# Chapter 11

# Some Basic Principles of Organic Chemistry and Purification and Characterisation of Organic Compounds

## HOMOLOGOUS SERIES

It is a series of similarly constituted organic compounds in which members possess the same functional group, have a similar or almost similar characteristics, can be represented by the same general formula, and the two consecutive members differ by $-CH_2-$ group in their molecular formula.

*e.g.,* General formula for saturated alcohol is $C_nH_{2n+1}-OH$

$$\underset{\text{Methanol}}{CH_3-OH} \xrightarrow{+(-CH_2-)} \underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow{+(-CH_2-)} \underset{\text{Propanol}}{CH_3-CH_2-CH_2-OH}$$

## ISOMERISM

Compounds having same molecular formula but different in their physical and chemical properties are called isomers. This phenomenon is called isomerism.

They are classified into two types

1. Structural isomerism or constitutional isomerism
2. Stereo isomerism

**1. Structural isomerism :** When same molecular formula represents two or more compounds which differ in the arrangement of atoms within the molecule, then such compounds are called structural isomers and the phenomenon is called structural isomerism. It is of the following types :

**(i) Chain isomerism :** When the same molecular formula represents two or more compounds which differ in the nature of carbon chain (straight or branched), the isomers are called chain isomers and the phenomenon is known as chain isomerism.

**Example :** $CH_3—CH_2—CH_2—CH_3$ and $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$ are chain isomers

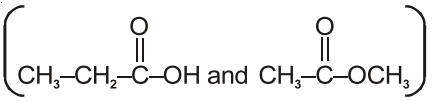
**(ii) Position isomerism :** Compounds having same structural formulae but differ only in the position of the substituent atoms or groups on the carbon chain are called position isomers.

**Example :** $C_3H_7OH$ has two position isomers

$\underset{\text{propan-1-ol}}{CH_3\,CH_2\,CH_2-OH}$ and $\underset{\text{propan-2-ol}}{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3}$

**(iii) Functional isomerism :** When any two compounds have same molecular formula but possess different functional groups, they are called functional isomers and the phenomenon is called functional isomerism. Examples of functional isomerism are

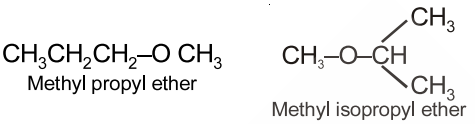
(a) Alcohol and ether ($CH_3–CH_2–CH_2–CH_2–OH$ and $CH_3–CH_2–O–CH_2–CH_3$)

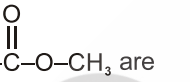
(b) Carboxylic acid and ester, etc. 

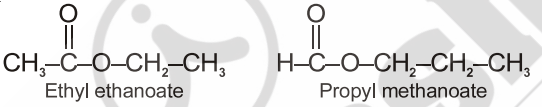
**(iv) Metamerism :** It arises due to different alkyl chains on either side of the functional group in the molecule. For example ethers, esters, amines, ketones etc. can exhibit metamerism.

**Example :**

(a) Metamers of $C_2H_5 – O – C_2H_5$ are



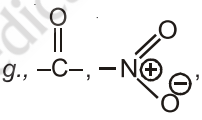

(b) Metamers of  are

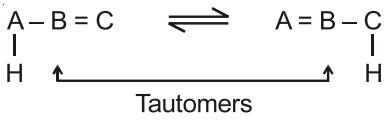



It is to be noted that $CH_3CH_2CH_2–C–O–H$ is not the metamer of above compounds. Because this compound is an acid while the above compounds are isomeric esters.

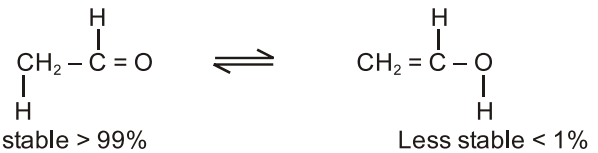
**(v) Tautomerism :** The phenomenon due to which two or more structurally distinct compounds are in dynamic equilibrium due to shift in the position of an atom or group in a molecule is known as tautomerism and the structural isomers are known as tautomers. Tautomerism may be catalysed by an acid, a base or traces of transition metal ions etc.

