12

Organic Chemistry—Some Basic Principles and Techniques

Facts that Matter

• Organic Chemistry

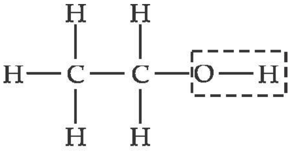
Organic chemistry is the branch of chemistry that deals with the study of hydrocarbons and their derivatives.

The Shapes of Carbon Compounds:

In organic or carbon compounds, s and p orbitals are involved in hybridisation. This leads to three types of hybridisation which are

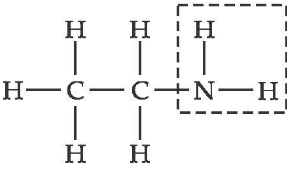
sp^3(in alkanes) – Tetrahedral in shape
sp^2(in alkenes) – Planar structure
sp(in alkynes) – Linear molecule

Functional Group: The functional group are atom or group of atoms joined in a specific manner which determines the chemical properties of the organic compound. The examples are hydroxyl group (—OH), aldehyde group (—CHO) and carboxylic acid group (—COOH) etc.



$$\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\boxed{O-H}}$$

Functional group



$$\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\boxed{\overset{H}{N}-H}}$$

Functional group

• Homologous Series

A homologous series may be defined as a family of organic compounds having the same functional group, similar chemical properties and the successive members differ from each other in molecular formula by $—CH_2$ units.

The members of a homologous series can be represented by same general molecular formula.

• Nomenclature of Organic Compounds

Common name (Common system): Before the IUPAC system of nomenclature, organic compounds were named after the sources of origin, for example, urea was so named because it was obtained from the urine of mammals. Formic acid was so named since it was extracted from red ants called formica.

Compound	*Common name*
CH_4	Methane
$H_3CCH_2CH_2CH_3$	*n*-Butane
$(H_3C)_2CHCH_3$	Isobutane
$(H_3C)_4C$	Neopentane
$H_3CCH_2CH_2OH$	*n*-Proply alcohol
HCHO	Formaldehyde
$(H_3C)_2CO$	Acetone
$CHCl_3$	Choloroform
CH_3COOH	Acetic acid
C_6H_6	Benzene
$C_6H_5OCH_3$	Anisole
$C_6H_5NH_2$	Aniline
$C_6H_5COCH_3$	Acetophenone
$CH_3OCH_2CH_3$	Ethyl methyl ether

• IUPAC (International Union of Pure and Applied Chemistry) System

According to IUPAC system, the name of an organic compound contains three parts: (*i*) word root, (*ii*) suffix, (*iii*) prefix.

(*i*) **Word root:** Word root represents the number of carbon atoms present in the principal chain, which is the longest possible chain of carbon atoms.

For special word roots for

meth	C_1
eth	C_2
Prop	C_3
but	C_4

(*ii*) **Suffix:** Suffix are of two types, primary suffix, secondary suffix.

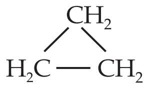
(*a*) **Primary Suffix:** It indicates the type of bond in the carbon atoms.

For example: Primary suffix ane for $C-C$ bond
ene for $C=C$ bond
yne for $C\equiv C$ bond

(*b*) **Secondary Suffix:** Secondary suffix is used to represent the functional group.

(*iii*) **Prefix:** Prefix is a part of IUPAC name which appears before the word root. Prefix are of two types:

(*a*) **Primary prefix:** For example, primary prefix cyclo is used to differentiate cyclic compounds.



cyclopropane

(*b*) **Secondary prefix:** Some functional groups are considered as substituents and denoted by secondary prefixes.

For example:

Substitutent Group	**Secondary prefix.**
$-F$	Fluoro
$-Cl$	Chloro

$-Br$	Bromo
$-NO$	Nitroso
$-NO_2$	Nitro
$-CH_3$	Methyl
$-OCH_3$	Methoxy

Naming of Compounds Containing Functional Groups: The longest chain of carbon atoms containing the functional group is numbered in such a manner that the functional group is attached at the carbon atoms possessing lowest possible number in the chain.

In case of polyfunctional compounds, one of the functional group is selected as principal functional group and the compound is named on that basis. The choice of principal functional group is made on the basis of order of preference.

The order of decreasing priority for the functional group is

$$-COOH,\ -SO_3H,\ -COOR\ (R = \text{alkyl group})\ COCl,\ -CONH_2,\ COCl,$$
$$-CONH_2,\ -CN,\ -C{=}O, > -C{=}O,\ -OH,\ -NH_2 > C{=}C<,\ -C{\equiv}C-$$

• Isomerism

When there are two or more compounds possessing the same molecular formula but different structural formula and different physical and chemical properties, the phenomenon is called isomerism. Such compounds are called isomers.

It is of two types:

(1) Structural Isomerism

(2) Stereoisomerism

(1) Structural Isomerism: Structural isomerism is shown by compounds having the same molecular formula but different structural formulae differing in the arrangement of atoms.

(2) Stereoisomerism: When isomerism is caused by the different arrangements of atoms or groups in space, the phenomenon is called stereoisomerism. The steroeoisomers have same structural formula but differ in arrangement of atoms in space. Stereoisomerism is of two types:

(*i*) Geometrical or Cis-Trans Isomerism

(*ii*) Optical Isomerism

• Fundamental Concepts in Organic Reaction Mechanism

Fission of a covalent bond: A covalent bond can undergo Fission in two ways:

(*i*) By Homolytic Fission or Homolysis

(*ii*) By Heterolytic Fission or Heterolysis

Homolytic Fission: In this process each of the atoms acquires one of the bonding electrons.

$$A-B \quad \text{or} \quad A:B \longrightarrow \dot{A} + \dot{B}$$

The products $\dot{A}$ and $\dot{B}$ are called free radicals. They are electrically neutral and have one unpaired electron associated with them. Homolytic fission is the most common mode of fission in vapour phase. Alkyl radicals are classified as primary, secondary or tertiary. Alkyl radical stability increases as we proceed from primary to tertiary.

$$\overset{\substack{\text{Methyl}\\ \text{free radical}}}{\dot{C}H_3} < \overset{\substack{\text{Ethyl}\\ \text{free radical}}}{\dot{C}H_3CH_2} < \overset{\substack{\text{Isopropyl}\\ \text{free radical}}}{\dot{C}H(CH_3)_2} < \overset{\substack{\text{Tert-butyl}\\ \text{free radical}}}{\dot{C}(CH_3)_3}$$

Heterolytic Fission: In this process one of atoms aquires both of the bonding electrons when the bond is broken.

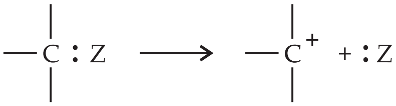
If B is more electronegative than A which thereby aquires both the bonding electrons and becomes negatively charged.

$A - B \longrightarrow \overset{+}{A} + :\overset{-}{B}$

The products of heterolytic fission are ions.

Reaction Intermediates: Heterolytic and homolytic bond fission results in the formation of short-lived fragments called reaction intermediates. Among the important reaction intermediates are carbonium ions, carbanions, carbon free radicals and carbenes.

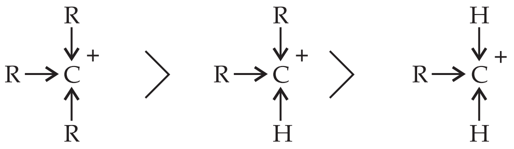
Carbonium Ions (carbocations): Organic ions which contain a positively charged carbon atom are called carbonium ions or carbocations. They are formed by heterolytic bond fission.



$-\overset{|}{\underset{|}{C}} : Z \longrightarrow -\overset{|}{\underset{|}{C}}{}^{+} + :Z$

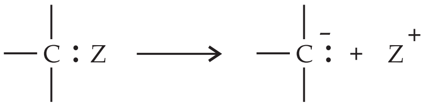
where Z is more electronegative than carbon.

Tertiary carbonium ion is more stable than a secondary, which in turn is more stable than a primary because of +I effect associated with alkyl group.



3° TERTIARY 2° SECONDARY 1°PRIMARY

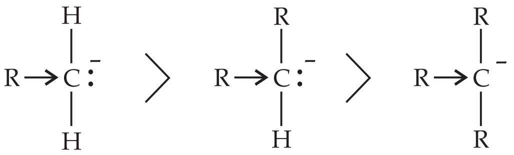
Carbanion: Organic ion which contains a negatively charged carbon atom are called carbanions. They are also formed by heterolytic bond fission.



$-\overset{|}{\underset{|}{C}} : Z \longrightarrow -\overset{|}{\underset{|}{C}}\overset{-}{:} + Z^{+}$

Carbanion

Where Z is less electronegative than carbon. A primary carbanion is more stable than a secondary, which in turn is more stable than a tertiary, because of +I effect associated with alkyl group.



Electrophile: It is positively charged or neutral species which is electron deficient. *e.g.,* H^+, H_2O^+, $\overset{+}{C}H_3$, NH_4^+, $AlCl_3$, SO_3, $CHCl_2$, CCl_3.

Nucleophile: It is negatively charged or neutral species with lone pair of electrons *e.g.,* (HO^-), Cyanide ($\ddot{C}\equiv N$), $H_2\ddot{O}:$, $R_3\ddot{N}$, $R_2\ddot{N}H$ etc.

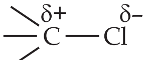
Electron Displacement Effects in Covalent Bonds: Electronic displacements in covalent bonds occurs due to the presence of an atom or group of different electronegativity or under the influence of some outside attaching group.

These lead to a number of effects which are as follows:

(*i*) Inductive effect (*ii*) Elecromeric effect

(*iii*) Resonance or Mesomeric effect (*iv*) Hyperconjugation effect.

