12. ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

Organic chemistry is the branch of chemistry that deals with carbon compounds. But all carbon compounds are not considered as organic compounds. (E.g. CO_2, CO, metal carbonates, bicarbonates etc.). So organic chemistry can be defined as *the branch of chemistry that deals with hydrocarbons and their derivatives*. Hydrocarbons are the major class of organic compounds and they *contain only carbon and hydrogen atoms*. All other organic compounds are formed by replacing one or more hydrogen atoms of hydrocarbons by other atoms or groups (They are called hydrocarbon derivatives).

All carbon compounds present in plants and animals are organic compounds. E.g. Carbohydrates, proteins, vitamins, nucleic acids, amino acids, fats and oils, natural polymers etc. petroleum and coal are the major source of organic compounds (hydrocarbons).

In ancient times, it was believed that a vital force (living body) is necessary for the production of an organic compound. But in 1828, Frederic Wohler proved that this belief was wrong. He prepared urea in the laboratory, by heating ammonium cyanate (NH_4CNO). It was the first organic compound prepared in the laboratory.

$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\text{Heat}} \underset{\text{Urea}}{NH_2CONH_2}$$

Then another scientist Kolbe synthesized acetic acid and Berthelot synthesized methane in the laboratory. Nowadays about 95% of the organic compounds are synthesized in the laboratory.

Chemistry behind the existance of large number Carbon compounds

Carbon is a unique element and it can form a large number of compounds due to the following reasons:

i) Tetravalency of carbon: In all of its compounds, the valency of carbon is four. Carbon has 4 electrons in its valency shell and requires 4 more electrons to complete the octet. So it attains the octet configuration by forming 4 covalent bonds.

ii) Ability to form single bond and multiple bonds: C can form single bond and multiple bond (double or triple bond) with itself and also with other elements like oxygen, nitrogen etc. This is possible by sp^3, sp^2 or sp hybridisation.

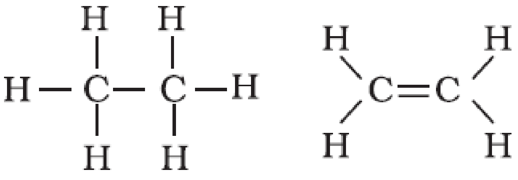
iii) Catenation: Carbon shows catenation. It is the self linking property of an element to form long chains and rings.

iv) Isomerism: Carbon compounds can show isomerism. It is the phenomenon in which compounds having same molecular formula but different structural formula or spatial arrangement of atoms.

Structural representation of organic compounds

An organic compound can be represented by the following ways:

1. **Complete structural formula**: Here all the bonds between atoms are denoted by dashes (----). A single dash represents a single bond, a double dash represents a double bond and a triple dash represents a triple bond. E.g.



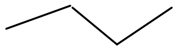
Ethane Ethene

2. **Condensed stuctural formula**: Here the carbon-hydrogen bonds or all the bonds are omitted except the multiple bonds. It is a simplified representation of an organic compound.
   E.g. ethane - CH_3CH_3, propane - $CH_3CH_2CH_3$, butane - $CH_3CH_2CH_2CH_3$, ethene - $CH_2{=}CH_2$ etc.

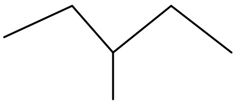
The condensed formula can again simplified as follows:
Butane – $CH_3(CH_2)_2CH_3$, Hexane- $CH_3(CH_2)_4CH_3$, Decane – $CH_3(CH_2)_8CH_3$ etc.

3. **Bond line representation**: It is the simplest form of representation of an organic compound. Here carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are drawn in a zig-zag fashion. The only atoms specifically written are oxygen, chlorine, nitrogen etc. The free terminals denote methyl ($–CH_3$) groups.

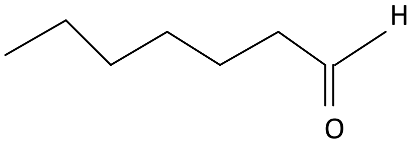
E.g. butane:



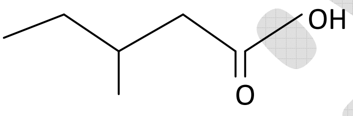
3-methyl pentane:



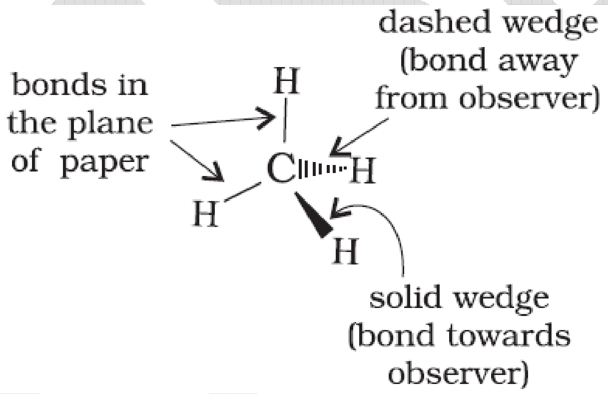
Heptanal:



3-Methyl pentanoic acid:



4. **Three-Dimensional Representation (Wedge Representation)**: Here the structure of an organic molecule can be represented by using solid (▬) and dashed (┆┆┆) wedges. The solid-wedge is used to indicate a bond projecting out of the plane of paper, towards the observer. The dashed-wedge indicates the bond projecting out of the plane of the paper and away from the observer. The broad end of the wedge is always towards the observer. The bonds lying in plane of the paper are depicted by using a normal line (—).
E.g. methane



Classification of Organic compounds

Organic compounds can be broadly classified into two – Acyclic or open chain compounds and cyclic or ring compounds.

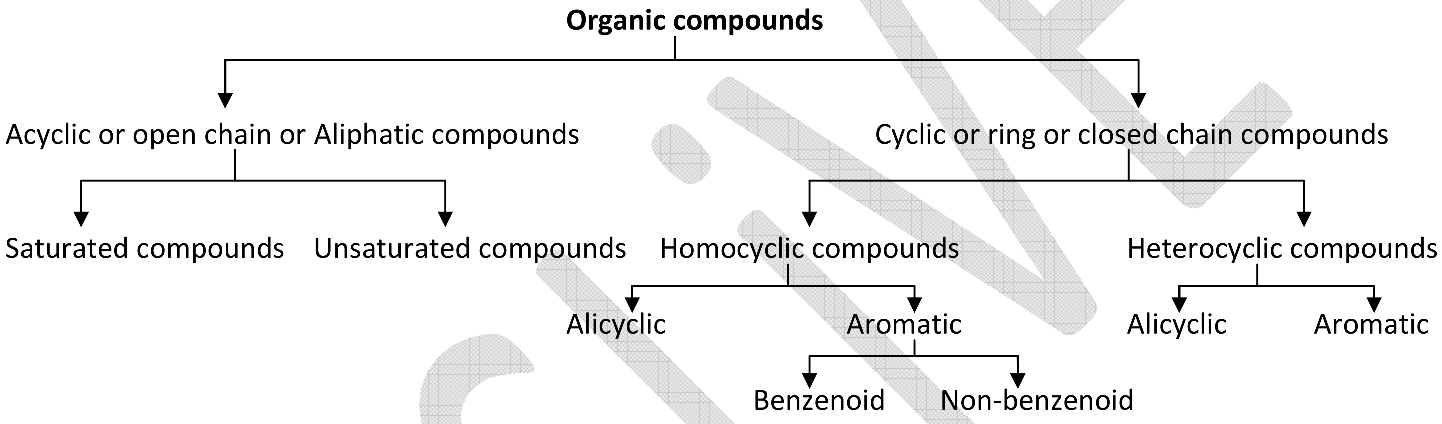
1. **Acyclic or open chain or aliphatic compounds**: In these compounds, the carbon atoms are joined together to form long chains which may be straight chain or branched chain. They are further classified as *saturated compounds* and *unsaturated compounds*. **Saturated compounds** contain only carbon – carbon single bonds. But **unsaturated compounds** contain atleast one carbon – carbon multiple bond (double or triple bond. Saturated hydrocarbons are called *alkanes* and unsaturated hydrocarbons are of two types – *alkenes and alkynes*.

