

2

SOME TERMS AND CONCEPTS

INTRODUCTION. In earlier courses you have learnt about the structure of atom (including shapes of s , p , d orbitals), nature of chemical bonds, polarity of covalent bonds, tetrahedral disposition of carbon valencies ; lengths and strength of covalent bonds; etc. It is now proposed to extend that information in this chapter by introducing some fundamental aspects relevant to modern organic chemistry. It is hoped that the knowledge gained here will be useful in understanding the subject and interpreting experimental facts about the organic compound to explain how and why organic compounds behave as they do.

HYBRIDISATION. To understand hybridisation, consider the electronic configuration of carbon ($1s^2; 2s^2, 2p_x^1, 2p_y^1$) which suggests that it may have a bonding capacity of two *i.e.*, *divalent*, but actually it has bonding capacity of four *i.e.*, *tetravalent* in most of its compounds (*e.g.*, CH_4 , CCl_4 etc.). A carbon can show the observed tetravalency only if the $2s$ electrons are involved in bond formation along with the $2p_x$ and $2p_y$ unpaired electrons. This is possible only if the *paired* $2s$ electrons are unpaired and then one of them is *promoted* to the empty $2p_z$ orbital. The new electronic configuration would then be $1s^2; 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$. The four unpaired electrons occupying atomic orbitals $2s^1, 2p_x^1, 2p_y^1, 2p_z^1$ can now *pair* with electrons of other atoms (say, s orbitals of 4H atoms or p -orbitals of 4Cl atoms) to form *four* covalent bonds. However, these four bonds would not be *equivalent* because of the component atomic orbitals are not equivalent. But the four bonds of carbon in methane and other related compounds are known to be equivalent. If we consider the redistribution of energy in these orbitals by some kind of *mixing*, we can get the resulting *equivalent orbitals* and hence *equivalent bonds*. This *mixing of the orbitals having nearly the same energies and the redistribution of their energies to form new orbitals having identical shapes and equivalent energies* is known as **hybridisation** and new orbitals are called **hybrid orbitals** to distinguish them from the *pure* atomic orbitals s , p , etc. This hybridisation in the orbitals of carbon can take place in three different ways, *viz.*, *tetrahedral* or sp^3 hybridisation, *trigonal* or sp^2 hybridisation and *digonal* or sp hybridisation. Let us consider these three types of hybridisation with their implications.

1. **sp^3 hybridisation (Tetrahedral hybridisation).** Here all the four orbitals (one s and three p) are hybridised to produce four *identical hybrid*

orbitals known as sp^3 orbitals with one unpaired electron in each. As the unpaired electrons in these hybrid orbitals repel one another, the four hybrid orbitals should keep at a maximum distance from one another. This is possible only if the four hybrid orbitals of carbon are directed towards the four corners of a regular tetrahedron (hence the name **tetrahedral hybridisation**) and the angle between any two sp^3 orbital is a tetrahedral angle 109.5° (see Fig. 1 and 2).

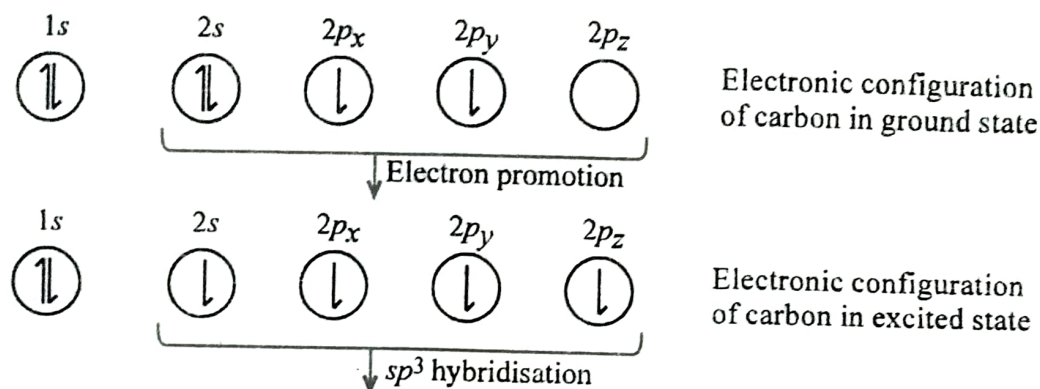


Fig. 1. sp^3 hybridisation of carbon.

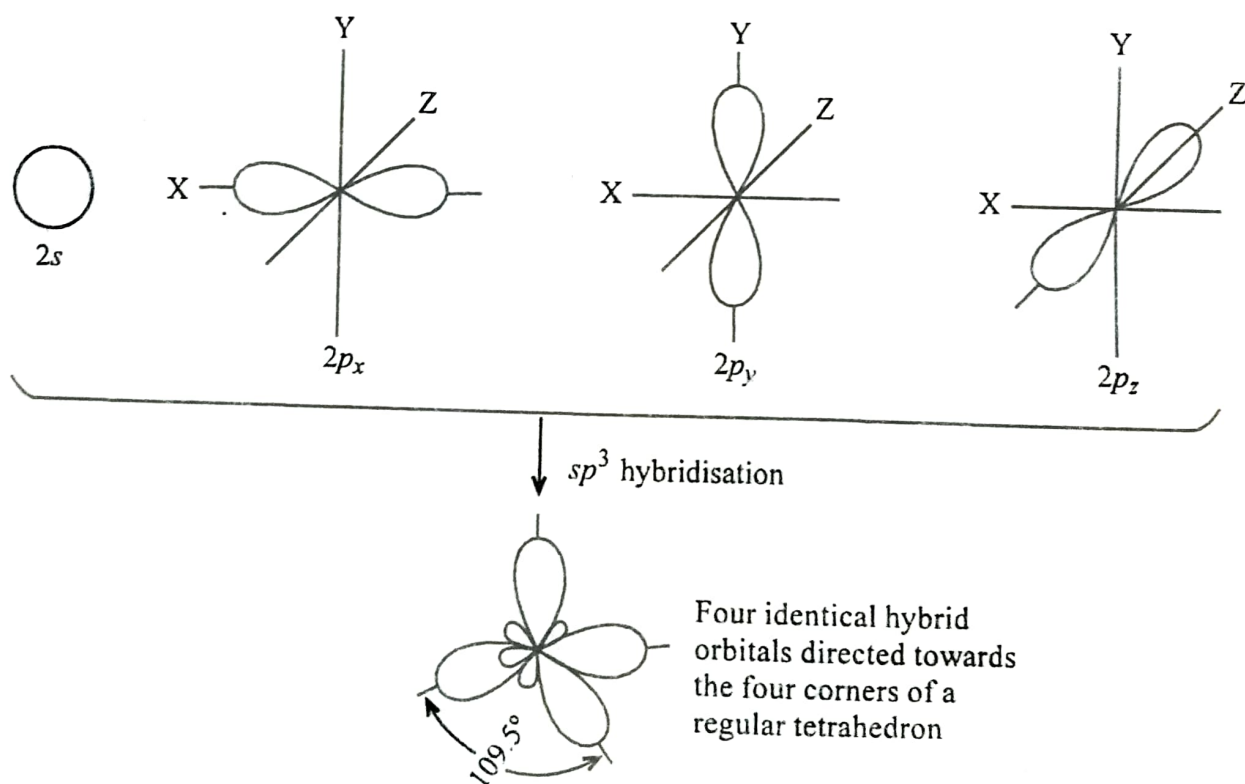


Fig. 2. Orbital picture of sp^3 hybridisation

It may be noted that each of the four sp^3 hybrid orbitals has $\frac{1}{4}s$ and $\frac{3}{4}p$ orbital character and form four (σ) bonds by pairing with electrons of other four atoms or groups at their axes.

Application. This type of hybridisation takes place in the formation of organic compounds containing only single bonds. This will be evident when we will consider the orbital picture of methane and ethane in due course. Formation of water, alcohol, ether and ammonia/amines also utilises sp^3 hybridisation.

2. sp^2 hybridisation (Trigonal hybridisation). Here, the $2s$ and two of the three $2p$ orbitals (say, $2p_x$ and $2p_y$) hybridise to form three *identical* hybrid orbitals called sp^2 orbitals, because they involve one s and two p orbitals. Since, the unpaired electrons in these hybrid orbitals repel one another the three hybrid orbitals should be so arranged that they keep at a maximum distance from one another and are directed to the corners of an equilateral triangle (hence the name **trigonal hybridisation**). The angle between any two sp^2 orbitals is 120° . The third $2p$ orbital remains unhybridised and perpendicular to the plane of the three hybrid orbitals (sp^2). See Fig. 3.

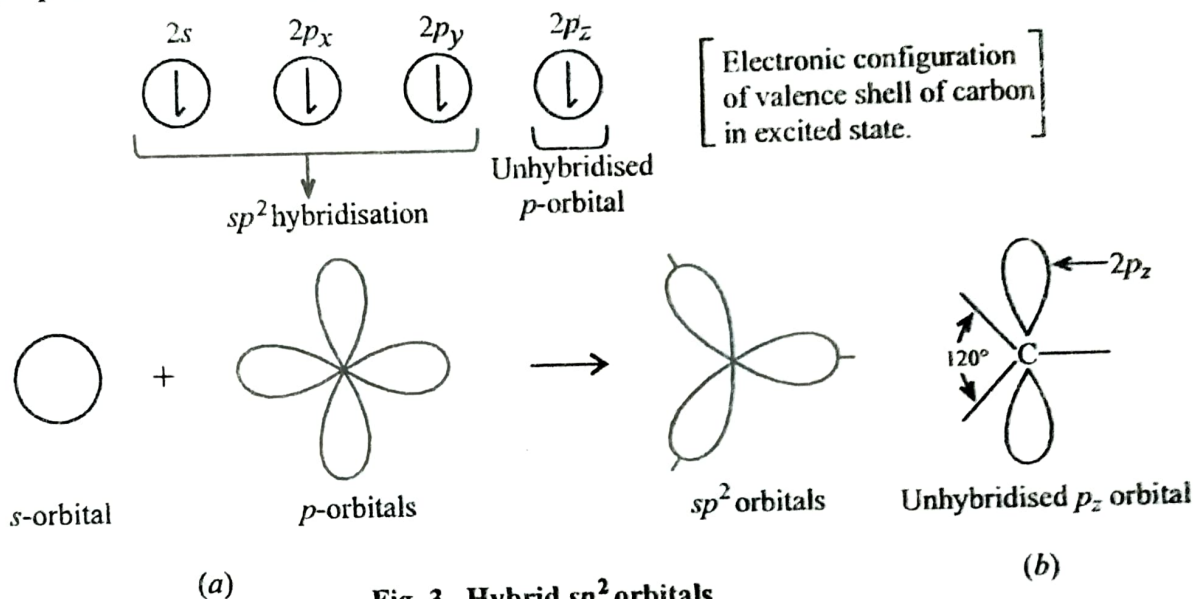


Fig. 3. Hybrid sp^2 orbitals

It may be noted that each of sp^2 hybrid orbitals has $\frac{1}{3}s$ and $\frac{2}{3}p$ orbital character. Also, the effective size of these sp^2 hybrid orbitals is slightly smaller than that of sp^3 hybrid orbitals.

Application. sp^2 hybridisation helps us to explain the structure of organic compounds having carbon linked by double bonds (e.g., ethylene and aldehydes/ketones). "Let us illustrate the bond formation in ethylene (C_2H_4), for example. An sp^2 hybrid orbital of one carbon overlaps the sp^2 hybrid orbital of the other carbon to form a carbon-carbon *sigma*(σ) bond in ethylene. The remaining two sp^2 hybrid orbitals of each carbon then overlap the $1s$ orbitals of hydrogen to form four carbon-hydrogen *sigma*(σ) bonds in ethylene (Fig 4a). Evidently, hybrid orbitals give (σ) bonds. The $2p_z$ orbitals of the two carbons then overlap each other *laterally* to form a carbon-carbon *pi*(π) bond (Fig 4b)".

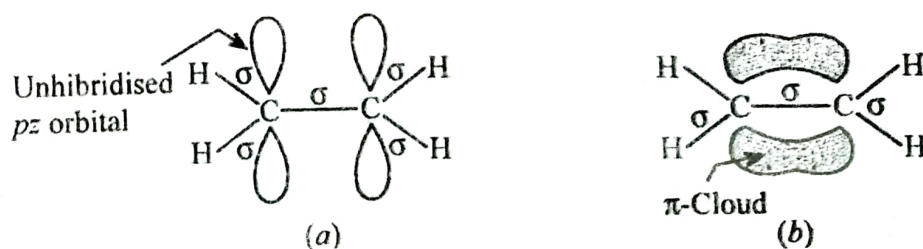


Fig. 4. Ethylene molecule (a) Sigma bonds formed by $2sp^2$ hybrid orbitals with unhybridised p_z orbital (b) formation of π -bond by $2p_z$ orbitals overlapping.

3. sp hybridisation (Digonal hybridisation). Here, the $2s$ orbital and one of the three $2p$ orbitals (say, $2p_x$) hybridise to give two *identical* orbitals

called *sp* orbitals (because they involve one *s* and one *p* orbital), which are collinear. The remaining two unhybridised *2p* orbitals containing an unpaired electron in each are perpendicular to one another and also to the plane of hybrid *sp* orbitals (see Fig. 5 and 6). The angle between any two *sp* orbital is 180° .

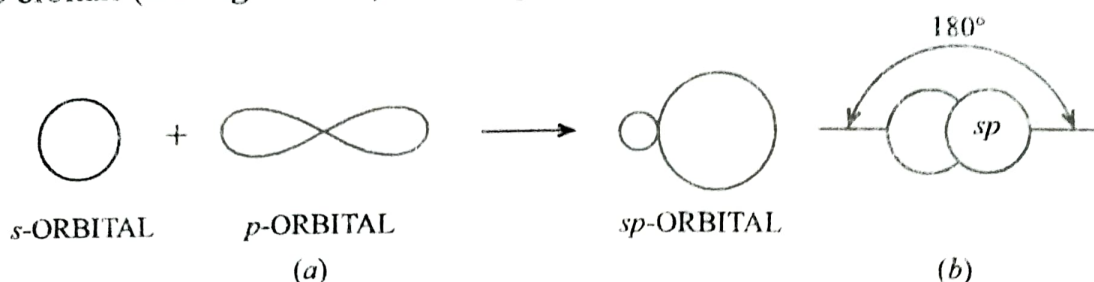


Fig. 5. Hybrid *sp* orbitals

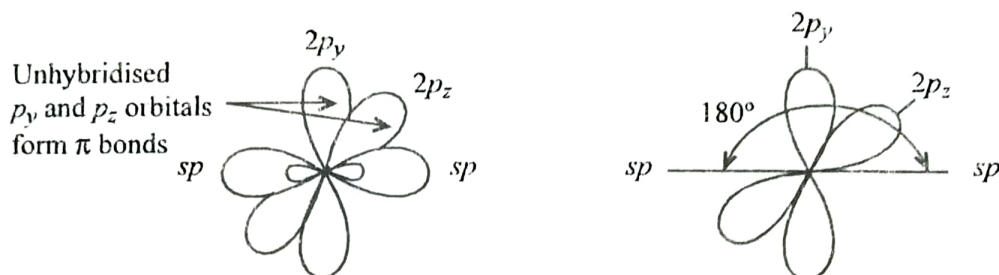


Fig. 6. Orbital picture of *sp* hybridisation

It may be noted that each of the *sp* hybrid orbitals has one-half *s* and one-half *p* orbital character. The *sp* hybrid orbitals are smaller in size than *sp*³ or *sp*² hybrid orbitals.

Application. *sp* hybridisation is used to explain the structures of organic compounds containing carbon linked by a triple bond (e.g., **acetylene**). The orbital picture of acetylene will be explained under chapter on **alkynes**.

It is important to remember that *hybridisation does not take place in isolated atoms. The hybrid orbitals are formed only at the time of bond formation.*

Sigma (σ) and Pi (π) bonds. The molecular orbitals or bond orbitals formed by overlap of *s* and *s* atomic orbitals, *s* and *p* atomic orbitals, *p* and *p* atomic orbitals along their axes are all *symmetrical* having the highest electron density along their internuclear axes. Since the overlap in all these molecular orbitals is very efficient, the resulting bonds are quite *strong* bonds. All these molecular orbitals (*s-s* e.g., H-H; *s-p* e.g., HF; and *p-p* e.g., Cl-Cl overlap along their axes) are called **sigma (σ) orbitals**, and the resulting bonds are known as **sigma (σ) bonds**. The electrons present in these sigma orbitals are referred to as **sigma (σ) electrons**.

When half-filled *p* orbitals forming a molecular orbital are oriented in a direction perpendicular to the internuclear axes, the two orbitals overlap laterally (or sideways) and the resulting molecular orbitals consist of two parts, one lying above and the other below the plane of the atoms. Such *sideways overlap* is necessarily poor and the resulting bond, unlike the sigma bond mentioned above, is *weak*. This type of molecular orbitals is called **pi (π) orbital**, and the resulting bond is known as **pi (π) bond**. The electrons present in a pi (π) orbital are referred to as **pi (π) electrons**.