Inductive Effect: It involues σ electron. The σ electrons which form a covalent bond are seldom shared equally between the two atoms. Due to different electronegatively electrons are displaced towards the more electronegative atom.
This introduces a certain degree of polarity in the bond.
The more electronegative atom acquires a small negative charge (δ^-). The less electronegative atom acquires a small positive charge (δ^+).
Consider the carbon-chlorine bond
As chlorine is more electronegative, it will become negatively charged with respect to the carbon atom.



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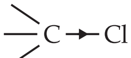


II

Structure I-indicates the relative charges on the two atoms.
Structure II-indicates the direction in which the electrons are drawn.
Atoms or groups which lose electrons towards a carbon atom are said to have a +I effect.
Those atoms or groups which draw electrons away from a carbon atom are said to have a –I Effect.
Some common atoms or groups which cause +I or –I effects are shown below:

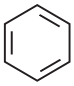
(*i*) –I Effect Groups (Electrons-attracting)
NO$_{2,}$ F, Cl, Br, I, OH, C_6H_5–
(*ii*) +I Effect Groups (Electron -releasing)
$(CH_3)_3$ C– , $(CH_3)_2$CH–, CH_3CH_2–, CH_3–

An inductive effect is not confined to the polarization of one bond.

$$-\underset{3}{C}-\underset{2}{C}\rightarrow\underset{1}{C}\twoheadrightarrow\underset{-1}{Cl}$$

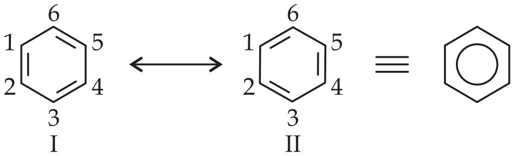
The inductive effect of C_1 upon C_2 is significantly less than the effect of the chlorine atom on C.

Resonance Structure: A number of organic compounds cannot be accurately represented by one structure.
For example, benzene is ordinarily represented as



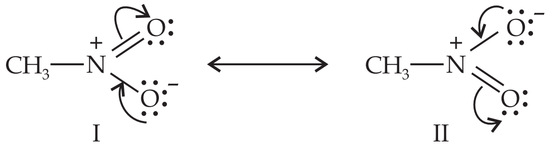
Benzene

This structure has three C—C bonds and three C$\equiv$C bonds.
Carbon-carbon double bond length = 1.34Å
Carbon-carbon single bond length = 1.54Å. But it has been determined experimentally that all carbon-carbon bonds in benzene are identical and have same bond length (1.39Å).
Thus the structure of benzene cannot be represented by single structure. It can be represented equally well by the energetically similar structures I and II. The two structures are called resonance structures.



Actual structure of benzene is resonance hybrid of structures I and II.

Another example of resonance is provided by nitromethane (CH_3NO_2) which can be represented by two Lewis structures.



The actual structure of nitromethane is a resonance hybrid of the two canonical forms I and II.

Resonance energy: The difference in the energy between the most stable contributing structure for a compound and its resonance hybrid is called as resonance energy or resonance stabilisation energy.

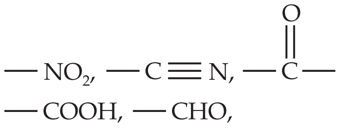
Resonance Effect: The polarity produced in the molecule by the interaction of two π-bonds or between a π-bond and a lone pair of electrons present on an adjacent atom. There are two types of resonance or mesomeric effects designated as R or M effect.

Positive Resonance Effect (+R effect):

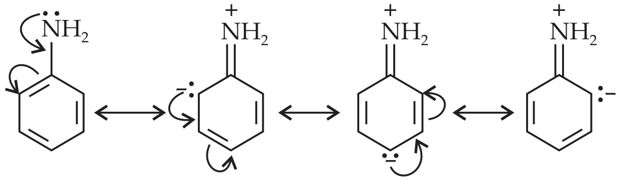
Those atoms which lose electrons towards a carbon atom are said to have a +M effect or +R effect. **For example:**

$$—Cl, —Br, —I, —NH_2, —NR_2, —OH, —OCH_3$$

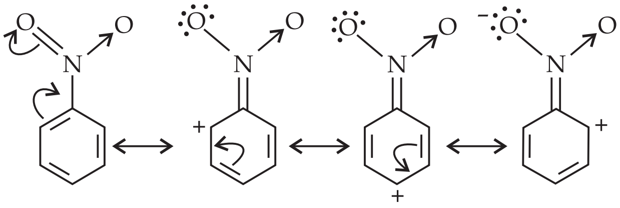
Negative Resonance Effect (–R effect): Those atoms or groups which draw electrons away from a carbon atom are said to have a –M effect or –R effect. **For example:**



$—NO_2,\ —C\equiv N,\ —\overset{O}{\overset{\|}{C}}—$
$—COOH,\ —CHO,$



+R effect in aniline



–R effect

Electromeric Effect (E Effect):

The electromeric effect refers to the polarity produced in a multiple bonded compound when it is attacked by a reagent when a double or a triple bond is exposed to an attack by an electrophile E^+ (a reagent) the two π electrons which from the π bond are completely transferred to one atom or the other.

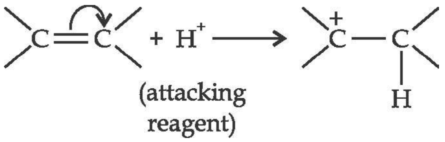
The electromeric effect is represented as:

$$A{=}B \xrightarrow[\text{REAGENT}]{E^+} \overset{+}{A}—\overset{-}{\ddot{B}}$$

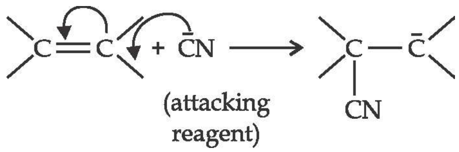
The curved arrow shows the displacement of the electron pair. The atom A has lost its share in the electron pair and B has gained this share. Therefore A acquires a positive charge and B a negative charge.

It is represented by E and the shifting of the electrons is shown by a curved arrow (↷). There are two distinct types of electromeric effect.

(*i*) **Positive Electromeric Effect (+E effect):** In this effect the π electrons of the multiple bond are transferred to that atom to which the reagent gets attached.



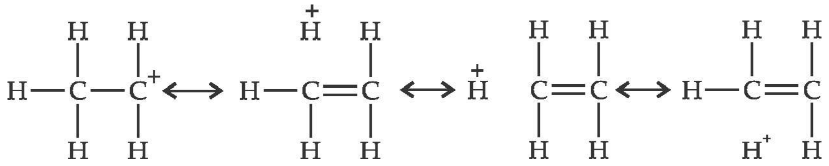
(*ii*) **Negative Electromeric Effect (–E effect):** In this effect the π electrons of the multiple bond are shifted to that atom to which the attacking reagent does not get attached.



Hyperconjugation or No Bond Resonance: When the alkyl group is attached to an unsaturated system such as $—CH=CH_2$ group the order of inductive effect gets reversed. The behaviour can be explained by hyperconjugation effect.

Such structures are arrived at by shifting the bonding electrons from an adjacent C—H bond to the electron deficient carbon. In this way, the positive charge originally on carbon is dispersed to the hydrogen.

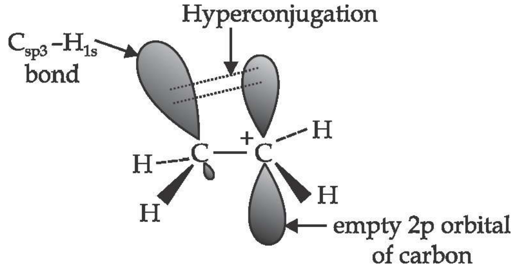
This way of electron release by assuming no bond character in the adjacent C—H bond is called No-Bond Resonance or Hyperconjugation.



• Orbital Concept of Hyperconjugation

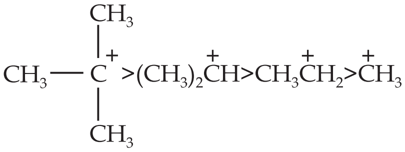
It involues delocalisation of σ electrons of C—H bond of an alkyl group which is attached directly to an atom of unsaturated system or to an atom with an unshared *p*-orbital.

Let us consider $CH_3\overset{+}{C}H_2$ (ethyl cation) in which the positively charged carbon atom has an empty *p*-orbital. One of the C—H bonds of the methyl group can align in the plane of this empty *p*-orbital and electron constituting the C—H bond in plane with this *p*-orbital can then be delocalised into the empty *p*-orbital as in Fig.

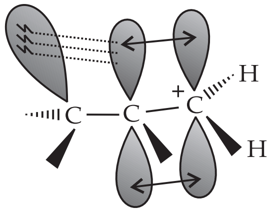


Orbital diagram showing hyperconjugation in ethyl cation

In general, greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation.



$$(CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$



Orbital diagram showing hyperconjugation in propene

• Qualitative Analysis of Organic Compounds

Detection of Carbon and hydrogen: Put Copper Oxide Test:

The organic substance is mixed intimately with about three times its weight of dry copper oxide. The mixture is then placed in a hard glass test-tube fitted with a bent delivery tube. The other end of which is dipping into lime water in another test tube.

The mixture is heated strongly and the following reactions take place.

$$C + 2CuO \longrightarrow CO_2 + 2Cu$$

$$2H + CuO \longrightarrow H_2O + Cu$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

Thus if carbon is present it is oxidised to carbon dioxide which turns lime water milky. If hydrogen is also present, it will be oxidised to water droplets on the cooler wall of the test tube.

Detection of other elements

Lassaigne's test: Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by 'Lassaigne's test'. Covalent compounds are converted into ionic form by fusing the compound with sodium metal. Following reaction occurs:

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} NaX \qquad (X = Cl, Br \text{ or } I)$$

(C, N, S and X come from organic compounds) compounds formed on sodium fusion are extracted by boiling it with distilled water.

