

There are six such unhybridised orbitals these can overlap laterally in pairs to form three π bonds as shown in Fig. 2.14 (a) and (b). But the same situation exists as in 1, 3-butadiene. All the six orbitals overlap together forming a circular electron cloud above and below the benzene ring as shown in Fig. 2.14 (c).

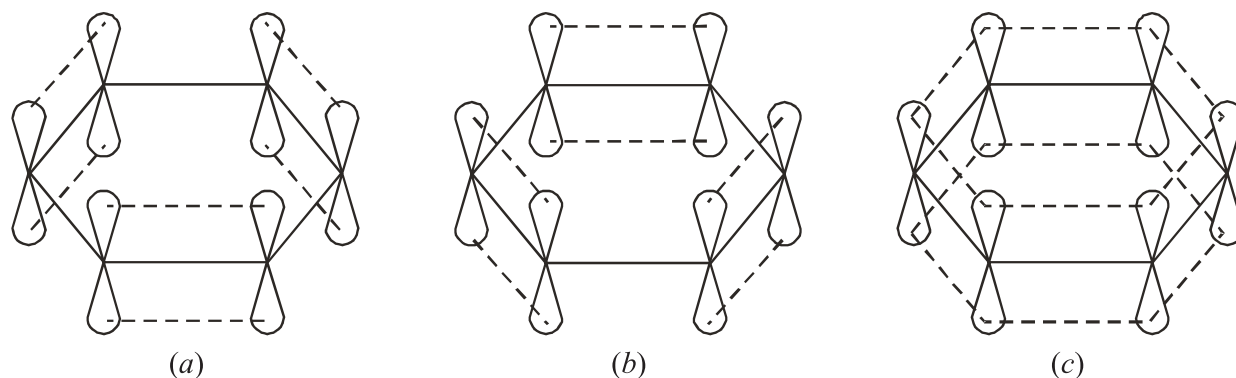


Fig. 2.14: Bond delocalisation in benzene

2.16 HOMOLYTIC AND HETEROLYTIC BOND BREAKING (FISSION)

Consider a covalent bond between atoms A and B.



The cleavage (or breaking) of this bond can take place in three possible ways depending upon the relative electronegativities of A and B.

- (i) $A : B \longrightarrow A\bullet + B\bullet$ (A• and B• of equal electronegativity)
- (ii) $A : B \longrightarrow \overset{-}{A} : + \overset{+}{B}$ (A more electronegative than B)
- (iii) $A : B \longrightarrow \overset{+}{A} + \overset{-}{B} :$ (B more electronegative than A)

The first type of cleavage is called *homolytic fission* or *homolysis* and leads to the formation of very reactive species called '*free radicals*' (atoms or groups of atoms containing odd or unpaired electrons).

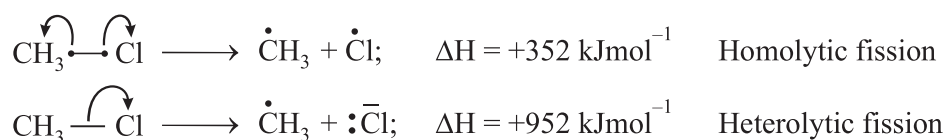
In homolytic fission the covalent bond breaks in such a way that each fragment carries one unpaired electron.

Homolytic fission usually occurs in non-polar bonds. High temperature, presence of ultraviolet radiations and radical initiators such as peroxide favour homolytic fission.

The second and third types of cleavage is called *heterolytic fission* and leads to the formation of ionic species. These ionic species are also very reactive and carry charges on carbon. Cationic species carrying positive charge on a carbon atom are called *carbonium ions* or *carbocations*. Anionic species carrying negative charge on carbon atom are called *carbanions*.

In heterolytic fission the covalent bond breaks in such a way that the pair of electrons stays on the more electronegative atom.

It may be realised that the same covalent bond can undergo homolytic fission or heterolytic fission depending upon the reaction conditions. Homolytic fission is generally associated with smaller bond dissociation energy compared to heterolytic fission. This can be understood by the fact, that in heterolytic fission, both the shared electrons are going to be shifted to one atom which requires a greater amount of energy.



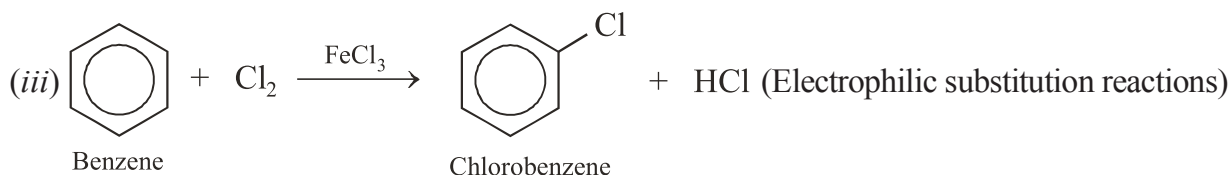
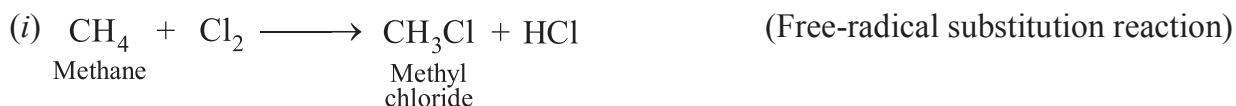
2.17 TYPES OF ORGANIC REACTIONS

Organic reactions may be classified into four main types:

- Substitution reactions
- Addition reactions
- Elimination reactions
- Rearrangements

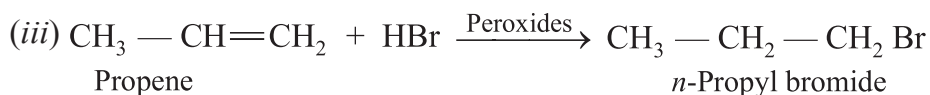
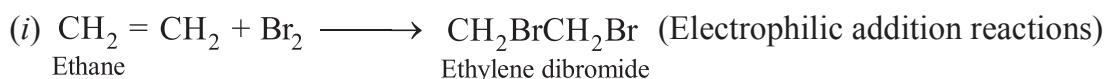
These are separately described as under.

(a) Substitution reactions. *A substitution reaction is one in which a part of one molecule is replaced by other atom or group without causing a change in the rest of the molecule.* Following are some examples of substitution reactions.



The substitution reactions may be brought about by free-radicals, nucleophilic or electrophilic reagents. Thus, there are free radical substitution reactions, nucleophilic substitution reactions and electrophilic substitution reactions.

(b) Addition reactions. *When two molecules of same or different substances combine together giving rising to a new product, it is an addition reaction.* Examples of addition reactions are:



Addition reactions could be brought about by free-radical, electrophilic or nucleophilic reagents.

As in the case of substitution, there are free radical, electrophilic and nucleophilic substitution reactions.

(c) Elimination reactions. *These reactions involve the removal of atoms or groups from a molecule to form a new compounds containing multiple bonds.* Dehydrohalogenation of alkyl halides is a common example of this type reaction.

2.19 TYPES OF REAGENTS—NUCLEOPHILES AND ELECTROPHILES

Nucleophilic reagents or nucleophiles

A nucleophilic reagent is a reagent with an atom having an unshared or lone pair of electrons. Such a reagent is in search of a point where it can share these electrons to form a bond. Nucleophiles are of two types:

(i) Neutral nucleophiles. These are the nucleophiles which are neutral in charge. But they carry some unshared electrons which they like to share with some positive centre or electron deficient centre. Ammonia $\overset{\cdot\cdot}{\text{N}}\text{H}_3$, water $\text{H}_2\ddot{\text{O}}$ and alcohols $\text{R} - \ddot{\text{O}} - \text{H}$ are examples of neutral nucleophiles.

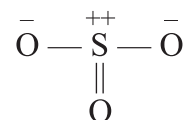
(ii) Negative nucleophiles. These are the nucleophiles which carry negative charge. Examples of this type of nucleophiles are hydroxyl ions (OH^-), halide ion (X^-), alkoxide ion (RO^-) and cyanide ion (CN^-). Carbanions also come in the category of negative nucleophiles.

Both neutral and negatively charged nucleophiles contain at least one lone pair of electrons which is donated to electron deficient species. Thus they behave as *Lewis bases*. It may be noted that nucleophiles attack the substrate molecule at a site which has the *least electron density*.

Electrophilic reagents or electrophiles

An electrophile is a reagent containing electron deficient atoms. Such species have a tendency to attach themselves to centres of high electron density. There are two types of electrophiles:

(i) Neutral electrophiles. These electrophile do not carry any net charge. Lewis acids like AlCl_3 , FeCl_3 and BF_3 belong to this category of electrophiles. Sulphonium ion (SO_3) carries no net charge, but it acts as an electrophile for sulphonation in benzene rings. This is because of its structure.



As the positive charge is concentrated and the negative charge is scattered, it acts as an electrophile. Substances like SnCl_4 which have vacant *d*-orbitals would like to accommodate electrons in them. Thus such substances also act as electrophiles.

(ii) Positive electrophiles. These electrophiles carry a net positive charge. Examples of this category of electrophiles are hydrogen ion (H^+), hydronium ion (H_3O^+), nitronium ion (NO_2^+), and chloronium ion (Cl^+). In the halogenation and nitration of aromatic systems, these electrophiles are involved.

Both positive and neutral electrophiles are short of one pair of electrons. Therefore, they have a tendency to seek electrons from other species. Thus, they behave as *Lewis acids*. They would attach to other molecules at the site of *highest electron density*.

Example 3: Classify the following as nucleophiles and electrophiles: H_3O^+ , NH_3 , AlCl_3 , ROH , BF_3 , CN^- , SO_3 .

Solution:	Nucleophiles	Electrophiles
	NH_3	H_3O^+
	ROH	AlCl_3
	CN^-	BF_3
		SO_3 (Sulphonium ion)

Example 4: Pick up from the following, the electrophiles and nucleophiles:



Solution: Electrophiles: $\text{AlCl}_3, \text{HNO}_3$.

Nucleophiles: $\text{PH}_3, \text{R}_3\text{N}$.

Example 5: Pick up from the following, the electrophiles and nucleophiles:



Solution: Electrophiles: $\text{BF}_3, \text{SnCl}_4$.

Nucleophiles: NH_3, ROH .

2.20 NUCLEOPHILICITY AND BASICITY

Nucleophilicity is the ability of a group with a lone pair of electrons to push another such group out of a carbon centre. Basicity is the ability of group to combine with a proton or to donate a lone pair of electrons.

Thus nucleophilicity involves donation of electrons to carbon while basicity involves donation to hydrogen.

Let us consider the nucleophilicity of halogen anions. These anions are solvated by means of hydrogen bonding. Fluorine is the smallest anion and has the largest charge density and therefore is solvated most heavily leading to the largest solution radius followed by chlorine, bromine and iodine.

For nucleophilic attack, this solvent cage has to be broken to enable to reaction to take place. Breaking the cage requires energy and that is shown up as activation energy and therefore iodide is most reactive because it is solvated the least. Then comes bromide, chloride and fluoride.

However, if we move to aprotic solvent like DMS, the situation is different. There is no hydrogen bonding, the anions are 'naked', no cage is to be broken. In such case smaller anions become better nucleophiles.

To sum up, basicity is a subset of nucleophilicity. All nucleophiles are Lewis bases, they donate a lone pair of electrons. A base is just the name we give to nucleophile when it is forming a bond to a proton (H^+). Nucleophile attacks carbon while a base attacks a proton.

2.21 REACTIVE INTERMEDIATES

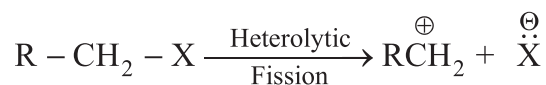
In organic reactions, reactants do not change into products in one step. The change normally takes place via an intermediate product, which is short-lived. From the intermediate product, the reaction passes on to the products. Various reaction intermediates that we come across in the study of organic reactions are:

- | | |
|------------------------------------|-----------------------|
| (i) Carbonium ion (or carbocation) | (ii) Carbanion |
| (iii) Free radical | (iv) Carbene |
| (v) Nitrene | (vi) Arynes (benzyne) |

2.22 CARBOCATIONS

These are defined as the species in which the positive charge is carried by the carbon atom with six electrons in its valence shell. These are formed by the heterolytic fission in which

an atom or group along with its pair of electrons leaves the carbon. In heterolytic fission, the shared pair of electrons between two atoms goes to one atom only.



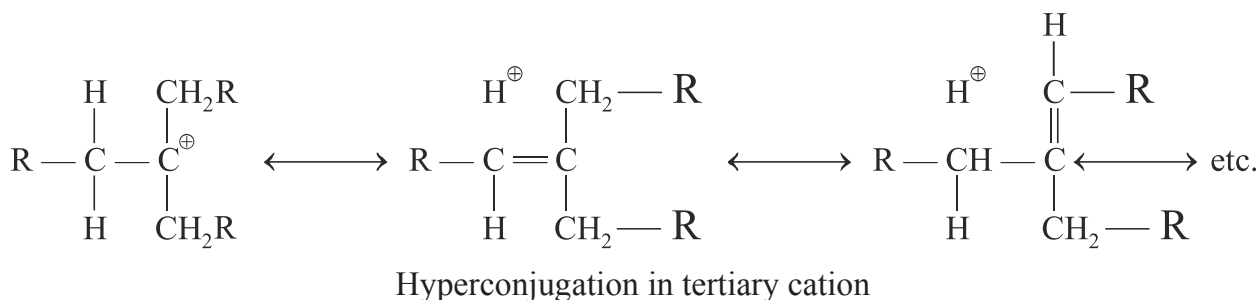
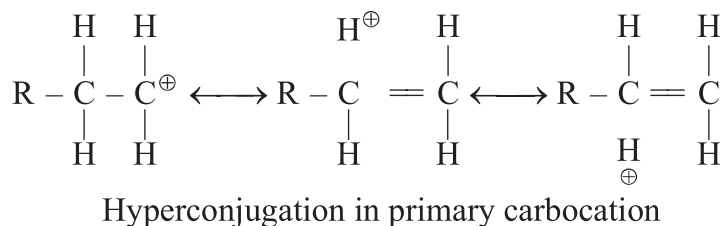
Stability of Carbocations

1. The order of stability among simple alkyl carbocations is: tertiary > secondary > primary. In most of the reactions, primary and secondary carbocations get rearranged to tertiary carbocations. Both *n*-propyl fluoride and isopropyl fluoride form the same isopropyl cation (2° carbocation). Similarly all the four butyl fluorides *viz.*, *n*-, iso-, sec. and tertiary butyl fluorides form the same tert-butyl cation. There are two factors which determine the stability:

- (i) *Hyperconjugation or resonance.*
- (ii) *Field effect or inductive effect of groups.*

Hyperconjugation

A large number of canonical forms can be written for tertiary carbocation compared to those for primary carbocation. Consider hyperconjugation in primary and tert-carbocation.