It may be noted that sigma bonds can also be formed by the mutual overlap of hybrid orbitals (see above), and also by the overlap of a hybrid orbitals and an *s* or *p* orbital. Pi (π) bonds are, however, formed only by the sideways overlap of *p* orbitals.

Multiple bonds are always made up of one strong sigma (σ) bond and one or more weak pi (π) bonds. It will be seen in due course that carbon-carbon double bond (as in ethylene), carbon-carbon triple bond (as in acetylene) and carbon-oxygen double bond (as in aldehydes/ketones) are made up of one σ bond and one or more π bonds.

Let us conclude this part with tabular comparison of sigma (σ) and pi (π) bonds (see Table 1).

Table 1. Comparison of Sigma and Pi bonds

S.No	Sigma (σ) Bond	Pi (π) Bond
1.	Formed by the overlap of two s orbitals, an s and p orbital, two p orbitals along their axes, two hybrid orbitals, a hybrid orbital and an s or p orbital.	Formed by the sideways overlap of two p orbitals.
2.	Strong bond due to efficient overlapping of orbitals.	Weak bond due to poor overlapping of orbitals.
3.	Its molecular orbital consists of a single electron cloud symmetrical about internuclear axis.	Its molecular orbital consists of two electron clouds, one above and the other below the plane of the participating atoms.
4.	Can have an independent existence.	Always exists alongwith a sigma bond.
5.	There is free rotation around the bond.	There is a restricted rotation around the bond.

4. Relative sizes of sp , sp^2 and sp^3 hybrid orbitals. Each of the four sp^3 orbitals has $\frac{1}{4}s$ and $\frac{3}{4}p$ character. In contrast, an sp^2 orbital has $\frac{1}{3}s$ and $\frac{2}{3}p$ character, and an sp orbital has $\frac{1}{2}s$ and $\frac{1}{2}p$ character. In other words, the decreasing order of s character in the three hybrid orbitals is :

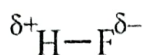
$$sp > sp^2 > sp^3$$

Since s orbitals are closer to the nucleus than p orbitals, it is reasonable to expect that *the greater the s character of an orbital, the smaller it would be.* In other words, *the decreasing order of the size of the three hybrid orbitals would be :*

$$sp^3 > sp^2 > sp$$

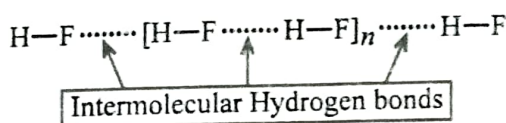
Therefore, an sp orbital should form the *shortest* and sp^3 orbital the *longest* bonds with other atoms. This is actually the case.

HYDROGEN BOND. Consider the hydrogen-fluorine bond in hydrogen fluoride, HF. It is a *polar* covalent bond in which hydrogen is attached to a strongly electronegative fluorine. As a result, fluorine acquires a formal negative charge and hydrogen acquires a formal positive charge, as shown below :



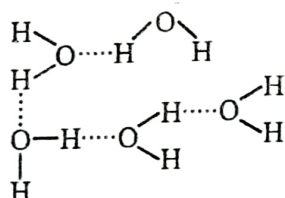
The positive charge on hydrogen in a molecule of hydrogen fluoride will be attracted *electrostatically* by the negative charge on the fluorine atom in another molecule of hydrogen fluoride. This electrostatic attraction between

different molecules of hydrogen fluoride continues resulting in the formation of large **molecular aggregates**, as shown below :

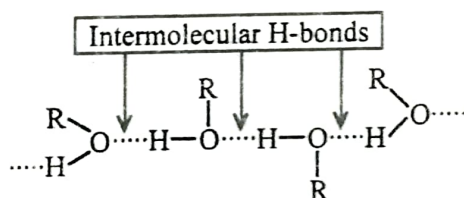


Thus, we see that hydrogen in hydrogen fluoride is bonded to two highly electronegative fluorine atoms, one of which is linked by a normal polar covalent bond and the other by electrostatic attraction (shown by dotted line to distinguish it from normal covalent bond shown by a solid dash). The bond in which hydrogen is linked to a highly electronegative atom like fluorine merely by electrostatic forces of attraction is called a **hydrogen bond** and it is denoted by a dotted line (see above).

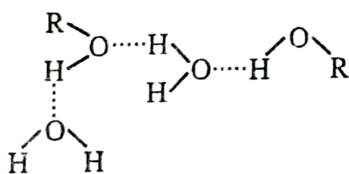
When hydrogen is bonded to other electronegative elements like oxygen (as in water, alcohols, etc.) and nitrogen (as in ammonia, amines, etc.), hydrogen bonds similar to those described above in the case of hydrogen fluoride can be visualised. For example,



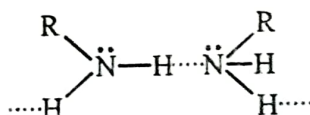
(a)



(b)



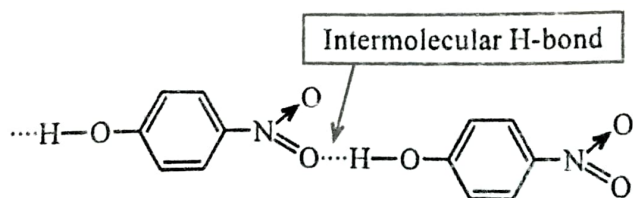
(c)



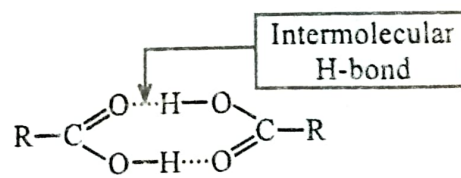
(d)

Intermolecular H-bonding (a) in water molecules (b) in alcohol (c) in alcohol and water molecules and (d) in amine molecules.

Organic compounds like *phenols*, and *carboxylic acids* also involve intermolecular hydrogen bonds. For example,

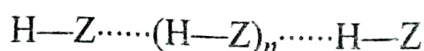


Intermolecular H-bonding
in *p*-Nitrophenol



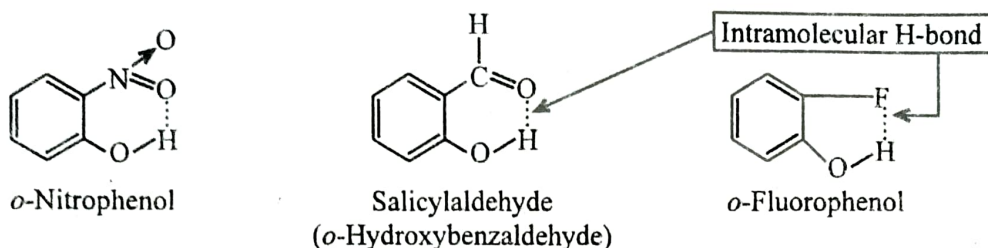
Intermolecular H-bonding
in carboxylic acid (Dimerisation)

In general, compounds represented by the general formula $\text{H}-\text{Z}$ (where Z is a strongly electronegative atom) would involve hydrogen bonds, as shown below :



When hydrogen bonds are formed between the two or more molecules of the same or different compounds they are called **intermolecular hydrogen bonds**.

However, when hydrogen bonds are formed between atoms of the same molecule, they are called **intramolecular hydrogen bonds**. For example,



The new five or six-membered rings formed above as a result of intramolecular hydrogen bonding are known as *chelate rings* and such compounds are often referred to as **chelate compounds**. To sum up,

✓(i) a hydrogen bond involves a strong dipole-dipole attraction.

(ii) the hydrogen atom in compounds containing a hydrogen bond serves as a bridge between two strongly electronegative atoms, holding one by the ordinary covalent bond and the other by mere forces of electrostatic attraction.

(iii) a hydrogen bond can be intermolecular or intramolecular.

Conditions for hydrogen bond. A hydrogen bond in $H-Z$ will be *effective* only when the hetero atom Z is *strongly electronegative* and *small* in size. When the electronegativity is not high or if the atom has a large atomic radius, the electrostatic forces of attraction will necessarily be weak and the hydrogen bond will not be very effective. In fact, *fluorine, oxygen and nitrogen* are the only three elements which have sufficiently high electronegativities and are small enough to form effective hydrogen bonds. Chlorine, which has electronegativity comparable to that of nitrogen, still does not form effective hydrogen bonds due to its relatively larger size.

Strength of hydrogen bonds. Hydrogen bonds, being electrostatic in character, are much weaker than ordinary covalent bonds. The strength of a hydrogen bond is of the order of $8-40 \text{ kJ mol}^{-1}$ whereas that of a normal covalent bond is $20-400 \text{ kJ mol}^{-1}$. *The greater the electronegativity and the smaller the size of the hetero atom, the stronger the hydrogen bond is.* Thus, hydrogen bonds involving fluorine or oxygen or nitrogen atom have strengths of about 40, 29 and 8 kJ mol^{-1} respectively.

Effect of hydrogen bonds on physical properties. The existence of hydrogen bonds in molecules has a marked effect on their physical properties, as illustrated below :

1. Effect on melting and boiling points. Ordinarily, compounds with similar molecular weights have similar melting/boiling points, and there is

regular gradation in these physical constants with rising molecular weights. Compounds containing intermolecular hydrogen bonds (e.g., water, alcohols, amines, carboxylic acids, etc.), show unusually high melting/boiling points for their molecular weights. For example,

Compound	Structure	Mol. wt.	Boiling point °C
<i>n</i> -Butane	$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$	58	0
<i>n</i> -Propylamine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	59	50
<i>n</i> -Propyl alcohol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	60	98
Acetic acid	CH_3COOH	60	118
Ethylene glycol	$\text{HOCH}_2\text{CH}_2\text{OH}$	62	197

n-Butane contains only carbon-hydrogen bonds which are almost non-polar due to little difference in the electronegativities of carbon and hydrogen. Consequently, there is little tendency for *association* in hydrocarbons due to intermolecular hydrogen bonding. In other words, these compounds do not form large *molecular aggregates*. In contrast, *n*-propyl alcohol, *n*-propyl amine, acetic acid and ethylene glycol contain strongly polar O—H or N—H bonds, and they tend to form large *molecular aggregates* due to intermolecular hydrogen bonding. These compounds, compared with *n*-butane are thus highly *associated* liquids. Consequently, much more energy would be needed to break apart these molecules constituting the molecular aggregates. The boiling points of these liquids therefore should be, and actually are, much higher than that of *n*-butane.

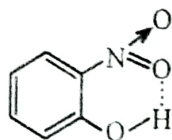
In the series mentioned above, all the compounds have similar molecular weights. Let us now consider a series (see below) in which related compounds have widely different molecular weights but abnormal boiling points for their molecular weights in certain cases.

Compound	Formula	Mol. wt.	Boiling point °C
Water	H_2O	18	100
Hydrogen sulphide	H_2S	34	-59.5
Hydrogen selenide	H_2Se	81	-42
Hydrogen telluride	H_2Te	130	-1.8

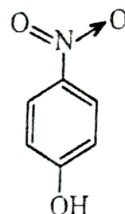
On the basis of its molecular weight, water (H_2O) is expected to have the lowest boiling point ($< -50^\circ\text{C}$) in the above series, but actually it has the highest boiling point (100°C). Water contains hydrogen bonds which are much more *effective* than those in the remaining compounds in the series because the hetero atom oxygen, compared with S, Se and Te, is not only more electronegative but also of small size. Thus, the abnormally high boiling point of water is understandable in terms of rather strong intermolecular hydrogen bonds in it.

Again, in the series, hydrogen fluoride (HF, mol. wt. 20), hydrogen chloride (HCl, mol. wt. 36.5), hydrogen bromide (HBr, mol. wt. 81) and hydrogen iodide (HI, mol. wt. 128), hydrogen fluoride despite its lowest molecular weights, is a liquid having a boiling point of 19.5°C whereas HCl, HBr and HI have boiling points of -85°C , -67°C and -36°C respectively. This abnormally high boiling point of HF is again understandable in terms of the much stronger hydrogen bonds due to the greater electronegativity and smaller size of the hetero element fluorine.

We have so far considered the examples of compounds containing only intermolecular hydrogen bonds and in each case the boiling point was much higher than that expected on the basis of its molecular weight. Let us now consider compounds which involve **intramolecular hydrogen bonds**. For example,



o-Nitrophenol (m.p. 44°C), (steam volatile) Forms a stable 6-membered chelate ring by intramolecular hydrogen bonding. **Association** due to intermolecular hydrogen bonding is **prevented**.



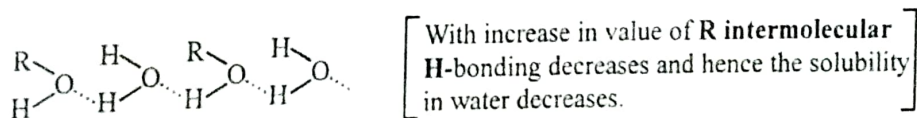
p-Nitrophenol (m.p. 114°C), (non-volatile in steam) O and H too distant to form stable chelate ring by intramolecular hydrogen bonding. **Association** due to intermolecular hydrogen bonding **occurs**.

The effect of intramolecular hydrogen bonding on melting and boiling points is thus opposite to that observed in the case of intermolecular hydrogen bonding. In due course, we shall come across many more examples of compounds with intramolecular hydrogen bonds having melting and boiling points lower than those of compounds with intermolecular hydrogen bonds.

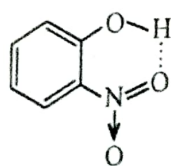
Thus we see that physical properties of molecules are affected markedly by hydrogen bonds.

2. Effect on Solubility. Compounds which can form **intermolecular hydrogen bonds** with a solvent (say, water) would be generally soluble in that solvent, but compounds in which hydrogen bonding with the solvent molecule is restricted or prevented due to **intramolecular hydrogen bonding** would be less soluble or insoluble in that solvent. For example,

(i) Hydroxy compounds like methyl alcohol, ethyl alcohol and sugars are highly soluble in water due to formation of **hydrogen bonds** between the solute and water molecules, as shown below :

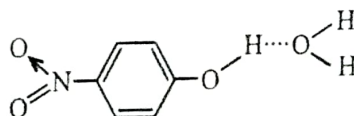


(ii) *o*-Nitrophenol, in which -OH group is not available to form hydrogen bonds with water due to formation of chelate ring by intramolecular hydrogen bonding, is **less soluble** in water **than** the non-chelate isomer *p*-Nitrophenol.



o-Nitrophenol

-OH group not available to form hydrogen bond with water

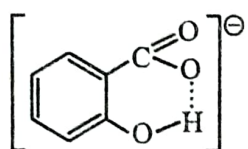


p-Nitrophenol

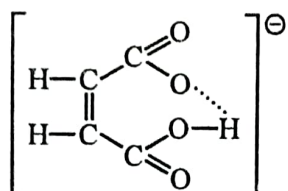
-OH group available to form hydrogen bond with water

3. Effect on spectral characteristics. It will be seen in due course that the spectral characteristics of compounds are affected significantly if these compounds contain hydrogen bonds. An IR band at about 3500 cm^{-1} , for example, is typical of an -OH group (*free*), but it shifts to lower frequencies (say, around 3200 cm^{-1} in alcohols and around 3000 cm^{-1} in carboxylic acids) as the -OH is *bonded*. Thus, the -OH group in alcohols and carboxylic acids is highly *associated*. The fact that the downward shift is much higher in carboxylic acids than in alcohols suggests that hydrogen bond in carboxylic acids is much stronger than that in alcohols. In due course, we shall see that hydrogen bonding in amides also causes a marked downward shift in their N—H stretching bands.

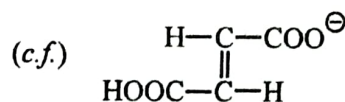
4. Strength of carboxylic acids. *o*-Hydroxybenzoic acid (salicylic acid) and maleic acid are stronger acids than their corresponding analogues *p*-hydroxybenzoic acid and fumaric acid due to greater stabilisation of salicylate and maleate anion *via intramolecular H-bonding*.



Salicylate anion : stabilised
by intramolecular H-bond



Maleate anion :
stabilised by intramolecular
H-bond



Fumarate anion

Importance of hydrogen bond. 1. The concept of hydrogen bond can explain the physical properties like melting and boiling points, solubility in water, spectral characteristics, etc. of molecules, as explained above.

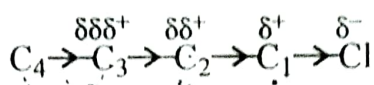
2. Hydrogen bonds in polypeptide chains in proteins play an important role in determining the precise structure and shape of proteins.

3. The concept of hydrogen bonds can explain diverse phenomena such as chemotherapeutic action of drugs, binding of dyes to textiles, adhesive action of paints, lacquers, etc..

ELECTRON DISPLACEMENTS IN ORGANIC COMPOUNDS. The behaviour of an organic compound is influenced to a large extent by the electron displacements taking place in its covalent bonds. These displacements may be of a **permanent** nature in a molecule or may be **temporary** taking place only in the presence of another molecule (reactant). The acidity and basicity of organic compounds, their stability, their reactivity towards other substances, etc. can easily be understood or even predicted by considering such electronic displacements. This chapter describes these electron displacements in organic molecules for a better understanding of their behaviour.