2. **Cyclic or closed chain or ring compounds**: In these compounds, the carbon atoms are joined together to form rings. These rings may be *homocyclic or heterocyclic*. If the ring contains only carbon atoms, it is called homocyclic compound and if it contains atoms other than carbon (like O, N, S etc), it is called heterocyclic compound.

   Homocyclic compounds are further classified into two – *Alicyclic compounds and Aromatic compounds*. **Alicyclic compounds** contain atleast one carbo-cyclic ring. *Alicyclic hydrocarbons* are of three types – *cycloalkanes, cycloalkenes and cycloalkynes*. **Aromatic compounds** are some special type of compounds. These are of two types. Aromatic compounds containing benzene ring are called *benzenoid compounds* and those which do not contain benzene ring are called *non-benzenoid compounds*. E.g. for a non-benzenoid aromatic compound is tropolone.

   Heterocyclic compounds may be alicyclic heterocyclic compounds or aromatic heterocyclic compounds.

The classification of organic compounds can be diagrammatically represented as follows:



Functional groups: Atoms or group of atoms (except hydrogen) which are bonded to carbon atoms are called functional groups. These groups are responsible for the characteristic chemical properties of the organic compounds. Some important functional groups, their names and name of the compounds are listed below:

Functional group	Name of the group	Name of compound
-OH	Hydroxyl group	Alcohol
$-NH_2$	Amino group	Amine
-X	Halo group	Halo compound
-CHO	Aldehydric (formyl) group	Aldehyde
-CO- or >CO	Carbonyl (keto) group	Ketone
-COOH	Carboxyl group	Carboxylic acid
-O-	Oxy group	Ether
-CN	Cyano group	Nitrile
$-NO_2$	Nitro group	Nitro compound

Homologous series: A series or group of organic compounds in which adjacent members are differed by a $-CH_2$ group is called a homologous series. The members of a homologous series are called *homologues*. They contain same functional groups, have similar chemical properties and show gradation in physical properties. They can be prepared by some general methods of preparation. E.g. for homologous series are alkanes, alkenes, alkynes, alcohols, ethers, carboxylic acids, aldehydes, ketones, amines, halo compounds etc.

Nomenclature of organic compounds

An organic compound has two types of names – Common name and IUPAC name. The common name is based on the source or some properties. For e.g. citric acid is named so because it is found in citrus fruits and the acid found in red ant is named formic acid since the Latin word for ant is formica.

IUPAC Nomenclature of organic compounds

A systematic name of an organic compound is generally derived by identifying the parent hydrocarbon and the functional group(s) attached to it. This name is called IUPAC name. It contains two parts – word root and suffix or prefix. The word root indicates the number of carbon atoms in the compound. The word roots for compounds containing 1 -12 carbon atoms are as follows:

No. of C atoms	Word root	No. of C atoms	Word root
C_1	Meth-	C_7	Hept-
C_2	Eth-	C_8	Oct-
C_3	Prop-	C_9	Non-
C_4	But-	C_{10}	Dec-
C_5	Pent-	C_{11}	Undec-
C_6	Hex-	C_{12}	Dodec-

There are two types of suffixes – primary suffix and secondary suffix. Primary suffix indicates saturation or unsaturation [for alkane the primary suffix is –ane, alkene –ene and for alkyne –yne]. Secondary suffix indicates the type of functional group. Some functional groups are also indicated as prefixes.

Nomenclature of branched chain alkanes:

A branch (side chain or substituent) is obtained by removing a hydrogen atom from an alkane. The resulting group is called an ***alkyl group*** [alkane – H = alkyl (i.e. ***word root + yl***)]. The names of some common branches are as follows:

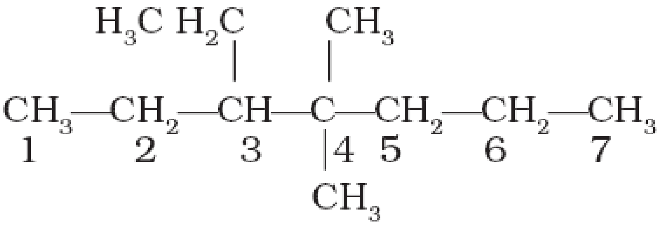
Branch	Name
$-CH_3$	Methyl
$-CH_2-CH_3$	Ethyl
$-CH_2-CH_2-CH_3$	n-propyl (normal propyl)
$(CH_3)_2CH-$	isopropyl
$-CH_2-CH_2-CH_2-CH_3$	n-butyl
$CH_3-\underset{\vert}{C}H-CH_2-CH_3$	sec-butyl (secondary butyl)
$(CH_3)_2CH-CH_2-$	isobutyl
$(CH_3)_3C-$	tert-butyl (tertiary butyl)
$(CH_3)_3C-CH_2-$	neopentyl

Rules for naming branched chain alkanes:

IUPAC recommenced the following rules for naming a branched chain alkane.

1. Select the longest continuous chain of carbon atoms. This chain is called parent chain or root chain. If there is more than one such chain, the chain that contains maximum number of branches is selected as the parent chain. Also identify all the branches or substituents.
2. Number the carbon atoms of the parent chain in such a way that the branched carbon atoms get the lowest possible numbers.
3. The names of alkyl groups attached as branches are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers.
4. If different alkyl groups are present, they are listed in alphabetical order. In alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes sec- and tert- are not considered to be the part of the fundamental name.

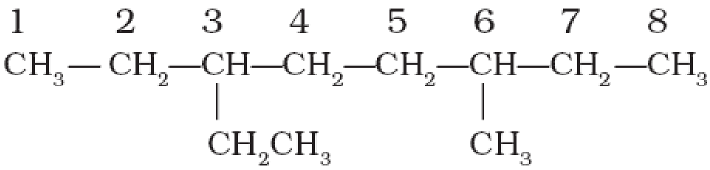
5. If two or more identical substituent groups are present then their numbers are indicated by prefixes like di (for 2), tri (for 3), tetra (for 4), penta (for 5) etc and the numbers are separated by commas. The number and word are separated by a hyphen. (The IUPAC name is written as a single word).
   For example:



$$\underset{1}{CH_3}-\underset{2}{CH_2}-\underset{3}{\overset{\overset{H_3C\,H_2C}{|}}{CH}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\underset{4}{C}}}-\underset{5}{CH_2}-\underset{6}{CH_2}-\underset{7}{CH_3}$$

3-Ethyl-4,4-dimethylheptane

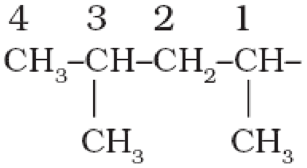
6. If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing.
   For example:



$$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{\underset{CH_2CH_3}{|}}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{6}{CH}}-\overset{7}{CH_2}-\overset{8}{CH_3}$$

   The above compound is *3-ethyl-6-methyloctane* and not 6-ethyl-3-methyloctane.