**Structural Requirement for Tautomerism**

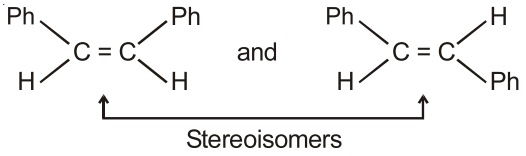
When unsaturated functional group (*e.g.,*  ) have $\alpha$-hydrogen, the compound may exhibit tautomerism.

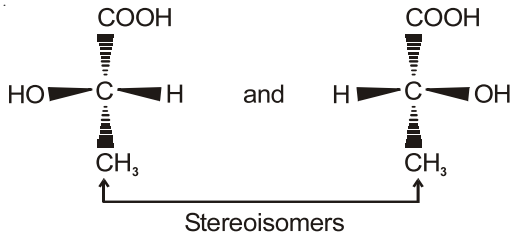



In simple keto-enol tautomerism generally keto form is more stable, the stability of enol form may increase due to extended conjugation, aromaticity or intramolecular hydrogen bonding.

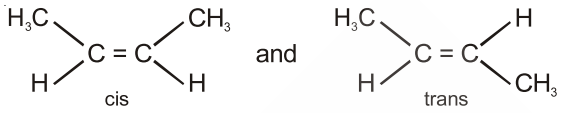
*e.g.,* 

2. **Stereo isomerism :** The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers and this type of isomerism is known as stereoisomerism. This isomerism can be further classified as **geometrical isomerism** and **optical isomerism**.




**Geometrical isomerism :** When stereoisomerism arises due to **restricted rotation** (because of the presence of double bond or ring), then it is known as geometrical isomerism.




These are geometrical isomers because they have different spatial arrangement due to the presence of restricted rotation (due to double bond).

***Note :*** *(i) Geometrical isomers may be named as cis-trans isomers, E-Z isomers or syn-anti isomers.*

*(ii) Geometrical isomers are also known as **diastereomers** (stereoisomers which are not the mirror images of each other). Therefore geometrical isomers have different physical properties and similar chemical properties.*

*(iii) Geometrical isomers do not rotate plane polarised light (unless they also happen to be chiral).*

**Enantiomers :** Nonsuperimposable mirror images are known as enantiomers. They have similar physical and chemical properties in symmetric environment. But they may behave differently in asymmetric environment. They also rotate plane polarised light in opposite directions but the magnitude of rotation is identical. Specific rotation of S-alanine is +8.5 while that of R-alanine is –8.5, while melting point of both the enantiomers are 297°C.

**Dextrorotatory substances :** Those substances which rotate the plane polarised light in clock-wise direction are known as dextrorotatory substances. The rotation is labelled as (+).

If the rotation is **counterclockwise**, the compound is called **Laevorotatory**. No relationship exists between D and L (represents relative configuration) and dextrorotatory and laevorotatory substances. A compound with D configuration may be (+) or (–). This information can be obtained only by putting the molecule in **Polarimeter** (instrument used to obtain direction and extent of rotation of plane polarised light).

**Specific rotation :** Specific rotation of a chiral compound is a constant at a particular temperature and wavelength (589 nm).

$$\text{Specific rotation} = [\alpha]_l^{\lambda} = \frac{\alpha}{c \times l}$$

$\alpha$ = observed rotation (in degree)
c = concentration (g/ml)
$l$ = length of sample tube (dm)

**Racemic mixture :** A mixture containing equal amount of two enantiomers is called racemic mixture or racemate. A racemic mixture is optically inactive due to external compensation. Racemic mixture can be resolved into optically pure form by several methods.

