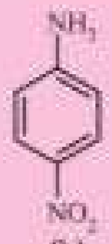
Problem 12.10

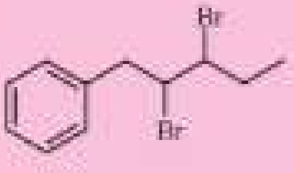
Write the structural formula of:
(a) *o*-Ethylanisole, (b) *p*-Nitroaniline,
(c) 2,3 - Dibromo -1 - phenylpentane,
(d) 4-Ethyl-1-fluoro-2-nitrobenzene.

Solution

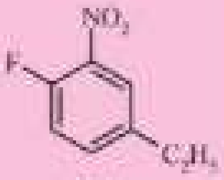
(a)



(b)



(c)



(d)

12.6 ISOMERISM

The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. Such compounds are called as isomers. The following flow chart shows different types of isomerism.

12.6.1 Structural Isomerism

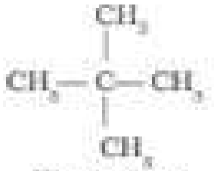
Compounds having the same molecular formula but different structures (manners in which atoms are linked) are classified as structural isomers. Some typical examples of different types of structural isomerism are given below:

(i) Chain isomerism: When two or more compounds have similar molecular formula but different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism. For example, C_5H_{12} represents three compounds:

$CH_3CH_2CH_2CH_2CH_3$
Pentane

$$CH_3-\overset{\overset{\large CH_3}{|}}{C}HCH_2CH_3$$

Isopentane
(2-Methylbutane)



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

Neopentane
(2,2-Dimethylpropane)

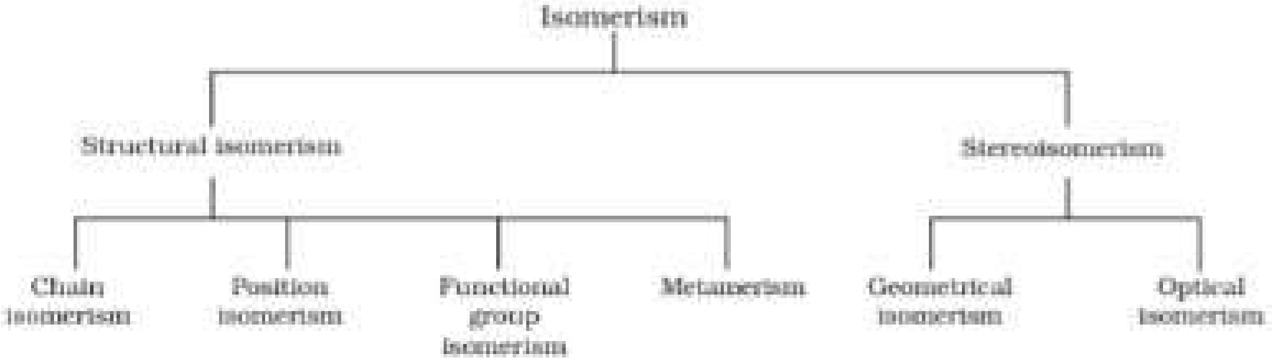
(ii) Position isomerism: When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism. For example, the molecular formula C_3H_8O represents two alcohols:

$CH_3CH_2CH_2OH$
Propan-1-ol

$$CH_3-\overset{\overset{\large OH}{|}}{C}H-CH_3$$

Propan-2-ol

(iii) Functional group isomerism: Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed as functional group isomerism. For example, the molecular formula C_3H_6O represents an aldehyde and a ketone:




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

Propanone


$$CH_3-CH_2-\overset{\overset{\displaystyle H}{|}}{C}=O$$

Propanal

(iv) Metamerism: It arises due to different alkyl chains on either side of the functional group in the molecule. For example, $C_4H_{10}O$ represents methoxypropane ($CH_3OC_3H_7$) and ethoxyethane ($C_2H_5OC_2H_5$).