7. While naming the branched alkyl groups, the carbon atom of the branch that attaches to the root alkane is numbered 1.
   For example:



$$\overset{4}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{3}{CH}}-\overset{2}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{1}{CH}}-$$

1,3-dimethyl butyl-

IUPAC nomenclature of compounds containing functional groups

For naming organic compounds containing functional group, the following rules are used:

1. Select the longest continuous chain containing the functional group.
2. Number the carbon atoms in such a way that the carbon to which the functional group is attached should get the lowest possible number. In the case of functional groups containing carbon atom like –CHO, -CN, -COOH, -CONH$_2$, -COX. -COOR etc. the numbering should start from the carbon atom of the functional group. (i.e. carbon atom of these groups should be numbered as 1). (But for ketones, the functional group –CO- should get the lowest possible number).
3. The name of the functional group is indicated by the following suffix or prefix.

Functional group	Name of compound	Suffix/Prefix	IUPAC name
-OH	Alcohol	-ol	Alkanol
-NH$_2$	Amine	-amine	Alkanamine
-X	Halo compound	Halo-	Haloalkane
-CHO	Aldehyde	-al	Alkanal
>CO	Ketone	-one	Alkanone
-COOH	Carboxylic acid	-oic acid	Alkanoic acid
-O-	Ether	Alkoxy-	Alkoxy alkane

-CN	Nitrile	-nitrile	Alkane ntrile
$-NO_2$	Nitro compound	Nitro-	Nitroalkane
$-C=C-$	Alkene	-ene	Alkene
$-C\equiv C-$	Alkyne	-yne	Alkyne
-COOR	Ester	-oate	Alkyl alkanoate
$-CONH_2$	Acid amide	-amide	Alkanamide
-COX	Acid halide	-oyl halide	Alkanoyl halide
-SO3H	Sulphonic acid	-sulphonic acid	Alkanesulphonic acid

In the case of suffixes, the ending –e of the corresponding alkane is replaced. E.g. IUPAC name of the alcohol CH_3-OH is methanol (methan~~e~~ + ol). But for nitriles, the –e of the corresponding alkane is retained. E.g. IUPAC name of CH_3-CH_2-CN is propanenitrile.

In the case of alkenes and alkynes, the suffix –ane of the alkane is replaced by –ene and –yne respectively. (i.e. word root + ene or yne). For naming alkenes or alkynes, the numbering is done in such a way that the double or triple bond should get the lowest possible number.

Some examples are:

Compound	**IUPAC Name**
$CH_3-CH_2-CH=CH_2$	1-Butene
$CH_3-CH=CH-CH_3$	2-Butene
$CH_3-CH_2-C\equiv C-CH_3$	2-Pentyne
$CH_3-CH_2-CH_2-CH_2-CH_2-C\equiv CH$	1-Heptyne
CH_3-CH_2-OH	Ethanol
$CH_3-CH_2-CHOH-CH_2-CH_2-CH_3$	3-Hexanol or Hexan-3-ol or Hexanol-3
$CH_3-CH_2-CH_2-CHO$	1-Butanal or Butanal
HCHO	Methanal
$CH_3-CO-CH_3$	Propanone
$CH_3-CO-CH_2-CH_2-CH_3$	2-Pentanone or Pentan-2-one
$CH_3-CH_2-CH_2-CO-CH_2-CH_2-CH_2-CH_3$	4-Octanone or Octan-4-one
HCOOH	Methanoic acid
CH_3-COOH	Ethanoic acid
$CH_3-CH_2-CH_2-COOH$	1-Butanoic acid or butanoic acid
CH_3-CH_2-Cl	Chloroethane
$CH_3-CH_2-CHBr-CH_3$	2-Bromobutane
$CH_2Cl-CH_2-CH_2-CH_2-CH_3$	1-Chloropentane
$CH_3-CH_2-CH_2-NO_2$	1-Nitropropane
$CH_3-CH_2-CH_2-CN$	Butanenitrile
$CH_3-CH_2-CH_2-CH_2-CH_2-CN$	Hexanenitrile
CH_3-O-CH_3	Methoxymethane
$CH_3-CH_2-O-CH_3$	Methoxyethane
$CH_3-CH_2-CH_2-O-CH_2-CH_3$	Ethoxypropane
$CH_3-CH_2-NH_2$	Ethanamine
$CH_3-CH_2-CHNH_2-CH_3$	2-Butanamine or Butan-2-amine
$CH_3-CH_2-COOCH_3$	Methylpropanoate
$CH_3-CH_2-COOCH_2-CH_3$	Ethylpropanoate

CH_3-CH_2-COCl	Propanoylchloride
CH_3-CH_2-CH_2-CH_2-COBr	Pentanoylbromide
CH_3-CH_2-CH_2-$CONH_2$	Butanamide
CH_3-$CONH_2$	Ethanamide

Nomenclature of organic compounds containing more than one functional groups (Poly functional compounds)

Here one of the functional groups is chosen as the principal functional group and the compound is named on that basis. The remaining functional groups (called subordinate functional groups) are named as substituents using the appropriate prefixes. The choice of principal functional group is made on the basis of order of preference. The order of decreasing priority for some functional groups is:

-COOH, –SO_3H, -COOR (R=alkyl group), -COCl, -$CONH_2$, -CN,-CHO, >CO, -OH, -NH_2, >C=C<, -C≡C-

The groups like alkyl (–R), phenyl (C_6H_5-), halogens (F, Cl, Br, I), nitro (–NO_2), alkoxy (–OR) etc. are always prefix substituents.

For example if a compound contains both alcoholic and aldehydic groups, it is named as hydroxyalkanal, since here aldehydic group is the principal functional group and –OH group is the subordinate functional group. The prefix names of some functional groups are as follows:

Functional group	Prefix name
-OH	Hydroxyl-
-NH_2	Amino-
-X	Halo-
-CHO	Formyl-
>CO	Oxo-
-COOH	Carboxy-
-O-	Alkoxy-
-CN	Cyano-
-NO_2	Nitro-
-COOR	Alkoxy carbonyl-
-$CONH_2$	Carbamoyl-
-COX	Halocarbonyl-

While numbering the carbon chain, the principal functional group should get the lowest possible number.
Some examples are:

Compound	IUPAC Name
CH_3-CHOH-CH_2-CO-CH_3	4-Hydroxy-2-pentanone
CH_2Cl-CH_2-CHBr- CH_2-CH_2OH	3-Bromo-5-chloropentan-1-ol *or,* 3-Bromo-5-chloro-1-pentanol
CH_3-CH_2-CO-CH_2-CH_2-CHO	4-Oxohexanal
CH_3-$CHNH_2$-CH_2-COOH	3-Aminobutanoic acid
CH_3-CH_2-CHCl-CH_2-CO-CH_2-COOH	5-Chloro-3-oxo-heptanoic acid

If a compound contains more than one same functional group, their number is indicated by adding the numeral prefixes di, tri, etc. before the suffix. In such cases the full name of the parent alkane is written before the suffix. However, the ending – ne of the parent alkane is dropped in the case of compounds having more than one double or triple bonds.

