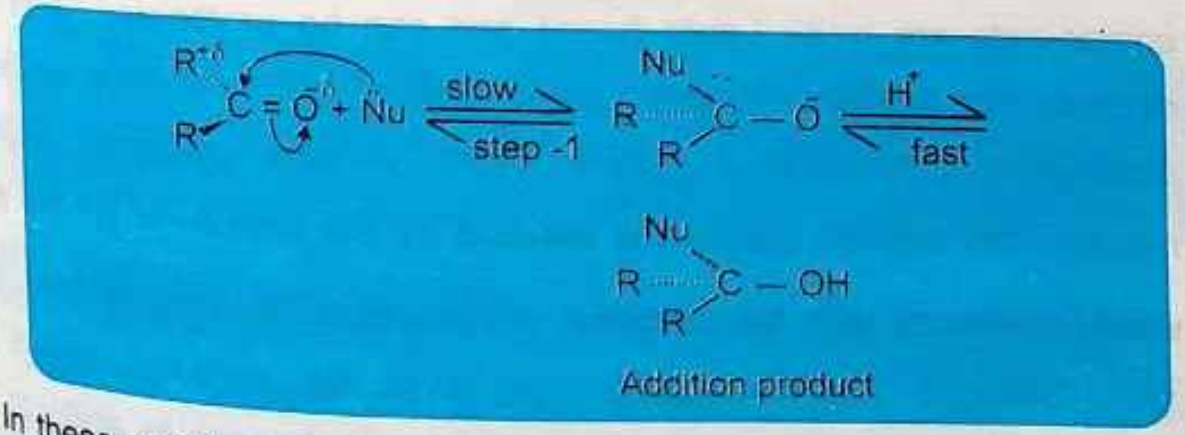
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

19.5 Reactivity of Carbonyl Group:

In carbonyl group ($>C=O$) oxygen is much more electronegative than carbon. Therefore, the π-electrons in $C=O$ bond are strongly attracted by the oxygen atom. As a result, the carbonyl group becomes highly polar with a partial negative charge on the oxygen atom and a partial positive charge on the carbon atom.

As a result of this polarization, most carbonyl reactions involve nucleophillic attacks at the carbonyl carbon often accompanied by addition of a proton to the oxygen. The aldehydes and ketones usually undergo nucleophillic addition reactions as compared to alkenes where C=C are not polarized and hence they usually involve electrophillic addition. The nucleophillic addition in aldehydes and ketones is generally shown as:



In these reactions, the nucleophillic end (negative part) of the reagent combines with the electrophillic carbon of carbonyl group, wherease the electrophillic end (positive part) of the reagent, usually a proton, goes to the oxygen. These reactions are catalysed either by an acid or by a base. The presence of base increase the nucleophillic character of the reagent while the presence of acid increase the electrophillic character of the carbonyl carbon atom.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

19.6 Reactions of Aldehydes and ketones:

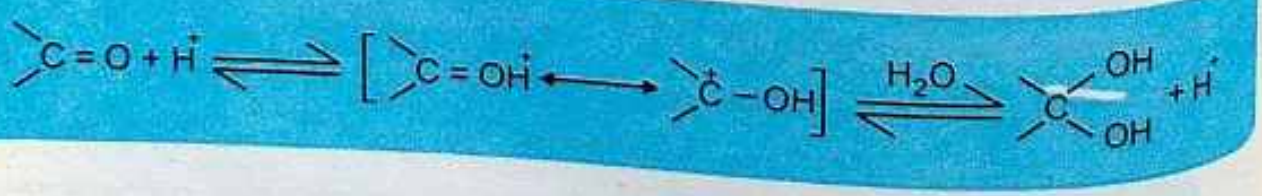
Aldehydes and ketones are very reactive substances mostly undergoing addition reaction across C= O bond. These can also be oxidized as well as reduced. Thus they undergo a very large variety of reactions. Some of their reactions are.

19.6.1 Nucleophilic Addition reactions: (Acid and Base catalyzed)

Aldehydes and ketones mainly undergo nucleophillic additions reactions. These reactions may be either acid catalyzed or base catalyzed.

a. Acid –Catalyzed Addition Reactions:

Because of the unshared electron pair on oxygen atom, carbonyl compounds are weak Lewis bases and can be protonated. Acid can catalyze the addition of weak nucleophiles to carbonyl compounds by protonating the carbonyl oxygen atom. In acid catalyzed addition reaction the addition process is initiated by the proton (H^+) of the acid which combines with the carbonyl oxygen atom to form oxonium ion. This increases the electrophillic nature of the carbonyl carbon by inducing more positive charge on it and thus enhances its ability to be attacked by weak nucleophiles.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The carbonyl carbon, which is trigonal and sp^2-hybridized in the starting aldehyde and ketones becomes tetrahedral and sp^3 – hybridized in the reaction product.

b. Base –Catalysed Addition Reactions:

A base catalyzed nucleophillic addition will take place with a strong nucleophile. The base reacts with the reagent and generates the nucleophile. This nucleophile attacks at the carbon atom of the carbon–oxygen double bond because that carbon has a partial positive charge and Pi electrons of C = O bond move to the oxygen atom, which, because of its electronegativity, can easily accommodate the negative charge. The reaction is completed by addition of proton to the negative oxygen.



19. 6. 2 Relative Reactivity:

Generally, Ketones are somewhat less reactive than aldehydes towards nucleophiles. There are two main reasons for this reactivity difference.

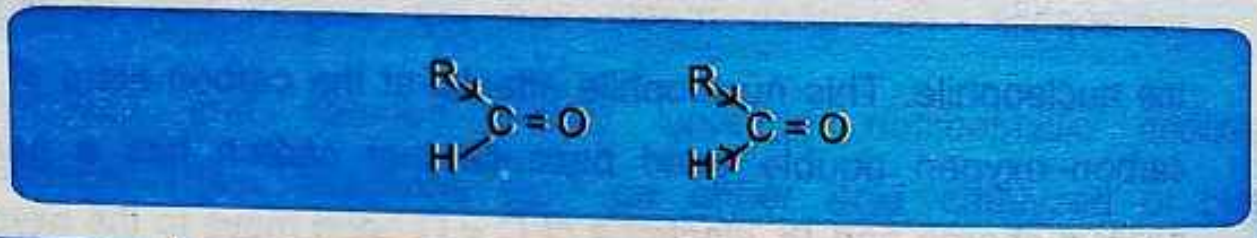
I. Steric Hindrance: The carbonyl carbon is more crowded in ketones as compared to aldehydes. In nucleophilic addition, the attached groups come even closer because in the product the hybridization

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

changes from sp^2 to sp^3 and the bond angles decrease from 120° to 109.5°.

II. Electronic Effect: As alkyl groups are usually electron donating compared to hydrogen. They, therefore, tend to neutralize the partial positive charge on the carbonyl carbon decreasing its reactivity towards nucleophiles. Ketones have two such alkyl groups; aldehydes have only one.



19.6.3 Reduction of Aldehydes and Ketones:

Addition of hydrogen to aldehydes and ketones is called reduction. Following are some important reactions of aldehydes and ketones that involve reduction.

1. Reduction of carbonyl compounds to Hydrocarbons:

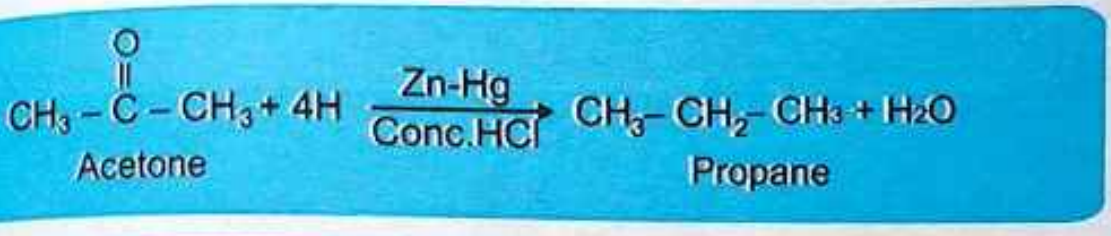
Aldehydes and ketones can be reduced to saturated hydrocarbons either by Clemmensen reduction or by Wolf – Kishner reduction.

a. Clemmenson Reduction: In this reaction aldehydes and ketones are reduced to alkanes in the presence of Zinc amalgam and HCl as reducing agent.



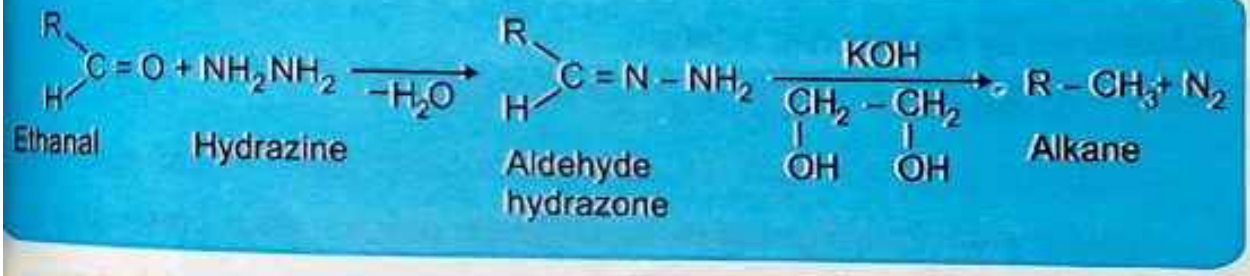
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



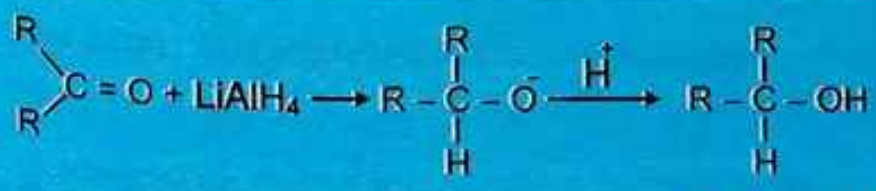
(b) Wolf-Kishner Reduction:

When an aldehyde or ketone is treated with hydrazine a corresponding hydrazone is obtained which on heating with KOH in boiling ethylene glycol gives corresponding alkane.



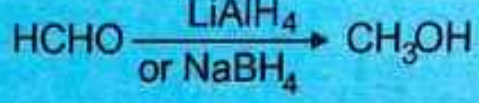
2. Reduction Using Hydrides to give Alcohols:

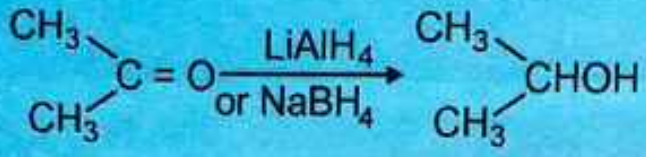
Aldehydes and ketones are easily reduced to primary and secondary alcohols respectively by using metal hydrides as reducing agents. The most common metal hydrides used to reduce carbonyl compounds are lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$).



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



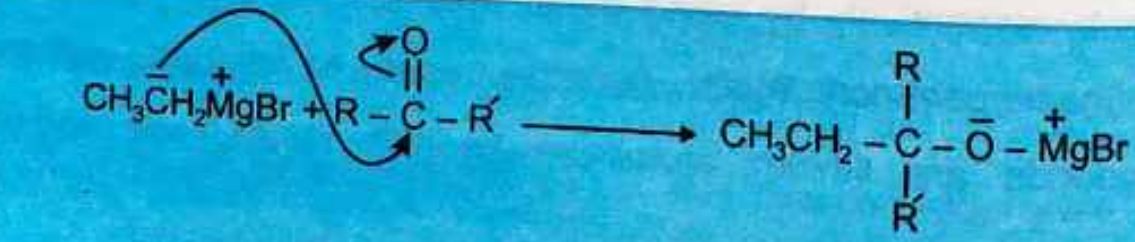


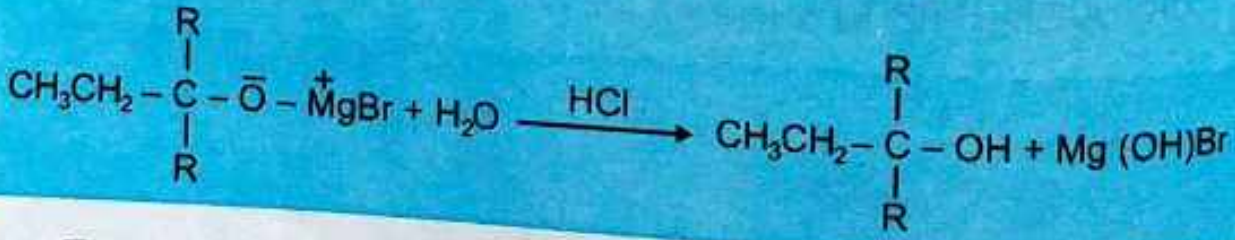
3. Reduction –Using Carbon Nucleophiles:

In organometallic compounds (e.g Grignard reagent) and hydrogen cyanide (HCN), the carbon acts as nucleophile and can reduce aldehydes and ketones by nucleophilic addition.

i. Reduction –Using Grignard Reagent:

Grignard reagents act as carbon nucleophiles toward carbonyl compounds. The R group of the Grignard reagent adds irreversibly to the carbonyl carbon, forming a new carbon –carbon bond that gives an intermediate alkoxide. The alkoxide can be protonated by dilute HCl to give alcohol.

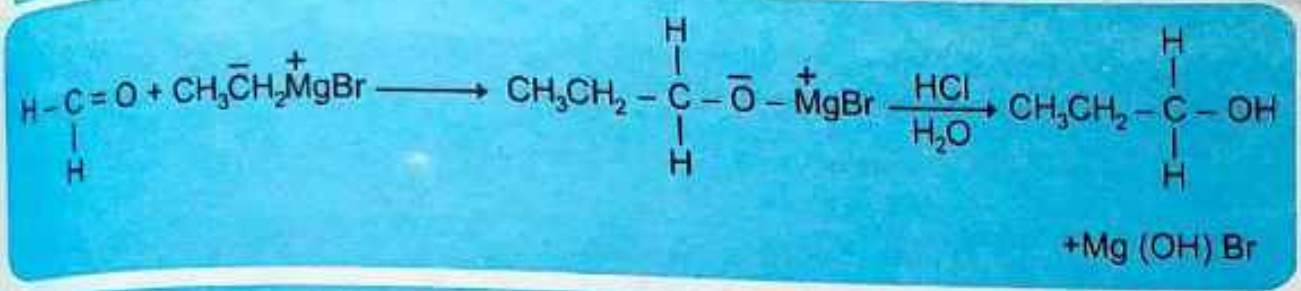




The type of carbonyl compound chosen, determines the class of alcohol produced e.g. formaldehyde gives primary alcohols.

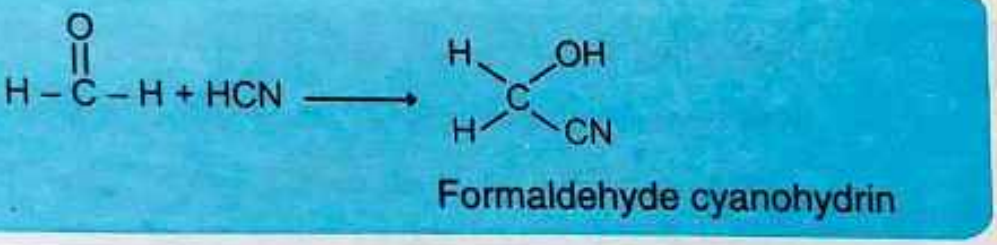
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

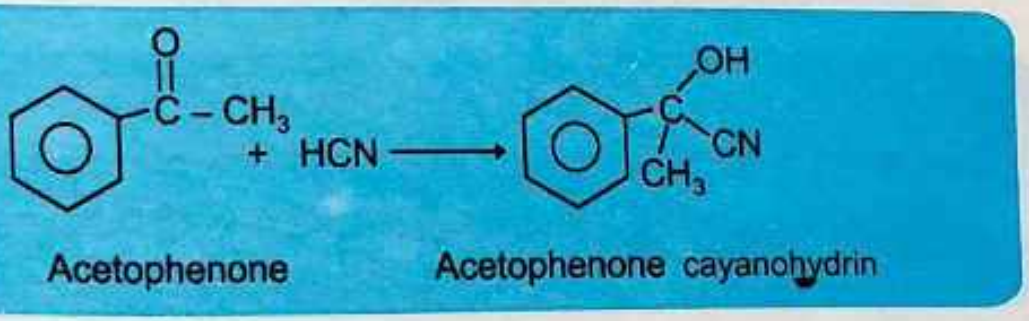


ii. Reduction –Using HCN:

The carbon in hydrocyanic acid also acts as carbon nucleophile and undergoes nucleophillic addition to aldehydes and ketones in the presence of base to yield cyanohydrins, compounds with a hydroxyl and a cyano group attached to the same carbon. The reaction is carried out in basic medium.



Formaldehyde cyanohydrin



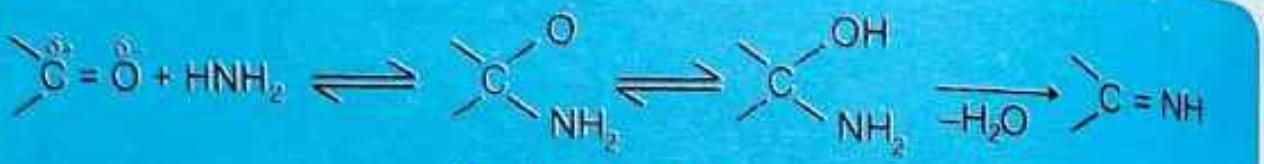
Acetophenone Acetophenone cayanohydrin

4. Reduction –Using Nitrogen Nucleophiles:

Ammonia, amines and some other related compounds have an unshared electron pair on nitrogen atom and therefore act as nucleophiles toward the carbonyl carbon atom.

a. Reaction with Ammonia: Aldehydes react with ammonia to form solid aldehyde ammonia.

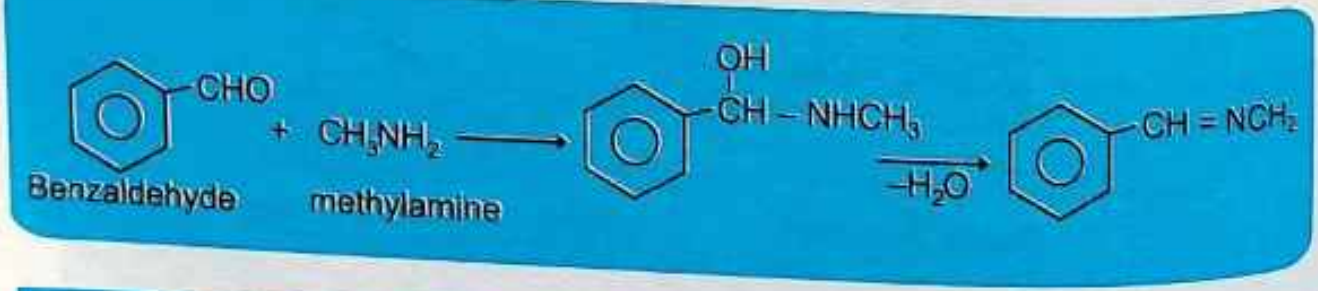
Scanned with CamScanner



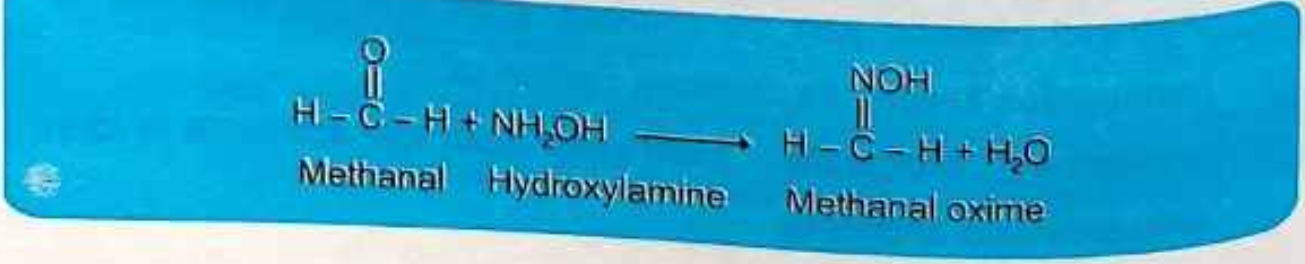
Ketones do not form addition product when treated with ammonia, rather it gives condensation products.

b. Reaction with ammonia derivatives: Some important ammonia derivatives are alkyl amines, hydroxyl amines (NH_2OH), hydrazine (NH_2NH_2), phenyl hydrazine etc. ($C_6H_5NHNH_2$)

i. Reaction with alkyl Amines: Primary amines react with aldehyde and ketones to form an unstable addition product which loses water to form a product with a carbon nitrogen double bond, called imines.



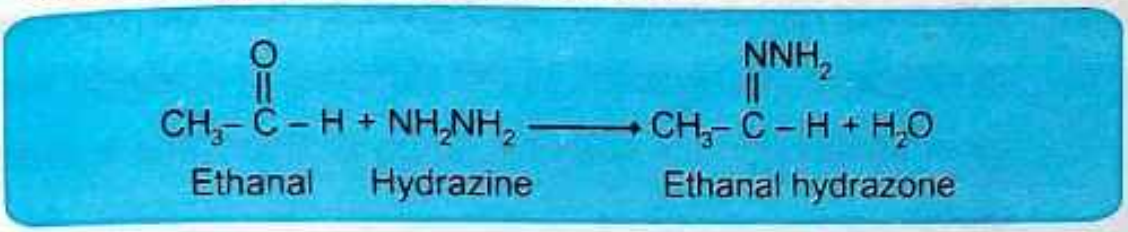
ii. Reaction with hydroxylamine: Aldehydes and ketones form oximes on reaction with hydroxylamine.



Scanned with CamScanner

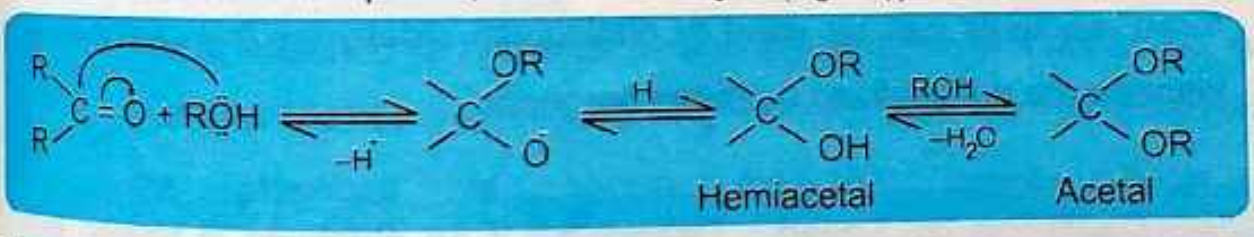
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

iii. Reaction with Hydrazine NH_2NH_2: Aldehydes and ketones reacts with hydrazine to form hydrazone.



5. Reduction –Using Oxygen Nucleophiles:

Alcohols are oxygen nucleophiles as alcohols are weak acids having O-H bond. The oxygen of the alkoxy group attacks the carbonyl carbon of aldehydes and ketones, resulting in addition to the C=O bond. Since alcohols are weak nucleophiles, an acid catalyst (H_2SO_4) is required.



The addition process is reversible and the product obtained is called hemiacetal, which contains both alcohol and ether functional groups on the same carbon. In the presence of excess alcohol, hemiacetal reacts further to form acetal, which has two ether functional groups (a gem–ether) at the same carbon.

19.6.4 Oxidation Reactions of Carbonyl compounds:

Both aldehydes and ketones undergo oxidation in the presence of oxidizing agents, however, aldehydes are more easily oxidized than ketones.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

a. Oxidation of Aldehydes: Oxidation of an aldehyde, in the presence of strong oxidizing agents like acidified $KMnO_4$ or acidified sodium / potassium dichromate, or Ag_2O gives an acid with the same number of carbon atoms. Actually, in the oxidation of aldehyde, the hydrogen atom attached to the carbonyl group in aldehydes is oxidized to OH group.

$$\underset{\text{Aldehyde}}{RCHO} + [O] \xrightarrow{KMnO_4} \underset{\text{Carboxylic acid}}{RCOOH}$$

Since aldehydes can be oxidized by much milder oxidizing agents such as Tollen's reagent, Fehling's solution and Benedict's solution. These three reactants can be used to distinguish aldehydes from ketones as ketones are not oxidized by these reagents.

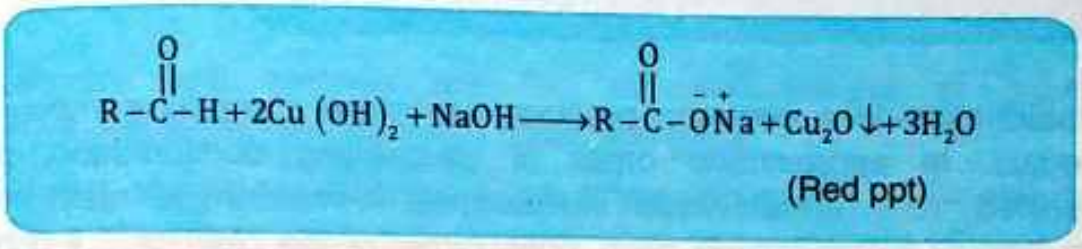
i. Oxidation by Tollen's Reagent: If an aldehyde is treated with Tollen's reagent, the silver ion present in Tollen's reagent is reduced to metallic silver which is deposited on the wall of test tube to form a silver mirror. Therefore, it is also known as silver mirror test.

$$\underset{\text{(Ammonical silver nitrate)}}{R-\overset{O}{\overset{\|}{C}}-H + 2\,Ag(NH_3)_2OH} \longrightarrow \underset{\text{Ammonium Carboxylate}}{R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{N}H_4} + \underset{\text{Silver mirror}}{2\,Ag} + H_2O + 3NH_3$$

Scanned with CamScanner

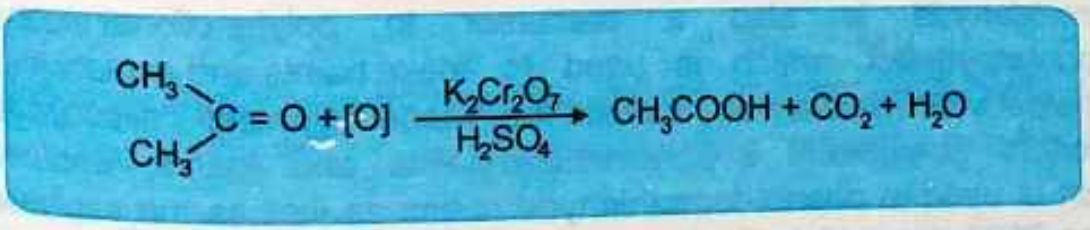
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

ii. Oxidation by Fehling's Solution: If aldehyde is treated with Fehling's solution, the deep blue colour of cupric ion is reduced to **red precipitates of cuprous** oxide. Ketones do not given this reaction.



This test is widely used for the estimation of glucose in blood and urine.

b. Oxidations of Ketones: In aldehydes, oxidation involve hydrogen that is attached to carbonyl carbon but in case of ketones no such hydrogen exists. Ketones having α–hydrogen can be oxidized in the presence of strong oxidizing agents such as $K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$ or concentrated HNO_3 etc which involves breaking of C–C bond.



In case of unsymmetrical ketones, the carbonyl group remain with smaller alkyl group as oxidation takes place at this site.

Scanned with CamScanner

Society, Technology and Science

Formaldehyde is a common precursor to more complex compounds and materials. In approximate order of decreasing consumption, products generated from formaldehyde include urea formaldehyde resin, melamine resin, phenol formaldehyde resin, polyoxymethylene plastics, 1,4-butanediol, and methylene diphenyl diisocyanate. The textile industry uses formaldehyde-based resins as finishers to make fabrics crease-resistant. Formaldehyde-based materials are key to the manufacture of automobiles, and used to make components for the transmission, electrical system, engine block, door panels, axles and brake shoes.

When treated with phenol, urea, or melamine, formaldehyde produces, respectively, hard thermoset phenol formaldehyde resin, urea formaldehyde resin, and melamine resin. These polymers are common permanent adhesives used in plywood and carpeting. It is used as the wet-strength resin added to sanitary paper products such as facial tissue, table napkins, and roll towels. They are also foamed to make insulation, or cast into moulded products. Production of formaldehyde resins accounts for more than half of formaldehyde consumption.

Formaldehyde is also a precursor to polyfunctional alcohols such as pentaerythritol, which is used to make paints and explosives. Other formaldehyde derivatives include methylene diphenyl diisocyanate, an important component in polyurethane paints and foams, and hexamine, which is used in phenol-formaldehyde resins as well as the explosive RDX. Since 2006, formaldehyde (methylene glycol) is also used in hair smoothing treatments in order to straighten wavy/curly hair and make hair less prone to frizz under high humid weather.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Key Points:

- Aldehydes and ketones are two different classes of organic compounds containing carbonyl functional group.
- Oxidation of primary alcohols gives aldehydes and that of secondary alcohol gives ketones.
- The $C = O$ bond in aldehydes and ketones is highly polar and hence they are very reactive compounds.
- Both aldehydes and ketones undergo nucleophillic addition reactions.
- Generally, ketones are somewhat less reactive than aldehydes towards nucleaphiles.
- Aldehydes and ketones undergo condensation reactions with ammonia and its derivatives to form compounds containing $>C = N -$ linkage.
- Aldehydes are oxidized to alcohols in the presence of oxidizing agents like $K_2Cr_2O_7$ in H_2SO_4, $KMnO_4$ in H_2SO_4. Howevere, ketones usually resist
- oxidation.
- Aldehydes form silver mirror with Tollen's reagent and gives red precipitates with Fehling's solution on heating. Whereas ketones do not undergo these reactions.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Exercise

Q.1 Choose the correct answer.

i. The carbon of the carbonyl group is

a. Sp^3 – hybridized
b. trigonal planar
c. Pyramidal in geometry
d. tetrahedral in geometry

ii. The reduction of $>C=O$ to $>CH_2$ is carried out with

a. Catalytic reduction
b. Zn-Hg and conc. HCl
c. Wolff Kishner reduction
d. $LiAlH_4$

iii. A compound $C_4H_{10}O$ yields a compound C_4H_8O on oxidation. The compound $C_4H_{10}O$ is.

a. An aldehyde
b. An alcohol
c. A ketone
d. An acid

iv. Formaldehyde gives an additive product with methyl magnesium iodide which on hydrolysis gives,

a. n–Propyl alcohol
b. Iso propyl alcohol
c. Methyl alcohol
d. Ethyl alcohol

v. Which of the following compounds can react with ammonical silver nitrate solution to form silver mirror?

a. Acetone
b. Ethanol
c. Ether
d. Ethanal

vi. Which of the following compounds precipitates Cu_2O from Fehling's reagent but does not react with sodium metal?

a. C_2H_5OH
b. C_2H_5CHO
c. $CH_3CH(OH)CH_3$
d. CH_3COCH_3

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

vii. When propanal is heated with Fehling's solution there is.

a. A colour change from green to orange.

b. A colour change from blue to red.

c. A negative test with Tollen's reagent

d. No colour change.

Q.2 Explain briefly.

i. Aldehyde contains the carbonyl group. ketones, carboxylic acids and esters also contain carbonyl group. What distinguishes these later compounds from an aldehyde?

ii. The mechanism of nucleophilic addition to a carbonyl compound.

iii. Aldehydes and ketones undergo nucleophilic addition while alkenes undergo electrophilic addition.

iv. Aldehydes are oxidized easily than ketones.

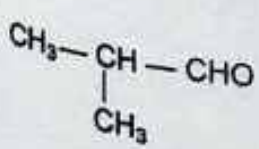
v. Ketones are somewhat less reactive than aldehydes towards nucleophile.

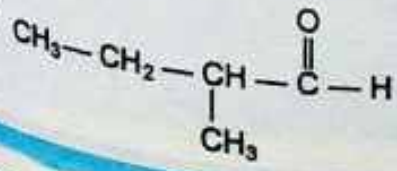
vi. Which test can be used for the identification of aldehydes from ketones in laboratory?

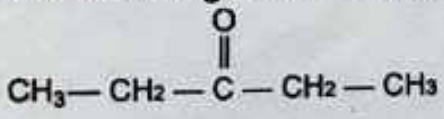
Q.3 Write the structural formulae and give IUPAC names for all aldehyde and ketone isomers of the molecular formula $C_5H_{10}O$.

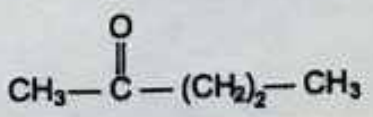
Q.4 Explain the structure and reactivity of carbonyl compounds.

Q.5 Name each of the following compounds according to IUPAC system.

(1) 

(2) 

(3) 

(4) 

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Q.6 Write structural formula for each of the following.

i. 2 – Octanone
ii. Di-n-propyl ketone
iii. 4 – Methyl pentanal
iv. 2,2 – Dibromohexanal
v. 3 – Ethylpentanal
vi. Hexane-2,4-dione

Q.7 Give a reaction to prepare each of the following.

i. Cyanohydrin
ii. Oxime
iii. Imine
iv. Hydrazone
v. Acetal

Q.8 Using Grignard reagent and the appropriate aldehyde or ketone how each of the following can be prepared?

i. 1– Butanol
ii. Ethyl alcohol
iii. 2 – Butanol
iv. 2 – Methyl –2 – butanol
v. 3 – Methyl –3 – pentanol

Q. 9 (a) Write any three methods for preparation of acetaldehyde.

(b) How does ethanal react with the following reagents?

i. Ethyl magnecium iodide
ii. Zinc – mercury amalgam and HCl
iii. Lithium Aluminium hydride
iv. Acidified $K_2Cr_2O_7$

Q. 10 (a) How aromatic ketones are prepared by Friedel-craft acylation?

(b) Starting from acetone, how will you prepare each of the following.

i. Propane
ii. 2 – Propanol
iii. Acetone cyanohydrin
iv. Acetone hydrazone
v. Hemiketal
vi. Acetic acid

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

UNIT 20

Carbonyl Compounds 2: Carboxylic Acids and Functional Derivatives

Learning Outcomes:

After Studying this unit Students will be able to:

- Describe Nomenclature, physical properties and structure of carboxylic acids.
- Discuss preparation of carboxylic acids by carbonation of Grignard's reagent, hydrolysis of nitriles, oxidation of primary alcohols, oxidation of aldehydes and oxidation of alkyl benzene.
- Discuss reactivity of carboxylic acids.
- Describe the chemistry of carboxylic acids by conversion to carboxylic acid i.e. acylhalides, acid anhydrides, esters, amides and reaction involving inter conversion of these.
- Describe reactions of carboxylic acid derivates.
- Describe isomerism in carboxylic acids.
- Identify carboxylic acid in the laboratory.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Introduction:

Carboxylic acids are organic acids containing the carboxyl group ($-\overset{\overset{O}{\|}}{C}-OH$ or $-COOH$) as a functional group. The carboxyl group itself consists of a carbonyl group ($\rangle C=O$) and a hydroxyl group ($-OH$) i.e. carb from carbonyl and oxyl from hydroxyl. Acids containing one such functional group are known as mono carboxylic acids, while those containing two carboxyl groups are called dicarboxylic acids. Carboxylic acids may be aliphatic or aromatic depending upon whether carboxyl group ($-\overset{\overset{O}{\|}}{C}-OH$) is attached to an alkyl group or an aryl group.

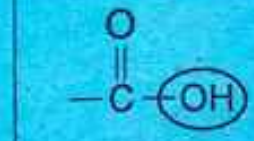
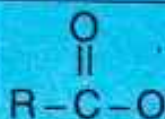
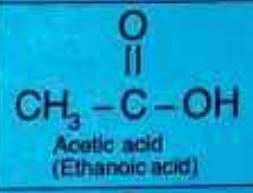
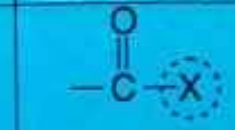
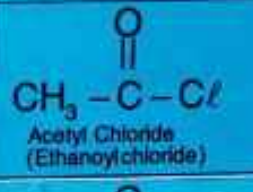
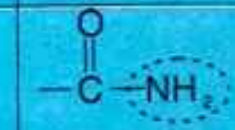
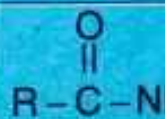
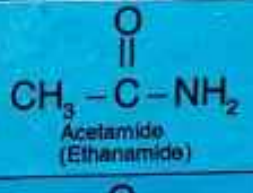
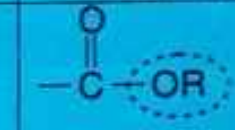
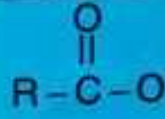
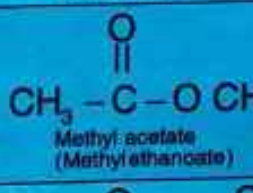
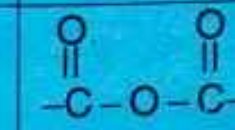
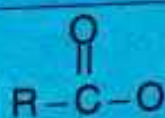
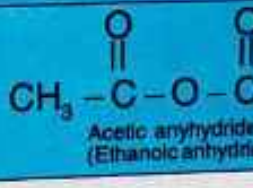
The general formula of an aliphatic carboxylic acid is RCOOH whereas that of aromatic carboxylic acid is ArCOOH.

Aliphatic carboxylic acids are also commonly called fatty acids because esters of several of their higher members are fats.

Carboxylic acids have many derivatives in which the –OH of an acid is replaced by other functional groups. This results in other classes of organic compounds. There derivatives alongwith their functional groups and general formulas are mentioned in the table 20.1 below;

Scanned with CamScanner

Table: 20.1 Derivatives of Carboxylic acids:

Acid Derivatives	Functional Group	General Formula	Examples
Acid			 Acetic acid (Ethanoic acid)
Acid Halide or Acyl Halide			 Acetyl Chloride (Ethanoyl chloride)
Acid amide			 Acetamide (Ethanamide)
Ester			 Methyl acetate (Methyl ethanoate)
Acid anhydrides			 Acetic anyhydride (Ethanoic anhydride)

20.1 Nomenclature:

Following two types of naming is employed in case of carboxylic acids.

Common or Trivial Names:

Many of the acids have common names. These names usually come from some Latin or Greek words that indicate the original source of the acid. Following table 20.2 lists some common aliphatic carboxylic acids, with their common names.

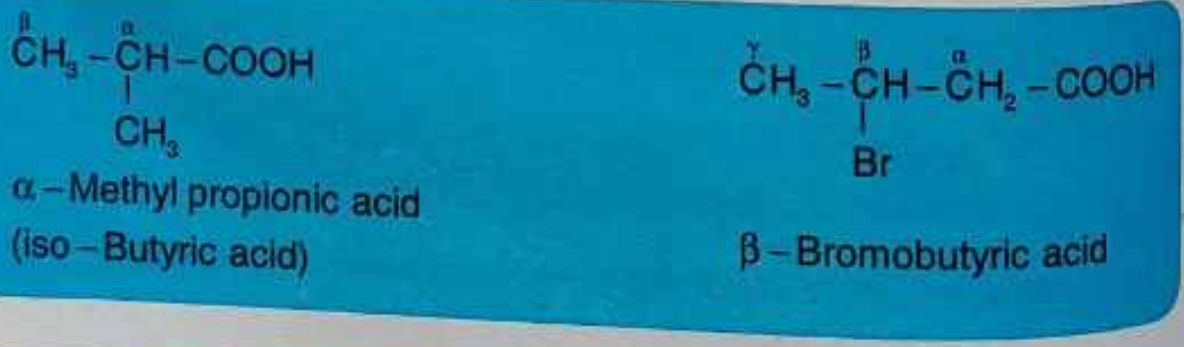
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Table: 20.2 Common Names of few Organic Acids:

Carbon atoms	Formula /common name	Sources
1.	HCOOH Formic acid	From Latin word 'Formica' means 'ant'
2.	CH_3COOH Acetic acid	From Latin word ' acetum means 'vinegar'
3.	CH_3CH_2COOH Propionic acid	From Greek word 'protos' means 'first' and 'pion' means 'fat'
4.	$CH_3CH_2CH_2COOH$ Butyric acid	From Latin word 'butyrum' means 'butter'

In case of branched acids, the common name of the acid is used. Substituents are located with Greek letters α, β, γ etc. as given below.



The IUPAC Nomenclature:

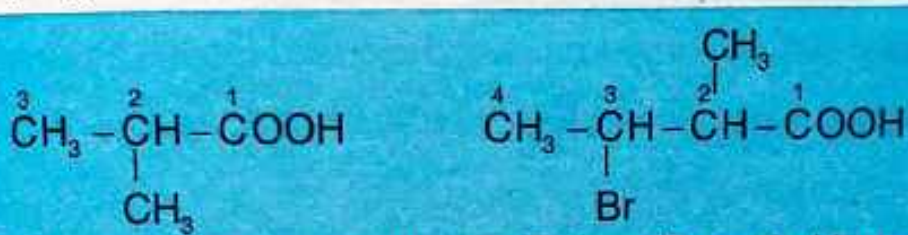
Aliphatic monocarboxylic acids are named as alkanoic acids. These are obtained by replacing the ending 'e' of the corresponding alkane with the suffix "oic acid". e.g.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$HCOOH$	CH_3COOH	CH_3CH_2COOH	$CH_3CH_2CH_2COOH$
Methanoic acid	Ethanoic acid	Propanoic acid	Butanoic acid

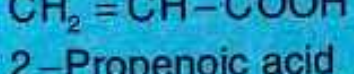
In case of branched acids, the chain is numbered starting from the carboxyl carbon atom i.e. $(-\overset{1}{\overset{\|}{\underset{\|}{C}}}-OH)$ and substituents are located in the usual way e.g.



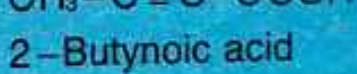
2–Methyl propanoic acid

3–Bromo–2–methyl butanoic acid

Similarly, the unsaturated carboxylic acids are named as alkenoic acid e.g.



2–Propenoic acid



2–Butynoic acid

Carboxylic acids containing two carboxyl groups are called dicarboxylic acids or dioic acids (IUPAC).

Table 20.3 Aliphatic dicarboxylic acids:

Formula	IUPAC Name
$HOOC-COOH$	Ethanedioic acid
$HOOC-CH_2-COOH$	Propanedioic acid
$HOOC(CH_2)_2COOH$	Butanedioic acid
$HOOC-(CH_2)_3-COOH$	Pentanedioic acid
$HOOC(CH_2)_4-COOH$	Hexanedioic acid

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

20.2 Physical Properties:

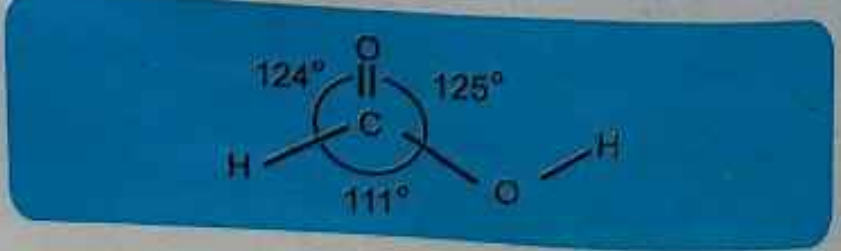
The lower members of the aliphatic acids $C_1 - C_{10}$ are liquids with distinctive penetrating odours. Acetic acid (ethanoic acid), which constitutes about 4 to 5 % of vinegar, has a characteristic smell which is recognizable in vinegar. Butyric acid (Butanoic acid) is the substance that can be smelled in rancid butter. Higher members of acid homologous series are wax-like solids. Anhydrous ethanoic acid (acetic acid) freezes at 17°C to form a solid which look like ice. It is, therefore, known as glacial acetic acid, (glacial means ice –like).

Carboxylic acids are more polar than alcohols. They form hydrogen bonds with themselves or with their own molecules. That is why they have high melting and boiling points.