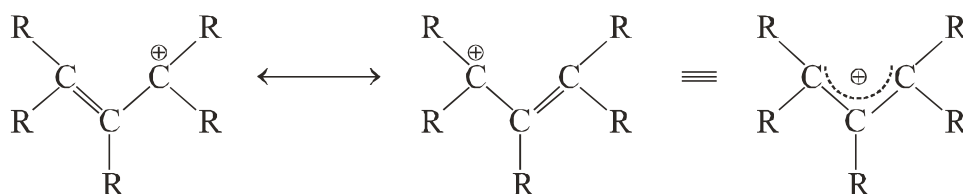
Greater the number of canonical forms, greater is the stability.

Field effect

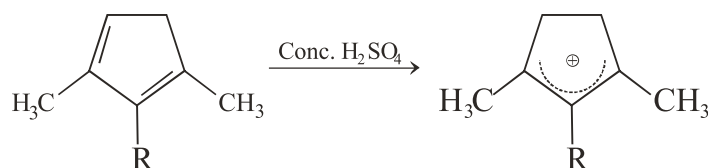
Electron donating effect of alkyl groups increases the electron density around the +vely charged carbon. This results in reducing the magnitude of positive charge on it and thus the charge is delocalised on α -carbon. Dispersal of positive charge increases the stability. Of carbocation of all the simple cation, *tert*-butyl cation being most stable. Even *tert*-pentyl and *tert*-hexyl cations produce *tert*-butyl cation at high temperature. Lower alkanes like methane, ethane and propane when treated with **super acid*** also yield *tert*-butyl cation as the main product. Salts of *tert*-butyl cation, like $(\text{CH}_3)_3\text{C}^+ \text{SbF}_3^-$ have been prepared from super acid solutions.

* A mixture of $\text{SbF}_5 + \text{HF}$ or $\text{SbF}_5 + \text{FSO}_3\text{H}$ dissolved in liquid SO_2 is one of the strongest acid solutions and are commonly called super acids.

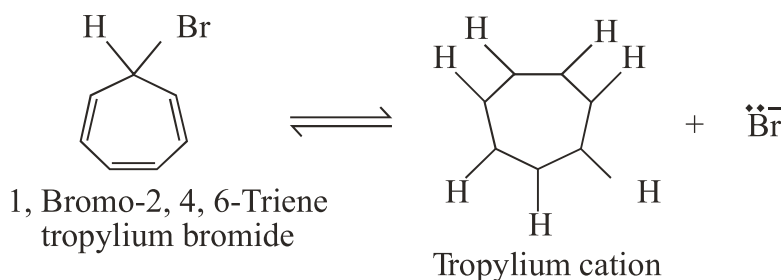
2. The stability of carbocation containing a conjugated double bond is usually greater due to increased delocalisation by resonance. In such carbocations, the positive charge is dispersed on at least two carbon atoms. Consider the following carbocation.



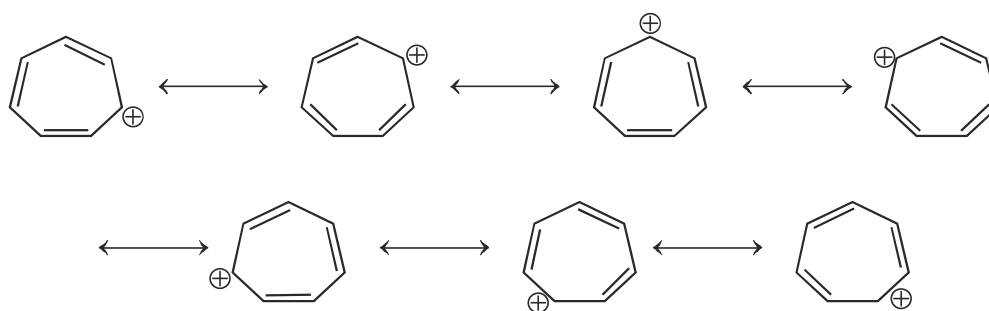
3. Allylic type carbocations have been prepared from the solution of conjugated diene in conc. sulphuric acid and are found to be most stable.



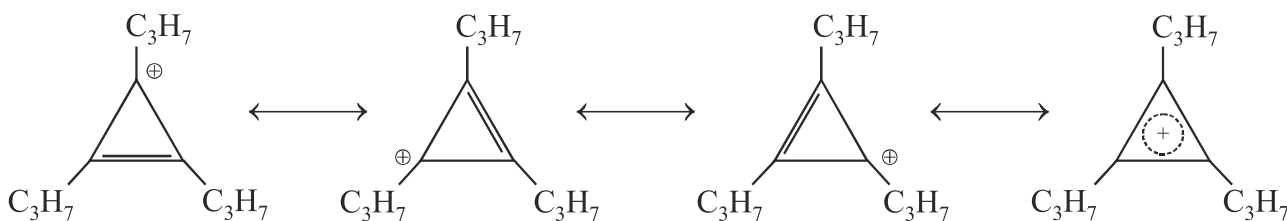
4. Carbocations can be stabilised through aromatisation also. 1-Bromocyclohepta-2, 4, 6-triene tropylium bromide is a crystalline solid. It is highly soluble in water and forms bromide ions in solution. Clearly, the compound is not covalent in nature. The reason for such a behaviour is the stability of tropylium cation which follows Huckel's rule (6π electrons) for aromaticity.



Its stability is also explained in terms of canonical structures which stabilise the tropylium cation.

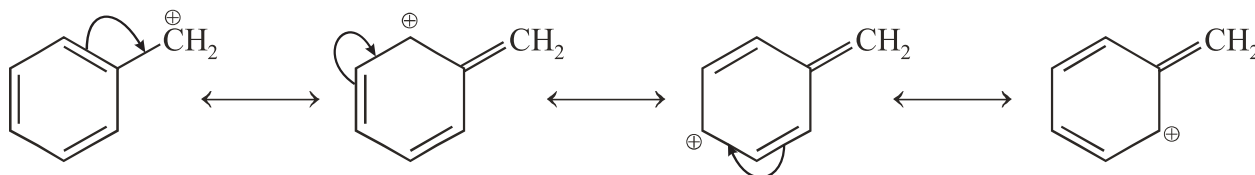


5. Substituted cyclopropenyl cation possesses even more aromatic stabilisation ($n = 0$).



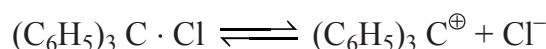
In the above tripropyl substituted cation, all the carbons are sp^2 hybridised. Thus all the p -orbitals including the vacant p -orbital of the positively charged carbon overlap forming a delocalised π molecular orbital, leading to stabilization.

6. Benzyl cation can be written in the following canonical forms:

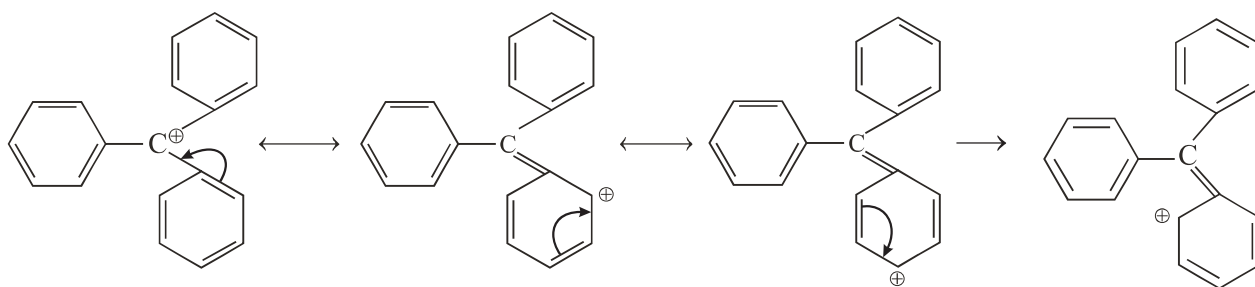


Due to larger number of canonical forms and greater dispersal of positive charge, benzyl carbocation is still more stable.

7. Triphenyl chloromethane ionises in SO_2 as



Triphenyl methyl cation has been isolated as solid salt as $(C_6H_5)_3 C^{\oplus} \cdot BF_4^{-}$. The stability of triarylmethyl cation is further increased if the rings are substituted at *ortho* and *para* positions by electron donating groups.

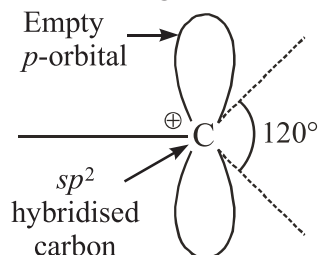


The extra stability of triphenyl methyl carbonium ion has been attributed to extensive resonance with three benzene rings. However, the benzene rings are slightly out of plane. They have a propeller shape.

Total contributing structures for triphenylmethyl carbonium ion will be $1 + (3 \times 3) = 10$ because 3 contributing structures result from one ring, one structure being the original one.

Structure and reactions of carbocations

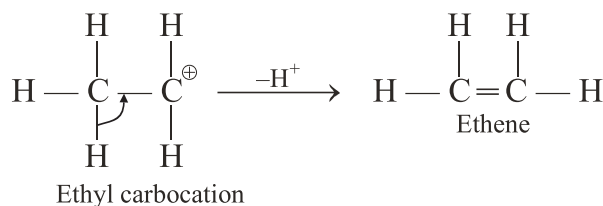
Structure. The carbon atom bearing the positive charge in a carbocation is sp^2 hybridised. The three sp^2 hybrid orbitals are utilised in the formation of sigma bonds with three atoms or groups. The third unused p -orbital remains vacant. Thus, the carbocation is a flat species having all the three bonds in one plane with a bond angle of 120° between them as shown below:



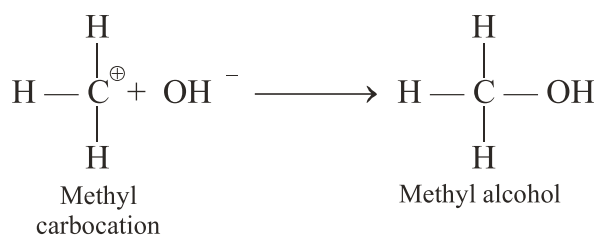
Reactions

Carbocations, which are shortlived species and very reactive give the following reactions:

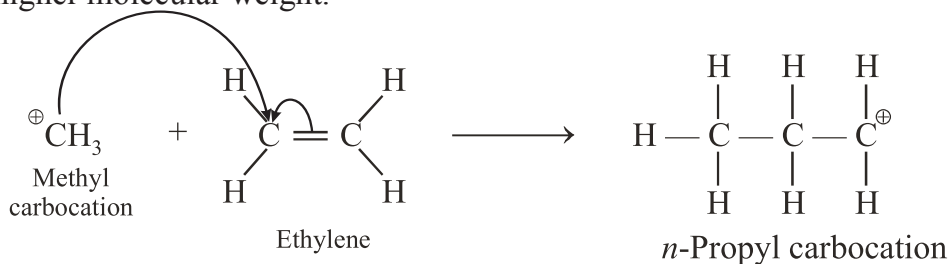
1. Proton loss. Carbocation may lose a proton to form an alkene. An ethyl carbocation loses a proton to form ethene.



2. Combination with nucleophiles. Carbocations combine with nucleophiles to acquire a pair of electrons. For example, a highly reactive methyl carbocation with hydroxyl ion to form methyl alcohol.

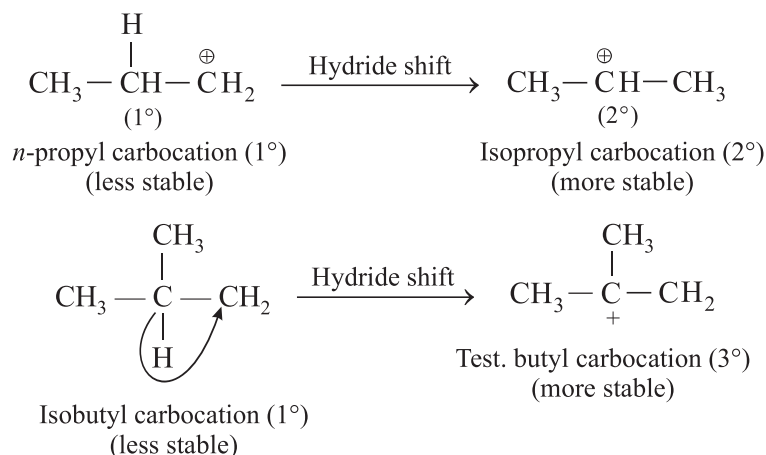


3. Addition to alkene. A carbocation may add to an alkene to produce another carbocation possessing higher molecular weight.