When both double and triple bonds are present, the double bonds are given the lowest numbers. Here first give the suffix of the double bond (-en) and then that of the triple bond (-yne) [the ending –e of the suffix –ene is avoided].

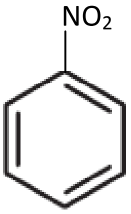
Examples:

Compound	IUPAC Name
CH_2OH-CH_2OH	Ethane-1,2-diol (Ethylene glycol)
$CH_2OH-CHOH-CH_2OH$	Propane-1,2,3-triol (Glycerol)
CHO-CHO	Ethane-1,2-dial (Glyoxal)
COOH-COOH	Ethane-1,2-dioic acid (Oxalic acid)
$CH_3-CO-CH_2-CO-CH_3$	Pentane-2,4-dione
$CH_2=CH-CH=CH_2$	1,3-Butadiene or Buta-1,3-diene
$CH\equiv C-CH_2-C\equiv CH$	1,4-Pentadiene or Penta-1,4-diene
$CH_2=CH-CH_2-C\equiv CH$	Pent-2-en-4-yne
$CH\equiv C-CH=CH-C=CH_2$	Hexa-1,3-dien-5-yne

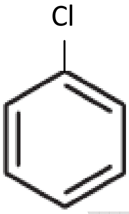
(The names given in the brackette are the common names)

Nomenclature of Substituted Benzene Compounds

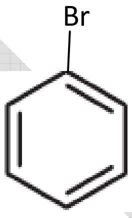
For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word benzene. But common names of some compounds are accepted by IUPAC.



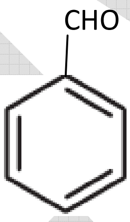
Nitrobenzene



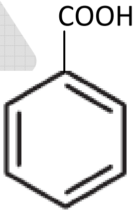
Chlorobenzene



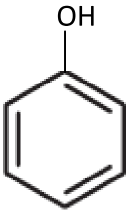
Bromobenzene



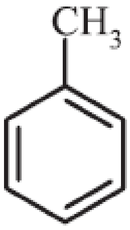
Benzaldehyde



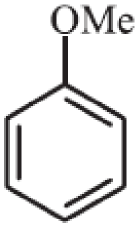
Benzoic acid



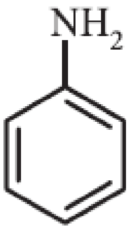
Phenol



Methylbenzene
(Toluene)



Methoxybenzene
(Anisole)

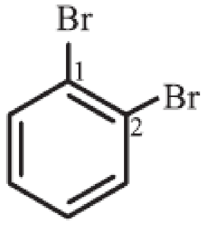


Aminobenzene
(Aniline)

Nomenclatrue of di or polysubstituted benzene

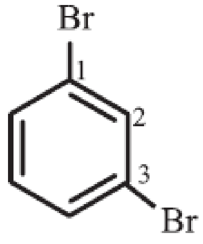
If benzene ring is disubstituted, the position of substituents is indicated by numbering the carbon atoms of the ring such that the substituents get the lowest possible numbers.

Example – Dibromobenzene



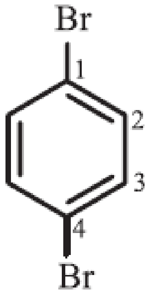
(a)

1,2-Dibromo-
benzene



(b)

1,3-Dibromo-
benzene

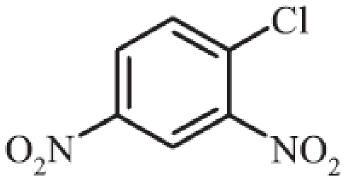


(c)

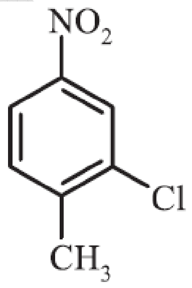
1,4-Dibromo-
benzene

In the common system of nomenclature the terms ortho (o), meta (m) and para (p) are used as prefixes to indicate the relative positions 1,2- 1,3- and 1,4- respectively. So 1,2-dibromobenzene is named as ortho (or just o-) dibromobenzene, 1,3-dibromobenzene as meta (or just m-) dibromobenzene and 1,4-dibromobenzene as para (or just p-)-dibromobenzene.

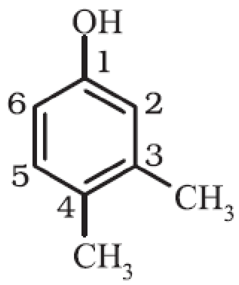
For tri - or higher substituted benzene derivatives, these prefixes cannot be used and the compounds are named by identifying substituent positions on the ring by following the lowest locant rule. In some cases, common name of benzene derivatives is taken as the base compound. Substituent of the base compound is assigned number1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents are named in alphabetical order.
Some examples are:



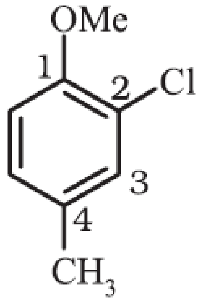
1-Chloro-2,4-dinitrobenzene

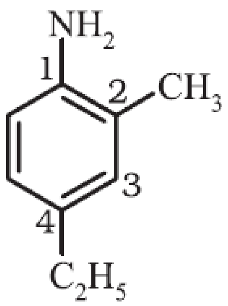


2-Chloro-1-methyl-4-nitrobenzene



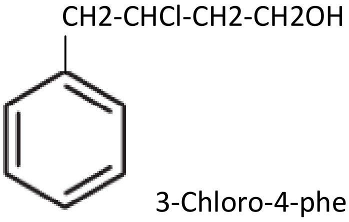
3,4-Dimethylphenol



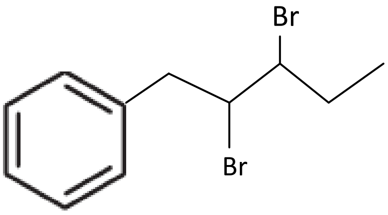


2-Chloro-4-methylanisole 4-Ethyl-2-methylaniline

When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. The name for benzene as substituent is phenyl (C_6H_5-, also abbreviated as Ph).
Example:



3-Chloro-4-phenyl-1-butanol



2,3-Dibromo-1-phenylpentane

Isomerism

The phenomenon of existence of two or more compounds having the same molecular formula but different structural formula or spatial arrangement of atoms is known as isomerism. Such compounds are called as *isomers*. Isomers have different physical and chemical properties. Isomerism can be broadly classified into two – structural isomerism and stereo isomerism.

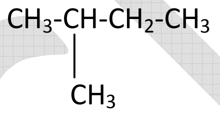
1. Structural isomerism

Compounds having same molecular formula but different structural formula (arrangement of atoms) are called structural isomers and the phenomenon is called structural isomerism. There are mainly four types of structural isomerism:

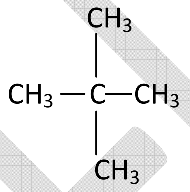
a) ***Chain Isomerism***: Isomers differ in carbon chain or skeleton are called chain isomers and the phenomenon is called chain isomerism.

E.g.: Pentane (C_5H_{12})

CH_3-CH_2-CH_2-CH_2-CH_3
n-pentane



$CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_2\text{-}CH_3$



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

isopentane
(2-Methylbutane)

neopentane (2,2-Dimethylpropane)

b) ***Position isomerism***: Isomers which differ in the position of the substituent or side chain are called position isomers and the phenomenon is called position isomerism.