**Percentage enantiomeric excess :** It tells us how much one enantiomer is present in excess of the racemic mixture.

$$\%\ ee = \%\ \text{of one enantiomer} - \%\ \text{of the other enantiomer}$$

**Number of Possible optical isomers in Compounds having n-chiral Carbon Atoms :**

**Case - I : When there is no symmetry in the structure of molecule.**

Number of *d* and *l* forms = $2^n$

Number of meso forms = 0

$\therefore$ Total number of optical isomers = $2^n$

**Case - II : When the molecule is structurally symmetric and n is even**

Number of *d* and *l* forms = $2^{n-1}$

Number of meso forms = $2^{n/2-1}$

$\therefore$ Total number of optical isomers = $2^{n-1} + 2^{n/2-1}$

**Case - III : When the molecule can be divided into two identical parts and n is odd**

Number of *d* and *l* forms = $2^{n-1} - 2^{\frac{n-1}{2}}$

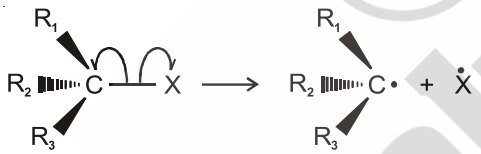
Number of meso forms = $2^{\frac{n-1}{2}}$

$\therefore$ Total number of optical isomers = $2^{n-1}$

## BOND FISSION

In any reaction, bond between the reactant molecule is broken, Bond fission in organic molecules can take place in one of the two ways.

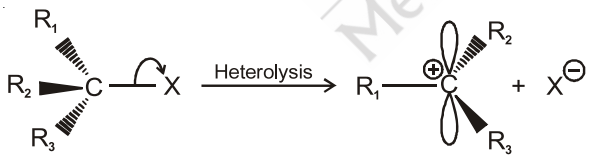
**1. Homolytic Bond Fission**



Result of homolytic fission is free radical. (Alkyl free radical may be $sp^2$ or $sp^3$ hybridised)

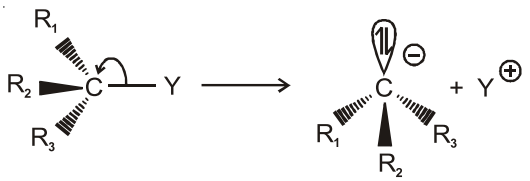
**2. Heterolytic Bond Fission**

(a) In the heterolytic bond fission bonding electron pair may move away from carbon, which results into the formation of carbocation.




[X is more electronegative than carbon]

(b) When bonding pair moves towards carbon



[Y is less electronegative than carbon]

This results in formation of carbanion. (Alkyl carbanion is $sp^3$ hybridised)

## ELECTROPHILE

Electrophiles are electron loving species having at least one vacant orbital in valence shell.

1. Charged electrophiles $X^{\oplus}$, $R^{\oplus}$
2. Neutral Electrophiles : *e.g.,* $BH_3$, $SO_3$, $AlCl_3$

> ***Note :*** *Electrophiles are Lewis acids.*

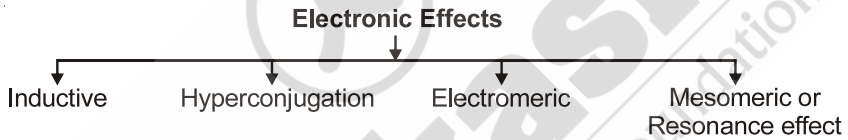
## NUCLEOPHILE

Nucleophiles are nucleus loving, they are electron rich having at least one non-bonding pair of electrons in valence shell.

It can be of three types.

1. Charged Nucleophiles - $\overset{\ominus}{H}$ :, $\overset{\ominus}{O}$–H, $\overset{\ominus}{I}$ etc.
2. Neutral Nucleophiles - $\ddot{N}H_3$, $R-\ddot{O}H$
3. Ambident Nucleophiles - $\overset{\ominus}{C} \equiv N$:, $\overset{\ominus}{O}$–C≡ N: (both atoms are nucleophilic centre)

## ELECTRONIC EFFECTS




### 1. Inductive Effect :

The permanent displacement of electrons in a bond towards the more electronegative element is called inductive effect. The effect provides polarity to the molecule. The property of electron withdrawal shown by an atom or group is its (–I) effect and that of donation is called (+I) effect. Electron donation or electron withdrawal is compared with respect to H.

$$\underset{\delta}{CH_3}-\underset{\gamma}{\overset{\delta\delta\delta+}{CH_2}}-\underset{\beta}{\overset{\delta\delta+}{CH_2}}-\underset{\alpha}{\overset{\delta+}{CH_2}}-\overset{\delta-}{Cl}$$

As shown above the charge decreases from $\alpha$ to $\beta$ to $\gamma$ position. Hence inductive effect decreases as number of bonds increases.