Hydrogen bonding also explains the water solubility of lower –molecular weight carboxylic acids which form hydrogen bond with water molecule. Solubility of these acids in water decrease as their relative molecular mass increases.

20.3 Structure

The Structural features of the carboxyl group are most apparent in formic acid. It is planar, with one of its carbon–oxygen bonds shorter than the other, and with bond angles at carbon close to 120°.



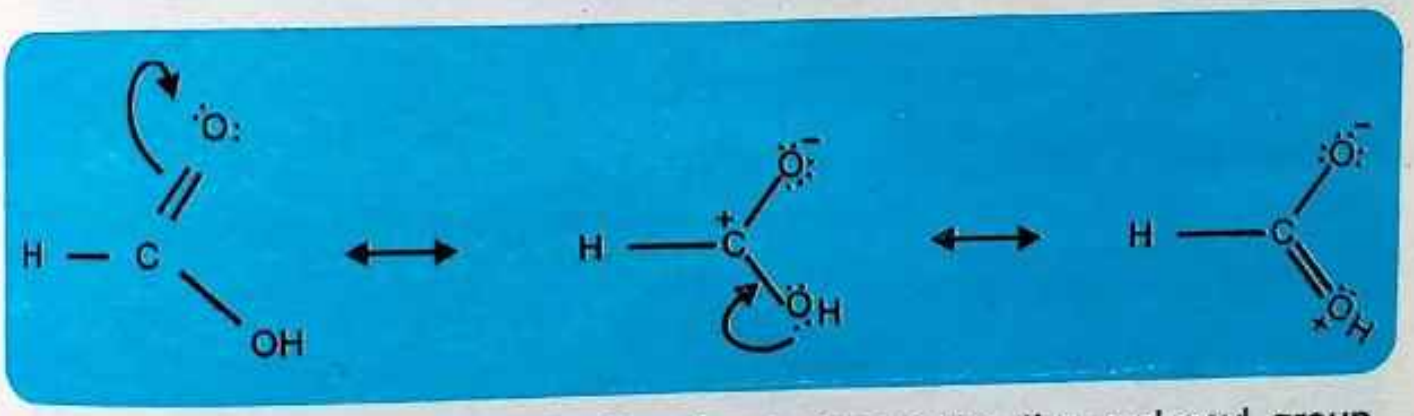
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The bond lengths between C = O is 120 pm and C — O is 134 pm. Similarly, the bond angles of H – C = O is 124°, H – C = O is 111° and O – C = O is 125°.

This suggest sp^2 hybridization at carbon, and a carbon oxygen double bond similar to that of aldehydes and ketones.

Additionally, sp^2 hybridization of hydroxyl oxygen allows one of its unshared electron pair to be delocalized by orbital overlap with the π system of the carbonyl carbon i.e.



Lone –pair donation from hydroxyl oxygen makes the carbonyl group less electrophillic than that of aldehyde and ketones.

20.4 Acidity:

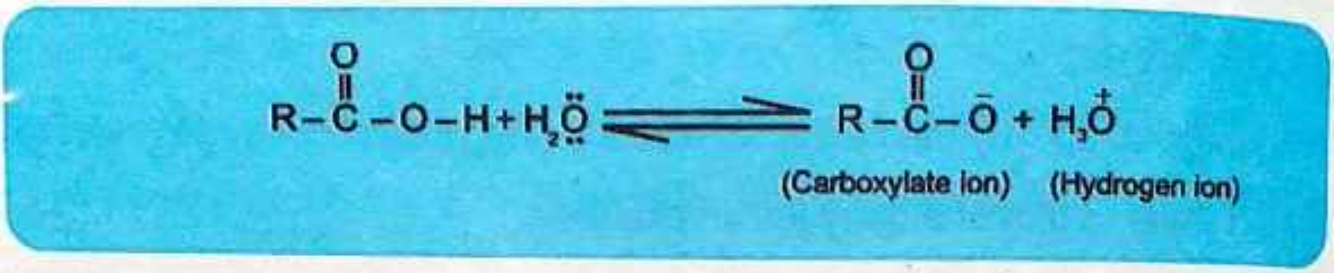
Carboxylic acids are the most acidic class of organic compounds. They are much stronger acids than water, alcohols and phenols but weaker than mineral acids.

Carboxylic acids dissociate in water, yielding carboxylate anion and a hydronium ion. The withdrawal of electrons away from the carboxyl hydrogen atom weakens the O–H bond. As a result the carboxyl group

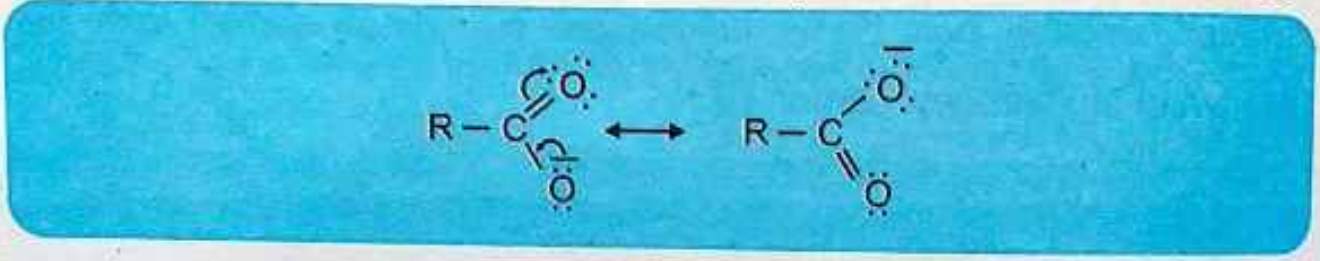
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

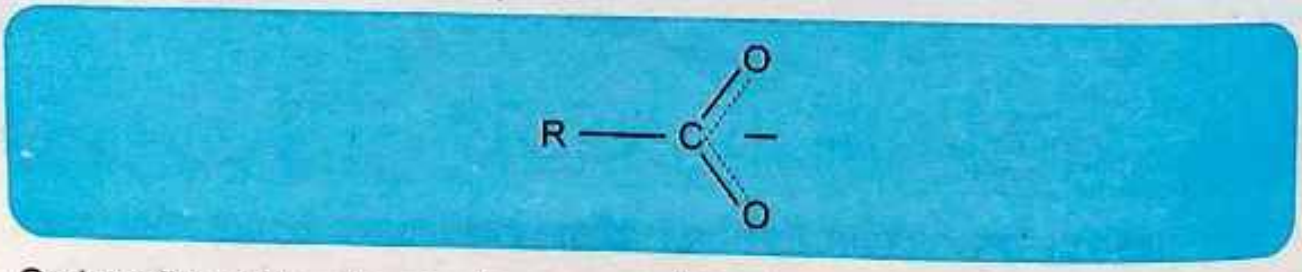
can lose a proton in aqueous medium. Mono carboxylic acids are thus monobasic acids. The following equilibrium is established.



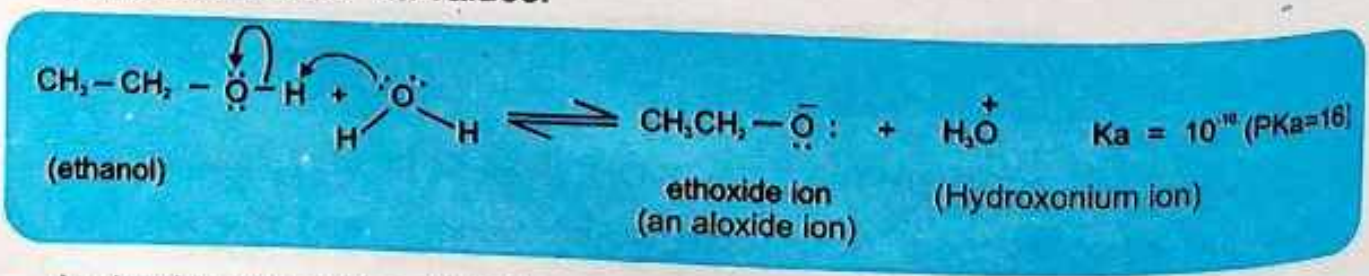
The carboxylate ion exists as a resonance hybrid of two canonical forms.



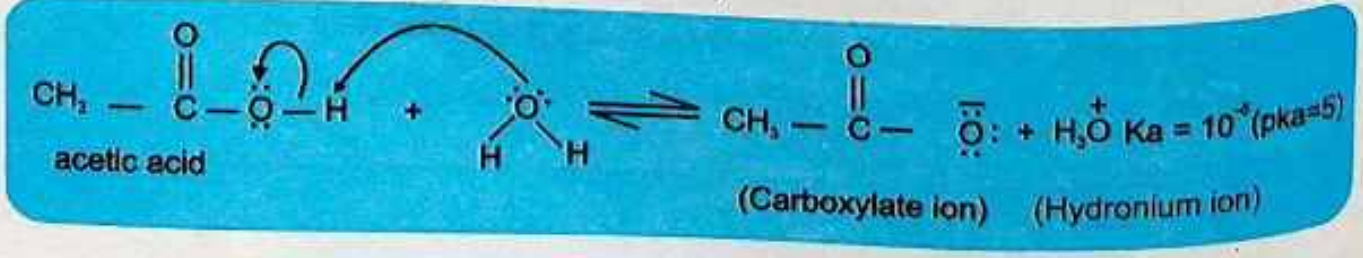
The resonance hybrid can be represented as



Carboxylic acids are much more acidic than alcohols and phenols as evident from their Ka values.



Ionization of acetic acid (ethanoic acid).



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The ionization of ethanol yields an alkoxide (ethoxide) ion in which the negative charge is localized on oxygen. However, the carboxylate ion is stabilized by the delocalization of negative charge on two oxygen atoms.

The acidities of the carboxylic acids vary considerably with the nature of the substituents present in the molecule. Any electron withdrawing substituent (e.g. Cl, NO_2 etc.) will tend to stabilize the carboxylate ion by dispersing its negative charge and thus increase the acidity of acid. Whereas an electron donating substituent (e.g alkyl group) will tend to destabilize the carboxylate ion and thus decrease the acidity of the acid.

Table 20.4 Increasing order of acids strength and ionization constants of some acids.

Carboxylic acid	Formula	pka
Propanoic acid	CH_3CH_2-COOH	4.87
Ethanoic acid	CH_3-COOH	4.76
Methanoic acid	$H-COOH$	3.68
Chloroacetic acid	$CH_2C\ell COOH$	2.86
Dichloroacetic acid	$CHC\ell_2COOH$	1.29
Trichloro acetic acid	$CC\ell_3COOH$	0.65

20.5 Preparations of carboxylic Acids:

Following methods of preparations are used for carboxylic acids.

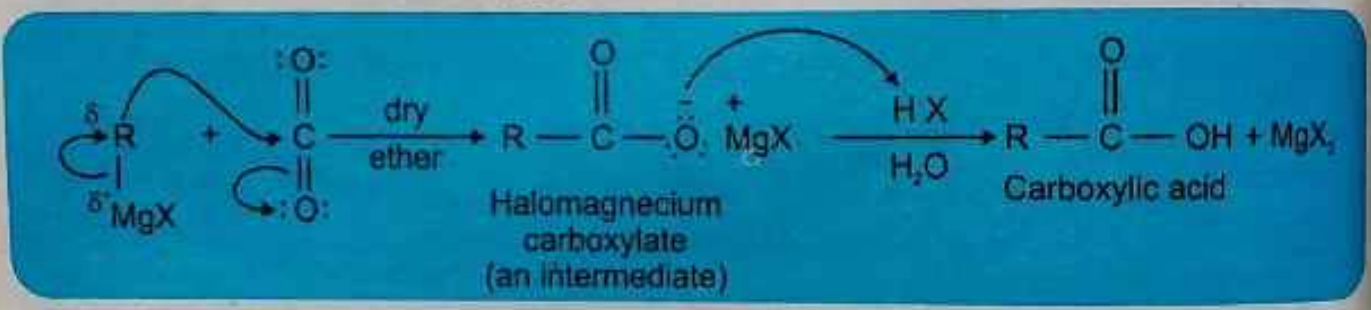
Scanned with CamScanner

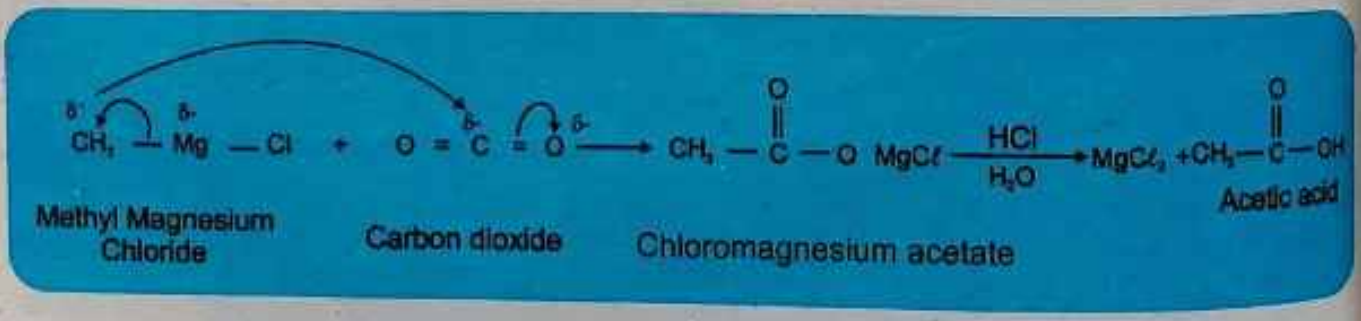
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

20. 5.1 Carbonation of Grignard Reagent:

Carboxylic acids can be prepared by the action of Grignard reagent (RMgX) with carbondioxide. This reaction is known as carbonation or carboxylation of Grignard reagent.

Grignard reagent reacts with carbon dioxide to give initially an intermediate magnesium salt of carboxylic acid which on hydrolysis in the presence of mineral acid ($HC\ell$) gives a carboxylic acid.





The acid obtained by the carboxylation of Grignard reagent has one more carbon atom than alkyl or aryl halide from which Grignard reagent is prepared, so the reaction provides a way to extend the length of a carbon chain.

20.5.2 Hydrolysis of Nitriles:

Compounds having a cyanide ($-C \equiv N$) group are called alkyl nitriles or alkyl cyanides. The carbon –nitrogen triple bond of alkyl nitriles can be hydrolyzed to a carboxylic acid in aqueous acid medium.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$R-C\equiv N+2H_2O \xrightarrow{HCl} R-\overset{O}{\overset{\|}{C}}-OH+\overset{+}{N}H_4+\overset{-}{Cl}$$

Alkyle Nitrile — an acid — ammonium ion

$$CH_3-C\equiv N+2H_2O \xrightarrow{HCl} CH_3-\overset{O}{\overset{\|}{C}}-OH+\overset{+}{N}H_4\ \overset{-}{Cl}_{(aq)}$$

Methyl nitrile (methyl cyanide) — acetic acid

20.5.3 Oxidation of Primary Alcohols:

Primary alcohols $(R-CH_2-OH)$ can be oxidized to carboxylic acids by oxidizing agents like acidified potassium permangnate or potassium dichromate etc.

Primary alcohol on oxidation, gives aldehyde which on further oxidation converts to carboxylic acid.

$$R-CH_2-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} R-\overset{O}{\overset{\|}{C}}-H$$

Aldehyde

$$R-\overset{O}{\overset{\|}{C}}-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} R-\overset{O}{\overset{\|}{C}}-OH$$

Carboxylic acid

$$CH_3-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-O-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{[O]} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

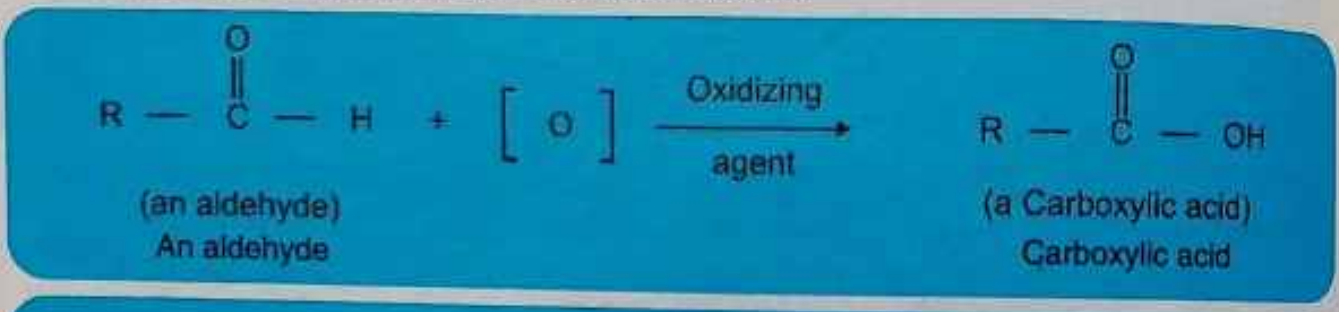
Ethyl alcohol — Acetaldehyde — Acetic acid

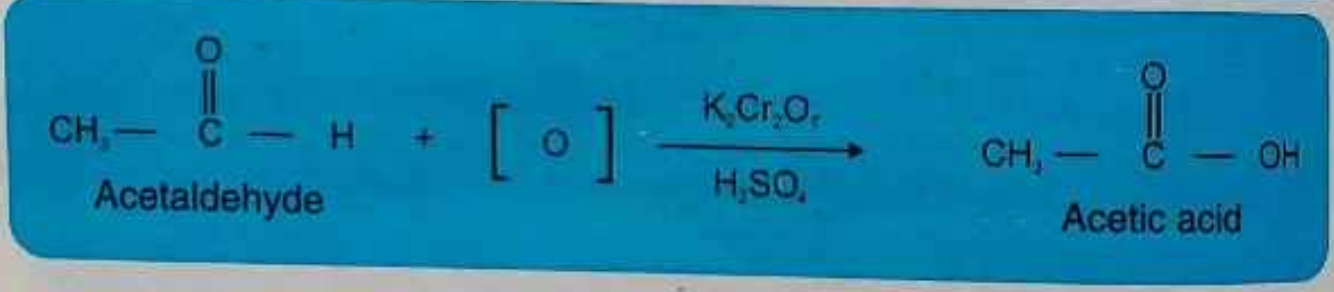
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

20.5.4 Oxidation of Aldehydes:

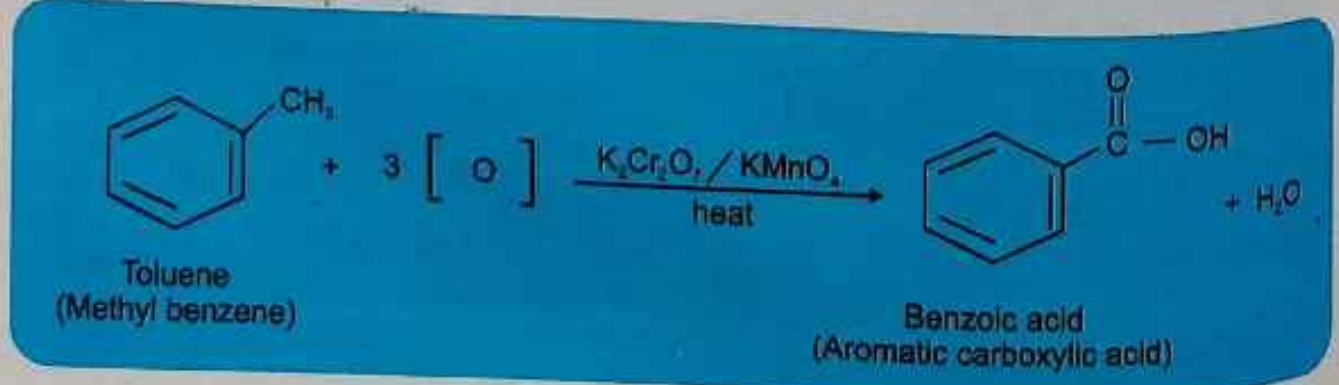
As mentioned earlier oxidation of aldehyde in the presence of oxidizing agents like acidified $KMnO_4$, $K_2Cr_2O_7$ or Ag_2O gives carboxylic acid with the same number of carbon atoms.





20.5.5 Oxidation of Alkyl Benzene:

Aromatic carboxylic acids can be prepared by the oxidation of aliphatic side chain (alkyl group) present on the benzene ring, with oxidizing agent like $KMnO_4$, $K_2Cr_2O_7$. Any side chain is converted to carboxyl group.



Scanned with CamScanner

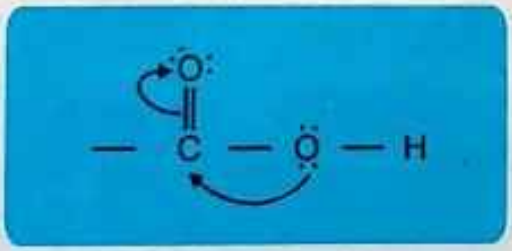
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The reaction illustrates the striking stability of aromatic rings towards oxidizing agents, it is methyl group, not the aromatic ring that is oxidized.

20.6 Reactivity:

The carboxylic group is so named because it contains a carboxyl group and a hydroxyl group. The two groups influence each other to such an extent that the reactivity of carboxylic acids shows little resemblance to those of carbonyl compounds (aldehydes and ketones) on one hand and alcohols on the other hand.

Although the carboxylic group contain the carbonyl group ($-\overset{\overset{O}{\|}}{C}-$) carboxylic acids do not exhibit the characteristic reactions of aldehyde and ketones. For example, they do not undergo addition or condensation reactions. This is because the carbon atom of the carboxyl group is less positive than in the aldehyde or ketone. The carboxylic group is given below.



The polar ($\rangle C = O$) group attracts the electrons away from the $-O-H$ bond, and make it easier for the hydrogen atom to ionize than in the case in the $O-H$ bond in alcohols. Hence carboxylic acids show different chemical reactivity than alcohols. Similarly, the flow of the electrons from the $-O-H$ group towards, the carbonyl carbon reduces the partial positive charge on the carbonyl carbon of carboxylic group. As a result it is not attacked by nucleophiles as compared to aldehyde or ketones.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

20.7 Reactions of Carboxylic Acids:

Following are some of the reactions of carboxylic acids that involve the conversion of the carboxylic acids to their derivatives as well as synthesis of some other compounds.

20.7.1 Conversion to Carboxylic Acid Derivatives

20.7.1.1 Acyl Halides / Acid Halides ($R-\overset{\overset{O}{\|}}{C}-X$)

Acyl halides or acid halides are the derivatives of carboxylic acids that are obtained by replacing the –OH of carboxylic acid by halogen atoms $(X = F, Cl, Br, I)$.

Acyl halides are the most reactive of carboxylic acid derivatives. Acyl chloride are more common and less expensive than bromides and iodides. They are usually prepared by the reaction of acids with thionyl chloride $(SOCl_2)$ or phosphorous pentachloride (PCl_5).

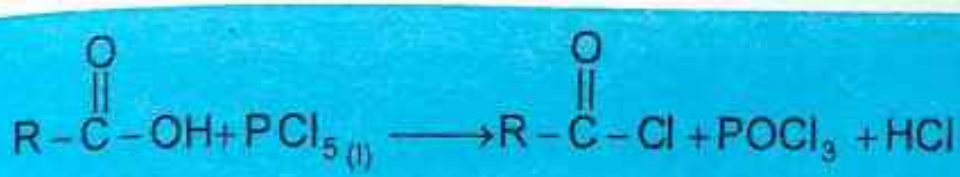
$$R-\overset{\overset{O}{\|}}{C}-OH + SOCl_2 \longrightarrow R-\overset{\overset{O}{\|}}{C}-Cl + HCl_{(g)} + SO_{2(g)}$$

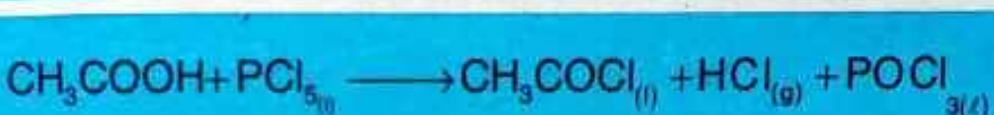
Carboxylic acid — Thionylchloride (Sulphur dichloride oxide) — Acylchloride

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + SOCl_{2(l)} \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-Cl_{(l)} + HCl_{(g)} + SO_{2(g)}$$

Acetic acid (Ethanoic acid) — (Sulphur dichloride oxide) — Acetyl Chloride (Ethanoyl Chloride)

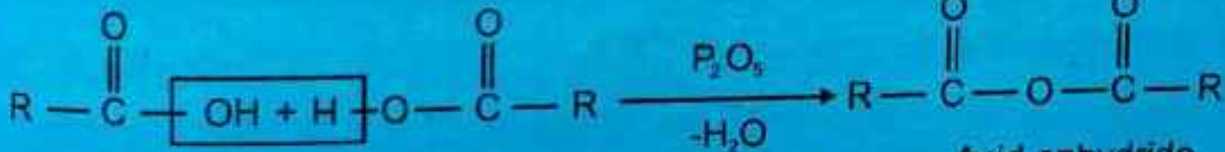
Scanned with CamScanner



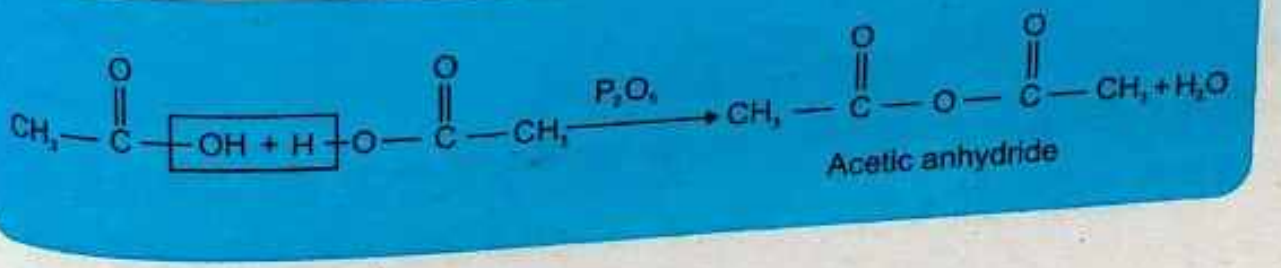


20.7.1.2 Acid Anhydrides:

Acid anhydrides are derived from acids by removing water from two carboxylic acid molecules.



As the name indicates, these are anhydrous carboxylic acids. The name of anhydride is obtained by naming the acid from which it is derived and replacing the word acid with anhydride. The most important and commercially available anhydride is acetic anhydride or ethanoic anhydride. It is prepared by heating acetic acid at high temperature in the presence of dehydrating agent, phosphorous pentoxide (P_2O_5).

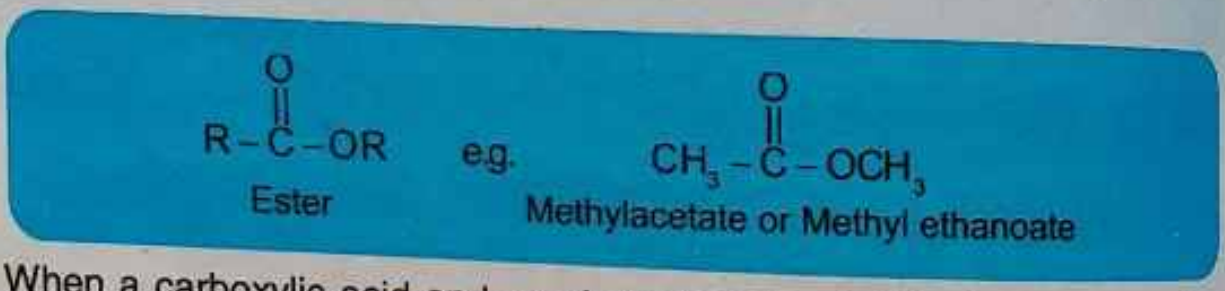


Scanned with CamScanner

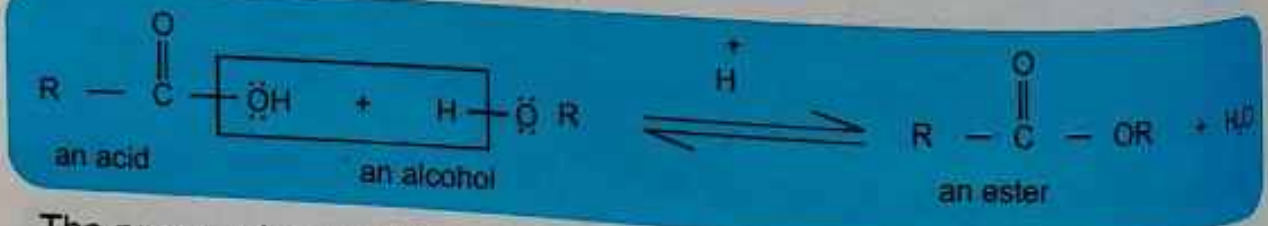
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

20.7.1.3 Esters (R – C(=O) – OR)

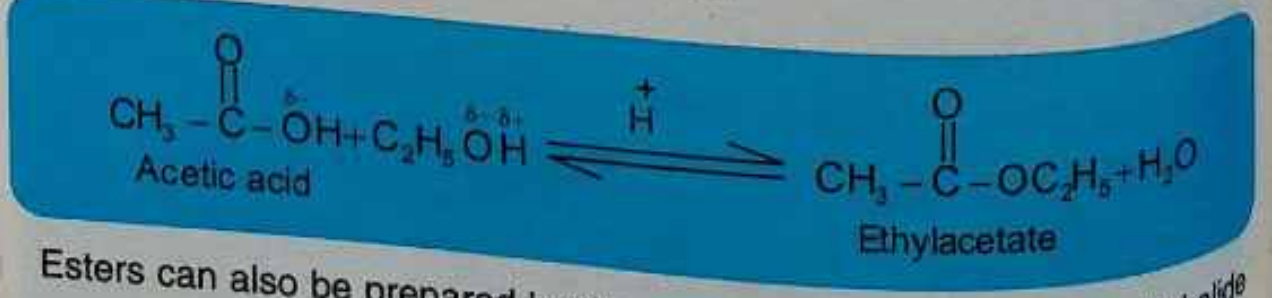
Esters are a class of organic compounds that are derived from acids by replacing the –OH group by an alkoxy (-OR) group. While naming ester the R part of the –OR group is named first, followed by the name of the acid, whereby "-ic acid" is replaced by "ate."



When a carboxylic acid and an alcohol are heated in the presence of an acid catalyst (usually H_2SO_4 or HCl) , an equilibrium is established with the formation of ester and water.

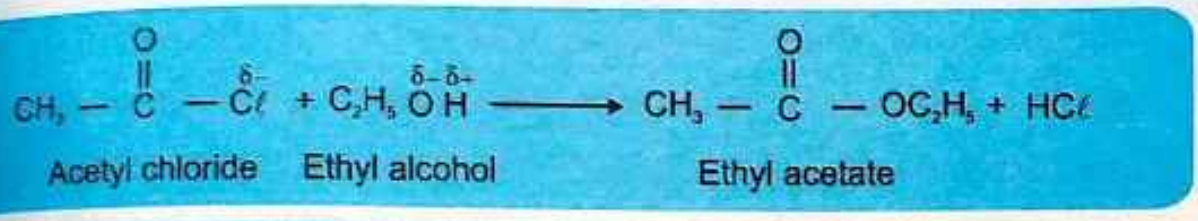


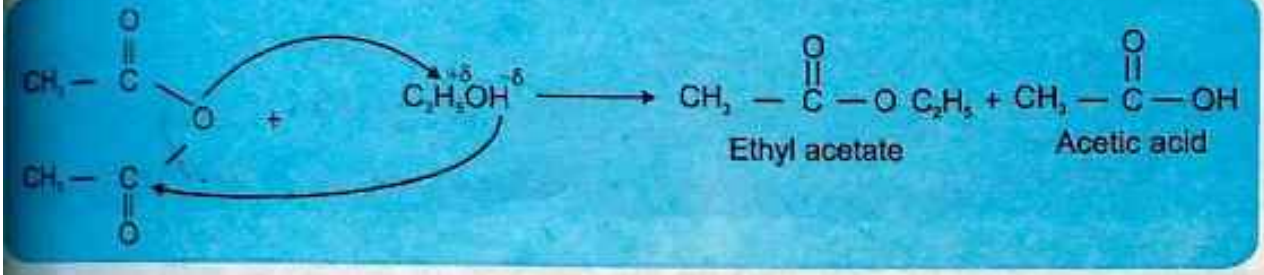
The process is called Fischer esterification after the name of Emil Fischer. Ethyl acetate is an important ester which can be prepared by this method by the reaction of acetic acid with ethanol.



Esters can also be prepared by the reaction of an alcohol with acid halide or acid anhydride.

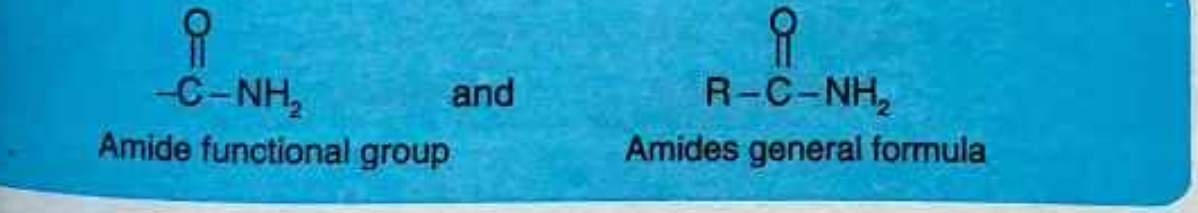
Scanned with CamScanner



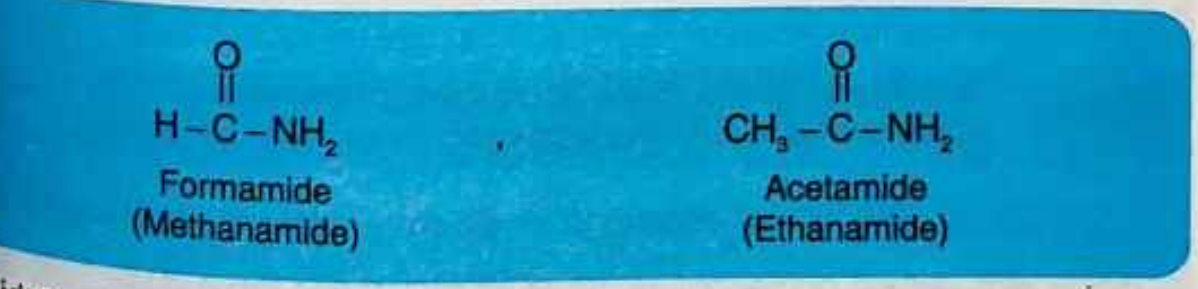


20.7.1.4 Amides:

Amides are the least reactive of the derivatives of carboxylic acid derivatives. These are obtained by replacing –OH of the acid with $-NH_2$ group.



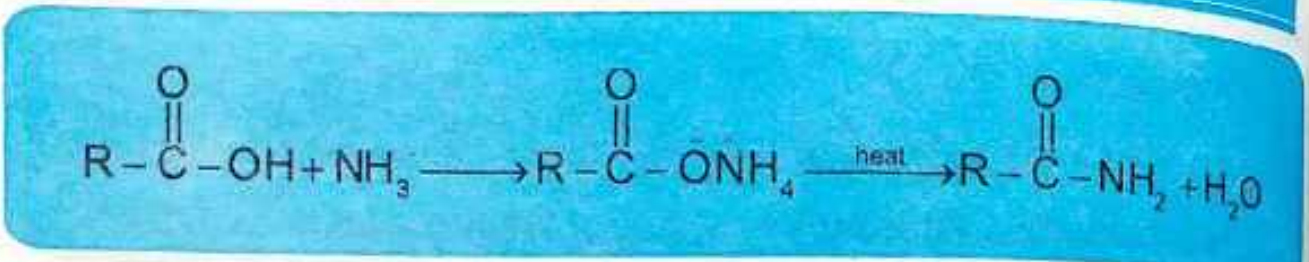
They are named by replacing "ic acid" or "Oic acid" of corresponding acid by word "amide".

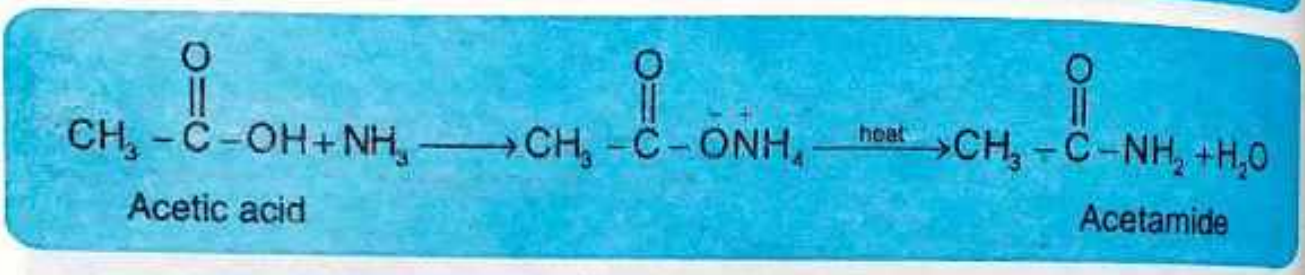


Amides can be prepared by the reaction of ammonia with carboxylic acid to form first ammonium salts which on heating produce acid amides.

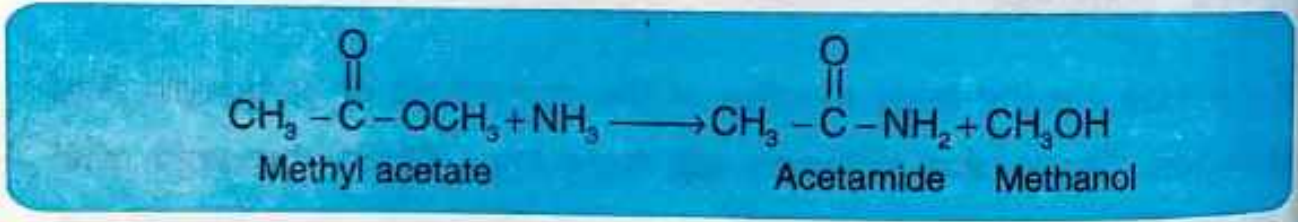
Scanned with CamScanner

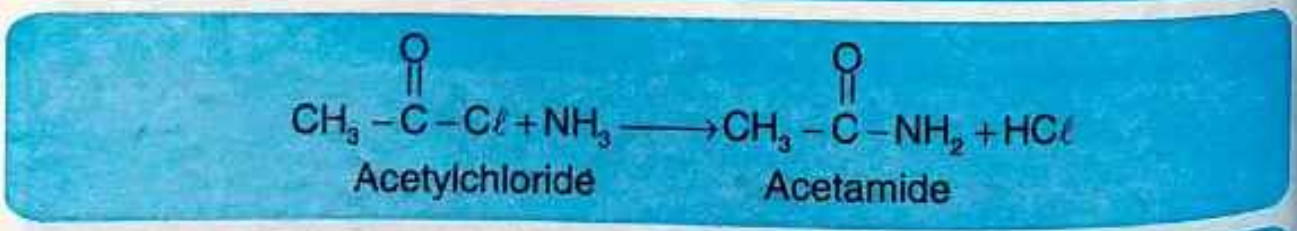
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

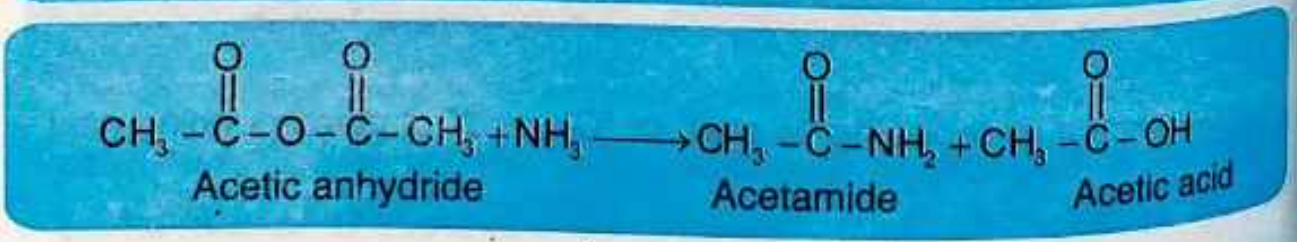




Amides can also be prepared by the reaction of ammonia with ester or acetyl chlorides.







20.7.2 Summary of the Reactions that Interconvert Carboxylic Acid Derivatives:

A summary of the reactions of different derivatives of carboxylic acids with certain nucleophiles, have been listed in table 20.5.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The different acids derivatives are listed at the left of the chart in order of decreasing reactivities towards nucleophiles. The common nucleophiles are listed across the top. In case of hydrolysis corresponding acid is obtained, we either start with an acyl halides, acid anhydride, ester, amide or nitrite. Similarly alcoholysis gives an ester and ammonolysis gives an amide. All of the reactions in table 20.5 take place via attack of the nucleophile on the carbonyl carbon of the acid derivative.

Table 20.5 Reactions of Acid Derivatives with Certain Derivatives Nucleophile:

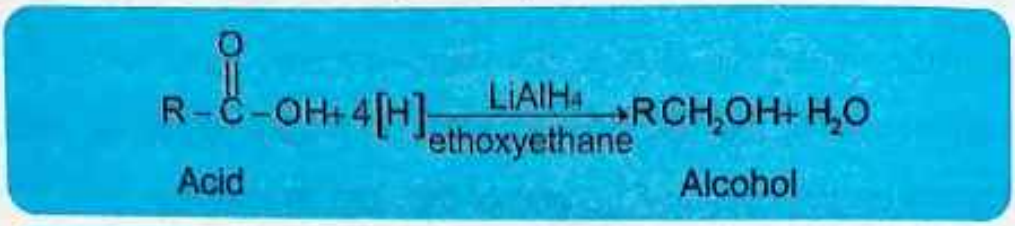
Acid Derivatives	HOH (Hydrolysis)	R'OH (Alcoholysis)	NH_3 (Ammonolysis)
$R-\overset{O}{\overset{\|}{C}}-C\ell$ Acylchloride	$R-\overset{O}{\overset{\|}{C}}-OH + HC\ell$	$R-\overset{O}{\overset{\|}{C}}-OR' + HC\ell$	$R-\overset{O}{\overset{\|}{C}}-NH_2 + \overset{+}{N}H_4\,\overset{-}{C}\ell$
$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ Acid anhydride	$2R-\overset{O}{\overset{\|}{C}}-OH$	$R-\overset{O}{\overset{\|}{C}}-OR' + R-\overset{O}{\overset{\|}{C}}-OH$	$R-\overset{O}{\overset{\|}{C}}-NH_2 + R-\overset{O}{\overset{\|}{C}}-OH$
$R-\overset{O}{\overset{\|}{C}}-O-R''$ Ester	$R-\overset{O}{\overset{\|}{C}}-OH + R''-OH$	–	$R-\overset{O}{\overset{\|}{C}}-NH_2 + R''OH$
$R-\overset{O}{\overset{\|}{C}}-NH_2$ Amide	$R-\overset{O}{\overset{\|}{C}}-OH + NH_3$	–	–
$R-C\equiv N$ Nitrile	$R-\overset{O}{\overset{\|}{C}}-OH + \overset{+}{N}H_4\,\overset{-}{C}\ell$ (in acid media)	–	–
Main organic product	Carboxylic acid	Ester	Amide

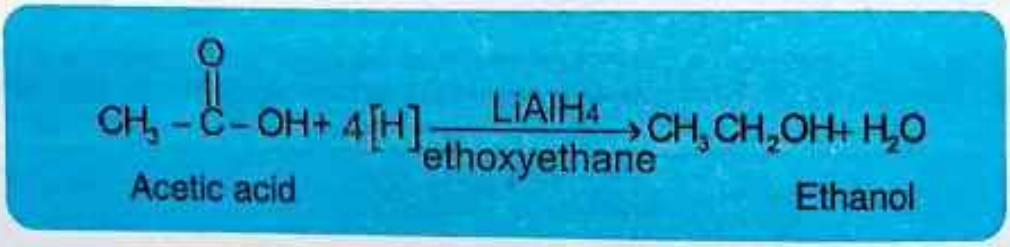
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

20.7.3 Reduction to Alcohols:

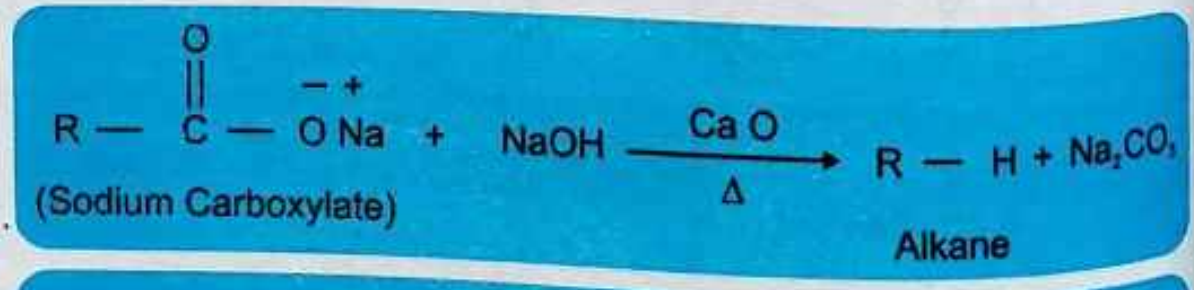
Carboxylic acids can be reduced to the corresponding alcohols using lithium aluminum hydride in dry ethoxy ethane.