E.g. : Alcohol with molecular formula $C_4H_{10}O$ may be 1-butanol or 2-butanol

CH_3-CH_2-CH_2-CH_2-OH — 1-Butanol

CH_3-CHOH-CH_2-CH_3 — 2-Butanol

c) ***Functional group isomerism***: Isomers which differ in the functional group are called functional group isomers and the phenomenon is called functional group isomerism. This isomerism is shown by alcohols and ethers and aldehydes and ketones.

E.g. compound with the molecular formula C_2H_6O may be an alcohol ethanol (CH_3-CH_2OH) or an ether methoxy methane (CH_3-O-CH_3).

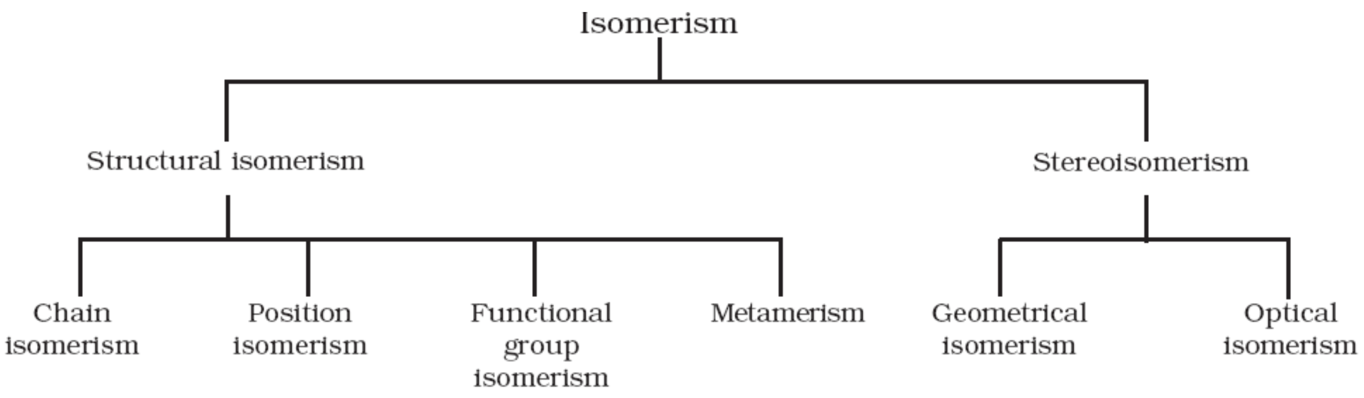
d) ***Metamerism***: Isomers which differ in the carbon chain (alkyl groups) around the functional group are called metamers and the phenomenon is called metamerism. It is commonly shown by ethers.

E.g.: Ether with molecular formula $C_5H_{12}O$ may be methoxybutane (CH_3-O-CH_2-CH_2-CH_2-CH_3) or ethoxypropane (CH_3-CH_2-O-CH_2-CH_2-CH_3).

2. Stereo isomerism

Compounds having same molecular formula but different spatial arrangement of atoms are called stereoisomers and the phenomenon is called stereoisomerism. They have same atom to atom bond. There are two types of stereo isomerism – *Geometrical isomerism and Optical isomerism*.

The diagrammatic representation of different types of isomerism is:



ORGANIC REACTION MECHANISM-Fundamental Concepts

In an organic reaction, the organic molecule (called substrate) reacts with an attacking reagent to form one or more intermediates and finally the products.

Substrate + attacking reagent → Intermediate → Products

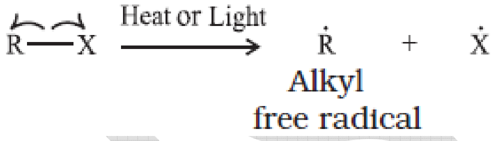
A sequential account of different steps in which the reactants are converted to products is called *reaction mechanism*.

Fission of a covalent bond

A covalent bond can be broken either by homolysis or by heterolysis.

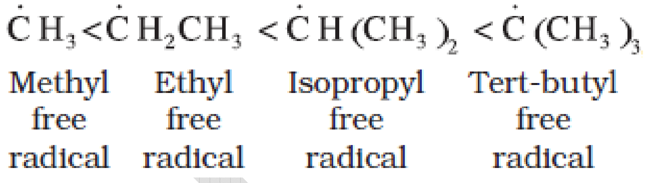
1. **Homolysis**:

In homolysis or homolytic cleavage, each of the bonded atoms gets one of the electrons of the shared pair. Here the movement of a single electron takes place. The single electron movement is shown by half – headed arrow or fish hook arrow ($\curvearrowright$).



$$R{-}X \xrightarrow{\text{Heat or Light}} \dot{R} + \dot{X}$$

The species formed as a result of homolysis is called ***free radical***. These are *species which contain an odd electron or an unpaired electron*. There are three types of free radicals – primary (1^0), secondary (2^0) and tertiary (3^0). Their stability increases in the order $1^0 < 2^0 < 3^0$.



$$\dot{C}H_3 < \dot{C}H_2CH_3 < \dot{C}H(CH_3)_2 < \dot{C}(CH_3)_3$$

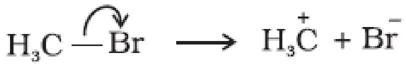
Organic reactions, which take place by homolytic fission are called ***free radical or homopolar or nonpolar reactions.***

2. **Heterolysis**:

In heterolysis or heterolytic cleavage, the bond breaks in such a manner that the shared pair of electrons remains with one of the parts.

After heterolysis, one atom has a sextet of electron and a positive charge and the other atom has an octet of electron with atleast one lone pair and a negative charge.

For example the bond cleavage in methyl bromide takes place in the following manner.

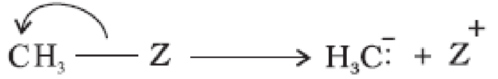


$H_3C-Br \longrightarrow H_3\overset{+}{C} + Br^-$

A species having a carbon atom possessing sextet of electrons and a positive charge is called a ***carbocation (carbonium ion)***. They are of three types – primary, secondary and tertiary.

Carbocations are highly unstable and reactive species. Their stability increases in the order $1^0 < 2^0 < 3^0$. The high stability of tertiary carbocations is due to inductive effect and hyper conjugation. In carbocations, carbon atom is in sp^2 hybridisation and hence they have trigonal planar (planar triangular) shape.

If the group attached to the carbon atom is less electronegative than C, due to heterolytic cleavage, a species with C atom containing a shared pair of electrons and negative charge is formed.



$CH_3-Z \longrightarrow H_3C{:}^- + Z^+$

Such a species carrying a negative charge on carbon atom is called ***carbanion***. They are also unstable and reactive. Their stability increases in the order : $3^0 < 2^0 < 1^0$.

The organic reactions which proceed through heterolytic bond cleavage are called ***ionic or heteropolar or polar reactions.***

Nucleophiles and Electrophiles

A reagent that brings an electron pair is called a nucleophile (:Nu) and the reaction is called nucleophilic reaction. Or, nucleophiles are electron rich species attack at electron deficient centre. (The word nucleophile means nucleus seeking).

Example for nucleophiles are OH^-, CN^-, NO_2^-, Cl^-, Br^-, I^-, H_2O, NH_3, $R-NH_2$ etc.