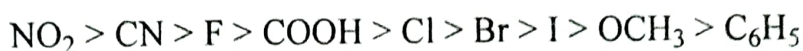
1. Inductive effect. This is a *permanent effect* operating in *polar* covalent bonds. In a carbon-chlorine bond, for example, the electron pair bonding the carbon and chlorine is displaced towards the chlorine atom due to much greater electronegativity of chlorine as compared with carbon. Thus, chlorine

atom acquires a small negative charge, and the carbon atom a small positive charge. If this carbon-chlorine bond forms the terminal of a carbon chain, the effect of this electron displacement gets relayed to other carbon atoms in the chain. The positive charge on C_1 attracts the electron pair bonding C_1 and C_2 . This will also cause C_2 to acquire a small positive charge but this charge on C_2 will be smaller than that on C_1 . Similarly, C_3 will acquire a positive charge that will be still smaller. This effect can be relayed still further although it would decrease in intensity considerably. This type of electron displacement along a chain is referred to as the **inductive effect** or **transmission effect** (I or T effect). *The process of electron shift along a chain of atoms due to the presence of a polar covalent bond in it is called Inductive effect (I effect) or Transmission effect (T effect).*

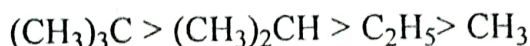


In the foregoing example, the atom Cl, is more electronegative than carbon. It can be less electronegative also sometimes and in that case the electron displacement will take place in the opposite direction. When this atom/group is such that it attracts the electron pair to itself, (e.g., chlorine), it is said to exert a **-I effect** or **electron-withdrawing inductive effect**. On the other hand, when the atom/group (say, alkyl groups) pushes the electrons away from itself, it exerts a **+I effect**, or **electron-releasing inductive effect**.

The decreasing order of the -I effect (electron-withdrawing inductive effect) of certain atoms/groups is :



The decreasing order of the +I effect (electron-releasing inductive effect) of certain atoms/groups is

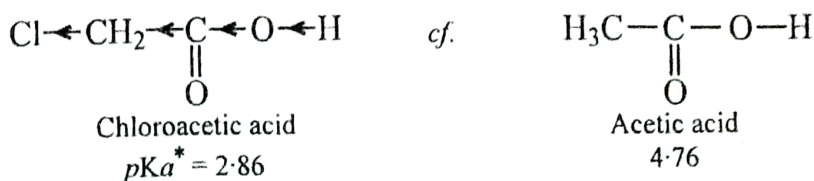


The inductive effect of an atom or a group of atoms diminishes rapidly with distance. In fact, the inductive effect is almost negligible beyond two carbon atoms from the active atom or group.

It is important to note that inductive effect does not involve actual transfer of electrons from one atom to other but merely helps in displacing them permanently.

Applications. Let us now consider a few representative example of organic compounds where the principles described above can be applied.

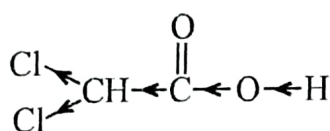
(i) **Acidity of Chloroacetic acid vis-a-vis Acetic acid**



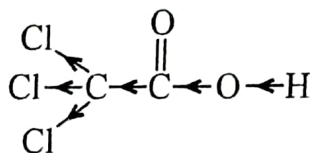
* pK_a value is used to express the strength of organic acids. The smaller the pK_a value, the stronger the acid is.

In chloroacetic acid, the electron-withdrawing inductive effect ($-I$ effect) of chlorine substituted in the methyl group of acetic acid sets up a relay of electrons as shown above. This facilitates the release of the proton from O atom, in chloroacetic acid as compared to acetic acid. Therefore, *chloroacetic acid is a stronger acid than acetic acid*.

In dichloroacetic acid and trichloroacetic acid the electron withdrawing inductive effect should be increasingly greater, as shown below :



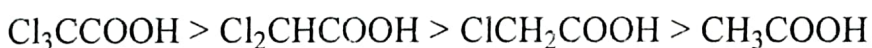
Dichloroacetic acid
($pK_a = 1.25$)



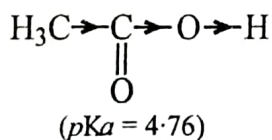
Trichloroacetic acid
($pK_a = 0.65$)

Therefore, *dichloroacetic acid should be stronger and trichloroacetic acid a still stronger acid than dichloroacetic acid*, and this is actually so.

To sum up, the decreasing order of acid strengths in the above series of acids should be, and actually is, as follows :

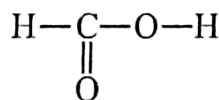


(ii) **Relative acid strengths of Formic acid and Acetic acid.**



($pK_a = 4.76$)

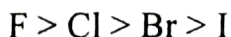
cf.



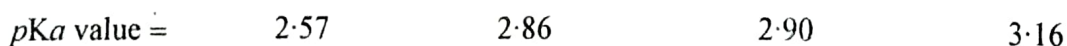
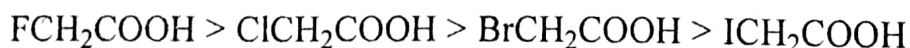
($pK_a = 3.77$)

Methyl group has an electron-releasing inductive effect ($+I$ effect). Therefore, acetic acid is a weaker acid than formic acid.

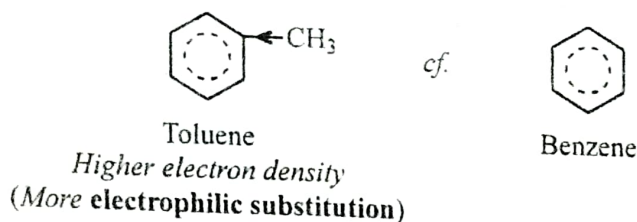
(iii) **Relative acid strengths of Fluoroacetic acid, Chloroacetic acid, Bromoacetic acid and Iodoacetic acid.** The decreasing order of electronegativity of different halogens is ;



This will also be the decreasing order of electron-withdrawing inductive effect ($-I$ effects) of these halogens when they are substituted in acetic acid. Consequently, the decreasing order of acid strengths of these halo acids is as follows :

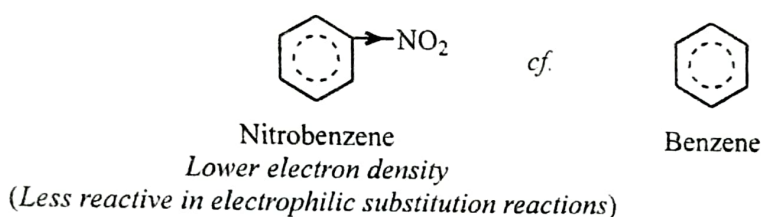


(iv) **Relative reactivity of Toluene (Methylbenzene) and Benzene in aromatic substitution reactions.** Aromatic substitution reactions are generally *electrophilic* in nature. Methyl has an electron-releasing inductive effect ($+I$ effect). Therefore, toluene with higher electron density than benzene enhances its reactivity in electrophilic substitution reactions.

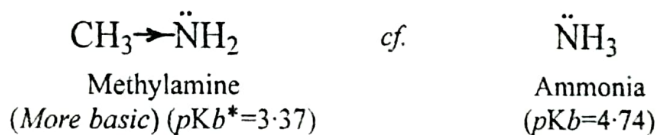


Therefore, toluene is more reactive than benzene in electrophilic aromatic substitution reactions.

(v) **Relative reactivity of Nitrobenzene and Benzene in Electrophilic aromatic substitution reactions.** $-\text{NO}_2$ group has an electron-withdrawing inductive effect ($-\text{I}$ effect). Therefore, nitrobenzene is less reactive than benzene in electrophilic substitution reactions.

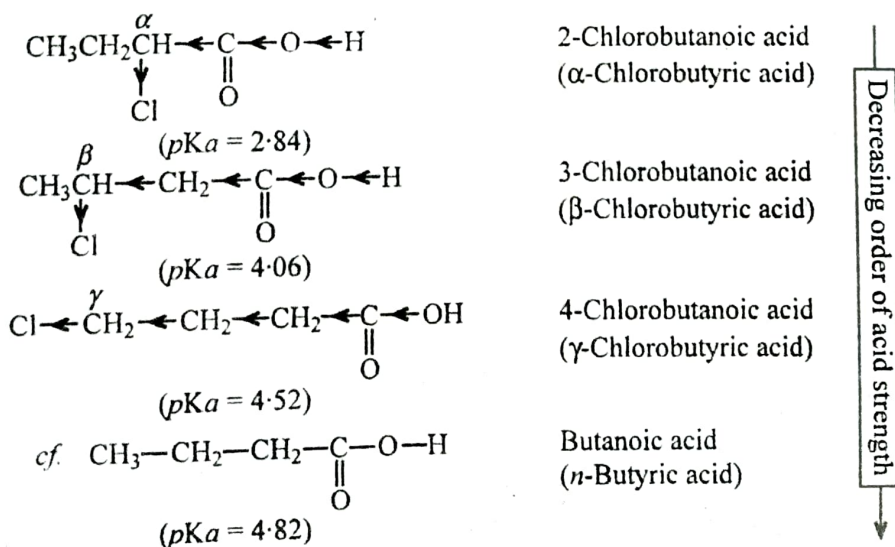


(vi) **Relative basicities of methylamine and ammonia.** Ammonia ($:\text{NH}_3$) is basic due to the presence of a lone pair of electrons on nitrogen.



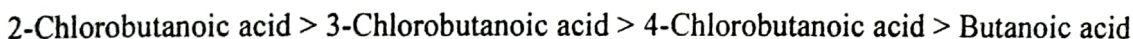
Due to the electron-releasing inductive ($+ \text{I}$ effect) of the methyl group, methylamine has higher electron density on nitrogen than in ammonia. Therefore, *Methylamine is a stronger base than ammonia.*

(vii) **Relative acidities of 2-chloro-3-chloro- and 4-chlorobutanoic acids vis-a-vis butanoic acid.**



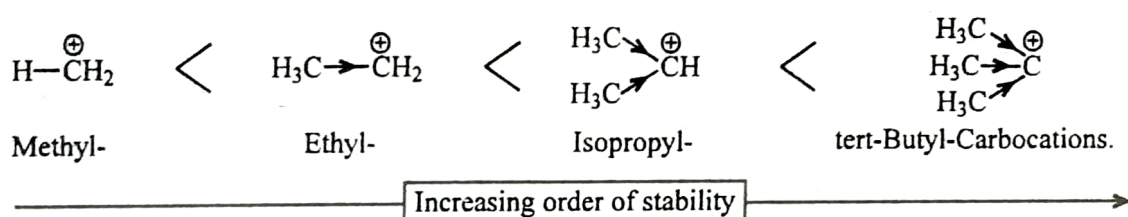
*The smaller the pK_b value stronger the base is.

Since chlorine has an electron-withdrawing inductive effect ($-I$ effect), all the three chlorobutanoic acids should be, and actually are, stronger acids than butanoic acid. However, the inductive effect of an atom/group diminishes rapidly with distance. Therefore, the decreasing order of acid strengths of the above series of acids is as follows :



Since the inductive effect is almost negligible beyond two carbon atoms from the active atom or group, 4-chlorobutanoic acid is therefore, slightly stronger acid than butanoic acid, whereas 2-chlorobutanoic acid is a much stronger acid than butanoic acid as is evident from their pK_a values.

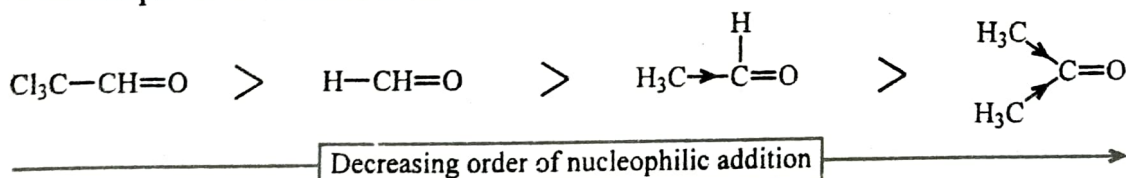
(viii) **Relative stabilities of methyl, ethyl, isopropyl and tert-butyl carbocations.**



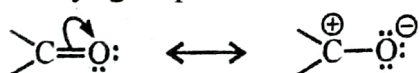
The electron-releasing inductive effect ($+I$ effect) of methyl group(s) *disperses* the positive charge of the carbocation to the greatest extent in *tert*-butyl carbocation and to the least extent in methyl carbocation. Therefore, the decreasing order of stabilities of this series of carbocations should be, and actually is, as follows :



(ix) **Relative reactivities of aldehydes and ketones.** Electron-releasing $+I$ effect increases electron availability on carbonyl carbon. This, therefore, *decreases* the rate of nucleophilic addition. On the other hand, electron withdrawing $-I$ effect *decreases* electron availability on carbonyl carbon and thereby increases the rate of nucleophilic addition. Thus, the decreasing order of nucleophilic addition reactions should be, and actually is, as follows :



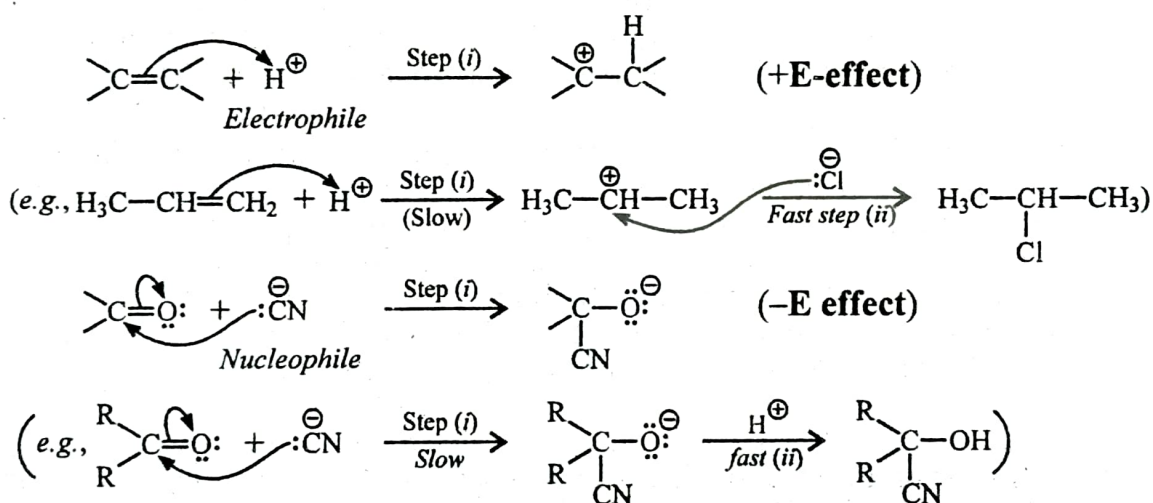
2. Electromeric effect. This is a *temporary* effect (*cf.* inductive effect) operating in unsaturated compounds *only* at the demand of a nearby reagent. It involves the *complete transfer** of π electrons of multiple bond. For example, *during the attack* of a carbonyl group by a nucleophile the π electron pair bonding the carbon and oxygen is transferred completely to oxygen, thereby polarising the carbonyl group as shown below :



*Such a transfer of electrons is usually denoted by means of curved arrow, as shown above.

The displacement of the electron pair to oxygen rather than to carbon is in accord with the greater electronegativity of oxygen atom as compared with carbon atom. The +vely charged carbon in the above polarised structure of the carbonyl group is then the centre of attack by the nucleophilic reagent (see reactions of the carbonyl compounds).

The complete transfer of the shared pair of π -electrons of a multiple bond to the more electronegative atom of the bonded atoms due to the requirement of an attacking reagent is called **Electromeric effect (E-effect)**. When the transfer of π electrons takes place towards the attacking reagent (*electrophile*), the effect is called **+E-effect**, and when the transfer of π electrons occurs away from the attacking reagent (*nucleophile*) in rate determining step (i), the effect is called **-E-effect**. For example,



When the I- and E-effects occur together in a molecule, they may be *assisting* or *opposing* each other. When they are opposing, the E-effect generally dominates over I-effect.

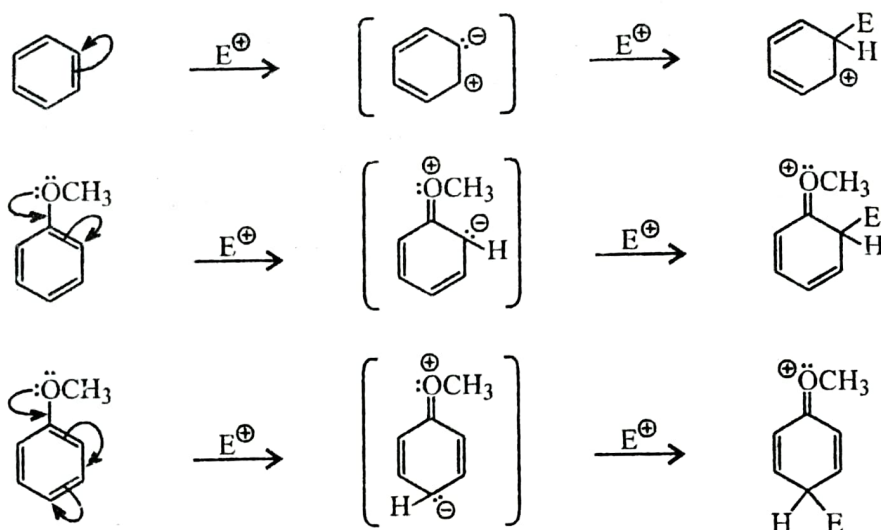
Applications. Organic chemistry is having ample examples of organic reactions involving electromeric effect.

