Isomerism

The phenomenon of existence of two or more compounds having the same molecular formula but different properties is known as isomerism.

Isomerism is broadly divided into two types:

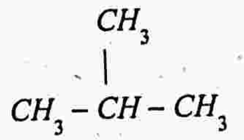
1. **Structural isomerism:** Isomers that differ from one another in the arrangement of atoms or groups of atoms within the molecule resulting in different structural formulae are known as structural isomers and the phenomenon is called structural isomerism. In other words, structural isomers have the same molecular formula but different structures. It is divided into four types.

   (a) **Chain isomerism or nuclear isomerism:** Isomers that differ in the arrangement of carbon chain within the molecule are called chain or nuclear isomers and the phenomenon is called chain or nuclear isomerism. The simplest compound that exhibits chain isomerism is butane (C_4H_{10}). There are two chain isomers for butane.

$CH_3 - CH_2 - CH_2 - CH_3$

butane

n–butane



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

2–methylpropane

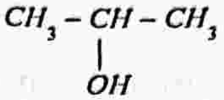
(isobutane)

The number or chain isomers increases with increase in the number of carbon atoms in the molecule. For example, pentane has three, hexane (C_6H_{14}) has five and heptane (C_7H_{16}) has nine chain isomers.

(b) **Position isomerism:** Isomers that differ only in the position of functional group or substituent atom are called position isomers and the phenomenon is called position isomerism. For example,

$CH_3\,CH_2-CH_2OH$ and

1 – *propan–1–ol*
(*n–propyl alcohol*)



$CH_3-\underset{|\atop OH}{CH}-CH_3$

propan–2–ol (*Isopropyl alcohol*)

(c) **Functional isomerism:** Compounds having the same molecular formula but different functional groups are called functional isomers and the phenomenon is called functional isomerism. For example,

CH_3-CH_2OH and CH_3-O-CH_3 ; CH_3-CH_2-CHO and $CH_3-CO-CH_3$

ethanol — *methoxymethane* — *propanal* (*propionaldehyde*) — *propanone* (*acetone*)

(d) **Metamerism:** Compounds having the same molecular formula but different arrangement of carbon atoms (or alkyl groups) on either side of the same functional group are called metamers.

$CH_3-CH_2-O-CH_2-CH_3$ and $CH_3-O-CH_2-CH_2-CH_3$

ethoxyethane (*diethyl ether*) — *1–methoxypropane* (*methyl n–propyl ether*)

2. **Stereo isomerism:** Isomers which have the same structural formula but differ in the relative arrangement of atoms or groups in space are called stereo isomers and the phenomenon is called stereo isomerism (Greek word 'stereo' means space).

Stereo isomerism is mainly of two types (i) optical isomerism and (ii) geometrical isomerism.

Reaction mechanism

An organic reaction takes place by the attack of a reagent on an organic compound which is designated as a substrate. *The steps of an organic reaction showing the breaking and formation of bonds in the substrate leading to the formation of the final product are referred to as its mechanism.*

Electron displacement effects in organic compounds

1. Inductive effect (I effect)

It is the permanent polarisation of a sigma bond in a molecule by the influence of an adjacent polar bond or group. It is due to electronegativity difference of atoms.

For illustration, let us consider a carbon chain in which one terminal carbon atom is joined to a chlorine atom. Since the chlorine atom is more electronegative than carbon, the sigma electrons of the *C–Cl* bond are displaced towards the chlorine atom. As a result, the chlorine atom acquires a small negative charge and C acquires a small positive charge as shown below. The magnitude of +charge is of the order $C_1 > C_2 > C_3$.

$$-\overset{\delta\delta\delta+}{C_3}-\overset{\delta\delta+}{C_2}-\overset{\delta+}{C_1}-\overset{\delta-}{Cl}$$

The permanent electron displacement of sigma electrons along a saturated carbon chain due to the presence of an electron withdrawing group (or electron donating group) is called inductive effect.

This effect decreases sharply with increasing distance from the substituent and becomes negligible after the third carbon in a chain. Atoms or groups of atoms that attract or withdraw electrons from a chain are said to have electron withdrawing inductive effect or **–I effect.**
e.g., $-NO_2 > -CN > -COOH > -F > -Cl > -Br > -I$

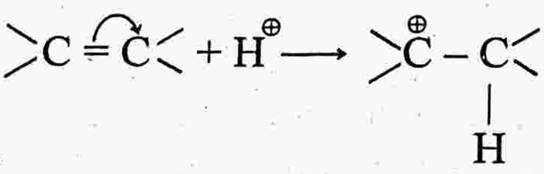
Atoms or groups which push or donate electrons to a carbon chain are said to have electron releasing inductive effect or **+I effect.** Alkyl groups have +I effect and the order of +I effect of alkyl groups is

$$\underset{\text{t–butyl}}{(CH_3)_3C-} > \underset{\text{isopropyl}}{(CH_3)_2CH-} > \underset{\text{ethyl}}{CH_3-CH_2-} > \underset{\text{methyl}}{-CH_3}$$

2. Electromeric effect (E - effect)

This is a temporary effect which involves the complete transfer of π electrons of a multiple bond to one of the bonded atoms in presence of an attacking reagent. However, when the attacking reagent is removed, the polarised molecule shifts back to its original electronic condition.