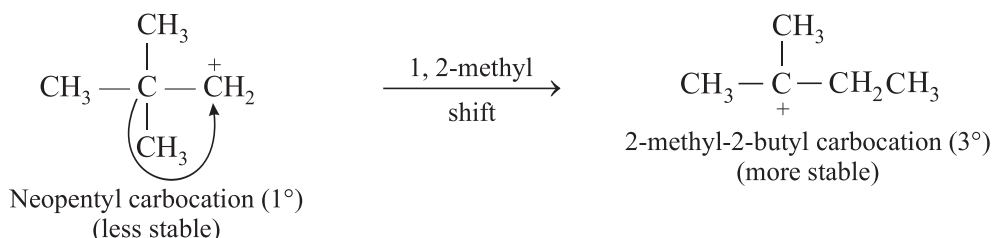


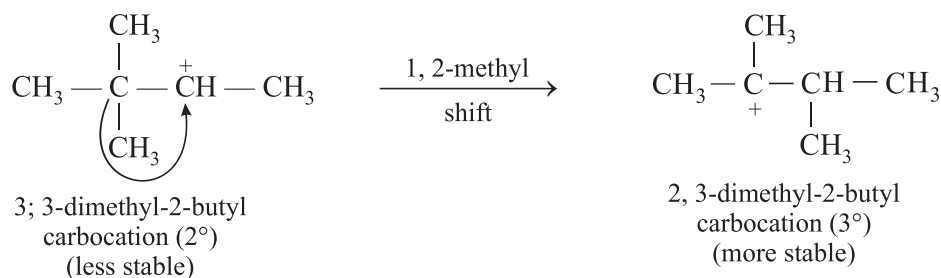
4. Rearrangement. The migration of alkyl or aryl or hydrogen along with an electron pair to the positive centre takes place which results in the formation of more stable carbocation. Some examples are given below:

1, 2-Hydride shift



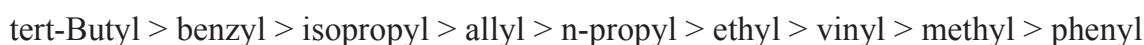
1, 2-Methyl shift



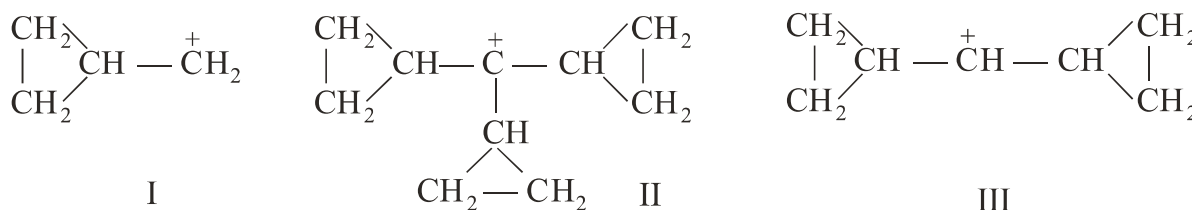


Such a rearrangement takes place because a tertiary carbocation is more stable than secondary carbocation, which in turn is more stable than primary carbocation. Similarly, a carbocation attached to a phenyl group (benzene ring) is more stable than others.

From the bond dissociation energy data, we can arrange various alkyl/aryl carbocations in order of decreasing stability as:



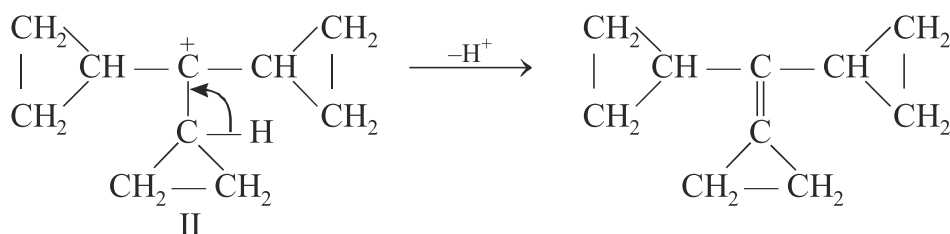
Example 6: Arrange the following in order of decreasing stability and give suitable explanation for it.



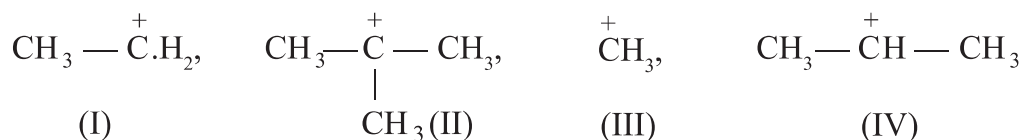
Solution: The stability of a carbocation depends upon two factors:

- (i) Hyperconjugation
- (ii) Inductive effect of groups attached.

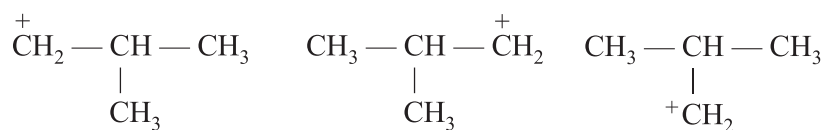
In this problem, it is hyperconjugation or resonance which is important. Structure II can form maximum number of resonating structures and hence this is most stable. It can form resonating structures with the help of hydrogen from three sides (from three cyclopropyl groups) whereas carbocations III and I can form resonating structures from two and one side respectively. Thus the order of stability in decreasing order is:



Example 7: Arrange the following in order of increasing stability and explain the order on the basis of hyperconjugation.

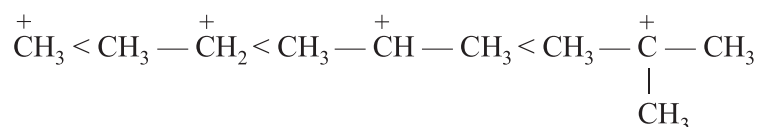


Solution: Greater the number of resonating structures, greater is the stability attached to a carbocation. Carbocation (II) which is a tertiary carbocation will give the maximum number of resonating structures involving hydride shift, like

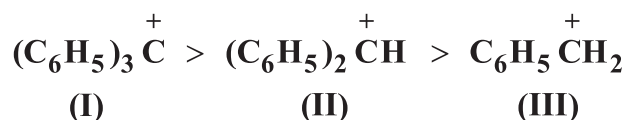


Greater the number of hydrogens on carbon atoms in the immediate neighbourhood of carbocation, greater the number of resonating structures and hence greater the stability.

This is followed by secondary carbocation IV, primary carbocation I and methyl carbocation (III). Hence the order of stability in increasing order is:



Example 8: Order of stability of carbocation is as under. Explain.



Solution: Carbocation (I) gives the maximum number of resonating structures, as this is linked to three benzene rings, hence this will have maximum stability.

For details, see Art. 2.8.

The order of stability in decreasing order is:



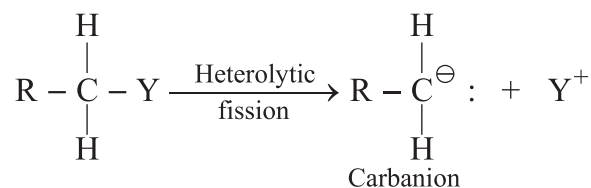
Example 9: Why tropyllium bromide gives precipitate with AgNO_3 and CH_3Br does not?

Solution: This is because tropyllium bromide behaves like an ionic compound whereas methyl bromide does not. Ionic nature of tropyllium ion is because of extra stability of tropyllium ion. For details refer to Art. 2.9.

2.23 CARBANIONS

These are defined as the *species with an unshared pair of electrons and a negative charge on the central carbon atom*. A carbanion may be formed in one of the following ways:

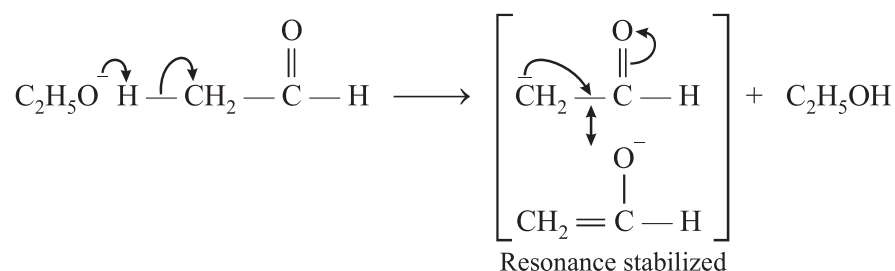
(i) An atom or group leaves carbon without the electron pair (Heterolytic fission).



(ii) An anion adds to a carbon-carbon double or triple bond



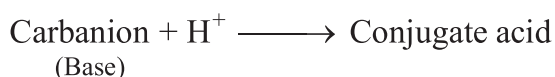
(iii) A strong base abstracts a proton from a carbonyl or cyano compound



(iv) A strong base abstracts hydrogen of terminal acetylenes



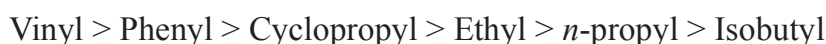
Every carbanion possesses unshared pair of electrons and is therefore a base. When the carbanion accepts a proton, it gives a conjugate acid. The stability of the carbanion is directly related with the strength of the conjugated acid.



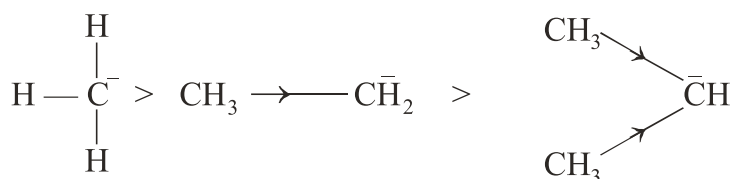
Stability of carbanions

1. It is important to note that weaker the acid, stronger is the base and hence lower is the stability of the carbanion. Clearly, the order of stability of carbanion can be determined from the order of the strength of conjugate acids. Carbanions are highly unstable in solution as compared to carbocations.

2. The order of stability of carbanions is:

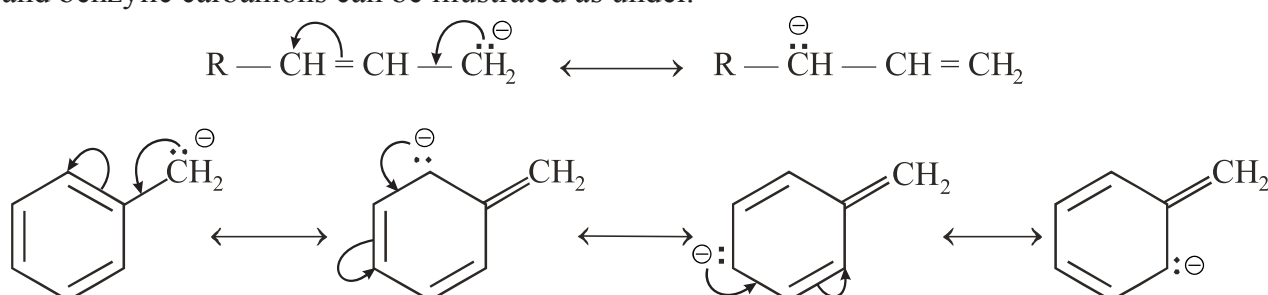


Also it has been found that the stability of carbanions decreases in the order methyl > prim-carbanion > sec-carbanion.



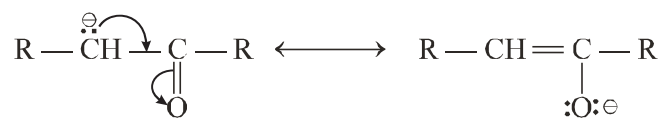
This stability order can be explained simply by the field effects. The presence of electron donating alkyl groups in secondary (Isopropyl) carbanion results in greater localisation of negative charge on the central carbon atom and hence the stability falls. Cyclopropyl carbanion has greater stability due to greater *s*-character on the carbanionic carbon.

3. Vinyl and phenyl carbanions are more stable due to resonance. In cases where a double or triple bond is located at α -position to the carbanionic carbon, the ion is stabilised by resonance in which the unshared pair overlaps with π -electrons of the double bond. The stability of allylic and benzylic carbanions can be illustrated as under.

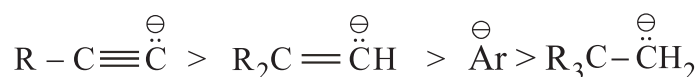


4. Diphenyl methyl and triphenyl methyl carbanions are more stable than even benzylic and can be kept in solution for a longer time if water is completely excluded.

5. When the carbanionic carbon is conjugated with a carbon-oxygen or carbon-nitrogen multiple bond, then the stability of carbanion is increased. The reason is that the presence of electronegative atoms helps in the dispersal of negative charge and thus such carbanions are better capable of bearing the negative charge. Thus,

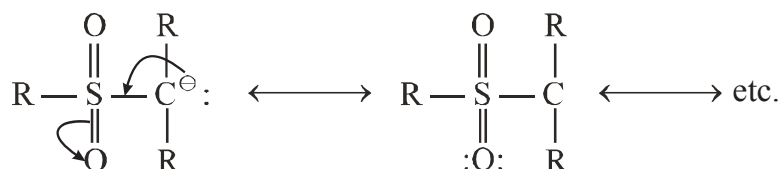


6. The increase in the *s*-character at the central carbon increases the stability of carbon. Thus, the order of stability is expressed as:



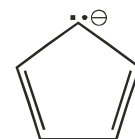
Acetylenic carbon contains 50% *s*-character being *sp*-hybridised.

7. **Stabilisation by Sulphur or Phosphorus:** The bonding of sulphur or phosphorus atom with carbanionic carbon increases the stability. It is probably due to the overlap of unshared pair with an empty *d*-orbital. Consider a carbanion containing sulphur atom:



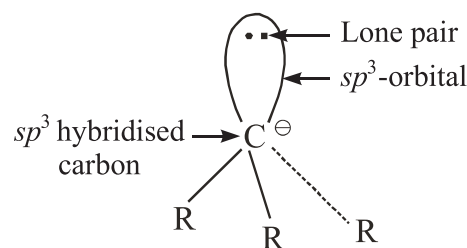
8. **Aromatic nature.** Some carbanions are stable as they are aromatic. *e.g.*, cyclopentadienyl anion is a stable carbanion.

Huckel's ($4n + 2$) rule is satisfied here with 6π electrons in the ring.