Test for Nitrogen:

(*i*) The substance is heated strongly with sodium metal.

$$Na + C + N \longrightarrow NaCN$$

(*ii*) The water extract of the fused mass is boiled with ferrous sulphate solution

$$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$

$$6NaCN + Fe(OH)_2 \longrightarrow \underset{\text{Sod. ferrocyanide}}{Na_4[Fe(CN)_6]} + 2NaOH$$

(*iii*) To the cooled solution is then added a little ferric choride solution and excess of concentrated hydrochloric acid.

$$\underset{\text{Sod. ferrocyanide}}{3Na_4[Fe(CN)_6]} + 4FeCl_3 \longrightarrow \underset{\text{Prussian Blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

The formation of prussian blue or green colouration confirms the presence of nitrogen.

Test for sulphur:

Sodium Test: Sulphur, if present, in the given organic compound, upon fusion with sodium reacts to form sodium sulphide

$$2Na + S \longrightarrow \underset{\text{Sodium Sulphide}}{Na_2S}$$

Thus the sodium extract obtained from the fused mass is tested as:

(*i*) Add freshly prepared sodium nitroprusside solution. A deep violet colouration indicates sulphur.

(*ii*) Acidify the portion of the extract with acetic acid and then add lead acetate solution. A black precipitate of lead sulphide confirms the presence of sulphur.

$$\underset{\text{Lead acetate}}{Pb(CH_3COO)_2} + Na_2S \longrightarrow \underset{\substack{\text{Lead sulphide}\\ \text{(Black)}}}{Pbs} + 2CH_3COONa$$

If nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood red colour and no prussian blue since there are no free cyanide ions.

$$Na + C + N + S \longrightarrow NaSCN$$
$$Fe^{3+} + SCN^- \longrightarrow \underset{\text{Blood red}}{[Fe(SCN)]^{2+}}$$

Test for Halogens

Sodium Test: Upon fusion with sodium, the halogens in the organic compound are converted to sodium halides.

$$Cl + Na \longrightarrow NaCl$$
$$Br + Na \longrightarrow NaBr$$
$$I + Na \longrightarrow NaI$$

Acidify a portion of 'sodium extract' with dilute nitric acid and add to it silver nitrate solution.
White ppt. soluble in ammonia indicates Chlorine.
Yellow ppt. sparingly soluble in ammonia indicates Bromine.
Yellow ppt. insoluble in ammonia indicates Iodine.
When nitrogen or sulphur is also present in the compound, the sodium extract before testing for halogens is boiled with strong nitric acid to decompose the cyanide and the sulphite formed during the sodium fusion. If not removed, these radicals will form a white and black precipitate respectively on the addition of silver nitrate.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$$
$$Na_2S + 2HNO_2 \longrightarrow 2NaNO_2 + H_2S\uparrow$$

Test for phosphorous

The compound is heated with an oxidising agent (sodium peroxide). The phosphorous present in the compound is oxidised to phosphate.

The solution is boiled with HNO_3 and treated with ammonium molybdate. A yellow coloured ppt. indicates the presence of phosphorous.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + \underset{\text{Ammonium molybdate}}{12(NH_4)_2MoO_4} + 21HNO_3 \longrightarrow 12H_2O + 21NH_4NO_3 + \underset{\text{Ammonium phosphomolybdate}}{(NH_4)_3PO_4 \cdot 12MoO_3}$$

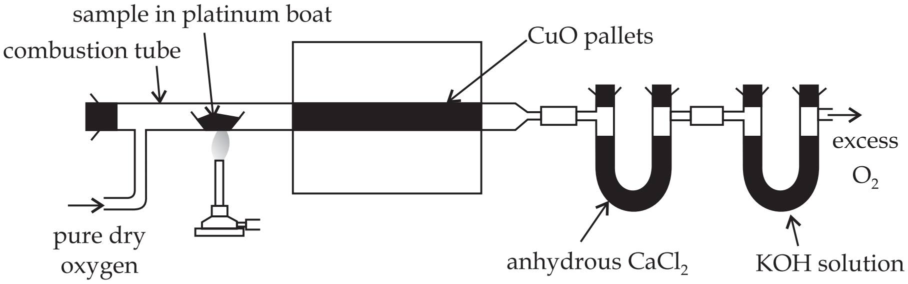
- **Quantitative Analysis**

Estimation of Carbon and Hydrogen

Both carbon and hydrogen are estimated together in one operation. A known weight of an organic compound is burnt in the presence of excess of oxygen and copper (II) oxide. Carbon and hydrogen are oxidised to carbon dioxide and water respectively.

$$C_xHy + \left(x + \frac{y}{4}\right) O_2 \longrightarrow xCO_2 + \left(\frac{y}{2}\right) H_2O$$

The weight of carbon dioxide and water thus formed are determined and the amounts of carbon and hydrogen in the original substance calculated.



Estimation of carbon and hydrogen. Water and carbon dioxide formed on oxidation of substance are absorbed in anhydrous calcium chloride and potassium hydroxide solutions respectively contained in U tubes.

Let the mass of organic compounds = mg

mass of water = m_1g

mass of CO_2 = m_2g

$$\text{\% of carbon} = \frac{12 \times m_2 \times 100}{44 \times m}$$

$$\text{\% of Hydrogen} = \frac{2 \times m_1 \times 100}{18 \times m}$$

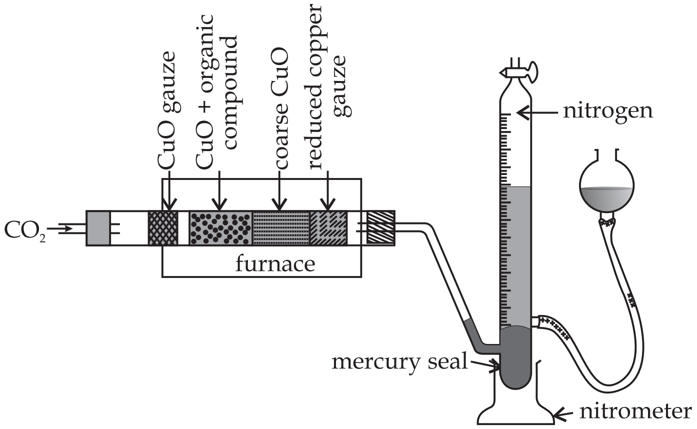
Estimation of Nitrogen

(*i*) **Dumas method:** This method is based on fact that the nitrogenous compounds when heated with copper oxide in an atmosphere of carbon dioxide yield free nitrogen,

$$C_xH_yN_z + \left(2x + \frac{y}{2}\right) CuO \longrightarrow xCO_2 + \frac{y}{2} H_2O + \frac{z}{2} N_2 + \left(2x + \frac{y}{2}\right) Cu$$

The traces of oxides of nitrogen, which may be formed in some cases, are reduced to elemental nitrogen by passing over heated copper spiral.

Apparatus can be shown as:



Dumas method. The organic compound yield nitrogen gas on heating it with copper (II) oxide in the presence of CO_2 gas. The mixture of gases is collected over potassium hydroxide solution in which CO_2 is absorbed and volume of nitrogen gas is determined.

Let the mass of organic compound = mg
Volume of nitrogen collected = V_1 ml
Room temperature = T_1K

volume of nitrogen at STP = $\dfrac{P_1V_1 \times 273}{760 \times T_1}$

$$\% \text{ of nitrogen } = \frac{28}{22400} \times \frac{\text{Volume of } N_2 \text{ at STP} \times 100}{\text{weight of organic compound}}$$

(*ii*) **Kjeldahl's Methods:** Kjeldahl's method is based on the fact that when an organic compound containing nitrogen is heated with con. H_2SO_4 the nitrogen in it is converted to ammonium sulphate. The resultant liquid is then treated with excess of alkali and the liberated ammonia gas absorbed in excess of standard acid. The amount of ammonia is determined by finding the amount of acid neutralised by back filtration with some std. alkali.

$$\begin{tikzcd} \text{Organic Compound} + H_2SO_4 \arrow[r] & (NH_4)_2\,SO_4 \arrow[d, "2NaOH"] \\ & Na_2SO_4 + 2NH_3 + 2H_2O \end{tikzcd}$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2\,SO_4$$

Volume of acid of normality N_1 neutralised by NH_3 = V_1 cm^3

1000 cm^3 of 1N NH_3 = 17 g of NH_3

V_1 cm^3 of N_1 acid = 14 g of Nitrogen

$$= \frac{14\,N_1V_1}{1000} \text{ g of Nitrogen}$$

$$\% \text{ of N } = \frac{14\,N_1V_1}{1000} \times \frac{100}{W} = \frac{1.4\,N_1V_1}{W}$$

Where N_1 is the normality of acid.
V_1 = volume of acid.
W = weight of organic compound.

Words that Matter

- All organic compounds contain carbon and hydrogen as essential constituents.
- In a homologous series two successive members differ in their molecular formula by $-CH_2$ unit.
- **Aliphatic Compounds** are open chain compounds contain straight or branched chain of carbon atoms.
- **Alicyclic Compounds:** Compounds containing closed ring of carbon compounds.
- **Aromatic Compounds:** Benzene and its derivatives are called aromatic compounds.
- **Functional group:** A functional group is an atom or group of atoms bonded together in a unique fashion and which determines the physical and chemical properties of the compounds.
- **Homolytic Bond Fission:** It leads to the formation of free radicals.

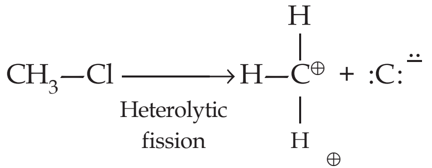
$$Cl—Cl \xrightarrow[\text{Homolytic fission}]{hv} \underset{\text{Free radical}}{Cl\cdot + Cl\cdot}$$

- **Heterolytic Bond Fission:**

$$A \text{———} B \longrightarrow A^{+} + :\bar{B}$$

Product of heterolytic fission are ions.