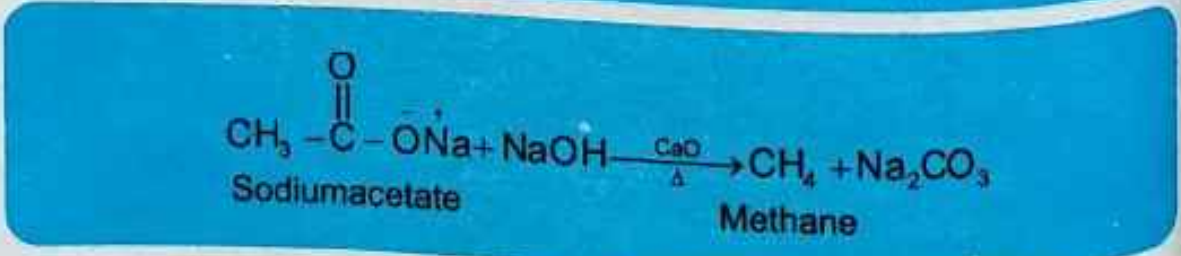




20.7.4 Decarboxylation Reactions:

The removal of carbon dioxide from a carboxylic acid is known as decarboxylation. Decarboxylation of carboxylic acid takes place when its sodium salt is heated with soda lime (dry mixture of caustic soda, NaOH and quick lime CaO) to form alkanes.





Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Society, Technology and Science

Ascorbic acid occur naturally in fruit, used as preservatives. It inhibits fungal growth but allow bacterial activity, hence it is useful for cheese. Benzoic acid and sodium benzoate have inhibitory effect on the growth of yeast, a major cause of food spoilage. You may have noticed the sharp sour taste of the lemonade. This tartness is a result of carboxylic acid. This is an organic acid found in variety of fruits including grapes, lemon, oranges (citric acid). This acid gives tangy taste. Acetic acid present in vinegar is responsible for giving its sour taste. Malic acid found in unripe fruit gives these fruit a sour or tart taste.

20.7.5 Reactions of Carboxylic Acid Derivatives:

20.7.5.1 Reactions of Acyl Halides:

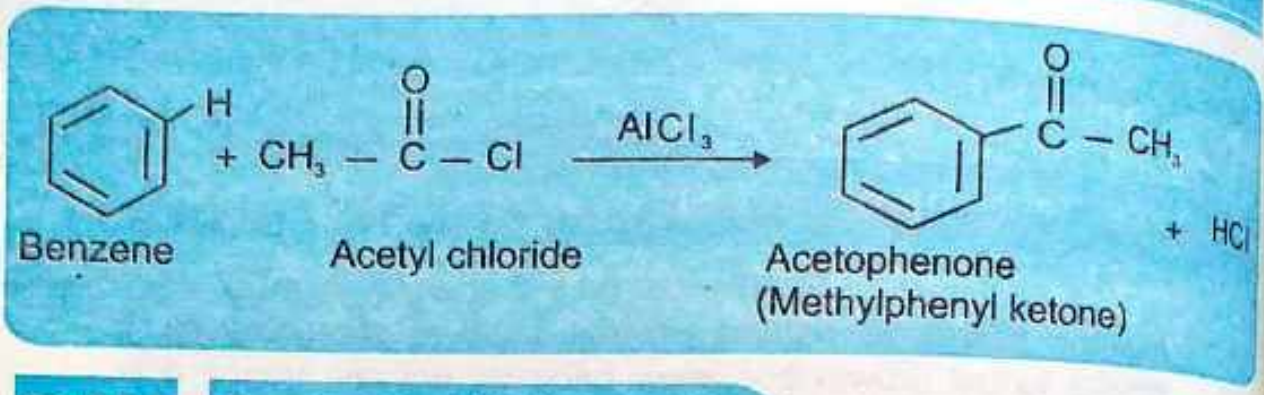
Acid halides are the most reactive of all derivatives of carboxylic acid.

Friedel –Crafts Acylation Reaction:

Acyl halides react with benzene in the presence of Lewis acid $AlC\ell_3$ to form aromatic ketones. The reaction involves the introduction of acyl group $(R-\overset{O}{\overset{\|}{C}}-)$ to the ring and is known as Friedel-Crafts acylation reaction.

Scanned with CamScanner

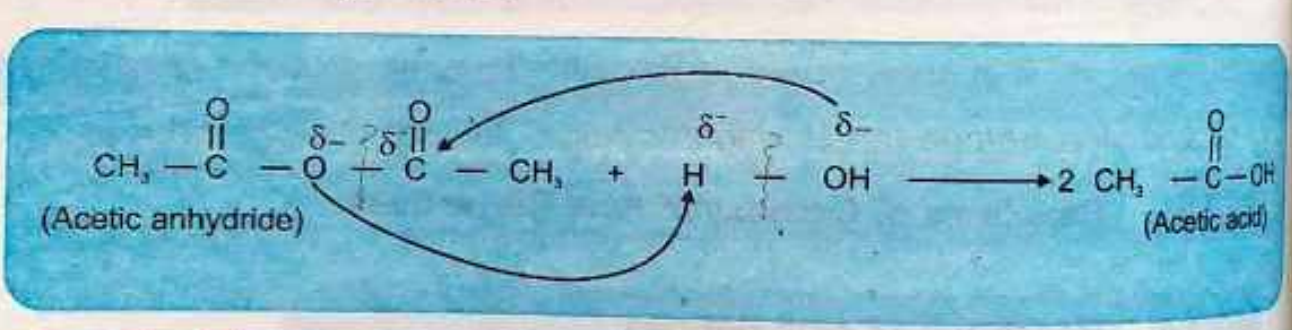
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



20.7.5.2 Reactions of Acid Anhydrides:

Acid Anhydrides are more reactive than esters, but less reactive than acid halides, toward nucleophiles.

i. Hydrolysis: On hydrolysis, anhydrides form corresponding carboxylic acids.

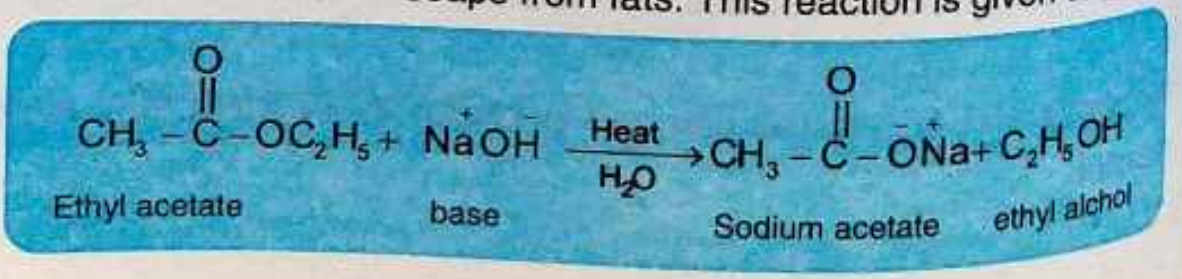


20.7.5.3 Reactions of Esters:

Following are some of the important reactions of esters.

i. Hydrolysis: (Saponification of Esters)

Esters are commonly hydrolyzed with bases. The reaction is called saponification (from the latin sapon, means soap) because this type of reaction is used to make soaps from fats. This reaction is given as;

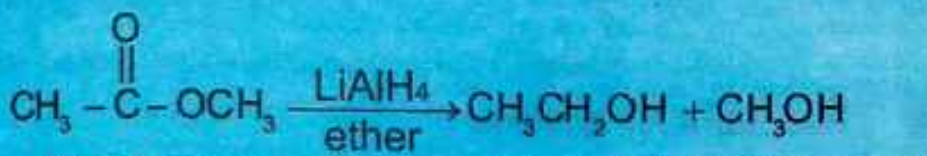


Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

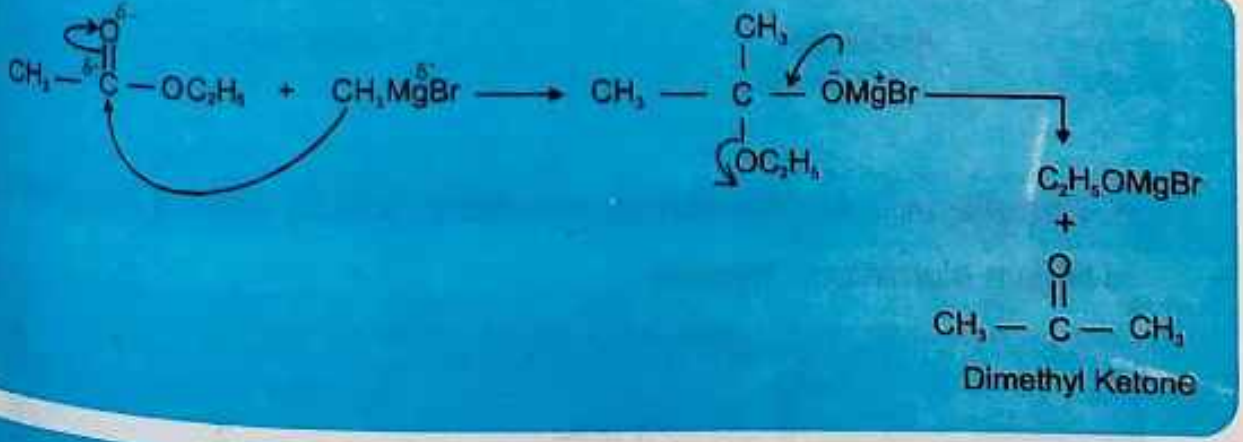
ii. Reduction of Esters:

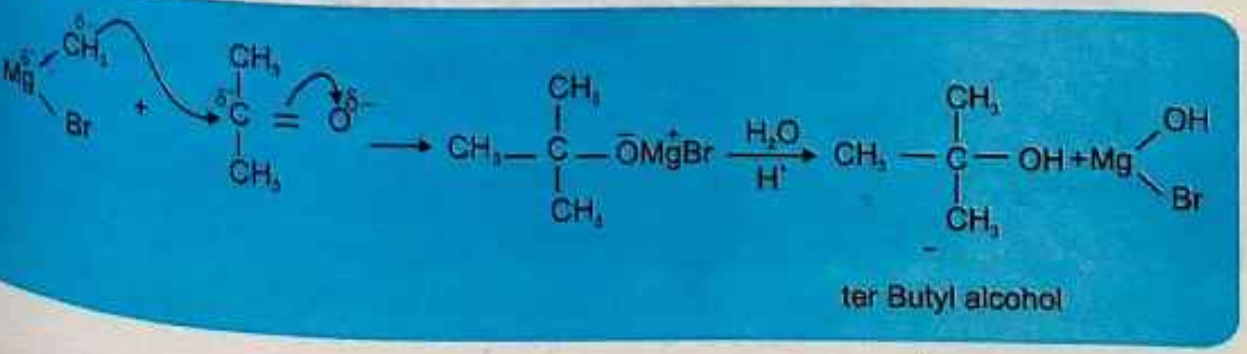
Ester can be reduced to primary alcohols in the presence of reducing agent (lithium aluminum hydride) in ether which is used as solvent.



iii. Reaction of Ester with Grignard Reagent:

Esters react with two equivalents of Grignard reagent to give tertiary alcohols. This involves two steps. In first step ester reacts with a molecule of Grignard reagent to form intermediate product, ketone. In second step, ketone reacts with another molecules of Grignard reagent to form tertiary alcohol. The reaction mechanism is given below.

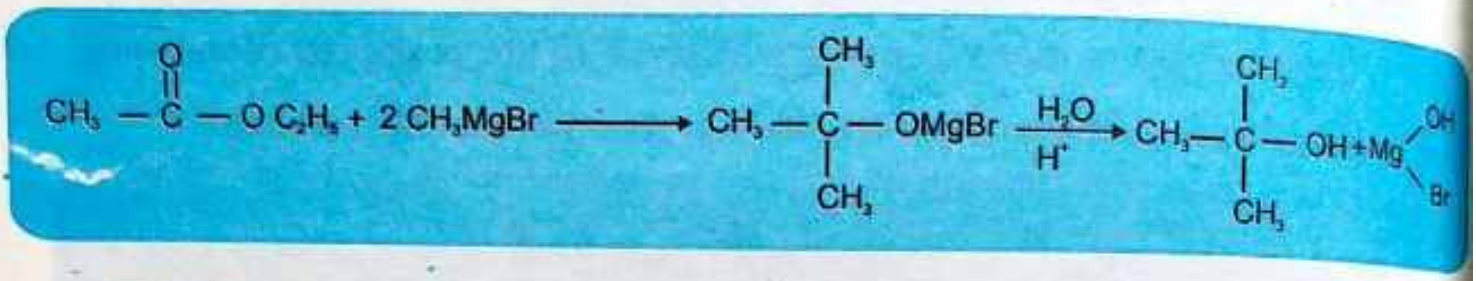




Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

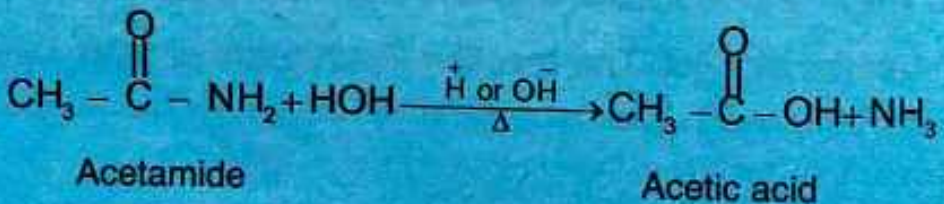
The overall reaction is given as;



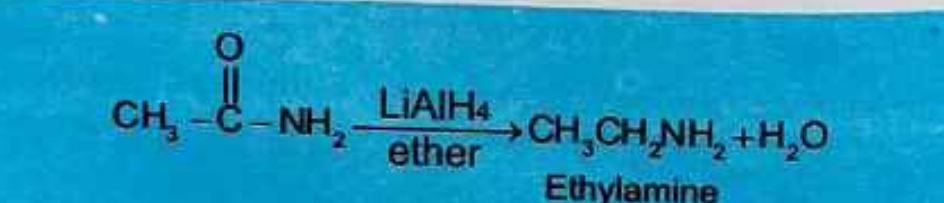
20.7.5.4 Reactions of Amides:

Amides are the least reactive of the common carboxylic acid derivatives. Like other acid derivatives, amides reacts with nucleophiles like water.

i. Hydrolysis: Amides on hydrolysis form the corresponding carboxylic acids. The reaction is slow and requires acid or base as catalyst.



ii. Reduction: Amides can be reduced to primary amines in presence of lithium aluminium hydride.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

20.7.5.5 Reactions of Nitriles:

Alkyl nitriles or simply nitriles (R – CN) are also considered as derivatives of carboxylic acid because they can be obtained from carboxylic acids, though they do not contain acyl group. The following are some of the important reactions of nitriles.

i. Hydrolysis: On boiling with a dilute minerals acid or dilute alkali, nitriles are hydrolysed forming carboxylic acid.

$$CH_3 - C \equiv N + 2H_2O + HCl \longrightarrow CH_3COOH + NH_4^+ Cl^-$$

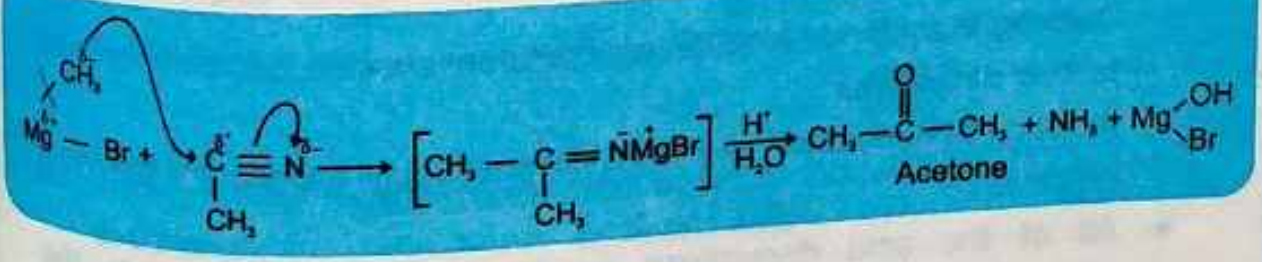
$$CH_3 - C \equiv N + H_2O + NaOH \longrightarrow CH_3COO^- Na^+ + NH_3$$

ii. Reduction: When treated with a reducing agent such as sodium and ethanol or lithium aluminium hydride (lithium tetra hydridoaluminate (III) in ethoxyethane, nitriles are reduced to primary amines.

$$CH_3 - C \equiv N \xrightarrow[\text{ether}]{LiAlH_4} CH_3CH_2NH_2$$

Methylcynide (methyl nitrile) — ethylamine

iii. Reaction with Grignard Reagent: Nitrites on reaction with Grignard reagent produce ketones.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Key Points:

- Carboxylic acids are organic acids having carboxyl group $\left(R-\overset{\overset{O}{\|}}{C}-OH\right)$ as the functional group ("carb" from carbonyl and "oxyl" from hydroxyl).
- Acyl halides, acid anhydrides, esters, amides etc. are the derivatives of acids obtained by replacing the OH of carboxyl group $(-COOH)$ by other functional groups.
- Some members of carboxylic acids have penetrating smells. They are water soluble and their solubility decreases with the increase in molecular mass.
- carboxylic acids, due to strong hydrogen bonds, have high boiling points than corresponding alcohols.
- The carbon atom of the carboxyl group is sp^2 hybridized.
- Carboxylic acids are the strongest organic acids, stronger than phenol, alcohols and water.
- Substituents in a carboxylic acid molecules strongly influence the strength of the acid due to the inductive effect of the substituent.
- Carboxylic acids can be prepared from Grignard reagent, by oxidation of alcohols and aldehydes and by hydrolysis of nitriles.
- Although the carboxylic group contains the carbonyl group, yet carboxylic acid do not exhibit some of the characteristic reactions of aldehydes and ketones.
- Carboxylic acids, on reaction with different species, can be converted to their derivatives.
- Among the derivatives of carboxylic acids, acyl halides are the most reactive.
- All of the acid derivatives can be converted back into the corresponding carboxylic acids on hydrolysis.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Exercise

Q.1 Multiple Choice question. Choose the correct answer from the given choices.

i. Which of the following represents the formula of an aromatic carboxylic acids?

a. HCOOH
b. C_6H_5OH
c. C_6H_5COOH
d. $C_6H_5CH_2OH$

ii. Which of the following acids is found in rancid butter?

a. $C_2H_4O_2$
b. $C_3H_6O_2$
c. $C_4H_8O_2$
d. $C_5H_{10}O_2$

iii. The compound with highest boiling point is.

a. Acetic acid
b. Water
c. Ethyl alcohol
d. Ether

iv. In which of the following compounds, the central atom does not show sp^2 hybridization?

a. Methanal
b. Methanol
c. Methanoic acid
d. Acetone

v. Which is the strongest acid?

a. Ethanol
b. Acetic acid
c. chloroacetic acid
d. Flouroacetic acid

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

vi. Acetic acid can be prepared by the hydrolysis of;

a. Methyl cyanide
b. Methylmagnecium chloride
c. Ethanal
d. Ethanol

vii. Esterification is the reaction between.

a. An acid and ester
b. An acid and alcohol
c. An acid halide and ester
d. An ester and Sodium hydroxide

viii. Acyl chloride can be prepared by the reaction of a carboxylic acid with.

a. Phosphorous pentoxide
b. Soda lime
c. Hydrochloric acid
d. Thionyl chloride

ix. The hydrolysis of an ester in presence of alkali (NaOH) is known as;

a. Saponification
b. Decarboxylation
c. Esterification
d. Transesterfication

x. All the acid derivatives can be converted back into the corresponding acid by one common reaction.

a. Ammonolysis
b. Alcoholysis
c. Reduction
d. Hydrolysis

Q.2 Explain Briefly.

i. Acetic acid is sometimes known as glacial acetic acid.

ii. Carboxylic acids have high boiling points than corresponding alcohols.

Scanned with CamScanner

iii. Why carboxylic acids are stronger acids than phenol, alcohols and water but weaker than mineral acids?

iv. Methanoic acid is stronger acid than ethanoic acid.

v. Chloroacetic acid is stronger acid than acetic acid.

vi. Carboxylic acids can be obtained readily by the oxidation of primary alcohols.

vii. Carboxylic acids do not undergo addition reactions as compared to aldehydes.

viii. Acid halide are most reactive of all acid derivatives towards nucleophiles.

Q.3 Write Structural formula for each of the following.

i. 3 – methylpentanoic acid

ii. 2,2–dichlorobutanoic acid

iii. 2,2 –dimethyl -3 –butenoic acid

iv. Ethan,1, 2-dioic acid

v. Buta,1, 4-dioic acid

vi. Acetamide

vii. Methanamide

viii. Ethanoic anhydride

ix. Methyl Methanoate

x. Ethylnitrile

Q.4 Write IUPAC names of the following.

i. $HCOOH$

ii. CH_3COOH

iii. $CH_3CH(Cl)COOH$

iv. $HOOC\ CH_2COOH$

v. $CH_2 = CHCOOH$

vi. CH_3CF_2COOH

vii. $HC \equiv C\ CH_2\ CO_2H$

viii. $(CH_3)_3\ CCOOH$

xi. $CH_3 - (CH_2)_4 - COOH$

x. $HCONH_2$

xi. $HCOCl$

xii. $HCOOCH_3$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Q.5 Explain the acidity of carboxylic acids. How their acid strength is affected by substitution?

Q.6 How will you prepare propanoic acid by using.

a. an alkyl nitrile
b. a Grignard reagent
c. an alcohol
d. an aldehyde

Q.7 (a) Is there any method used for the preparation of formic acid? If yes explain with example.

(b) How benzoic acid can be prepared from toluene (methyl benzene)?

Q.8 Write an equation for.

a. Hydrolysis of acetyl chloride
b. Reaction of benzoyl chloride with methanol.
c. Esterification of But,1-ol with acetic anhydride.
d. Ammolysis of butanoyl chloride.
e. Fischer esterfication of pentanoic acid with ethanol.
f. Reaction of formic acid with ammonia.
g. Hydrolysis of ethanoic propanoic anhydride.
h. Reduction of ethyl cyanide.

Q. 9 Complete the following reactions.

i. $CH_3CH_2CH_2COOH + PCl_5 \longrightarrow$

ii. $CH_3CH_2COOH + SOCl_2 \longrightarrow$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

iii. $CH_3CH_2CONH_2 + LiAlH_4 \longrightarrow$

iv. $2CH_3CH_2COOH + P_2O_5 \longrightarrow$

v. $CH_3CO\,OCOCH_3 + NH_3 \longrightarrow$

vi. $CH_3CH_2COOCH_3 + NaOH \xrightarrow{heat}$

vii. $CH_3CH_2COONa + NaOH \xrightarrow{CaO}$

viii. $CH_3CH_2\,COOC_2H_5 + Li\,Al\,H_4 \longrightarrow$

ix. $CH_3\,CH_2\,MgBr + CH_3CH_2CN \longrightarrow$

Q. 10 Starting from acetic acid, how will you prepare each of the following.

i. Ethanoyl chloride ii. Ethanoic anhydride iii. Ethanamide

iv. Ethyl ethanoate v. Ethanol

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

UNIT 21

BIOCHEMISTRY

Learning Outcomes:

After Studying this unit Students will be able to:

- Explain the basis of classification and structure –function relationship of carbohydrates.
- Explain the role of various carbohydrates in various diseases.
- Identify the nutritional importance and their role as energy storage.
- Explain the basis of classification and structure functional relationship of proteins.
- Describe the role of various proteins in maintaining body functions and their nutritional importance.
- Describe the role of energy as biocatalyst and relate this role to various functions such as digestion of food.
- Identify factors that affect energy activity such as effect of temperature and P^H.
- Explain the role of inhibitors of energy catalysed reactions.
- Describe the basis of classification and structure function relationship of lipids.
- Identify the nutritional and biological importance of lipids.
- Identify the structural components of DNA and RNA.
- Recognize the structural differences between DNA polymer (double strand) and RNA (single strand).
- Relate DNA sequence to its function as storage of genetic information.
- Relate RNA sequence (transcript) to its role in transfer of information to protein (translation).
- Identify the source of minerals such as iron, calcium, phosphorous and zinc.
- Describe the role of iron, calcium, phosphorus and zinc in nutrition.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

21.1 Carbohydrates:

Carbohydrates form an important class of naturally occuring organic compounds. They are widely distributed in plants and animals. Plants are the major sources of carbohydrates which comprise upto 80% of their dry weight. In contrast animals contains very small amount of carbohydrates e.g about 1%. Carbohydrates include glucose (grape sugar), fructose (honey), starch (potatoes), cellulose (wood) and glycogen (liver) etc. Plants use these carbohydrates both as energy sources and as supporting materials while animals, use them for production of energy.

Carbohydrates are the organic compounds of carbon, hydrogen and oxygen. Most of them can be represented by a general formula $C_n(H_2O)_n$, therefore, they were for the first time defined as the hydrates of carbon. For example glucose, $(C_6H_{12}O_6)$ can be written as $C_6(H_2O)_6$. But, however, there are some compounds which are carbohydrates but they do not conform to this general formula for example 2–deoxyribose having molecular formula $C_5H_{10}O_4$ cannot be represented by $C_n(H_2O)_n$ formula. On the other hand, there are also some compounds which follow this $C_n(H_2O)_n$ formula but they are not carbohydrates, for example formaldehyde, CH_2O and acetic acid $C_2H_4O_2$.

On the basis of the above facts, the name carbohydrates is not a correct name to be used for this class of compounds. But this name still persists because it is firmly rooted in the chemical nomenclature. Now carbohydrates are precisely defined as, the poly, hydroxy aldehydes or

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

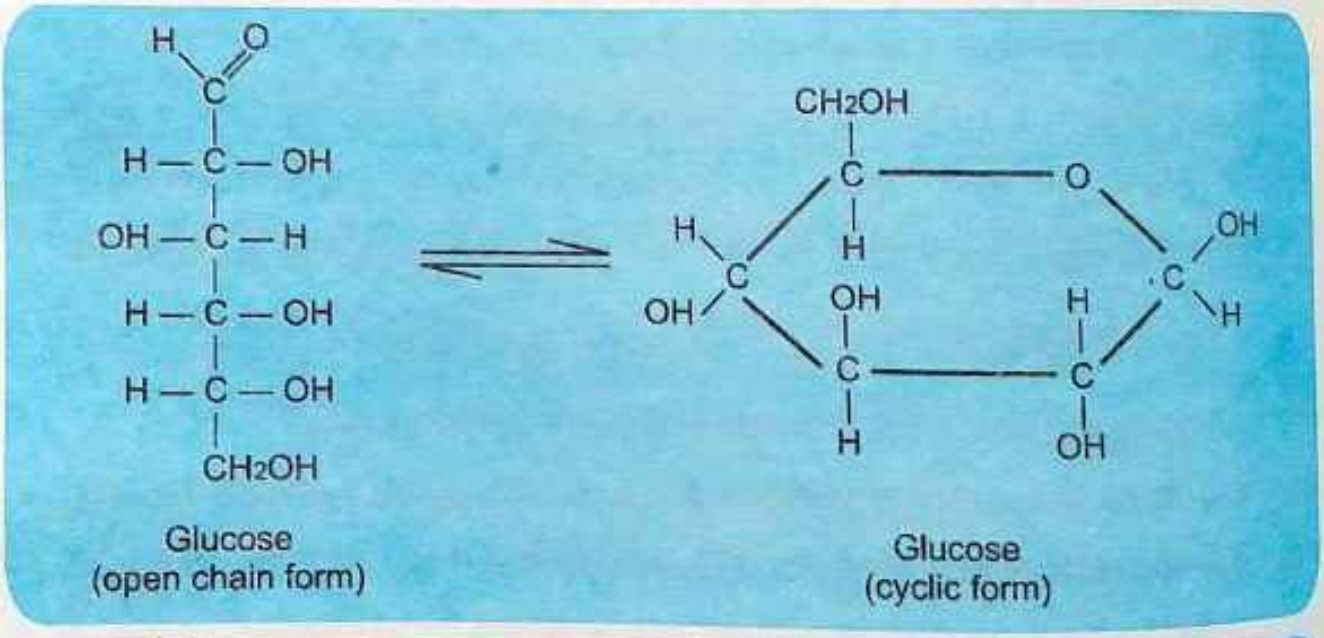
poly hydroxyketones or the molecules which yield these compounds on hydrolysis.

21.1.1 Classification of Carbohydrates:

On the basis of the number of simple sugar units present per molecules, carbohydrates are divided into three major classes. These are,

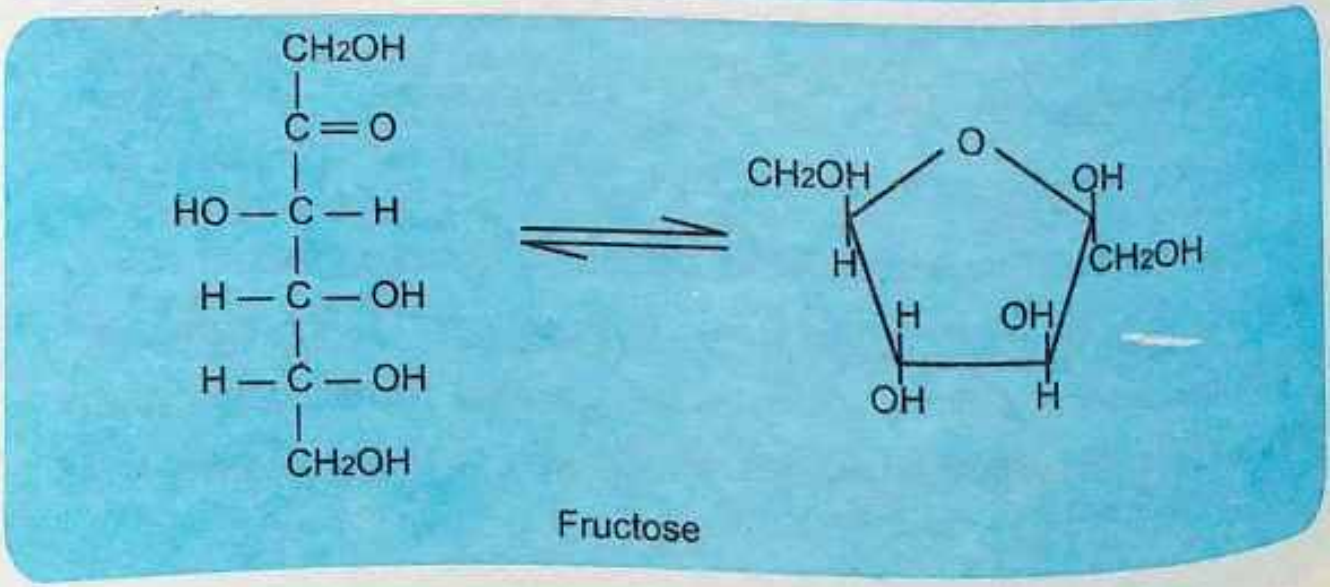
1. Monosaccharides:

They are also called simple sugars. They contain only one sugar unit per molecule. They cannot be broken down into more simpler carbohydrates on hydrolysis. For example, glucose, fructose etc,



Glucose (open chain form)

Glucose (cyclic form)



Fructose

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The monosaccharides are again subdivided on the basis of the type of functional group and the number of carbon atoms in the molecule. On the basis of type of functional group monosaccharides may be classified as aldoses or ketoses.

Similarly on the basis of number of carbon atom in a molecule monosaccharides may be trioses, tetroses, pentoses, hexoses.

2. Oligosaccharides:

These are those carbohydrates which contain 2–10 units of monosaccharides or simple sugars per molecule. They are hydrolysable carbohydrates. They are broken down into two to ten simpler carbohydrates or monosaccharides upon acid hydrolysis. Those oligosaccharides which contain two monosaccharide units per molecule are called disaccharides while those containing three and four units of monosaccharides per molecule are called trisaccharides and tetrasaccharides respectively. Upon hydrolysis they may yield similar or different types of monosaccharides. For example maltose yields the same kind of two glucose units upon hydrolysis.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{(Acid)} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

While sucrose yields two different types of monosaccharides e.g glucose and fructose upon hydrolysis.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{(Acid)} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

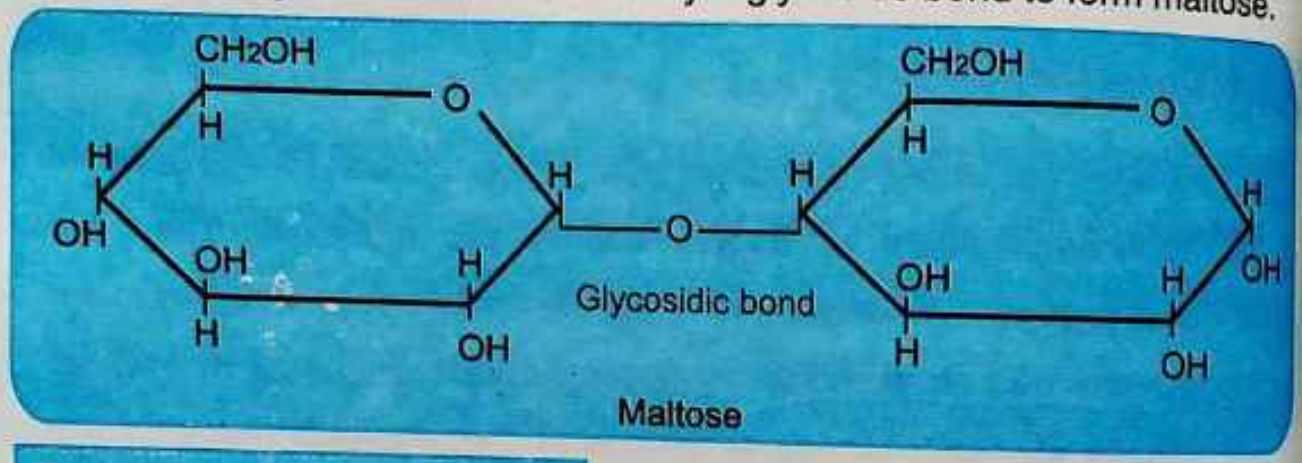
Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Glycoside Linkage or Bond:

During the formation of a disaccharides the two monosaccharide units combine together by an oxygen atom with the elimination of one water molecule. This type of linkage is called glycoside linkage or glycoside bond. This is shown as under.

Similarly two glucose units combine by a glycoside bond to form maltose.



Maltose

3. Polysaccharides:

They are the complex class of carbohydrates. They contain more than ten (10) units of monosaccharides per molecule. They are also hydrolysable. Upon hydrolysis they yield a large number of similar or different kinds of monosaccharides. For example starch, cellulose, glycogen etc.

$$\underset{\text{Starch or Cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{(Acid)} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

21.1.2 Functions of Carbohydrates:

Basic function of carbohydrates is the production of energy for the performance of vital activities in living organisms. They are also known as "fuel of life". They produce energy by the process of oxidation.

$$\text{Carbohydrate} + O_2 \xrightarrow{(Oxidation)} CO_2 + H_2O + \text{Energy}$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

These are chief sources of energy and, therefore spare proteins and lipids for other important functions of the body. Some important uses are given below.

1. Glucose is used as an immediate source of energy for the sick and sportsmen. It is also used in the manufacture of jams and sweets.
2. Fructose is used as a sweetening agent in confectionary, in medicinal syrup. It is also used to prevent sandiness in ice –creams. It is also used as a substitute of table sugar (sucrose) for the obese and the diabetic.
3. Sucrose is used as a food and as ingredient of jams, jellies, confectionaries, syrup. It is also used in the preparation of sucrose octaacetate which is used for the denaturation of alcohols and for making anhydrous adhesives.
4. Starch is principally used as a food. It is industrially used for manufacturing of ethanol by the process of fermentation. It is also used as a stiffening agent in textile industry and in laundry. It is also used as an adhesive to fasten paper.
5. Cellulose has no food value. But it is used as a roughage in our diet for promoting the peristaltic motion of digestive tract. It is used for the manufacturing of paper.
6. Oligosaccharides are involved in the formation of secreted proteins like antibodies and blood clotting factors.
7. The receptors on the cell membranes are the complexes of carbohydrates with certain proteins. The receptors are involved in molecular targeting or molecular recognition.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

8 The derivatives of carbohydrates such as protein glycol heparin sulfate are involved in the attachment or adhesion of neurons to one another during the development of nervous system.

21.1.3 Role of Various Carbohydrates in Health and Diseases:

There are different types of carbohydrates which are involved in the health and diseases of living beings. Some of these are given as under.

1. Sucrose:

Sucrose is a disaccharide. Since long, it has been used as a sweetening agent and as a source of production of energy for living organism. But the use of sucrose is the primary cause of tooth decay and obesity.

The material known as "plaque" which sticks to our teeth is caused by sucrose.

2. Lactose:

It is a disaccharide of glucose and galactose. If is also called milk sugar. It is found in the milk of mammals. Human milk contains about 6.8% while cow milk contains about 4.8% lactose. Lactose is digested by a special type of enzyme called lactase. Lactase is secreted by the intestinal mucosal cells of young mammals. Although milk is a universal food of new born mammals and one of the most complete human diet, still many human adults are unable to digest milk due to deficiency of lactase-intolerance. The general symptoms of this disease are abdominal bloating, cramps, flatulence, colic pains, abnormal intestinal flow, nausea and watery diarrhea. These symptoms appear within 30 – 90 minutes after the ingestion of milk.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

To avoid this disease fermented milk products such as yogurt and cheese should be consumed.

3. Glucose:

It is the most common and popular monosaccharide that can be found in sweet fruits such as grapes, which contains 20 – 30 % glucose. It is mainly used by the living bodies for the production of instant energy. It is an important constituent of human blood. Human blood contains normally about 65 -110 mg of glucose per 100ml. The surplus glucose is converted to a polymer called glycogen in human beings. Glycogen is then stored in the liver and muscles. When the body is deficient in glucose, this liver and muscle glycogen is hydrolyzed to glucose according to the body requirement.

Human pancreas secretes a hormone known as insulin. Insulin helps in the metabolism of glucose to produce energy. In some cases defects in the metabolism of glucose occurs due to which blood glucose level rises from the normal level. This condition results in a disease known as diabetes mellitus.

The consequences of unchecked diabetes include hardening of blood vessels, dysfunction of kidneys, diabetic coma which cause pre–mature death.

21.1.4 Nutritional Importance:

Carbohydrates are the most important energy containing nutrients for living organisms. Plant contains stored carbohydrates called starch while animals contain stored carbohydrates called glycogen. Both these

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

polymers are broken down into the simplest monosaccharide units known as glucose before oxidation. Then glucose is oxidized in the body cells by different types of pathways (series of enzymatic chemical reactions) to release energy. This energy is stored in the form of molecules known as ATP (adenosine triphosphate) in the different parts of the body.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \underset{(ATP)}{Energy}$$

One mole of glucose on complete oxidation by cirtic acid cycle produces 36 ATPs.

21.2 Proteins:

This term protein is derived from the Greek word proteios which means "first, prime or chief", as proteins are of primary importance as food source, in the tremendous variety of physiological functions they perform and as the object of genetically controlled synthesis.

Proteins are complex nitrogenous organic compounds which are associated with the concept of life itself.

By chemical composition, proteins are composed of carbon, hydrogen, oxygen and nitrogen. Percentage of nitrogen is fairly constant and is about 16% of the molecular weight of protein. Some proteins also contain smaller quantities of sulphur and phosphorous. Proteins are large molecules which are made up of smaller basic units called amino acids. There are about 20 different amino acids which combine in different sequence and different numbers and produce an infinite number of

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

different types of proteins. It is analogous to the infinite number of words which can be formed with 26 letters of the alphabets.

The bacterium, Escherichia coli (E. coli) has been estimated to contain about 3000 different types of proteins. Similarly human organism contains about 100,000 different kinds of proteins. But none of the proteins of E. coli is identical with any of the human proteins.

21.2.1 Functions of proteins

1. Proteins are the most abundant intra –cellular macromolecules and form more than 50% of the dry weight of most organisms. They are present in all animals, plants, bacteria and viruses.
2. They act as catalysts in the shape of enzymes, as barriers such as skin and bacterial cell walls, as protective agents in immune system, as storage depots such as ferritin for iron storage in blood, as transporting agent such as hemoglobin as oxygen carrier.
3. They also act as receptors of chemically transmitted informations as well as the carrier of these information in the form of substances known as pheromones.
4. They are also involved in the activities of muscles (contraction and relaxation) and in the transmission of heredity characters from parents to offsprings (in the form of genes).

21.2.2 Classification of Proteins:

Proteins have been classified into the following three major classes.

1. Simple Proteins
2. Compound or Conjugated Proteins
3. Derived Proteins

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Simple Proteins:

These are proteins which upon hydrolysis produce only simple amino acids or their derivatives. Examples of such proteins are Albumins, Globulins, Legumin, Collagen, Globins, Histones etc.

Conjugated Proteins:

The proteins of this group are bonded or conjugated to some non proteins known as prosthetic groups. These are sub divided into the following types.

	Conjugated Protein	Prosthetic Group
1.	Nucleoproteins	DNA or RNA
2.	Phosphoproteins	Phosphoric acid
3.	Lipoproteins	Lipids
4.	Glycoproteins	Carbohydrates
5.	Chromoprotein	Coloured compounds
6.	Metalloproteins	Metals eg. Zn, Cu, Fe, Mn etc.

Derived proteins:

These are proteins which are produced by the partial digestion of simple or conjugated proteins. They may be proteins, meta proteins, coagulated proteins etc.