A reagent that takes away an electron pair is called an electrophile (E^+) and the reaction is called electrophilic reaction. Or, electrophiles are electron deficient species attack at electron rich centre. (The word electrophile means electron seeking).

Example for electrophiles are carbocations (R^+), -CHO, >CO etc.

Electron displacement effects in covalent bonds

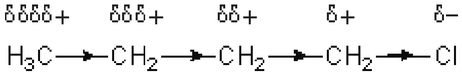
In an organic molecule, the electron displacement may take place either under the influence of an atom or in the presence of an attacking reagent. The important types of electron displacement effects are inductive effect, electromeric effect, resonance effect and hyper conjugation.

1. **Inductive effect (I effect):**

It is a permanent effect arising due to the shifting of sigma electrons through a carbon chain in presence of an atom or group of atom (having different electronegativity) attached to a carbon chain. This effect propagates only through C – C σ bonds. This effect decreases rapidly as the number of C atoms increases.

E.g. 1-chlorobutane $CH_3 – CH_2 – CH_2 – CH_2 –Cl$

Here Cl is more electronegative than C. So the electron pair in the C – Cl bond is shifted towards Cl and it gets a slight –ve charge (δ^-) and C gets a slight +ve charge (δ^+). This carbon attracts the electron density from the second carbon and so the 2nd carbon gets a relatively smaller positive charge ($\delta\delta^+$).



$\overset{\delta\delta\delta\delta+}{H_3C} \rightarrow \overset{\delta\delta\delta+}{CH_2} \rightarrow \overset{\delta\delta+}{CH_2} \rightarrow \overset{\delta+}{CH_2} \rightarrow \overset{\delta-}{Cl}$

Here Cl atom attracts electron towards it. So we can say that Cl atom has electron withdrawing effect or – I effect (negative inductive effect). So groups which have the ability to attract electron pairs towards it are called – I effect. Example for such groups are –X (F, Cl, Br, I), nitro ($-NO_2$), Cyano (CN^-), Carboxy (-COOH), ester (-COOR), aryloxy (-OAr) etc.

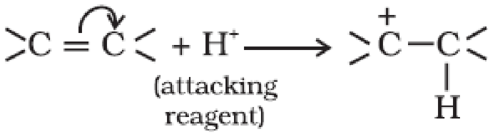
Groups which donate electron pairs towards the carbon chain are said to have +I effect or electron donating (releasing) groups. Example for such groups are alkyl groups like methyl ($-CH_3$), ethyl ($-CH_2-CH_3$) etc.

2. Electromeric effect (E effect):

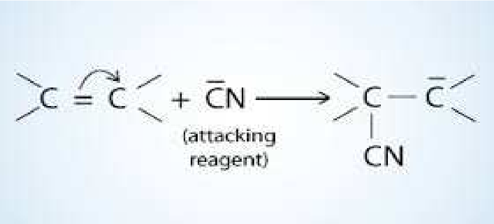
It is defined as the complete transfer of a shared pair of π-electrons to one of the atoms joined by a multiple bond in presence of an attacking reagent. It is a temporary effect. It is possible only in compounds containing multiple bonds(alkene or alkyne). This effect cancels when the attacking reagent is removed from the reaction site. The shifting of the electrons is shown by a curved arrow (↷).

There are two types of E effects:

a) ***Positive Electromeric effect (+E effect*)**: Here the pi electrons are transferred to that atom to which the attacking reagent gets attached.



b) ***Negative Electromeric effect (-E effect):*** Here the pi electrons of the multiple bonds are transferred to that atom to which the attacking reagent does not get attached.

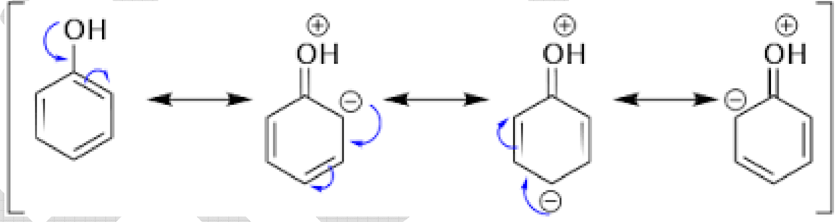


When inductive and electromeric effects operate in opposite directions, the electromeric effect predominates.

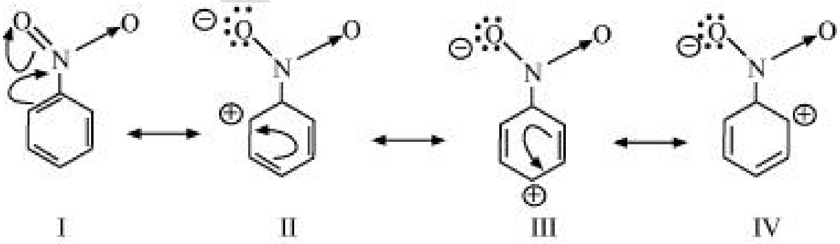
3. Resonance Effect (R effect):

It is defined as 'the polarity (charge) produced in the molecule by the interaction of two π-bonds or between a π-bond and lone pair of electrons present on an adjacent atom'. The effect is transmitted through the chain. There are two types of resonance or mesomeric effect (R or M effect):

a) ***Positive Resonance effect (+R effect):*** Here the transfer of electrons is away from an atom or substituent group attached to the conjugated system. E.g. + R effect in phenol:



b) ***Negative Resonance Effect (- R effect):*** Here the transfer of electrons is towards the atom or substituent group attached to the conjugated system. E.g. – R effect in nitrobenzene:



The presence of alternate single and double bonds in an open chain or cyclic system is termed as a conjugated system.

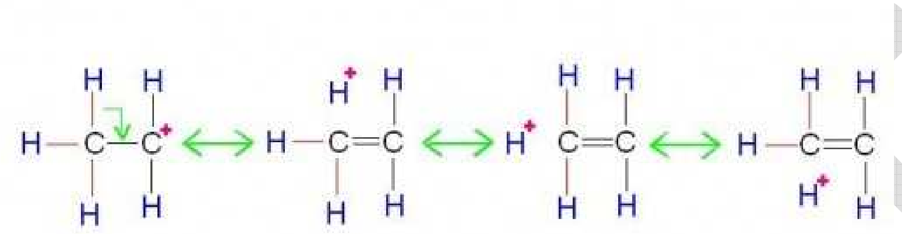
E.g. for +R effect groups: – halogen, –OH, –OR, –OCOR, $–NH_2$, –NHR, $–NR_2$, –NHCOR etc.

E.g. for – R effect groups: – COOH, –CHO, >C=O, – CN, $–NO_2$ etc.

4. Hyper conjugation:

It is a permanent effect. In this effect the σ electrons of C—H bond of the alkyl group enter into partial conjugation with the unsaturated system or with the unshared p orbital. i.e. the σ electrons of C –H bonds get delocalised.

e.g. ethyl cation (CH_3-CH_2^+)



Hyper conjugation stabilises the carbocation because electron density from the adjacent σ bond helps in dispersing the positive charge. In general, the greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyper conjugation interaction and stabilisation of the cation.

Thus the relative stability of carbocations is in the order: $(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3\text{-}CH_2^+ . CH_3^+$.

Here tertiary carbocation has 9, isopropyl has 6, ethyl carbocation has 3 and methyl carbocation has zero hyper conjugative structures.

Hyper conjugation is also called no-bond resonance and it is also possible in alkenes and alkyl arenes.