12.6.2 Stereoisomerism

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. This special type of isomerism is called as stereoisomerism and can be classified as *geometrical* and optical *isomerism*.

12.7 FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

In an organic reaction, the organic molecule (also referred as a substrate) reacts with an appropriate attacking reagent and leads to the formation of one or more intermediate(s) and finally product(s)

The general reaction is depicted as follows :

Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both the reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called *substrate.*

In such a reaction a covalent bond between two carbon atoms or a carbon and some other atom is broken and a new bond is formed. **A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism.** The knowledge of reaction mechanism helps in understanding the reactivity of organic compounds and in planning strategy for their synthesis.

In the following sections, we shall learn some of the principles that explain how these reactions take place.

12.7.1 Fission of a Covalent Bond

A covalent bond can get cleaved either by : (i) ***heterolytic cleavage***, or by (ii) ***homolytic cleavage.***

In ***heterolytic cleavage***, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

After heterolysis, one atom has a sextet electronic structure and a positive charge and the other, a valence octet with at least one lone pair and a negative charge. Thus, heterolytic cleavage of bromomethane will give $\overset{+}{C}H_3$ and Br^- as shown below.


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

A species having a carbon atom possessing sextext of electrons and a positive charge is called a *carbocation* (earlier called *carbonium ion).* The $\overset{+}{C}H_3$ ion is known as a methyl cation or methyl carbonium ion. Carbocations are classified as primary, secondary or tertiary depending on whether one, two or three carbons are directly attached to the positively charged carbon. Some other examples of carbocations are: $CH_3\overset{+}{C}H_2$ (ethyl cation, a primary carbocation), $(CH_3)_2\overset{+}{C}H$ (isopropyl cation, a secondary carbocation), and $(CH_3)_3\overset{+}{C}$ (*tert*-butyl cation, a tertiary carbocation). Carbocations are highly unstable and reactive species. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects, which you will be studying in the sections 12.7.5 and 12.7.9. The observed order of carbocation stability is: $\overset{+}{C}H_3 < CH_3\overset{+}{C}H_2 < (CH_3)_2\overset{+}{C}H < (CH_3)_3\overset{+}{C}$. These carbocations have trigonal planar shape with positively charged carbon being sp^2 hybridised. Thus, the shape of $\overset{+}{C}H_3$ may be considered as being derived from the overlap of three equivalent $C(sp^2)$ hybridised orbitals with 1s orbital of each of the three hydrogen atoms. Each bond may be represented as C(sp^2)–H(1s) sigma bond. The remaining carbon orbital is perpendicular to the molecular plane and contains no electrons. (Fig. 12.3).

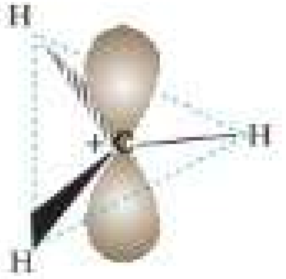


Fig. 12.3 *Shape of methyl cation*

The heterolytic cleavage can also give a species in which carbon gets the shared pair of electrons. For example, when group Z attached to the carbon leaves without

$$\overset{\curvearrowleft}{CH_3 - Z} \longrightarrow H_3\ddot{C}^{-} + \overset{+}{Z}$$

electron pair, the methyl anion $\left(H_3\ddot{C}^{-}\right)$ is formed. Such a carbon species carrying a negative charge on carbon atom is called *carbanion*. Carbanions are also unstable and reactive species. The organic reactions which proceed through heterolytic bond cleavage are called **ionic** or **heteropolar** or just polar reactions.