21.2.3 Structure of Proteins:

Proteins being very complicated macromolecules have very complicated structures. In short all the proteins appear in any of the following four different structures.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

i. Primary Structure:

This structure shows the sequence and number of different amino acid units along the peptide chain. It also shows whether the polypeptide chain is open, branched or cyclic.

ii. Secondary Structure:

X –ray diffraction experiments have shown that long running polypeptide chains tend to twist or coil upon themselves in a special pattern. Secondary structure shows this folding of the polypeptide chain to form a specific coiled structure held together by strong hydrogen bondings. Secondary structure may assume any of the following two different forms.

a) Alpha –helix form b) β – pleated sheets.

iii. Tertiary Structure:

The long polypeptide chain of protein molecule undergo folding and re –folding on itself and gives rise to a definite three dimensional structure. This is called tertiary structure. This structure makes proteins rounded and some what rigid molecule.

iv. Quaternary Structure:

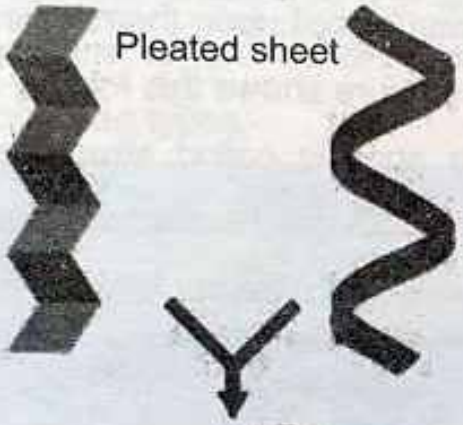
This structure shows the association of many individual protein sub –units, each with its own tertiary structure into a complex functional unit. Examples are myoglobin (oxygen storage) and hemoglobin (oxygen carrier)

Scanned with CamScanner

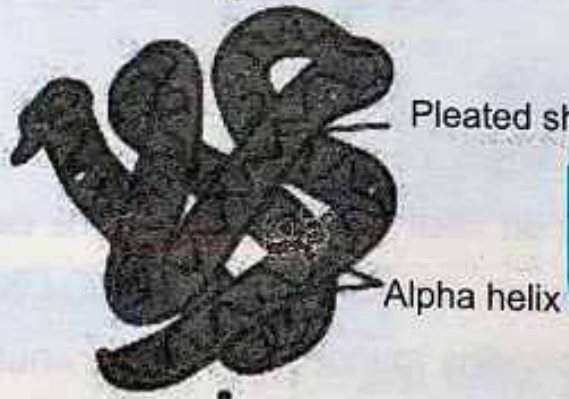
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



Primary protein structure
is sequence of a chain of amino acids.



Secondary protein structure
occurs when the sequence of amino acids are linked by hydrogen bonds.



Tertiary protein structure
occurs when certain attractions are present between alpha helices and pleated sheets.



Quaternary protein structure
is a protein consisting of more than one amino acid chain.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

21.2.4 Properties of Proteins:

i. They are complex heavy molecular weight organic compounds.

ii. They are amphoteric in nature because they contain both acidic (–COOH) and basic (amino) group. They react with both acids and bases.

iii. They can be precipitated from their solution by salts of heavy metals, heat and alcohols etc.

iv. When proteins are strongly heated or treated with certain reagents they lose their structural organization and their biological functions. This is known as coagulation of proteins.

21.2.5 Importance of Proteins:

Proteins are the most significant biological compounds of living beings. These are most critical to life and perform different types of functions. Some of these are.

i. Many of the proteins act as living catalysts called enzymes. These enzymes increase the rate of biological reactions to the extent required by the body.

ii. The nucleoproteins act as carrier of genetic information or characters. They serve as basis of inheritance of traits.

iii. Hormones are proteins in nature. They regulate the growth of living organisms and control a number of other physiological functions.

iv. Some proteins serve as carrier of different substances inside the body. For example haemoglobin (heme containing protein) acts as

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

carrier of oxygen, ceruloplasmin acts as carrier of copper in the blood plasma.

v. Some proteins contribute to the structure of tissues for example collagen, elastin and keratin.

vi. Proteins play vital role in the immune system of living organisms.

21.3 Enzymes:

The catalysis of biological reactions is probably the most important task assigned to proteins by nature. Hundreds of biological reactions are taking place every minute in different parts of the body for obtaining energy, synthesizing the protoplasmic and other structural materials, digestion, absorption and assimilation of food etc. These and so many other biological reactions are catalyzed by certain special proteins known as enzymes. The word enzyme was originated from a Greek word "en" means "in" and 'zyme' means yeast after studying the catalytic properties of yeast. Enzyme is defined as a complex organic substance which alter the rate of an already initiated biochemical reaction without itself being altered permanently during the reaction. Enzymes are soluble, colloidal organic catalysts produced by living cells but they are capable of acting independently of the cells. Most of the enzymes are protein in nature and show all the properties of proteins. They are precipitated by the usual protein precipitating agents. They are non–hydrolysable with nitrogen contents of about 16%. They are de–activated by extreme alteration of pH and high temperature. Enzymes are highly specific in nature. It means that

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

an enzyme can work only for one type of reaction in the body. The substance upon which an enzyme acts is called substrate of that enzyme.

21. 3.1 Role of Enzymes as bio-catalyst:

Enzymes are playing the decisive role in the digestion of food in different parts of the alimentary canal. For example

In the Digestion of Carbohydrates:

After ingestion food meets saliva. Saliva contains an enzyme called salivary amylase or ptyalin. This enzyme catalyses the hydrolysis of carbohydrates of food without affecting proteins and fats. When food reaches stomach, the action of amylase comes to an end due to acidic pH of the stomach. When food enters the intestine, pancreatic juice is secreted. This juice contains pancreatic amylase which has the same action as salivary amylase.

In the Digestion of Fats:

There is only slight hydrolysis of fats in the mouth and stomach because no lipase is secreted by the salivary glands while the lipase of the gastric juice is weak and can hydrolyse only small fat molecules. The lingual lipase enzyme secreted by the Ebner's glands on the dorsum of the tongue remains active in stomach and can hydrolyse or digest about 30% of the ingested fats. When the fats reaches the intestine, they face pancreatic juice. This juice contains a pancreatic lipase enzyme also known as steapsin. This enzyme completely hydrolyses or digests all the fats of the food.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

In the Digestion of Proteins:

Digestion of proteins starts in stomach because the saliva contains no enzymes for the digestion of proteins. The first enzyme that acts upon the proteins of the ingested food is called pepsin present in the gastric juice of stomach. It is best active in acidic pH of 1–2 range. Pepsin has also milk curdling properties.

When food enters the intestine, pancreatic juice comes into action. This juice contains numerous enzymes for the digestion of proteins. These enzymes include trypsin, chemotrypsin. These enzymes are secreted in their inactive forms which are then activated by the action of other enzymes. For example the inactive trypsinogen is activated to active trypsin by the action of enzyme enterokinase. Besides, trypsin and chymotrypsin pancreatic juice contains, carboxypeptidase's A and B, elastase, collagenase etc.

21.3.2 Factors Affecting Enzyme Activity:

A number of factors influence the activity of enzymes. Some of these are.

i. Effect of Temperature:

Temperature is an important factor in both for enzymatic and non –enzymatic reactions. This is because temperature increases or decreases the kinetic energy and hence changes the number of fruitful collisions among reactants. Enzymatic reactions, being chemical in nature, their rates increase with increase in temperature. But it holds good upto a certain increase in temperature. Above that temperature the enzymes undergo denaturation and their activity decreases rapidly. On the other

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

hand, decreasing the temperature, the activity of the enzyme is decreased. An enzymes becomes less active when cooled and is altogether inactive at 0°C. But their activity can be restored by raising the temperature. Enzymes can be stored for years in frozen state.

The temperature at which the enzymes shows maximum activity is called optimum temperature. For most animal enzymes optimum temperature is around body temperature (37°C). Some plants enzymes such as urease has optimum temperature even upto 60°C. If we plot a graph between temperature and rate or velocity of enzymatic reaction we get the curve as shown in the figure21.1

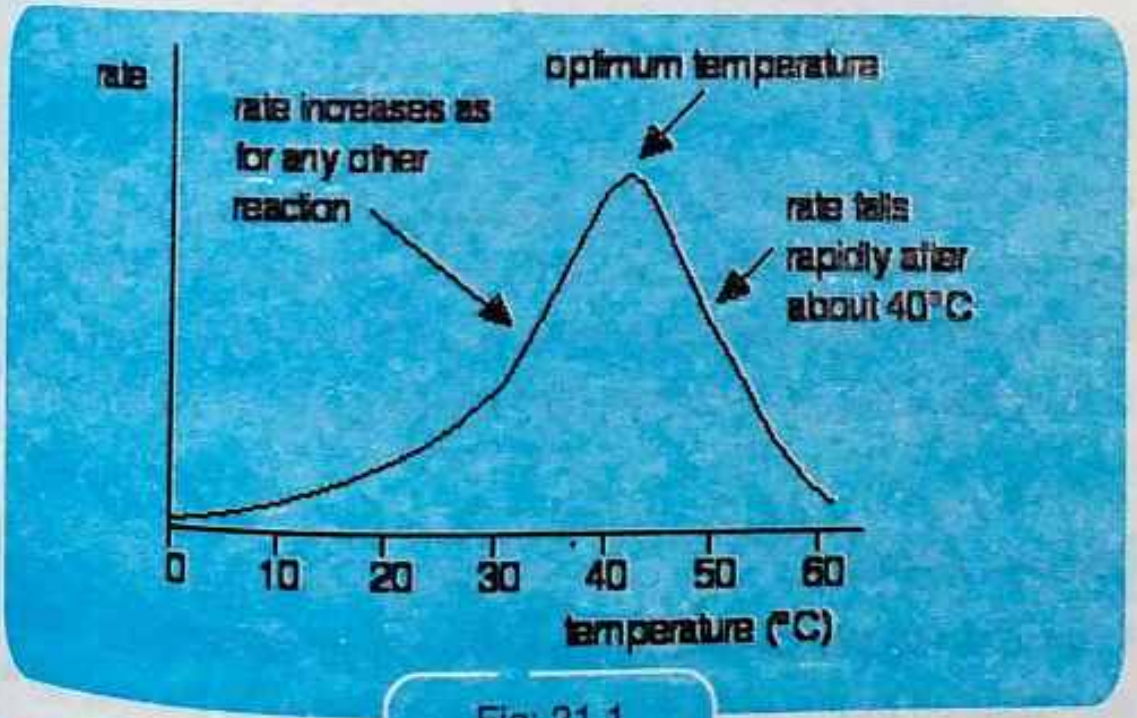


Fig: 21.1

ii. pH:

Some enzymes work best in an alkaline pH while others in acidic pH. For every enzyme there is a pH at which it shows the maximum activity. This pH is called optimum pH. For example the

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

optimum pH of pepsin is around 2.0 while that of trypsin varies from 8–9 pH. There is a pH below which the enzyme loses its activity and at which the enzymes shows the lowest activity. This pH is called minimum pH. Most of the enzymes have optimum activities in the range between 5–9. Pepsin is an exception to this rule Plotting a graph between enzyme activity and pH, we get a curve as shown in the figure 21.2.

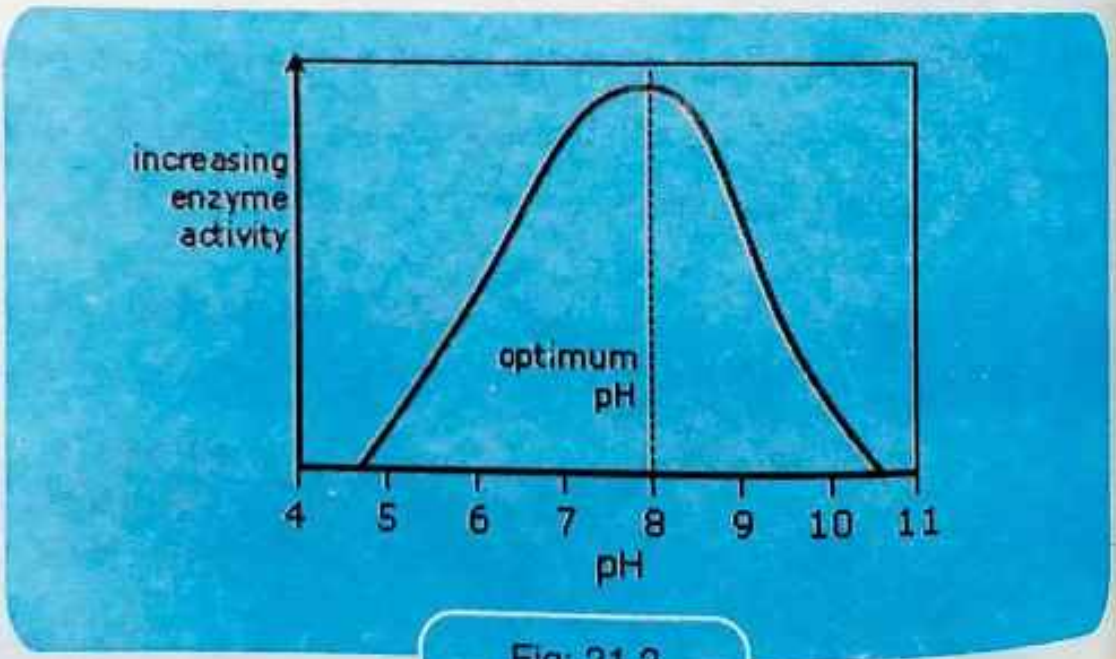


Fig: 21.2

Enzyme Inhibition:

The process by which the activity of an enzyme is decreased or inhibited by the addition of certain substances to the reaction is called enzyme inhibition. The different substances which inhibit the activity of enzymes are known as inhibitors. There are two major types of enzyme inhibition. These are

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

I. Irreversible Inhibition:

When the inhibitor reacts and form a strong covalent bond with the active site of the enzyme this is termed as irreversible inhibition. The inhibitors forms a stable and irreversible complex with the enzyme. This complex con not be broken down by physical or chemical methods to restore the active form of the enzyme.

II. Reversible Inhibition:

It is a temporary type of inhibition. That is the activity of the inhibited enzyme can be restored or the inactive form of the enzyme can be converted back to the same active form. It is sub –divided into.

(a) Competitive Inhibition:

The inhibitor competes with the substrate for the active sites of the enzyme. The inhibitor binds to the same active sites of enzymes to which the actual substrate binds. By this way the active sites of the enzyme are blocked and then the substrate is unable to bind to the enzyme.

(b) Non – Competitive Inhibition:

The inhibitor has no structural resemblance with the substrate of the enzyme and, therefore, does not compete with the substrate for the active sites of the enzyme. The inhibitor does not bind to the active sites of enzyme. Inhibitor binds to the site other than active sites of the enzyme therefore, two complexes the enzyme – substrate and enzyme – substrate inhibitor are formed.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

(c) Uncompetitive Inhibition:

In this type, the inhibitor does not react directly with the enzyme but it binds to the enzyme substrate complex.

21.3.3 Industrial application of Enzymes

Enzymes are used in the chemical industry and other industrial applications when extremely specific catalysts are required.

Useful enzymes are obtained from both plants and animals, but most enzymes are obtained from microorganisms, mainly bacteria and fungi. Some applications of enzymes are given below:

1. Biological detergents: Most of the enzymes for washing come from bacteria adapted to live in hot springs. The enzymes are used for presoak condition and direct liquid applications helping removal of protein and starch stains. They are also able to digest fat, oil and grease stains.

2. Fruit Juice production: During the manufacture of fruit juice the cells of the fruits have to be broken down before the bulk of the juice can be extracted. Plant cell wall is built of cellulose fibres which are held together by pectins and hemicelluloses and they are extremely tough. When very high temperatures are used to break down the fruit tissues, this will affect colour and flavor of the juice. Instead, the fruit is crushed and enzymes preparation containing cellulases and hemicellulases are added. These cause cell wall break up and most of the liquid is released.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

3. Production of Ethanol: In Biofuel industry, cellulase are used to break down cellulose into sugar and which can then be fermented to produce ethanol.

4. High Fructose syrup: A sweetner that is widely used in food and drinks is high fructose corn syrup. It is manufactured from starch in corn fruit. The grains are milled to a starch slury and the enzyme amylase is added. Finally the syrup is passed down a column of immobilized glucose isomerase enzymes. This converts much of glucose to fructose. It is added to sweeten foods without adding too many calories.

5. Paper Industry: In paper industry enzymes like amylases, xylanases, cellulases and ligninase are used. Amylases degrade starch to lower viscosity, aiding sizing and coating of paper. Xylanases produce bleach required for decolourizing. Cellulases smoothen fibers, enhance water drainage and promote ink removal. Lipases reduce pitch and lignin degrading enzymes remove lignin to soften paper.

21.4 Lipids:

Lipids are a heterogeneous class of organic compounds. They are greasy substances which are relatively insoluble in water but considerably soluble in organic solvents like ether, chloroform benzene etc. Lipids perform several important functions in living organisms. They act as storehouses of metabolic energy, as structural components of membranes, as protective and insulating coatings. Nervous tissues are rich in lipids where they play important role in their functions. The sub–cutaneous fat serves the role of insulating

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

against atmospheric heat and cold. Lipids may be saponifiable or unsaponifiable. Fats, oils and and waxes are saponifiable while terpenes and steroids are unsaponifiable lipids.

21.4.1 Classification of Lipids:

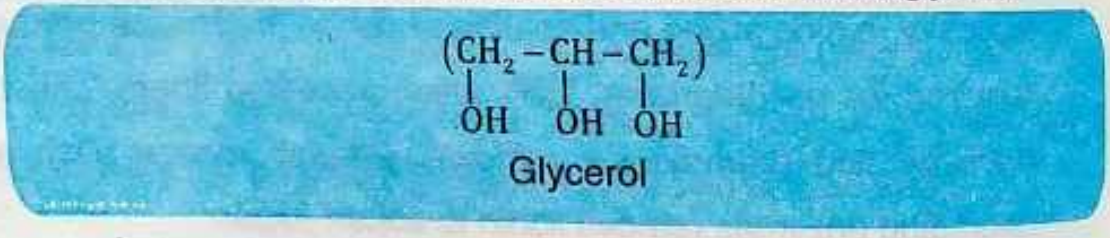
Lipids have been classified into the following three major classes.

1. Simple Lipids:

These are the esters of fatty acids with different types of alcohols. These include.

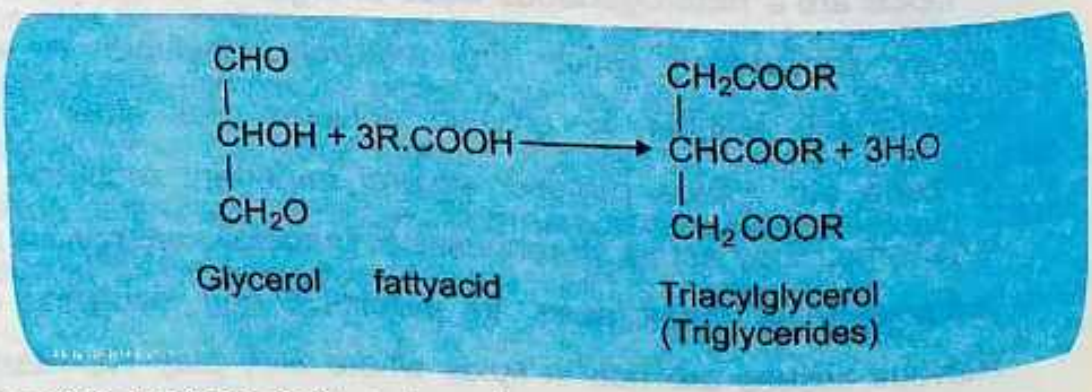
i. Fats and Oils:

These are the esters of fatty acids with trihydroxy alcohol called glycerol



Glycerol

Fat is solid at room temperature while oil is liquid at room temperature. Oils contain more unsaturation in the alkyl part of fatty acids than fats. These are also known as triglycerides or triacylglycerols.



Glycerol fattyacid Triacylglycerol (Triglycerides)

Fatty acids are long chain carboxylic acids containing usually 12–18 carbon atoms per molecule.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

ii. Waxes:

These are the esters of fatty acids with high molecular weight monohydroxy alcohols. For example bee wax carnauba wax etc.

2. Compound Lipids:

These are the esters of fatty acids with alcohols containing some additional groups, as well. They are further divided into

i. Phospholipids:

These lipids contains fatty acids, phosphoric acid, nitrogenous bases alongwith some other constituents. They are also called phosphatide.

ii. Glycolipids:

They contain fatty acid, alcohol and carbohydrate. They are present in large amount in the white matter of the brain and in the myelin sheaths of nerves.

iii. Sulpholipids:

They contains a sulphate group in addition to fatty acids, alcohol and carbohydrate.

iv. Lipo–proteins:

These are the complexes of lipids with proteins.

3. Derived Lipids:

These are the substances derived by the hydrolysis of simple and compound lipids. These include fatty acids, alcohols, mono and triglycerides, steroids, terpenes and arytenoids.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

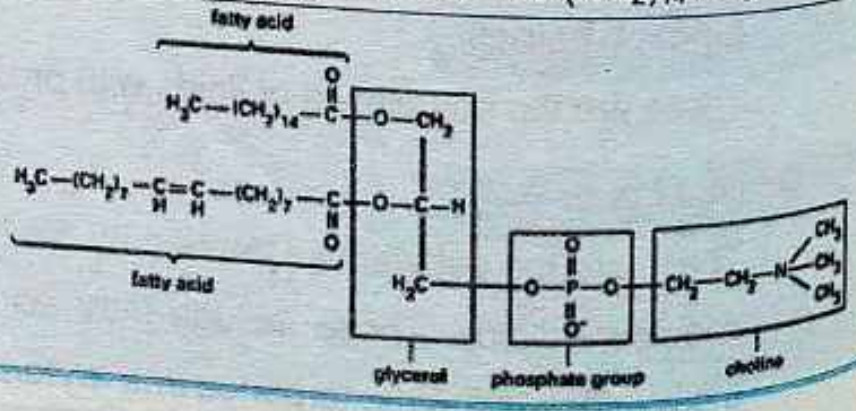
21.4.2 Structure:

Lipid has no common structure. The most common occurring lipids are triglycerides and phospholipids.

Triglycerides are fats and oils. Triglycerides have a glycerol backbone bonded to three fatty acids. If the three fatty acids are similar, the fats are called simple triglycerides. If the fatty acids are not similar, they are known as mixed triglycerides.

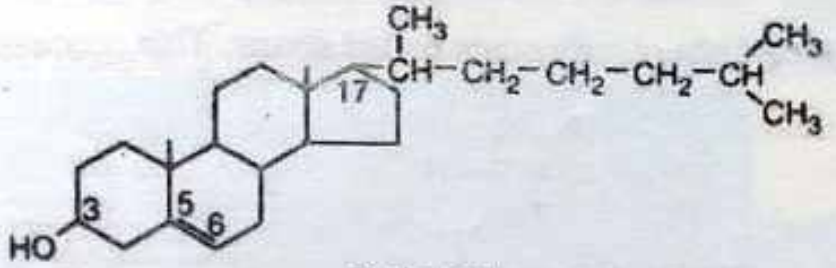
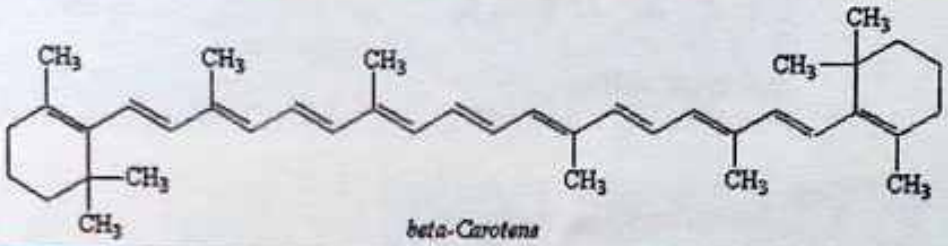
The second most common lipids are phospholipids. They are found in cell membrane of animals and plants. Phospholipids contain glycerol and fatty acids as well as phosphoric acid and low molecular weight alcohol.

Some lipids and their structures are given in table.

Name of Lipid/ Fatty acids	Structure
Stearic acid	$CH_3(CH_2)_{16}COOH$ (saturated)
Oleic acid	$CH_3(CH_2)_7$ $(CH_2)_7\,COOH$ $C = C$ $H \quad H$
Wax (From bee hive)	$CH_3(CH_2)_{28}\,CH_2 - O - C\,(CH_2)_{14}CH_3$ (O double bonded to C)
Phospholipids	

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Cholesterol	 Cholesterol
β-carotene	 beta-Carotene

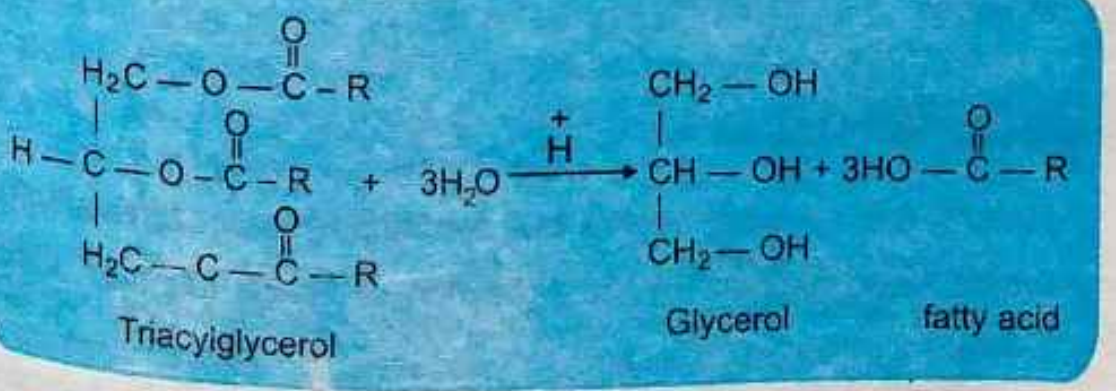
21.4.3 Physical Properties:

1. Natural fats are colourless, odourless and tasteless.
2. They are insoluble in water but are highly soluble in organic solvents like benzene, ether, chloroform etc.
3. They have well defined melting and solidifying points.
4. They have low specific gravity and, therefore, float on the surface of water.

21.4.4 Chemical Properties:

1. **Hydrolysis:**

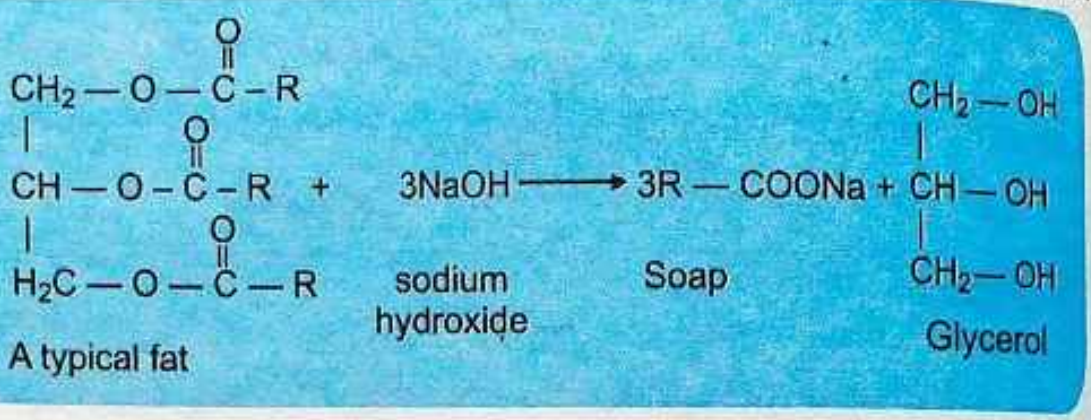
Natural fats undergo hydrolysis with acids or bases in boiling water where they produce free acids and glycerol.



Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

In case of base hydrolysis, the base reacts with free fatty acids and produce salts of fatty acids called soaps. This process is called saponification.



2. Addition Reactions:

Unsaturated fatty acids of fats and oils undergo addition reactions at the points of unsaturation and produce addition products. The oils which contain more unsaturation are hydrogenated to produce solid ghee. By this way inedible and cheap oils such as cotton seed oils are hydrogenated and converted to solid and edible ghee.

3. Oxidation:

Fats rich in unsaturated fatty acids (linseed oil) undergo spontaneous oxidation at their double bonds and produce aldehydes, ketones and resins. They form a thin transparent coating on the surface to which the oil is applied. These are known as drying oils. They are used in manufacture of paints and varnishes.

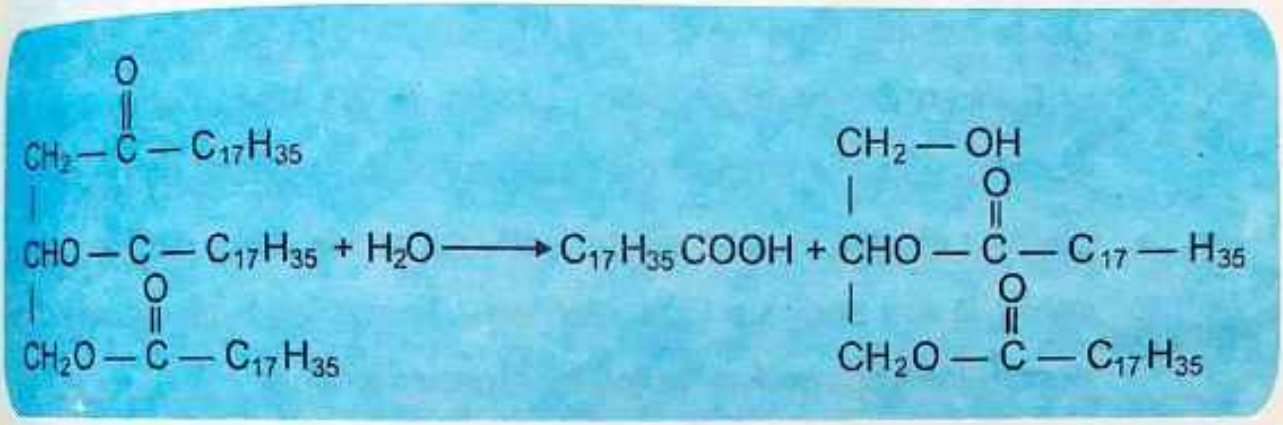
4. Rancidification:

Natural and specially animal fats contains lipase enzyme. By the action of atmospheric oxygen, in the presence of lipase the fats undergo partial

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

hydrolysis and oxidation at their double bonds. This produces volatile carboxylic acids of sour taste and unpleasant smell. This process is called rancidification and the fat is said to have become rancid.



Tristearian + H_2O ⟶ Stearic Acid + Distearian

SST

Society, Technology and Science

Insulin is peptide hormone secreted by the Beta cell of pancreatic islets of Langer Hans and maintain blood glucose level by facilitating cellular glucose uptake, regulating carbohydrate and lipid and protein metabolism.

Diabetes miletus is the group of metabolic disease in which patient has high blood sugar level which is either due to the fact that pancreas does not produce enough insulin or cells do not respond to the insulin that is produced.

Cholesterol is the precursor of five major classes of steroid hormones, progesterone, glucocorticoids, mineralocorticoids, androgen and estrogen. These hormones are powerful signal molecules. While aminoacid derivatives hormones are commonly derived from tyrosine and tryptophan. The tyrosine derived hormones are thyroid hormones and catecholamines.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

21.4.5 Nutritional and Biological Importance of Lipids:

Lipid perform a number of different functions in living organisms. Some of these are listed below.

- Lipids provide food which is highly rich in calorific value. One gram of lipid on complete oxidation produces 9.3 kcal of heat which is about double the amount produced by carbohydrates and proteins.
- Lipids are insoluble in water and, therefore, they can be stored easily in the body as food reserves. These food reserve are then used by the organisms during hibernation periods.
- Lipids in association with different proteins form the important constituents of cell membranes.
- Fats have high insulating capacity. Great quantities of fats are deposited in the sub–cutaneous layers in aquatic mammals such as whale and in animals of cold climates. These fat deposits protect these animals from severe cold and severe temperature changes.
- Some lipids specially phospholipids play a key role in the absorption and transportation of fatty acids in the body.
- Sex harmones, adrenocorticoids, cholic acids are synthesized from a steroidal lipid known as cholesterol.
- Lipids serve as carrier of fat soluble vitamins such as vitamin A,D and E in the body.
- Squealing, a steroid present in the blood of shark has antibiotic and antifungal properties. This explains why sharks rarely contract infections and almost never get cancer.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

21.5 Nucleic Acids:

Friedrich Miescher a 25 year old Swiss chemist isolated nuclei from pus cells (white blood corpuscles). He found that these nuclei contained an unknown phosphate rich substance. He named it as nuclein. This newly discovered substance was quite different in properties from carbohydrates, proteins and fats. He also isolated a nucleoprotein complex from ripe salmon sperm. It was a basic protein which he named protamine. It was Altmann who for the first time used the word nucleic acid in 1889. He also discovered the existence of two different types of nucleic acids namely DNA (deoxyribonucleic acid) and RNA (ribonucleic acid). Later on Watson and Crick determined the structure of nucleic acids. They are present in every living organism as well as in viruses. They have been found to be the essential substance of the genes and the apparatus by which the genes act or express themselves. They contain in their structure the blueprints for the normal growth and development of each and every organism. They are responsible for storing, expressing and transmitting genetic information and mutation in living organisms.

21.5.1 Types of Nucleic Acids:

There are two different types of nucleic acids. DNA (deoxy ribonucleic acid) it is present in nuclei and in some viruses. It is the main constituent of chromosome.

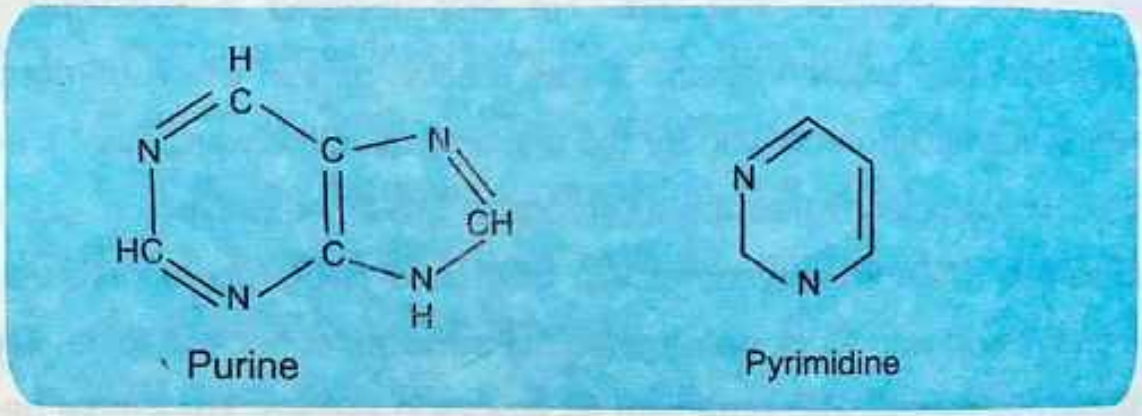
RNA (Ribonucleic acid) is present in the cytoplasm and in some viruses.

Scanned with CamScanner

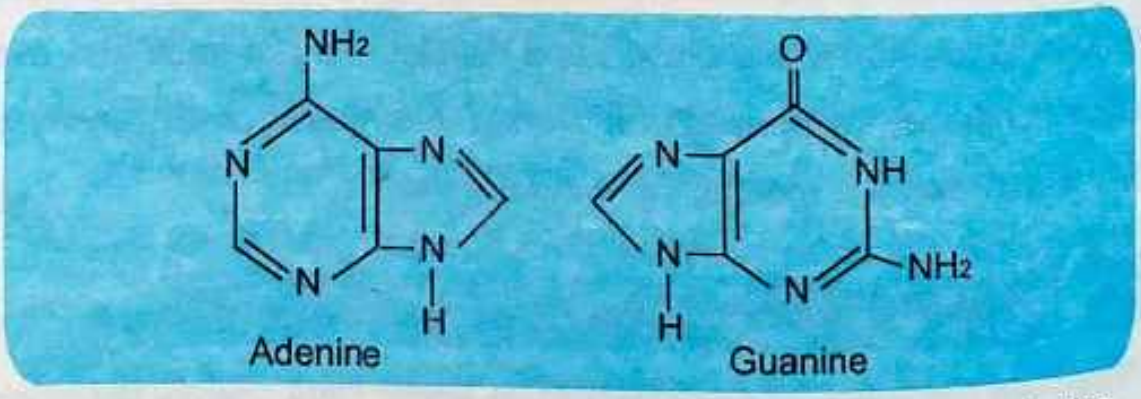
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

21.5.2 Structural Components of DNA and RNA:

Both DNA and RNA are formed by the polymerization of large number of units known as nucleotides. That is why DNA and RNA are polynucleotides. A nucleotide is composed of a nitrogenous base, a sugar and a phosphate group. DNA differs from RNA in the type of nitrogenous base and type of sugar unit. The nitrogenous bases are of two types, purine and pyrimidine.



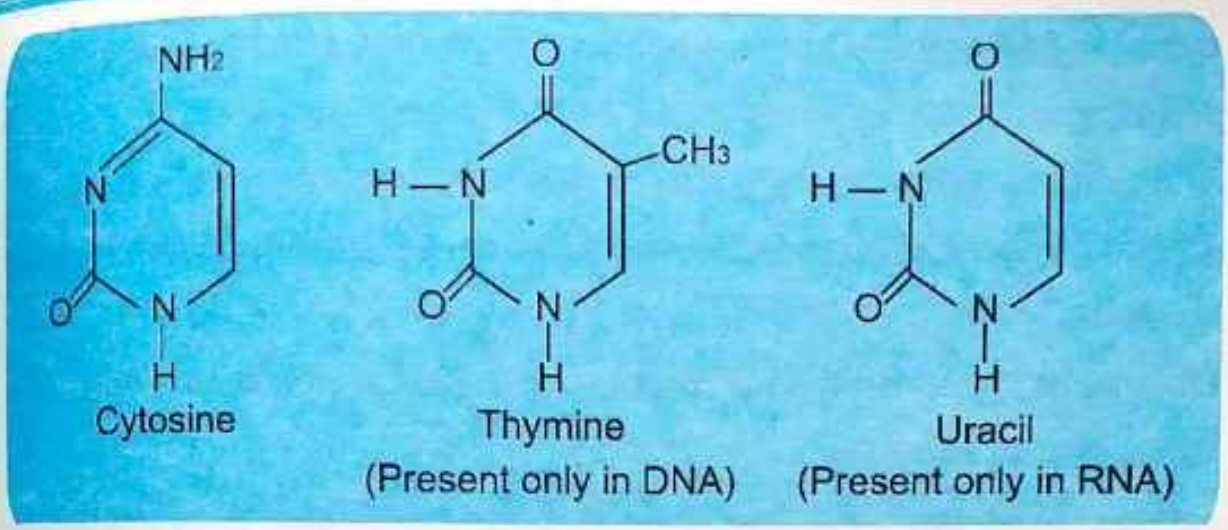
There are two different types of purine derivatives. These are adenine and guanine.



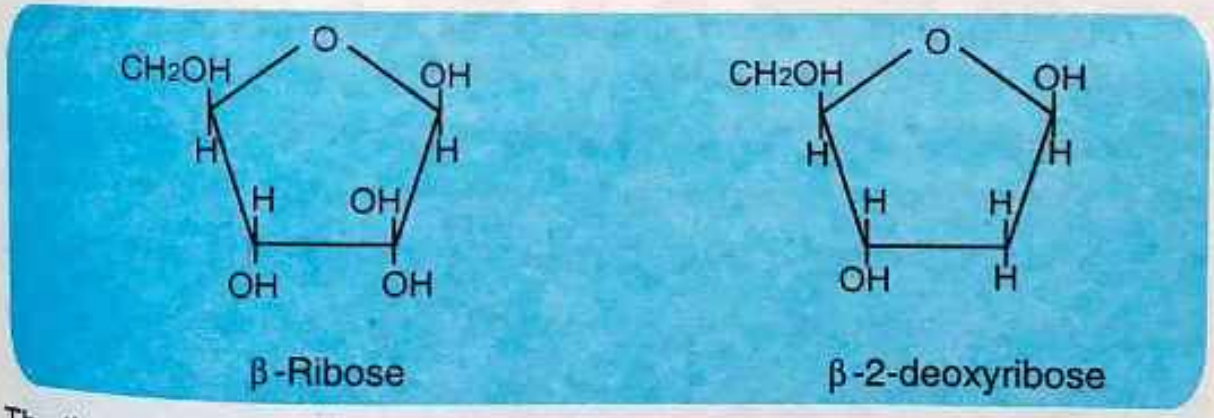
Similarly there are three derivatives of pyrimidine. These are cytosine, thymine and uracil.

Scanned with CamScanner

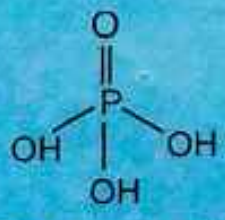
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



DNA and RNA contain two different types of sugars. One is deoxyribose and the other is ribose sugar. Both these sugars are in cyclic furanose form.



The third component of nucleic acid is phosphoric acid



21.5.3 Difference between DNA and RNA

1. The DNA differs from RNA in the sense that the pyrimidine bases of DNA are cytosine and thymine while the pyrimidine bases of RNA are

Scanned with CamScanner

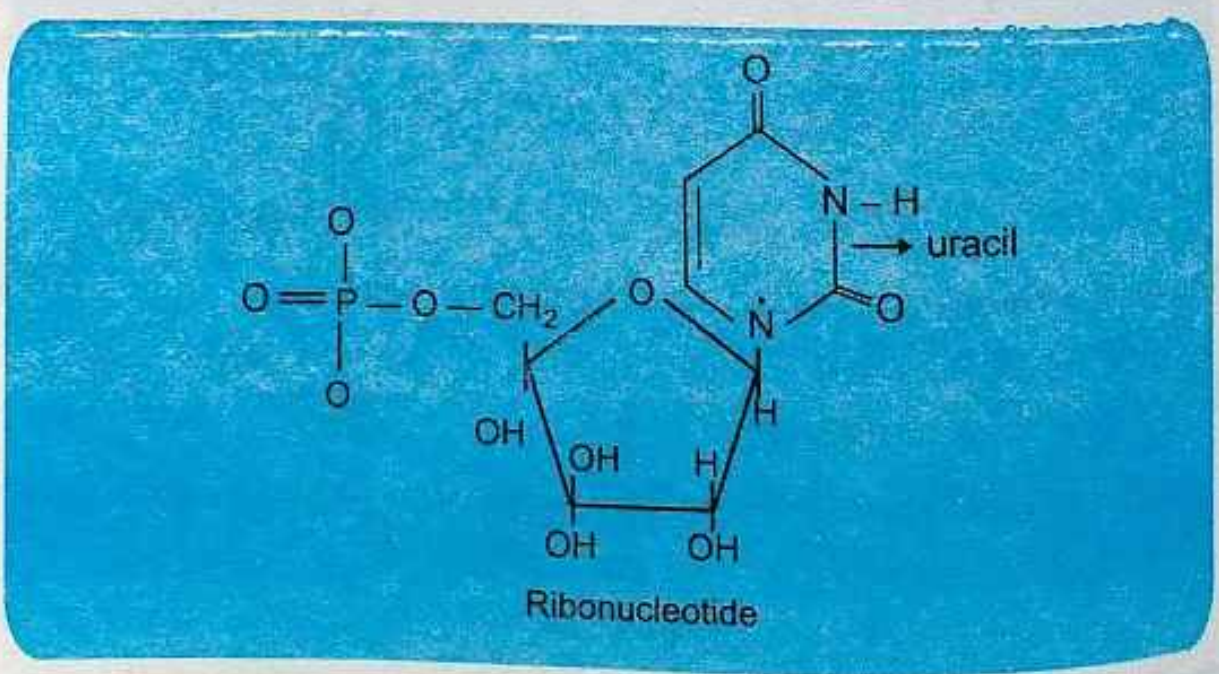
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

cytosine and uracil. On the other hand both DNA and RNA contain the same types of purine bases called adenine and guanine.

2. The pentose sugar of DNA is deoxyribose while that of RNA is ribose.
3. DNA is a double stranded molecule while RNA is a single stranded molecule.
4. DNA is mainly present in the nucleus while RNA is mainly present in the cytoplasm of the cells.

Both DNA and RNA are polynucleotide molecules. A nucleotide is formed by the combination of nitrogenous base (Purine and Pyrimidine), ribose sugar (ribose or deoxyribose) and phosphoric acid.