**Order of –I effect :** $(CH_3)_3\overset{+}{N} > -NO_2 > -CN > -F > -COOH > -Cl > -Br > -I > -OR > -OH > -NH_2 > C_6H_5- > -H$

**Order of +I effect :** $(CH_3)_3C- > (CH_3)_2CH- > CH_3-CH_2- > -CH_3 > -H$

**Uses of Inductive Effect :**

**(i) Stability of ions:** Stability of ions can be explained by using the concept of inductive effect and hyperconjugation.

(a) Stability of Carbocation

*e.g.,* $(CH_3)_3C^{\oplus} > (CH_3)_2\,CH^{\oplus} > CH_3CH_2^{\oplus} > CH_3^{\oplus}$

(b) Stability of Carbanions

$(CH_3)_3C^{\ominus} < (CH_3)_2CH^{\ominus} < CH_3CH_2^{\ominus} < CH_3^{\ominus}$ (groups with +I effect decrease the stability of anion)

**(ii) Acidic Properties :** It is possible to compare the acidic strength of various organic compounds using the inductive effect concept, *e.g.*, in carboxylic acid

The strength of an acid depends upon the ease with which it can ionize to give proton or on the stability of the conjugate bases formed, *i.e.* if the conjugate base formed is more stable, then the acid is more acidic.

| Name of Acid | Formula | $K_a$ | Conjugate Base |
|---|---|---|---|
| Fluoroacetic acid (most acidic) | $FCH_2COOH$ | $217 \times 10^{-5}$ | $FCH_2COO^-$ (most stable) |
| Chloroacetic acid | $ClCH_2COOH$ | $155 \times 10^{-5}$ | $ClCH_2–COO^-$ |
| Bromoacetic acid | $BrCH_2COOH$ | $138 \times 10^{-5}$ | $BrCH_2COO^-$ |
| Iodoacetic acid | $ICH_2COOH$ | $75 \times 10^{-5}$ | $ICH_2COO^-$ |
| Acetic acid (least acidic) | $CH_3COOH$ | $1.8 \times 10^{-5}$ | $CH_3-COO^{\ominus}$ (least stable) |

Increasing stability of conjugate base increases the acidity of acids.

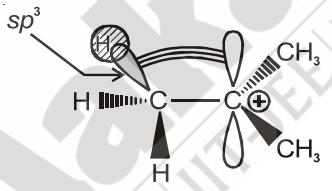
Furthermore, the inductive effect in di and trihalogenated acids is still more marked with the result they are progressively more acidic than the corresponding monohalogenated acids.