In ***homolytic cleavage***, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. Thus, in homolytic cleavage, the movement of a single electron takes place instead of an electron pair. The single electron movement is shown by 'half-headed' (fish hook: ⇁) curved arrow. Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called *free radicals*. Like carbocations and carbanions, free radicals are also very reactive. A homolytic cleavage can be shown as:

$$\overset{\frown\ \frown}{R - X} \xrightarrow{\text{Heat or Light}} \underset{\substack{\text{Alkyl}\\ \text{free radical}}}{\dot{R}} + \dot{X}$$

Alkyl radicals are classified as *primary*, *secondary*, or *tertiary*. Alkyl radical stability increases as we proceed from primary to tertiary:

$\dot{C}H_3 <$	$\dot{C}H_2CH_3 <$	$\dot{C}H(CH_3)_2 <$	$\dot{C}(CH_3)_3$
Methyl free radical	Ethyl free radical	Isopropyl free radical	Tert-butyl free radical

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

12.7.2 Nucleophiles and Electrophiles

A reagent that brings an electron pair is called a **nucleophile** (Nu:) i.e., nucleus seeking and the reaction is then called **nucleophilic**. A reagent that takes away an electron pair is called **electrophile** (E^+) i.e., electron seeking and the reaction is called **electrophilic**.

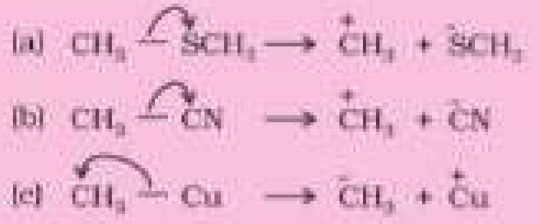
During a polar organic reaction, a nucleophile attacks an electrophilic centre of the substrate which is that specific atom or part of the electrophile that is electron deficient. Similarly, the electrophiles attack at nucleophilic centre, which is the electron rich centre of the substrate. Thus, the electrophiles receive electron pair from nucleophile when the two undergo bonding interaction. A curved-arrow notation is used to show the movement of an electron pair from the nucleophile to the electrophile. Some examples of nucleophiles are the negatively charged ions with lone pair of electrons such as hydroxide (HO^-), cyanide (NC^-) ions and carbanions ($R_3C:^-$). Neutral molecules such as $H_2\ddot{O}:$, $R_3\ddot{N}:$, $R_2\ddot{N}H$ etc., can also act as nucleophiles due to the presence of lone pair of electrons. Examples of electrophiles include carbocations ($\overset{+}{C}H_3$) and neutral molecules having functional groups like carbonyl group (>C=O) or alkyl halides (R_3C-X, where X is a halogen atom). The carbon atom in carbocations has sextet configuration; hence, it is electron deficient and can receive a pair of electrons from the nucleophiles. In neutral molecules such as alkyl halides, due to the polarity of the C-X bond a partial positive charge is generated on the carbon atom and hence the carbon atom becomes an electrophilic centre at which a nucleophile can attack.

Problem 12.11

Using curved-arrow notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage.

(a) $CH_3–SCH_3$, (b) $CH_3–CN$, (c) $CH_3–Cu$

Solution



$$\text{(a)}\ CH_3-SCH_3 \longrightarrow \overset{+}{C}H_3 + \overset{-}{S}CH_3$$

$$\text{(b)}\ CH_3-CN \longrightarrow \overset{+}{C}H_3 + \overset{-}{C}N$$

$$\text{(c)}\ CH_3-Cu \longrightarrow \overset{-}{C}H_3 + \overset{+}{C}u$$

Problem 12.12

Giving justification, categorise the following molecules/ions as nucleophile or electrophile:

$H\overset{-}{S}, BF_3, C_2H_5\overset{-}{O}, (CH_3)_3N:,$

$\overset{+}{C}l, CH_3-\overset{+}{C}=O, H_2N\overset{-}{:}, \overset{+}{N}O_2$

Solution

Nucleophiles: $H\overset{-}{S}, C_2H_5\overset{-}{O}, (CH_3)_3N:, H_2N\overset{-}{:}$

These species have unshared pair of electrons, which can be donated and shared with an electrophile.

Electrophiles: $BF_3, \overset{+}{C}l, CH_3-\overset{+}{C}=O, \overset{+}{N}O_2$.

Reactive sites have only six valence electrons; can accept electron pair from a nucleophile.

Problem 12.13

Identify electrophilic centre in the following: $CH_3CH=O$, CH_3CN, CH_3I.