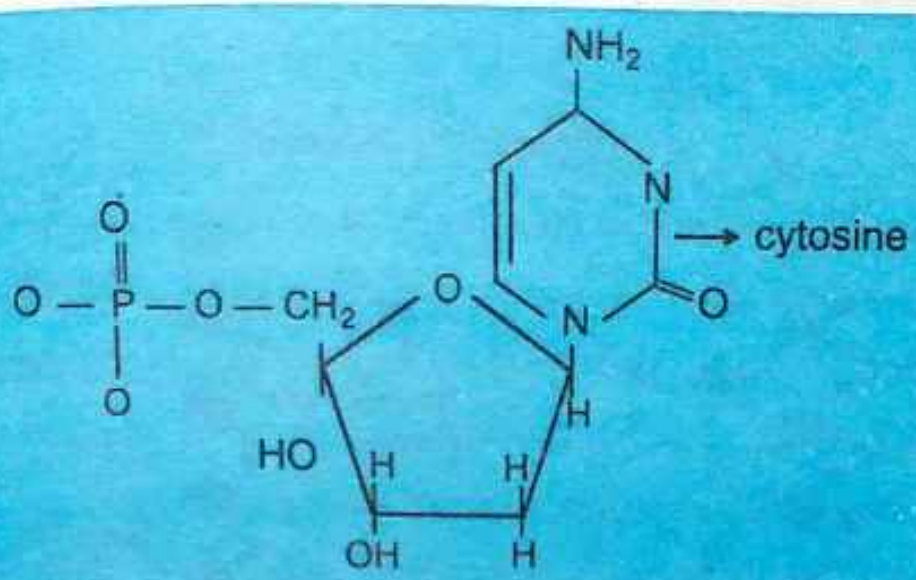
Nucleotide = Nitrogenous Base + Sugar + Phosphoric acid. DNA is made up of repeating units of deoxyribonucleotides while RNA is a polyribo nucleotide.



Ribonucleotide

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



Deoxyribonucleotide

A DNA molecule is formed by two antiparallel long polyde oxyribonucleotide chains which wind on each other. These two chains are held together throughout the whole length by hydrogen bondings present between their nitrogenous bases. Adenine joins only to thymine while guanine joins only to cytosine. Adenine joins to thymine by two while cytosine joins to guanine by three hydrogen bondings. This pairing of bases is highly specific. Adenine will never join cytosine and guanine never joins thymine.

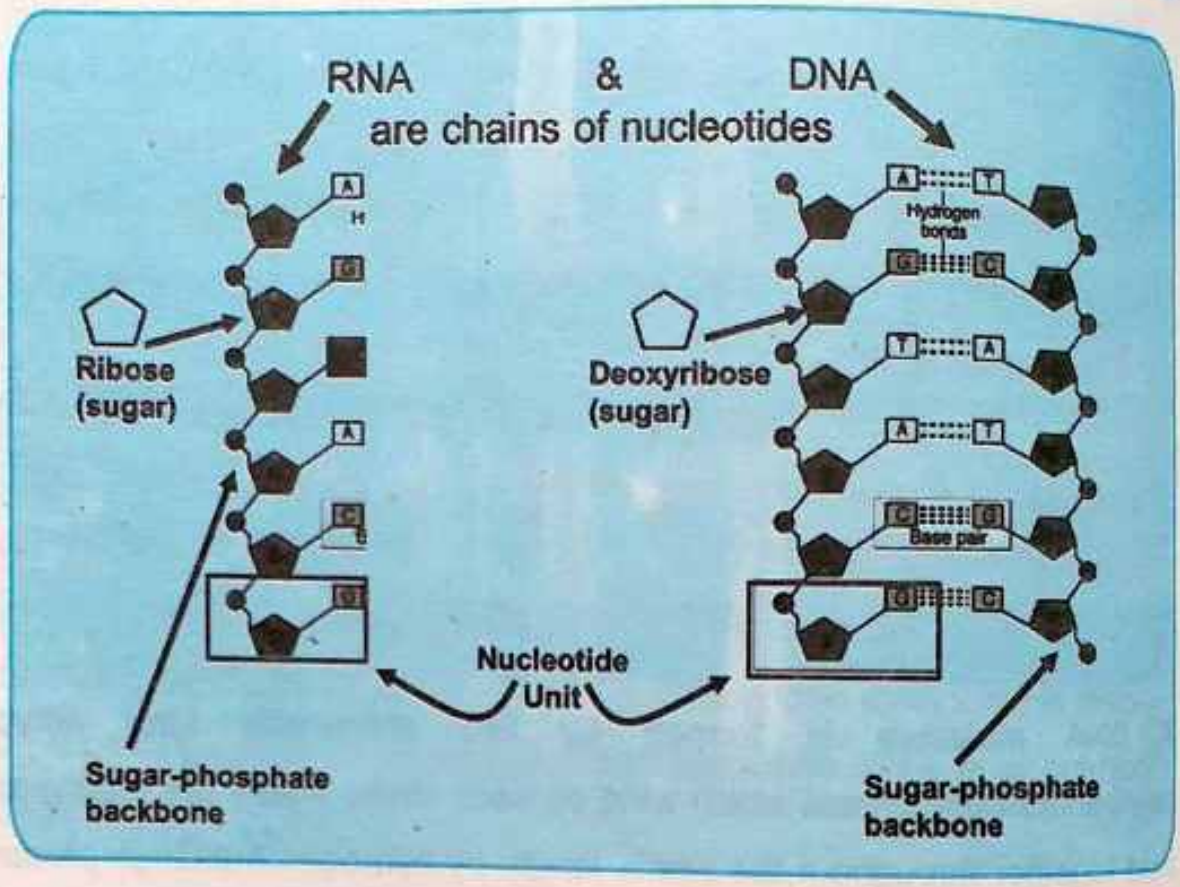
21.5.4 Nucleic Acid Polymers

Monomer means one unit, while polymer means many units. In chemistry many compounds are polymers (large molecules) that consist of repeating, identical or very similar units.

Nucleic acid polymers are DNA or RNA. The polymer DNA has deoxyribonucleotides as its monomer. While polymer RNA has ribo nucleotides as its monomers.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



21.5.5 Storage of Genetic Information:

DNA is the ultimate carrier of heredity in all the living organisms. Genes are composed of DNA which contains genetic information in the form of codes. A sequence of three nitrogenous bases on DNA strands contains code for one amino acid synthesis of proteins which occurs inside ribosomes present in the cytoplasm of living cells. The information stored in the form of genes which are parts of DNA are transmitted to the cytoplasm in the form of messenger RNA or mRNA. There is another type of RNA called transfer RNA (tRNA) which reads out the message of mRNA and brings the amino acids to the ribosome in the form of amino acid tRNA complexes. Then these amino acids are incorporated into the peptide chain. This process is called translation.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

21.6 Minerals of Biological Significance

21.6.1 Sources of Important Minerals

Minerals essential for life are the inorganic nutrients, which are needed by living organism for vital functions but cannot be synthesized by them. They are naturally present in the soil and river water. Plants take up minerals from the soil. Animals get their minerals in drinking water and eating plants as food. We receive these inorganic substances from both animals and plants in our diet. Sometimes drinking water also supplies appreciable quantity of minerals. Purified salts such as NaCl is used in food preparation is also good source of minerals for human consumption.

Minerals are mainly classified as macronutrients (calcium, phosphorus, magnesium and sulphur etc) and micronutrients (Iron, zinc, Iodine, cupper and manganese).

21.6.2 Biological significance of Iron, Calcium, Phosphorus and Zinc

1. Iron:

Iron is one of the important element because it is a part of haemoglobin, a carrier of oxygen in the body. An adult man requires about 10mg of iron in his daily diet. Growing children, pregnant and lactating women require greater concentrations of iron due to the loss of blood in menstruation. Liver, heart, kidney, egg yolk, green leafy vegetables, wheat etc. are good sources of iron. The daily synthesis of haemoglobin, requires about 27mg of iron but the same quantity of iron is liberated by the break down of body haemoglobin, therefore, only a small quantity of iron is required unless there is a loss of blood from the body. About 300 mg of iron is transferred to the fetus in

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

uterus. Since there is no loss by excretion, therefore, this amount is sufficient during uterine life.

Deficiency of iron produces a disease called anemia. This may be due to the lack of iron in the diet or a deficiency in its absorption by the body.

Excess of iron is stored in the form of hemosiderin in the skin, pancreas, liver, spleen etc. This leads to bronzed appearance of the skin, diabetes mellitus and cirrhosis. This state is called hemochromatosis or hemosiderosis.

2. Calcium:

Calcium is present in largest quantity on account of being the main constituent of bones and teeth. About 1 kg of calcium is present in man, 99% of which is present in bones in the form of hydroxyapatite crystals. Small amount of calcium is also present in blood. The main sources of calcium are milk, and milk products, egg yolk, legumes, nuts and green leafy vegetables.

Calcium is required for the regulation of a large number of cellular activities, muscle and nerve functions, hormonal action, blood coagulation and cell motility. Increase in the concentration of calcium in plasma leads to a condition known as hyperparathyroidism. Decrease in plasma calcium level leads to a condition known as hypocalcaemia.

3. Phosphorous:

Phosphorous is also the major constituent of bones and teeth. It is present in all the body cells in association with proteins, lipids and carbohydrates in the form of phosphoproteins, phospholipids and similar

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

compounds. It has a unique role in the storage and transformation of energy in the body.

An adult requires about 800mg per day of phosphorous. It is present in association with calcium in its sources. Proteins of food also provide good amount of phosphorous to the body. An increase in the plasma phosphate level due a decrease in its excretion leads to kidney dysfunction. But a decrease in the plasma phosphate level due to an increase in its excretion leads to renal rickets.

4. Zinc:

Zinc is an important element for the normal growth, reproduction and longevity of animals. It is a constituent of several types of enzymes such as alkaline phosphatase, carbonic anhydrase etc. It also forms a complex with insulin and helps in its storage and release according to the need of the body. It is also required for maintaining the plasma concentration of vitamin A.

The different sources of zinc include, meat, liver, eggs, fish, milk and cereals.

Deficiency of zinc results in delayed wound healing and impairment of acuity of taste.

Scanned with CamScanner

Key Points:

- Biochemistry studies the chemistry of life.
- Carbohydrates, proteins, lipids, nuclic acids and enzymes are called biomolecules.
- Carbohydrates are organic compounds of carbon, hydrogen and oxygen and have general formula $Cn(H_2O)_n$.
- Carbohydrates are classified into monosaccharide, oligosaccharide and polysaccharide.
- Glucose is known as "aldose" and has a aldehyde structure at carbon atom number 1.
- Fructose is known as ketose and has a "keto" structure at carbon atom number 2.
- Monosaccharides and oligosaccharides are collectively called sugars.
- Polysaccharides are known as non-sugars.
- When two monosaccharide units combine together by an oxygen atom with elimination of one water molecule, this type of linkage is called glycosidic linkage or glycoside bond.
- Amino acids are monomers of proteins and they are connected by peptide bond.
- The structure of protein is considered at four levels: primary, secondary tertiary and quaternary.
- Lipids are heterogenous class of organic compounds. They may be saponifiable or non-saponifiable.
- The oils which contain more unsaturation are hydrogenated to produce solid ghee.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

- DNA and RNA are two examples of nucleic acids and their function is replication and protein synthesis.
- Enzymes are protein in nature which can speed up a chemical reaction.
- Enzyme inhibition may be irreversible or reversible.
- Minerals essential for life are the inorganic nutrients that are needed by living organism for vital function, but cannot be synthesized by them.

EXERCISE

Q 1: Choose the correct option for each statement.

1. The most abundant carbohydrate in nature is
   (a) Cellulose (b) Glycogen
   (c) Pectin (d) Chitin
2. The glycosidic linkage is present between the molecules of
   (a) Glucose (b) Glycine
   (c) Fatty acid (d) Non of these
3. Steriods belong to family of
   (a) Carbohydrates (b) Protein
   (c) Lipid (d) Enzymes
4. Protein present in haemoglobin has the structure known as ____ structure
   (a) Primary (b) Secondary
   (c) Tertiary (d) Quaternary

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

5. The optimum p^H of pepsin is
   (a) 1.5 (b) 1
   (c) 2.5 (d) 2.0
6. Which carbohydrate does not conform the general formula $Cn(H_2O)_n$
   (a) Deoxyribose (b) Ribose
   (c) Glucose (d) Fructose
7. Ethanol is produced from starch by the process of
   (a) Hydrolysis (b) Hydrogenation
   (c) Decomposition (d) Fermentation
8. Human are unable to digest
   (a) Glucose (b) Cellulose
   (c) starch (d) Denatured protein
9. Which one of the following term is not related to term aldohexose?
   (a) Aldehyde (b) Ketone
   (c) Six (d) Sugar
10. Synthesis of DNA is also known as
    (a) Transcription (b) replication
    (c) Translation (d) Transmutation
11. RNA is primarily seen in
    (a) Nucleus (b) Cytoplasm
    (c) Cell wall (d) Cell membrane
12. Specificity of enzymes depend upon
    (a) Active site (b) linear sequence
    (c) Turn over number (d) Non of these

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

13. The best source of iron is
(a) Organ meat (b) Milk
(c) Tomato (d) Potato

14. In which of following disaccharides both the basic structural units are the same?
(a) Maltose (b) Lactose
(c) Sucrose (d) All of these

15. In competitive inhibition, the inhibitor
(a) Competes with enzyme
(b) Irreversibly binds with the enzyme
(c) Binds with substrate
(d) Competes with substrate

16. In DNA, adenine forms a complementary pair with what other nitrogen base?
(a) Uracil (b) Cytosine
(c) Thymine (d) Guanine

17. The primary structure of protein represents
(a) Linear sequence of amino acids joined together by peptide bonds
(b) 3-dimensional structure of protein
(c) Helical structure of protein
(d) Sub units structure of protein.

18. Liquid forms of triglycerides at room temperature are called
(a) Oils (b) Fats
(c) Solid (d) None of these

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Q II. Short questions

1. Why vegetable oil is sensitive to rancidity?
2. Give brief reason why melting point of saturated fatty acid is higher than unsaturated fatty acid.
3. Draw the open and cyclic structure of the following compounds
   (a) Glucose (b) Fructose (c) Mannose (d) Galactose
4. Differentiate between
   (a) Aldose and ketose
   (b) Sugar and non sugar
   (c) Competitive and non-competitive inhibition.
   (d) DNA and RNA
5. What is meant by the term "fuel of life".
6. What happens when protein is denatured?
7. What are chemical entities that compose the nuclic acid?
8. Describe briefly the primary, secondary, Tertiary and quaternary structure of protein.
9. What is the importance of protein in our daily life?
10. Why zinc is important for human being?
11. State the medical problem that may relate to calcium and phosphorus.

Scanned with CamScanner

Q III. Long question

1. (a) What are carbohydrate? Describe the properties of each kind of carbohydrates with example.
   (b) Explain the role and nutritional importance of carbohydrates.
2. (a) Describe various classes of protein along with example.
   (b) Enlist the properties of protein.
3. (a) What are lipids? Describe the classification and role in human body.
   (b) Write down at least three chemical properties of lipids.
4. (a) Define enzymes. Describe the role of enzymes in digestion of fat, carbohydrates and protein.
   (b) What are the factors affecting enzyme activity?
5. Write notes on
   (a) Nucleic acid
   (b) Biological significance of minerals.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

UNIT 22

INDUSTRIAL CHEMISTRY

Learning Outcomes:

After carefully studying this unit and working the exercise, students will be able to:

- Discuss the importance of the chemical industries in the economy of Pakistan.
- Describe the raw materials available in Pakistan for various chemical industries.
- Describe the chemical processes of addition and condensation polymerization.
- Interpret difference between petrochemical and chemicals derived from them.
- Describe the fractional distillation of refining of petroleum.
- List the various raw materials for petrochemical industry.
- Identify the important fraction.
- Describe the basic building block processes in petrochemical technology.
- Describe the petrochemical process technology.
- List some major petrochemicals.
- Discuss types and applications of hair dyes.
- Discuss the formation and uses of PVC and Nylon.
- Describe preparation and applications of various cosmetics like nail varnish, nail polish remover and lipsticks.
- Describe types and application of synthetic adhesives.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Introduction:

22.1 Industrial chemistry

Industrial chemistry is concerned with chemical processing of raw materials to useable and profitable products. Certain of these marketable products will be consumer goods and enter directly into economic life of the country. Others will be intermediates chemicals for the manufacture of consumer's items. Manufacturers of chemicals utilize some twenty percent of the total chemical output. In as much as the products of one become raw materials for further fabrication in another. Thus, the industry as a whole is its own best customer.

The chemical industry today is a very diverse sector of manufacturing industry with in which it plays a central role. It makes thousand of different chemicals which the general public only usually encounter as end or consumer products. These products are purchased because they have the required properties which make them suitable for particular applications e.g non stick coating for pans or weed killer. Thus chemicals are ultimately sold for the effect they produce.

Chemical processing may be defined as the industrial processing of the chemical raw materials leading to the products of enhanced industrial value. Generally this involve the chemical conversion, as in manufacture of sulphuric Acid from sulphur by oxidation and hydration, but the production of fibers from chemicals is also included such as nylon from hexamethylene diamine and adipic acid by more complicated chemical reactions. In all these chemical changes physical operations are initmately involved such as heat transfer and temperature control which are necessary to secure good yield required by competitive industry as for example the oxidation of SO_2 to SO_3.

Economy of Pakistan

Chemical sector plays a fundamental role in economic development of any nation. The globalization forms the structure of the modern world. It converts the essential raw materials into more than seventy thousand variety products for indursty as well as the goods of consumers, that people depend upon their daily lives.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Pakistan trades in chemicals with other countries to earn foreign exchange in the field of chemical industry such as a fertilizers, plastics, rubber, medicine, dyes and pigments, soaps and detergents.

The increase in imports is from 760 million US $ in 2002-2003 to 5160 million US $ in 2008-2009. The increment in export was shown from 118 million US $ in 2002-2003 to 411 million US $ in 2008-2009.

Chemical industry supply the farmers the fertilizers and pesticides which are essential for the crop growing and other agriculture products. Chemical industry also produces fibers and dyes which are used in textile industry and supply synthetic sweeteners and synthetic flavours which are used by food manufacturing companies.

The provision of essential chemicals to the pharmaceutical industry and health care industry is also a major role of chemical industry.

Artificial rubber requirement of Pakistan industry are also met by the very same chemical industry.

Chemical industry contributes indirectly to almost every sector of economy.

22.2 SAFETY CONSIDERATION IN THE PROCESS OF INDUSTRY

The following safety consideration in the process of industry must be kept in view before launching any industrial activity.

- To keep away the factory itself from corroding away, proper material of construction should be selected by the designing chemical engineers.
- To avoid harmful impurities in raw materials, to follow the course of chemical reactions and to secure the requisite yield and purity of products, careful process control by periodic anylysis is required as well as modern instrumentation and automatic control.
- To transmit goods in a clean and economical manner from the manufacturer to the customer, suitable containers must be provided.
- To affect the safety of workmen and the plant all procedures, must be carried on in a non-hazardous manner.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

- To secure the processes from excessive competition and to ensure an adequate return for a large sums spent on the research and plant.
- To guarantee progress to continue profits and to replace obsolescent processes and equipments much attention and money must be spent upon continuing research and development.
- To prevent the contamination of water and air, factories must avoid discharge of toxic material into the air and water of their localities.

22.3 Dyes

A dye is a substance which adds value to products for their cost. In most of the cases the colour of a product is the reason for its sale. The purpose of a dye is usually to help the purchaser sell his product to his customer. A dye must be coloured, but it must also be able to impart colour to something else on a reasonably permanent base before it can be considered as a dye.

Chemical Composition of a dye:

A dye consists of a colour producing structure called "The chromogen" (electron acceptor) and a part to regulate the solubility and dying properties called the auxochrome (electron donor). Without both parts, the material is simply a coloured body.

The chromogen is an aromatic body containing a colour giving group, commonly called the "chromophore". Chromophores groups cause colour by altering absorption bands in the visible spectrum. Some common chromospheres are given in the table 22.1 Dyes are usually classified on the basis of chromophore groups.

Table 22.1 Some common chromophore groups.

S. No	Chromophore	Structure
1.	Nitrosogroup	$-NO\ (or = N-OH)$
2.	Nitro group	$-NO_2\ (or\ NOOH)$
3.	Azo group	$-N=N-$
4.	Ethylene group	$-C=C-$
5.	Carbonyl group	$\begin{matrix} O \\ \| \\ -C- \end{matrix}$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

6.	Carbon–nitrogen group	$-C\equiv N, -\overset{\overset{N}{\|\|}}{C}-$
7.	Carbon–sulphur groups	CH_3-SH

The auxochrome, the part of the dye which causes it to adhere to the material which it colours (usually textiles) are $-NH_2, -OH, -NR_2, -COOH$ and $-SO_3H$ of these groups. $-NH_2$ and $-NR_2$ cause solubility in acids while $-OH, -COOH$ and $-SO_3H$ cause solubility in basic solutions.

Classification of Dyes:

Dyes are of many types. They may be classified into the following classes. The basis of classification being the "use" or "application" of the dye.

1. Acid dyes:

They are used for dyeing protein fibers such as wool, silk, nylon; also leather and paper. They contain one or more sulfuric acid substituents or other acidic groups. An example of the class is acid yellow 36 (Metanil yellow).

2. Basic Dyes:

These dyes can be used to dye wool or cotton with a mordant but are usually used for duplicator inks, carbon paper and typewriter ribbons. In solvents other than water, they form writing and printing inks. Basic dyes are mostly amino compounds soluble in acids and made insoluble by the solution being made basic.

Basic dyes were the first dye class made synthetically; "mauve" was a basic dye. Examples of the basic dyes are basic brown 1 (bismark brown), basic violet 3 (crystal violet) etc.

3. Azo dyes:

These are brilliant and long –lasting dyes and are used primarily for printing on cotton. These "ice colours" are made right on the fiber by coupling diazotized materials while in contact with the fibers.

4. Direct dyes:

These are used to dye cotton directly i.e. without the addition of a mordant. They are also used to dye union goods (mixed cotton and wool

Scanned with CamScanner

or silk). These are generally azo dyes and their solubility in the dyes bath is often reduced by adding salt. Direct orange 26 and direct black 22 are typical direct dyes.

5. Disperse dyes:

Some fibers such as plastics, cellulose acetate, polyesters, nylon fibers, are difficult to dye. Disperse dyes are applied as very finely divided materials which are absorbed on to these fibers with which they then form a solid solution. The dye dissolves into the fiber at or near the glass transition temperature of the polymer. Some typical examples of the disperse dyes are disperse red 4, disperse red 77, disperse orange 25, disperse blue 27 etc.

6. Fiber –reactive dyes:

These dyes react with the substrate, usually cellulose to form a covalent link (bond) between the dye and the fiber. Cotton, rayon and some nylons are dyed by these dyes. Examples of this type include vinyl sulfone (sulfatoethyl sulfone)

7. Mordant dyes (and lakes):

Some dyes combine with metallic salts to form highly insoluble coloured materials, called lakes. Lakes are usually used as pigments. If a cloth made of cotton, wool or other protein fiber is impregnated with an Al, Cr or Fe salt and then contacted with a lake forming dye, the metallic precipitate forms in the fiber and the colours become far more resistant to light and washing. The azo and anthraquinone nuclei, having attached the groups like $-OH$ *and* $-COOH$, can act as mordant dyes.

8. Sulphur dyes (sulphide dyes):

These dyes have been used for a long time. They are large low costing group of dyes which produce dull shades on cotton. The chromophore is complex and not well defined. Sulphur dyes are usually colourless when in the reduced form in a sodium sulfide bath but gain colour on oxidation.

9. Solvent dyes:

Solvent dyes, sometimes called the spirit –soluble dyes are usually azo, triarylmethane or anthraquinones. They are used to colour oil, waxes, varnishes, shoe polishes and gasolines.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

10. Vat –dyes:

Vat-dyes are water insoluble organic pigments that become water – soluble when mixed with powerful reducing agents in the dyeing process. The reducing operation formerly was carried in wooden vats and hence the name vat –dyes. These have highly complex chemical structures and mostly are derivatives of anthraquinone or indanthrone. Vat –dyes are quite expensive and are most often used on cotton fabrics that are to be subjected to severe conditions of washing and bleaching, such as men's shirts. Some vats are supplied as pastes for printing. The best known dyes of this class is indigo, which is one of the most popular colours in the world.

22.4 Pesticides:

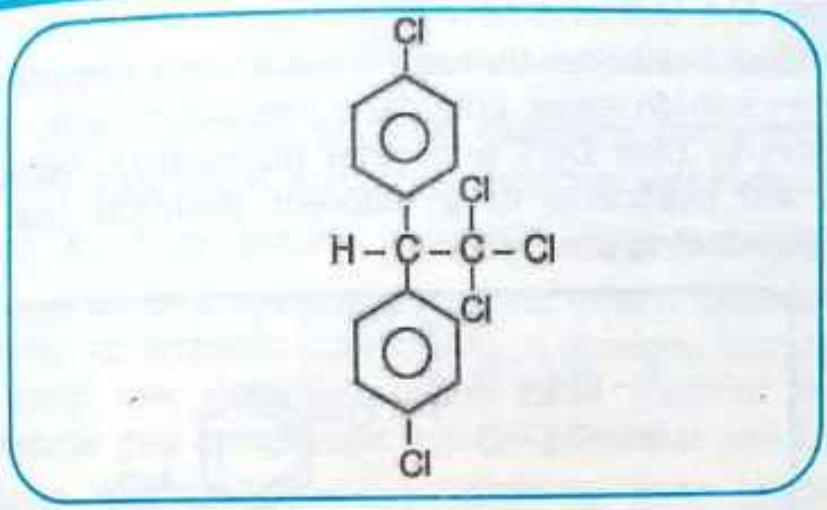
The use of chemical pesticides has been a major feature of modern agriculture. Our modern system of agriculture depends not only on our ability to stimulate plant growth, but also on our ability to control various insects or more generally, "pests" that would eat or destroy the crops in the fields or the harvest in the storage sheds.

It is not difficult to kill all the troublesome creatures that we include as pests. Poisons such as lead arsenate, $Pb_3(AsO_4)_2$ have been in use for a long time. Both lead and arsenic are damaging to a wide variety of living systems. Another traditional insecticide is nicotine sulphate, which is obtained from plants but is extremely poisonous to most pests and to man. Pesticides such as these general poisons are not really satisfactory. We would prefer a substance that destroys specific pests without injuring other insects, wild life, or man. Secondly a pesticide that breaks down in nature into harmless products is preferred.

Modern insecticides were ushered in by DDT in 1943. Its remarkable effectiveness against mosquitoes, which carry malaria and lice was immediately demonstrated in the world war II campaigns in Italy and the pacific. DDT has the formula.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



and the name "dichlorodipheny trichloroethane". It is good in specificity in that it acts directly on insects and not on mammals. But it does not distinguish between bad insects that destroy our crops and good insects, like bees, that assist them.

Unfortunately DDT fails to meet the second criterion i.e it, does not readily break down in nature to give harmless substances. DDT is a very stable chemical. Its half life is estimated to be 10 -15 years. It means that half of any DDT applied in any year still exists, somewhere, 10 or 15 years later. The persistence of DDT is more troublesome by its tendency to become concentrated in all forms of animal life. (The process is some times referred to as biological magnification). As is clear from its structure, DDT can not become involved in hydrogen bonding to water molecules, so it is water –insoluble. Further more the DDT molecule is non – polar. If a sample of DDT is shaken up with a two layer oil –and –water system, almost all the DDT will be found in the oil layer. In nature this distribution occurs and DDT accumulates in animals and in particular in their fatty tissues. Thus, although DDT can be used in very small quantities to control insects, it accumulates in the fatty tissues of each successive member of the food chain. An area may be sprayed with DDT so that the concentration of the DDT in the waters of the area might be much less than 1 ppm. But the food chain that proceeds from insects through fish to fish–eating birds can concentrate the DDT until it is at the 100 or 1000 ppm level. Even man is not immune from this DDT accumulation and our fatty tissues now contain something over 10 ppm of DDT more than would be tolerated in the foods we eat.

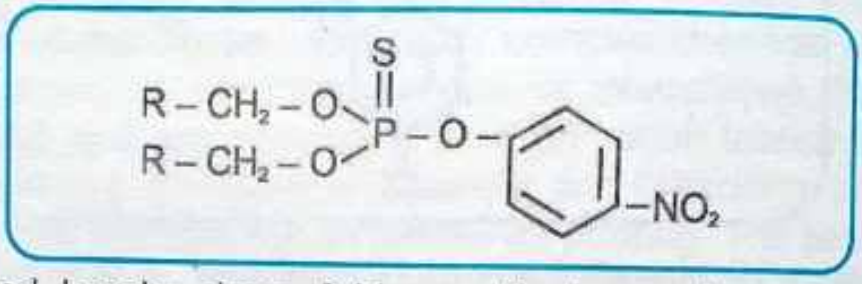
Generally, it has been found, that almost all chlorinated pesticides including DDT appear to have a variety of undesirable effects. That is why pressure from environmentalists has lead to the nearly total ban of the

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

use of DDT in the U.S and all over the world. However, there are still some chlorinated pesticides that are used for more specific targets than was DDT. They include mirex, chlordane, heptachlor, aldrin and dieldrin.

The controversy over DDT and other chlorinated hydrocarbons spurs attempts to find pesticides of a different chemical type. One of the important alternatives is parathion.



This compound breaks down fairly readily to products that appear to cause no biological damage. It is, however, toxic to man and other animals as well as to insects. Thus it avoids long term damage but unless handled carfully it can make for that by short term effects.

In short, the ideal pesticide is clearly not yet available. In fact, chemical poisons will probably turn out to be only one route to the control of the pests that compete with us for our crops.

22.5 Petrochemicals:

Formerly, it was easy to define petrochemicals. They were relatively pure identifiable substances derived from petroleum and used in the chemical trade. But now the original products, separated from petroleum are converted into more desirable sometimes complex, products. That is the oil companies are entering the chemical business; chemical companies are entering the oil business, and the whole group is expanding greatly. So most organic chemical substances could be considered petrochemicals.

The first organic chemical made on large scale from a petroleum base was isopropyl alcohol (isopropanol), first produced by Standard Oil of New Jersey in 1920. By 1925 Standard Oil of New Jersey was making 75 tons per year of isopropyl alcohol and the emergence of petrochemical industry was established in many minds. Currently well over 80 per cent of all organic chemicals are petrochemicals.

While separating individual species from petroleum, the processes involve well refined engineering methods. The most important of these methods are (i) distillation and (ii) selective adsorption. Once separated,

Scanned with CamScanner

however, most materials then undergo chemical conversion into more desirable products. Alkylations involving propenes and butenes yield C_6 to C_8 hydrocarbons for high octane gasoline. Propylene becomes poly propylene, polyamines or propylene glycol and others. Likewise 98 percent of the raw material, for aromatic compounds, is obtained from petroleum.

The most basic raw materials (table 22.2) supplied by petroleum refineries or natural gas companies are LPG, natural gas from cracking operations, liquid distillate(C_4 *to* C_6), distillate from special cracking processes and selected or isomerized cyclic fractions for aromatics. Most of these substance are of high value for fuel use.

Table 22.2: Primary Precursors petroleum –petrochemicals:

Raw materials by Distillation	Precursors (basic Chemicals) by conversion.	Intermediates by conversion	Finished Products By conversion
Paraffins And cyclics	Olefins, diolefins, Acetylene, aromatics	Various inorganics and organics,	Inorganic And organics
Natural gas Sulfides Hydrogen Methane	H_2S	S, H_2S synthesis gas	Carbon black H_2SO_4, NH_3 Methanol
Refinery gases	Acetylene Isobutene Ethylene Propylene n –butanes	Acetic acid Acetic anhydride Isoprene Ethylene – oxide etc Butadiene Adipic acid Ethyl benzene Styrene	Formaldehyde Acetates Fibers Rubber Rubber & fiber Rubber Fibers Styrene Rubber
Ethane Propane N –butane Hexane Heptanes Refinery naphtha's			

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Naphthalene		Cumene	Phenol, acetone
Benzene	Cyclohexadiene	Alkyl benzene	Nylons
Toluene	Toluene	Phenol	Plastics
Xylems	Toluene	Benzoic acid	Phenol
Methyl naphthalene's	O -, m -, p -, xylene , toluene naphthalene	Pthalic anhydride	Plastics

The lower members of the paraffine and olefin series have been the preferred and most economical sources of organic raw materials for conversion. So tables are shown concerning the derivations from methane (Table 22.3) and ethylene (table 22.4)

Table 22.3 Petrochemicals from Methane

Basic	Uses, (Percent)
Ammonia	Fertilizers (80%) plastics and fibers (10 %) explosives (5%)
Carbon black	Tyres (65%) other rubber (25%) colorant and fillers (10%).
Methanol	Polymers (50%), solvents (10%), derivatives $(HCHO, CH_3COOH)(40\%)$
Chloromethane	
Methyl chloride (CH_3Cl)	Silicones (57%),tetramethyl lead (19%)
Methylene chloride (CH_2Cl_2)	Paint remover (30%) aerosol propellant (20%) degreaser (10%)
Chloroform $(CHCl_3)$	Fluorocarbons (90%)
Carbon tetrachloride (CCl_4)	Fluorocarbons (95%) degreasing, fumigant etc (5%)
Acetylene	VCM (37%), 14, - butanediol (25%) v . acetate (14%), v fluoride and acetylene black (5%)
Hydrogen Cyanide	MMA (58%), cyanuric chloride (17%), chelating agents (13%), NaCN (9%).

Scanned with CamScanner

Table 22.4 Petrochemicals from Ethylene:

Basic Derivatives	Uses, (Percent)
Ethyl Benzene	Styrene (99%) , solvent (1%)
Ethyl chloride	TEL (90%), ethyl cellulose of pharmaceuticals (5%)
Ethylene dichloride	VCM (84%) solvent (7%)
Ethylene glycol	Antifreez (38%), polyester fibers and films (49%)
Ethylene oxide	Glycol (60%) Rthoxylates (10%) glycol ethers (10%)
Perchloro ethylene	Textile cleaning (40%) metal cleaning (21%) chemical intermediates (6%).
Polyethylene	
Low	Film, sheet, molding and extrusion plastics.
High density	Film sheet molding and extrusion plastics
Styrene	Polystyrene (52%) ABS (9%), SBR (7%) polyester resins (6%) SB latex (6%)
1,1,1 – trichloroethane	Cold cleaning (40% Vapour degreasing (22%) Adhesives (12%), aerosols (10x), electronics (6%)

Fractional Distillation of Petroleum:

Petroleum in the unrefined from is called crude oil. It is a naturally occurring thick viscous brown or greenish black liquid which is obtained from earth crust. It consists of mostly hydrocarbons along with some other elements, mainly sulphur, nitrogen and oxygen. Crude oil is first treated to remove sulphur or sulphur compounds that may be present. The cleaned hydrocarbon material is then distilled, and fractions with various boiling ranges are collected. (figure 22.1). The principal goal of refinery operations is the production of gasoline.

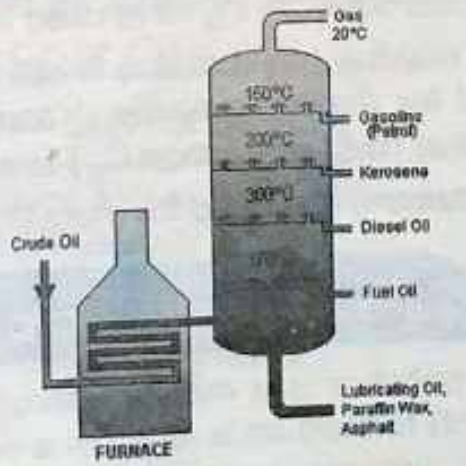


Fig: 22.1 Fractional distillation

The principal fractions and some of the principal routes in the treatment of crude oil in an oil refinery during fractional distillation are :

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

1. **Refinery gas:** It is a mixture of hydrocarbons containing methane, ethane, propane, and butane, i.e, C_1 *to* C_4 atoms per molecule. It is obtained at a temperature below $20°C$, and is used as "fuel" and for making other organic compounds.
2. **Petroleum ether:** It is obtained in the boiling range $20°-60°C$, contains pentane and hexane (C_5-C_6) and is used as solvent.
3. **Light naphtha:** It is obtained in the boiling range $60-100°C$, contains hexane and heptane (C_6-C_7) and is used as solvent.
4. **Gasoline:** This is the most important fraction containing hydrocarbons from C_7 *to* C_{10}. It is obtained in the boiling range $80°-180°C$ and is used as motor fuel.
5. **Kerosine (Paraffin oil):** It is obtained in the boiling range $160°-300°C$ and contains hydrocarbons from C_{11} to C_{15}. It is used as jet fuel, and for oil –fired domestic heating. It can also be used for cracking to produce gasoline (motor fuel).
6. **Heavy oil (Diesel oil, fuel, oil, gas oil):** This fraction is obtained in the boiling range $300°$ to $400°C$ and contains hydrocarbon from C_{15} to C_{18}. It is used as industrial fuel and as fuel for diesel engines.
7. **Lubricating oil:** It is a mixture of non-volatile liquids which is obtained at a temperature above $400°C$. It contains hydrocarbons from $C_{18}-C_{20}$. It is used for lubricating heavy machinery.

The residue (solid mass) is still a mixture of higher hydrocarbons which is used for making greases, Vaseline, waxed paper and candles. The final residue (with more than C_{30}) is a black coal tar and is called asphalt, pitch or bitumen. It is used for metalling roads.

22.6 Synthetic polymers (PVC and Nylon):

A polymer is a macromolecule (sometimes with a very high molecular weight) formed as a result of a process known as polymerization whereby small organic molecules combine together to form large molecules (polymers). The small molecules which under go polymerization are called "the monomers." Thus a polymer is a large molecule built up from many

Scanned with CamScanner

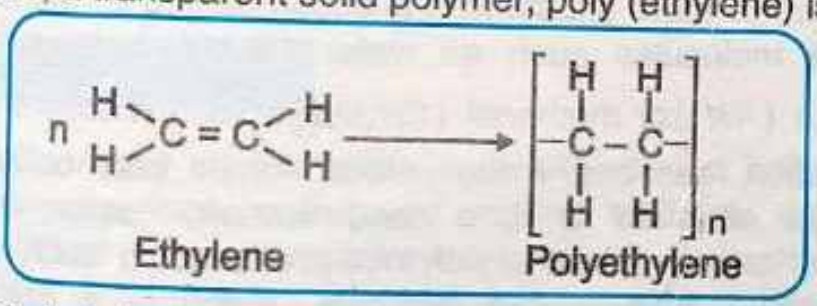
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

hundreds or thousands of monomer units joined together. The well known plastic polyethylene or polythene is composed of large molecules formed by the repeated combination of ethene molecules.

Polymers are classified as either "addition polymers" or "condensation polymers" depending on their method of formation.

a. Addition Polymers:

In these polymers, the repeating unit (monomer) keeps on adding to itself or to the growing polymer so that a long chain polymer is produced. That is to say addition polymer results from the self –combination of many monomer units into a substance with a molecular weight which is a multiple of the monomer. The empirical formula of the addition polymer is the same as that of the monomer. For example, when ethylene is heated under pressure, a transparent solid polymer, poly (ethylene) is obtained.



An endless chain is built up by successive addition of the C_2H_4 units. The product has an average molecular weight of $2000 - 20{,}000$, depending on the temperature and pressure. Acetylene forms an addition product with HCl called vinyl chloride in the presence of $HgCl_2$ or $CuCl$.

$$H-C\equiv C-H + HCl \xrightarrow[CuCl]{HgCl_2} H_2C = CH - Cl \text{ (Vinyl chloride)}$$

Vinyl chloride molecules combine with themselves to produce molecules of very high molecular weight, called poly (vinyl chloride) or PVC.

$$nCH_2{=}CHCl \longrightarrow \left[CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH}} - \right]_n \text{ (Polyvinyl chloride)}$$

Industrial Preparation of PVC:

The largest branch of the vinyl family is polyvinyl chloride (PVC). The popularity of PVC is due to its excellent physical properties, its ability to be compounded for a wide range of applications, its ease of processing and

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

its relatively low cost. The liquid monomer is formed into tiny globules by vigorous stirring in water containing a suspending agent. A typical recipe lists 100 parts of water, 100 parts of liquid vinyl chloride, 1 part of a persulphate catalyst and 1.5 parts of an emulsifier such as sodium lauryl sulphate. The autoclave operates at approximately $50°C$ for 72 hours to give a yield of 90 percent of polymer with a particle size of 0.1 to 1.0 μm. Recovery of these particles may be accompanied by spraying or by coagulation by acid addition. A PVC compound can be tailer –made to achieve whatever balance of properties is desired by using plasticizers, stabilizers, lubricants and fillers.

b. Condensation Polymers:

In the chemistry of carbon there are many reactions where the combination of two or more substances is accompanied by the elimination of small simple molecules such as water (H_2O), hydrogen chloride $(HC\ell)$, ammonia (NH_3) or methanol (CH_3OH). Such reactions are often called condensation reactions. If the carbon –chain back bone has two functional groups attached to it, a condensation reaction can occur involving polymerization. And the polymer produced in such a case is called condensation polymer. For example, Nylon is a condensation polymer, produced by the reaction between a diamine and a dibasic organic carboxylic acid. If the diamine is hexamthylene diamine (1,6 – diaminohexane) and the dibasic acid is adipic acid (hexanedioic acid) then the condensation polymer is nylon (6, 6) (six carbon atom in each monomer).

$$-NH-(CH_2)_6\,NH-\overset{\overset{O}{\|}}{C}\,(CH_2)_4-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_6-NH-$$

Preparation of Nylon (6, 10) (the nylon rope trick)

$50\ cm^3$ of a 2% (by volume) solution of decanedioyl dichloride (sebacoyl chloride) in $CC\ell_4$ is measured into a 100 cm^3 tall –form beaker 25 cm^3 of an aqueous solution containing 2.2g of 1,6 –diamino hexane (hexamethylene diamine) is added carfully to the beaker so that the aqueous solutions floats on top of the $CC\ell_4$ solution, without mixing. A thread of the nylon is drawn from the interface between the two liquids, using a pair of forceps and wound around thick glass rod. (Figure 22.2)

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

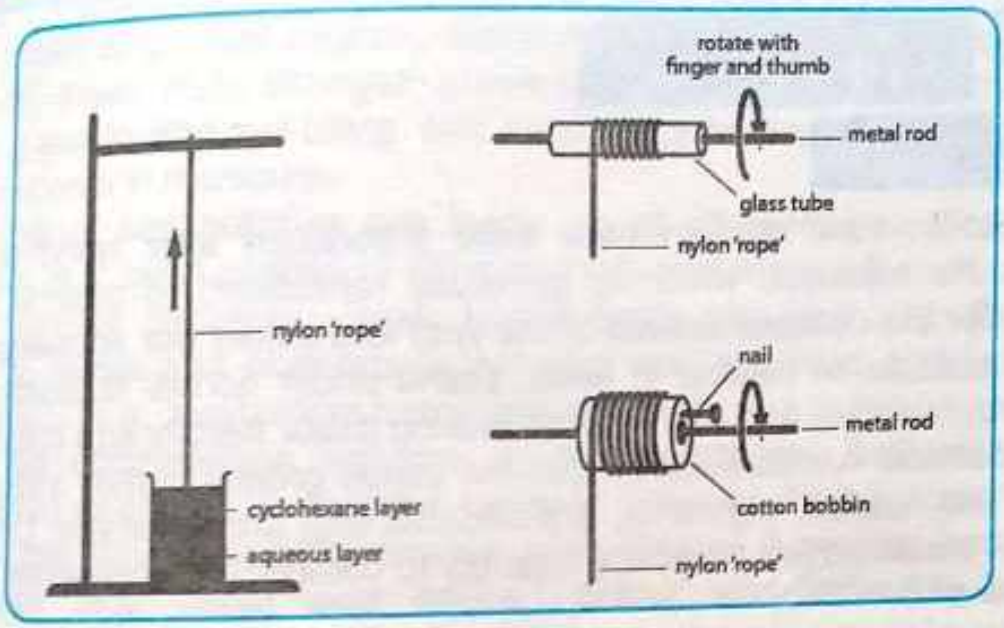


Fig: 22.2

Uses of PVC and Nylon

1. PVC or poly vinyl chloride is widely used in imitation leathers, floor coverings, corrugated roofing material, drainage pipes, electrical pipes, gramophone records etc.
2. Nylon is well known as synthetic fiber in carpets, fabrics, rope, stockings and other clothings. Because of its mechanical strength, nylon is also used in moulded machine parts such as gears and bearings.