Types of Organic reactions

Organic reactions can be classified into the following categories:

i. Substitution reactions
ii. Addition reactions
iii. Elimination reactions
iv. Rearrangement reactions

PURIFICATION OF ORGANIC COMPOUNDS

An oganic compound may contain impurities and is essential to purify it. Various methods used for the purification of organic compounds are based on the nature of the compound and the impurity present in it.

The common techniques used for purification are as follows:

i. Sublimation
ii. Crystallisation
iii. Distillation
iv. Differential extraction and
v. Chromatography

1. Sublimation

It is the process of conversion of a solid substance directly to vapour by heating. It is used to separate sublimable compounds from non-sublimable impurities.

In this method, the substance is placed in a sublimation apparatus and heated under vacuum. Under this reduced pressure, the solid sublimes and condenses as a purified compound on a cooled surface. The impurities left behind on the apparatus.

This method is used for the purification of naphthalene, iodine, camphor etc.

2. Crystallisation

This is one of the most commonly used techniques for the purification of solid organic compounds. *It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent*. The impure compound is dissolved in a solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature. The solution is concentrated to get a nearly saturated solution. On cooling the solution, pure compound crystallises out and is removed by filtration. *If the compound is highly soluble in one solvent and very little soluble in another solvent, crystallisation can be satisfactorily carried out in a mixture of these solvents*.

3. **Distillation**

This method is used to separate (i) volatile liquids from non-volatile impurities and (ii) the liquids having sufficient difference in their boiling points. The principle of this method is that liquids having different boiling points vaporise at different temperatures. The vapours are cooled and the liquids so formed are collected separately.

In this method, the liquid mixture is taken in a round bottom flask and heated carefully. On boiling, the vapours of lower boiling liquid are formed first. The vapours are condensed by using a condenser and the liquid is collected in a receiver. The vapours of higher boiling liquid form later and it can be collected separately.

Chloroform (b.p 334 K) and aniline (b.p. 457 K) are separated by this technique.

There are different types of distillation methods. They are:

a) ***Fractional distillation***:

Fractional distillation is used to separate two or more liquids that are miscible. It is a special type of distillation designed to separate a mixture of two or more liquids that have different boiling points. The process involves heating the mixture and partial condensation of the vapours along a fractionating column. The column is set up such that components with lower boiling points pass through the column and are collected earlier than components with higher boiling points. Repeated vaporization and condensation result in the separation of the components of the mixture. The efficiency of fractional distillation depends on the use of the fractionating column. The fractionating column is packed with glass beads. It provides a large surface area for vaporization and condensation of the liquid mixture.

Ethanol and water, crude oil, toluene and cyclohexane etc are separated by this method.

b) ***Distillation under reduced pressure***:

This method is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points. Such liquids are made to boil at a temperature lower than their normal boiling points by reducing the pressure on their surface. The pressure is reduced with the help of a water pump or vacuum pump. Glycerol can be separated from spent-lye in soap industry by using this technique.

c) ***Steam Distillation:***

This technique is applied to separate substances which are steam volatile and are immiscible with water. In steam distillation, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and the volatile organic compound is condensed and collected. The compound is later separated from water using a separating funnel. Aniline – water mixture is separated by this method.

4. **Differential Extraction**

When an organic compound is present in an aqueous medium, it is separated by shaking it with an organic solvent in which it is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other. So they form two distinct layers which can be separated by separating funnel. The organic solvent is later removed by distillation or by evaporation to get back the compound.

5. **Chromatography**

This method is used to separate mixtures into their components, to purify compounds and to test the purity of compounds. Here the mixture to be separated is passed through a stationary phase, which may be a solid or a liquid. A pure solvent (sometimes a mixture of solvents or a gas) is allowed to move slowly over the stationary phase. The moving phase is called the mobile phase. The components of the mixture get gradually separated from one another.

Based on the principle involved, there are mainly two types of chromatography:

(a) Adsorption chromatography, and
(b) Partition chromatography

a) **Adsorption Chromatography*:*** Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent in different degrees. Commonly used adsorbents are silica gel and alumina.
Here a mobile phase is allowed to move over a stationary phase (adsorbent). Based on the adsorbing power, the components of the mixture are adsorbed at different places over the stationary phase. Following are two main types of chromatographic techniques based on the principle of differential adsorption.

i) Column chromatography, and
ii) Thin layer chromatography.

***i) Column Chromatography*:**

It involves the separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end. The mixture to be separated is passed through the column. Based on the adsorbing power, the components are adsorbed at different places over the column. The most readily adsorbed substances are retained near the top and others come down to various distances in the column. Then an appropriate eluant (solvent) is allowed to flow down the column slowly. Different solvents are used to separate different components. So the components can be collected separately and they can be separated.

ii) Thin Layer Chromatography (TLC:

It is another type of adsorption chromatography. It involves separation of substances of a mixture over a thin layer of an adsorbent coated on a glass plate. A thin layer (about 0.2mm thick) of an adsorbent (silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as *thin layer chromatography plate or chromaplate*. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate. The glass plate is then placed in a closed jar containing the eluant. As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its ***retardation factor (R_f value)***.

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

The spots of coloured compounds are visible on TLC plate due to their original colour. The spots of colourless compounds can be detected by putting the plate under ultraviolet light. Another detection technique is to place the plate in a covered jar containing a few crystals of iodine. Spots of compounds, which adsorb iodine, will show up as brown spots. Sometimes an appropriate reagent may also be sprayed on the plate.

b) **Partition Chromatography:**

It is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography. In paper chromatography, a special quality paper known as chromatography paper is used. Chromatography paper contains water trapped in it, which acts as the stationary phase.

A strip of chromatography paper, spotted at the base with the solution of the mixture, is suspended in a suitable solvent or a mixture of solvents. This solvent acts as the mobile phase. The solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram. These spots can be visible by u.v. light or by spraying suitable reagents.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

An organic compound mainly contains carbon and hydrogen. Some compounds may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

Detection of Carbon and Hydrogen

Organic compound is heated with copper (II) oxide [CuO]. Carbon present in the compound is oxidised to carbon dioxide and hydrogen to water. CO_2 can be tested by passing through lime-water, which turns milky and water can be tested with anhydrous copper sulphate, which turns blue.

$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$

$2H + CuO \xrightarrow{\Delta} Cu + H_2O$

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

Detection of Nitrogen, Sulphur and Halogens

Nitrogen, sulphur and halogens present in an organic compound are detected by "***Lassaigne's test***". Here the organic compound is fused with metallic sodium in a fusion tube. It is then plunged into distilled water taken in a china dish. The solution is boiled and filtered. The filtrate is known as sodium fusion extract.