Structure and reactions of carbanions

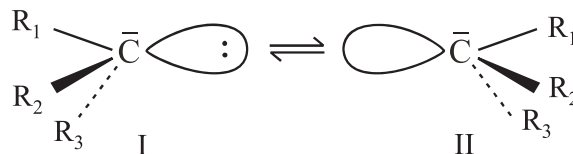
Structure. The carbanions, being unstable have not been isolated. Therefore, their structure is not known with certainty. Most likely, the central carbon atom with an unshared pair of electrons (and negative charge) is *sp*³ hybridised. The three *sp*³ hybrid orbitals are used in forming three sigma bonds with the other atoms. The fourth *sp*³ -orbital is occupied by a lone pair of electron. In fact, the structure of carbanion is quite similar to that of ammonia as shown in the figure.



Carbanions which get stabilized by resonance involving the lone pair of electrons and the π electrons of multiple bonds, should be planar as this is the necessary condition for resonance to take place.

Carbanions of $\text{R}_1\text{R}_2\text{R}_3\text{C}^-$ are optically inactive. Why?

If the *sp*³ orbital containing the lone pair of electrons is considered as fourth substituent, then carbanions of the type $\text{R}_1\text{R}_2\text{R}_3\text{C}^-$ should be optically active as the carbon is linked to four different groups (chiral) and it should be possible to obtain two optical forms. But in actual practice, these forms have not been obtained. We explain it by saying that the pyramid structure of the carbonion is not rigid and it undergoes rapid inversion as shown below:

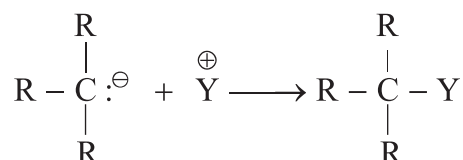


Consequently, one optical form (say structure I) gets converted to structure II and a racemic mixture is obtained which is not easily resolvable.

Reactions

Some important reactions of carbanions are described below:

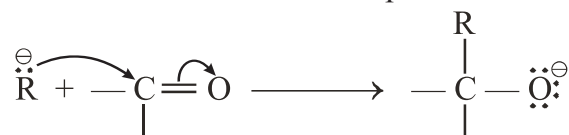
1. Reaction with positive species or electrophiles. A carbanion reacts with a proton or with another action.



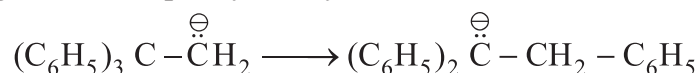
2. Reactions involving the displacement of an atom or a group. Such reactions are nucleophilic substitution (S_{N}^2) reactions observed in alkyl halides.



3. Addition to carbonyl compounds. Carbanions attack an electron deficient carbon in the carbonyl compounds. Such reactions are called nucleophilic addition reactions.



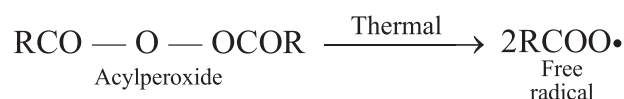
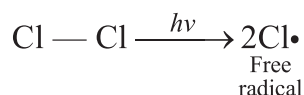
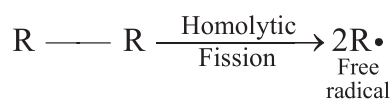
4. Rearrangement. In some cases, carbanions may rearrange to form more stable species. Consider the rearrangement in triphenylmethyl carbanion.

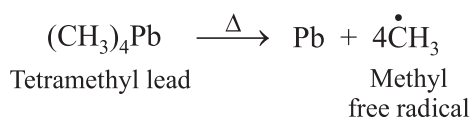


Here the two phenyl groups directly attached to the central carbon help in dispersing the negative charge.

2.24 FREE RADICALS

Free radicals are produced by the homolytic fission of a covalent bond. These are odd electron neutral species which are formed by the homolytic fission of a covalent bond. Free radicals are paramagnetic due to the presence of unpaired electron. Formation of free radicals is favoured by the presence of UV light, heat and organic peroxides. Reactions involving radicals widely occur in the gas phase. Such reactions also occur in solutions, particularly if carried in non-polar solvents. An important characteristics of free radical reactions is that, once initiated, they proceed very fast. The free radicals can be detected by magnetic susceptibility measurements.



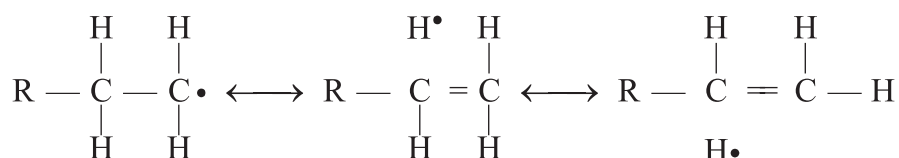


Stability of free radicals

1. Simplest alkyl free radicals are highly reactive like carbocations and carbanions. Their life time is extremely short in solution. The relative stability of simple alkyl radicals has the order:

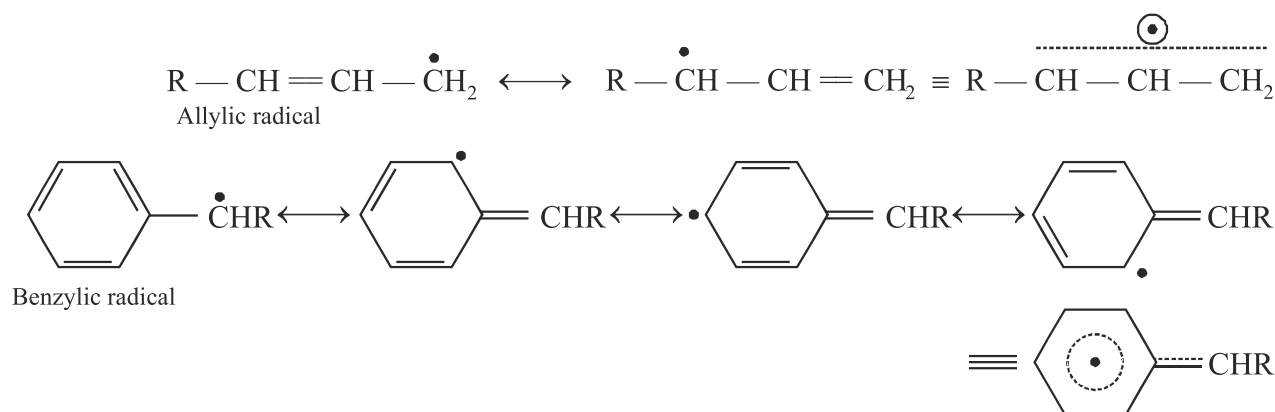


It can be explained on the basis of hyperconjugation similar to that in carbocations.

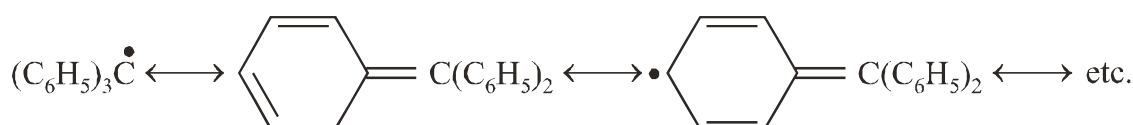


Greater the number of the resonating structures, greater is the stability of the free radical.

2. Allylic and benzylic type of free radicals are more stable and comparatively less reactive than simple alkyl radicals. The reason is the delocalisation of the unpaired electron over the π -orbital system.



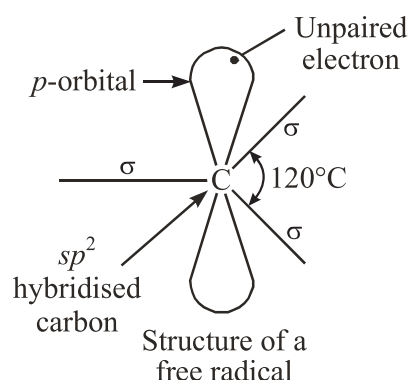
3. Triphenyl methyl and triarylmethyl radicals are much more stable in solution at room temperature. The stability of such radicals is due to resonance.



Steric hindrance to dimerisation is probably the major cause of their stability. If each aromatic nucleus in the radical has a bulky *p*-substituent, then irrespective of any substitution at the *o*-positions, dimerisation will be greatly inhibited and hence radical stability increases.

Structure and reactions of free radicals

Structure. The state of hybridisation of carbon atom having the unpaired electron is not clearly established. However, it is believed to be either pyramidal (like ammonia)

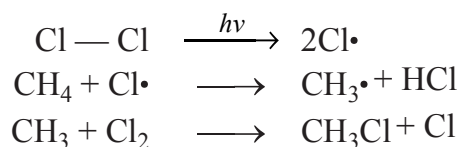


or planar. But experimental evidence suggests strongly that the alkyl radicals such as methyl radical are actually planar with sp^2 hybridisation. The three coplanar hybrid orbitals are used in the formation of three sigma bonds with other atoms. The unhybridised orbital which lies in a plane at right angles to the plane of the hybrid orbitals, carries the unpaired electron. ESR spectra of $\dot{\text{C}}\text{H}_3$ and other simple alkyl radicals indicate that these radicals have planar structures. This is also in accordance with the fact that optical activity is lost when a free radical is generated at an asymmetric carbon. As a general rule, we can say that simple alkyl free radicals prefer a planar or near planar shape. However, the free radicals in which the carbon is connected to atoms of high electronegativity prefer a pyramidal shape. The increase in electronegativity causes the deviation from the planar geometry.

Reactions

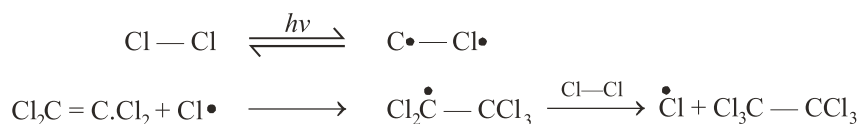
Some important reactions of free radicals are described below:

1. Halogenation of aliphatic hydrocarbons



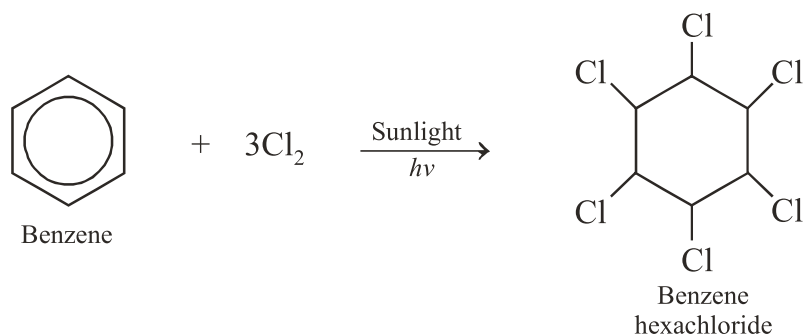
In the presence of sunlight, chlorination of methane gives chloromethane, dichloromethane, chloroform and carbon tetrachloride.

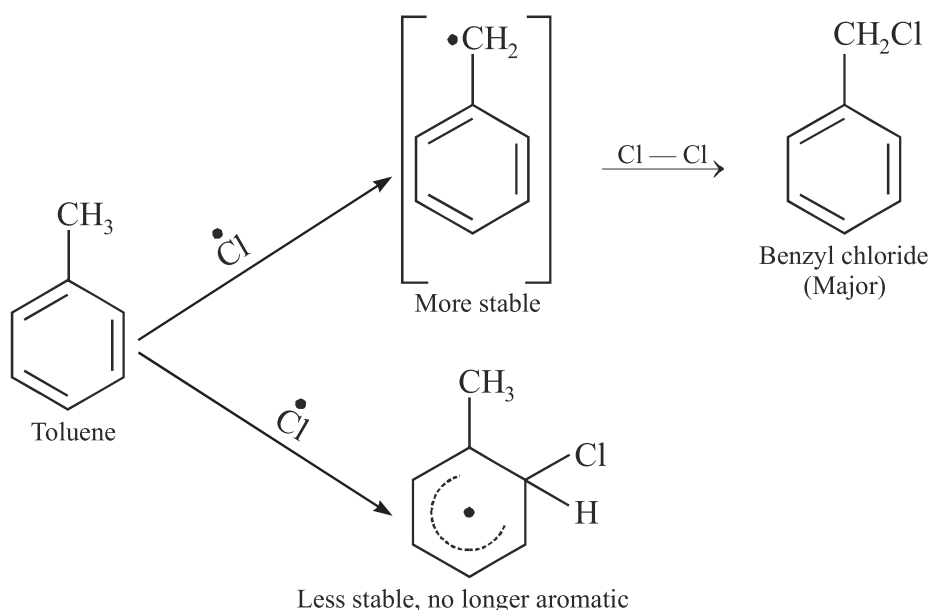
2. Addition. Halogen addition to alkenes takes place with free radical mechanism. The addition of chlorine to tetrachloroethene is photochemically catalysed. A molecule of chlorine undergoes homolytic fission giving two chlorine radicals. Each radical is capable of initiating a reaction chain.



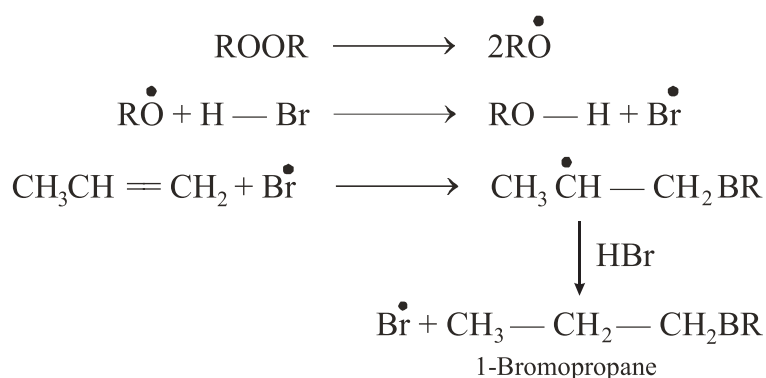
$\dot{\text{C}}\text{Cl}$ radical further adds to tetrachloroethene. This continues till the whole of tetrachloroethene has been converted into hexachloroethane. Chain termination occurs through radical-radical collision. The radical reactions are inhibited by the presence of oxygen. The reason is that the molecule of oxygen has two unpaired electrons and behaves as a biradical. This biradical combines with highly reactive radical intermediate and converts it to less reactive peroxy radical which is unable to propagate the chain reaction.