- **Carbonium Ion (Carbon cation):**



$$CH_3—Cl \xrightarrow[\text{Heterolytic fission}]{} H—\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C^{\oplus}}} + :\overset{..}{C}:^{-}$$

relative order of stability = $(CH_3)_3\overset{\oplus}{C} > (CH_3)_2\overset{\oplus}{C}H > CH_3\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3$

- **Carbanions:** The relative order of stability

$(C_6H_5)_3\overset{\ominus}{C} < (C_6H_5)_2\overset{\ominus}{C}H < C_6H_5\overset{\ominus}{C}H_2 < \overset{\ominus}{C}H_3 < \overset{\ominus}{C}H_3 < CH_3\overset{\ominus}{C}H_2 < (CH_3)_2\overset{\ominus}{C}H < (CH_3)_3\overset{\ominus}{C}$

- **Electrophiles** are positively charged electron deficient species.

Ex: $H^{\oplus}$, $H_3O^{\oplus}$, NO_2^{+}

- **Nucleophiles** are negatively charged or electron rich species.

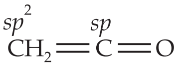
$R—COO^{\ominus}$, $R—\underset{..}{\ddot{O}}—H$, $H—C\equiv\overset{\ominus}{C}$

- **Crystallisation** is used to purify organic solids by dissolving them in suitable solvents.
- **Simple distillation** is used to purify liquids with non-volatile impurities.
- **Steam distillation** is used to purify organic compounds which give sufficient vapours at the boiling of water and are insoluble in water.
- **Chromatography** is used to purify and separate the constituents from a sample.
- **Lassaigne's test** is used to detect carbon, nitrogen, sulphur and halogen in organic compound.
- **Dumas or Kjeldahl's method:** Nitrogen is estimated by this method.
- **Halogens:** Halogens are estimated by Carius method.
- **Sulphur and phosphorous:** Sulphur and phosphorous are estimated by oxidising them to sulphuric and phosphoric acid respectively.
- **Oxygen:** The percentage of oxygen is usually determined by difference between the total percentage (100) and the sum of the percentages of all other elements present.

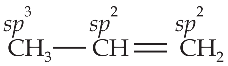
NCERT TEXTBOOK QUESTIONS SOLVED

Q1. *What are hybridisation states of each carbon atom in the following compounds?* $CH_2{=}C{=}O$, $CH_3CH{=}CH_2$, $(CH_3)_2CO$, $CH_2{=}CHCN$, C_6H_6.

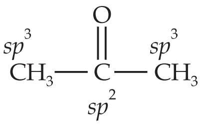
Ans.



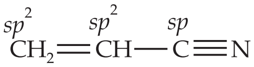
$\overset{sp^2}{CH_2}{=}\overset{sp}{C}{=}O$



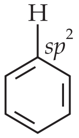
$\overset{sp^3}{CH_3}{-}\overset{sp^2}{CH}{=}\overset{sp^2}{CH_2}$



$\overset{sp^3}{CH_3}{-}\underset{sp^2}{\overset{\overset{O}{\|}}{C}}{-}\overset{sp^3}{CH_3}$



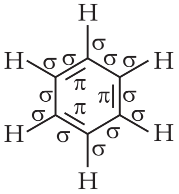
$\overset{sp^2}{CH_2}{=}\overset{sp^2}{CH}{-}\overset{sp}{C}{\equiv}N$

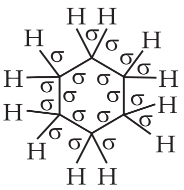


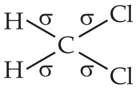
Each C is sp^2-hybridized

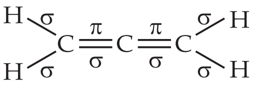
Q2. *Indicate the σ- and π-bonds in the following molecules:*
C_6H_6, C_6H_{12}, CH_2Cl_2, $CH_2{=}C{=}CH_2$, CH_3NO_2, $HCONHCH_3$

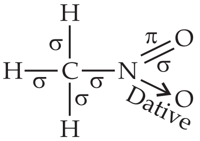
Ans.

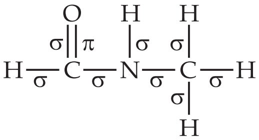








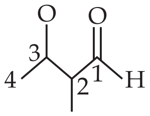




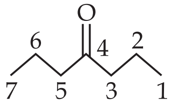
Q3. *Write bond-line formulas for: Isopropyl alcohol, 2,3-Dimethylbutanal, Heptan-4-one.*

Ans.

Isopropyl alcohol



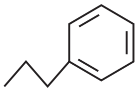
2,3-Dimethylbutanal



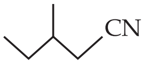
Heptan-4-one

Q4. *Give the IUPAC names of the following compounds:*

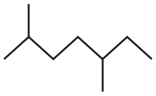
(*a*)



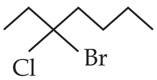
(*b*)



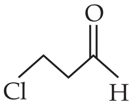
(*c*)



(*d*)



(*e*)



(*f*) Cl_2CHCH_2OH

Ans. (*a*) Propylbenzene (*b*) 3-Methylpentanenitrite (*c*) 2, 5-Dimethylheptane (*d*) 3-Bromo-3-chloroheptane (*e*) 3-Chloropropanal (*f*) 2, 2-Dichloroethanol

Q5. *Which of the following represents the correct IUPAC name for the compounds concerned? (a) 2, 2-Dimethylpentane or 2-Dimethylpentane (b) 2, 4, 7-Trimethyloctane or 2, 5, 7-Trimethyloctane (c) 2-Chloro-4-methylpentane or 4-Chloro-2-methylpentane (d) But-3-yn-1-ol or But-4-ol-yne.*

Ans. (*a*) 2, 2-Demethylpentane (*b*) 2, 4, 7-Trimethyloctane. For two alkyl groups on the same carbon its locant is repeated twice, 2, 4, 7-locant set is lower than 2, 5, 7. (*c*) 2-Chloro-4-methylpentane. Alphabetical order of substituents. (*d*) But-3-yn-1-ol. Lower locant for the principal functional group, *i.e.,* alcohol.

Q6. *Draw formulas for the first five members of each homologous series beginning with the following compounds. (a) H—COOH (b)* CH_3COCH_3 *(c)* $H—CH{=}CH_2$.

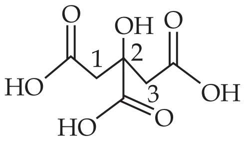
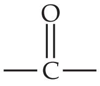
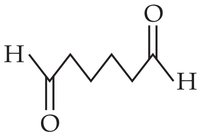
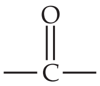
Ans. (*a*) $CH_3—COOH$
$CH_3CH_2—COOH$
$CH_3CH_2CH_2—COOH$
$CH_3CH_2CH_2CH_2—COOH$

(*b*) CH_3COCH_3
$CH_3COCH_2CH_3$
$CH_3COCH_2CH_2CH_3$
$CH_3COCH_2CH_2CH_2CH_3$
$CH_3CO(CH_3)_4CH_3$

(*c*) $H—CH{=}CH_2$
$CH_3CH{=}CH_2$
$CH_3CH_2CH{=}CH_2$
$CH_3CH_2CH_2CH{=}CH_2$
$CH_3CH_2CH_2CH_2CH{=}CH_2$

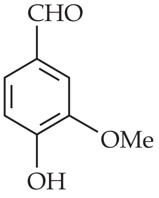
Q7. *Give condensed and bond line structural formulas and identify the functional group(s) present, if any, for: (a) 2, 2, 4-Trimethylpentane (b) 2-Hydroxy-1, 2, 3-propanetricarboxylic acid (c) Hexanedial.*

Ans.

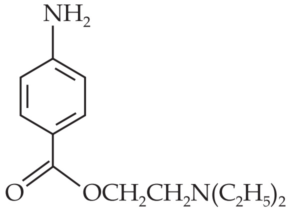
Condensed formula	**Bond line formula**	**Functional group/s**
(*a*) $(CH_3)_3CCH_2CH(CH_3)_2$		–
(*b*) $HOOCCH_2C(OH)$ $(COOH)CH_2COOH$		 $—\overset{\overset{\displaystyle O}{\|}}{C}—OH$ (carboxyl) and —OH (hydroxyl)
(*c*) $OHC(CH_2)_4CHO$		 $—\overset{\overset{\displaystyle O}{\|}}{C}—H$ (aldehyde)

Q8. *Identify the functional groups in the following compounds:*

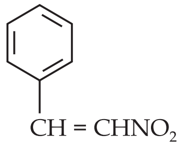
(*a*)



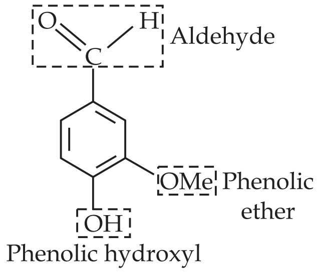
(*b*)



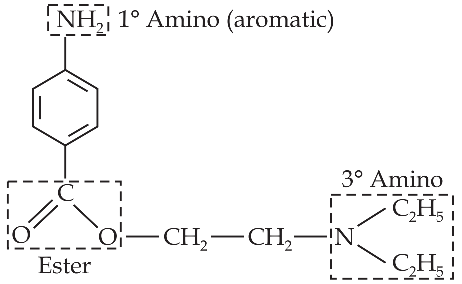
(*c*)



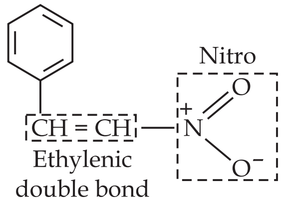
Ans. (*a*)



(*b*)



(*c*)

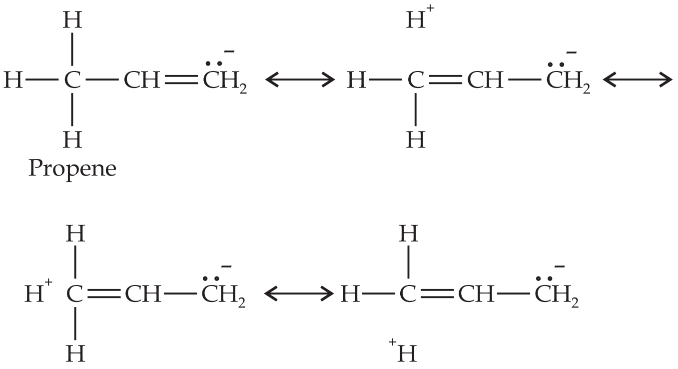


Q9. *Which of the two: $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ is expected to be more stable and why?*

Ans. $O_2N \leftarrow CH_2 \leftarrow CH_2 \leftarrow O^-$ is more stable than $CH_3 \rightarrow CH_2 \rightarrow O^-$ because NO_2 group has –I-effect and hence it tends to disperse the –ve charge on the O–atom. In contrast, CH_3CH_2 has +I-effect. It, therefore, tends to intensify the –ve charge and hence destabilizes it.