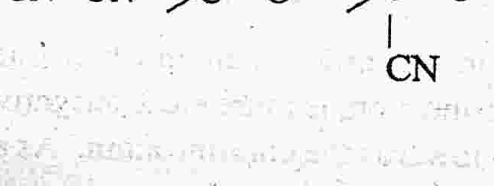
For example, when an alkene is treated with *HCl*, H^+ of the acid first attacks the double bond and π – electron shift takes place as follows:



$$>C=C< + H^{\oplus} \longrightarrow >\overset{\oplus}{C}-\underset{\displaystyle H}{\underset{|}{C}}<$$

This type of electromeric effect in which π – electrons are transfered to the atom to which the attacking reagent gets attached is called **+ *E* effect.**

When a compound containing carbonyl group (*C* = *O*) is treated with cyanide (CN^-), the π – electrons are transferred to the atom to which the attacking reagent does not get attached.



$$\bar{CN} + CN^{\circ}_{\circ} + >C=\ddot{O} \longrightarrow >\underset{\displaystyle CN}{\underset{|}{C}}-O^{\ominus}$$

This is called **– *E* effect.**

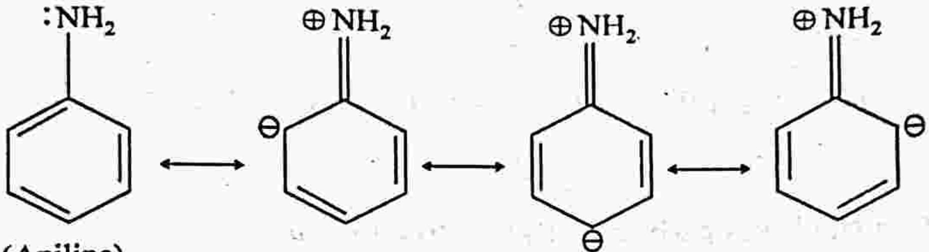
3. Resonance effect (Mesomeric effect)

Resonance effect may be defined as the electron displacement from one part of a conjugated system to the other creating polarity in the molecule due to the phenomenon of resonance.

It may also be defined as the polarity produced in a molecule by the interaction of two π – bonds or between a π – bond and lone pair of electrons.

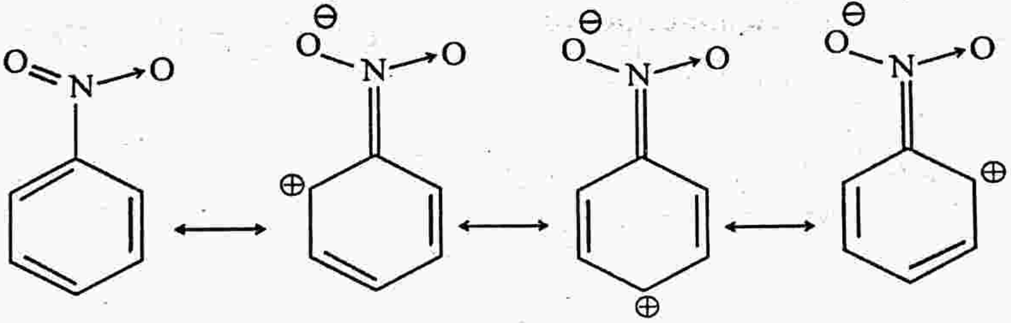
There are two types of resonance or mesomeric effects:

(i) When atoms or groups containing lone pair electrons are linked to an unsaturated system, they displace electrons towards the multiple bond or conjugated system. This type of mesomeric (or resonance) effect is called positive resonance effect. It is represented as **+*R* effect.** Groups such as $-OH$, $-NH_2$, halogens etc. show +*R* effect. For example,



(Aniline)

(ii) When electronegative atoms or groups are bonded to a conjugated system, they attract electrons from the multiple bond due to resonance. This effect is called negative resonance effect and is designated as **–R effect.** For example,