Society, Technology and Science

Nylon was the first truly synthetic fiber, resulting from the brilliant research of the late Wallace H-Carothers of the Du Pont company. The introduction of synthetic fibers changed the textile industry because their properties differ from natural fibers. Nylon creates draperies, flame-resistant product and clothes. Other uses include, carpets, tyres of vehicles, stockings and tights etc. Kevlar is used in ropes, tyres, sports equipment and bullet-proof vests. Polyester is used in outer wears because of its tenacity and durability. Its hydrophobic property makes it ideal for garments and jackets. It is also used for making sails of sailboat, water hoses for fire fighting.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

22.7 COSMETICS

a) Lipstick

Lipsticks in their modern form were introduced after world war I. Lipstick is the cosmetic which is generally formulated to provide both protection (for the delicate tissues of the lips) and colour (for appearance). They are made to be neutral in taste, stable under normal fluctuation of temperature, moisture and air flow and lacking major toxicity and irritancy.

The chemical composition of lipsticks varies greatly. It may include a mixture of oils, waxes, pigments, antioxidants and preservatives. Usually perfumes are also added in minute quantity to combat the unpleasant fatty odour of the oil.

Lipstick is mainly composed of a mixture of non-volatile oil (e.g. castor, vegetable, mineral or wool fat, lanolin oil) and solid wax (e.g; bees wax or carnauba). The addition of oil makes the wax-based product to be softened and easily applied. To reduce the "stickiness", usually, esters of fatty acids (like 2-propyl myristate) is also added.

The most important characteristic of a lipstick is considered to be its colouration. The colours and dyes of lipsticks include many water-soluble (also fat soluble) products, such as erythrosine (redish pink synthetic dye), amaranth (dark red to purple azodyes), brilliant blue eosin or tetrabromo fluorescein.

The dyes must be water-insoluble, otherwise, the colour would quickly fade or be removed in a short time by the consumer through the movement of the saliva-soaked tongue across the lips. Water-soluble dyes such as green or blue food dyes can be used to provide lipstick colouration, but they are, usually, first combined with metal oxides such as aluminum hydroxide [$Al(OH)_3$] to form an insoluble precipitate that is then suspended in the oil base of the lipstick.

b) Nail Varnish and Remover

i. Nail Varnish

Nail varnish or Nail Polish is a lacquer applied to human finger nails or toe nails to decorate or protect the nail plate.

Nail polish started traditionally in clear red, pink and brown colour. Since that time, many new colours and techniques have been developed, resulting in nail polish that is found in an extremely diverse variety of

Scanned with CamScanner

colours. Beyond solid colours, nail polish has also developed an array of other designs and colours. Such as nail polish stamps, crackled, magnetic, nail polish strips and stickers. Some nail polishes are used to cause nail growth, make nails stronger, prevent nails from breaking, cracking and slitting and to stop nail biting. Nail polish may be applied as one of several components in manicure.

Most of nail polishes are made up of nitrocellulose dissolved in a solvent (e.g; butyl acetate or ethyl acetate) and either left clear or coloured with various pigments. Basic components included are: film forming agents, resins and plasticizers, solvents and colouring agents. Adhesive polymers (e.g; tosylamide-formaldehyde resin) are added to make sure that the nitrocellulose adheres to the nail surface. Plasticizers (e.g. camphor) or chemicals that link between polymer chains, spacing them to make the film sufficiently flexible after drying. Pigments and sparkling particles (e.g; mica) add desired colour and reflecting properties. Thickening agents (e.g; stearalkonium hectorite) are added to maintain the sparkling particles in suspension within the bottle. Ultraviolet stabilizers (e.g; benzophenone-I) resist colour changes when the dry film is exposed to direct sunlight.

Nail polish ingredients often include toluene, formalin etc. Solvents such as toluene and xylene and petroleum based products have been linked to cancer. Formaldehyde (formalin) may cause allergic reactions and is unsafe for use by asthmatic people. It is a carcinogen. However, the nail polish industries (makers) are under pressure and are now trying to reduce or eliminate toxic ingredients, including phthalates, toluene and formaldehyde.

Water based nail polish is based on acrylic polymer emulsion (e.g; styrene-acrylate copolymer) and pigments similar to those used in water colour paints. This is marketed as environmentally conscious products, since nail polish is considered a hazardous waste by some regulatory authorities. When applied, the solvent (water) does not completely evaporate as in the case of the traditional nail polish; part of water is absorbed through the fingernail.

ii. Nail Polish Remover

Nail polish is removed with nail polish remover or nail pads which is an organic solvent, but may also include oils, scents and colouring. The most

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

common type of nail polish remover contains acetone $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$. It is powerful and effective but is harsh on skin and nails which can even make them more brittle. Acetone is a volatile organic compound which can also be used to remove artificial nails, that are usually made of acrylic. There are many different types of nail polish removers in the market and different brands may have different chemical compositions. However, the principal ingredients in most of them are acetone, ethyl acetate or butyl acetate and alcohol. The "non-acetone nail polish remover" usually contains ethyl acetate which is less aggressive solvent and can therefore, be used to remove nail polish from artificial nails. These chemicals used are known to dehydrate the skin, cause irritation to eyes and make nails dry and brittle. They also have a distinct chemical smell and are highly inflammable. To counter the dehydration and brittleness effects, many removers also contain conditioning ingredients like castor oil, ethyl palmitate or lanolin.

Application:

With liquid removers, the remover is taken on a cotton ball or tissue and wiped over the nail to strip away the finger nail polish on it. Depending upon the type of finger nail polish, the number of applied coats and the type of remover, one application may suffice for removal or several application may be necessary.

To understand how nail polish remover works, it is necessary to know that a finger nail polish remover and a finger nail polish both contain similar organic solvents; the nail polish also contains drying agents, thickeners, hardening agents and colouring agents. The organic solvent in a nail polish keeps them in a liquid state, while the solvent present in remover, dissolve the hardened polish and transforms it back into its original liquid form. When the nail polish remover is applied to the nail polish that is to be removed, the solvent molecules of the remover interrupt, loosen and break the polymer chains of the polish. This dissolves the hardened polish and transforms it back into its original liquid form. It can then be wiped off from the nail.

c)Hair Dyes

Hair dyes are the dyes, used for hair colouring. The purpose of this practice is to change the hair colour to a colour regarded as more fashionable or desirable and or to restore the original hair colour after it has been discoloured by hair dressing processes or sun bleaching.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Types of Hair Dyes:

Hair dyes, also called hair colouring are commonly classified into four groups.

1. Permanent hair dyes.
2. Semi-permanent hair dyes.
3. Demi-permanent hair dyes.
4. Temporary hair dyes.

These are briefly discussed here.

1. Permanent Hair Dyes:

Permanent hair colouring is usually carried out with oxidation dyes. The ingredients of these products include an oxidizing agent (usually hydrogen peroxide), coupling agents or couples (which are meta-substituted derivatives of aniline) and the primary intermediate (which are aromatic para-compounds such 1,4-diaminobenzene or 4-aminophenol or 2,5-diaminotoluene). The process is essentially performed under basic conditions, for which ammonia is usually used.

The combination of H_2O_2 and the primary intermediate causes the natural hair to be lightened which provides a blank canvas for the dye. Ammonia opens the hair shaft so that the dye can actually bond with the hair and ammonia speeds up the reaction of the dye with the hair.

The couplers (meta-substituted derivatives of aniline) are the chemical compounds that define the colour of the hair dye. Various combinations of primary intermediates and couplers provide different shades of hair colours.

2. Semi-permanent hair dyes:

These dyes have smaller molecules than temporary and are therefore, able to partially penetrate the hair shaft. That is why these colours can survive washing with typically 4-5 shampoos. Semi-permanent hair dyes contain no or very low levels of developers, peroxide or ammonia and are thus, safer for damaged or fragile hair. However, they may still contain the toxic compound p-phenylenediamine or other such ingredients.

The final colour of each strand of hair depends on its original colour and porosity, so there will be a large variations in shade across the whole head. This gives a more natural result than that of a solid permanent colour. Semi-permanent colour can lighten the hair.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

3. Demi-permanent hair dyes:

These are in fact, permanent hair colours that contain an alkaline agent other than ammonia (e.g; ethanolamine, sodium carbonate) and the concentration of H_2O_2 in the developer may be lower than used in a permanent hair colour. Since the alkaline agents employed in these colours are less effective in removing the natural pigment of hair than ammonia, these products provide no lightening of hair colour during dyeing.

As a result, they can not colour hair to a lighter shade than it was before dyeing and are less damaging to hair then permanent counterpart.

4. Temporary hair dyes:

Temporary hair dyes are most oftenly used to colour hairs for special occasions such as weddings, costume parties etc. They are available in various forms, such as resins, shampoos, gels, sprays and foams. A temporary hair colour is typically brighter and more vibrant than semi-permanent and permanent hair colour. The dye molecules in temporary hair colour are large and can not penetrate the cuticle layer. The colour particles remain absorbed (closely adherent) to the hair shaft and are easily removed with a single shampooing.

22.8 ADHESIVES

Adhesives are the materials, usually in liquid or semi-liquid states, that adhere or bond items together. They come from either natural or synthetic sources. Although a large number of materials can be bonded by means of adhesives, they are specially useful for bonding thin materials.

Adhesives cure (harden) by either evaporating a solvent or by chemical reactions that occur between two or more constituents.

Importance

With the passage of time and during their development, adhesives have gained an important position in an increasing number of production processes. There is hardly any product in our surroundings that does not contain at least one adhesive in it. For example the label on a beverage bottle, protective coating on automobiles, profiles on window frames, bonding formica to wooden counters or attaching out soles to uppers in foot wear.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

TYPES OF ADHESIVES

Adhesives are mainly classified into two classes.

1. Non-reactive adhesives.
2. Reactive adhesives.

The basis of classification is their method of adhesion.

1.NON-REACTIVE ADHESIVES:

These adhesives may be either of natural or synthetic origin. Drying adhesives, pressure sensitive adhesives, contact adhesives and hot adhesives are some examples of this class.

Drying Adhesives:

There are two types of adhesives that harden by drying;

(i) Solvent based adhesives:

Which are a mixture of ingredients (typically polymers) dissolved in a solvent. White glue, contact adhesives and rubber cements are the members of the drying adhesive family.

(ii) Polymer dispersion adhesives:

These are also known as emulsion adhesives and are milky white dispersions often based on polyvinyl acetate (PVAc). They are extensively used in the wood working and packing industries; also used in fabrics and fabric based components and in the engineered products such as loudspeaker cones.

Pressure Sensitive Adhesive (PSA):

These adhesives form a bond by the application of light pressure to adhere the adhesive with the adherent. Once the adhesive and the adherent are in close proximity, molecular interactions, such as "Van der Waals forces" become involved in the bond, contributing significantly to its ultimate strength. Major raw materials for PSA's are acrylate based polymers.

Contact Adhesives:

These are used in strong bonds with high "shear-resistance" like laminates, such as bonding formica to a wooden counter and in footwear, as in attaching outsoles to uppers. Examples of contact adhesives are

Scanned with CamScanner

natural rubber and polychloroprene (Neoprene). It must be remembered that contact adhesives must be applied to both surfaces and allowed for some time to dry before the two surfaces are pushed together. Once the surfaces are pushed together, the bond forms very quickly.

Hot Adhesives:

These are also known as hot melt adhesives or thermoplastics and are applied in molten form ($65^0C - 180^0C$ range) which solidify on cooling to form strong bonds between a wide range of materials. Hot adhesives containing "ethylene vinyl acetate", are particularly popular for crafts because of their ease of use and the wide range of common materials they can join. A glue-gun is one method of applying hot adhesive. The glue-gun melts the solid adhesive, then allows the liquid to pass through its barrel onto the material where it solidifies. Thermoplastic glue may have been invented around 1940 by "Proctor & Gamble" as a solution to water based adhesives commonly used in packing at that time failing in humid climates, causing packages to open.

2.Reactive Adhesives:

These adhesives chemically react with the material, when harden. They may be;

(i) Multiparts Adhesives
(ii) One Parts Adhesives

i. Multiparts Adhesives:

These adhesives harden by mixing two or more components which chemically react. This reaction causes polymers to cross link into acrylics, urethanes and epoxies. Commercially, there are several combinations of multi-component adhesives that are used in the industry. Some of these combinations are:

a)Polyester resin-Polyurethane resin.
b)Polyols-Polyurethane resins.
c)Acrylic Polymers-Polyurethane resins.

The individual components of these adhesives do act as adhesive by nature. These components, however, react with each other after being mixed and show full adhesion only on curing.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

II. One Part Adhesives:

These adhesives harden via a chemical reaction with an external energy source such as radiation heat or moisture. Light curing adhesives are generally acrylic based, and due to their rapid action, they are significantly used in electronics, telecommunications, medical, aerospace, glass and in optics.

Heat curing adhesives include epoxies, urethanes and polyimides, while moisture curing adhesives cure when they react with moisture present on the substrate surface or in the air. This type of adhesives include cyanoacrylates and urethanes.

Scanned with CamScanner

Key Points:

- Dye is a substances which adds value to product for their cost.
- Pesticides are chemical substances used for destroying insect and other organisms harmful to cultivated plants or to animals.
- Petrochemicals are relatively pure identifiable substances derived from petroleum and used in the chemical trade.
- A polymer is a macromolecule formed as a result of a process known as polymerization.
- Addition polymer are long chain giant organic compounds which are assembled from many smaller molecules.
- Condensation polymer formed through a condensation reaction, releasing small molecules as by-products.
- Industrial Chemistry is the study of fundamental chemical processes used in industry for transferring raw material to useful commercial products for society.
- Lipstick is mainly composed of a mixture of non-volatile oil and solid wax.
- Nail varnish or nail polishes is a lacquer applied to human finger nails or toe nails to decorate or protect the nail plate.
- The most common type of nail polish remover contains acetone.
- Permanent hair colouring is usually carried out with oxidation dyes.
- Adhesive are the material usually in liquid or semi-liquid state, that adhere or bond items together.
- Adhesives are of two types non-reactive adhesive and reactive adhesives.
- Non-reactive adhesives may be of natural or synthetic origin.
- Reactive adhesives chemically react with material, when harden.
- Cosmetic products apply to body, especially the face, to improve its appearance.
- Hair dye is usually soluble substance for staining or colouring.

Scanned with CamScanner

Exercise

Q1. Choose the correct one.

(i) "Mauve" is an example of _____ dye.

a) Acidic b) Basic
c) Direct d) Azo

(ii) Which is true for DDT? It is

a) Not a pollutant b) an antibiotic
c) an antiseptic d) a non-degradable pollutant

(iii) Which one of following is not petrochemicals?

a) Naphthalene b) Mineral oils
c) Wax d) table salt

(iv) What is called "black gold"?

a) Petroleum b) Coal
c) Coal Tar d) Natural gas

(v) Petrochemicals are used in the manufacture of

a) Polythene b) Detergents
c) Fibers d) All of these

(vi) Which one of the following is synthetic polymer?

a) Cellulose b) Protein
c) Rubber d) Polythene

(vii) Which one of the following is condensation polymer?

a) PVC b) Polythene
c) Nylon d) None of these

Q2. **Short questions.**

(i) Differentiate between reactive and non-reactive adhesives.
(ii) How nail-polish remover removes the nail-polish?
(iii) Why temporary hair dyes are removed with single shampooing?

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

(iv) What are the uses of PVC and nylon?
(v) Write down the four applications of pesticides.
(vi) How DDT reaches to animals fatty tissues?
(vii) Differentiate between addition and condensation polymers.

Long question

Q1. (a) Define Dyes. What is its chemical composition?
(b) How dyes are classified.
Q2. Explain the fractional distillation of petroleum.
Q3. What is meant by hair dyes. Classify it into different groups?
Q4. What are adhesives. Discuss its importance in our daily life?
Q5. Explain the types of adhesive.
Q6. Write a note on following:

a) Petrochemicals
b) Synthetic polymers
c) Lipsticks
d) Nail polish and its removers

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

UNIT 23

ENVIRONMENTAL CHEMISTRY

Learning Outcomes:

After carefully studying this unit students will be able to:

- Recognize various reactions, occurring in the atmosphere.
- Recognize that the release CO_x, SO_x, NO_x, VOC_x are associated with the combustion of hydrocarbon fuels.
- Outline problems associated with release of pollutants, including acid rain and the formation by free radical reactions of hazardous inorganic and organic compounds e.g PAN.
- Describe causes and impacts of urban smog.
- Explain greenhouse effect and global warming as resulting in climate change.
- Explain the build up to and recognize the adverse effects of ozone in the atmosphere.
- Describe the role of CFC's in destroying ozone in the atmosphere.
- Describe the role of ozone in the stratosphere in reducing the intensity of harmful UV radiation reaching the earth.
- List possible alternatives to the use of CFC's.
- Recognize and describe alternatives to the use CFC'c.
- Recognize and describe various water pollutants.
- Explain the various parameters of water analysis.
- List some major products of the petrochemicals industry, together with their uses.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Introduction:

In this chapter, we will turn our attention to environmental issues, associated with earth's atmosphere. Air and water pollutions are the major problems in most of the world's cities and they often take on regional dimensions. The atmosphere, a part of the environment, acts as repository for emissions from combustion and from many other human activities. The air can be cleansed by natural mechanisms but these can be overwhelmed by the amount of pollutants being produced. Human activities are increasing the atmosphere concentration of carbon dioxide and other greenhouse gases. In addition, the stratospheric ozone shield, which protects us from the ultraviolet rays, is threatened by the emission of ozone destroying chemicals.

Likewise, water quality is as important issue as water quantity. Although most of the water supply is returned to the stream flow after use, its quality is inevitably degraded. The quality of surface and ground water is of concern due to two distinct points of view that is human health and welfare and the health of aquatic ecosystems. Both aspects of water quality are enhanced by minimizing the impacts of human activities, but the specific issues and control measures are different.

Atmosphere is one of the four spheres of our environment. The other three being lithosphere, hydrosphere and biosphere. Atmosphere is the envelop of gases, surrounding the earths surface. It plays a key role to sustain life on earth and save it from the hazardous environment of the outer space. The atmosphere absorbs most of the cosmic rays from the outer space and harmful radiation such as U.V through ozone (O_3) layer.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

In addition, the atmosphere maintains the heat balance of the earth through absorption of energy from the sun and re-emitted.

The atmosphere can be divided into:

i. Troposphere ii. Stratosphere

iii. Mesosphere iv. Thermosphere and

v. Exosphere

S. No.	Zone/Sphere	Altitude (in km)	Temperature range (^{0}C)	Important Chemical Species
1.	Troposphere	0-11	15 to -56	N_2,O_2, CO_2,H_2O, Ar
2.	Stratosphere	11-50	-56 to -2	O_3 (ozone), N_2, O_2
3.	Mesosphere	50-85	-2 to -92	NO^+, O_2^+
4.	Thermosphere	85-500	-92 to 1200	O_2^+, NO^+, O, O^+

Fig: 23.1 The atmospheric division

23.1 CHEMISTRY OF THE TROPOSPHERE:

Troposphere extends from the surface of the earth upto 11 kilometers. It constitutes about 10% of the atmosphere's height but contains 80% of its mass. The temperature in this sphere ranges from 15^{0}C to -56^{0}C. (Table, 23.1). The important chemicals that exist in this sphere are N_2, O_2,CO_2 and H_2O. It is also a region of much turbulence, due to the global energy flow that results from the imbalances of heating and cooling rates between the equator and the poles. The temperature in troposphere falls off uniformly with increase in altitude. That is why the air it contains is mixed rapidly by convection.

23.1.1 Chemical Reactions in The Atmosphere:

As mentioned earlier, atmosphere can be divided into four spheres/zones (Table 23.1). The main chemical species in the

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

atmosphere are N_2, O_2, $H_2O_{(v)}$, O_3, NO^+ and O_2+ etc. In some areas (particularly the industries zones), the atmosphere (troposphere) may also contain SO_x and NO_x gases which are the gases responsible for the acid rain.

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

$$SO_2 + H_2O + \frac{1}{2}O_2 \rightarrow H_2SO_4$$

The concentration of the acid thus formed can be quite higher, which ultimately reduce the pH of rain water substantially. This results in producing what is called acid rain (Topic 23.2.7). The CO_2 present in the atmosphere (0.036%) also reacts with the rain water, making it slightly acidic (pH ≅ 5.6).

$$H_2O + CO_2 \rightarrow H_2CO_3$$

Carbonic acid

The lightening in air and also in combustion engine of motor vehicles may also ignite reaction between stable molecules of N_2 and O_2, producing NO.

$$N_2 + O_2 \rightarrow 2NO$$

Incomplete combustion of the carbonaceous compounds (hydrocarbons, coal etc) result in the formation of carbon monoxide. e.g

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$\text{Hydrocarbon} + O_2 \rightarrow CO + H_2O + \text{Energy}$$
(limited)

CO, like other pollutants such as SO_x, NO_x, etc pollute the fresh air. At concentration higher than 750 ppm (0.1% of the air), CO may cause loss of consciousness and death occurs quickly.

Many more chemical reactions, occurring in the atmosphere, are involved in the formation of industrial and photochemical smog (Topic 23.2.4 and 23.2.5) similarly the main reaction occurring in the stratosphere (11-50 km) are due to the production and destruction of ozone.

23.1.2 Air Pollutants and Their Effects (COx, NOx, VOC's, SO_x O_3)

The term air pollution generally refers to substances that on local and regional scales directly harm animals, plants and people and their artifacts. Clean and dry air contains 78.09% nitrogen, 20.94% oxygen by volume. The remaining 0.97% is comprised of gaseous mixture of CO_2, He, Ar, Kr, Xe and nitrous oxide (N_2O). A wide range of chemicals can pollute the air. They include carbon monoxide, sulphure dioxide, toxic organics, nitrogen oxides and volatile organic compound (VOC's).

- **Carbon Monoxide**

Carbon monoxide mainly results from the incomplete combustion of carbonaceous compounds. It is termed as asphyxiating pollution because it can displace (O_2) bound to hemoglobin (Hb).

$$HbO_2 + CO \rightarrow COHb + O_2$$

Oxyhaemoglobin complex — Carboxyhaemoglobin complex

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The Fe binding sites in hemoglobin bind CO 320 times more tightly than O_2. The main source of CO to the environment are the vehicles, which emit the exhaust gases containing CO. When the concentration of the CO inhaled, reaches 100 ppm particularly in the closed spaces like tunnels, parking garages etc. It may result in headaches and shortness of breath. The severity of the effects depends on the duration of the exposure and level of exertion. At a concentration higher than 750 ppm (0.1% of the air molecules), loss of consciousness and death occurs quickly.

- **Sulphur Dioxide (SO_2):**

The main sources of sulphur dioxide (SO_2) emission to contaminate air, are combustion of coal and the smelting of metals (metallurgy) particularly copper. The sulphur content of the refined petroleum is generally quite low but the sulphur content of coal is quite high. The sulphur in coal is converted to SO_2 at high temperatures of combustion. SO_2 itself is a lung irritant and is harmful to people suffering from respiratory diseases. However, the most damaging health effects in urban atmosphere are not by SO_2 but by the sulphuric acid aerosol formed from its oxidation. Sulphuric acid not only irritates the fine vessels of the pulmonary region, causing them to swell and block the passages, but is also the major contributor to the acid rain (see 23.2.7).

- **Nitrogen oxides NOx and Volatile Organic Compound (VOC's):**

Nitrogen oxide (NO_x) and volatile organic compounds (VOC's) are not the direct air pollutants in that they rarely affect health directly. Rather, they are the main ingredients in the formation of photochemical smog (see

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

23.2.5) which is a brown blanket, covering many cities world wide. Although most damage from smog results from the action of ozone (O_3) and other oxidants, these oxidants can not build up without the combined action of NO_x and VOC's. Controlling smog formation requires reducing emission of NO_x and VOC's. Almost all NO_x emissions are due to fossil fuel combustion, whereas the major sources of VOC's emissions are the industrial processes, solvent utilization and on-road and non-road vehicles.

- **Ozone (O_3) as Pollutant:**

While anthropogenic emissions or man made activities are destroying ozone in the stratosphere (Fig: 23.1 of table 23.1), they are helping to create ozone in the troposphere through the phenomenon of photochemical smog. While ozone in the stratosphere protects us from the harmful effects of U.V rays, ozone at ground level is quite harmful. Producing cracks in rubber, destroying plants, and causing respiratory distress and eye irritation in humans. These effects set in at quite low concentrations, around 100 ppb.

23.1.3 Automobile, Pollutants and the Catalytic Converter:

The major pollutants, present in the exhaust gases emitted by automobiles, are carbon monoxide (CO), nitric oxide (NO) and the hydrocarbons (HC's). These gases disturb the stoichiometric ratio of the clean air and thus cause air pollution. When present in sufficient amount, they cause damage to human health and plants life.

One way of reducing emissions is to remove the pollutants from the exhaust gases. In automobiles, this is accomplished with a three-way

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

catalytic converter, so named because it reduces emissions of hydrocarbons (HC's), carbon monoxide (CO) and nitric oxide (NO). In order to deal with both NO and unburned gases, the converter has two chambers in succession (Fig: 23.4).

In the reducing chamber NO is reduced to N_2 by hydrogen. Hydrogen is generated at the surface of a rhodium (Rh) catalyst by the action of water on unburned fuel molecules.

$$HC's + H_2O \rightarrow H_2 + CO$$
$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

In the oxidation chamber, air is added and the CO and unburned hydrocarbons are oxidized to CO_2 and H_2O at the surface of pt/pd catalyst.

$$2CO + O_2 \xrightarrow{pt/pd} 2CO2$$
$$HC's + 2O_2 \xrightarrow{pt/pd} CO_2 + 2H_2O$$

The catalytic converter is quite effective in reducing automobile emission of pollutants.

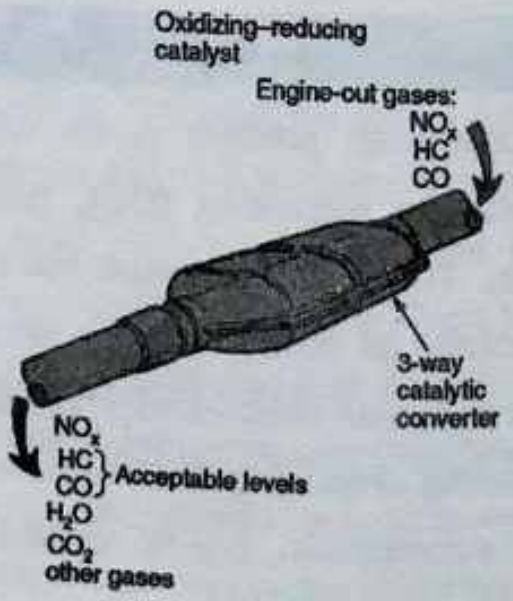


Fig. 23.2

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Fig: 23.4: The three-way catalytic remover for HC's, NO and CO, from automobile exhaust.

23.1.4 Industrial Smog:

Smog, in simple words, is the combination of smoke and fog. Smog causes a brownish coloration in the atmosphere, and thus reduces the visibility in the area. This situation ultimately leads to an increased death rates, particularly in large cities such as Los Angeles, Tokyo, Chicago, Lahore, Faisal Abad and Islamabad etc.

Industrial smog is formed, when exhaust pipes throw smoke and other materials into the air, produced by burning of the fossil fuels such as coal, oil and natural gas. The major products are CO_2, H_2O and smoke (carbon) particles.

The fossil fuel, coal, contributes large amounts of combustion products to the atmosphere. Coal is a complex substance made up primarily of carbon containing materials. Its burning produces mostly CO_2.

$$C + O_2 \rightarrow CO_2$$

CO_2 and H_2O in some ways may be considered pollutants. They cause relatively little trouble. Other minor combustion products are the major pollutants. For instance, most of the fossil fuels contain small amounts of sulphur compounds. These, on combustions, form sulphur dioxide, SO_2

$$S + O_2 \rightarrow SO_2$$

The tremendous quantities of coal that are burned for power production and in the blast furnace for making steel release a sizeable SO_2 to the atmosphere which causes to pollute the clean air. SO_2 is an obnoxious pollutant primarily because it gradually reacts further to form sulphur trioxide SO_3. Then in the presence of water or water vapours,

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

droplets of H_2SO_4 are formed as a result of this reaction.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

H_2SO_4 is corrosive to such diverse materials as building stones and the human respiratory tract.

Another coal-burning power station pollutant is soot, (primarily particles of carbon) which gives smoke its persistent dark colour. The soot also plays its role in the industrial smog. Incomplete combustion of the coal and natural gas may result in the formation of carbon monoxide gas or soot. CO is a lethal gas and at a concentration of 750 ppm in air, it may kill a person, if inhaled. At a level of above 100 ppm, carbon monoxide causes nausea, headache and shortness of breath. If exposed for a bit longer period, it causes loss of consciousness. CO plays vital role in the formation of smog. It is evident, that industrial activities are now so great that they can seriously modify the earths atmosphere, and thus can affect the earths average temperature and our climates.

23.1.5 Photochemical Smog:

Air pollution can be divided into two types. In one type, materials produced from the combustion of coal, oil and gasoline directly create trouble. In the other type, sunlight acts on air pollutants to produce photochemical smog. Photochemical smog can form wherever large quantities of automobile and industrial exhausts are trapped by an inversion layer over a locality that is exposed to sunshine. Photochemical smog is characterized by an accumulation of brown, hazy fumes, containing ozone (O_3) and other oxidants. Nitrogen oxides (NO_x) and volatile hydrocarbons (HC's), photochemical smog, a condition that affect an increasing number of cities and their surroundings.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Nitrogen dioxide, NO_2 is the only common atmospheric molecule capable of absorbing visible light near the ground level. Its spectrum (Fig: 23.3) has maximum absorption at about 400 nm, in the blue region. It is this absorption that gives smoggy air its brown tint. The unstable photo exited NO_2 dissociates to NO and O atoms.

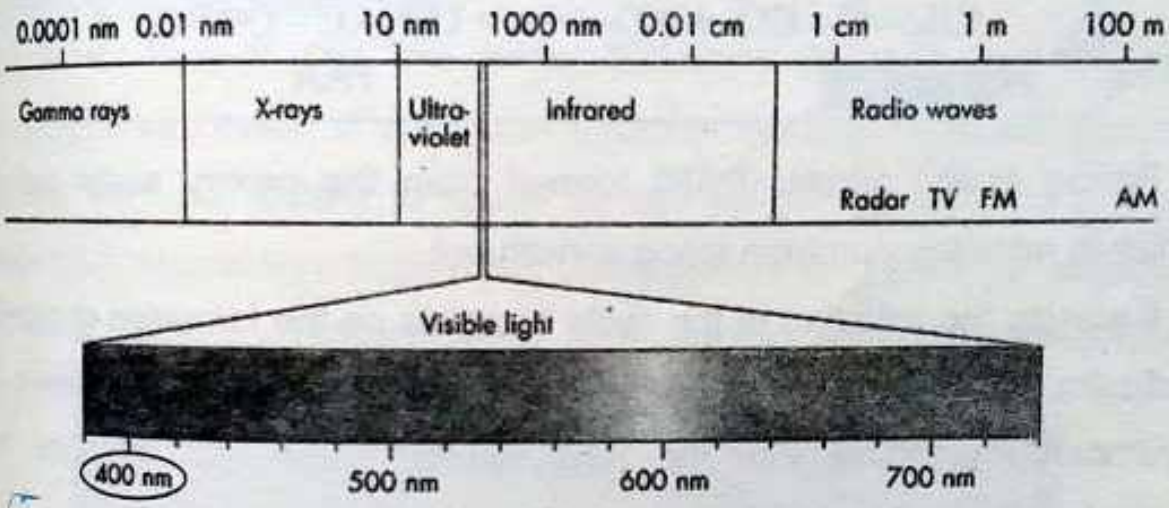


Fig. 23.3

$$NO_2 + h\upsilon \xrightarrow{<400nm} NO_{(g)} + O$$

The oxygen atoms (O) react immediately with the surrounding O_2 molecules to produce ozone (O_3).

$$O_2 + O \rightarrow O_3$$

The O_3 can react with NO to regenerate NO_2. A photochemical cycle is thus, established in these reactions. Hydrocarbons are also needed for smog formation. They produce carboxyl radicals by the reaction of O_3 with hydrocarbon.

$$O_3 + NO \rightarrow NO_2 + O_2$$

The organic radical react with O_2 and produce acylperoxy radical which react with NO_2 and produce PAN.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

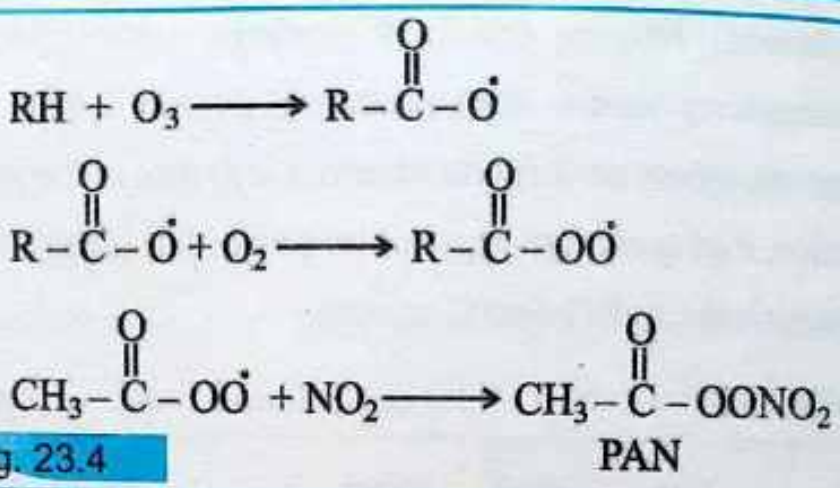


Fig. 23.4

Peroxy acetyl nitrate (PAN) formed from the peroxy acetyl radical, which is relatively common smog constituent.

Because the initiation of the cycle depends on the formation of organic radicals, the extent of smog formation depends on the reactivity of hydrocarbons (HC's) with the (O_3) radical. Some HC's produce few radicals, others many more.

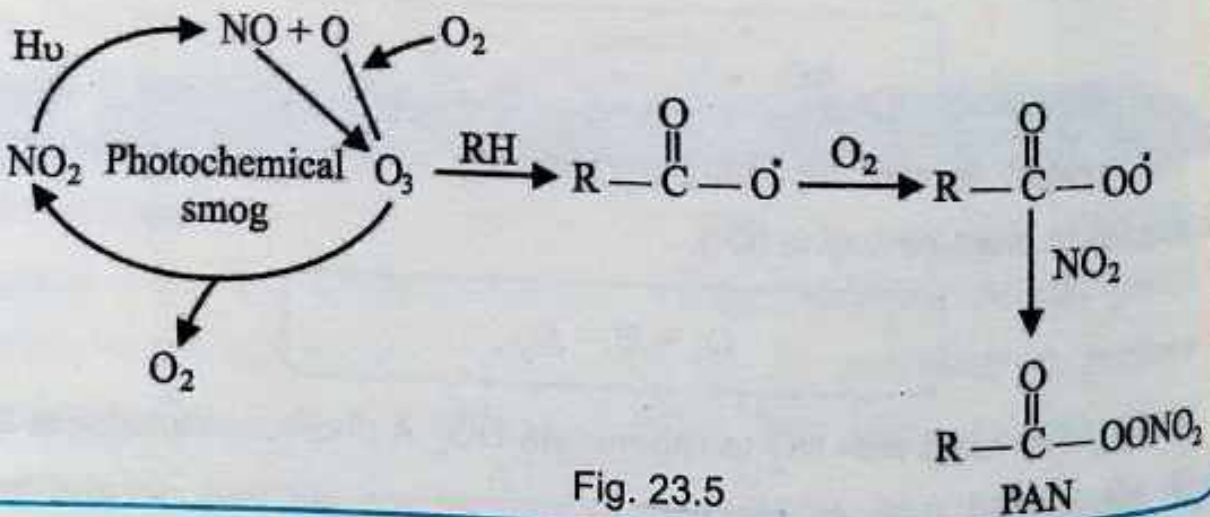


Fig. 23.5

23.1.6: Global Warming and Climate Change:

Several climatic changes are attributed to the large emissions of pollutants into the atmosphere. Generally, the global climate changes are studies from two aspects.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

i. Global warming or the greenhouse effect.

ii. Destruction of the ozone layer in the stratosphere. The later will be discussed at length in "the chemistry of stratosphere" (topic 23.3).

The Green House Effect:

Scientists believe that the earth maintains its long-term average temperature as a result of a balance between the heat received from the sun and the heat emitted to space by the earth. The sun like a high-temperature electric light bulb, emits ultraviolet (U.V) and visible radiation. The earth like a cool radiant heater, emits mostly infrared (IR) radiation.



(Fig. 23.6).

Carbon dioxide gas is colourless and, like all the other colourless matter, it does not absorb visible radiation. Consequently it doesn't absorb much of the sunlight, which is mostly in the visible region, that penetrates the outer atmosphere. However, atmosphere richer in CO_2 would capture a larger proportion of the radiation being emitted by the earth's surface. As a result

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

the temperature of the atmosphere and of the earth's surface would gradually increase. Like the glass, in a green house, CO_2 lets sunlight enter, but prevents the I.R radiation from escaping.

The increase in the temperature of the earth's surface that is expected to result from an increase in CO_2 in the atmosphere is said to be a "green house effect". The major gas contributing 50% to green house effect is CO_2. Other gases (CH_4, CFC's, SO_2, and NOx) together contribute the rest of 50%.

Human activities are increasing the atmospheric concentration of CO_2 and other green house gases, thereby altering the way the sun's heat is distributed on the earth's surface and in the atmosphere. In addition, the stratospheric ozone shield, which protects us from the sun's U.V radiation, is threatened by the emission of ozone destroying chemicals. The earth's average temperature is being increased (global warming) which ultimately changes our climates. Human health will also be affected due to spread of infectious diseases, such as yellow fever, dengue and malaria. The most serious outcome would be rise in sea level, floods and pattern of rain fall.

23.1.7 Acid Rain:

The concept of acid rain is also associated with polluted air. The term acid rain is referred to all precipitation (rain, dew and snow) which is more acidic then natural water with pH = 7.0. Rain water is generally, slightly acidic (pH = 5.6). it is due to the varying amounts of the dissolved CO_2 which is a common constituent (0.036%) of the earth's atmosphere.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$H_2O + CO_2 \rightarrow H_2CO_3$$

Carbonic acid

Therefore, any precipitation having a pH of less than 5.6, would be classified as acid rain. To the acidifying effect of CO_2, must be added the contribution other than acidic constituents of the atmosphere, particularly HNO_3 and H_2SO_4. These acids can both be formed naturally. HNO_3 derives from NO produced in lightening and forest fires, while H_2SO_4 derives from volcanoes and from biogenic sulphur compounds. The oxides of nitrogen and sulphur emitted within the atmosphere react with the moisture in the air or rain water to form nitric acid and sulphuric acid.

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

$$SO_2 + H_2O + \frac{1}{2}O_2 \rightarrow H_2SO_4$$

In polluted areas, the concentrations of these acids can be much higher and can reduce the pH of rain water substantially over extended regions, producing what is known as "acid rain". Acid rain can fall quite far from the sources of pollution, due to long-range atmospheric transport. In particular, acid rain is a serious problem for areas down-wind of coal-fired power plants.

Acid rain, on one hand, is a serious threat to the human life as it contaminates the drinking water and on the other hand is a pressing problem for plants, animals aquatic life and building material. Heavy metals e.g. Cu, Hg and Pb are also dissolved by acid rain producing various toxic effect.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Acidic streams and lakes or rivers affects the aquatic life. High acidity may result in killing of fish, reduces their growth and causes their reproductive failure. Hatching of fish eggs is prevented due to change in pH of water. Moreover, green algae and many forms of beneficial bacteria, which are essential to aquatic life, are also killed as a result of acidity in water. Plant growth is seriously inhibited due to acid rain. In addition, the acid rain also corrodes buildings monuments, statues and metals.

$$CaCO_{3(s)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(ppt)} + CO_2 + H_2O$$

23.2: CHEMISTRY OF THE STRATOSPHERE:

As mentioned earlier in this chapter (Table 23.1) stratosphere is the part of atmosphere which extends from 11-50 km. The temperature of the stratosphere ranges from -56^0C to -2^0C. The important chemical species that exists in this sphere is ozone (O_3), which acts as a protective shield (layer) for the survival of life on the earth from the harmful effects of sun's U.V radiation. The temperature of this sphere increases with increasing altitude.

Production and Distruction of Ozone:

The formation of ozone requires both oxygen atoms and oxygen molecules. Ozone is formed in the stratosphere when O_2 molecules absorb solar energy (radiation). The U.V photons of the sun have enough energy to split O_2 molecules into oxygen atoms high in the atmosphere.

$$\lambda < 242nm$$
$$O_2 + h\upsilon \rightarrow 2O$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

(The symbol "hυ" is used for photon and $\lambda < 242\text{nm}$ indicates the wave length range in which photons can induce the reaction).

The oxygen atoms produced in the reaction, then combine with oxygen molecules to form ozone.

$$O + O_2 \rightarrow O_3$$

In the atmosphere ozone layer occurs as a band at intermediate altitudes, between 25 and 30 km. At low altitudes, there are ample oxygen molecules but few unattached oxygen atoms. At high altitudes free oxygen atoms are more prevalent but there are few oxygen molecules. Conditions most suitable for ozone formation are found at intermediate altitudes, where both oxygen molecules and free oxygen atoms are present.

Ozone is also destroyed by solar radiation. When O_3 absorbs a solar U.V photons it dissociates into O_2 and O.

$$O_3 + h\upsilon \rightarrow O_2 + O$$

Also when O_3 encounters a free oxygen atom (O), the two can combine to form two O_2 molecules.

$$O_3 + O \rightarrow 2O_2$$

The concentration of O_3 depends on the relative rates of the formation and destruction reactions.

Depletion of Ozone layer

Certain man-made organic compounds such as chlorofluro carbons, CFC's (Freon) and the bromine-containing halons are used for many purposes. CFC's have been widely used as refrigerants, blowing agents for plastic foams, propellants for aerosol sprays and solvents for cleansing

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

micro electronic components. The halons have used as fire extinguishers. The heavy bromine-containing molecules provide a blanket of the gas that effectively smothers flames. The CFC's and halons have been enormously useful in these applications because they are nontoxic and nonflammable. Moreover they are not subject to oxidation, either in flame or biochemical. CFC's and halons are, therefore, not destroyed in the troposphere when released. They are only destroyed in the stratosphere by the action of U.V photons. The result of absorbing U.V photons is to break the weakest bond in the molecules either C – Cl or C-Br.

$$RX + h\upsilon \rightarrow R + X$$

Once released, chlorine and bromine destroy ozone via the following reactions.

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O \rightarrow X + O_2$$
$$or\ O_3 + O \rightarrow 2O_2$$

Scientists have noted a big hole in the ozone layer due to ozone depletion over Antarctica, for which they believe the CFC's are mostly responsible. Others have put a great deal of effort to find substitutes for CFC's. The main strategy has been to explore the suitability of hydro chlorofluro carbons (HCFC's) and hydrofluoric carbons (HFC's). These molecules have hydrogen as well as chlorine and fluorine substitutions on the carbon. The presence of C-H bonds allows the HCFC's and HFC's to be attacked by the OH radicals and thereby destroyed in the troposphere. At the same time the Cl and/or F substituent's lend these chemicals some of the desirable properties of CFC's, such as low reactivity and fire suppression, good insulating and solvent characteristics and boiling points suitable for use in refrigerator.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Society, Technology and Science

Chlorofluorocarbons (CFCs) are anthropogenic compounds that have been released into the atmosphere since the 1930s in various applications such as in air-conditioning, refrigeration, blowing agents in foams, insulations and packing materials, propellants in aerosol cans, and as solvents.