3. Consider the addition of chlorine to benzene in the presence of light. The reaction proceeds by radical intermediates and gives benzene hexachloride. But the attack of chlorine radical on toluene results in preferential hydrogen abstraction giving substitution in CH_2 group. Clearly, it is because of the greater stability of benzyl radical due to delocalisation.

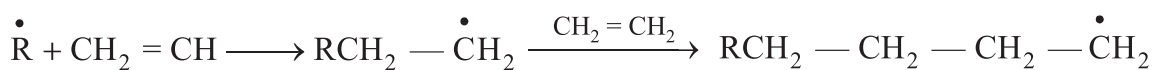




4. The addition of HBr to propene in presence of peroxides yields 1-Bromopropane. The reaction involves the formation of radical intermediates giving anti-Markownikoff addition. In this reaction, Br^\bullet radical attacks propene to form a more stable secondary free radical.

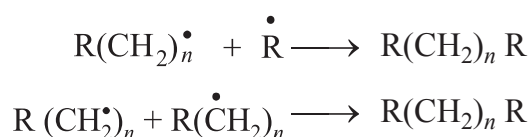


5. **Vinyl polymerisation.** Radical reactions also produce polymers of great importance. Like other radical reactions, polymerisation reactions also constitute three step viz.; initiation, propagation and termination. In initiation step, a free radical is formed under the influence of peroxide. The radical formed then propagates the chain reaction.



and so on.

In the final step, the collisions between the radicals terminate the reaction

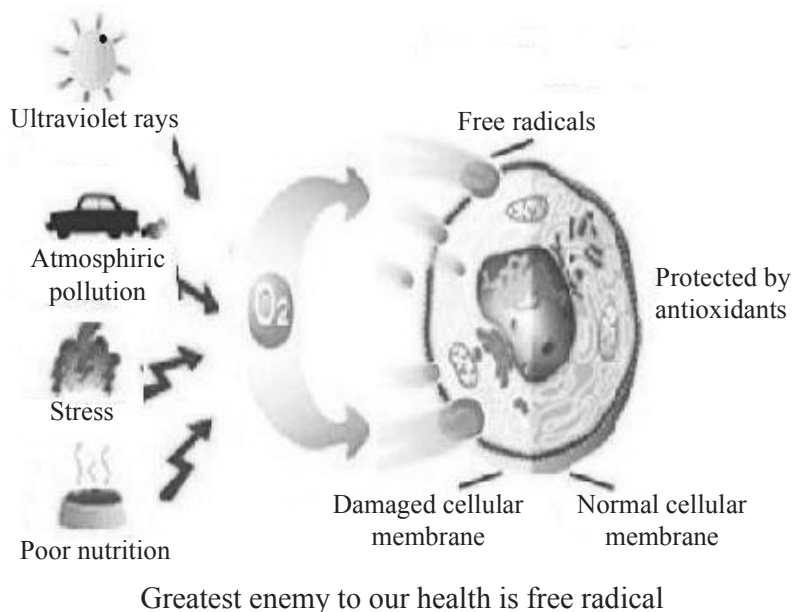


Polythene, PVC, teflon etc. are the polymers which are formed from the respective monomers by radical pathways.

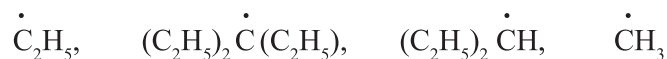
Applying Chemistry to Life

Most common form of free radicals comes from oxygen. When an oxygen molecule becomes electrically charged, it causes damage to your DNA and other molecules. Over time this damage may become irreversible and lead to diseases like cancer.

Antioxidants are our friends, they protect the cells from damage caused by free radicals. Antioxidants can be found in foods containing beta-carotene (carrots) lycopene (tomatoes) and foods with high amounts of vitamin C (kiwi, berries, dark leafy greens) and vitamin E (seeds, nuts and apricots).

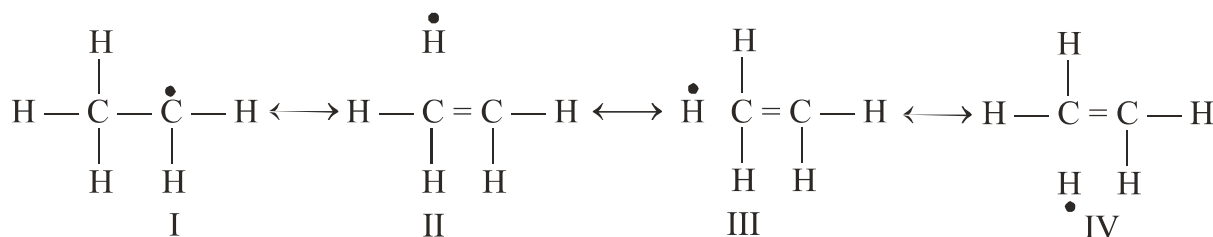


Example 10: Arrange the following free-radicals in increasing order of stability and explain your answer.



Solution: The order of stability can be given considering the hyperconjugation phenomenon.

(i) Ethyl radical is a hybrid of four resonating structures.



2.25 CARBENES

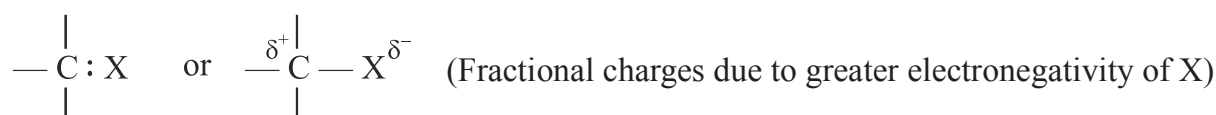
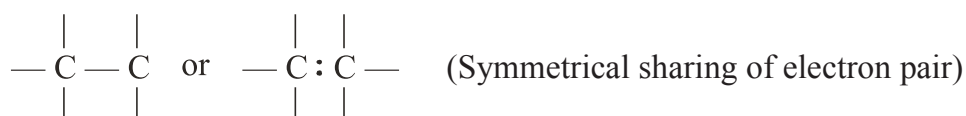
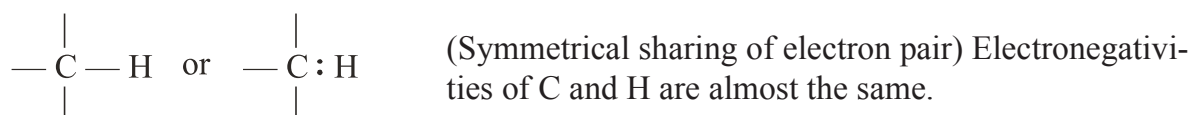
These are defined as the neutral organic species containing a divalent carbon atom having a set of electrons but no charge on it. For example,



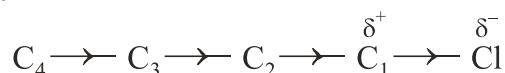
Formation of carbenes

They can be generated by the following methods:

called the inductive effect. The development of partial +ve and -ve charges is due to shift of the shared pair of electrons towards the more electronegative atom. This results in small fractional charges on the constituent atoms. When a carbon atom is bonded to a hydrogen (C-H) or another carbon (C-C) atom by a covalent bond as in alkanes, the sharing of electron-pair is symmetrical between them. Thus, no charges are induced on the atoms. However, when carbon is bonded to a halogen (X), charges are created.



The direction of displacement is shown by placing an arrow head midway along the line representing the sigma bond.



The inductive effect of an atom or a group of atoms diminishes rapidly with distance. Infact, the inductive effect is almost negligible beyond two carbon atoms from the active atom or group.

Inductive effect does not involve actual transfer of electrons from one atom to another but simply helps in displacing them permanently.

Groups with - I effect:



Decreasing order of - I effect \longrightarrow

Groups with + I effect:



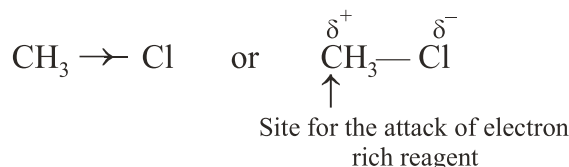
Decreasing order of + I effect \longrightarrow

Characteristics of inductive effect

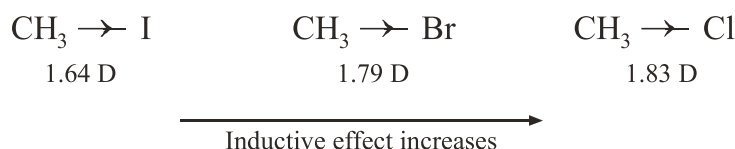
1. Inductive effect arises due to displacement of σ -electrons only and occurs in molecules containing polar and single bonds only.
2. Inductive effect is permanent and irreversible.
3. Inductive effect diminishes progressively as we move away from electron-donating or electrons withdrawing group/atom along the molecule chain.
4. The electrons that are displaced do not leave their orbital. A little distortion of the orbital occurs which causes polarisation.
5. Depending upon the electrons-withdrawing or electron-donating strength, different atoms or groups polarize the covalent bonds to different extent.

Applications

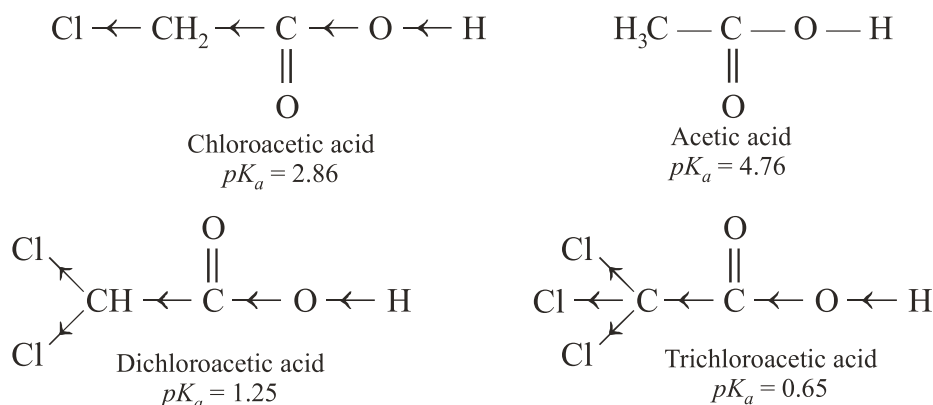
(i) **Reactivity of alkyl halides:** The presence of halogen atoms in the molecule of alkyl halide creates a centre of low electron density on adjacent carbon which is readily attacked by the negatively charged reagents.



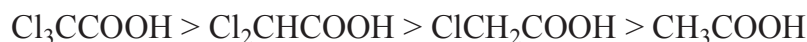
(ii) **Dipole moment:** As the inductive effect increases, the dipole moment increases. This is because the dipole moment is the product of distance and charge.



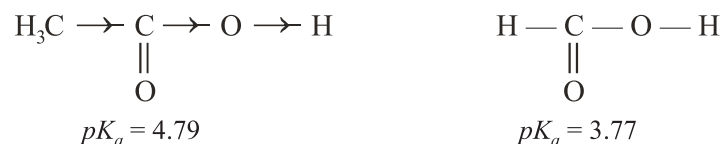
(iii) (a) **Acidity of acetic acid and halogen substituted acetic acid:** Electron-attracting groups increase the acid strength of the acid as such groups help in the removal of protons. Greater the number of such electron withdrawing group, greater is the acid strength of the acid. pK_a values of some acids are given below. It may be remembered that smaller the pK_a value, higher is the acid strength



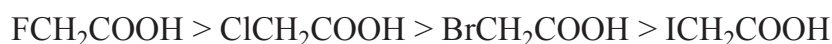
The decreasing order of acid strength



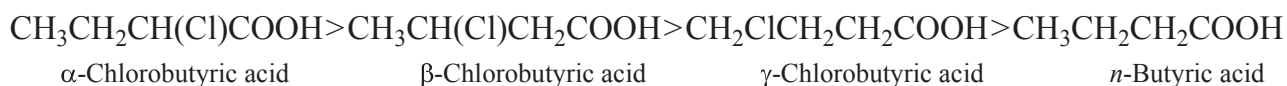
(b) **Relative acid strength of formic acid and acetic acid:** Methyl group has an electron-releasing inductive effect (+I effect). It reduces the release of protons. Therefore acetic acid is a weaker acid than formic acid.



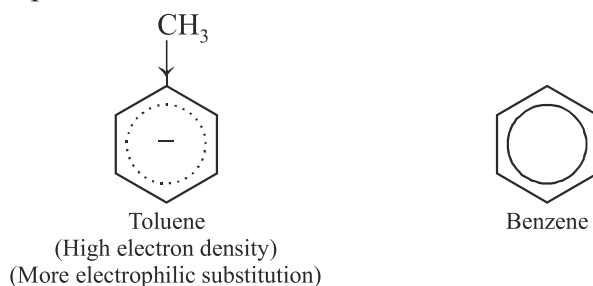
(c) **Relative acid strength of fluoroacetic acid, chloroacetic acid, bromoacetic acid and iodoacetic acid:** Halogenated acids are much stronger acids than the parent acid and the acidity increases with the increase in electronegativity of the halogen present which helps in the release of protons. Thus, the strength of halogenated acids follows the order:



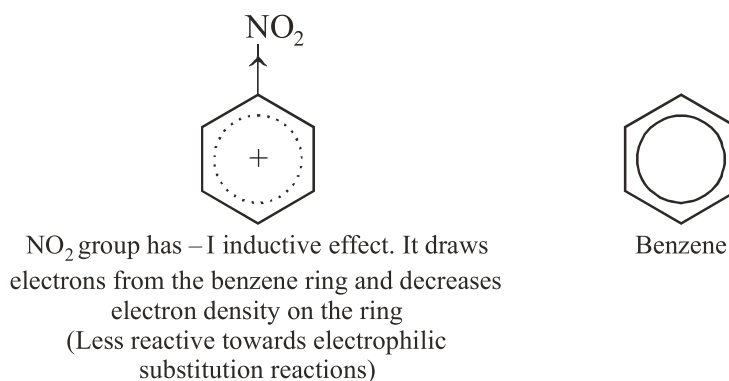
Inductive effect decreases with increase in distance of halogen atom from the carboxylic group, hence the strength of the acid is proportionally decreased. Thus,



(iv) (a) Relative reactivity of toluene and benzene in aromatic substitution reactions:
 Aromatic substitution reactions are electrophilic in nature. Methyl has an electron-releasing inductive effect (+I effect). Therefore, toluene with higher electron density than benzene has greater reactivity in electrophilic substitution reactions.