Examples of groups showing +R effect

$-OH, -OR, -OCOR, -NH_2, -NHR, -NHCOR,$ – halogens

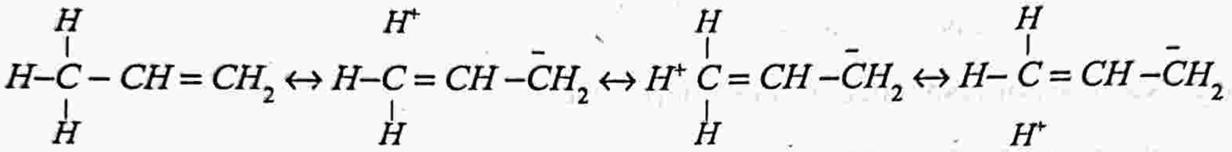
Examples of groups showing –R effect

$-COOH, -CHO, \quad C = O, -CN, -NO_2$

4. Hyper conjugation

When C–H bond of an alkyl group is directly attached to an unsaturated carbon atom, or a carbon atom containing unshared p-orbital, partial delocalisation of σ electrons of the C – H bond *with the unsaturated system or with the unshared p-orbital takes place.* This is known as hyper conjugation or no bond resonance.

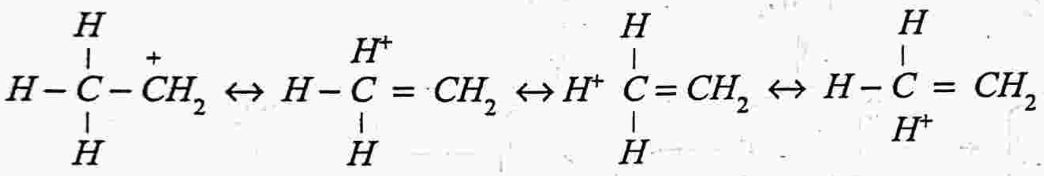
Hyperconjugation is possible in alkenes, alkyl substituted arenes, carbocations and free radicals. For example, the hyperconjugation in propene is shown below:



$$H-\underset{H}{\overset{H}{C}}-CH=CH_2 \leftrightarrow H-\underset{H}{\overset{H^+}{C}}=CH-\overset{-}{C}H_2 \leftrightarrow H^+\ \underset{H}{\overset{H}{C}}=CH-\overset{-}{C}H_2 \leftrightarrow H-\underset{H^+}{\overset{H}{C}}=CH-\overset{-}{C}H_2$$

Since there is no bond between carbon and one of the hydrogen atoms in the hyperconjugation forms, hyperconjugation is also known as *no bond resonance.*

Hyperconjugative structures of ethyl carbocation are shown below:



$$H-\underset{H}{\overset{H}{C}}-\overset{+}{C}H_2 \leftrightarrow H-\underset{H}{\overset{H^+}{C}}=CH_2 \leftrightarrow H^+\ \underset{H}{\overset{H}{C}}=CH_2 \leftrightarrow H-\underset{H^+}{\overset{H}{C}}=CH_2$$

Hyperconjugation stabilises carbocations and free radicals.

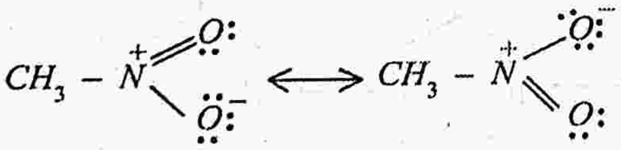
Relative stabilities of alkenes, alkyl free radicals and alkyl cations are explained on the basis of hyperconjugation.

Example 12.5: Write the resonance structures of the following molecules

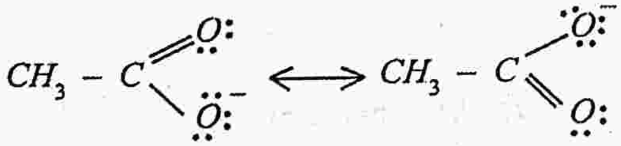
(a) CH_3NO_2 (b) CH_3COO^- (c) $CH_2=CH-CHO$

Ans:

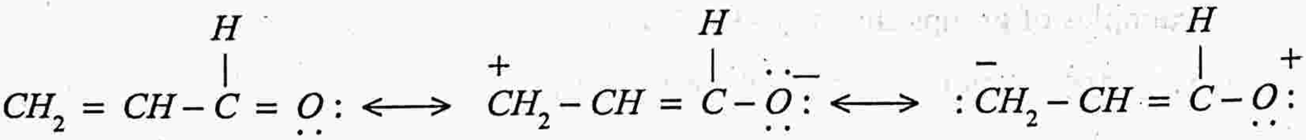
(a)



(b)