CFCs play a major role in ozone depletion. However, the atmospheric impacts of CFCs are not limited to its role as an active ozone reducer. This anthropogenic compound is also a greenhouse gas, with a much higher potential to enhance the greenhouse effect than CO_2.

Smog is a kind of air pollution. Classic smog results from large amounts of coal burning in an area caused by a mixture of smoke and sulfur dioxide. Modern smog does not usually come from coal but from vehicular and industrial emissions that are acted on in the atmosphere by ultraviolet light from the sun to form secondary pollutants that also combine with the primary emissions to form photochemical smog.

The effect of radiation pollution can include increase risk of developing cancer. Such as lung cancer, skin cancer and thyroid cancer etc and skin burns, genetic changes mutation, change in physical characteristics in animals and human.

The water is purified naturally by distillations, sand filtration, charcoal filtration, reverse osmosis and also by ultraviolet light.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

23.3: Water Pollution and Water Treatment:

The quality of surface and ground water is of great concern from two but distinct points of view:

1)Human health and welfare

2)Aquatic ecosystem.

Although most of the water is returned to the stream flow, yet its quality is inevitably degraded. Industrial and mining activities contaminate water with a variety of toxic materials. Agriculture can foul surface and ground waters with excess nutrients and can lead to salinization of soil when irrigation water evaporates, leaving salts behind. The cooling of power plants by circulating water raises the temperature (thermal pollution), with adverse effects on the biota of the receiving waters. Discharge of sewage from homes and commercial establishments, reduces the dissolved oxygen contents, again upsetting the biological balance of surface waters.

All such activities and many more, make water unfit for drinking and public use. Such water is said to be polluted water which needs treatment before it is made fit for public use.

23.3.1 Types of Water Pollutants:

Water that we either use or discard generally contains the following categories of undesirable substances (pollutants).

23.3.1.1 Suspended Solids and Sediments:

Two sub-categories of the undissolved solid material present in water can be recognized. One consists of particles large enough to be

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

removed by running the water through a filter paper or any other filtering apparatus. The second, consists of particles so small that they can not be removed by such treatments. Those in the second category are called colloids, which are too small to be seen, even with a microscope. They can, however, be detected, because they give water a turbid or cloudy appearance. They are most easily detected by passing a beam of light through the water and observing the scattering of light they produce like a beam of light passing through smoky or foggy air.

23.3.1.2 Dissolved Solids:

The dissolved solid material, present in water, may either be organic or inorganic. The dissolved organic compounds, acting as impurities, enter into water as a result of the growth and the death of aquatic plants, such as algae. Others are contributed by sewage from domestic sewage systems and by industrial wastes. The total amount of organic substances can be estimated from the amount of oxygen or any other chemical (oxidizing agent) needed to oxidize these substances to CO_2 and H_2O.

The dissolved inorganic materials present in water are mostly salts. These on one hand, are essential for human body, but on the other hand, if their concentrations are greater than about 500 ppm, they make water unfit for drinking, and such water is considered to be polluted. The most common salts present in water are carbonates, bicarbonates, sulphates and sulphides of calcium and magnesium. Hardness of water depends primarily on the Ca^{+2} and Mg^{+2} ion contents.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Source of Water Pollution:

Industrial effluents, domestic consumption and agricultural wastes contaminate the surface and ground waters making it unfit for drinking.

Industrial Effluents:

Industries like paper industry, metal industry and petrochemical industries discharge pollutants such as non-degradable organic substances, metals, mineral oils, benzene, toluene, xylene and phenols etc, which contaminate water. Textile industries, tanneries and slaughter houses also contribute towards water pollution. Metals that are released by various industries to pollute water, mainly include arsenic, mercury, lead and cadmium.

a) Smelting of gold, lead, copper, iron and nickel ores can be a source of arsenic pollution. Arsenic in drinking water is a slow poison. It decolorizes the skin (keratoses) which leads to cancer.

b) Mercury's toxicity is associated with almost entirely with eating fish. Sulphate reducing bacteria in sediments generate methyl mercury and release it into the water above, where it is absorbed by fish from the waters passing across their gills or from their food supply. The poisoning of mercury causes numbness of limbs, blurring and even loss of vision and loss of hearing and muscle coordination.

c) Leaded paints, leaded gasoline and lead solder (to seal food and drinks in cans) are the main sources of lead pollution. Lead poisons many thousands of people yearly. Once absorbed in the body, lead enters the blood stream and moves from there to soft tissues.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Higher exposures produce anemia. It also inhibits the enzymes involved in the biosynthesis of haemoglobin.

d) Cadmium inputs to soils and ultimately to surface waters, are mainly from airborne deposition (wet plus dry) and from commercial phosphate fertilizers which contain cadmium as a natural constituent of phosphate ore. Chronic exposure to cadmium causes heart and lung diseases (including lung cancer at high levels), immune system suppression and liver and kidney diseases.

- **Domestic Activities:**

Domestic water contains mainly soaps and detergents. Phosphates, used in the detergent formulation, affects the water quality. Likewise the use of synthetic washing powder has a drastic effect on fresh water, when domestic sewers are discharged into river. In general the domestic pollutants, make water turbid, increase the growth of pathogen causing diseases, impart bad and foul smell to fresh water (eutrophication) and may affect the aquatic life by screening off the sun's light due to the presence of suspended matter.

- **Agricultural Wastes:**

Agricultural areas can have water problems associated with the wide spread application of fertilizers, herbicides and pesticides. Drainage from poultry farms creates an extremely high potential for water pollution. Some herbicides and pesticides can accumulate in the ground water, occasionally threatening farm wells. Fertilizers, used by farmers to increase their yield, can increase the level of nitrate ions in the ground water. The main nitrate hazard is "blue baby syndrome", a condition of respiratory failure in babies having excessive nitrate in their diet.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

23.3.1.3 Thermal Pollution:

The heavy machinery and power plants get heated when frequently and continuously used for making various industrial products. Some parts of the plants are heated due to friction when they are in contact with each other while manufacturing the industrial products. For high efficiency and to elongate their life time, these parts (components) must be cooled. This is done with cold water. The cooling of power plants and other machinery by circulating water, raises the temperature of the water. This is called "thermal pollution".

Thermal pollution has adverse effects on the biota of the receiving waters. The high-temperature water, when mixed with cold water, increases the solubility of many pollutants (organic and inorganic), salts, ions, causing the water to be more easily polluted, thus affecting the quality of water and make it unfit for drinking and public use.

- **Parameters of Water Analysis:**

Drinking water should qualify the following qualities or parameters. That is it should be.

1. Odorless tasteless and colourless.
2. Free from turbidity causing agents such as suspended solids, dissolved solids, excess of chlorides, sulphates, phosphates etc.
3. Turbidity, not more than 10 ppm.
4. Free from bacteria causing diseases.
5. Slightly alkaline (pH = 7.0 – 8.5).

Water quality is consistently monitored. Many water quality parameters are used to decide weather or not, the given sample of water is fit for drinking. These include the biological oxygen demand (BOD) and

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

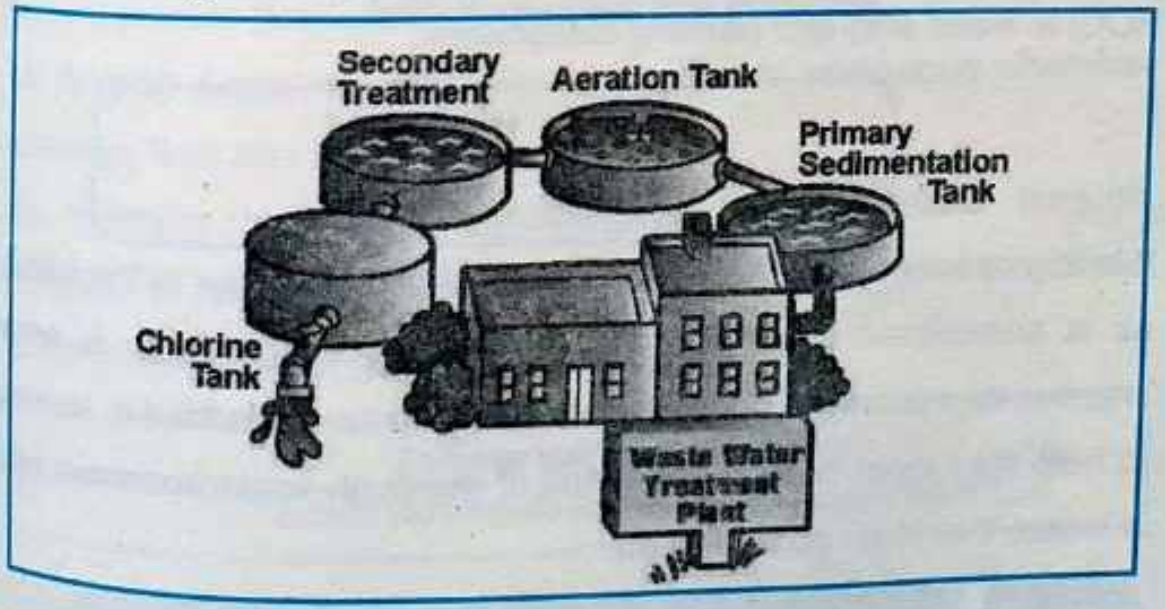
chemical oxygen demand (COD). In BOD, the amount of dissolved oxygen is determined by adding bacteria to the water while in COD it is done by adding chemical oxidizing agents, to the water.

Other parameters, used to check the quality of water, include the determination of total organic carbon (TOC), total dissolved solids (TDS), total suspended solids (TSS), pH and alkalinity, colour and odour etc.

23.3.2 Waste Water Treatment:

Water from a lake or river, that must meet the qualities of drinking water, undergoes a purifying treatment, involving several steps.

1. First, the undissolved (floating and visible) solid materials, if present in water, are removed. Coarse objects are removed by running the water through screens/filters.



2. The finer, colloidal particles that make water turbid, can not be removed by simple filtration. So a flocculating agent that is a substance that forms large gelatinous particles, is added. The

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

common flocculating agent is aluminium sulphate, $Al_2(SO_4)_3$, often referred to as alum, some lime, $Ca(OH)_2$, is generally also added so that precipitate of aluminium hydroxide, $Al(OH)_3$ which has the desired gelatinous form, is produced.

$$Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_{3\,ppt} + 2CaSO_4$$

This precipitate traps both inorganic solid particles and bacteria in the large curd like particles. These particles are then easily removed by filtration through a sand-bed or charcoal.

3. After filtration through the sand-bed, the water is usually treated with chlorine to kill remaining bacteria and other microbes. Chlorination is the widely used method to disinfect water for longer duration of time. The reactions involved are;

$$H_2O + Cl_2 \rightarrow H^+ + Cl^- + HOCl$$

HOCl is weak acid and partially dissociates.

$$HOCl \rightarrow H^+ + OCl^-$$
$$HOCl \rightarrow [O] + HCl$$

It is this nascent oxygen, [O], that gives taste and odour to the water. Thus air is sometimes blown through the water, i.e. the water is aerated to improve its odour and taste. A fluoride compound is added in some plants, to help fight tooth decay. The result of thorough water treatment operation is water, that is as good as new.

23.4 Green Chemistry:

The concept of green chemistry was coined by Paul Anestas of America. He enunciated twelve principles of Green chemistry in 1994

Scanned with CamScanner

towards ideal synthetic methods to save natural resources. Green Chemistry is the use of chemistry for pollution prevention by environmentally conscious design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry, also called sustainable chemistry, is a philosophy of chemical research and engineering that minimizes the use and generation of hazardous substances.

Goals of Green Chemistry:

The goal of "Green Chemistry" perspective include the following:

1. To reduce adverse environmental impacts by appropriate and innovative choice of materials and their chemical transformations.
2. Develop processes based on renewable (plant-based) rather than non-renewable (fossil carbon-derived) raw materials.
3. To develop processes that are less prone to obnoxious chemical releases, fires and explosions.
4. To minimize byproducts in chemical transformations through redesign of reactions and reaction sequences. In other words, to achieve better "Atom economy".

$$\% \text{ Atom economy} = \frac{\text{Formula weight of the product}}{\text{sum of the formula weights of all the reactants}} \times 100$$

(Good atom economy means most of the atoms of the reactants are incorporated in the desired products and only small amounts of unwanted byproducts are formed and hence lesser problems of waste disposal or waste treatment).

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

5. To develop products that are less toxic or which require less toxic raw materials/feed stocks.
6. To develop products that degrade more readily in environment than the current products.
7. To reduce the requirements for hazardous or environmentally persistent solvents and extractants in chemical processes.
8. To improve energy efficiency by developing low temperature and low pressure processes by using new/improved catalysts.
9. To develop efficient and reliable methods to monitor processes (e.g. monitoring reactions and releases) for improved control.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Key Points:

- Environmental chemistry is the branch of chemistry which deals with chemical and biochemical occurrence in nature.
- Pollutant is any substance which contaminate our environment.
- Atmosphere is a big tank of gases, surrounding the earth's surface.
- The term acid rain is referred to all precipitation (rain, snow or dew) which is more acidic than natural water (pH = 7.0).
- Smog is the combination of smoke and fog.
- Water is an important natural resource on this planet.
- An important aspect of water quality is the amount of dissolved oxygen in it.
- The term green chemistry is defined as the invention, design and application of chemical product and process to reduce or to eliminate the use and generation of hazardous substances.
- The smog consisting of high concentration of photochemical oxidants is known as photochemical or oxidizing smog.
- Increased concentration of CO_2 increase the earth's temperature, by greenhouse effect. This in turn result in climate changes and global warming.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Exercise

1. Which one of the following is not a secondary pollutant?

a) Ozone b) H_2CO_3

c) H_2SO_4 d) CO_2

2. Pollutants have adverse effect over

a) Biosphere b) ecosystem

c) Hydrosphere d) All

3. Ozone layer in upper atmosphere is being destroyed by.

a) Chlorofluoro Carbons b) SO_2

c) Smog d) Photochemical Oxidant.

4. Drained sewage has B.O.D.

a) More than that of water b) Less than that of water

c) Equal to that of water d) Non of above

5. Photochemical smog is primarily caused by

a) CO b) CO_2

c) O_3 d) NO_2

6. Result of ozone hole is

a) Acid rain b) Global warming

c) Increased amount of CO_2 d) Greater exposure of earth to U.V

7. Which one of following substances is not present in acid rain?

a) H_2SO_4 b) HNO_3

c) H_2SO_3 d) CH_3COOH

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

8.Photochemical oxidant PAN is formed by

a)The action of oxide of nitrogen on hydrocarbons in presence if sunlight.

b)Action of carbon dioxide on hydrocarbon in presence of sunlight

c)Action of hydrogen sulphide on hydro carbon in presence of sunlight

d)Action of SO_2 and hydro carbons.

9.Which compound is base for corrosion resistance paints

a)White lead b) Red lead

c)Lead chromate d) All of these

10.The temperature (C°)range of troposphere is

a)15 to -56 b) 56 to -2

c)-2 to -92 d) -92 to 1200

Short Questions:

1.Why is acid rain considered as a threat to historical monuments?

2.Define the following

a)Contaminants b) Pollutant

c)Eutrophication d) Acid rain

f) B.O.D g) Smog

3.What is importance of dissolved oxygen in water?

4.What methods are employed for control of SO_2 pollution?

5.What are applications of Green Chemistry?

6.Name four major greenhouse gases.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

7. Out of CFC's and CO_2 which one has higher potential to cause global warming and why?
8. Why does the rain water normally have pH of about 5.6? When does it become acid rain?

Long Questions:

1. 'Green Chemistry is a new route to the protection of environment'. Comment on it.
2. What is greenhouse effect? How is it causing global warming?
3. What is meant by atmosphere? Explain the various layers of atmosphere.
4. Define air pollutant and discuss its effect.
5. A) What is role of ozone layer in upper atmosphere?
   B) What will happen if ozone is no more present in upper atmosphere?
6. What is water pollution? What are the main sources of water pollution?
7. Write note on the following.
   a) Acid rain
   b) Smog
   c) Water treatment
   d) Chemistry of stratosphere

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

UNIT 24

ANALYTICAL CHEMISTRY

Learning Outcomes:

After Studying this unit Students will be able to:

- compare the classical method of analysis with modern methods.
- discuss the procedure/purpose of combustion analysis.
- define spectroscopy and discuss its applications in analytical chemistry.
- explain the origin of electromagnetic spectrum used in IR and uv-vis spectroscopy.
- explain the origin of IR absorption by the simple molecules.
- determine structures of phenol, toluene, acetone and ethanol by their IR spectrum.
- predict whether a given molecule will absorb in the uv-visible/IR region or not.
- predict the color of a transition metal complexe from its uv-vis spectra.
- outline in simple terms the principles of proton NMR spectroscopy.
- explain how chemical environment of proton affects the magnetic field it experiences and hence the absorption of energy at resonance frequency.
- describe standard scales used in proton NMR.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

- explain instrumentation and working of MS.
- outline the use of MS in determination of relative isotopic masses and isotopic abundance.
- define and explain atomic emission and atomic absorption spectrum.
- calculate the average atomic mass of an element from isotopic data.
- calculate percentage of C,H and O from given data and determine empirical and molecular formula.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Analytical Chemistry:

Analytical chemistry is a branch of chemistry which deals with the identification of substances and finding their weights. A set of experiments used to know about the quality of a substance is called qualitative analysis. The methods used for finding the quantities of substances are called quantitative analysis. Analytical chemistry deals with both qualitative and quantitative analysis.

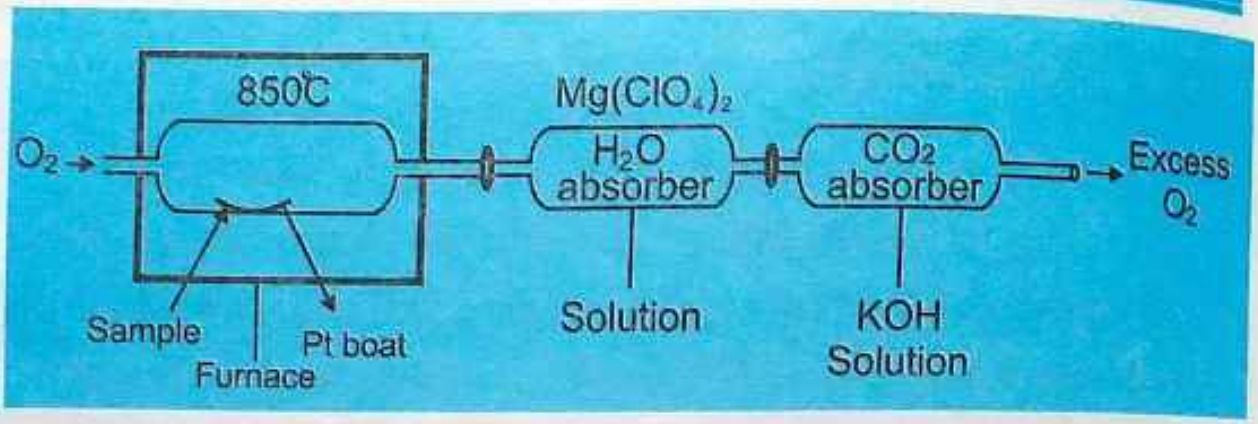
Identification of acidic and basic radicals in a salt involves qualitative chemical analysis. On the other hand, volumetric analysis (titrations) and gravimetric analysis are quantitative chemical analysis.

24.1 Classical methods of Analysis, Combustion analysis and determination of Molecular formula:

Burning of a substance in the presence of oxygen is called combustion. Combustion is an exothermic process in which heat energy is evolved.

Combustion analysis is carried out for finding the percentage composition of an organic compounds cantaining C,H or C,H and O. If any other element such as N,S,Cl etc. is present in the compound, combustion analysis can not be used. In combustion analysis a known weight of an organic compound is mixed with CuO and taken in a platinium boat, which is placed in a furnace heated to about 850°C, and a stream of oxygen gas is passed over the sample.

Scanned with CamScanner



Organic compound on burning produces CO_2 and H_2O vapours which are swept out of the furnace and traped in a pair of absorbers. The water is absorbed in a sample of Magnesium perchlorate [$Mg(ClO_4)_2$] of known mass. The carbon dioxide is absorbed in a known mass of KOH. Percentage of C and H are calculated by the following formulae.

$$\%C = \frac{\text{mass of } CO_2}{\text{mass of org.compound}} \times \frac{12}{44} \times 100$$

$$\%H = \frac{\text{mass of } H_2O}{\text{mass of org.compound}} \times \frac{2.02}{18.02} \times 100$$

Percentage of oxygen is calculated as %O = 100 – (%C + %H). If percentage of oxygen comes out to be zero, it means the organic compound does not contain oxygen.

Calculation of Empirical formula:

Empirical formula is the formula that gives the simplest whole number ratio of the atoms of elements present in the compound.

In order to find the empirical formula of a compound, number of moles of carbon, hydrogen and oxygen is calculated by the following formulae.

$$\text{Moles of C} = \frac{\%\text{age of C}}{\text{At. mass of C}}$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$\text{Moles of H} = \frac{\%\text{age of H}}{\text{At. mass of H}}$$

$$\text{Moles of O} = \frac{\%\text{age of O}}{\text{At. mass of O}}$$

In second step the simplest ratio between the number of moles is found out by dividing the number of moles of each element by the smallest number of moles. If the ratio is not in whole numbers then number of moles of each element is multiplied by a suitable small number to get the whole number ratio.

Finally the symbol of each element are written and their number of moles are written as subscripts. This gives the empirical formula of a compound.

Example 24.1: The combustion analysis of 0.003g of Aspirin produced 0.0066g of CO_2 and 0.0012g of H_2O. Calculate the empirical formula of aspirin.

Solution: Calculate the percentage of elements

$$\text{Percentage of C} = \frac{\text{mass of } CO_2}{\text{mass of org. compound}} \times \frac{12}{44} \times 100$$

$$= \frac{0.0066}{0.003} \times \frac{12}{44} \times 100$$

$$= 60.0\ \%$$

$$\text{Percentage of H} = \frac{\text{mass of } H_2O}{\text{mass of org. compound}} \times \frac{2.02}{18.02} \times 100$$

$$= \frac{0.0012}{0.003} \times \frac{2.02}{18.05} \times 100 = 4.48\%$$

$$\text{Percentage of O} = 100 - (60.0 + 4.48)$$

$$= 35.5\ \%$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Let us find the number of moles of elements

$$\text{Moles of C} = \frac{\%\text{age of C}}{\text{At.mass of C}} = \frac{60.0}{12.01} = 4.99$$

$$\text{Moles of H} = \frac{\%\text{age of H}}{\text{At.mass of H}} = \frac{4.48}{1.01} = 4.43$$

$$\text{Moles of O} = \frac{\%\text{age of O}}{\text{At.mass of O}} = \frac{35.5}{16.0} = 2.21$$

Molar ratio :	C	:	H	:	O
	4.99		4.43		2.21
Simplifying the molar ratio	$\frac{4.99}{2.21}$	:	$\frac{4.43}{2.21}$	:	$\frac{2.21}{2.21}$
	2.25		2.00		1.00

To convert the fractional number into whole number, each value is multiplied by 4.

C	:	H	:	O
(4 x 2.25)		(4 x 2.00)		(4 x 1.00)
9.00	:	8.00	:	4.00

Thus empirical formula of Aspirin is $C_9H_8O_4$. Empirical formula of a compound shows the simplest ratio between different kinds of atoms present in a compound. It does not show the exact number of atoms.

Calculation of Molecular formula:

Molecular formula shows the actual number of atoms of each kind of element in molecule of a compound. Molecular formula is either same to empirical formula or integral multiple of the empirical formula.

Molecular formula = n x (empirical formula)

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

Example: Empirical formula of a compound is CH_2O. Molecular weight of this compound as obtained from other experiments is 180.12 g/mol. Find the molecular formula of the compound.

Solution: Let find the value of n

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}} = \frac{180.12}{30.02} = 6$$

Thus molecular formula = n (empirical formula)

$= 6\ (CH_2O)$

$= C_6H_{12}O_6$

24.2 Modern methods of Analysis:

In inorganic chemistry, a molecular formula is informative enough to distinguish one substance from another. However, this is not the case in organic chemistry, where molecular formula may represent more than one substance e.g. C_2H_6O is a molecular formula, the atom may be arranged as:

$CH_3 - CH_2 - OH$	$CH_3 - O - CH_3$
Ethanol	Dimethyl ether

So in organic chemistry structural formula is often used to represent a particular organic substance. Previously, the structure of newly discovered organic compounds was based almost entirely on its molecular formula and chemical reactions. This way of finding the structure of organic compounds was time consuming and not always 100% accurate. Now a

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

days spectroscopic methods are used for analysis and structure determinations.

Modern methods of analysis include infrared spectrophotometry, ultraviolet and visible spectrophotometry, Atomic abosption and emission spectrophotometry and mass spectrometry. Modern methods of analysis are superior to classical methods because of the following reasons.

(i) Small amounts of chemical are required.
(ii) Chemicals are not wasted in large amounts.
(iii) These methods are rapid and less time consuming.
(iv) They give more accurate results.
(v) These methods are simple and do not involve much chemistry as compared to the classical methods.

24.2.1 Spectroscopy:

After finding the molecular formula of an organic compound, we need to find its exact structural formula. For structural formula of a compound mainly three aspects are considered;

i. Physical properties of the compound.

Physical properties are dependent on the structure and provides enough information about the structure formula of the compound. For example C_2H_6O is the molecular formula of both ethanol and diethyl ether. Ethanol (C_2H_5–OH) at room temperature is liquid and its boiling point is 341K, while dimethyl ether ($CH_3 — O — CH_3$) is gas at room temperature having a boiling point of 248K.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

ii. Chemical properties:

Functional group is defined as "an atom or a group of atoms that gives certain characteristic properties to the compound". Different compounds having the same molecular formula but different functional groups (structural formula) behave differently to the same reactants. For example ethanol reacts with sodium metal liberating hydrogen, while demethyl ether do not react with it.

iii. Instrumental methods of analysis.

Modern chemistry laboratories use instruments that help to identify atoms/group of atoms in the organic compound to elucidate its structure. Spectroscopy is one of these instrumental methods.

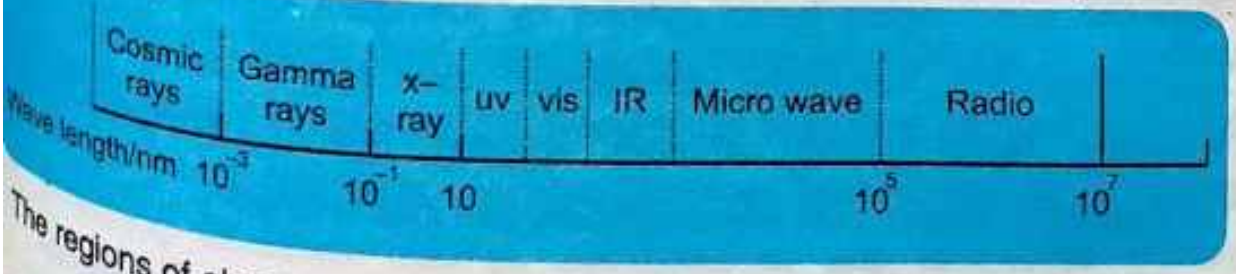
Organic compounds absorb energy on interaction with electromagnetic radiations. The electromagnetic radiation (emr) extend from high-energy cosmic rays to low-energy radio waves, according to the equation

$E = h\nu$ and

$\nu = c/\lambda$

So $E = hc/\lambda$

That is energy of the e.m.r depends on its frequency and wave length.



The regions of electromagnetic spectrum of e.m.r is given in above figure.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

During the interaction of organic compounds with electromagnetic radiations certain wavelengths are absorbed, which excites the molecules/atoms to higher energy level. In atoms the transition results due to changes in distribution of electrons, while in molecules along with changes in electronic distribution, changes in the molecular rotations and bonds vibration (stretching, bending) also occurs.

The bond vibration and rotation of molecules need less energy, i.e. in IR region, than the electronic excitation i.e. in uv/vis region.

The instrument used to record the wavelengths absorbed and the concentration of the absorbing species is called spectrophotometer.

Spectrophotometry is a technique used to identify the different substances as a result of their interactions with the electromagnetic radiations, spectrophotometry is used both for qualitative as well as quantitative analysis. Before discussing the different spectrophotometric techniques let us study the electromagnetic spectrum.

Electromegnetic spectrum.

The electromagnetic spectrum covers a wide range of wavelengths of different radiations. Electromagnetic radiations are divided into different regions, each region being defined by the limits of any of the four parameters, i,e. frequency, wavelength, wave number or energy. The following table shows different spectral regions alongwith their wavelength, frequencies, wave numbers and their energies.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Table 24.1: Gamma Rays and the Electromagnetic Spectrum

Name of Wave	Wavelength (m = meters)	Frequency (Hz)	Energy per Photon (eV)
AM Radio	10^{2}	10^{6}	10^{-9}
FM, TV	1	10^{8}	10^{-7}
Radar	10^{-1}	10^{9}	10^{-6}
Microwaves	10^{-2}	10^{10}	10^{-5}
Infrared	10^{-5}	10^{13}	10^{-2}
Visible Light	10^{-7}	10^{15}	1
Ultraviolet	10^{-8}	10^{16}	10^{1}
X-Rays	10^{-10}	10^{18}	10^{3}
Gamma Rays	10^{-13}	10^{21}	10^{6}

24.2.2 Spectroscopic method:

24.2.2.1 Infrared (IR):

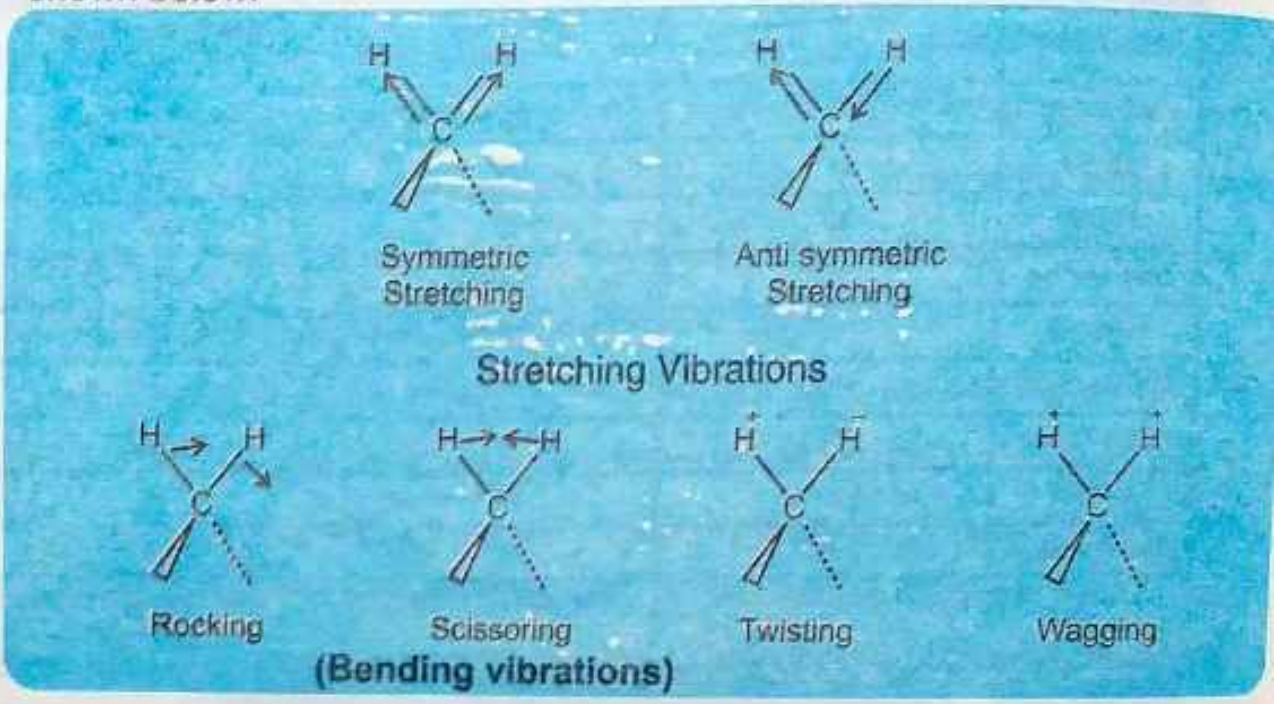
In IR spectroscopy organic compounds are exposed to weak radiations in the range 5000–667cm^{-1} (wave number $\bar{\upsilon}$), which increases vibration of bonds in its molecules and also rotation of molecules.

Atoms in a molecule do not maintain fixed positions with respect to each other, the bonds undergo stretching and bending vibrations about the average value of interatomic distance. Such vibrations are particularly important with bonds involving H atoms, because of its low atomic mass. Vibrations may be stretching or bending. In stretching vibrations the bond angle does not change but only the distances between the atoms change. Stretching vibrations may be symmetric or anti symmetric. Bending vibrations do not change the interatomic distance but change the angles between the atoms. The various stretching and bending vibrational modes

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

for Ax_2 system, e.g, the methylene group in a hydrocarbon molecule are shown below.



An infrared spectrum, commonly referred to as IR spectrum is usually expressed in microns (μ) or in the form of wave number (cm^{-1}). Wave number is plotted on *x-axis* and % transmittance on *y-axis*. Each dip in a spectrum is called a band or peak. A 100% transmittance means no absorption.

IR spectrum of an organic compound is characteristic of the structure of the compound, and is of great assistance in establishing its identity. No two different organic compounds would give rise to identical spectra.

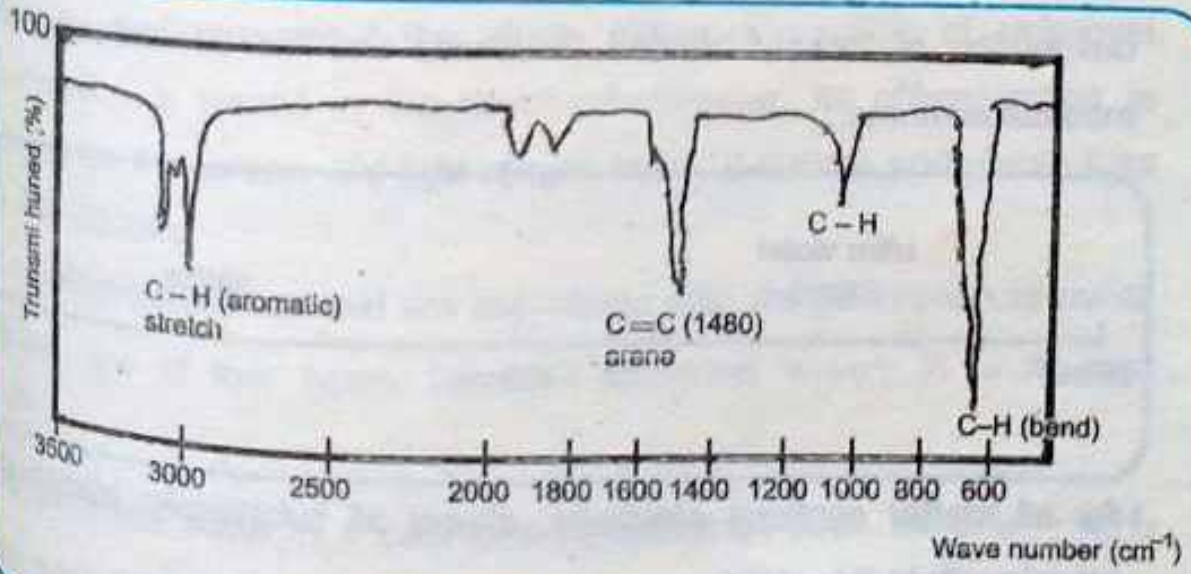
IR region is divided into two. The region between 600 – 1500 cm^{-1} is called finger print region because the absorption in this region is characteristic of a compound. Two different compounds will give different absorptions peaks in this region. This region is used to identify a compound. The region between 1500 – 4000 cm^{-1} is called functional group region. Different functional groups show absorption at different

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

frequencies. The following table shows the IR absorption frequencies of different functional groups.

Functional group	Wave number/cm^{-1}
O – H aliphatic and aromatic	3600 – 3000
N – H primary, secondary, tertiary amines	3600 – 3100
C – H aliphatic	3000 – 2850
C – H aromatic	2280 – 2200
C – C arene	1600
C – O	1300 – 1000
O – H free	3670 – 3580
C ≡ C alkynes	2250 – 2070
COOR ester	1750 – 1700
COOH carboxylic acid	1740 – 1670
C = O aldehydes, ketones and esters	1750 – 1680
$CONH_2$ amides	1720 – 1640



IR spetrum of benzene

Scanned with CamScanner

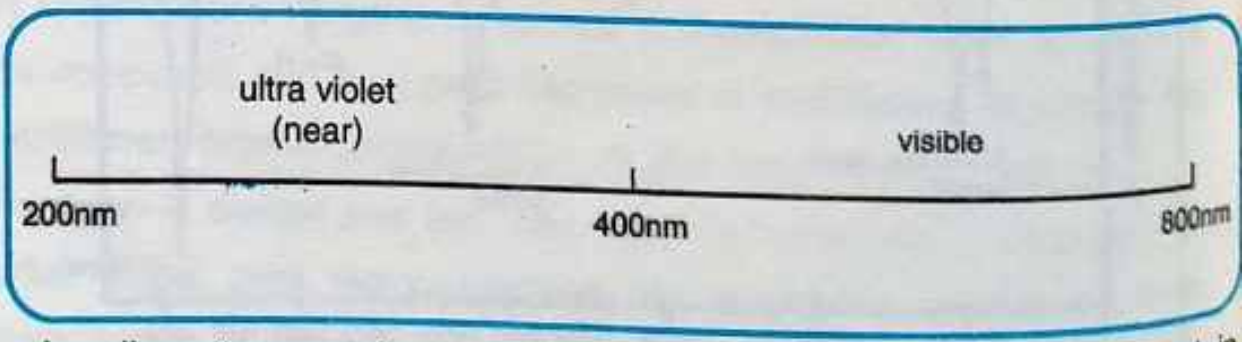
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Uses

1. IR spectroscopy is helpful in identification of unknown compounds.
2. It is used for detection of impurities. The presence of absorption peak at positions where the compound does not absorb indicates the presence of impurities e.g. the presence of cyclohexanone is readily detected in cyclohexanol by the intense carbonyl band.
3. The progress of most reactions can be followed by examining the infra-red spectra of aliquots withdrawn from the reaction mixture. For example, the oxidation of secondary alcohol to ketone is accompanied by the disappearance of the O–H band near 3600cm^{-1} and the appearance of C = O band near 1715cm^{-1}.

24.2.2.2 Ultraviolet and visible (uv/vis) spectrophotometry:

In uv/vis spectroscopy radiation having wavelength in the range 200–800nm are used. These are more energetic and therefore, can change the distribution of loosely bonded (π – bond) and non-bonded electrons in molecules/atoms.



As all matter contains electrons, almost all substances absorb certain wavelength in this range.

The absorption is according to Beer-Lambert's law

$$A = Ecl$$

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

where A is the absorbance, c is the concentration of solution in mole per litre and l is the path length of the sample solution in centimetres. E is called molar absorptivity or molar extinction coefficient, a constant characteristic of the solute at a given wavelength.

Uv-vis spectrophotometry is used both for qualitative and quantitative analysis. For quantitative analysis we use Beer Lambert law. The absorption of uv-vis light by a solution kept in a quartz cell of known path length is directly proportional to the concentration of solution. Solutions of different concentration are prepared and are introduced into the uv-vis spectrophotmeter in order to record their absorbances.

A graph is constructed by plotting the concentrations on x-asis and absorbances on y-axis. This graph is called working curve. During this experiment a selected wavelength λ (max) at which maximum absoption occurs is used throughout the study. When a solution of unknown concentration is placed in the spectrophotometer, its concentration is displayed on the screen. UV light ranges from 10-400nm and visible light from 400-800mn.

The electronic transition that are associated with the absorption of uv/vis radiation, are of four types. i,e $\sigma \rightarrow \sigma^*$ saturated $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$

$\sigma \rightarrow \sigma^*$ transition occur in a saturated hydrocarbon such as $CH_3 - CH_3$ which contain only sigma bonds. $\sigma \rightarrow \sigma^*$ transition requires greater energy, thus C–C bond absorbs 135nm and C – H bond absorbs at about 125nm.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The $n \rightarrow \sigma^*$ transition occurs in a saturated molecules containing hetero atoms, such as oxygen, sulphur, nitrogen or halogens. This transition requires slightly less energy than required for $\sigma \rightarrow \sigma^*$ transition.

The $\pi \rightarrow \pi^*$ transitions occur in molecule, containing double or triple bonds or aromatic rings. Ethylene absorbs at 171nm. However, a conjugated system of unsaturated bonds absorbs at much longer wavelength, e.g. butadiene absorbs at 217mn. ($CH_2 = CH - CH = CH_2$)

The $n \rightarrow \pi^*$ transitions occur in molecules that contain double or triple bonds involving hetero atoms e.g. $>C=O$:, $-C \equiv N$: etc.

Transition metal complexes are usually coloured due to d-d transition. Such compounds absorb radiations in the visible region. When a compound absorbs viclet light (400-435nm), it refects all the remaining (six) colours which electively appear as a single colour (complementary colour). Complementary colour of violet colour is yellow green. The following table shows relationship between the colour of transition metal complexes and the wavelength of light absorption.

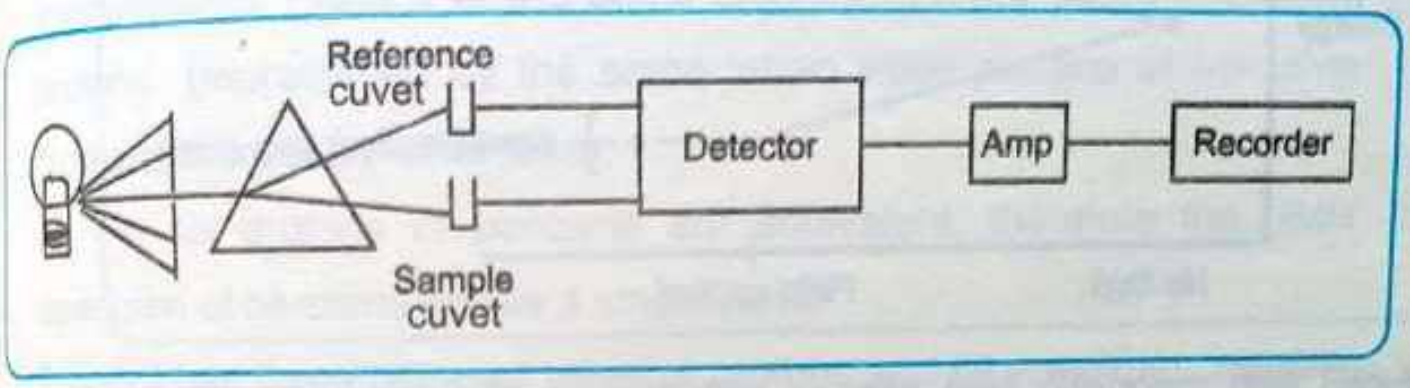
Colour of light absorbed	Wave length (nm)	Colour of complex
Violet	400 – 435	Yellow green
Blue	435 – 480	Yellow
Blue green	490 – 500	Red
Green	500 – 560	Purple
Yellow	580 – 595	Blue
Orange	595 – 650	Green blue

From the above discussion it is concluded that from the uv-vis spectrum of transition metal complex, the colour of the compound can be predicted. A

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

schematic diagram of double beam uv-vis spectrophotometer is given below.