(i) **Electrophilic addition reactions of unsaturated compounds** (say, alkenes and alkynes) involve the *polarisation* of the carbon-carbon double bond in the presence of the attacking electrophiles like H^+ etc., as shown above. Electrophilic additions involving +E effect are discussed in detail under chapter on alkenes and alkynes.

(ii) **Nucleophilic addition reactions of carbonyl compounds.** They involve the *polarisation* through -E electromeric effect of the carbon-oxygen double bond in the presence of a nucleophile, as illustrated above. These reactions are discussed in detail under aldehydes/ketones and in unsaturated carbonyl compounds.

(iii) **Electrophilic substitution reactions of benzenoids.** They involve polarisation through electromeric effect of the benzene ring when an electrophile

(E^+) approaches them. For example,



Polarisation of the double bond in the benzene nucleus has been shown above as a distinct step just to make the presentation lucid. However, polarisation and the attack by E^+ may actually take place concurrently in a concerted mechanism.

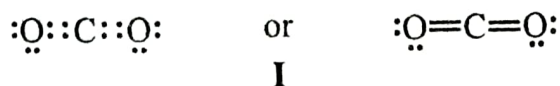
✓ **Electromeric effect versus Inductive effect.** The main features of these two effects can be summarised as follows :

(1) Whereas inductive effect is a **permanent effect** involving only a *displacement* of electrons, electromeric effect is a **temporary effect** involving a *complete transfer* of shared pair of electrons.

(2) Whereas electromeric effect operates only under the *influence of a suitable attacking reagent*, inductive effect has no such requirement.

(3) Whereas inductive effect in a molecule requires only a *polar bond* (it need not be a multiple bond), electromeric effect is shown only by compounds containing one or more *multiple bonds* (they may or may not be polar).

3. Resonance and resonance effect. Let us first consider the concept of *resonance*. If we examine the structure of a simple molecule, carbon dioxide, we find that it can be depicted as follows :

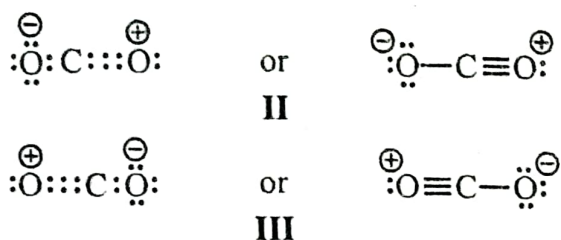


The structure I does not account for all the known properties of carbon dioxide molecule although it can explain many. The carbon-oxygen bond length in carbon dioxide molecule, for example, is 115 pm* whereas it is expected to be 121 pm on the basis of structure I. Again, the heat of formation of carbon dioxide molecule is 1590 kJ mol⁻¹, whereas on the basis of structure I, it is expected to be about 1464 kJ mol⁻¹**. These discrepancies cannot be

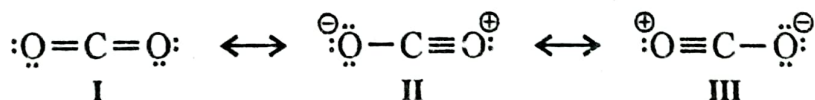
*pm (picometer) is the unit to express bond lengths. It has almost displaced the earlier unit Angstrom (Å). 1 Å = 100 pm

**The term kJ mol⁻¹ means *k* Joules/mole. It has also been used in place of *kcal* values. 1 kcal = 4.184 k Joules/mole.

accounted for even by the alternative possible structures II and III**.



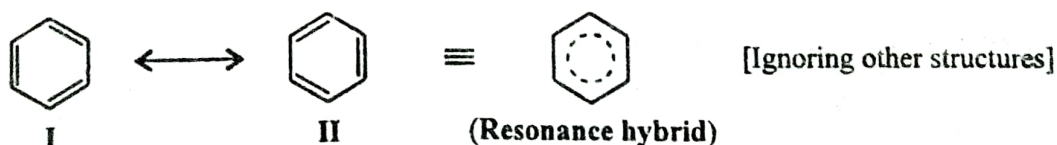
Although each of the three structures given above for carbon dioxide conforms with the *octet rule* for bond formation but none of them can explain completely all the known properties of carbon dioxide molecule. In other words, none of these structures represents the *true* structure of carbon dioxide. Possibly, the true structure of carbon dioxide lies somewhere in between the structures shown above. It is, therefore, difficult to assign a rigid structure to a molecule like carbon dioxide. It is, therefore, suggested that the true structure of carbon dioxide is a *resonance hybrid* of structures I, II and III. These structures (I, II and III) do not represent the true structure but they only *contribute* to the true structure of carbon dioxide (these structures are referred to as *contributing structures* or *canonical structures* or *resonance structures*). It is also emphasized that the true structure of carbon dioxide does not correspond to an equilibrium mixture of these contributing structures. In fact, a carbon dioxide molecule has a *hypothetical* structure which cannot be depicted on paper. This hypothetical structure may show certain similarity to the contributing structures, I, II and III but it is *new* and *different* from them. The resonance hybrid is generally represented by putting double-headed arrows between the contributing structures, as shown below in the case of carbon dioxide :



Occasionally, the term **mesomerism** is also used for synonymously with resonance.

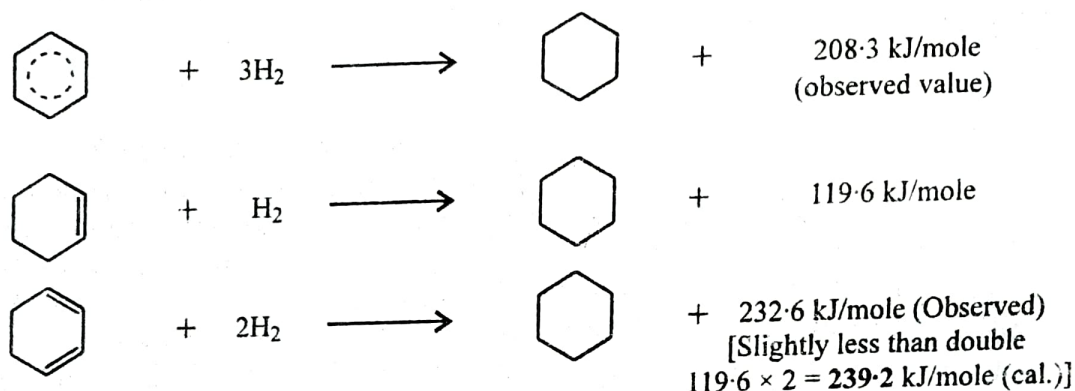
It is clear that a molecule showing resonance involves overlap of *p* orbitals in both directions and there is participation of each *p* electron in more than one bond. In other words, resonance hybridisation involves **delocalisation of electrons** and the terms resonance and delocalisation are often used in the same sense.

Similarly, benzene can be represented as a resonance hybrid of two **Kekule'** structures I and II to explain all its properties like **unusual stability** and equal bond lengths of all six C—C bonds (139 pm) that is intermediate between single (154 pm) and double (133 pm) bonds.



**Apparently, the structure II and III are identical, but each structure shows a particular oxygen to be in a different state of combination and, therefore, they are treated as separate possible structures of carbon dioxide.

Resonance energy. It is observed that a resonance hybrid is more stable than any single *discrete* structure. This can be explained in terms of energy of stabilisation known as **resonance energy**. This can be quantitatively measured from the heat of hydrogenation released on addition of hydrogen to double bonds. If we hydrogenate one double bond of say, cyclohexene the energy released on hydrogenation is $= 119.6 \text{ kJ mol}^{-1}$. Therefore, if we consider benzene with three double bond structure (1,3,5-hexatriene) it should release energy equal to $119.6 \times 3 = 358.8 \text{ kJ mol}^{-1}$ as the heat of hydrogenation but actual value of heat of hydrogenation (*observed*) is 208.3 kJ/mole . This difference between the observed and calculated value $358.8 - 208.3 = 150.5 \text{ kJ/mole}$ is called the **resonance energy** due to more stable hybrid structure. Similar comparison can also be achieved from the heat of hydrogenation of 1,3-cyclohexadiene as shown below :



1,3-Cyclohexadiene

Thus, a hybrid structure of benzene molecule with minimum energy content should be, and actually is, more stable than any discrete 1,3,5-cyclohexatriene (high energy content) structure. The above observations can be diagrammatically visualised as shown below (Fig. 7) :

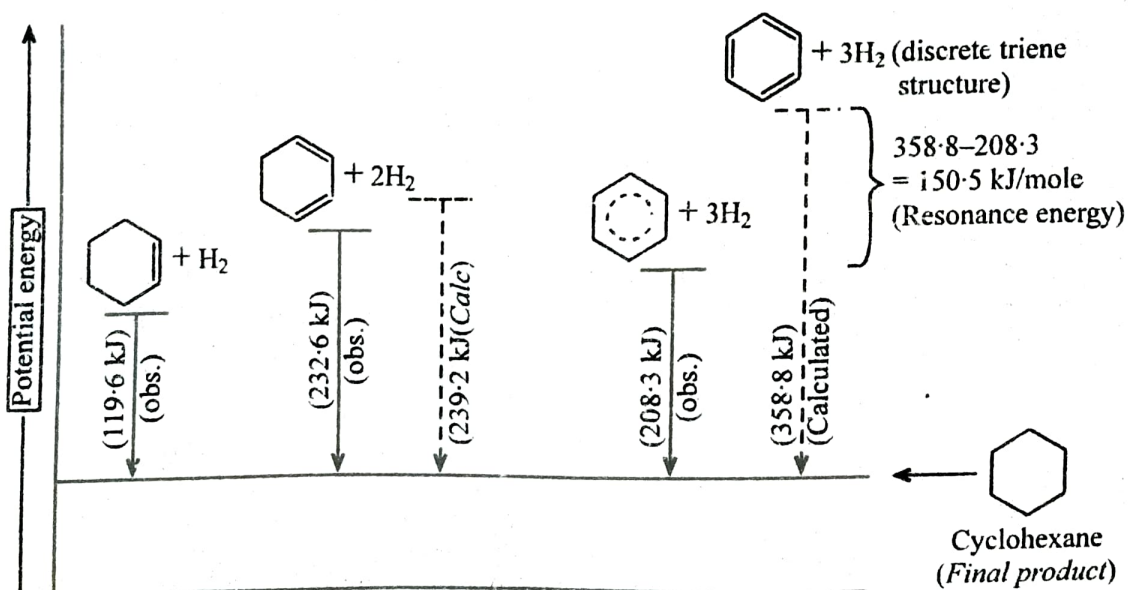


Fig. 7. Diagrammatic presentation of resonance energy.

4. Resonance theory. It has been explained what the concept of *resonance/mesomerism* is and what the term *contributing structure* as applied to a resonance hybrid is. Let us now consider some postulates of the theory known as *resonance theory*. These postulates will serve as guidelines to writing the possible contributing structures for a resonance hybrid. They will also help us to tell which of the contributing structures would be reasonable or important. The main postulates of resonance theory are :

(i) *Whenever a molecule can be represented by two or more structures that differ from one another in the arrangement of electrons and not in atomic nuclei, the molecule is said to involve resonance. The molecule is said to be a resonance hybrid of all these structures. None of these structures represent the actual molecule, but each of these structures contribute to the hybrid (hence the name contributing structures, for such structures).*

(ii) *Each contributing structure must have the same number of unpaired electrons.*

(iii) *The greater the stability of a contributing structure, the greater is its contribution to the hybrid.*

(iv) *Resonance is most important when the contributing structures are equivalent, i.e., they have the same stability or the same energy content.*

(v) *The resonance hybrid is more stable than any of the contributing structures. This increase in the stability of the hybrid vis-a-vis the most stable contributing structures is called resonance energy, or delocalisation energy.*

(vi) *The smaller the difference in the energy contents (or stabilities) of the contributing structures, the greater the resonance energy of that hybrid.*

(vii) *The polar contributing structures involving distinct charges are less stable (and hence less important) than those which do not involve any charges.*

(viii) *The greater the number of contributing structures that can be written for a hybrid molecule, the greater is its stability.*

(ix) *The larger the number of bonds in a contributing structure, the greater the stability of that structure.*

Characteristics of a Resonance Hybrid. A resonance hybrid is characterised by (i) **stability**, and (ii) **bond lengths** distinct from those of contributing structures, as illustrated below :

(i) **Stability.** A resonance hybrid is more stable than any of the contributing structures. The resonance hybrid of benzene, for example, is more stable than 1,3,5-cyclohexatriene by about 151 k Joule/mole.

(ii) **Bond lengths.** All the carbon-carbon bonds in benzene, for example, are *equivalent* (there are not true single and double bonds as expected from the contributing structure 1,3,5-cyclohexatriene) and are of exactly the same length (139 pm). These are obviously intermediate between single (154 pm) and double (134 pm) bonds present in the cyclohexatriene.

Application. Let us consider a few organic molecules where the concept of resonance has been useful in understanding their chemistry.

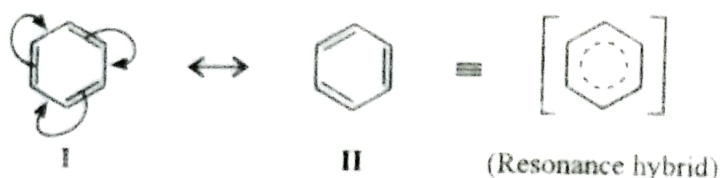
(i) **1, 3-Butadiene.** This diene can be regarded as a resonance hybrid of structures I, II and III.



These structures explain 1, 2 and 1, 4-addition products of 1, 3-butadiene (which could not be explained by a single structure).

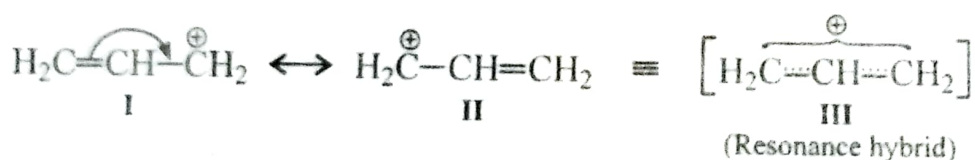
The contributing structures II and III provide a satisfactory explanation for 1,2- and 1,4-addition and stability of **conjugated dienes** over simple alkenes.

(ii) **Benzene.** Benzene is a resonance hybrid of several structures, important being the two Kekule' structure I and II.



A large *resonance energy* and hence *stability* is expected for this system, and it is actually so (151 k Joule/mole). Bond lengths in benzene have already been commented upon.

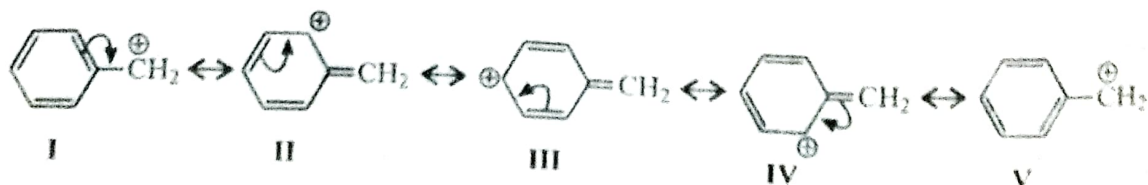
(iii) **Allyl carbocation.** Allyl carbocation is a resonance hybrid of structures I and II.



This explains the **marked stability** of the allyl cation and hence the driving force for the formation of allyl cation intermediate in many reactions of allyl compounds.

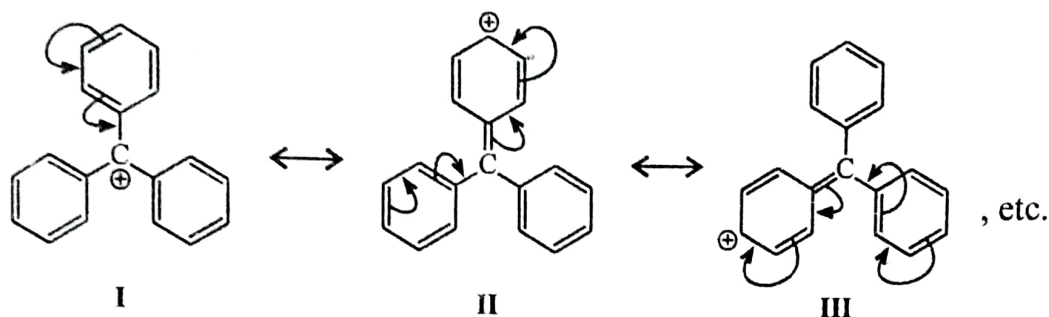
Absence of a true carbon-carbon single bond and a true carbon-carbon double bond in allyl cation is easily understood by reference to structure III above. Rather, structure III actually contain two *identical* carbon-carbon bonds which are intermediate between a single and a double bond. This new type of bond, called the **hybrid bond**, possesses one-half single bond character and one-half double bond character. The π electrons in this structure are completely *delocalised* and equally distributed over the whole system. This *delocalisation* as expressed by the concept of **resonance** is responsible for the **stability** of allyl carbocation.