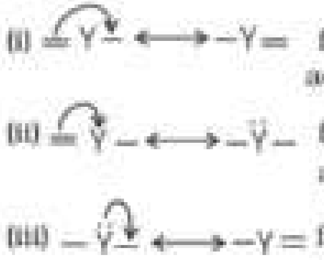
Solution

Among $CH_3H\overset{*}{C}=O$, $H_3C\overset{*}{C}\equiv N$, and $H_3\overset{*}{C}-I$, the starred carbon atoms are electrophilic centers as they will have partial positive charge due to polarity of the bond.

12.7.3 Electron Movement in Organic Reactions

The movement of electrons in organic reactions can be shown by curved-arrow notation. It shows how changes in bonding occur due to electronic redistribution during the reaction. To show the change in position of a pair of electrons, curved arrow starts from the point from where an electron pair is shifted and it ends at a location to which the pair of electron may move.

Presentation of shifting of electron pair is given below :

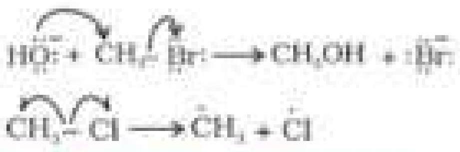


(i) from π bond to adjacent bond position

(ii) from π bond to adjacent atom

(iii) from atom to adjacent bond position

Movement of single electron is indicated by a single barbed 'fish hooks' (i.e. half headed curved arrow). For example, in transfer of hydroxide ion giving ethanol and in the dissociation of chloromethane, the movement of electron using curved arrows can be depicted as follows:



$$H\ddot{O}:^- + CH_3-Br: \longrightarrow CH_3OH + :Br:^-$$

$$CH_3-Cl \longrightarrow \dot{C}H_3 + \dot{C}l$$

12.7.4 Electron Displacement Effects in Covalent Bonds

The electron displacement in an organic molecule may take place either in the ground state under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent. The electron displacements due to the influence of an atom or a substituent group present in the molecule cause permanent polarlisation of the bond. Inductive effect and resonance effects are examples of this type of electron displacements. Temporary electron displacement effects are seen in a molecule when a reagent approaches to attack it. This type of electron displacement is called electromeric effect or polarisability effect. In the following sections we will learn about these types of electronic displacements.

12.7.5 Inductive Effect

When a covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom of the bond. Such a shift of electron density results in a polar covalent bond. Bond polarity leads to various electronic effects in organic compounds.

Let us consider cholorethane (CH_3CH_2Cl) in which the C–Cl bond is a polar covalent bond. It is polarised in such a way that the carbon-1 gains some positive charge (δ^+) and the chlorine some negative charge (δ^-). The fractional electronic charges on the two atoms in a polar covalent bond are denoted by symbol δ (delta) and the shift of electron density is shown by an arrow that points from δ^+ to δ^- end of the polar bond.

$$\overset{\delta\delta^+}{\underset{2}{CH_3}} \longrightarrow \overset{\delta^+}{\underset{1}{CH_2}} \longrightarrow \overset{\delta^-}{Cl}$$

In turn carbon-1, which has developed partial positive charge (δ^+) draws some electron density towards it from the adjacent C-C bond. Consequently, some positive charge ($\delta\delta^+$) develops on carbon-2 also, where $\delta\delta^+$ symbolises relatively smaller positive charge as compared to that on carbon – 1. In other words, the polar C – Cl bond induces polarity in the adjacent bonds. Such polarisation of σ-bond caused by the polarisation of adjacent σ-bond is referred to as the **inductive effect**. This effect is passed on to the subsequent bonds also but the effect decreases rapidly as the number of intervening bonds increases and becomes vanishingly small after three bonds. The inductive effect is related to the ability of substituent(s) to either withdraw or donate electron density to the attached carbon atom. Based on this ability, the substitutents can be classified as *electron-withdrawing* or *electron donating* groups relative to hydrogen. Halogens and many other groups such as nitro (- NO_2), cyano (- CN), carboxy (- COOH), ester (-COOR), aryloxy (-OAr, e.g. – OC_6H_5), etc. are electron-withdrawing groups. On the other hand, the alkyl groups like methyl (–CH_3) and ethyl (–CH_2–CH_3) are usually considered as electron donating groups.