24.2.2.3 Nuclear Magnetic Resonance (NMR) :

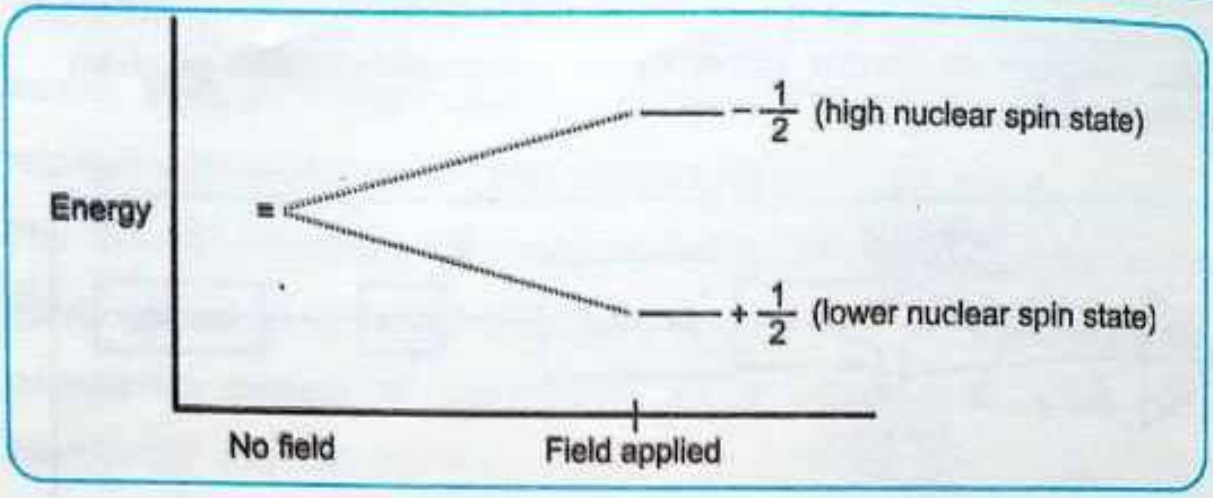
Like electrons atomic nucleus also spin about an axis. Thus the atomic nuclei behave like tiny magnets, as the spinning charged bodies produce magnetic field. The nuclear spin is quantised, therefore, the magnetic moment of nucleus is also quantised. In a proton (H) the spin quantum number is = ½. Other nuclei which contain odd number of protons or neutrons or both also have a spin quantum number = ½ e.g. ^{13}C ^{15}N ^{19}F ^{31}P.

Nuclei which have even number of protons and neutrons have zero spin and zero magnetic moment e.g. ^{12}C and ^{16}O. Such nuclei are invisible in NMR spectrometry.

The spin states of a nucleus have equal energies, in the absence of applied magnetic field. If a magnetic field is applied, the spin states are no longer of equal energy. Thus two nuclear spin states, one of lower energy (+ ½) and other of high energy (– ½) are produced. Proton with magnetic field aligned with the applied field is at a lower energy than that which aligns against the field.

Scanned with CamScanner

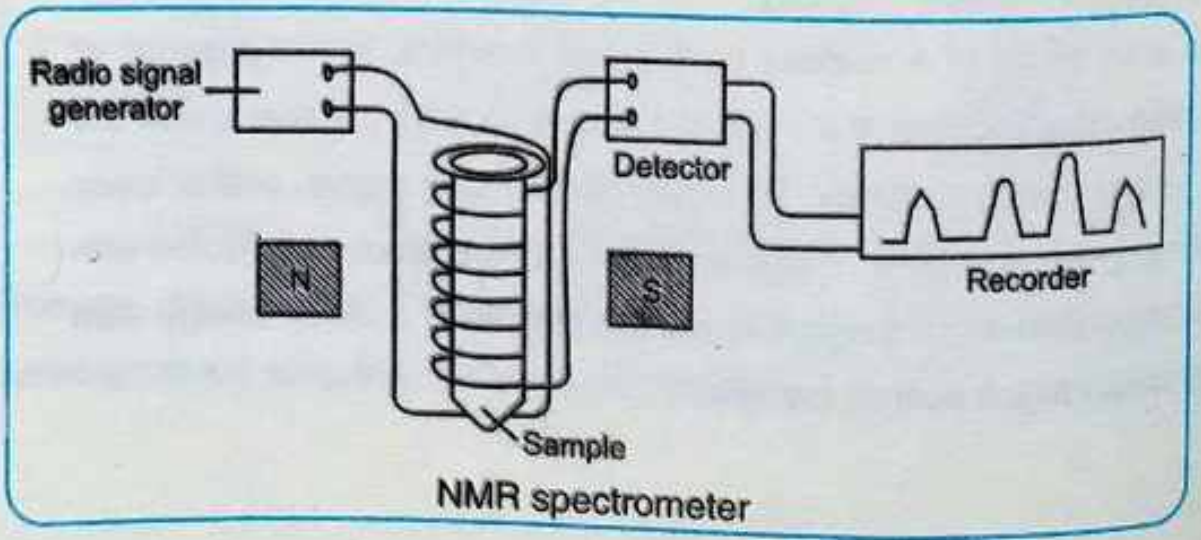
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



Nuclei with magnetic field aligned with the applied field can absorb energy and change their spin state (high energy state). The phenomenon is called flipping. The quantity of energy absorbed depends on the energy gap between the two states.

$E_{absorbed} = E_{(-½)} - E_{(+½)}$.

In this case energy absorbed belongs to radio frequency region of the electromagnetic spectrum. The absorption of energy is recorded an a chart paper. When a sample is placed in NMR spectrophotometer, the magnetic field is varied and energy of a specific frequency is absorbed. A schematic diagram of NMR spectrophotometer is shown in the following figure.



NMR spectrometer

Scanned with CamScanner

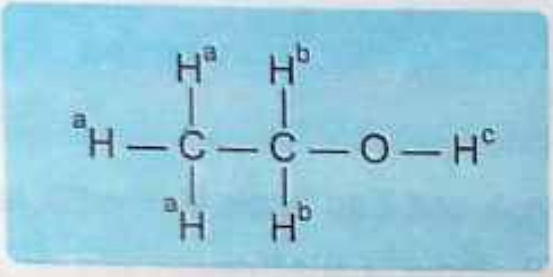
MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Position of signals (chemical shift)

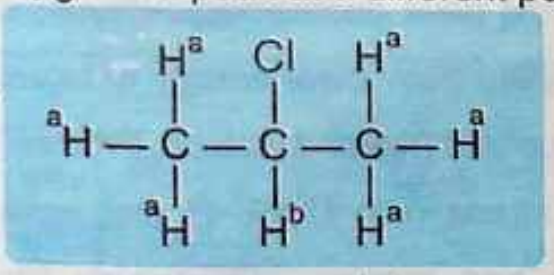
NMR spectrophotometer can differentiate between protons of different environments. Protons of the same environment are called equivalent protons (represented by the same letter) while protons of the other type are indicate by other letter.

All the six protons of benzene are equivalent, therefore the NMR spectrum of benzene shows a single peak.

Ethanol has three different types of protons and its spectrum contains three peaks.



Isopropyl chloride has six equivalent protons which give a single peak. The remaining proton, gives a peak at a different position.



The area under the peak is directly proportional to the number of protons.

For taking the NMR spectrum of a substance a little amount of TMS (Tetramethyl silane $(CH_3)_4Si$) is added to it. It has been chosen as a standard. NMR spectrum is a plot of absorption (y-axis) and chemical shift on x-axis. For TMS the value of chemical shift (δ) has been chosen as zero arbitrarily. Chemical shifts of other compounds are compared with this reference value. All other compounds have

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

chemical shift (δ) value higher than zero. TMS has been chosen as a standard because its all protons are equivalent and show absorption at lowest δ value. Moreover it is highly volatile and can be separated from the compound after its spectrum has been recorded. Chemical shift is expressed as delta (δ) or Tau (τ) scale. NMR spectrum is rectangular chart paper with a linear scale of δ (delta) usually arranging from 0 to 12 ppm, the TMS signal is taken as $\delta = 0$.

$$\delta = \frac{\text{Observed shift from TMS in (Hz)}}{\text{Operating frequency of spectrophotometer (Hz)}} \times 10^6 \text{ ppm}$$

The relationship between δ and Tau scale is $\tau = 10 - \delta$. Usually ppm scale is used, where TMS signal is at 10 ppm.

Different protons give peaks at different δ value. Protons with greater electron clouds are called (less deshielded protons) and they require higher frequency for flipping from lower energy to higher energy states. Such peaks appear as upfield (lower δ value). Protons in the vicinity of higher electronegative atoms (like Cl, F, O etc) have lower electron densities around them and require little energy for flipping. Such protons are called more deshielded protons. Such protons show peak at higher δ value (downfield). From the values of δ, the different protons of a compound can be differentiated from one another.

24.2.2.4 Atomic emission and absorption spectra:

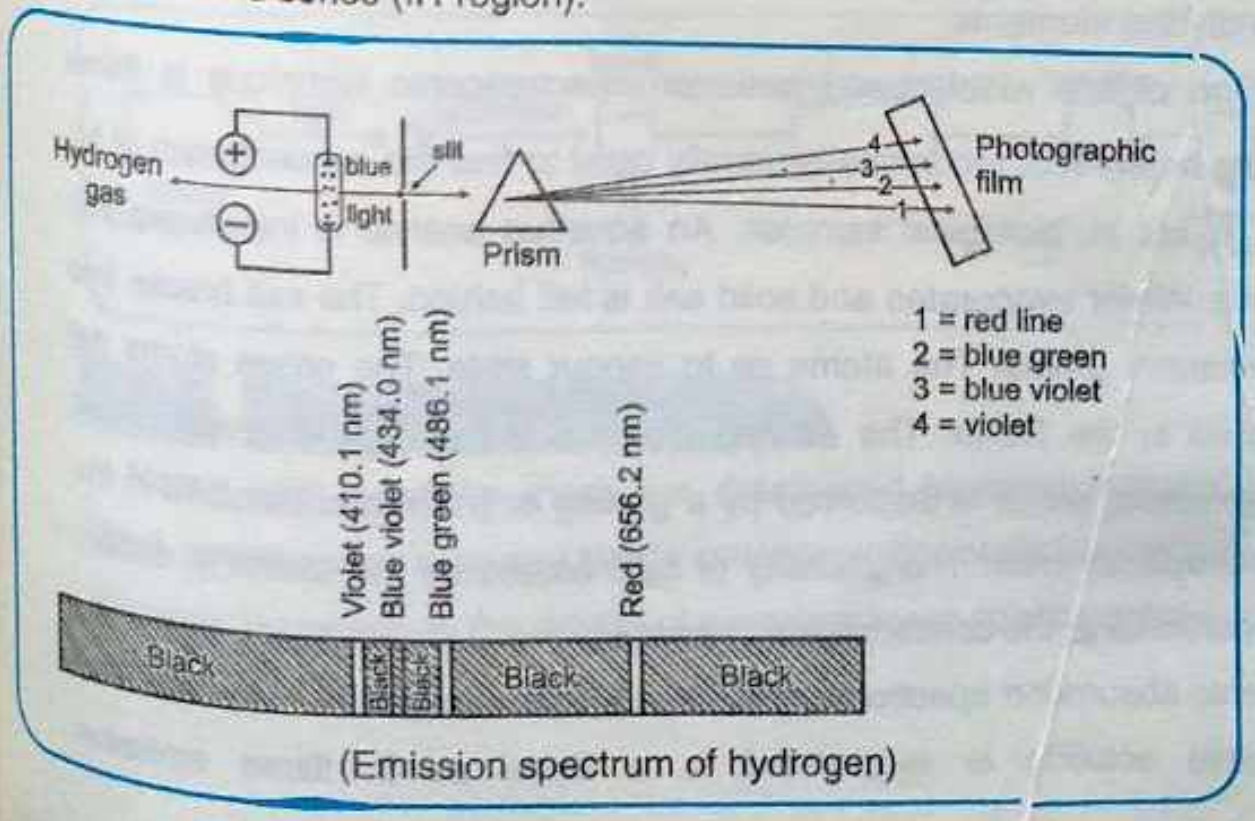
When a metal is strongly heated, it starts glowing. The light emitted from the metal when passed through a prison forms a continuous spectrum (emission spectrum) ranging from violet to red.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

The emission spectra of atoms in the gas phase on the other hand, do not show a continuous spread of wavelength from red to violet, rather the atoms produce bright lines in different parts of the visible spectrum. Such spectra are called line emission spectra. Each element has a characteristic line spectrum.

When hydrogen gas is taken in a discharge tube under low pressure it emits blue light. The light is emitted by atoms when they go from excited to ground state. When this blue light is passed through a prism, four bright lines against a dark background are produced. The colours and wave lengths of these are red (656.2nm), blue green (486.1 nm), blue-violet (434.0 nm) and violet (410.1 nm). This spectrum is called emission spectrum of hydrogen. These lines of hydrogen spectrum are collectively called Balmer series. In the invisible part of H-spectrum four more series are also obtained; Lyman (uv-region), Paschen (IR-region), Brackett (IR region) and P fund series (IR-region).



(Emission spectrum of hydrogen)

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Wavelength of the different bright lines of Balmer series can be calculated by the formula

$$\frac{1}{\lambda} = R_H \left[\frac{1}{(2)^2} - \frac{1}{n^2} \right]$$

R_H is called Rydberg constant. Its value is 2.18×10^{-18} J.

Red, blue green, blue violet and violet lines of Balmer series actually correspond to the electronic transition from 6^{th}, 5^{th}, 4^{th} and 3^{rd} orbit to 2^{nd} orbit respectively.

Emission spectrum of sodium can be obtained when sodium salt is added to the Bunsen flame, yellow flame is produced. When this yellow light is passed through a prism, two closely spaced yellow lines are produced. These lines are called D_1 (589 nm) and D_2 (589.6nm).

For every element there is a unique emission or absorption spectrum. Thus the emission or absorption atomic spectra are used as finger print to identify the elements.

One of the widely used emission spectroscopic technique is flame photometer. This technique is usually used to find the concentration of Ni, Na, K etc in, biological samples. An aqueous analyte is introduced into flame. Water evaporates and solid salt is left behind. The salt breaks into constituent atoms. The atoms go to vapour state. The gases atoms get excited in the flame. The excited atoms loose energy of characteristic wavelength, which is dispersed by a grating or prism and detected in the spectrophotometer. The intensity of light emited by the atoms is directly proportional to the concentration of analyte.

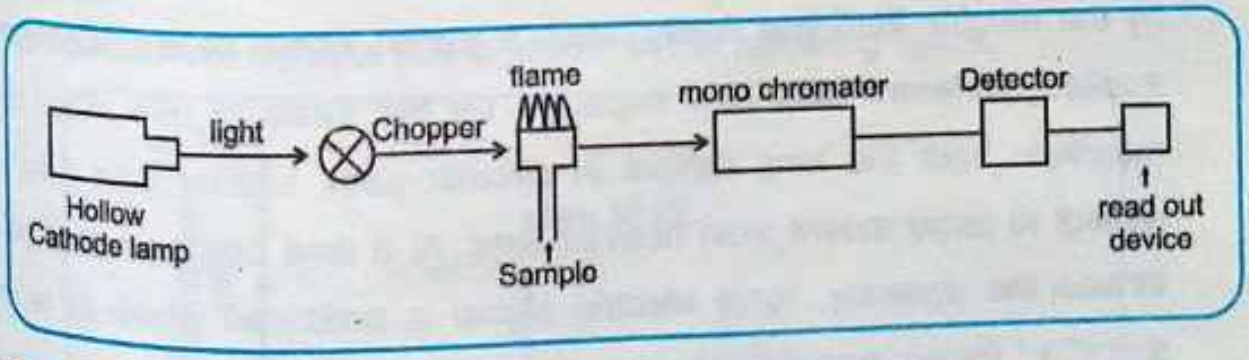
Atomic absorption spectrometry is used for the analysis of elements. The sample solution is evaporated in a flame as in flame emission

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

spectrometry and the sample is converted to atomic vapour. Some of the atoms in the flame get excited but majority of them are in ground state. When a light of particular wave length from the Hollow cathode lamp is passed through these atoms, they absorb the light for excitation from ground state to high energy state. The absorbance of light by atoms is directly proportional to the concentration of atomic vapours in the flame. For the analysis of different elements different types of lamps are used which produce light of different wave lengths. Each element shows absorption of particular wave length.

Before introducing the sample of unknown concentration, solution of known concentrations of that element are aspirated into the flame one by one. Their absorbances are recorded and a working curve is constructed. Then sample of unknown concentration is aspirated into the flame and its concentration is read from instrument. The simple diagram of an atomic absorption spectrometer is shown below.

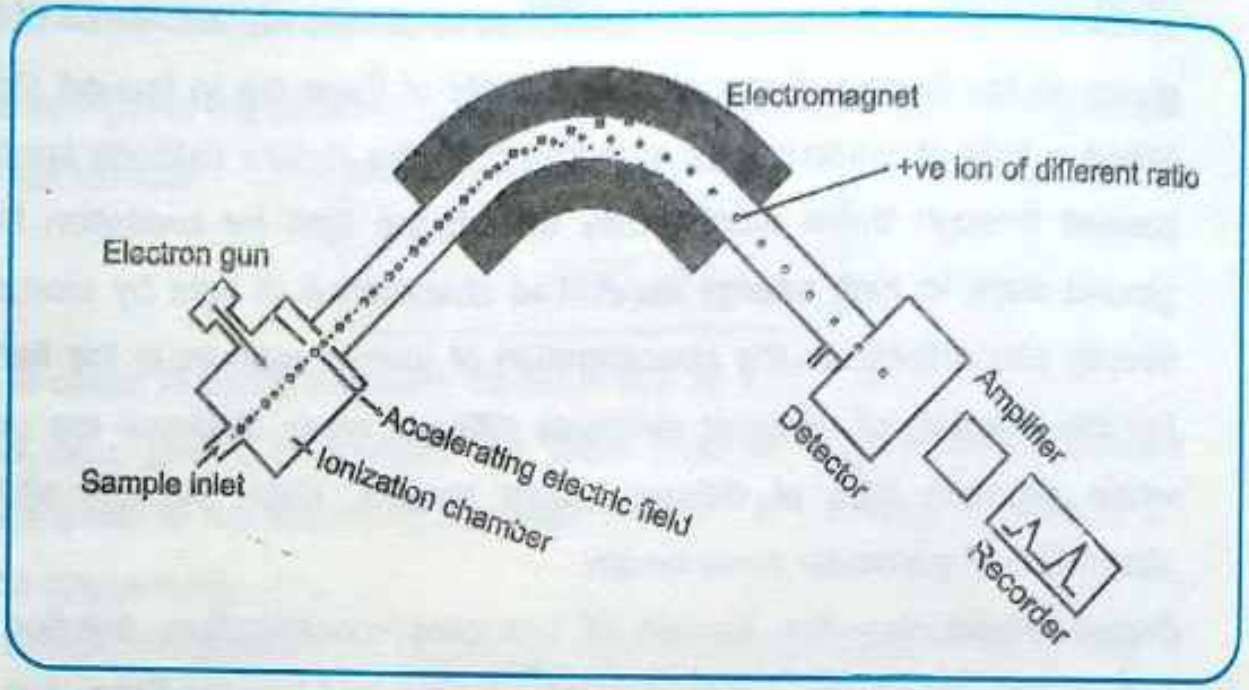


24.2.2.5 Mass spectrometry:

Atomic and molecular mass are determined by mass spectrometry. Mass spectrometer is a very highly sensitive instrumental technique. The following figure shows the design of a modern mass spectrometer.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



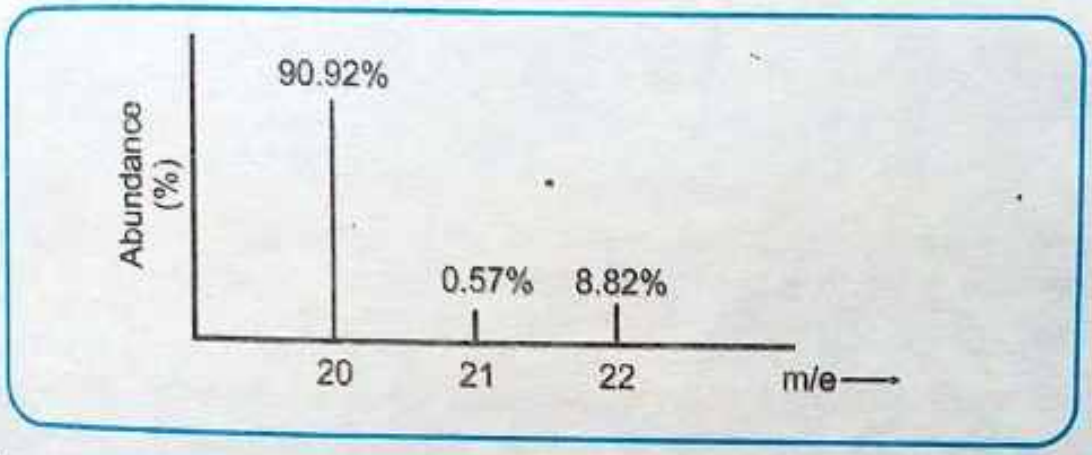
The sample is injected as a gas into the ionization chamber. Electrons, come from the electron gun collide with the sample atoms or molecules. As a result of these collisions electrons from the sample atoms or molecules are knocked out and they become positive ions. Usually oppositely charged ions are produced. The positive ions are accelerated by the electric field and finally reach a region where an electromagnet is applied. Different ions now separate on the basis of m/e ratio. In the magnetic field the ions deflect in circular path. Lighter ions (low m/e) deflect to large extent than heavier ions. At a time only one kind of ions strikes the detector. Here electric signal is produced which is later on amplified by an amplifier. In recorder the electric current operates a pen which traces peaks on a chart. The intensity of the electric signal is directly proportional to the number of ions striking the detector.

If the magnetic field is kept constant while the accelerating voltage is continuously changed, one kind of ions after other will reach detector and thus more peaks are produced on the chart.

Scanned with CamScanner

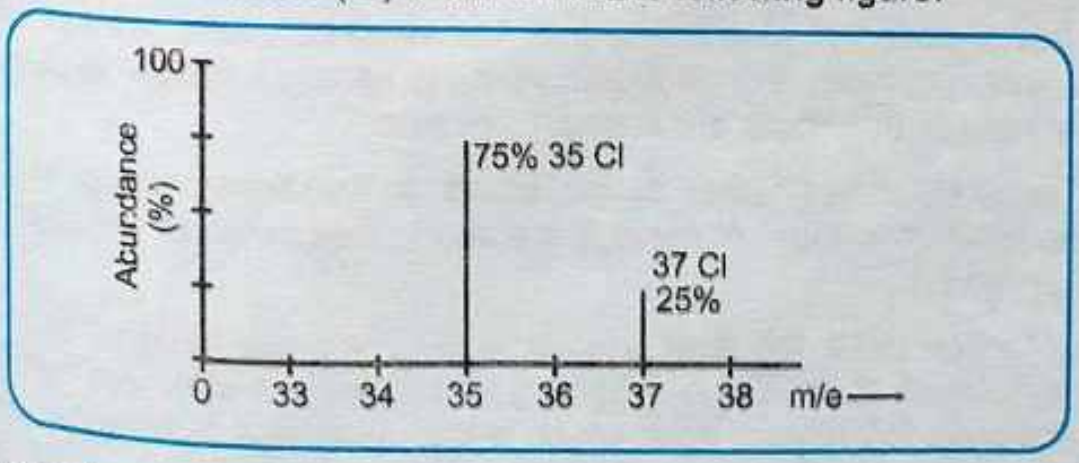
Mass spectrum is a chart in which m/e is taken on x-axis and relative abundance is taken on y-axis. Higher is the peak of a species higher is its abundance.

Mass spectrum helps in finding the number of isotopes of an element and also their relative abundances. Following the mass spectrum of Neon.



The above spectrum shows three peaks with m/e equal to 20,21, and 22 which correspond to ^{20}Ne, ^{21}Ne and ^{22}Ne. Neon –20 is the most abundant and Neon –21 is the least abundant isotope as clear from the heights of their peaks.

Mass spectrum of chlorine (Cl) is shown in the following figure.



When a molecule is introduced into mass spectrometer, the molecular ion (M^+) is produced due to loss of an electron. In addition to the molecular

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

ion, more ions are produced due to fragmentation of the molecule. Fragmentation occurs due to rupture of chemical bonds.

The fragmentation pattern of a molecule gives an idea of the structure of the molecule. Thus mass spectrometry is very helpful in the identification of molecular structures as well.

Science, Technology and Society

In Analytical Chemistry classical method use separations such as precipitation, extraction and distillation and qualitative analysis by color, odor or melting point. Quantitative analysis is achieved by measurement of weight or volume.

Whereas instrumental method use an apparatus to measure physical quantities of the analyte such as light absorption, fluorescence, or conductivity. The separation of materials is accomplished using chromatography, electrophoresis or Field Flow Fractionation methods.

Analytical chemistry has applications in forensics, bioanalysis, clinical analysis, environmental analysis, and materials analysis.

A method frequently used in forensic chemistry is that employing luminol, a derivative of phthalic acid, which reacts with metal cations and hence to detect traces of blood. The process involves mixing luminol with a dilute solution of hydrogen peroxide, which is spread carefully in places where it is thought that there are remnants of blood.

Thus, the iron-shaped cation found in the heme group of hemoglobin reacts with luminol observing a blue luminescence of the reaction itself is carried out.

In this process, the final product is the 3-aminophthalate anion which is in an excited state. Upon returning to the ground state (or basal) releases energy in the form of light, which is known as blue luminescence.

One particularly useful method for the simultaneous separation, identification, and quantitation of one or more individual components of an unknown substance or mixture is the use of a gas chromatograph-mass spectrometer (GC-MS). A GC-MS is actually two instruments that are

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

attached together physically, and together comprising one of the so-called "tandem" or "hyphenated" techniques. A combined GC-MS instruments has a very high sensitivity and can analyse sample present at concentration of 1ppb. MS uses high voltage to produce charged ions. Gas ions or isotopes are separated in magnetic field according to their masses.

The gas chromatograph (GC) is essentially a hot (150-350°C), temperature-controlled oven holding a bent or coiled, specially packed or coated glass column between one and a few dozen meters long. A small volume of a drug sample is quickly injected into the hot column. Volatile components in the sample are vaporized by the heat of the oven and are forced toward the end of the column by the flow of an inert "carrier gas" (typically helium). The special chemical component(s) within the column bind to substances contained in the moving vaporized sample mixture with slightly different force. As a result, different substances eventually are "eluted" (i.e. emerge from the end of the column) in differing amounts of time, which is known as the "retention time". In general the GC portion of the technique is used as a separation and quantitation tool, not an identification tool.

Scanned with CamScanner

3. Which one of the following technique is used for determination of functional group in a compound?

(a) IR Spectroscopy (b) NMR

(c) UV Spectroscopy (d) Mass spectroscopy

4. Two different compounds will give different absorption peaks in _____ region of IR ?

(a) 600-1500cm^{-1} (b) 1500-4000cm^{-1}

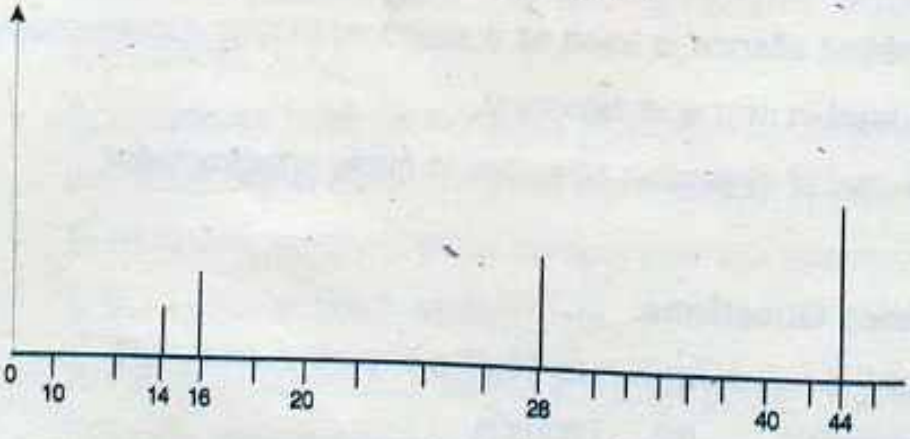
(c) 3000-2500cm^{-1} (d) 2500-3500cm^{-1}

5. Which one of the following methods would be best for finding the identity of an organic compound.

(a) Mass spectroscopy (b) NMR

(c) IR (d) uV

6. A mass spectrunm is shown below.



Which one of the following gives complete mass spectrum illustrated?

(a) CO_2 (b) N_2O

(c) C_3H_8 (d) mixture of CH_4 and N_2

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

7. UV ranges from

(a) 400nm-800nm (b) 800-1200 nm

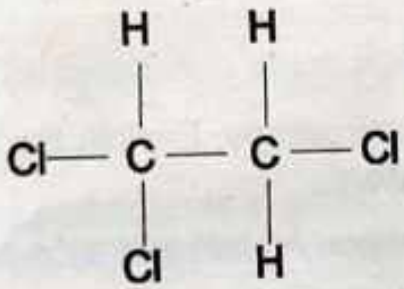
(c) 1200-1600nm (d) 10-400nm

8. Which one of the following hydrocarbon produces an NMR spectrum with more than one peak.

(a) Methane (b) Ethane

(c) Butane (d) Cyclobutane

9. For the compound below, how many single peaks would you expect in its NMR spectrum?



(a) 2 (b) 4

(c) 6 (d) 8

10. How many types of "NMR" protons are there in butanoic acid?

(a) 8 (b) 2

(c) 6 (d) 4

Q11 Short Questions

(i) Why magnesium perchlorate is used as H_2O absorber?

(ii) Acetic acid contains only C, H and O.A 5gm sample of acetic acid is completely burnt. It gives 3.00gm of water and 7.33gm of CO_2 is produced. What is the mass precentage of each elements in acetic acid. Also calculate the empirical formula of acetic acid.

(iii) Isoprene is a liquid compound that can be polymerized to form synthetic rubber. It is composed of 88.17% carbon and 11.83%

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

hydrogen. Its molar mass is 68.11g/mole. What are its empirical and molecular formulae?

(iv) Why modern method of analysis is superior over classical methods of analysis?

(v) Write down the main functions of IR, UV-visible and NMR spectroscopy?

(vii) Why it is necessory to use quartz cuvets in the U.V region, but less expensive glass or plastic cuvets are acceptable in the visible region.

Q12 Long Question

(i) Define mass spectroscopy. Explain the construction and working of mass spectrometery.

(ii) Differentiate between Atomic emission and absorption spectra.

(iii) What is meant by NMR. Explain chemical shift in different cases.

(iv) Explain in detail spectroscopy. Write down its applications.

(v) Write notes on the following.

(a) IR spectroscopy

(b) uv visible spectroscopy

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Alcohols:- Alcohols are organic compounds, in which a hydroxyl group is attached to alkyl group.

Alkanes:- These are salurated hydrocarbons which contain all carbon carbon single bonds.

Alkyl halide:- The organic compounds in which one or more hydrogens of an alkane are replaced by halogen atoms.

Alkylation of Ammonia :- The reaction in which Hydrogen atoms of NH_3 are replaced by alkyl groups.

Amines:- These are organic compounds in which one or more hydrogens of NH_3 molecule have been replaced by alkyl groups.

Beer Lambert's Law: Bear Lambert's Law is the linear relationship between absorbance and concentration of an absorber of electromagnetic radiations. Mathematically A=ECl

Bond enthalpy: Bond enthalpy is the amount of heat required to break one mole of covalent bonds to form individual atoms.

Carbocation:- The ion in which carbon atom bears positive charge.

Carbonyl group :- It is chemically an organic functional group composed of carbon atom doubly bonded to an oxygen atom.

Catenation:- The ability of an element to form chains of atoms bonded together.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Chiral Carbon atom:- Such a carbon atom which has four different groups attached to it.

Coal:- It is an important solid fossil fuel of black or brownish colour normally occuring in rock strata in layers called coal beds.

Complex Ion: An ion in which a metal ion is surrounded by a group of negative ions or molecules.

Contact process: Method of producing sulphuric acid in high concentration needed for industrial purposes.

Dextrorotatory isomer:- The isomer which rotates the plane polarized light in clockwise direction (to right).

Diamagnetism: If a substance is slightly repelled by an external magnetic field, this property is called diamagnetism.

Diazonium Salt :- Organic compounds of the general formula $R-N_2^+X^-$ are called diazonium salts, where R is an alkyl or aryl group and $\bar{X}$ is a halide ion.

Electronic effect:- Effect by which the reactivity at one part of a molecule is affected by electronic attraction or repulsion originating in another part.

Electrophile:- (Electron-Loving) A reagent which can accept an electron pair in a reaction.

Elimination reaction:- Those reactions which involve the elimination or removal of atoms or group of atoms from two adjacent carbon atoms in the substrate molecule to form a multiple bond.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Electromagnetic spectrum: The range of wave lengths and frequencies over which electromagnetic radiation extends.

Empirical formula: The formula that gives the simplest whole number ratio of the atoms of elements present in compound.

Enantiomers:- Such stereoisomers which are nonsuperimposable mirror image of each other.

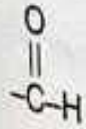
Entering Group:- The atom or ion or group which attacks the substrate molecule and forms a new bond with its carbon atom.

Esterification:- Formation of ester from carboxylic acid and alcohol.

Ether:- Ethers are a class of compound in which two alkyl groups or two aryl groups or one alkyl and one aryl group are attached to oxygen atom.

Fatty Acid:- It is a carboxylic acid with long aliphatic chain, which is either saturated or unsaturated.

Formyl group :- The aldehyde functional group is called formyl group



Fullerenes:- The molecules composed entirely of carbon in the form of a hallow sphere, ellipsoid or tube.

Functional group: It is specific group of atoms within a molecule that is responsible for characteristic chemical reactions of that molecule.

Gasification:- The conversion of coal into coal gas (H_2,CO_2,CO,$H_2O_{(g)}$)

Scanned with CamScanner

Grignard reagent:- Alkyl Magnesium halides are commonly known as Grignard reagent.

Hemiacetal/Hemiketal :- These are compound derived from aldehyde or ketone. The Greek word hemi means half.These are formed by addition of an alcohol molecule to carbonyl group.

Heterolysis:- Here unsymmetrical bond breaking takes place where one atom retains both the electrons. This gives rise to positive and negative ions.

Homologous series:- Series in which two adjacent members differ from each other only in length of the carbon chain by a CH_2 group.

Homolysis:- When bond breaks symmetrically such that each atom gets an electron each.

Inductive Effect:- The type of polarization of a bond induced by an adjacent polar bond.

Iso-alkane:- When CH_3 group attaches to second last carbon of the continuous chain, the alkane is an iso alkane.

Isomerism:- The phenomenon in which different compounds have the same molecular formula but different structures.

Inert pair effect: The existence of a positive oxidation state corresponding to the group number and of another state two units lower is an illustration of the inert pair effect. The term referring to the valence shell s electrons, used in bonding in the higher oxidation state but not in the lower.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Keto group :- Ketone functional group is called keto group (>C= O)

Leaving group:- The group or species which leaves the substrate or which is being replaced by the entering group.

Levorotatory isomer:- which rotates plane polarized light in anticlock wise direction (to left).

Lucas Test :- This test is used to distinguish between primary, secondary and tertiary alcohols in which the alcohol is treated with HCl in the presence of anhydrous $ZnCl_2$.

Markovnikove's Rule:- When unsymmetrical (or polar) reagent is added to unsymmetrical alkene, the positive part of the reagent attaches itself to the carbon atom involved in the double bond, holding greater number of hydrogen atoms.

Mass spectrometry: An analytical technique that produces spectra of the masses of the atoms or molecules comprising a sample of metarial.

Scanned with CamScanner

Meta directing group:- The substituents which direct the second incoming substituent to meta position.

Metamerism:- This type of isomerism is exhibited due to unequal distribution of carbon atoms of alkyl groups on either side of a functional group.

Monochromatic light:-Light consisting of single wavelength.

Molecular formula: It shows actual number of atoms of each kind of elements in a molecule of a compound.

Neo-alkane:- Those alkanes which have two methyl groups attached to second last carbon of continous chain.

Nitriles :- Compounds having a cyanide (-C≡N) group.

Nuclephilic Substitution:- The type of reaction in which part of a molecule is replaced by a nucleophile.

Nuclear Magnetic Resonance (NMR): It is the research technique that exploits the magnetic properties of certain atomic nuclei.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Nucleophile:- (Nucleus-Loving) A reagent which can donate electron pair in a reaction.

Ortho-para directing groups:- Substituents which direct the second substituent to the ortho or para position simultaneously.

Paramagnetism: Paramagnetism is caused by the presence of unpaired electrons in the substance. Paramagnetic substances and attracted by an external magnetic field.

Petroleum:- It means "rock oil" present in underground porous rocks.

Phenol :- The organic compounds is which –OH group is attached directly to the aromatic ring.

Polarimeter:- Optical activity of a compound is measured by an instrument called polarimeter.

Polymerization:-The process by which small molecules chemically join together to form large molecule with high molecular weight.

Resonance Energy:- The resonance energy of a molecule is the difference between the energy of the most stable canonical form and that of the actual molecule.

Resonance:-The representation of a real structure as weighted average of two or more contributing structures is called resonance.

Saturated Hydrocarbon:- It contains single covalent bonds between carbon atoms.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Saytzeff Rule:- This rule states that the alkene formed preferentially is the one containing greater number of alkyl groups attached to doubly bonded carbons.

Spectroscopy Infra Red: It is the characterization tool used to determine the molecular structure.

SN^1, Mechanism:- The nucleophilic substitution reaction in which only one molecule is involved in the rate determing slow step.

Stearic Hindrance:- Stearic effect arises from the fact that each atom within molecule occupies certain amount of space.

Stereoisomerism:- The stereoisomerism is exhibited by the compounds that have same connectivity but different arrangement of the atoms in space.

Spectroscopy: The techniques widely used in chemical analysis and the study of the properties of the atoms, molecules and ions etc.

Substrate : The molecule which is attacked by a reagent in a chemical reaction.

Sulphydryl or Marcapto :- The function group of thiol (-SH).

Tautomerism:- It is special type of functional group isomerism, in which isomers are in dynamic equilibrium with each other.

Ultra violet spectroscopy: An instrumental scanning method that analyse the absorption of light within uv spectrum.

Unsaturated Hydrocarbon:- Hydrocarbons containing one or more multiple (double or triple) covalent bonds.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

Vitalism : The belief that organic compounds can only be obtained from living organism as they possess a super natural force called vital force.

Williamson synthesis :- In this method sodium alkoxide is treated with an alkyl halide, to form an ether.

Variable oxidation state: The property of an element to show two or more oxidation states in its compounds.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)

AUTHORS PROFILE

Mushtaq-ur-Rehman

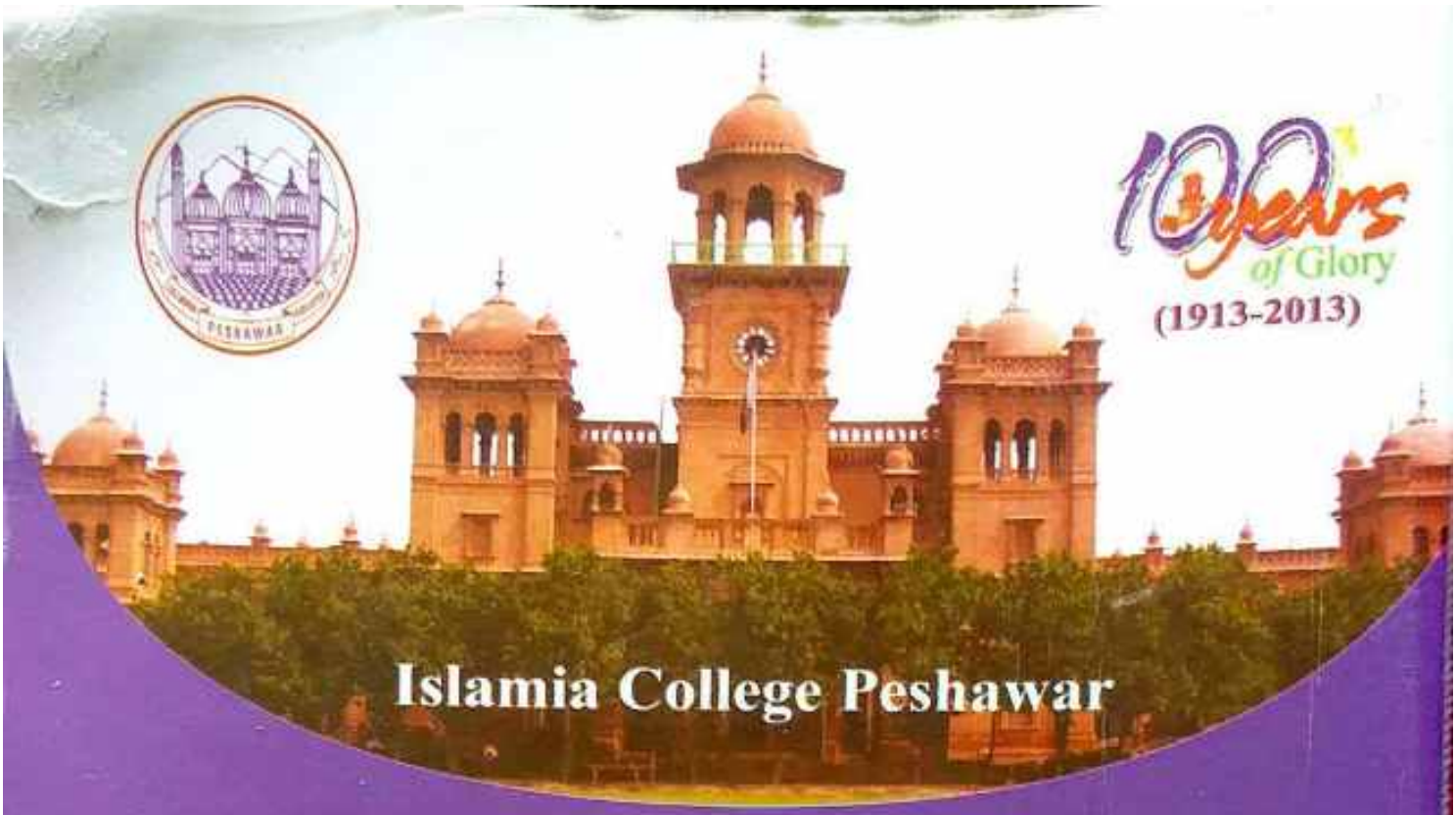
Mushtaq-ur-Rehman is working as Assistant Professor in Chemistry at Govt. College Peshawar. He got his M.Phil Degree in Chemistry from N.C.E in Physical Chemistry from Peshawar University. He has attended numerous seminars and workshops concerning education and development of Textbooks.

Muhammad Amin

Muhammad Amin is working as Instructor in RITE (M) Peshawar. He got his M.Phil Degree in Chemistry. He has attended numerous seminars and workshops concerning Writing Textbook Development. He is author of Chemistry Textbook for Textbook Board. He has also worked as Subject Specialist (Science) in Textbook Board, Peshawar.

Scanned with CamScanner

MDCAT BY FUTURE DOCTORS (TOUSEEF AHMAD)



100 Years of Glory
(1913-2013)

Islamia College Peshawar

قومی ترانہ

پاک سَر زمین شاد باد — کشورِ حَسین شاد باد
تو نشانِ عَزمِ عالی شان — ارضِ پاکستان
مرکزِ یقین شاد باد

پاک سَر زمین کا نظام — قُوتِ اُخوتِ عوام
قوم، ملک، سلطنت — پائندہ، تابِندہ باد
شاد باد منزلِ مُراد

پرچمِ سِتارہ و ہلال — رَہبرِ ترقی و کمال
ترجُمانِ ماضی شانِ حال — جانِ اِستقبال
سایۂ خدائے ذُوالجلال

LEADING BOOKS PUBLISHER
University Road Peshawar

Printer	Price	Quantity	Code No.
Leading Books Publishers	191.00	20,000	LBP - 2020-21(O)

Scanned with CamScanner