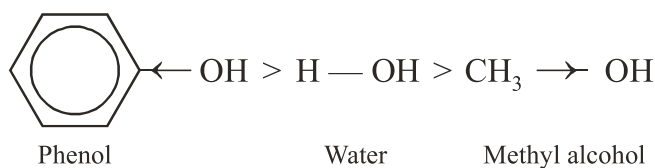


(b) Relative reactivity of nitrobenzene and benzene in electrophilic aromatic substitution reactions



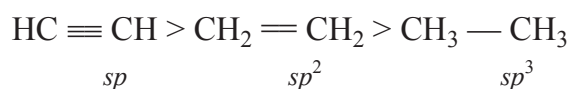
(v) Compared to water, phenol is more acidic ($-I$ effect) but methyl alcohol is less acidic ($+I$ effect):

This is because phenyl group has $-I$ effect while methyl group has $+I$ effect.



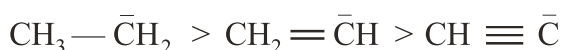
(vi) Inductive effect is dependent on state of hybridisation of the atoms linked by covalent bond:

Relative acidity of hydrocarbons may be given as



Electron density on *s*-orbital is more than on, *p*-orbital. Percentage of *s* character decrease from left to right.

Relative basicity of corresponding carbanions is as:

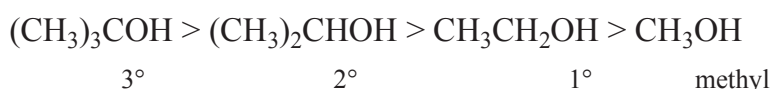


(vii) Strength of base: Base strength is defined as the tendency to donate an electron pair for sharing. Strength of a base can be explained on the basis of inductive effect.

- (a) As compared to ammonia, methyl amine is more basic (+I effect) but aniline is less basic and diphenyl amine is a still weaker base (–I effect).



- (b) The decreasing order of base strength in alcohols from tertiary to primary is due to +I effect of alkyl groups.



- (c) Greater the tendency to donate electron pair for coordination with proton, more is the basic nature, or in other words more the negative charge on nitrogen atom (due to +I effect of alkyl group), higher is the basic strength.

Aliphatic 1°, 2° and 3° amines contain one, two and three alkyl groups attached to the nitrogen atom respectively as shown below:



On the basis of +I effect of alkyl groups alone, the expected order of basicity should be: 3° amine > 2° amine > 1° amine. This order is really followed by the amines in **gaseous state**. However, the observed order of basicity **in aqueous solution** is:



Explanation for the above observation is as under:

Basicity of an amine in aqueous solution does not depend only on the electron density on nitrogen in the compound but it also depends upon the stability of the conjugate acid obtained on accepting a proton which is in the order



The combined effect of electron density on N and the stability of the conjugate acid formed is that the observed order of basicity in aqueous solution is

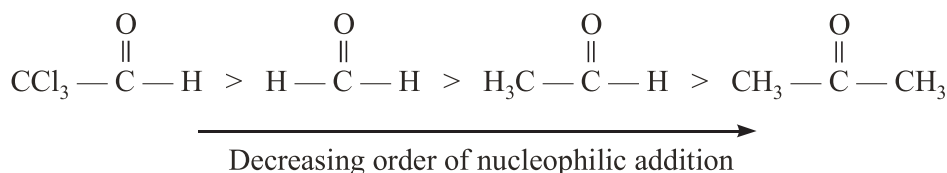
secondary amine > primary amine > tertiary amine

(viii) Relative stabilities of carbocations: Greater the number of alkyl groups attached to positive carbon, greater the dispersal of charge and hence greater is the stability.



(ix) +I group increases electron availability on carbonyl carbon: This therefore decreases the rate of nucleophilic addition.

On the other hand, electron-withdrawing –I group decreases electron availability on carbonyl carbon and therefore increases the rate of nucleophilic addition



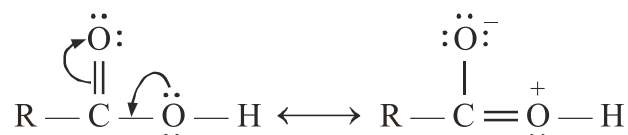
If a compound having a certain molecular formula can be represented by different structural formulae which differ only in the arrangement of the electron pairs and not of the atoms, such like structures are called **resonating** or **contributing** or **canonical structures** and the phenomenon is known as **resonance**. The compound cannot be represented completely by any of the resonating or contributing structures but by a mixture of all of them which is called **resonance hybrid** (cannot be actually represented). Resonance is indicated by the sign \longleftrightarrow .

It may be noted that the various resonating or contributing structures do not actually exist i.e., they are all hypothetical structures. They have been given simply to explain certain properties of the compounds which cannot be otherwise explained.

Examples of Resonance

A common analogy of a resonance hybrid is that of a mule which is a hybrid of horse and donkey.

1. Monocarboxylic acid. The acidic character of monocarboxylic acid is explained with the help of resonance. The following contributing structures for the monocarboxylic acid are possible which differ in the position of the electron pairs.

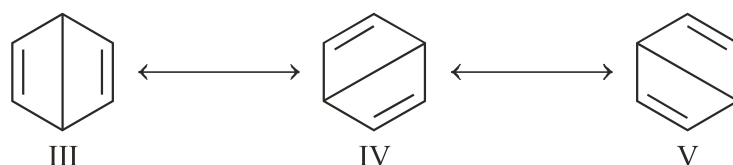


As a result of resonance, the oxygen atom of the O—H group acquires a positive charge i.e., it draws the electrons pair towards itself resulting in the release of protons.

2. Benzene. Benzene is a hybrid of two equivalent contributing structures (I and II) which differ in the position of the π -electron pairs representing double bonds. These were suggested by Kekule.

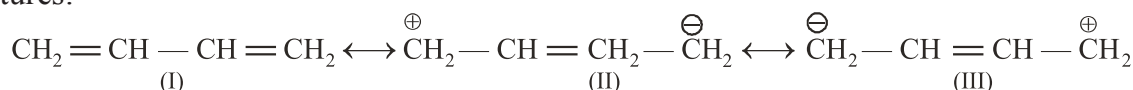


Three more contributing structures (III, IV and V) have been proposed by **Dewar**. Being less symmetrical they have small contribution (28% only) towards the hybrid. Benzene exists mainly in the form of **Kekule structures** (I and II). Benzene is, in fact, quite stable and its stability is explained



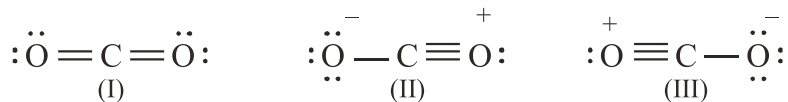
with the help of resonance. As the π -electron charge is distributed over greater area i.e., it gets delocalised.

3. 1, 3-Butadiene. The diene can be regarded as the hybrid of the following contributing structures:



The charged structures II and III make lesser contribution towards the hybrid. However, they do explain the 1, 4-addition in the conjugated dienes.

4. Carbon dioxide. The structural formula of carbon dioxide (CO_2) molecule is $\text{O} = \text{C} = \text{O}$. The standard $\text{C} = \text{O}$ bond length is 122 pm but the bond length which is obtained for the molecule from spectroscopic studies is 115 pm. The difference in the bond length values can be explained by considering the following structures for carbon dioxide which are known as the *resonating structures*, or *contributing structures* or *canonical structures*.



The carbon-oxygen bond length is the mean of all the bond length values. Carbon dioxide cannot be represented by any of the contributing structures but by an average of all. Carbon dioxide is said to be a resonance hybrid of these structures.

Conditions of resonance

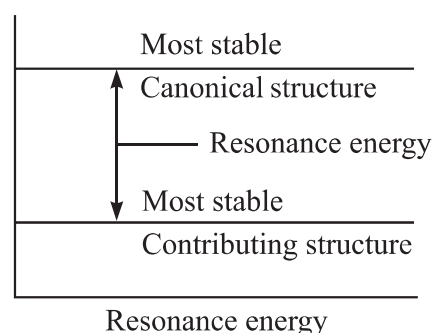
Wheland has suggested the following conditions for resonance:

- (i) The resonance or the contributing structures must differ only in the position of the electron pairs and not of the atomic nuclei.
- (ii) The resonating structures must have the same number of paired and unpaired electrons.
- (iii) The energies of the various resonating structures must be either same or nearly the same.
- (iv) All the contributing or resonating structures do not contribute equally towards the hybrid. The equivalent structures have greater contribution. The contribution of any resonating structure towards the hybrid depends upon the following factors:
 - (a) Structures with more covalent bonds are more stable than the structures with less covalent bonds.
 - (b) The charged contributing structure is less stable as compared to the structure without any charge.
 - (c) Structure with negative charge on more electronegative atom is more stable than the structure with negative charge on less electronegative atom.

Effects of resonance

Some effects of the resonance are explained as under:

1. Stability. As a result of resonance, the energy of the hybrid decreases and its stability, therefore, increases. Greater the number of contributing structures, greater will be the stability of the hybrid. The stability also depends upon the equivalence of the contributing structures. Moreover, the charged structures have less contribution than the uncharged structures.



2. Resonance energy. The relative stabilities of two different resonance hybrids may be compared in terms of **resonance energy**. It may be defined as the difference in the energy content of the hybrid and its most stable contributing structure. It may be expressed either as the difference in the heat of combustion of the contributing structures and the hybrid or in terms of the difference in the heat of hydrogenation values. Consider the following examples:

(a) **Heat of combustion value.** In benzene, the heat of combustion of the contributing structure is calculated by determining the values for different bonds mathematically.

Heat of combustion of 6 C — H bonds = $6 \times 225.5 = 1355$ kJ / mole

Heat of combustion of 3 C — C bonds = $3 \times 206.0 = 618$ kJ/mole

Heat of combustion of 3 C = C bonds = $3 \times 491.0 = 1473$ kJ/mole

3446 kJ/mole.

The value as determined experimentally for the hybrid is 3300 kJ/mole. Thus, the resonance energy for benzene is $(3446 - 3300)$ kJ or **146 kJ/mole**.

Similarly, resonance energies for some typical molecules are as follows:

1, 3-Pentadiene (17.6 kJ / mole); 1, 3-Butadiene (14.6 kJ/mole) and 1, 3-Cyclohexadiene (7.5 kJ/mole).

(b) Heat of hydrogenation value. In benzene, the expected heat of hydrogenation value is 376 kJ/mole. But the value for the hybrid as determined experimentally is 230 kJ/mole *i.e.* the resonance energy is the same *i.e.* $(376 - 230)$ kJ or (146 kJ/mole).

The relative stabilities of two hybrids can be compared in terms of the resonance energy value.

3. Bond length values. The resonance causes a change in bond length values. For example, the standard C — C bond length is 154 pm and C = C bond length is 134 pm. But the value as determined for benzene is 139 pm which does not coincide with any of the two values and is intermediate between the two values.

Types of resonance or mesomeric effect

Depending upon the nature of the functional group present adjacent to the multiple bond, the resonance effect (R) or mesomeric effect (M) is of two types depending upon the nature of the group which is present.

(i) Groups having electron-withdrawing resonance effect. Groups such as — NO₂, > C = O, — C ≡ N, — COOH etc. tend to withdraw the electrons from the multiple bond through resonance and are said to have — M or — R effect. For example, in the following compound, the aldehyde group (— CH = O) has — R effect.



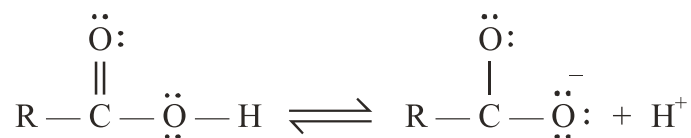
(ii) Groups having electron-releasing resonance effect. Groups such as — $\ddot{\text{N}}\text{H}_2$, — NHR, — NR₂, — $\ddot{\text{O}} - \text{H}$, — $\ddot{\text{O}} - \text{R}$ etc. which can release electrons through resonance are said to have + M or + R effect. For example, the amine group (— NH₂) in the following compound has + R effect



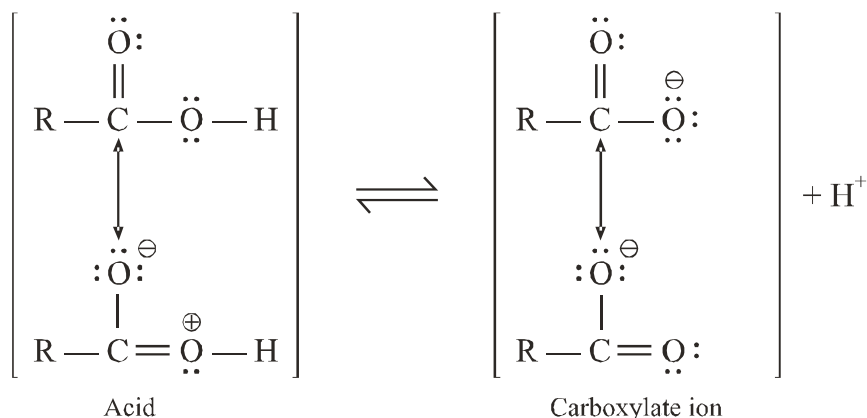
Applications of resonance effect

Resonance effect or mesomeric effect is quite useful in explaining many observations in organic compounds. A few typical applications are being listed as follows:

1. Explanation for the acidic character of carboxylic acids. The acidic character of carboxylic acids is due to release of H⁺ ion in aqueous solution.