(iv) **Benzyl cation.** The stability of this carbocation is also explained by the resonance as shown below :

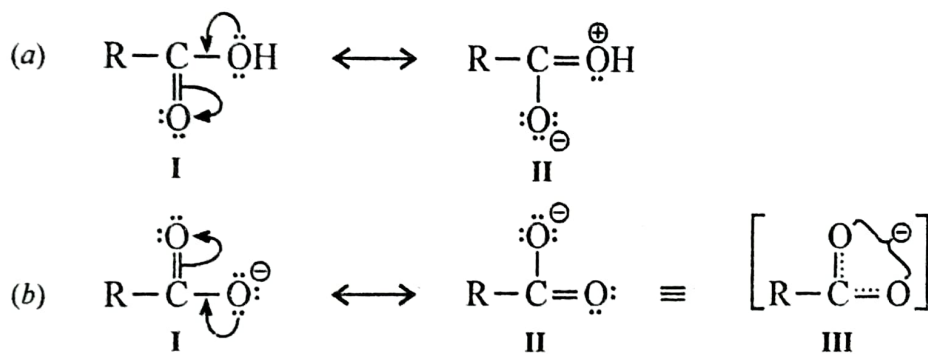


The formation of benzyl cation intermediates in reactions of benzyl compounds is also understandable in terms of the resonance-stabilisation of benzyl cation.

(v) **Triphenyl cation.** This is one of the most stable carbocations known. Its stability is due to the *extensive delocalisation of the positive charge*, as shown below :



(vi) **Carboxylic acids and Carboxylate anions.** Carboxylic acid and carboxylate anion are both resonance-stabilised as shown below :

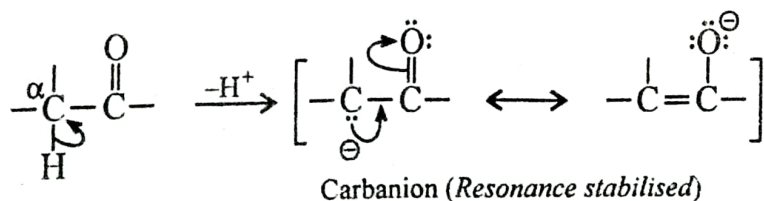


Since structures I and II in (b) are *equivalent*, the carboxylate anion is much more resonance stabilised than the parent carboxylic acid. This high resonance-stabilisation of the carboxylate anion would provide the driving force for the ready dissociation of carboxylic acids to form the carboxylate anion and release a proton (hence the acidic character of carboxylic acids).

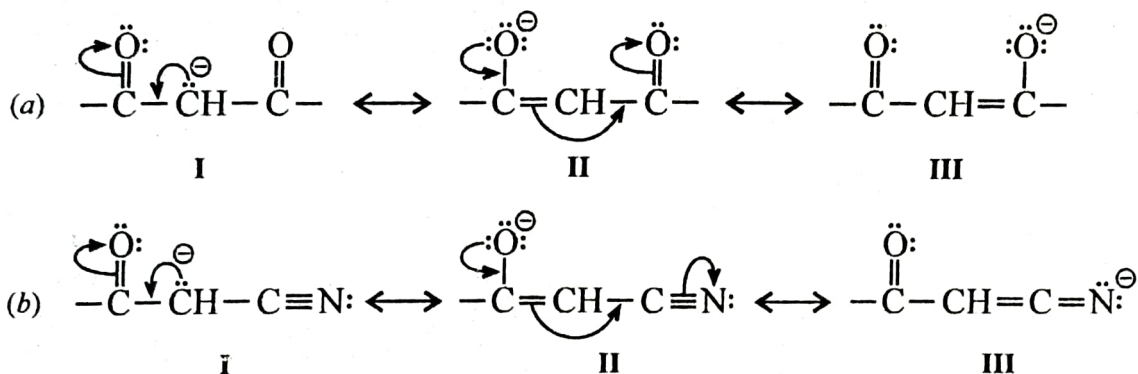
Structure III would explain why the two carbon-oxygen bonds in carboxylate anion should be identical and equal in length.

The double bond character of the carbon-oxygen linkage in carboxylic acids and carboxylates is reduced considerably in the above noted resonance structures of these compounds. Therefore, *carboxylic acids and carboxylates do not show the reactions typical of the carbonyl group*.

(vii) **Acidity of alpha hydrogen in carbonyl compounds.** This is understandable because the resulting *carbanions* (*cf.* carboxylate anion described above) are resonance-stabilised, as shown below :



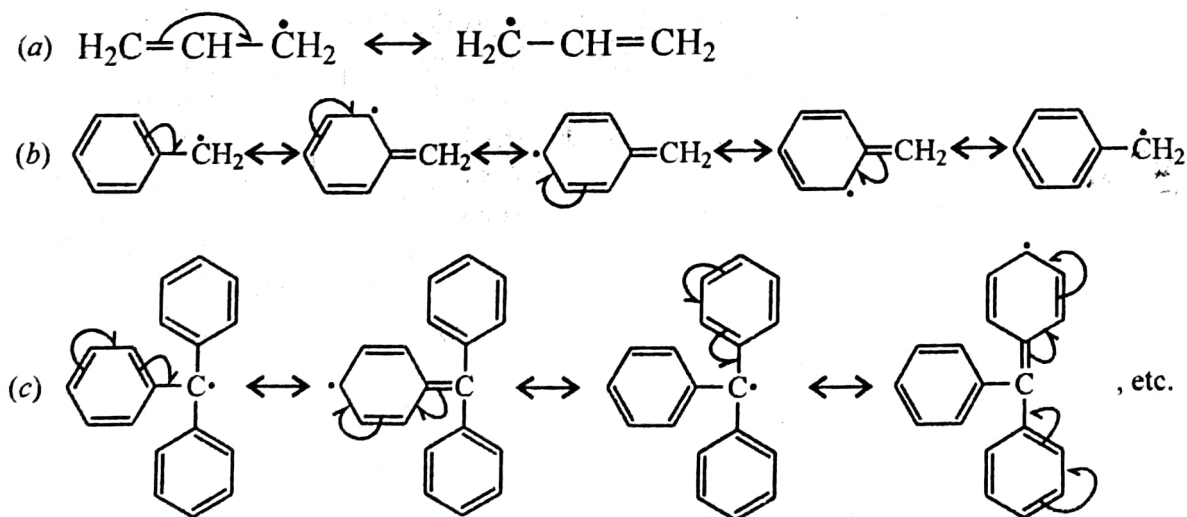
(viii) **Active methylene compounds.** The methylene hydrogens in compounds like malonic ester ($\text{EtOOC}-\text{CH}_2-\text{COOEt}$), acetoacetic ester ($\text{CH}_3\text{COCH}_2\text{COOEt}$), cyanoacetic ester ($\text{N}\equiv\text{C}-\text{CH}_2-\text{COOEt}$) etc. should be even more acidic than the alpha hydrogens in simple aldehydes/ketones. The carbanions formed from these compounds are *resonance-stabilised* to a greater extent, as shown below :



This forms the basis of high reactivity and synthetic importance of these active methylene compounds, as we shall see in chapter 18.

(ix) Acidic character of **phenols**, base weakening effect of **aromatic amines** and directive influence of group(s) present on benzene ring can also be explained by **resonance effect**. These are discussed in detail in concerned chapters.

(x) **Free radicals.** The concept of resonance has also been used to explain the stability and reactivity of many free radical intermediates in organic reactions. Allyl, benzyl and triphenylmethyl radicals are all resonance stabilised as shown below :

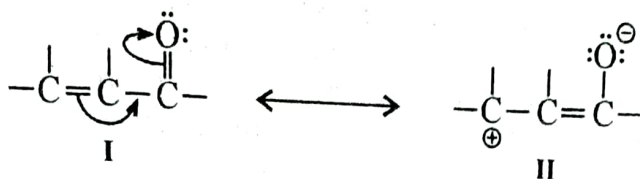


[It may be noted that in these free-radicals, there is displacement of an odd electron rather than a pair of electrons observed. Whereas in earlier examples the movement of electron pairs was shown by the curved arrow (\curvearrowright), the movement of the odd electron is usually shown by a fish-hook arrow (\frown)].

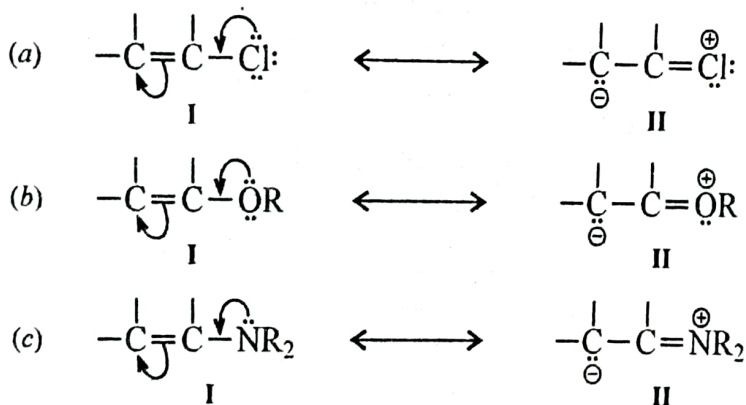
Resonance effect (Mesomeric effect). We have seen above that resonance or mesomerism involves displacement of electrons. This electronic displacement generates centres of high or low electron density and thereby affects the

reactivity of those molecules. The effect caused by the phenomenon of resonance or mesomerism in a molecule is called the **Resonance effect (R-effect)** or **Mesomeric effect (M-effect)**. Like the inductive effect, but unlike the electromeric effect, resonance effect is a *permanent* effect.

Importance. This effect is important in systems with an extended conjugation of multiple bonds such as polyenes, α , β -unsaturated carbonyl compounds, benzenoid compounds, etc. When groups such as $-\text{C}=\text{O}$, $-\text{NO}_2$, $-\text{C}\equiv\text{N}$, $-\text{COOR}$, etc. are adjacent to a multiple bond, they withdraw π -electron from the multiple bond through R- or M-effect as illustrated below.



Such groups which *withdraw* electrons from the adjacent multiple bonds through resonance or mesomerism are said to cause **-R (or -M)-effect** or **electron-withdrawing resonance effect**. Similarly, groups such as $^{\ominus}\ddot{\text{O}}\text{H}$, $^{\ominus}\ddot{\text{O}}\text{CH}_3$, $^{\ominus}\ddot{\text{N}}\text{H}_2$, $^{\ominus}\ddot{\text{C}}\text{I}$, HSO_4^{\ominus} , $-\ddot{\text{O}}\text{H}$, $-\ddot{\text{O}}\text{R}$, $-\ddot{\text{N}}\text{H}_2$, $\ddot{\text{N}}\text{HR}$, $-\ddot{\text{C}}\text{I}$ etc. which can *release* or donate electrons through resonance or mesomerism, are said to cause **+R (or +M) -effect** or **electron-releasing resonance effect**. For example,



Resonance effect versus Inductive effect. Both are *permanent effects*, but there are significant differences between the two which are outlined below :

1. Resonance effect operates only in unsaturated (preferably one with a conjugated system) compounds, but inductive effect operates in compounds containing only σ bonds. In other words, π electrons are involved in resonance effect but only σ electrons are involved in inductive effect.

2. Inductive effect is *distance dependent* (its intensity decreases sharply with distance from the crucial atom in the chain), but resonance effect is not.

3. Resonance effect involves *delocalisation* of electrons, but there is no such delocalisation in compounds showing inductive effect.

HYPERCONJUGATION. We have seen that the conjugated dienes like 1, 3-butadiene have been found to be more stable than simple alkenes (monoenes) like 1-butene. This has been explained in terms of *delocalisation*

of π electrons. Besides conjugation, even alkyl groups bearing hydrogen on the carbon that is attached to doubly-bonded carbon atoms tend to increase the stability of alkenes. Propene ($\text{H}_3\text{C}-\text{CH}=\text{CH}_2$), for example, has been found to be more stable than ethene ($\text{H}_2\text{C}=\text{CH}_2$) by about 11 kJoule/mole.

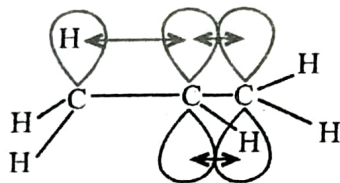
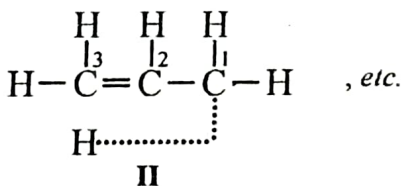
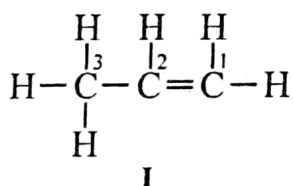


Fig. 6. Hyperconjugation in propene.

This can be explained in terms of *delocalisation of electrons* which takes place by the overlapping between a π -orbital of carbon and a σ -orbital of the H of the methyl group (Fig. 6). As a result of this overlapping, each pair of electrons does not bind together just two atoms—the doubly bonded carbons or the carbon and hydrogen—but binds together all four atoms. This delocalisation which involves σ -bond orbitals also is referred to as **hyperconjugation**, or **σ - π conjugation**.



The dotted line in II represents a *formal bond* between the two atoms, indicating that the electrons on the two atoms are paired.

Viewed in terms of resonance, structures like II contribute to structure of propene. Two more equivalent structures (arising from the other two hydrogen atoms of the methyl group in propene) would contribute similarly to the overall structure of propene. Thus, propene can be regarded as resonance hybrid of three structures like II. On the face of it, structure II is unusual because it has no real bond joining the hydrogen to carbon. However, it does indicate the C—H bond is something *less than* a single bond, C_2-C_3 bond has a slight double bond character, and the C_1-C_2 bond has some single bond character. This picture finds support in actual measurements of different bond lengths in propene. The C_2-C_3 bond in propene for example, is 148 pm long, and not 154 pm as expected for a pure single bond.

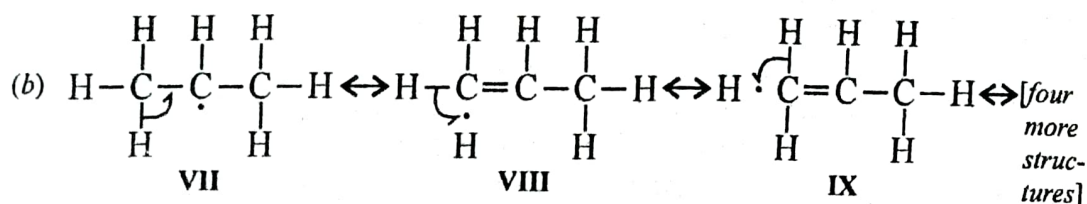
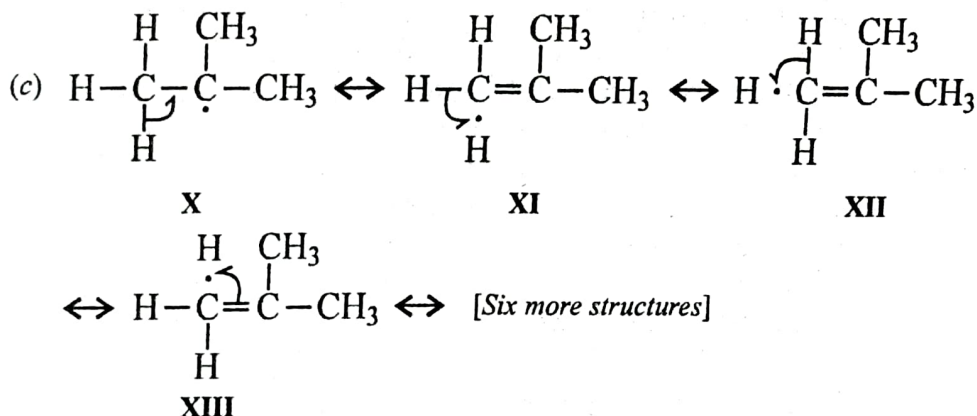
Since there is no real bond between the hydrogen on C_3 and C_1 and yet electrons on these two atoms are paired in II, the term **no bond resonance** is also used for hyperconjugation and the contributing structures like II are called **no-bond contributing structures**.

It may be noted that structure II has one *less* real bond than I. In other words the hyperconjugation given above has involved a sort of “*sacrifice*” of a bond and such hyperconjugation is therefore known as **sacrificial hyperconjugation also**.