*e.g.*, $CHCl_2 – COOH$ ; $K_a = 514 \times 10^{-5}$

$CCl_3 – COOH$ ; $K_a = 12100 \times 10^{-5}$

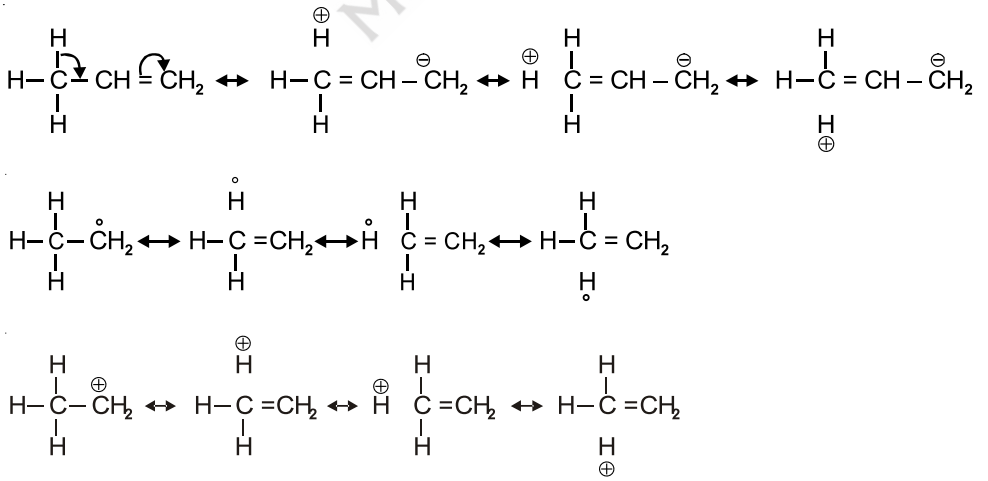
In general, dicarboxylic acids are stronger acids than monocarboxylic acids, since one of the –COOH group shows –I effect.

**2. Hyperconjugation :** It is also known as **no-bond resonance**. It involves delocalisation of σ-electrons of C – H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared orbital (*p* or *d* orbital). Depending on the number of α-H, various hyperconjugative structures are possible. Greater the number of hyperconjugative structures, higher would be the stability of given system. It is also a permanent effect.




Less effective $\sigma - \pi$ overlap (responsible for hyperconjugative effect).

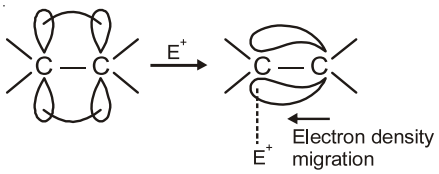
Stability of substituted alkenes, alkyl carbocations, and free radicals can be explained on the basis of hyperconjugation.



3. **Electromeric Effect :** The temporary electron density charge in substrate in presence of attacking reagent facilitate the attack of attaching reagent is called electromeric effect.

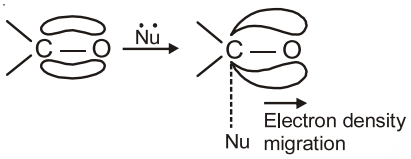
**+E effect**: When electron density pilled on centre to which attacking reagent attacks then electromeric effect is +E effect, observed in presence of electrophile.

*e.g.,*




**–E effect**: When electron density is removed from the centre to which attacking reagent attacks then electronic effect is –E effect, observed in presence of nucleophile.

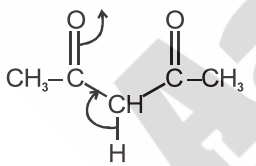
*e.g.,*



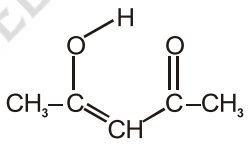

4. **Mesomeric or Resonance Effect :** The effect involves permanent delocalization of conjugated π electrons in a conjugated system. Intermediate structures formed are called resonating structures. The structure that collectively represents all resonating structures is called the resonance hybrid.

Resonating structures are imaginary having no physical significance. The average structure i.e. resonance hybrid represents the actual molecule. Resonance is also known as π-electron delocalisation, which is a permanent effect, it is distance independent effect. Normally this effect is more powerful than hyperconjugative effect.

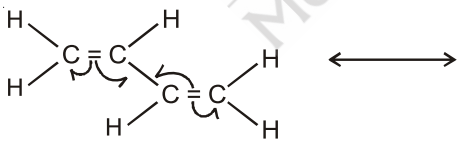
Resonating structures must be valid Lewis structures, they must have same position of atomic nuclei, same number of paired and unpaired electrons and the part of molecule taking part in resonance must be planar.