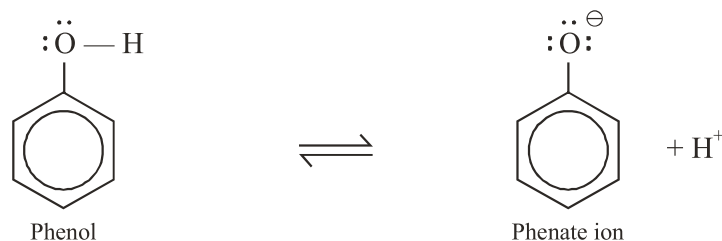


This is explained with the help of resonance. Both the acid and the carboxylate ion are resonance stabilised as shown below:

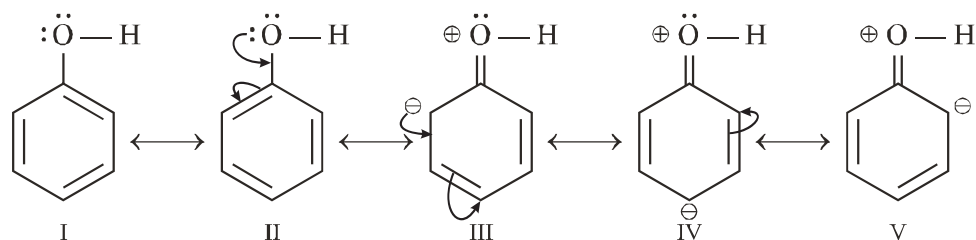


While the contributing structures for the carboxylate ion are exactly equivalent, they are not so for the acid. *Therefore, hybrid for the ion is more stable than hybrid for the acid. The acid changes to a more stable ion by releasing a proton and this accounts for the acidic character of carboxylic acid.*

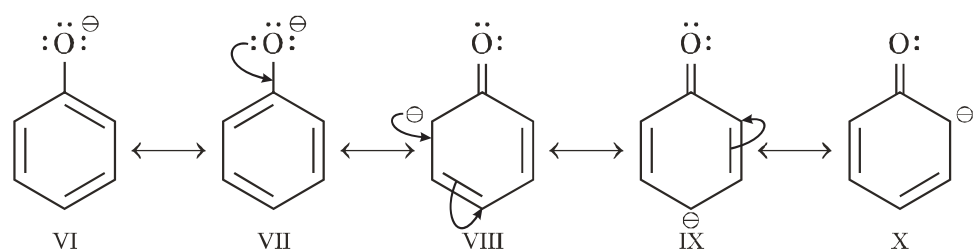
2. Explanation for acidic character of phenols. The acidic nature of phenols is due to the release of H^+ ion in aqueous solution.



The acidic character in phenol is exhibited on the basis of resonance both in phenol and phenate ion. They exist as hybrid of a number of contributing structures as follows:



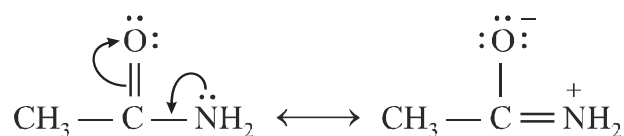
Resonating structures of phenol



Resonating structures for phenate ion

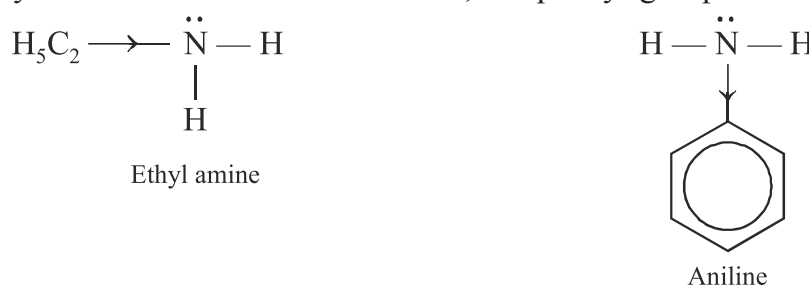
In case of phenol, contributing structures (III), (IV) and (V) involve charge separation *i.e.* they have both positive and negative charges. Energy is needed to separate the opposite charges. But no such structures are noticed in case of phenate ion. Therefore, the hybrid for the phenate ion is more stable and phenol changes to phenate ion by releasing proton. This accounts for the acidic character of phenol.

3. Comparison of relative basic strength of ethyl amine and acetamide. Ethyl amine is a stronger base than acetamide. In ethyl amine, the ethyl group with + I effect increases the electron density on the nitrogen atom. As a result, its electron releasing tendency is more. In acetamide the carbonyl group is an electron withdrawing group and takes away the electron pair from the nitrogen atom because of resonance as shown below:

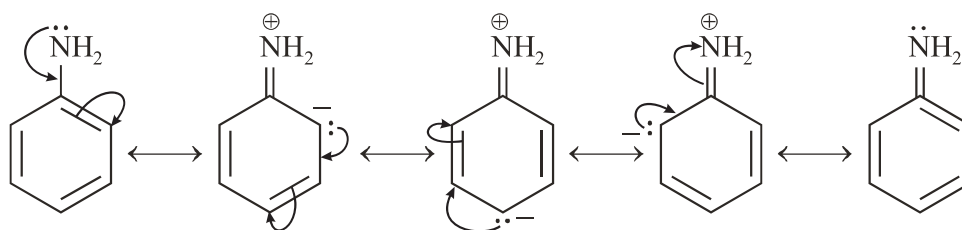


Resonance hybrids of acetamide

4. Comparison of relative basic strength of ethyl amine and aniline. Ethyl amine ($K_b = 5.6 \times 10^{-4}$) is much more basic than aniline ($K_b = 3.8 \times 10^{-10}$). In the former, the ethyl group with + I effect increases the electron density on the nitrogen atom and, thus, increases electron releasing tendency or basic character. In the latter, the phenyl group with – I effect tends to



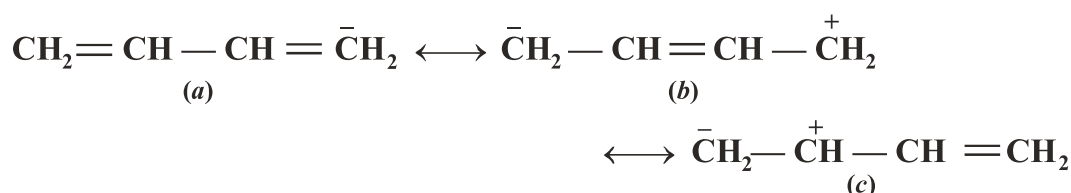
decrease the electron density on the nitrogen atom resulting in a decreased basic strength. Aniline is a hybrid of following contributing structures:



The electron density on the nitrogen atom decreases, consequently, the electron releasing tendency or basic strength decreases.

Solved Examples

Example 1: Which of the following canonical forms would contribute most towards resonance? Explain.



Solution: The resonance structures fulfilling the following conditions are more stable.

1. Greater number of covalent bonds
2. Less separation of charges
3. Negative charge on electronegative atom
4. Positive charge on electropositive atom
5. More dispersal of charges

Structure (b) takes care of dispersal of charge.

Hence, it is more stable and contributes more towards resonance.

Example 2: By what electronic effect can you explain the low reactivity of halogen atom in vinyl bromide.

or

On the basis of resonance, how will you explain low reactivity of vinyl bromide as compared to ethyl bromide?

Solution: Low reactivity of halogen in vinyl bromide can be explained on account of the phenomenon of resonance or mesomerism.



Halogen compounds generally give nucleophilic substitution reactions, in which the halogen is removed as halide ion.

But in the case of vinyl bromide, resonance takes place as illustrated above. This creates a double bond between carbon and bromine. Removal of bromine thus becomes difficult. Moreover, bromine, acquires a positive charge and hence cannot be substituted by a nucleophile. That is why vinyl bromide shows low reactivity.

2.7 COMPARISON OF INDUCTIVE, ELECTROMERIC AND RESONANCE EFFECTS

Sl. Nos.	Inductive effect	Electromeric effect
1	It involves a permanent displacement of the electron pairs in the molecule.	It involves a temporary transference of the electron pair towards more electronegative atom in the molecule.
2	The displaced electron pair does not leave its molecular orbital. There is only a distortion in shape of the molecular orbital.	The electron pair which gets transferred, completely leaves its molecular orbital and takes up a new position.
3	The presence of the outside attacking reagent is not needed.	The presence of the outside attacking reagent is essential.
4	There is a partial separation of the charges.	There is a complete separation of the charges.
5	No ions are formed.	Ions are formed.
6	The presence of multiple bond is not essential.	The presence of multiple bond is essential.

Sl. Nos.	Resonance Effect	Inductive Effect
7	It occurs in conjugated systems.	It occurs in saturated compounds.
8	It involves the transference of the π -electrons.	It involves the displacement of the σ -electrons.
9	It involves delocalisation of electrons.	It does not involve any delocalisation of electrons.
10	It does not undergo any change in charge density with distance.	It decreases as we move away from the atom involved in the initial polar bond.

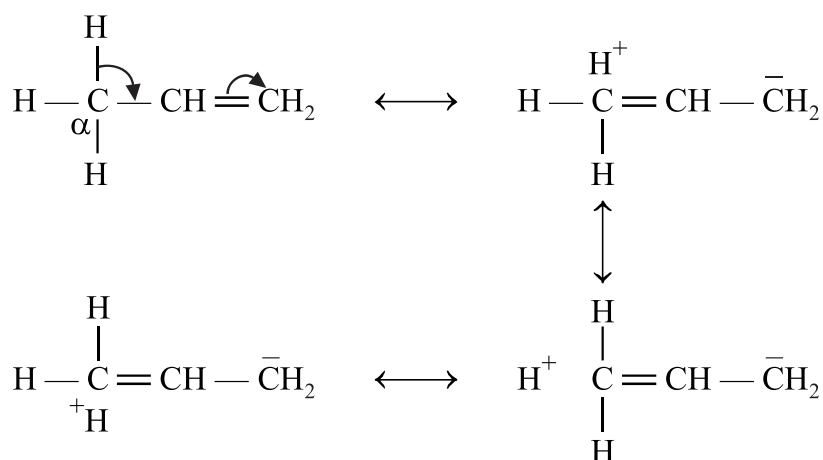
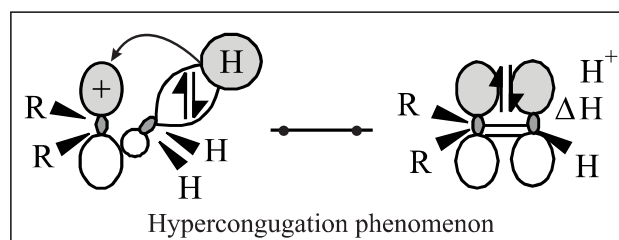
2.8 HYPERCONJUGATION OR NO-BOND RESONANCE

In the study of inductive effect, we have observed that the alkyl group has + I effect and the order of + I effects of different alkyl groups is as under:



But when the alkyl group is attached to an unsaturated system such as $-\text{CH}=\text{CH}_2$ group, or a benzene ring the order of the inductive effect simply gets reversed. This anomaly in the electron releasing tendency of the alkyl groups is explained on the basis of **hyperconjugation** which was developed by *Baker* and *Nathan*. It is also called *Baker-Nathan effect* or *no-bond resonance*.

Explanation. According to the concept, if an alkyl group carrying at least one hydrogen is attached to an unsaturated carbon atom, it releases the electrons of the $\text{C}-\text{H}$ bond towards the multiple bond. For example, in propene ($\text{CH}_3-\text{CH}=\text{CH}_2$), the following contributing structures are involved.



Since there is no bond between the α -carbon atom and one of the hydrogen atoms, the hyperconjugation is also called **no-bond resonance**. Now, hyperconjugation due to CH_3- group is expected to be more than due to CH_3CH_2- group since the latter has only two hydrogen atoms attached to the α -carbon atom directly linked to the double bonded carbon atom. Therefore, the

number of contributing structures for ethyl group will be less. Similarly, the electron releasing tendency in $(\text{CH}_3)_2\text{CH}$ — group will be still less as it has only one hydrogen atom attached to the α -carbon atom and this tendency will be the least when the $(\text{CH}_3)_3\text{C}$ — group is attached to the $\text{CH} = \text{CH}_2$ group. Thus, the order of the electron releasing tendency or inductive effect of the alkyl groups get reversed because of the phenomenon of hyperconjugation.

Orbital concept of hyperconjugation

The orbital concept of hyperconjugation is illustrated with the help of propene ($\text{H}_3\text{C} - \text{CH} = \text{CH}_2$). As mentioned earlier the electron pair of $\text{C} - \text{H}$ bond (σ -bond) is involved in conjugation with the π -electron pair of the double bond. This may be shown with the help of Fig. 2.14.

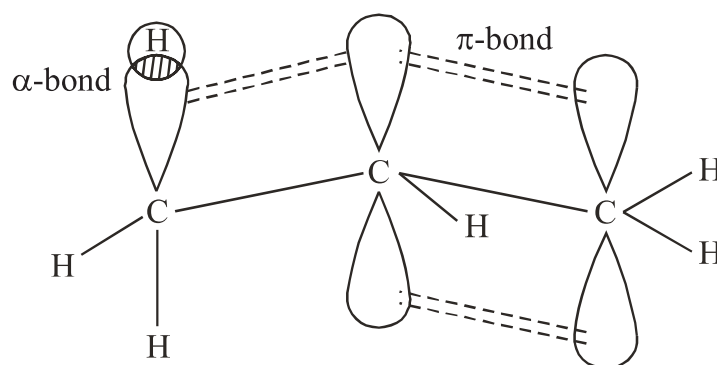


Fig. 2.1: Hyperconjugation in propene.

The $\sigma - \pi$ conjugation is called hyperconjugation. Though hydrogen atom of the methyl group is not forming any real bond with the double bonded carbon atom but it is not actually free to leave its original position. From the orbital structure, it is evident that there is interaction between the electrons of the $\text{C} - \text{H}$ bond and the π -electrons of the adjoining double bond. This will bring about a change in the bond lengths of $\text{C} - \text{H}$ and $\text{C} = \text{C}$ bonds. This has been supported by the experimental determination of the bond lengths.