It is obvious that greater the number of available hydrogen on alkyl carbon that is attached to doubly bonded carbon, the greater the number of contributing

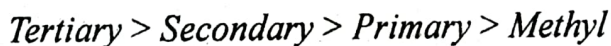
$$\begin{array}{ccccccc}
 \begin{array}{c} \text{H}_3\text{C} \diagup \text{C}=\text{C} \diagdown \text{CH}_3 \\ \text{H}_3\text{C} \diagdown \text{C}=\text{C} \diagup \text{CH}_3 \end{array} & > & \begin{array}{c} \text{H}_3\text{C} \diagup \text{C}=\text{C} \diagdown \text{CH}_3 \\ \text{H}_3\text{C} \diagdown \text{C}=\text{C} \diagup \text{H} \end{array} & > & \text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}_3 & > & \\
 (110 \text{ kJ mol}^{-1}) & & (112 \text{ kJ mol}^{-1}) & & (115 \text{ kJ mol}^{-1}) & & \\
 & & & & & & \\
 & & & & & & \\
 \begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CH}_2-\text{C}=\text{CH}_2 \end{array} & > & \text{CH}_3-\text{CH}=\text{CH}_2 & > & \text{CH}_3\text{CH}_2-\text{CH}=\text{CH}_2 & > & \\
 (119 \text{ kJ mol}^{-1}) & & (125.9 \text{ kJ mol}^{-1}) & & (126.8 \text{ kJ mol}^{-1}) & & \\
 & & & & & & \\
 & & & & & & \\
 \text{H}_2\text{C}=\text{CH}_2 & & & & & & \\
 (137.2 \text{ kJ mol}^{-1}) & & & & & &
 \end{array}$$

Hyperconjugative forms of Ethyl radical (1°)

Hyperconjugative forms of Isopropyl radical (2°)Hyperconjugative forms of tert-Butyl radical (3°)

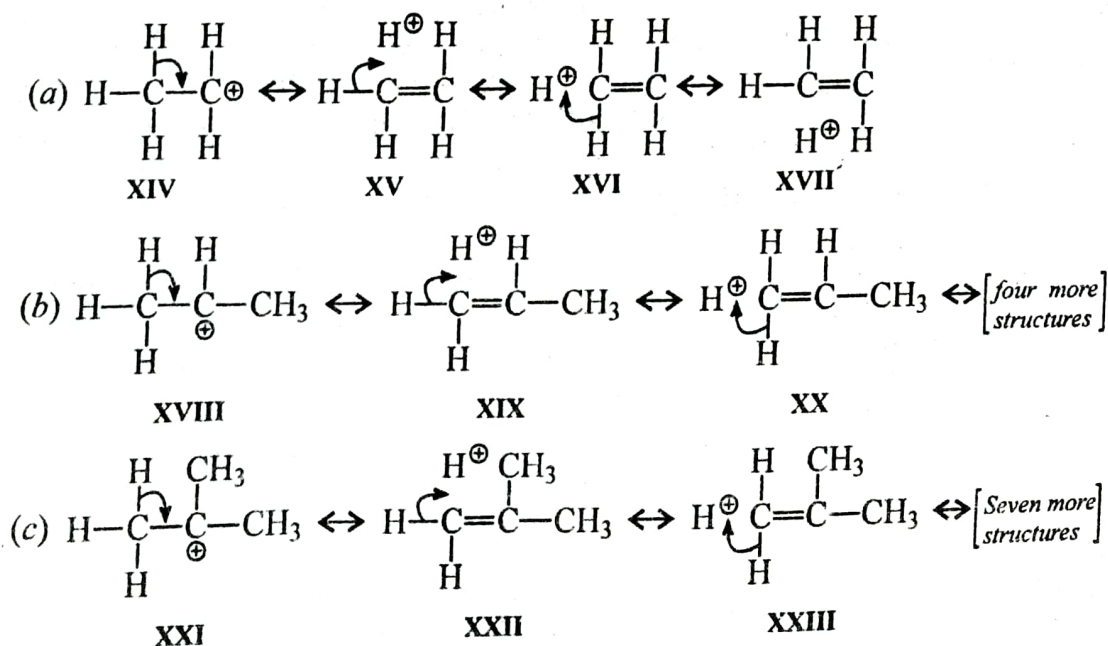
Thus, *ethyl*, *isopropyl* and *tertiary butyl* radicals have 3, 6 and 9 hyperconjugative forms or no-bond contributing structures respectively. Therefore, in the above series, *tert*-butyl radical should be the most stable and the ethyl radical the least stable, and this is so.

Relative stabilities of simple alkyl cations. Among simple alkyl cations, the decreasing order of stability is :



Explanation. It can be explained as follows :

A tertiary carbocation has more *hyperconjugative forms* than a secondary carbocation, and a secondary carbocation has more hyperconjugative forms than a primary carbocation, as illustrated below :



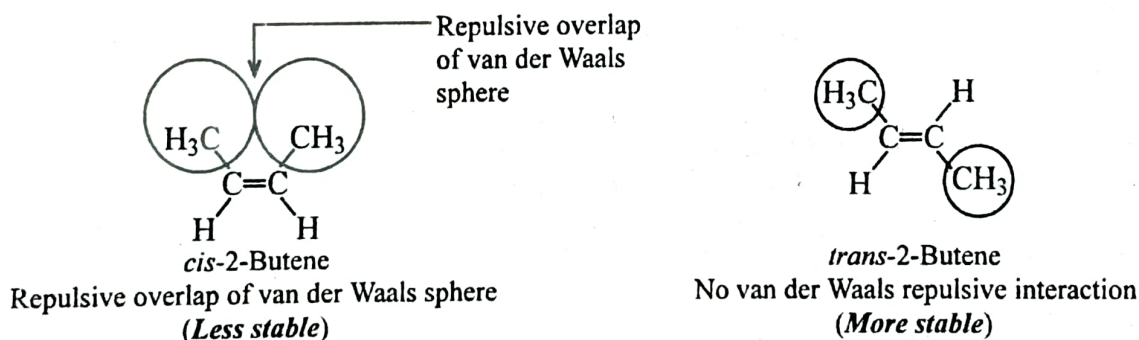
Thus, ethyl, isopropyl and *tert*-butyl cations have 3, 6 and 9 no-bond contributing structures. Therefore, they should show an increasing order of stability mentioned above.

In due course, we shall come across many examples of organic compounds where the concept of hyperconjugation explains their behaviour satisfactorily.

It may be noted that in contrast to the hyperconjugative form II in propene the hyperconjugative forms IV to VI in ethyl radical have the same number of real bonds as the classical structure III. Similarly, hyperconjugative forms of secondary and tertiary alkyl free radicals and carbocations involve no 'sacrifice' of the bonds as observed in the case of propene (all the possible hyperconjugative forms in these cases are not drawn, but it can be easily seen that there is no loss of bonds in them). This kind of hyperconjugation involving **no sacrifice** of bonds is called **isovalent hyperconjugation** to distinguish it from the term sacrificial hyperconjugation used in the case of alkenes like propene.

STERIC EFFECT / INHIBITION / HINDRANCE. It is observed that molecules require specific spatial geometry for the reactions to occur. This 'geometry' is disturbed by the presence of bulky groups on an atom or due to the rigidity of a covalent bond. The repulsive forces arise because of *van der Waals radii*. Such alteration in the geometry of the molecule can markedly modify or even nullify the physical and chemical properties of organic compounds. These modifications arising in a molecule *due to spatial crowding* within the *periphery of van der Waals radii* are called **steric effects** or **steric hindrance**. For example,

(a) The greater stabilisation of *trans*-2-butene as compared with *cis*-2-butene can be explained in terms of steric effect, as shown below :



(b) **Steric hindrance in nucleophilic substitution reactions (S_N^2).** The observed relative rates of nucleophilic substitution reaction for CH_3^- , C_2H_5^- , $(\text{CH}_3)_2\text{CH}^-$ and $(\text{CH}_3)_3\text{C}^-$ halides are in the order :

Alkyl halide	$\text{CH}_3\text{-X}$	$\text{CH}_3\text{CH}_2\text{-X}$	$(\text{CH}_3)_2\text{CH-X}$	$(\text{CH}_3)_3\text{C-X}$
Relative rate	30	1	0.03	≈ 0

This reaction order can be interpreted in terms of **steric hindrance**. The back side of methyl group is relatively more exposed to nucleophilic attack than when hydrogens of methyl group in methyl halide is replaced by bulky methyl group(s). In other words, the area close to *leaving group* becomes more hampered. Therefore, it becomes difficult for attacking nucleophile to approach the back side of C-X bond for reaction to occur. The rate of

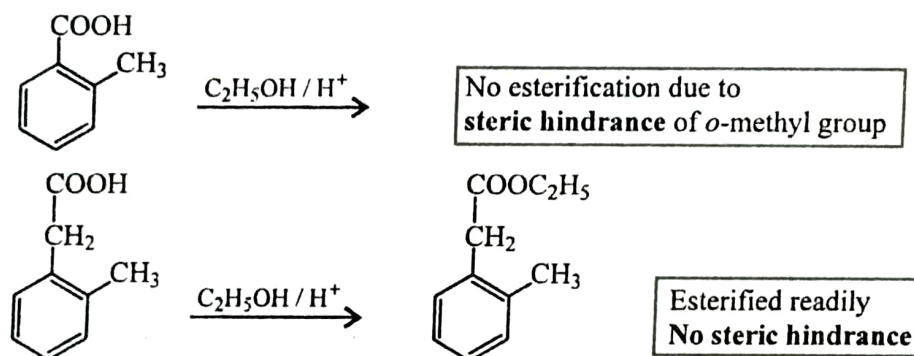
reaction, therefore diminishes, as shown above.

(c) **Steric hindrance in esterification of acids.** On similar grounds, if a $-\text{COOH}$ group is attached to a carbon atom containing bulky group(s), the rate of esterification of the acid with alcohol decreases. The rate of esterification follows the following decreasing order, and is expected to be so.

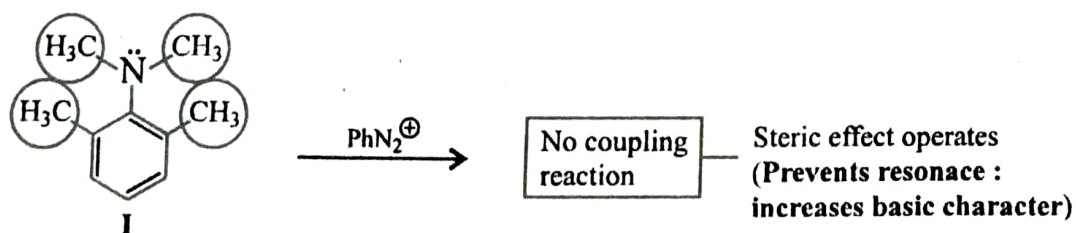


Similarly, *o*-methyl benzoic acid cannot be esterified due to steric effect exerted by the *ortho* methyl group. However, if $-\text{COOH}$ group is far away from the steric influence of *o*-methyl group as in *o*-methyl phenyl acetic acid, it can be easily esterified.

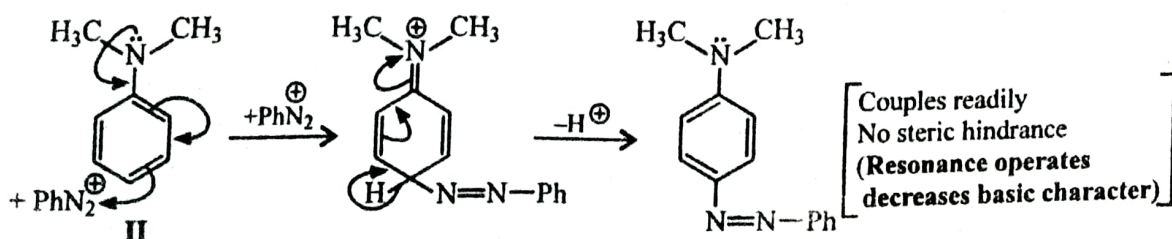
Such steric hindrance was referred by Victor Meyer as **mechanical hindrance**.



(d) **Relative coupling reactions of N,N-dimethylaniline and its 2,6-dimethyl derivative.** It is observed that 2,6-dimethyl derivative of N,N-dimethylaniline does not couple with diazocation PhN_2^+ (electrophile) due to steric hindrance exerted by two methyl groups at *ortho*-position to $-\text{NMe}_2$. Steric hindrance prevents the benzene ring from lying in the same plane and inhibit the interaction of unshared electron pair of nitrogen with π -electrons of the benzene nucleus. In other words, resonance is prevented and the electrons are not available to be attacked by the electrophile, PhN_2^+ . Consequently the reaction is hampered.

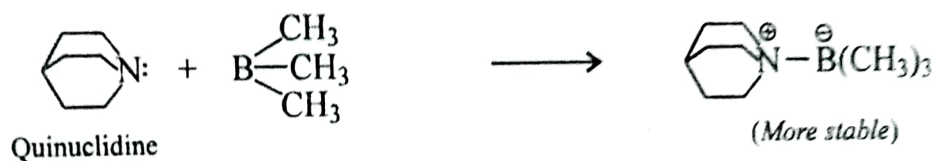
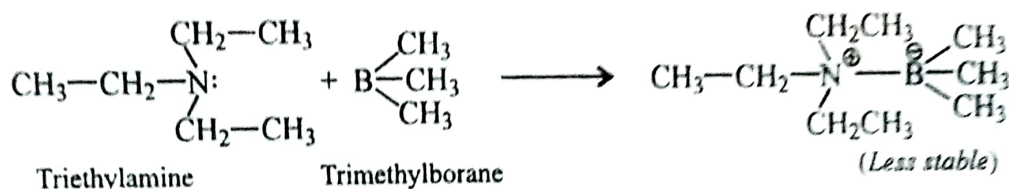


Such steric hindrance is not seen in N,N-dimethylaniline. The lone pair of electron on nitrogen is available in this case, and N,N-dimethylaniline, therefore, couples readily with PhN_2^+ as shown below :



(e) **Relative basicities of N,N-dimethylaniline and its 2,6-dimethyl derivatives.** As seen in the preceding diagrams, there is resonance inhibition (due to steric hindrance) in I and the lone pair of electrons on nitrogen is easily available. This should, and actually does, make the compound I (2,6-dimethyl derivative of N,N-dimethylaniline) more basic than II (N,N-dimethylaniline).

(f) **Relative stability of complexes.** Both triethylamine and quinuclidine having comparable base strength with almost similar structural environment, form complexes with trimethyl borane. However, the complex formed by triethylamine is unstable compared with the complex formed by quinuclidine. This difference in complex stabilities can be rationalized as follows. The substituents in quinuclidine are held back by the ring system whereas in triethylamine the substituents can rotate freely. This can block the reaction site and the resulting steric effect destabilises the complex so formed (see below).



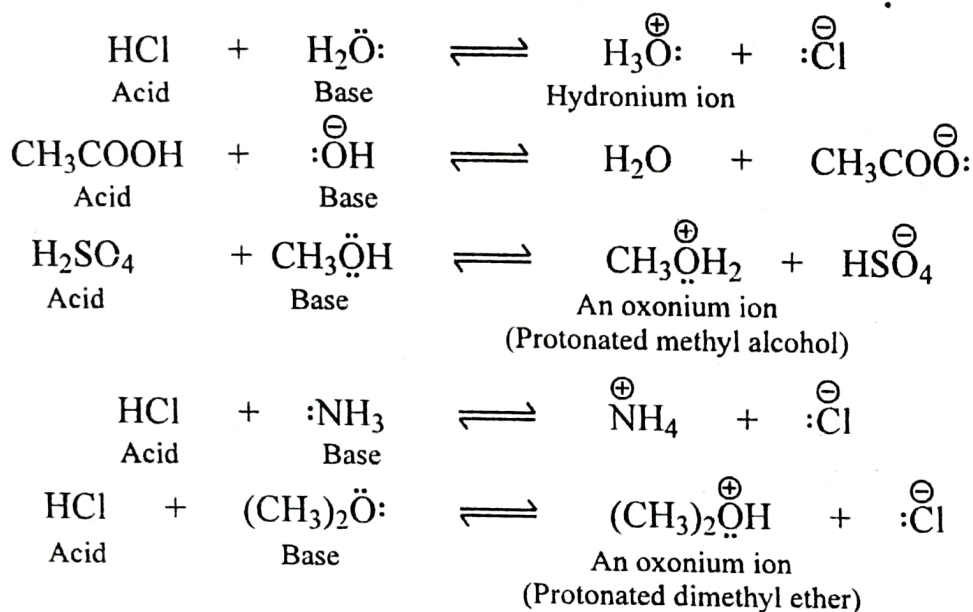
(g) **Basic characters of tertiary amines and aromatic amines.** These will be taken up in due course in the concerned chapters.

ACIDS AND BASES. The concept of acids and bases is of fundamental importance in understanding organic chemistry. It is, therefore, relevant if we define here the terms *acid* and *base* and examine briefly the factors which affect their strengths.

The two concepts of acids and bases which are much used by organic chemists are due to **Lowry-Brønsted** and **Lewis**. Let us consider these briefly.