Problem 12.14

Which bond is more polar in the following pairs of molecules: (a) H_3C-H, H_3C-Br (b) H_3C-NH_2, H_3C-OH (c) H_3C-OH, H_3C-SH

Solution

(a) C–Br, since Br is more electronegative than H, (b) C–O, (c) C–O

Problem 12.15

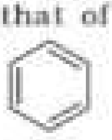
In which C–C bond of $CH_3CH_2CH_2Br$, the inductive effect is expected to be the least?

Solution

Magnitude of inductive effect diminishes as the number of intervening bonds increases. Hence, the effect is least in the bond between carbon-3 and hydrogen.

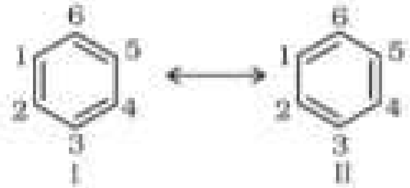
12.7.6 Resonance Structure

There are many organic molecules whose behaviour cannot be explained by a single Lewis structure. An example is that of benzene. Its cyclic structure containing alternating C–C single and C=C double bonds shown is inadequate for explaining its characteristic properties.



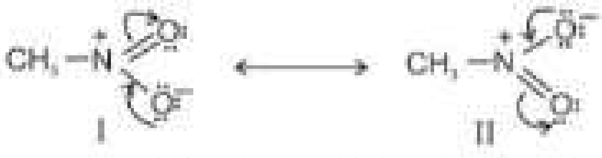
Benzene

As per the above representation, benzene should exhibit two different bond lengths, due to C–C single and C=C double bonds. However, as determined experimentally benzene has a uniform C–C bond distances of 139 pm, a value intermediate between the C–C single(154 pm) and C=C double (134 pm) bonds. Thus, the structure of benzene cannot be represented adequately by the above structure. Further, benzene can be represented equally well by the energetically identical structures I and II.



Therefore, according to the resonance theory (Unit 4) the actual structure of benzene cannot be adequately represented by any of these structures, rather it is a hybrid of the two structures (I and II) called *resonance structures*. **The resonance structures (canonical structures or contributing structures) are hypothetical and individually do not represent any real molecule.** They contribute to the actual structure in proportion to their stability.

Another example of resonance is provided by nitromethane (CH_3NO_2) which can be represented by two Lewis structures, (I and II). There are two types of N-O bonds in these structures.



However, it is known that the two N-O bonds of nitromethane are of the same length (intermediate between a N-O single bond and a N=O double bond). The actual structure of nitromethane is therefore a resonance hybrid of the two canonical forms I and II.

The energy of actual structure of the molecule (the resonance hybrid) is lower than that of any of the canonical structures. The difference in energy between the actual structure and the lowest energy resonance structure is called the ***resonance stabilisation energy*** or simply the ***resonance energy***. The more the number of important contributing structures, the more is the resonance energy. Resonance is particularly important when the contributing structures are equivalent in energy.

The following rules are applied while writing resonance structures:

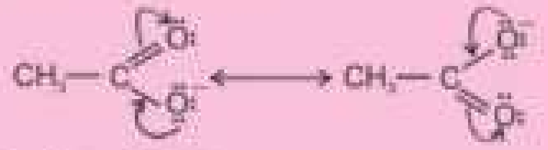
The resonance structures have (i) the same positions of nuclei and (ii) the same number of unpaired electrons. Among the resonance structures, the one which has more number of covalent bonds, all the atoms with octet of electrons (except hydrogen which has a duplet), less separation of opposite charges, (a negative charge if any on more electronegative atom, a positive charge if any on more electropositive atom) and more dispersal of charge, is more stable than others.