(c)



$$CH_2=CH-\overset{H}{C}=\underset{\cdot\cdot}{O}: \longleftrightarrow \overset{+}{C}H_2-CH=\overset{H}{C}-\underset{\cdot\cdot}{\overset{\cdot\cdot\,-}{O}}: \longleftrightarrow :\overset{-}{C}H_2-CH=\overset{H}{C}-\underset{\cdot\cdot}{\overset{+}{O}}:$$

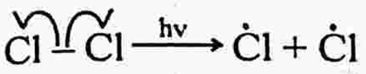
Note: The last structure for (c) contributes little

Fission of a Covalent Bond

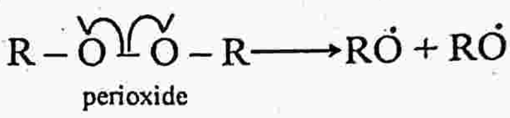
A covalent bond can be broken in two different ways.

(i) Homolytic fission

If a covalent bond breaks in such a way that each atom takes away one electron of the shared pair, it is called homolytic fission or homolysis. The fragments with odd or unpaired electrons formed by homolysis are known as free radicals. For example,



$$Cl-Cl \xrightarrow{h\nu} \dot{C}l + \dot{C}l$$

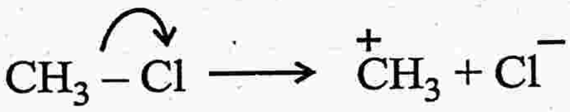


$$R-O-O-R \longrightarrow R\dot{O} + R\dot{O}$$

Usually homolysis occurs at high temperature or in presence of high energy radiations. Reactions occuring through homolytic fission are known as free radical reactions.

(ii) Heterolytic fission

When a covalent bond breaks in such a way that both the electrons of the covalent bond are taken away by one of the bonded atoms, the mode of cleavage is called heterolytic cleavage or heterolysis. The products of heterolysis of a covalent bond are positive and negative ions. e.g.,



$$CH_3-Cl \longrightarrow \overset{+}{C}H_3 + Cl^-$$

Reaction Intermediates

1. Free radicals

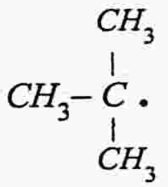
An atom or group of atoms which contains an unpaired electron is known as a free radical. Alkyl free radicals are of three types; primary, secondary and tertiary free radicals. For example,

$CH_3-\dot{C}H_2$

ethyl free radical (1°)

$CH_3-\dot{C}H-CH_3$

iso propyl free radical (2°)



$CH_3-\dot{C}(CH_3)_2$

tert–butyl free radical (3°)

The decreasing order of stability of alkyl free radicals is : Tertiary (3°) > Secondary (2°) > Primary (1°) > methyl

This order of stability can be explained in terms of delocalisation of the unpaired electron through hyperconjugation. The carbon atom in alkyl free radical is *sp*^{2} **hybridised** and the unpaired electron lies in the unhybridised *p*–orbital.

2. Carbocations

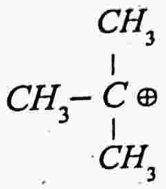
Carbocation may be defined as a species that contains a positively charged carbon atom having only six electrons in its valence shell. Carbocations are formed by heterolytic fission of covalent bonds containing carbon. For example,

$CH_3-\overset{\oplus}{C}H_2$

ethyl carbocation (1°)

$CH_3-\overset{\oplus}{C}H-CH_3$

iso propyl carbocation (2°)



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

tert–butyl carbocation (3°)

The decreasing order of stability of carbocations is Tertiary (3°) > secondary (2°) > primary (1°) > methyl.

This order can be explained in terms of inductive effect and hyperconjugation effect of alkyl groups. The positively charged carbon atom in carbocation is in the ***sp*^{2} hybridised** state. The three hybrid orbitals form three σ bonds while the unhybridised 2*p* orbital remains vacant.

3. Carbanions

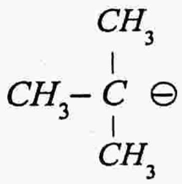
Carbanion may be defined as a species that contains a carbon atom bearing negative charge. Carbanions are also formed by heterolytic cleavage of a covalent bond involving carbon atom.

$CH_3-\overset{\ominus}{C}H_2$

ethyl carbanion (1°)

$CH_3-\overset{\ominus}{C}H-CH_3$

iso propyl carbanion (2°)



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

tert–butyl carbanion (3°)

The decreasing order of stability of carbanions is methyl carbanion > primary (1°) > secondary (2°) > tertiary (3°).

This order is explained on the basis of electron releasing inductive effect (+I) of alkyl groups. In carbanions, the carbon atom carrying the negative charge is ***sp*^{3} hybridised.** Three of the hybrid orbitals form σ bonds with other atoms while the fourth hybrid orbital contains a lone pair of electrons.