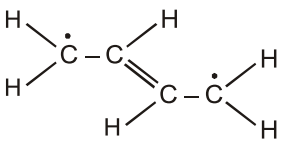


Position of H atom is changing



∴ Invalid resonating structure

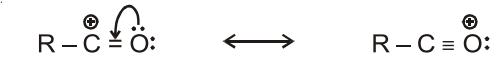




∴ Invalid resonating structure
Number of unpaired electrons is changing

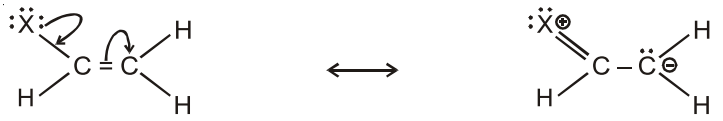
**Extent of contribution of various resonating structures:**

(a) Resonating structures having maximum number of covalent bonds are more contributing



Less contributing More contributing

(b) Non charge separated resonating structures are more contributing than charge separated resonating structures.

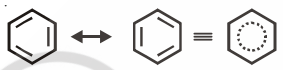


More contributing ⟷ Less contributing

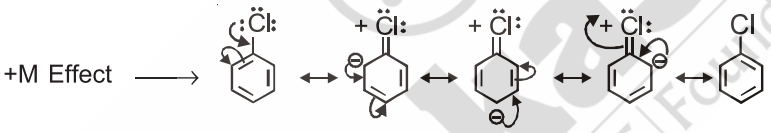
(c) Resonating structure which places negative charge on more electronegative atom is more contributing as compared to resonating structure which places negative charge on less electronegative atom.

More contributing ⟷ Less contributing

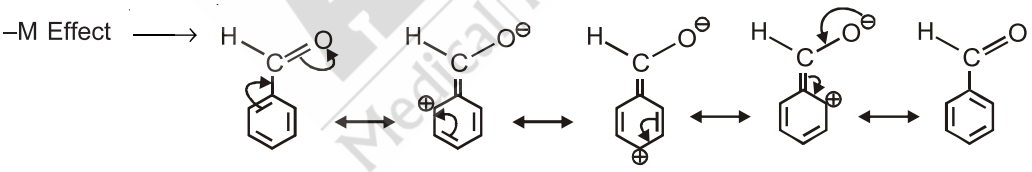
The difference between energies of most stable resonating structure and the resonance hybrid is called the resonance energy of the molecule.



**Electron Donating Mesomeric Effect (+M Effect) :** Groups with +M effect releases $\pi$-electron towards unsaturated system. This effect makes certain positions in the molecule of high electron densities. This effect in chlorobenzene is shown as



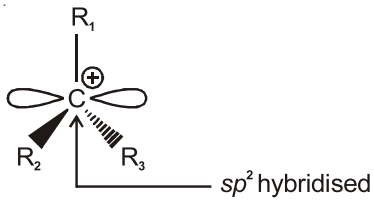

**Electron Withdrawing Mesomeric Effect (–M Effect) :** This effect is observed when the displacement of $\pi$-electrons from unsaturated system is towards the atom or group. This effect in benzaldehyde is shown as




## REACTION INTERMEDIATES

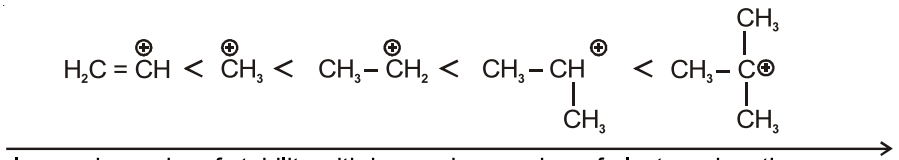
**Carbocations :**

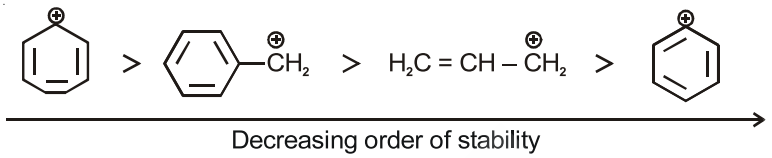
**Structure :**




Trigonal planar

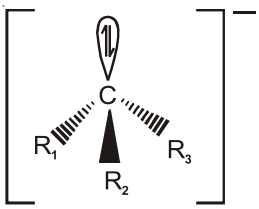
**Stability:** Carbocations are stabilised by electron donating groups and are destabilised by electron withdrawing groups.