Q10. *Explain why alkyl groups act as electron donors when attached to a π-system.*

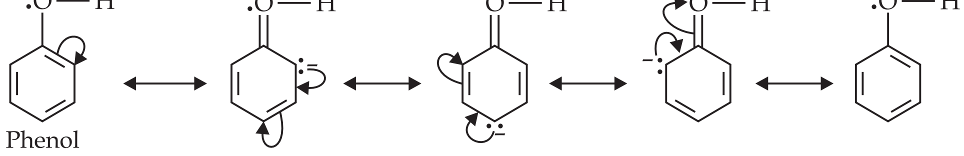
Ans. Due to hyperconjugation, alkyl groups act as electron donors when attached to a π-system as shown below:



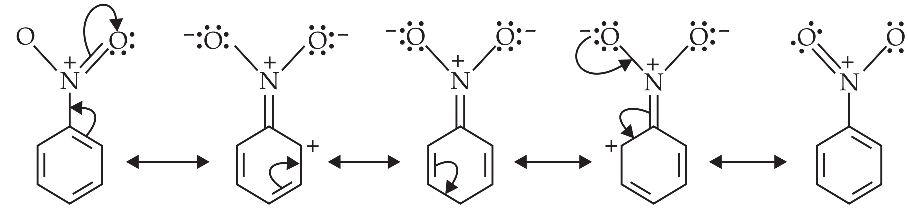
Q11. *Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.*

(a) C_6H_5OH (b) $C_6H_5NO_2$ (c) $CH_3CH{=}CHCHO$ (d) $C_6H_5{-}CHO$ (e) $C_6H_5{-}\overset{+}{C}H_2$
(f) $CH_3CH{=}CH\overset{+}{C}H_2$

Ans. (*a*)

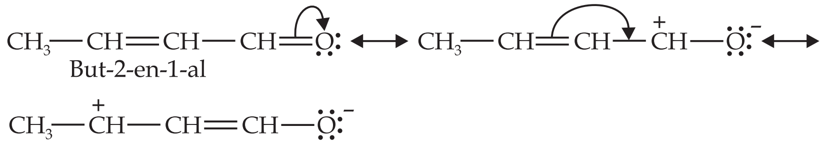


(b)



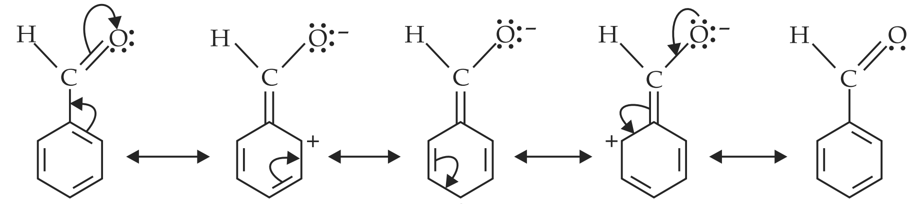
Nitrobenzene

(c)



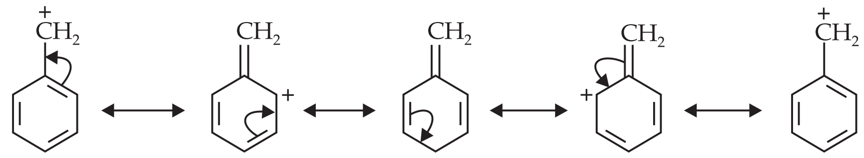
But-2-en-1-al

(d)



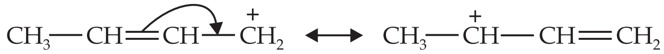
Benzaldehyde

(e)



Benzyl carbocation

(f)



But-2-en-1-yl carbocation

Q12. *What are electrophiles and nucleophiles? Explain with examples:*

Ans. **Electrophiles:** The name electrophiles means electron loving. Electrophiles are electron deficient. They may be positive ions or neutral molecules.

Ex: H^+, Cl^+, Br^+, NO_2^+, R_3C^+, RN_2^+, $AlCl_3$, BF_3

Nucleophiles: The name nucleophiles means 'nucleus loving' and indicates that it attacks the region of low electron density (positive centres) in a substrate molecule. They are electron rich they may be negative ions or neutral molecules.

Ex: Cl^-, Br^-, CN^-, OH^-, RCH_2^-, NH_3, RNH_2, H_2O, ROH etc.

Q13. *Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles*

(a) $CH_3COOH + \mathbf{HO^-} \longrightarrow CH_3COO^- + H_2O$

(b) $CH_3COCH_3 + \mathbf{{}^-CN} \longrightarrow (CH_3)_2\, C(CN)(OH)$

(c) $C_6H_5 + \mathbf{CH_3\overset{+}{C}O} \longrightarrow C_6H_5COCH_3$

Ans. **Nucleophiles:** (*a*) and (*b*) and **Electrophile** : (*c*)

Q14. *Classify the following reactions in one of the reaction type studied in this unit.*

(a) $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$

(b) $(CH_3)_2C{=}CH_2 + HCl \longrightarrow (CH_3)_2CCl{-}CH_3$

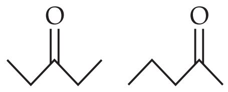
(c) $CH_3CH_2Br + HO^- \longrightarrow CH_2{=}CH_2 + H_2O + Br^-$

(d) $(CH_3)_3C{-}CH_2OH + HBr \longrightarrow (CH_3)_2C\,Br\,CH_2CH_2CH_3 + H_2O$

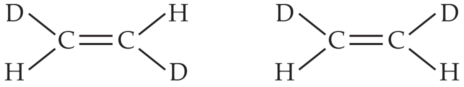
Ans. (*a*) Nucleophilic substitution (*b*) Electrophilic addition
(*c*) Bimolecular elimination (*d*) Nucleophilic substitution with rearrangement.

Q15. *What is the relationship between the members of following pairs of structures? Are they structural or geometrical isomers or resonance contributors?*

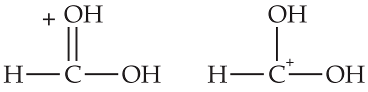
(a)



(b)



(c)



$H-\overset{+OH}{\overset{\|}{C}}-OH \quad H-\overset{OH}{\overset{|}{\overset{+}{C}}}-OH$

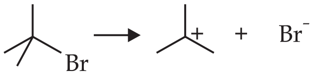
Ans. (*a*) Structural isomers (actually position isomers as well as metamers)
(*b*) geometrical isomers
(*c*) resonance contributors because they differ in the position of electrons but not atoms

Q16. *For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.*

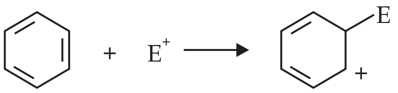
(a) $CH_3O-OCH_3 \longrightarrow CH_3\dot{O} + \dot{O}CH_3$

(b)

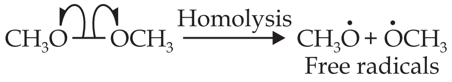
(c)



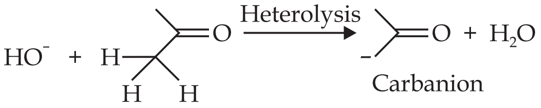
(d)



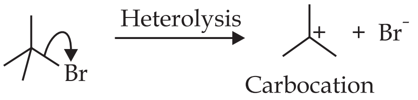
Ans. (*a*)



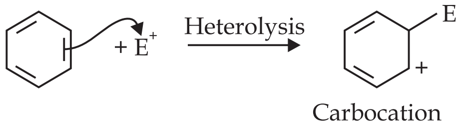
(*b*)



(*c*)



(*d*)



Q17. *Explain the terms inductive and electromeric effects. Which electron displacement effect explain the following correct orders of acidity of the carboxylic acids?*
(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$
(b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C{\cdot}COOH$

Ans. **Inductive Effect:** The inductive effect refers to the polarity produced in a molecule as a result of higher electronegativity of one atom compared to another.
Atoms or groups which lose electron towards a carbon atom are said to have + I Effect.

Those atoms or groups which draw electron away from a carbon atom are said to have –I Effect.

Common examples of –I effect are:

NO_2, F, Cl, Br, I, OH etc.

Examples of +I effect are (Electron releasing)

$(CH_3)_2C—$, $(CH_3)_2CH—$, $CH_3CH_2—$, $CH_3—$ etc.

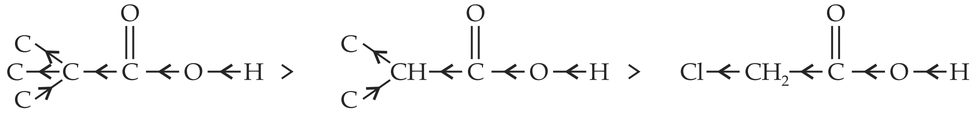
Electromeric effect: The electromeric effect refers to the polarity produced in a multiple bonded compound as it is approached by a reagent.