Principle: In an organic compound, nitrogen, sulphur and halogen atoms are present in covalent form. By heating with metallic sodium, these elements are converted to ionic form as follows:

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

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

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

For the detection of the elements, the following tests are done:

No.	Experiment	Observation	Inference
1.	To one part of sodium fusion extract add freshly prepared ferrous sulphate ($FeSO_4$) solution. Heated to boiling, cooled and acidified with dil. H_2SO_4.	Blue or green coloration or precipitate (ppt)	Presence of nitrogen
2.	A little of the sodium fusion extract is acidified with dil. HNO_3 and then silver nitrate ($AgNO_3$) is added.	White ppt soluble in ammonium hydroxide (NH_4OH)	Presence of Chlorine
		Pale yellow ppt slightly soluble in NH_4OH	Presence of Bromine
		Yellow ppt insoluble in NH_4OH	Presence of Iodine
3.	To a little of the sodium fusion extract, add sodium nitroprusside solution	Violet colouration	Presence of sulphur

Test for Phosphorus

The organic compound is heated with an oxidising agent like sodium peroxide. The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The percentage composition of elements present in an organic compound is determined by the following methods:

1. Estimation of Carbon and Hydrogen

Carbon and hydrogen are estimated by ***Liebig's combustion method***. In this method, a known mass of an organic compound is burnt in the presence of excess of oxygen and copper(II) oxide. Then carbon is oxidised to CO_2 and hydrogen is oxidised to H_2O.

$$C_xH_y + (x + y/_4)\,O_2 \longrightarrow x\,CO_2 + (y/_2)\,H_2O$$

The water so produced is absorbed in a weighed U-tube containing anhydrous calcium chloride and carbon dioxide is absorbed in another U-tube containing concentrated solution of potassium hydroxide. These tubes are connected in series. The increase in masses of calcium chloride and potassium hydroxide gives the amounts of water and carbon dioxide from which the percentages of carbon and hydrogen are calculated.

Calculations:

Let the mass of organic compound be m g, mass of water and carbon dioxide produced be m_1 and m_2 g respectively.

Percentage of hydrogen = $\frac{2 \times m_1 \times 100}{18 \times m}$

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

2. Estimation of Nitrogen

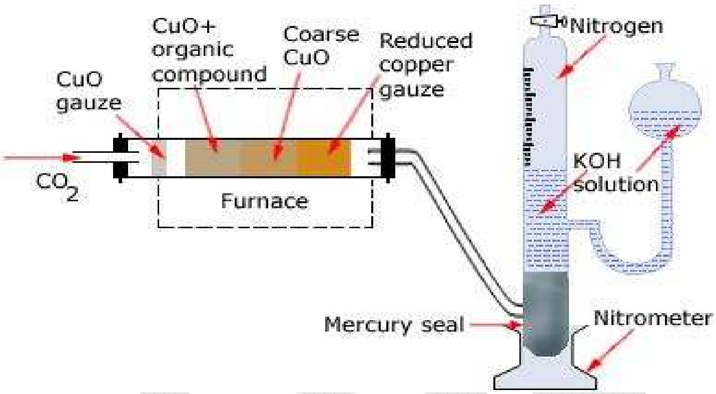
There are two methods for estimation of nitrogen: (i) Dumas method and (ii) Kjeldahl's method.

i) Dumas method:

Here the organic compound is heated with copper oxide in an atmosphere of carbon dioxide so that free nitrogen, carbon dioxide and water are produced.

$$C_xH_yN_z + (2x + y/_2)\ CuO \longrightarrow x\ CO_2 + y/_2\ H_2O + z/_2\ N_2 + (2x + y/_2)\ Cu$$

This mixture of gases is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide. Nitrogen is collected in the upper part of the graduated tube



Calculations:

Let the mass of organic compound = m g

Volume of nitrogen collected = V_1 mL

Room temperature = T_1 K

Volume of nitrogen at STP = $\frac{P_1V_1 \times 273}{760 \times T_1}$ = V mL

Where P_1 and V_1 are the pressure and volume of nitrogen gas.

P_1= Atmospheric pressure – Aqueous tension

We know that 22400 mL N_2 at STP weighs 28 g.

Therefore, VmL N_2 at STP weighs = $\frac{28 \times V}{22400}$ g

Percentage of nitrogen = $\frac{28 \times V \times 100}{22400 \times m}$ %

ii) Kjeldahl's method:

Here the organic compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen in the compound gets converted to ammonium sulphate. The resulting acid mixture is then heated with excess of sodium hydroxide. The liberated ammonia gas is absorbed in an excess of standard solution of sulphuric acid. The amount of ammonia produced is determined by estimating the amount of sulphuric acid consumed in the reaction. It is done by estimating unreacted sulphuric acid left after the absorption of ammonia by titrating it with standard alkali solution. The difference between the initial amount of acid taken and that left after the reaction gives the amount of acid reacted with ammonia.

$$\text{Organic compound} + H_2SO_4 \longrightarrow (NH_4)_2SO_4 \xrightarrow{2\ NaOH} Na_2SO_4 + NH_3 + H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

Calculations:

Let the mass of organic compound taken = m g

Volume of H_2SO_4 of molarity M, taken = V mL

Volume of NaOH of molarity M, used for titration of excess of H_2SO_4 = V_1 mL

V_1mL of NaOH of molarity M = $V_1/2$ mL of H_2SO_4 of molarity M

Volume of H_2SO_4 of molarity M unused = $(V - V_1/2)$ mL = y mL

y mL of H_2SO_4 of molarity M = 2y mL of NH_3 solution of molarity M.

1000 mL of 1 M NH_3 solution contains 17g NH_3 or 14 g of N

2y mL of NH_3 solution of molarity M contains $\frac{14 \times M \times 2y}{1000}$ g N

Percentage of N = $\frac{14 \times M \times 2y \times 100}{1000 \times m}$ %

Note: Kjeldahl's method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does not change to ammonium sulphate under these conditions.

3. Estimation of halogens (Carius method):

Here a known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as Carius tube, in a furnace. Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water. The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried and weighed.

Calculations:

Let the mass of organic compound taken = m g

Mass of AgX formed = m_1 g

1 mol of AgX contains 1 mol of halogen

Mass of halogen in m_1g of AgX = $\frac{\text{Atomic mass of halogen} \times m_1}{\text{molecular mass of AgX}}$ g

Percentage of halogen = $\frac{\text{Atomic mass of halogen} \times m_1 \times 100}{\text{Molecular mass of AgX} \times m}$ %

4. Estimation of Sulphur (Carius method):

A known mass of an organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid. Sulphur present in the compound is oxidised to sulphuric acid. It is precipitated as barium sulphate by adding excess of barium chloride solution. The precipitate is filtered, washed, dried and weighed. The percentage of sulphur can be calculated from the mass of barium sulphate ($BaSO_4$).

Calculations:

Let the mass of organic compound taken = m g and the mass of barium sulphate formed = m_1 g

1 mol of $BaSO_4$ = 233 g $BaSO_4$ = 32 g sulphur

m_1 g $BaSO_4$ contains $\frac{32 \times m_1}{233}$ g sulphur

Percentage of sulphur = $32 \times m_1 \times 100$ %

$$\overline{233 \times m}$$

5. Estimation of Phosphorus

A known mass of an organic compound is heated with fuming nitric acid. Phosphorus present in the compound is oxidised to phosphoric acid. It is precipitated as ammonium phosphomolybdate [$(NH_4)_3PO_4.12MoO_3$] by adding ammonia and ammonium molybdate.

Calculations:

Let the mass of organic compound taken = m g and mass of ammonium phosphomolydate = m_1g

Molar mass of $(NH_4)_3PO_4.12MoO_3$ = 1877 g

Percentage of phosphorus = $\frac{31 \times m_1 \times 100}{1877 \times m}$ %

6. Estimation of Oxygen

The percentage of oxygen in an organic compound is usually found by difference between the total percentage composition (100) and the sum of the percentages of all other elements.

i.e. percentage of oxygen = 100 – sum of the percentage of all the other elements.

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