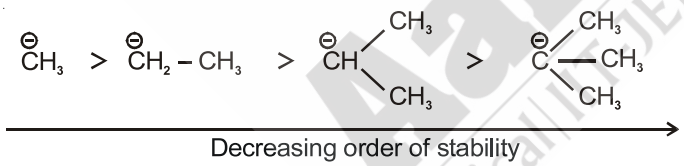

**Carbanions :**

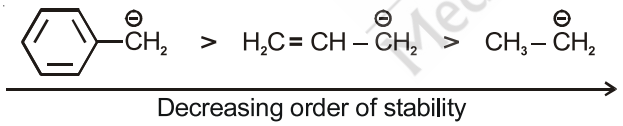
**Structure :**

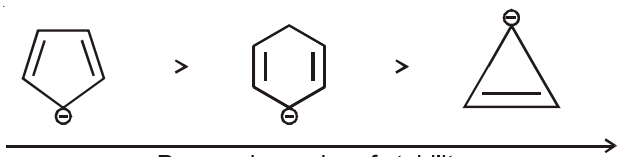



Carbon bearing the negative charge is $sp^3$ hybridised, when lone pair on carbon not involve in resonance.

**Stability:** Carbanions are stabilised by electron withdrawing groups and they are destabilised by electron donating groups



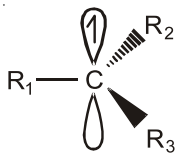




## Carbon Free Radicals

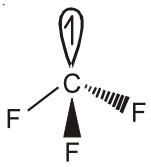
Free radicals are obtained through homolysis of a bond. They have unpaired electron associated with carbon.

**Structure :** The exact type of hybridisation of the carbon atom bearing an unpaired electron depends on the nature of the substituent. Generally alkyl radicals are planner and as electronegativity of bonded group increase it adopts pyramidal shape *e.g.*, $\dot{C}F_3$ is pyramidal. In presence of resonance it surely adopts planner shape.



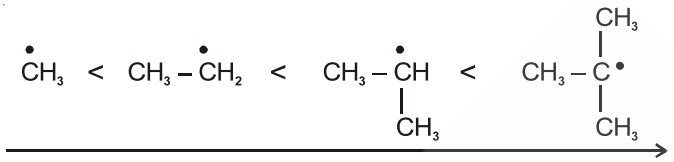

Trigonal planar

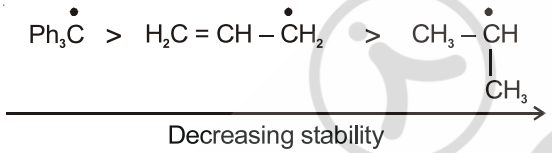
Unpaired electron is present in unhybridised $p_x$ orbital



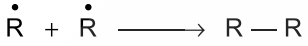

Unpaired electron is present in $sp^3$ hybridised orbital

**Stability :** Free radicals are stabilised by resonance, hyperconjugation and steric effect. Both electron donating and electron withdrawing groups stabilize free radicals.




(a) A free radical combines with other free radical




(b) Free radicals may give disproportionation reaction


## DETECTION OF ELEMENTS (Qualitative Analysis)

| Element | Sodium Fusion Extract (S.E) | Confirmed Test | Reactions |
|---|---|---|---|
| Nitrogen | $Na + C + N \xrightarrow{\Delta} NaCN$ (S.E) | S.E + $FeSO_4$ + NaOH, boil and cool, + $FeCl_3$ + conc. HCl → Prussian blue or green | $FeSO_4 + 6NaCN \rightarrow Na_4[Fe(CN)_6] + Na_2SO_4$ $3Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 6\ Na_2SO_4$ Prussian blue (Ferri Ferrocyanide) |
| Sulphur | $2Na + S \xrightarrow{\Delta} Na_2S$ (S.E) | (i) S.E + Sodium nitroprusside → Deep violet colour<br>(ii) S.E + $(CH_3COO)_2Pb$ → Black ppt. | $Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NOS]$ deep violet<br>$Na_2S + (CH_3COO)_2Pb \rightarrow PbS\downarrow + 2CH_3COONa$ (black ppt) |