1. The Lowry-Brønsted concept. According to this concept, *an acid is a substance that gives up a proton, and a base is a substance that accepts a proton*. Thus **an acid is a proton donor and a base is a proton acceptor**. All hydrogen compounds (e.g., HCl, H₂SO₄, CH₃COOH, H₂O, CH₃OH, NH₃, CH₃NH₂ etc.) can act as acids (even hydrocarbons are *potential* acids according to this concept), and all anions or substances containing at least one pair of unshared electrons (e.g., $\text{:}\ddot{\text{O}}\text{H:}^-$, $\text{:}\ddot{\text{O}}\text{CH}_3^-$, $\text{:}\ddot{\text{N}}\text{H}_2^-$, $\text{:}\ddot{\text{Cl}}^-$, HSO_4^- , CH_3COO^- , $\text{H}_2\ddot{\text{O}}^-$, $\text{CH}_3\ddot{\text{O}}\text{H}$, $\text{CH}_3\text{---}\ddot{\text{O}}\text{---CH}_3$, :NH_3 , $\text{CH}_3\text{---}\ddot{\text{N}}\text{H}_2$, etc.) can act as bases. Substances like $\text{H}_2\ddot{\text{O}}^-$, $\text{CH}_3\ddot{\text{O}}\text{H}$, :NH_3 , $\text{CH}_3\ddot{\text{N}}\text{H}_2$ etc., which contain hydrogen as well as electron pair (s), can act both as acids and bases and some times they do.

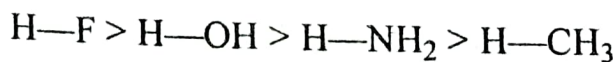
An acid and a base must necessarily react with each other. For example,



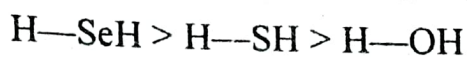
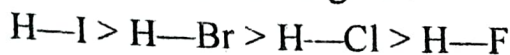
Strengths of acids and bases. The strength of an acid depends upon its tendency to *give up* a proton, and the strength of a base depends upon its tendency to *accept* a proton. *The greater the tendency of an acid to give up its proton, the stronger the acid is.* Also, *the greater the tendency of a base to accept a proton, the stronger the base is.* Hydrochloric acid is a *strong* acid because it gives up its proton very readily. Hydroxide ion is a *strong* base because it accepts a proton very readily.

Factors affecting the strength of acids and bases. The strength of an acid or a base depends on several factors. The role of a few of these factors is described below :

(a) **Nature of the atom bearing hydrogen in acids.** The strength of a Lowry-Brønsted acid depends on the nature of the atom that holds the hydrogen. The ability of this atom to accommodate the electron pair left behind after the departure of the proton is important in determining the strength of the acid. This ability to accommodate the electron pair would naturally depend on factors such as *electronegativity* and *size* of the atom. *The acid strength should increase with the increase in the electronegativity of the atom holding the hydrogen.* That this is so is borne out by the following decreasing order of acid strengths actually observed :



Also, *the acid strength increases as the size of the atom holding the hydrogen increases.* This expectation is also realised when we actually observe the following decreasing order of acid strengths :

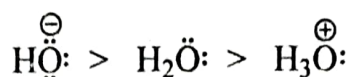


Thus, we should expect appreciable Lowry-Brønsted acidity in organic compounds containing O—H (e.g., alcohol/phenols), N—H (amines/amides) and S—H (e.g., thiols) bonds and this is actually so.

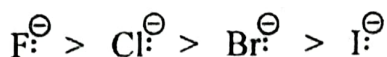
(b) **Availability of the electron pair(s) in bases.** The *availability* of the unshared electrons in a base depends on the *electronegativity, size and charge* (if any) of the atom holding them.

(i) **Electronegativity.** *The greater the electronegativity (the ability to accommodate electrons) of the atom holding the electron pair(s), the less available the pair(s) is for sharing with the proton.* Thus, $\text{H}_2\ddot{\text{O}}:$ should be and actually is, more basic than $\text{HF}:$.

(ii) The positive charge, if present on the atom holding the electron pair (s), will make the unshared electron on the atom *less* available than those on the atom bearing no charge. Similarly, if the atom holding the unshared electrons carries a negative charge, the availability of the electrons should be more than that of electrons on the atom bearing no charge. Thus, the decreasing order of basicity in the group $\text{H}_2\ddot{\text{O}}:$, H_3O^+ , HO^- should be, and actually is, as follows :



(iii) The larger the size of the atom holding the unshared electrons, the lesser the availability of the electrons is. Thus, the decreasing order of basicity in the series F^- , Cl^- , Br^- , I^- should be, and actually is, as follows :



Thus, we see that the factors of electronegativity, size and charge operate for basicity opposite to what we have seen above for acidity.

(c) **Intrinsic basicity of the atom holding the unshared electrons.** The intrinsic basicity of an atom is a measure of the degree to which the electron pair on it is under the control of the positively charged nucleus. Oxygen, compared with nitrogen, has a very low degree of *intrinsic basicity*. Thus, water, alcohols and ethers are very weak bases, but ammonia and amines are rather strong bases.

(d) **Inductive effects.** Earlier we have seen why

(i) Chloroacetic acid is a much stronger acid than acetic acid.

(ii) Dichloroacetic acid (Cl_2CHCOOH) and trichloroacetic acid (Cl_3CCOOH) are even stronger acids.

(iii) α -Chlorobutyric acid [$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{COOH}$] is a much stronger acid than butyric acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$), but isomeric β - and γ -chlorobutyric acid [$\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{COOH}$ and $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$] are only slightly stronger.

(iv) Acetic acid (CH_3COOH) is a weaker acid than formic acid.

(v) Methylamine is a stronger base than ammonia.

(e) **Steric effects.** It has been found that triethylamine, $(\text{C}_2\text{H}_5)_3\text{N}$, is a weaker base than diethylamine, $(\text{C}_2\text{H}_5)_2\text{NH}$, although it should have been otherwise on the basis of inductive effects alone. This apparent anomaly is

explained in terms of steric factors. In NH_4^+ , formed by the protonation of NH_3 , the four H-N bonds are disposed *tetrahedrally* due to their sp^3 hybridisation. Similarly, $(\text{C}_2\text{H}_5)_3\text{NH}^+$ formed by the protonation of $(\text{C}_2\text{H}_5)_3\text{N}$ would be approximately tetrahedral. However, the three bulky CH_3CH_2^- groups cause a crowding of these groups when they are forced into a tetrahedral arrangement and consequently the protonation of N in $(\text{C}_2\text{H}_5)_3\text{N}$ would be relatively more hindered than in $(\text{C}_2\text{H}_5)_2\text{NH}$.

Conjugate pairs of acids and bases, and their relative strengths. Consider the compound hydrochloric acid, HCl . It is a *strong* acid because it gives up its proton very readily. The chloride ion Cl^- , which is a *base* by definition and is also referred to as the **conjugate base** of HCl , must necessarily be a *weak* base because it has little tendency to hold on to proton. Methane (CH_4) is an extremely weak acid (it is not even considered as an acid in common usage) since it has little tendency to part with its proton. Its conjugate base, $^-\text{CH}_3$, must be necessarily a very *strong* base since it has a strong tendency to hold on to proton. *The stronger an acid, the weaker its conjugated base is. Conversely, the stronger a base, the weaker its conjugate acid is.* This relationship between the strengths of conjugate pairs of acids and bases is evident from the following examples :

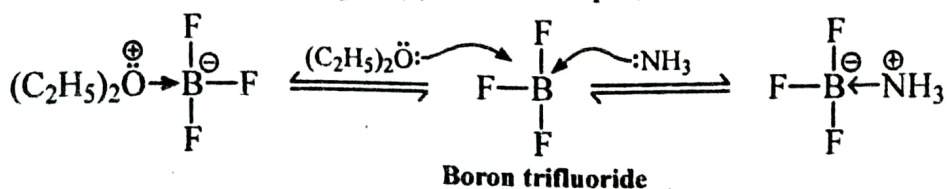
Decreasing strengths of acids $\text{HCl} > \text{H}_3\text{O}^+ > ^+\text{NH}_4 > \text{H}_2\text{O}$

Increasing strength of conjugate bases $:\bar{\text{Cl}} < \text{H}_2\ddot{\text{O}} < \ddot{\text{N}}\text{H}_3 < :\bar{\text{O}}\text{H}$

2. The Lewis concept. According to this concept, an acid is a substance that can take up an electron pair to form a covalent bond, and a base is a substance that can furnish an electron pair to form a covalent bond. In other words, according to Lewis, an acid is an electron-pair acceptor and base is an electron-pair donor.

This is the most comprehensive concept of acids and bases. It includes also the Lowry-Brønsted concept discussed above. The proton (H^+), Lowry-Brønsted acid, is an acid because it is an electron-deficient substance needing an electron-pair to complete its valency shell. Similarly, hydroxide ion, ammonia, amines, water, alcohols and others are bases because they are electron rich substances which can donate their electron pairs for sharing with electron-deficient substances.

Consider the substance boron trifluoride, BF_3 . In it, boron has only a *sextet* of electrons and hence tends to accept an electron pair to complete its *octet*. Boron trifluoride is, therefore, an acid according to the Lewis concept. As an acid, boron trifluoride should, and actually does, combine with bases containing unshared electron pair(s). For example,

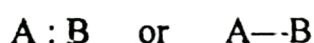


Similarly, substances like aluminium chloride (AlCl_3), ferric chloride (FeCl_3), in which Al or Fe have incomplete octets have a tendency to accept an electron pair to complete their octets, are acids in the Lewis sense. Stannic chloride (SnCl_4) in which Sn has a complete octet but can still accept another pair of electrons to form SnCl_6 , is also an acid in the Lewis sense. Thus, we see that an acid in the Lewis sense is not necessarily a substance which contains hydrogen capable of dissociating as a proton (*cf.* Lowry-Brønsted concept). All substances which are *electron acceptors* are acids in the Lewis sense. They are called **Lewis acids** to distinguish them from the more familiar proton acids like HCl , CH_3COOH , etc.

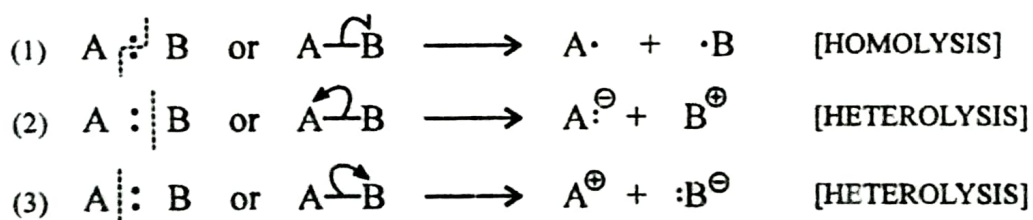
The Lewis concept of bases is similar to the Lowry-Brønsted concept of bases, except that Lowry-Brønsted bases donate an electron pair to form a covalent bond with a *proton* only but the **Lewis bases** donate an electron pair to form a covalent bond with any electron deficient substance/species. Thus, the Lewis concept of bases is also more comprehensive than the Lowry-Brønsted concept.

HOMOLYTIC AND HETEROLYTIC CLEAVAGE OF A COVALENT BOND (FORMATION OF REACTIVE INTERMEDIATES).

Consider the covalent bond between A and B :



The breaking or cleavage of this bond can take place in three ways :



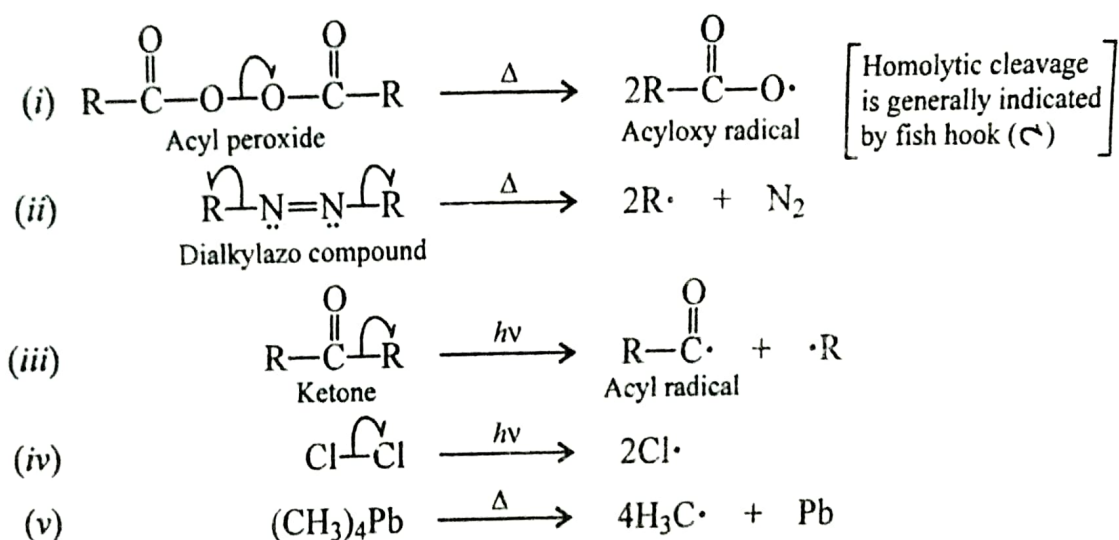
The first type of cleavage also known as *homolytic cleavage* or homolysis is obviously *symmetrical* and bond breaks in such a way that each atom or group of atoms separates with odd unpaired electrons called *free radicals*. They are generally too unstable to be isolated and are *paramagnetic*.

The second and third type of cleavage is known as *heterolytic cleavage* or *heterolysis* and lead to the formation of electron rich and electron deficient species. These ionic species are also highly reactive. These ionic species mentioned above when bear a positive charge on a carbon atom are referred to as **carbocations**. Anionic species in which the negative charge is borne by carbon are called **carbanions**.

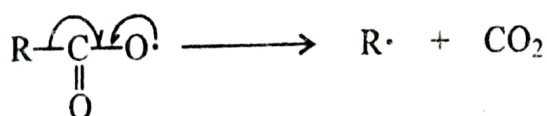
There are yet another reactive species namely carbenes, nitrenes and benzyne which are generally short lived and formed in situ. These species are often intermediates in organic reactions and the name reactive species are used for such species. Let us now consider a few aspects of such reactive intermediates.

1. Free radicals. *The paramagnetic species containing an atom or a group of atoms with one or more odd and unpaired electrons is called a free radical.* Organic reactions which are either initiated by free radicals or involve free radical intermediates are called **free radical reactions**.

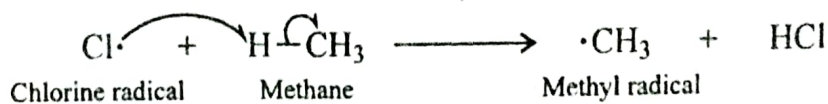
(a) Formation. Free radicals are generally formed in reactions carried out at high temperature or under the influence of high energy radiations such as ultraviolet light. The formation of free radicals is particularly easy if the bonds undergoing symmetrical cleavage are relatively weak. For example,



Occasionally, a free radical cleaves further to give yet another radical. For example,

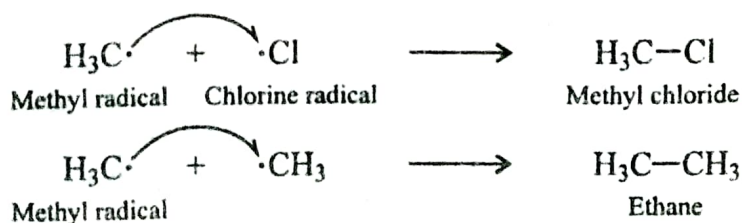


Free radicals are sometimes formed also by the reaction between radical and a molecule. For example,

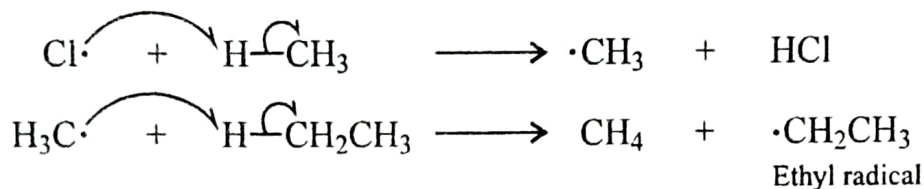


(b) Reaction. The important reactions of free radicals can be outlined as follows :

(i) Coupling of free radicals to form neutral molecules. Two free radicals readily couple (or combine) to form a stable, neutral molecule. These are the usual **termination reactions in free radical chemistry**. For example,

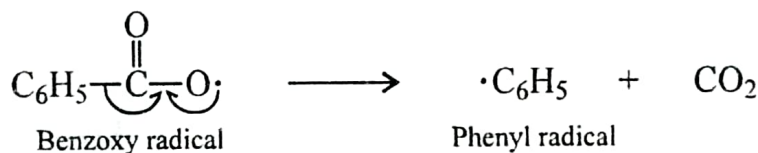


(ii) **Reaction with a neutral molecule.** A free radical may abstract an atom from a neutral molecule to form a *new* free radical. The new radical so formed usually reacts further to *propagate* a free radical reaction. For example,

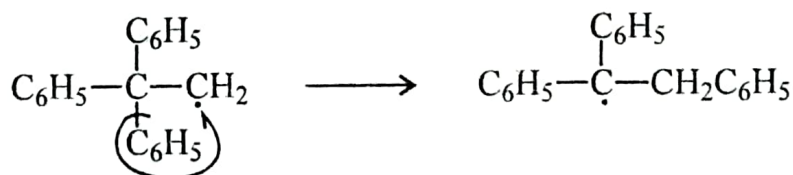


Such reactions are usually referred to as **propagation reactions** in free radical chemistry.