The atom A has lost its share in the electron pair and B has gained this share.

As a result A acquires a positive charge and B a negative charge. It is a temporary effect and takes place only in the presence of a reagent.

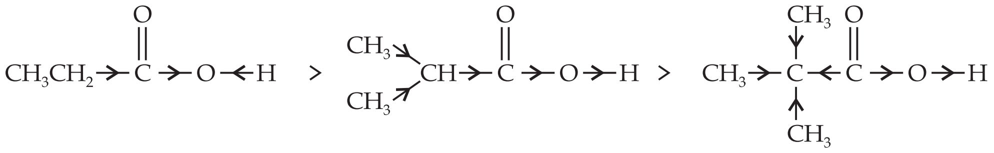
(*a*) **–I-effect** as shown below:

As the number of halogen atoms decreases, the overall –I- effect decreases and the acid strength decreases accordingly.



(*b*) **+I-effect** as shown below:

As the number of alkyl groups increases, the +I-effect increases and the acid strength decreases accordingly.



Q18. *Give a brief description of the principles of the following techniques taking an example in each case:*

(a) Crystallisation (b) Distillation (c) Chromatography

Ans. (*a*) **Crystallisation:** In this process the impure solid is dissolved in the minimum volume of a suitable solvent. The soluble impurities pass into the solution while the insoluble ones left behind. The hot solution is then filtered and allowed to cool undisturbed till crystallisation is complete. The crystals are then separated from the mother liquor by filtraration and dried.

Example: crystallisation of sugar.

(*b*) **Distillation:** The operation of distillation is employed for the purification of liquids from non-volatile impurities. The impure liquid is boiled in a flask and the vapours so formed are collected and condensed to give back pure liquid in another vessel. Simple organic liquids such as benzene toluene, xylene etc. can be purified.

(*c*) **Chromatography:** Chromatography is based on the principle of selective distribution of the components of a mixture between two phases, a stationary phase and a moving phase. The stationary phase can be a solid or liquid, while the moving phase is a liquid or a gas. When the stationary phase is solid the basis is adsorption and when it is a liquid the basis is partition.

Chromatography is generally used for the separation of coloured substances such as plant pigments or dyestuffs.

Q19. *Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.*

Ans. Fractional crystallisation is used for this purpose. A hot saturated solution of these two compounds is allowed to cool, the less soluble compound crystallises out while the more soluble remains in the solution. The crystals are separated from the mother liquor and the mother liquor is again concentrated and the hot solution again allowed to cool when the crystals of the second compound are obtained. These are again filtered and dried.

Q20. *What is the difference between distillation, distillation under reduced pressure and steam distillation?*

Ans. **Distillation** is used in case of volatile liquid mixed with non-volatile impurities.

Distillation under reduced pressure: This method is used to purify such liquids which have very high boiling points and which decompose at or below their boiling points.

Steam distillation is used to purify steam volatile liquids associated with water immiscible impuritites.

Q21. *Discuss the chemistry of Lassaigne's test.*

Ans. **Lassaigne's test:** Nitrogen, sulphur, halogens and phosphorous present in an organic compound are detected by Lassaigne's test.

First of all compounds are converted to ionic form by fusing the compound with sodium metal.

$$\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$$

$$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$$

$$\text{Na} + \text{X} \xrightarrow{\Delta} \underset{[\text{X} = \text{Cl, Br, I}]}{\text{NaX}}$$

Cyanide, sulphide or halide of sodium are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract.

Q22. *Differentiate between the principle of estimation of nitrogen in an organic compound by (i) Dumas method (ii) Kjeldahl's method.*

Ans. (*i*) **Dumas method:** The organic compound is heated strongly with excess of CuO (Cupric Oxide) in an atmosphere of CO_2 when free nitrogen, CO_2 and H_2O are obtained.

(*ii*) **Kjeldahl's method:** A known mass of the organic compound is heated strongly with conc. H_2SO_4 , a little potassium sulphate and a little mercury (a catalyst). As a result of reaction the nitrogen present in the organic compound is converted to ammonium sulphate.

Q23. *Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound.*

Ans. **Estimation of halogens:** It involves oxidising the organic substance with fuming nitric acid in the presence of silver nitrate. The halogen of the substance is thus converted to silver halide which is separated and weighed:

Weight of organic compound = W gm

weight of silver halide = x g.

$$\%\text{ of halogen} = \frac{\text{At. wt. of halogen} \times 100x}{\text{Mol. wt of silver halide} \times w}$$

Estimation of sulphur: The organic substance is heated with fuming nitric acid but no silver nitrate is added. The sulphur of the substance is oxidised to sulphuric acid which is then precipitated as barium sulphate by adding excess of barium chloride solution. From the weight of $BaSO_4$ so obtained the percentage of sulphur can be calculated.

$$\% \text{ of sulphur} = \frac{32 \text{ (At. weight of S)}}{233 \text{ (mol weight of } BaSO_4)} \times \frac{\text{weight of} \times 100 \text{ } BaSO_4}{\text{weight of organic compound}}$$

Estimation of phosphorous: The organic substance is heated with fuming nitric acid whereupon phosphorous is oxidised to phosphoric acid. The phoshoric acid is precipitated as ammonium phosphomolybdate, $(NH_4)_3 PO_4 \cdot 12MoO_3$, by the addition of ammonia and ammonium molybdate solution which is then separated, dried and weighed.

$$\% \text{ of P} = \frac{31 \times w_1 \times 100}{1877 \times w}$$

where Molar mass of $(NH_4)_3 PO_4.12MoO_3$ = 1877 g

If phosphorous is estimated as $Mg_2P_2O_7$

$$\% \text{ of P} = \frac{62 \times w_1 \times 100}{222 \times w} \%$$

Q24. *Explain the principle of paper chromatography.*

Ans. This is the simplest form of chromatography. Here a strip of paper acts as an adsorbent. It is based on the principle which is partly adsorption. The paper is made of cellulose fibres with molecules of water adsorbed on them. This acts as stationary phase. The mobile phase is the mixture of the components to be identified prepared in a suitable solvent.

Q25. *Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens ?*

Ans. Nitric acid is added to sodium extract so as to decompose

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN$$

$$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S$$

Q26. *Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.*

Ans. Organic compound is fused with sodium metal so as to convert organic compounds into NaCN, Na_2S, NaX and Na_3PO_4. Since these are ionic compounds and become more reactive and thus can be easily tested by suitable reagents.

Q27. *Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.*

Ans. Sublimation. Because camphor can sublime whereas $CaSO_4$ does not.

Q28. *Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation?*

Ans. It is because in steam distillation the sum of vapour pressure of organic compound and steam should be equal to atmospheric pressure.

Q29. *Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.*

Ans. No. CCl_4 is a completely non-polar covalent compound whereas $AgNO_3$ is ionic in nature. Therefore they are not expected to react and thus a white ppt. of silver chloride will not be formed.

Q30. *Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?*

Ans. CO_2 is acidic in nature and therefore, it reacts with the strong base KOH to form K_2CO_3.

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O.$$

Q31. *Why is it necessary to use acetic acid and not sulphric acid for acidification of sodium extract for testing sulphur by lead acetate test?*

Ans. For testing sulphur sodium extract is acidified with acetic acid because lead acetate is soluble and does not interfere with the test.

$$\underset{\text{lead acetate}}{Pb(OCOCH_3)_2} + H_2SO_4 \longrightarrow PbSO_4\downarrow + 2CH_3COOH$$

Q32. *An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this compound is subjected to complete combustion.*

Ans. **Step I. Calculation of mass of CO_2 produced**

Mass of compound = 0.20 g

Percentage of carbon = 69%

$$\text{Percentage of carbon} = \frac{12}{44}\times\frac{\text{Mass of carbon dioxide formed}}{\text{Mass of compound}}\times 100$$

$$69 = \frac{12}{44}\times\frac{\text{Mass of carbon dioxide formed}}{(0.20\text{ g})}\times 100$$

$$\therefore\ \text{Mass of } CO_2 \text{ formed} = \frac{69\times 44\times(0.20\ g)}{12\times 100} = \mathbf{0.506\ g}$$

Step II. Calculation of mass of H_2O produced

Mass of compound = 0.20 g

Percentage of hydrogen = 4.8%

$$\text{Percentage of hydrogen} = \frac{2}{18}\times\frac{\text{Mass of water formed}}{\text{Mass of compound}}\times 100$$

$$4.8 = \frac{2}{18}\times\frac{\text{Mass of water formed}}{(0.20\text{ g})}\times 100$$

$$\therefore\ \text{Mass of } H_2O \text{ formed} = \frac{4.8\times 18\times(0.20\ g)}{2\times 100} = \mathbf{0.0864\ g}$$

Q33. *0.50 g of an organic compound was Kjeldahlished. The ammonia evolved was passed in 50 cm^3 of 1N H_2SO_4. The residual acid required 60 cm^3 of N/2 NaOH solution. Calculate the percentage of nitrogen in the compound.*

Ans. **Step I.** *Calculation of volume of unused acid*

Volume of NaOH solution required = 60 cm^3

Normality of NaOH solution = 1/2 N

Normality of H_2SO_4 solution = 1/N

Volume of unused acid can be calculated by applying normality equation

$$\underbrace{N_1V_1}_{\text{Acid}} = \underbrace{N_1V_1}_{\text{Base}}$$

$$1 \times V = \frac{1}{2} \times 60 = 30 \text{ cm}^3$$

Step II. *Calculation of volume of acid used*

$$\begin{aligned} \text{Volume of acid added} &= 50 \text{ cm}^3 \\ \text{Volume of unused acid} &= 30 \text{ cm}^3 \\ \text{Volume of acid used} &= (50 - 30) = 20 \text{ cm}^3 \end{aligned}$$