Applications of hyperconjugation

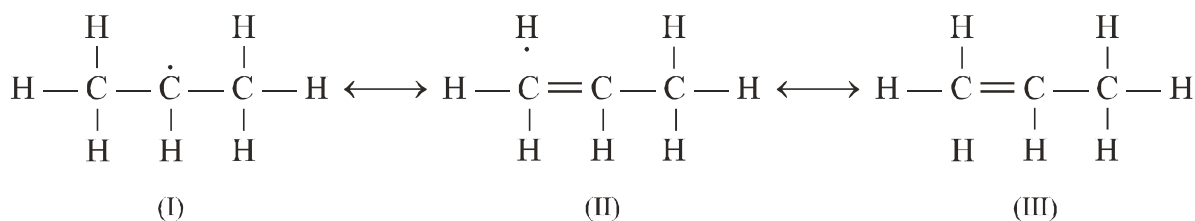
The concept of hyperconjugation is quite useful in explaining relative stabilities of a number of species such as alkyl free radicals, carbocations and alkenes. These are briefly discussed as follows:

1. Relative Stabilities of Alkyl Free Radicals

The order of the relative stabilities of different alkyl free radicals is:

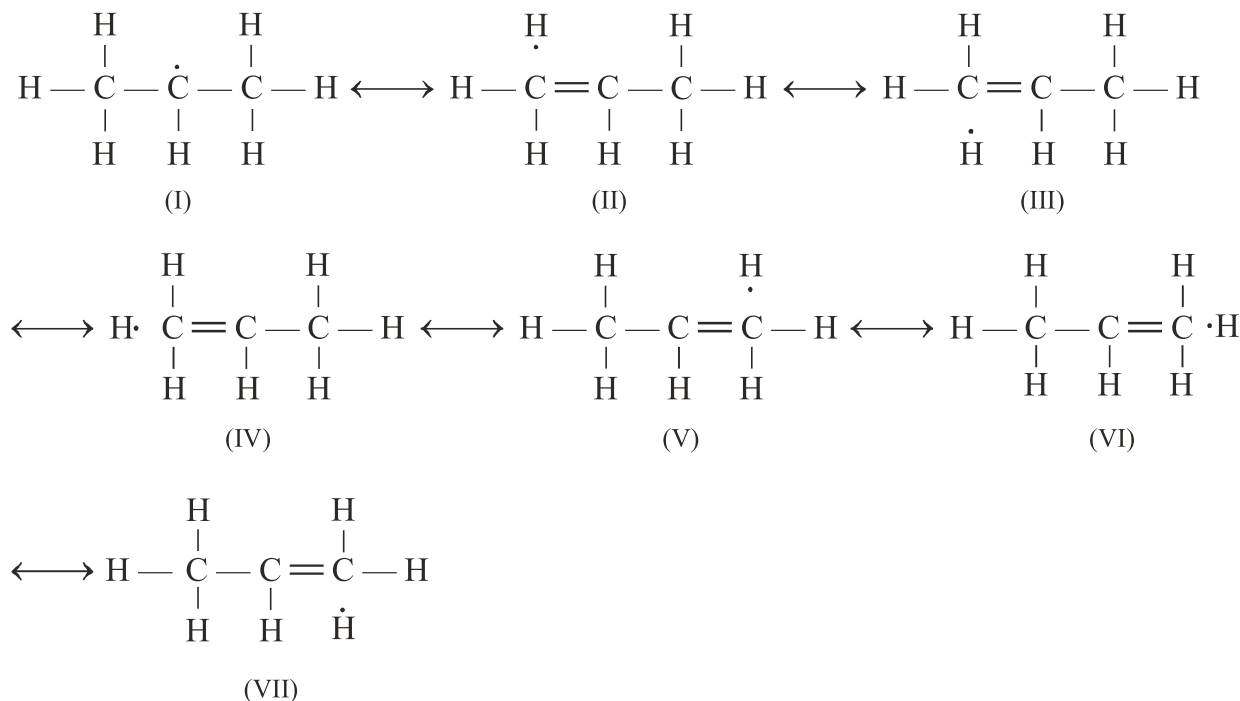


Ethyl free radical is regarded as a hybrid of four contributing structures.



But there is no possibility of any hyperconjugation in methyl free radical. Therefore, ethyl free radical is more stable than the methyl free radical.

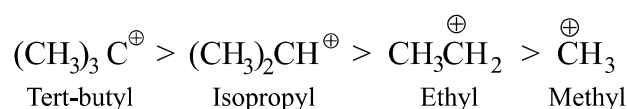
In isopropyl free radical, there are two methyl groups attached to the carbon atom which has single electron. As a result, six contributing structures in addition to normal structure are possible as shown below:



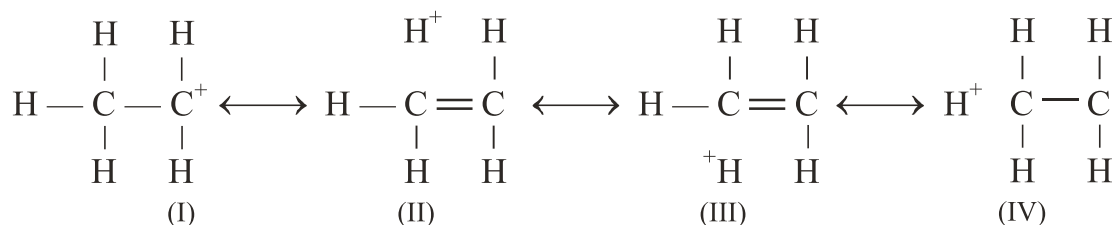
Similarly, *nine contributing structures* are possible for the tertiary butyl free radical in addition to its normal structure. Therefore, it is still more stable and thus, the order of the relative stabilities of the different alkyl free radicals can be explained.

2. Relative Stabilities of Alkyl Carbocations

The order of relative stabilities of the alkyl carbocations is

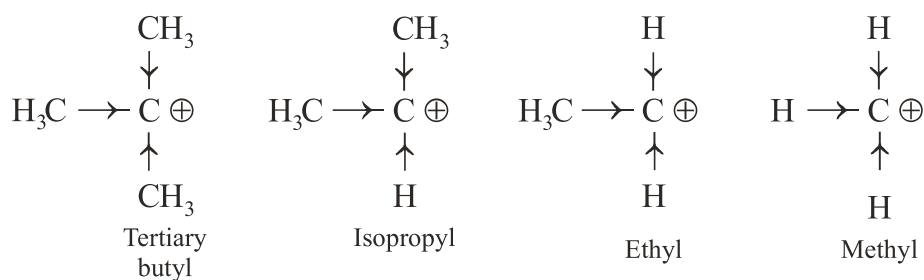


and the order is the same as in case of free radicals. This can also be explained with the help of hyperconjugation. The ethyl carbocation (primary) has three contributing structures in addition to its normal structure based upon hyperconjugation.



It is more stable than methyl carbocation where no resonance is possible. Similarly, the contributing structures in isopropyl carbocation and tertiary butyl carbocation are six and nine respectively in addition to the normal structure. Hence these are more stabilised and relative order of their stabilities is justified.

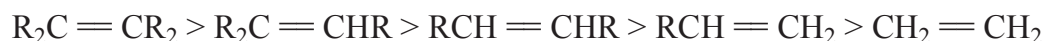
The order of the relative stabilities of the different alkyl carbocations can also be explained with the help of inductive effect (+I effect).



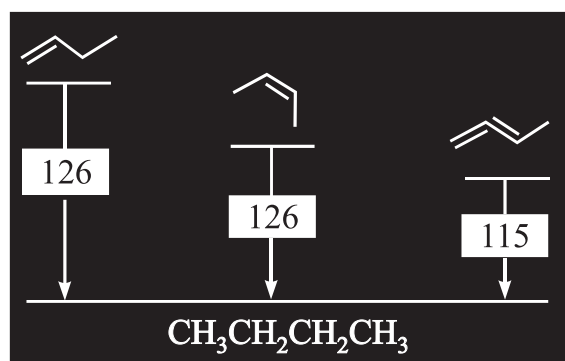
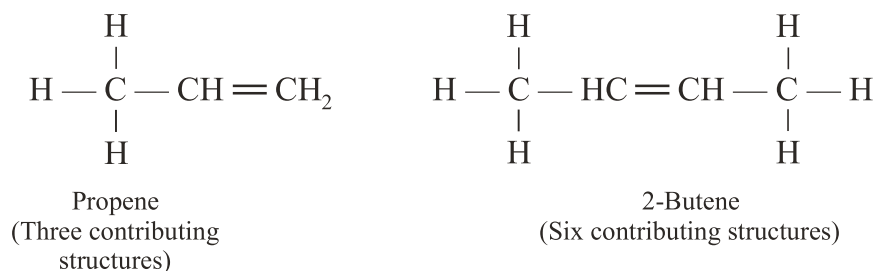
Because of the +I effect, the alkyl group will tend to increase the electron density on positively charged carbon atom neutralising its +ve charge to some extent. As the reactivity of carbocation is due to the positive charge on it, the reactivity will tend to decrease and the stability will correspondingly increase. Thus, greater the number of the alkyl groups present, greater will be the stability of carbocation and lesser will be the reactivity. Thus, the relative stabilities of different alkyl carbocations can be explained.

3. Relative Stabilities of Alkenes

The order of the relative stabilities of different alkenes is:



This can be explained on the basis of hyperconjugation. The presence of alkyl group (say methyl group) on the double bonded carbon atom is likely to increase the number of contributing structures due to hyperconjugation.

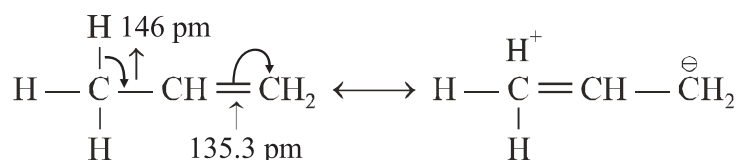


Stability of isomeric alkenes

Thus, greater the number of the contributing structures, greater will be the stability of the alkene.

4. Bond length

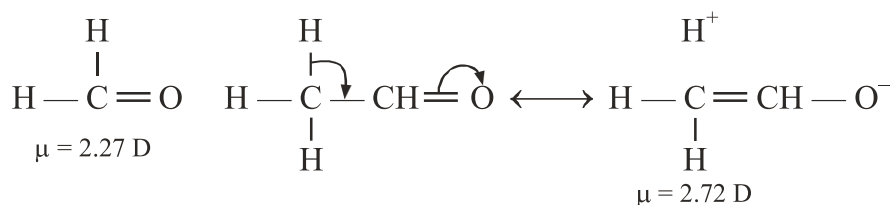
Hyperconjugation, like conjugation and resonance, also affects bond length.



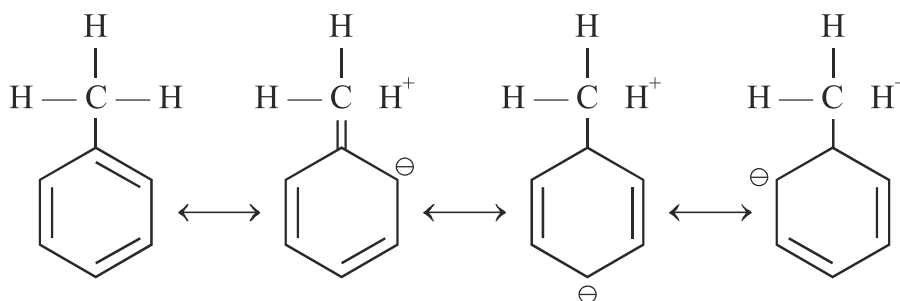
Bond length in propene is 1.46 pm in contrast to normal 1.54 pm (in propane). It is due to the partial double bond character acquired and hence a little shorter.

5. Dipole moment

Since hyperconjugation causes the separation of charges, it also affects the dipole moment in the molecule. Thus the dipole moment values of C — O bond in methanal and ethanal are quite different.



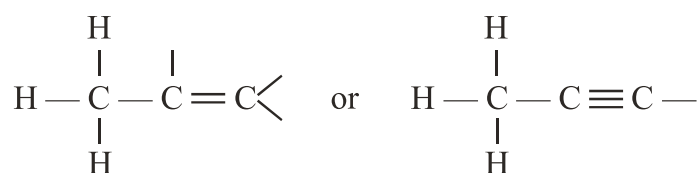
6. Ortho-para directing property of methyl group in toluene is partly due to +I effect and partly due to hyperconjugation.



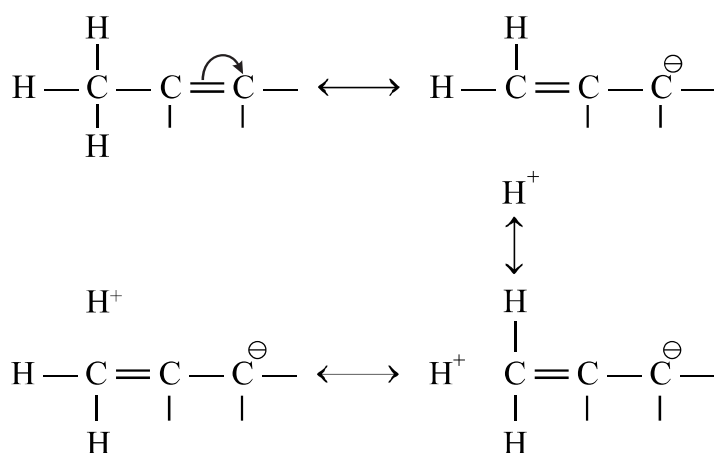
Types of Hyperconjugation

(a) Sacrafacial hyperconjugation

The essential condition is the attachment of alkyl group to double bond or triple bond.



Carbon atom of alkyl group attached to double bond must contain atleast one hydrogen atom in hyperconjugation.



It involves a sort of sacrifice of bond and hence the name sacrafacial.