Problem 12.16

Write resonance structures of CH_3COO^- and show the movement of electrons by curved arrows.

Solution

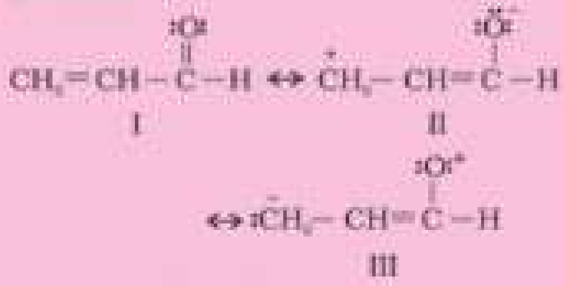
First, write the structure and put unshared pairs of valence electrons on appropriate atoms. Then draw the arrows one at a time moving the electrons to get the other structures.



Problem 12.17

Write resonance structures of CH_2=CH-CHO. Indicate relative stability of the contributing structures.

Solution

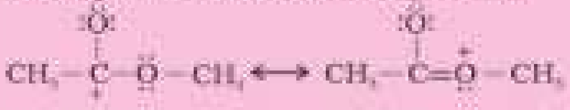


Stability: I > II > III

[I: Most stable, more number of covalent bonds, each carbon and oxygen atom has an octet and no separation of opposite charge II: negative charge on more electronegative atom and positive charge on more electropositive atom; III: does not contribute as oxygen has positive charge and carbon has negative charge, hence least stable].

Problem 12.18

Explain why the following two structures, I and II cannot be the major contributors to the real structure of CH_3COOCH_3.



$$\underset{\text{I}}{CH_3-\overset{\overset{\large :\ddot{O}:^-}{|}}{\underset{+}{C}}-\ddot{O}-CH_3} \longleftrightarrow \underset{\text{II}}{CH_3-\overset{\overset{\large :\ddot{O}:^-}{|}}{C}=\overset{+}{\ddot{O}}-CH_3}$$

Solution

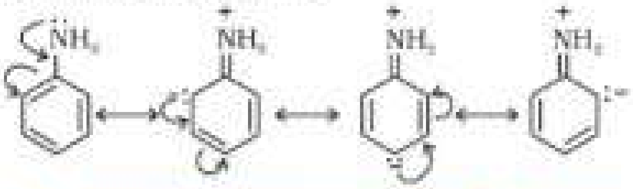
The two structures are less important contributors as they involve charge separation. Additionally, structure I contains a carbon atom with an incomplete octet.

12.7.7 Resonance Effect

The resonance effect is defined as 'the polarity 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 designated as R or M effect.

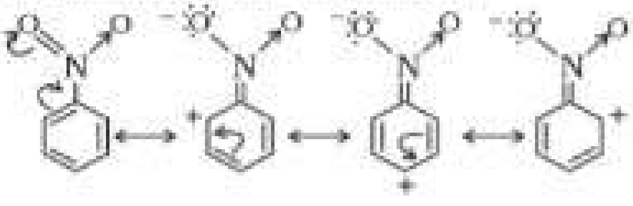
(i) Positive Resonance Effect (+R effect)

In this effect, the transfer of electrons is away from an atom or substituent group attached to the conjugated system. This electron displacement makes certain positions in the molecule of high electron densities. This effect in aniline is shown as :



(ii) Negative Resonance Effect (- R effect)

This effect is observed when the transfer of electrons is towards the atom or substituent group attached to the conjugated system. For example in nitrobenzene this electron displacement can be depicted as :



The atoms or substituent groups, which represent +R or –R electron displacement effects are as follows :

+R effect: – halogen, –OH, –OR, –OCOR, $-NH_2$, –NHR, $-NR_2$, –NHCOR,

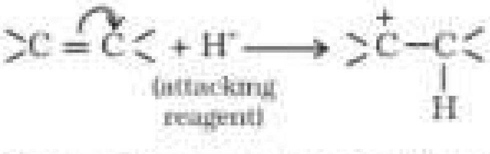
– R effect: – COOH, –CHO, >C=O, – CN, $-NO_2$

The presence of alternate single and double bonds in an open chain or cyclic system is termed as a conjugated system. These systems often show abnormal behaviour. The examples are 1,3- butadiene, aniline and nitrobenzene etc. In such systems, the π-electrons are delocalised and the system develops polarity.