Step III. *Calculation of percentage of nitrogen*

$$\begin{aligned} \text{Mass of compound} &= 0.50 \text{ g} \\ \text{Volume of acid used} &= 20 \text{ cm}^3 \\ \text{Normality of acid used} &= 1 \text{ N} \\ \text{Percentage of N} &= \frac{1.4 \times \text{Volume of acid used} \times \text{Normality of acid used}}{\text{Mass of the compound}} \\ &= \frac{1.4 \times 20 \times 1}{0.50} = \mathbf{56\%} \end{aligned}$$

Q34. *0.3780 g of an organic compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine in the compound.*

Ans.

$$\begin{aligned} \text{Mass of the compound} &= 0.3780 \text{ g} \\ \text{Mass of silver chloride} &= 0.5740 \text{ g} \\ \text{Percentage of chlorine} &= \frac{35.5}{143.5} \times \frac{\text{Mass of siliver chloride}}{\text{Mass of compound}} \times 100 \\ &= \frac{35.5}{143.5} \times \frac{(0.5740 \text{ g})}{(0.3780 \text{ g})} \times 100 = \mathbf{37.57 \text{ g}} \end{aligned}$$

Q35. *In an estimation of sulphur by Carius method, 0.468 of an organic sulphur compound gave 0.668 g of barium sulphate. Find the percentage of sulphur in the compound.*

Ans. Mass of the compound = 0.468 g

Mass of barium sulphate = 0.668 g

$$\begin{aligned} \text{Percentage of sulphur} &= \frac{32}{233} \times \frac{\text{Mass of barium sulphate}}{\text{Mass of compound}} \times 100 \\ &= \frac{32}{233} \times \frac{(0.668 \, g)}{(0.468 \, g)} \times 100 = \mathbf{19.60\%} \end{aligned}$$

Q36. *In the organic compound $CH_2{=}CH{-}CH_2{-}CH_2{-}C{\equiv}CH$, the $CH{-}CH_2$ bond is formed by the interaction of a pair of hybridised orbitals:*

(a) $sp - sp^2$ *(b)* $sp - sp^3$

(c) $sp^2 - sp^3$ *(d)* $sp^3 - sp^3$

Ans. (*c*) is the correct answer. $(CH_2{=}\overset{(sp^2)}{CH} - \overset{(sp^3)}{CH_2} - CH_2{-}C{\equiv}CH)$

Q37. *In the Lassaigne's test for ntrogen in an organic compound, the Prussian blue colour is obtained due to the formation of:*

(a) $Na_4[Fe(CN)_6]$ (b) $Fe_4[Fe(CN)_6]_3$

(c) $Fe_2[Fe(CN)_6]$ (d) $Fe_3[Fe(CN)_6]_4$.

Ans. (*b*) is the correct answer.

Q38. *Which of the following carbocation is most stable?*

(a) $(CH_3)_3C\overset{\oplus}{C}H_2$ (b) $(CH_3)_3\overset{\oplus}{C}$

(c) $CH_3CH_2\overset{\oplus}{C}H_2$ (d) $CH_3\overset{\oplus}{C}HCH_2CH_3$.

Ans. (*b*) is the most stable since it is a tertiary carbocation.

Q39. *The best and latest technique for isolation, purification and separation of organic compounds is:*

(a) Crystallisation (b) Distillation

(c) Sublimation (d) Chromatography.

Ans. (*d*) is the correct answer.

Q40. *The following reaction is classified as:*

$$CH_3CH_2I + KOH\ (aq) \longrightarrow CH_3CH_2OH + KI$$

(a) electrophilic substitution (b) nucleophilic substitution

(c) elimination (d) addition

Ans. (*b*) It is a nucleophilic substitution reaction. KOH (*aq*) provides OH^- ion for the nucleophile attack.

MORE QUESTIONS SOLVED

I. VERY SHORT ANSWER TYPE QUESTIONS

Q1. *How will you separate a mixture of two organic compounds which have different solubilities in the same solvent?*

Ans. By fractional crystallisation.

Q2. *An organic liquid decomposes below its boiling point. How will you purify it?*

Ans. By distillation under reduced pressure.

Q3. *Suggest a suitable technique for separating naphthalene from kerosene oil present in a mixture.*

Ans. Simple distillation.

Q4. *Arrange the following in increasing order of C—C bond length:*

C_2H_6, C_2H_4, C_2H_2.

Ans. C_2H_2 (120 pm) < C_2H_4 (134 pm) < C_2H_6 (154 pm)

Q5. *Name the process used to separate sugar and salt.*

Ans. Fractional crystallisation using ethanol as a solvent.

Q6. *Which gas is liberated in Kjeldhal's method?*

Ans. Ammonia gas (NH_3)

Q7. *What is Lassaigne's extract?*

Ans. When organic compound is fused with sodium metal and then extracted by water, it is called Lassaigne's extract.

Q8. *What type of solids are separated by fractional crystallisation?*

Ans. Those solids which are soluble in the same solvent but to a different extent *i.e.,* differ in their solubility.

Q9. *Name a suitable adsorbent used in the process of column chromatography.*

Ans. Al_2O_3 (alumina)

Q10. *Name three types of chromatography.*

Ans. Column chromatography, paper chromatography and thin layer chromatography.

Q11. *Which method is used to extract a compound in aqueous solution?*

Ans. Differential extraction.

Q12. *In Carius method, sulphur is estimated by precipitating it as which compound?*

Ans. $BaSO_4$.

Q13. *Which elements are estimated by Liebig's Method?*

Ans. Carbon and hydrogen.

Q14. *Which type of compounds are purified by steam distillation?*

Ans. Steam volatile and insoluble in water.

Q15. *Complete the following:*

$$(CH_3COO)_2\,Pb + Na_2S \longrightarrow$$

Ans. $(CH_3COO)_2\,Pb + Na_2S \longrightarrow \underset{\text{black ppt}}{PbS} + 2CH_3COONa$

Q16. *How will you separate a mixture of Iodine and sodium chloride?*

Ans. Sublimation.

Q17. *Why is an organic compound fused with sodium in Lassaigne's test?*

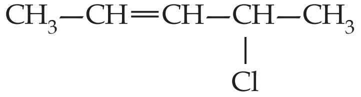
Ans. It is because sodium is highly reactive and it reacts with elements to form ionic compounds.

Q18. *Write the name of element which is confirmed on adding $Na_2[Fe(CN)_5NO]$ in sodium extract solution due to appearance of violet colouration.*

Ans. Sulphur.

Q19. *Write the structural formula of 4-chloro-2-pentene.*

Ans.



$$CH_3{-}CH{=}CH{-}\underset{\substack{|\\ Cl}}{CH}{-}CH_3$$

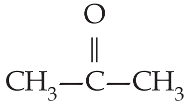
Q20. *What is the basic principle of chromatography?*

Ans. Chromatography is based on the principle of differential adsorption.

II. SHORT ANSWER TYPE QUESTIONS

Q1. *Write all structural isomers of molecular formula C_3H_6O.*

Ans. CH_3CH_2CHO



$$CH_3{-}\overset{\substack{O\\ \|}}{C}{-}CH_3$$

Q2. (*a*) *What do you understand by Homolytic fission?*

(*b*) *What are carbanions? Give an example.*

Ans. (*a*) Homolytic fission is breaking of a bond in such a manner that each atom takes one electron each to form free radicals.

$$A \text{——} B \longrightarrow A\cdot + \cdot B$$

(*b*) Organic ions which contain a negatively charged carbon atom are called carbanions. *e.g.*, $\overset{\ominus}{C}H_3$ is carbanion.

Q3. *How will you detect the presence of nitrogen and sulphur in Lassaigne's extract?*

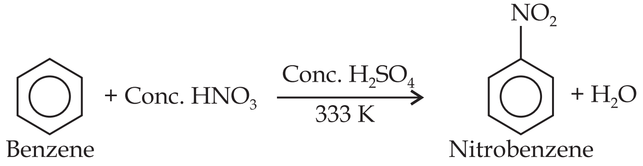
Ans. If freshly prepared $FeSO_4$ and then dil. H_2SO_4 is added to Lassaigne's extract, a blue green colouration confirms the nitrogen.

Q4. *Give equation for the following:*

(*i*) Electrophilic Substitution

(*ii*) Nucleophilic Substitution

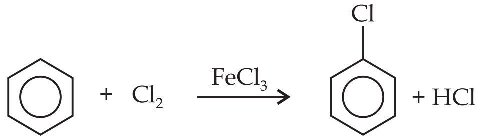
Ans. (*i*)



(*ii*) $CH_3CH_2I + KOH(aq) \longrightarrow \underset{\text{ethanol}}{CH_3CH_2OH} + KI$

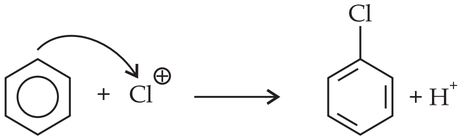
Q5. *What are electrophiles? Explain electrophile substitution reaction with the help of example.*

Ans. A reagent which can accept an electron pair in a reaction is called an electrophile. Examples are, H^+, Cl^+, NO_2^+, R_3C^+, $RN_2^{\oplus}$



Mechanism

$Cl_2 + FeCl_3 \longrightarrow FeCl_4^{\ominus} + Cl^{\oplus}$



Q6. *0.25 g of an organic compound gave 38 cm³ of N_2 at 300 K and 96 k Pa pressure. Calculate % of N in the sample.*

Ans.

$$V_1 = 38 \text{ cm}^3$$
$$V_2 = ?$$
$$P_1 = 96 \text{ k Pa}$$
$$P_2 = 101.3 \text{ Pa}$$
$$T_1 = 300 \text{ K} \qquad T_2 = 273 \text{ K}$$
$$V_2 = \frac{96 \times 38 \times 273}{300 \times 101.3}$$
$$= \frac{995904}{30390} = 32.77 \text{ cm}^3$$
$$\% \text{ of N} = \frac{28}{22400} \times \frac{100 \times V_2}{W}$$
$$= \frac{1}{8} \times \frac{V_2}{W} = \frac{1}{8} \times \frac{32.77}{0.25} = 16.38\%$$

Q7. *0.15 g of an organic compound gave 0.12 g of Ag Br by the Carius method. Find percentage of Br in the compound.*

Ans.
$$\% \text{ of Br} = \frac{80}{188} \times \frac{\text{weight of Ag Br} \times 100}{\text{weight of organic compound}}$$

$$= \frac{80}{188} \times \frac{0.12}{0.15} \times 100$$

$$= 34\%$$

Q8. *0.12 g of an organic compound containing phosphorous gave 0.22 g of $Mg_2\, P_2O_7$ by usual analysis. Calculate the percentage of phosphorous in the compound.*

Ans.
$$\% \text{ of P} = \frac{62}{222} \times \frac{\text{weight of } Mg_2P_2O_7 \text{ formed} \times 100}{\text{weight of organic compound}}$$

$$= \frac{62}{222} \times \frac{0.22}{0.12} \times 100$$

$$= 51.20\%$$

Q9. *(a) Which is more suitable method for the purification of a compound in liquid state which decomposes at or below its boiling point?*

(b) How will you separate a mixture of ammonium chloride and common salt?