| | | | |
|---|---|---|---|
| Halogens | $Na + Cl \xrightarrow{\Delta}$ NaCl (S.E) | S.E + $AgNO_3 \rightarrow AgX$ (X=Cl, Br, I)<br>(i) White ppt soluble in $NH_3$(liq)<br>Cl confirms<br>(ii) Pale yellow ppt partially soluble in $NH_3$(liq)<br>Br confirms<br>(iii) Yellow ppt, insoluble in $NH_3$(liq)<br>I confirms | $NaX + AgNO_3 \rightarrow \underset{ppt}{AgX}$ |
| Nitrogen and Sulphur together | $Na + C + N + S \xrightarrow{\Delta}$ NaCNS (S.E) | As in test for nitrogen instead of green or blue colour, blood red colouration confirms presence of N and S both | $3NaCNS + FeCl_3 \rightarrow Fe(CNS)_3 + 3NaCl$<br>blood red (Ferric thiocyanate) |

## QUANTITATIVE ESTIMATION OF ELEMENTS IN ORGANIC COMPOUNDS

| Element | Technique | Formula |
|---|---|---|
| Carbon and Hydrogen | (Method)<br>Liebig's Method | $C \rightarrow CO_2$ (12g, 44g); $\%\ C = \frac{12 \times \text{wt. of } CO_2 \times 100}{44 \times \text{weight of organic compound}}$<br>$2H \rightarrow H_2O$ (2g, 18g); $\%\ H = \frac{2 \times \text{wt. of } H_2O \times 100}{18 \times \text{wt. of organic compound}}$ |
| Nitrogen | (i) Duma's method<br>(ii) Kjeldahl method | (i) $2N \rightarrow N_2(g)$<br>22.4 L at S.T.P. $\%\ N = \frac{28 \times V \times 100}{22.4 \times \text{wt. of organic compound}}$<br>where V is the volume of $N_2$ gas in L at S.T.P.<br>(ii) $N \rightarrow NH_3 \equiv H_2SO_4$<br>$\%\ N = \frac{1.4\ N_1V_1}{\text{wt. of organic compound}}$<br>where, $N_1V_1$ is the meq. of $H_2SO_4$ used |
| Sulphur | Carius method | $S \rightarrow H_2SO_4 \rightarrow BaSO_4$ (32g, 233g); $\%\ S = \frac{32 \times \text{wt. of } BaSO_4}{233 \times \text{wt. of org. comp.}} \times 100$ |
| Halogens | Carius method | $Cl \longrightarrow AgCl$ (35.5g, 143.5g); $\%\ Cl = \frac{35.5 \times \text{wt. of AgCl} \times 100}{143.5 \times \text{wt. of organic comp.}}$<br>$Br \longrightarrow AgBr$ (80g, 188g); $\%\ Br = \frac{80 \times \text{wt. of AgBr} \times 100}{188 \times \text{wt. of organic comp.}}$<br>$I \longrightarrow AgI$ (127g, 235g); $\%\ I = \frac{127}{235} \times \frac{\text{wt. of AgI}}{\text{wt. of organic comp.}} \times 100$ |
| Oxygen | | 100 – (sum of % of all elements) |
| Phosphorus | Carius method | $\%\ P = \frac{62}{222} \times \frac{\text{wt. of } Mg_2P_2O_7 \text{ formed}}{\text{wt. of organic comp.}} \times 100$ |

## EMPIRICAL AND MOLECULAR FORMULA

(i) **Empirical Formula of a compound** is the simplest whole number ratio of the atoms of elements constituting its one molecule. The sum of atomic masses of the atoms representing empirical formula is called **empirical** formula mass.

(ii) **Molecular Formula** of a compound shows the actual number of the atoms of the elements present in its one molecule. The sum of atomic masses of the atoms representing molecule is called **molecular mass**.

(iii) **Relationship between Empirical Formula and Molecular Formula**

Molecular formula = n × empirical formula where n is a simple whole number having values of 1, 2, 3... etc.

Also, n = Molecular formula mass/Empirical formula mass.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