12.7.8 Electromeric Effect (E effect)

It is a temporary effect. The organic compounds having a **multiple bond** (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of π-electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. The effect is annulled as soon as the attacking reagent is removed from the domain of the reaction. It is represented by E and the shifting of the electrons is shown by a curved arrow (↷). There are two distinct types of electromeric effect.

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



$$>C=C< + \underset{\text{(attacking reagent)}}{H^+} \longrightarrow >\overset{+}{C}-\underset{\underset{\large H}{|}}{C}<$$

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

$$>C=C< + \underset{\text{(attacking reagent)}}{\bar{C}N} \longrightarrow >\underset{\underset{\large CN}{|}}{C}-\bar{C}<$$

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

12.7.9 Hyperconjugation

Hyperconjugation is a general stabilising interaction. 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 *p* orbital. The σ electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared *p* orbital. Hyperconjugation is a permanent effect.

To understand hyperconjugation effect, let us take an example of $CH_3\overset{+}{C}H_2$ (ethyl cation) in which the positively charged carbon atom has an empty *p* orbital. One of the C-H bonds of the methyl group can align in the plane of this empty *p* orbital and the electrons constituting the C-H bond in plane with this *p* orbital can then be delocalised into the empty *p* orbital as depicted in Fig. 12.4 (a).

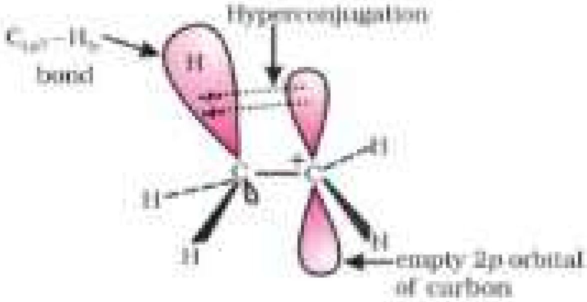
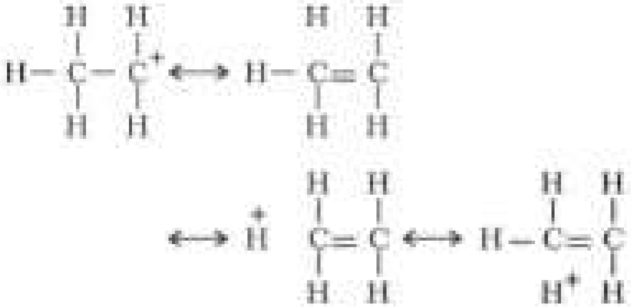


Fig. 12.4(a) *Orbital diagram showing hyperconjugation in ethyl cation*

This type of overlap stabilises the carbocation because electron density from the adjacent σ bond helps in dispersing the positive charge.



In general, greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and stabilisation of the cation. Thus, we have the following relative stability of carbocations :

$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{\overset{+}{C}}} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$

Hyperconjugation is also possible in alkenes and alkylarenes.

Delocalisation of electrons by hyperconjugation in the case of alkene can be depicted as in Fig. 12.4(b).

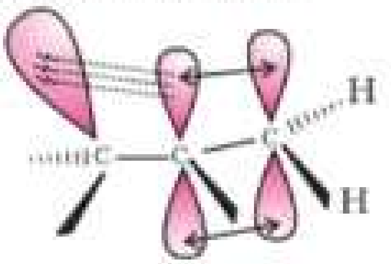


Fig. 12.4(b) *Orbital diagram showing hyperconjugation in propene*

There are various ways of looking at the hyperconjugative effect. One of the way is to regard C—H bond as possessing partial ionic character due to resonance.