Ans. (*a*) Distillation under reduced pressure or vacuum distillation

(*b*) Sublimation.

Q10. *(i) Arrange the following carbocation in increasing order of their stability.*

$(CH_3)_2\overset{\oplus}{C}H$, $CH_3CH_2^+$, $(CH_3)_3C^+$, $\overset{+}{C}H_3$

(ii) Write the IUPAC name of following compound.

(a)

$$CH_3{-}\underset{\underset{OH}{|}}{CH}{-}CH_2{-}OC_2H_5$$

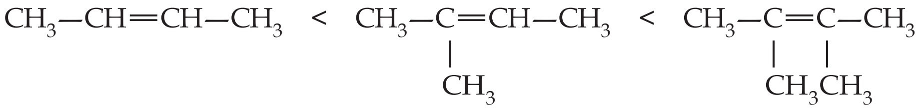
Ans. (*i*) $\overset{\oplus}{C}H_3 < CH_3\overset{\oplus}{C}H_2 < (CH_3)_2\overset{\oplus}{C}H < (CH_3)_3\overset{\oplus}{C}$

(*ii*) 1-Ethoxypropan-2-ol

III. LONG ANSWER TYPE QUESTIONS *(5 marks)*

Q1. *Explain hyperconjugation effect. How does hyperconjugation effect explain the stability of alkenes?*

Ans. **Hyperconjugation:** The relative stability of various classes of carbonium ions may be explained by the number of no-bond resonance structures that can be written for them. Such structures are arrived by shifting the bonding electrons from an adjacent C—H bond to the electron–deficient carbon. In this way, the positive charge originally on carbon is dispersed to the hydrogen. This manner of electron release by assuming no-bond character in the adjacent C—H bond is called Hyperconjugation or No-Bond Resonance. The greater the hyperconjugation, the greater will be the stability of the compound. The increasing order of stability can be shown as.



$$CH_3{-}CH{=}CH{-}CH_3 < CH_3{-}\underset{\underset{CH_3}{|}}{C}{=}CH{-}CH_3 < CH_3{-}\underset{\underset{CH_3}{|}}{C}{=}\underset{\underset{CH_3}{|}}{C}{-}CH_3$$

Q2. *(a) What is the basic principle involved in the estimation of nitrogen by Dumas method.*

(b) In a Dumas nitrogen estimation method, 0.30 g of an organic compound gave 50 cm^3 *of* N_2 *collected at 300 K and 715 mm Hg pressure. Calculate the percentage composition of nitrogen in the compound. (Vapour pressure of water at 300 K is 15 mm Hg)*

Ans. (*a*) This method is based upon the fact that nitrogenous compound is heated with copper oxide in an atmosphere of carbon dioxide yield free nitrogen.

$$C_xH_yN_z + CuO \longrightarrow xCO_2 + \frac{y}{2}\ H_2O + \frac{z}{2}N_2 + (Cu)$$

(*b*) $P_1 = 715 - 15 = 700$ mm Hg, $P_2 = 760$ mm Hg

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$T_1 = 300$ K, $T_2 = 273$ K

$V_1 = 50$ cm^3, V_2 = ?

$$V_2 = \frac{700 \times 50 \times 273}{300 \times 760}$$

$$= 41.9 \text{ cm}^3$$

$$\% \text{ of N} = \frac{28}{22400} \times 41.9 \times \frac{100}{W}$$

$$= 17.46\%$$

Q3. *(a) What is Lassaigne's extract? Will NaCN give a positive Lassaigne's test for nitrogen?*

(b) Which colour will appear in the Lassaigne's test if the compound contains both nitrogen and sulphur.

(c) Why is Lassaigne's extract prepared in distilled water? Can we detect oxygen in a compound by Lassaigne's test?

Ans. (*a*) When organic compound is fused with sodium metal and then extracted by water, it is called Lassaigne's extract. Yes.

(*b*) Blood red colour.

(*c*) Lassaigne's extract is prepared in distilled water since tap water contains Cl^- ions. No, oxygen cannot be detected by Lassaigne's test.

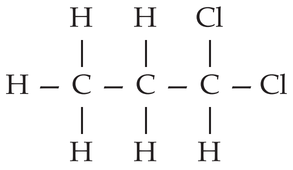
IV. MULTIPLE CHOICE QUESTIONS

1. The large number of organic compounds is due to

(*a*) the valency of carbon (*b*) a small size of carbon

(*c*) a special property of carbon known as catenation

2. The IUPAC name of

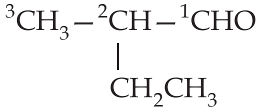


$$\begin{array}{ccccccc} & & H & & H & & Cl \\ & & | & & | & & | \\ H & - & C & - & C & - & C - Cl \\ & & | & & | & & | \\ & & H & & H & & H \end{array}$$

(*a*) 1, 2-dichloropropane (*b*) 3, 3-dichloropropane

(*c*) 1, 1-dichloropropane (*d*) dichloropropane

3. The IUPAC name of



$$^{3}CH_3-{}^{2}\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}-{}^{1}CHO$$

(*a*) 2-methyl butanal (*b*) butan-2-aldehyde
(*c*) 2-ethylpropanal (*d*) 3-methyl isobutraldehyde

4. The bond that undergoes heterolytic cleavage most readily is

(*a*) C–C (*b*) C–O (*c*) C–H (*d*) O–H

5. The reaction

$CH_3CH = CH_2 + HBr \xrightarrow[CH_3\,CH_2\,CH_2\,Br]{\text{Peroxide}}$ can be explained by

(*a*) carbocation formation (*b*) free-radical mechanism
(*c*) carbanion formation (*d*) none of these

6. The hybridization state of a carbocation is

(*a*) sp^4 (*b*) sp^3 (*c*) sp^2 (*d*) sp

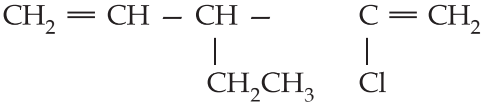
7. Which of the following are electrophiles?

(*a*) Dimethyl sulphide (*b*) Bromides (*c*) Carbon dioxide (*d*) Ammonia

8. Which of the following compounds will exhibit cis-trans isomerism?

(*a*) 2-Butene (*b*) 2-Butyne (*c*) 1-Butene (*d*) 2-Butanol

9.



$$CH_2 = CH - \underset{\displaystyle CH_2CH_3}{\underset{|}{CH}} - \underset{\displaystyle Cl}{\underset{|}{C}} = CH_2$$

The IUPAC name of this compound is

(*a*) 3-ethyl-4-chloro-1, 4-pentadiene (*b*) 2-chloro-3-ethyl-1, 4-pentadiene
(*c*) 4-chloro ethyl-1-pentene (*d*) 3-ethyl-4-chloro-4-pentene

Ans. 1. (*c*) 2. (*c*) 3. (*c*) 4. (*d*) 5. (*b*)
6. (*c*) 7. (*a*) and (*c*) 8. (*a*) 9. (*b*)

V. HOTS QUESTIONS

Q1. *Write the hybridized state of C atoms in the following* $CH_2 = CH - C - N$

Ans. $\overset{sp^2}{CH_2} = \overset{sp^2}{CH} - \overset{sp}{C} - N$

Q2. *Explain why* $(CH_3)_3C^+$ *is more stable than* $CH_3C^+H_2$.

Ans. $(CH_3)_3C^+$ has nine alpha hydrogens and has nine hyperconjugation structures while $CH_3C^+H_2$ has three alpha hydrogens and has three hyperconjugation structures, therefore $(CH_3)_3C^+$ is more stable than $CH_3C^+H_2$.

Q3. *Why is an organic compound fused with Sodium for testing nitrogen, halogens and sulphur?*

Ans. On fusing with sodium metal the elements present in an organic compound are converted into sodium salts which are water soluble which can be filtered and detected by the respective tests.

Q4. *Under what conditions can the process of steam distillation is used?*

Ans. Steam distillation is used to purify the liquids which are steam volatile and not miscible with water.

Q5. *Explain hyperconjugation effect. How does hyperconjugation effect explain the stability of alkenes?*

Ans. The relative stability of various classes of carbonium ions may be explained by the number of no-bond resonance structures that can be written for them. Such structures are obtained by shifting the bonding electrons from an adjacent C-H bond to the electron deficient carbon so the positive charge originally on carbon is dispersed to the hydrogen. This manner of electron release by assuming no bond character in the adjacent C-H bond is called Hyperconjugation. Greater the hyperconjugation, greater will be the stability of alkenes.

❑❑❑