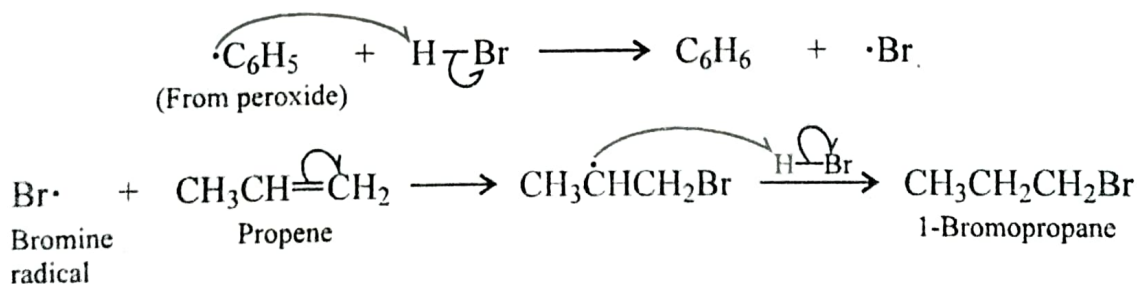
(iii) **Decomposition.** A free radical may cleave to give another radical. For example,



(iv) **Rearrangement.** A free radical may rearrange, though less readily than a carbocation, to another radical. For example,



(v) **Addition to a multiple bond.** A free radical can add to a multiple bond like a typical electrophile. The abnormal addition of HBr to propene in the presence of peroxide is one such example.



(vi) **Disproportionation.** A free radical may undergo disproportionation to form two or more neutral molecules. For example,



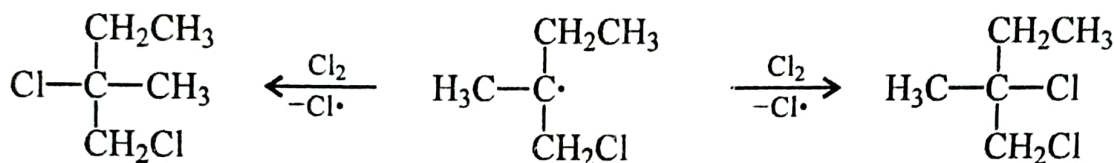
In due course we shall see the formation of these intermediates in Wurtz reaction, halogenation of alkanes, Gomberg reaction, pyrolysis, etc. at proper places.

The loss of optical activity in the above reaction is easily understood in terms of the planar structure of the alkyl radical intermediate. The chlorine molecule can attack the *flat* alkyl radical from both sides with equal ease and the product should be a racemic compound (see below).



(+)-1-Chloro-2-methylbutane

1-Chloro-2-methylbutyl
radical (3°) (*flat*)

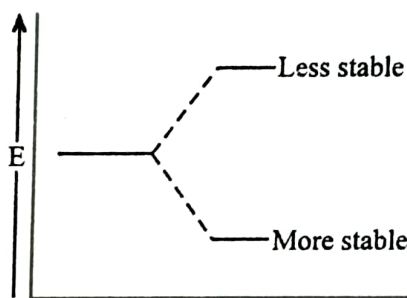


(+)-1,2-Dichloro-
2-methylbutane

1-Chloro-2-methylbutyl
radical (3°) (*flat*)

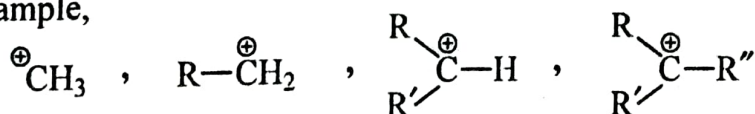
(-)-1,2-Dichloro-
2-methylbutane

(e) **Detection.** The latest technique used to detect free radicals even at low concentration (10^{-8}M) is called **electron spin resonance spectroscopy (ESR)***. The basic principle of this spectroscopy is that a free radical with *unpaired electron* has a spin associated with magnetic moment, when placed in a magnetic field, the magnetic moment generated by the spinning electron can align with or against the applied field. It prefers to align with the field of low energy content (more stable) than the other with high energy content (less stable). But however, by the absorption of light in microwave region, the spin of electron shifts against the applied field (unstable orientation). The transition between these two states produces a line in ESR spectrum. The number of such lines are equal to $n+1$ where n is the number of coupling protons. For example, methyl radical ($\cdot\text{CH}_3$) shows $3+1 = 4$ resonance lines (as shown in ESR spectrum).



ESR spectrum of $\cdot\text{CH}_3$ radical

2. Carbocations/Carbonium ions. The cationic species in which the positive charge is borne by carbon is called a **carbocation** or a **carbonium ion**. For example,



(R, R' and R'' are alkyl/aryl groups, simple or substituted. They may contain multiple bonds also).

Limitation of Definition. In examples given above, carbon is trivalent. The ending *onium ion* is generally used for a covalency higher than normal

*Spectroscopic techniques will be learnt in a separate chapter on Spectroscopy.

covalency of the charged atom (e.g., ammonium ion for NH_4^+ , oxonium ion for ROH_2^+ , etc.). Therefore, the name *carbonium ion* for the carbocation with trivalent carbon is misleading. Recently, a carbocation with *pentavalent* carbon (CH_5^+) has also been reported. Therefore, it has been suggested that the term **carbocations** be used for *carbonium ions* with **trivalent** carbon and for carbocations such as CH_5^+ , the term **carbonium ion** should be used. Since this suggestion has not been adopted universally so far, the term carbonium ion continues to be used in literature for carbocations with even trivalent carbon.

Caution ! Although the more scientific term *carbocation* has been used in this book, users of the book should keep this limitation in view while reading other books or even examination papers.

(a) **Nomenclature.** Two systems of nomenclature have been proposed. Under the **carbonium ion system**, the simplest carbocation CH_3^+ is called 'carbonium ion' and the related carbocations are named as derivatives of this 'carbonium ion'. Under the **cationic system**, these species are named as alkyl (or aryl) cations, as illustrated below :

Formula	Name Under	
	Carbonium ion system	Cationic system
CH_3^+	Carbonium ion	Methyl cation
CH_3CH_2^+	Methylcarbonium ion	Ethyl cation
$(\text{CH}_3)_2\text{CH}^+$	Dimethylcarbonium ion	Isopropyl cation
$(\text{CH}_3)_3\text{C}^+$	Trimethylcarbonium ion	<i>tert</i> -Butyl cation
$\text{H}_2\text{C}=\text{CH}-\text{CH}_2^+$	Vinylcarbonium ion	Allyl cation
$\text{C}_6\text{H}_5-\text{CH}_2^+$	Phenylcarbonium ion	Benzyl cation

Caution ! (1) Avoid using names like isopropyl carbonium ion for dimethylcarbonium ion, and *tert*-butylcarbonium ion for trimethylcarbonium ion. Under the carbonium ion system, the correct formulae for isopropyl and *tert*-butyl carbonium ions are really $(\text{CH}_3)_2\text{CH}-\text{CH}_2^+$ and $(\text{CH}_3)_3\text{C}-\text{CH}_2^+$ respectively. It may be noted that many of these names are still used in current literature rather loosely.

(2) Encourage the use of names recommended under the cationic system.

(b) **Structure.** The central carbon of a carbocation is sp^2 hybridised. The three sp^2 hybrid orbitals are utilised in forming bonds to three atoms or groups. The remaining unused p orbital remains vacant. The carbocation is thus a flat species having all the three bonds in one plane with a bond angle of 120° between them (Fig. 8).

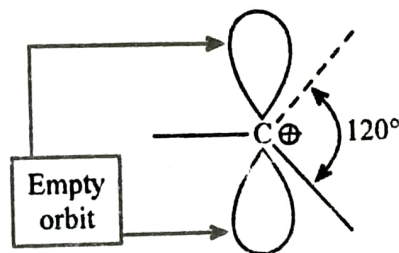
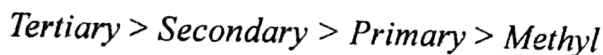


Fig. 8. Structure of a carbocation.

(c) **Stability.** The stability of a carbocation is determined to a large extent by its structure (see ahead).

(i) **Simple alkyl cations.** Among simple alkyl cations, the decreasing order of stability is :



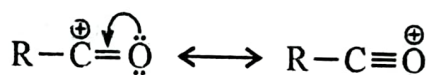
It has already been explained in terms of **hyperconjugation** and the concept of **inductive effect**.

(ii) **Allyl cation.** It is highly **resonance-stabilised**, as already explained.

(iii) **Benzyl cation.** This is also **resonance-stabilised species**, as already explained.

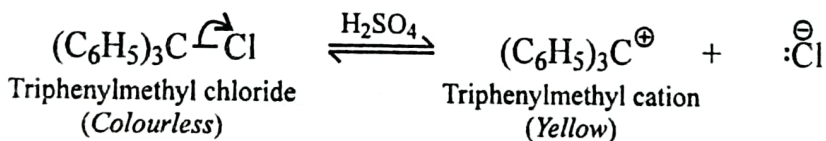
(iv) **Triphenylmethyl cation.** This is among the most stable carbocations known due to *extensive dispersal of the positive charge*, as already explained.

(v) **Acyl cations (Acylium ions).** These carbocations are also resonance-stabilised, as shown below :

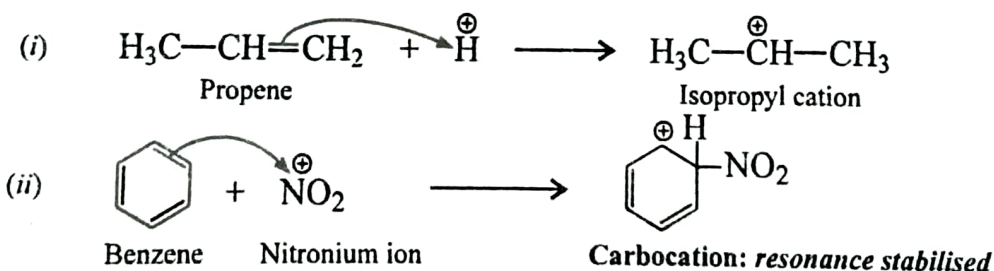


(d) **Formation.** Carbocations are formed in one of the following ways :

(1) **Unsymmetrical cleavage.** For example,

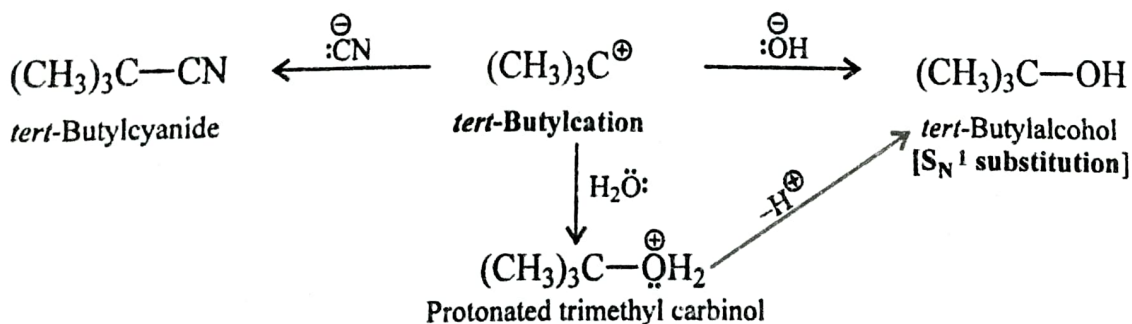


(2) **Polar additions to multiple bonds.** For example,



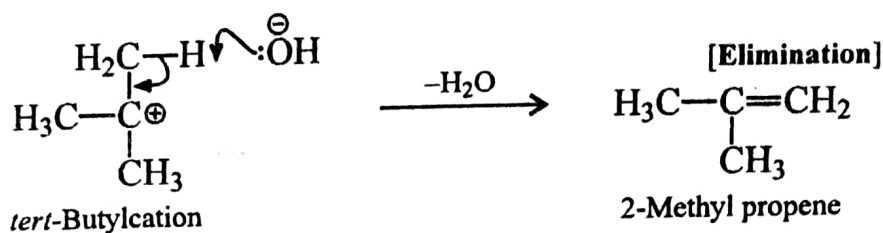
(e) **Reactions.** Some representative reactions of carbonium ions/ carbocations are :

(i) **Combination with anions or electron-rich species (nucleophiles).** For example,



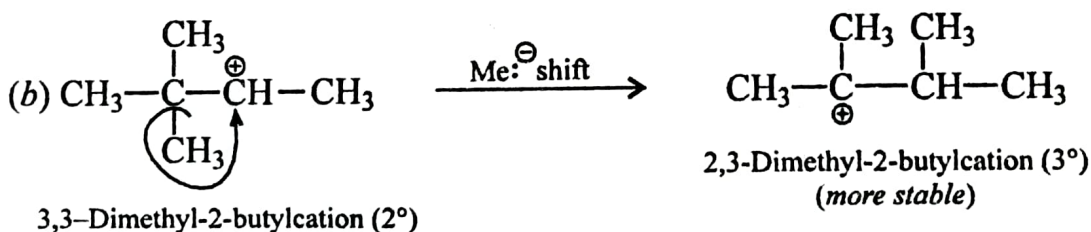
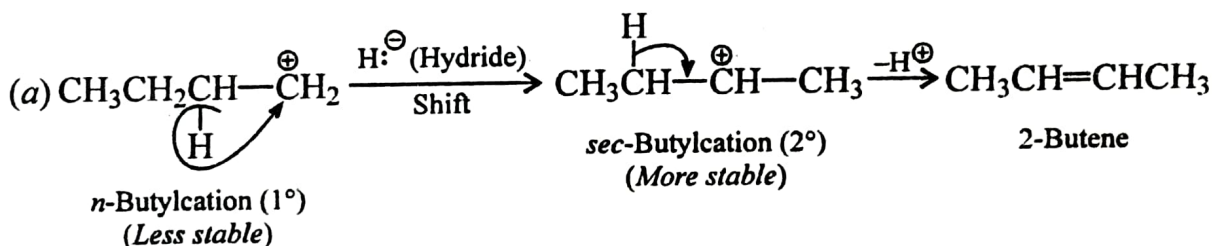
These **cations** are formed as intermediates in the **nucleophilic substitution** reaction of alkyl halides following S_N1 mechanism. For detail, see chapter 9.

(ii) **Loss of a proton or a cation from the adjacent atom.** For example,



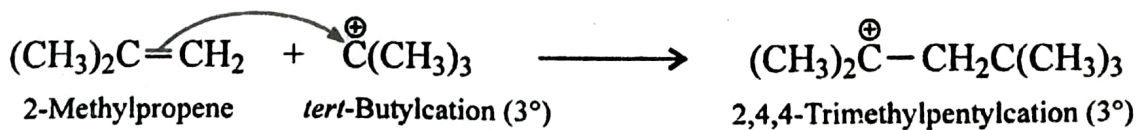
Such *carbocation intermediates* are formed in elimination reactions of **alkyl halides** and **alcohols** in the presence of alc. KOH and conc. H_2SO_4 respectively.

(iii) **Rearrangement.** A hydrogen or an alkyl/aryl group may migrate along with its electron pair to the positive centre in the carbocation and a new carbocation may be formed, provided the new carbocation is more stable than the original carbocation. For example, (a) the **dehydration** of 1-butanol to form 2-butene in the presence of conc. H_2SO_4 involves such **hydride ion** (H^\ominus) shift.



Such rearrangements involving alkyl shift R^\ominus can be seen in **pinacolpinacolone** rearrangement, **Wagner-Meerwein** rearrangement and in isomerisation of *n*-alkanes to branched chain alkanes, etc.

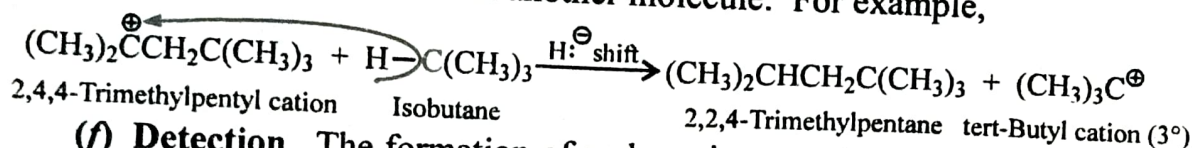
(iv) **Addition to a multiple bond.** A carbocation may add to a multiple bond to form a new carbocation. For example,



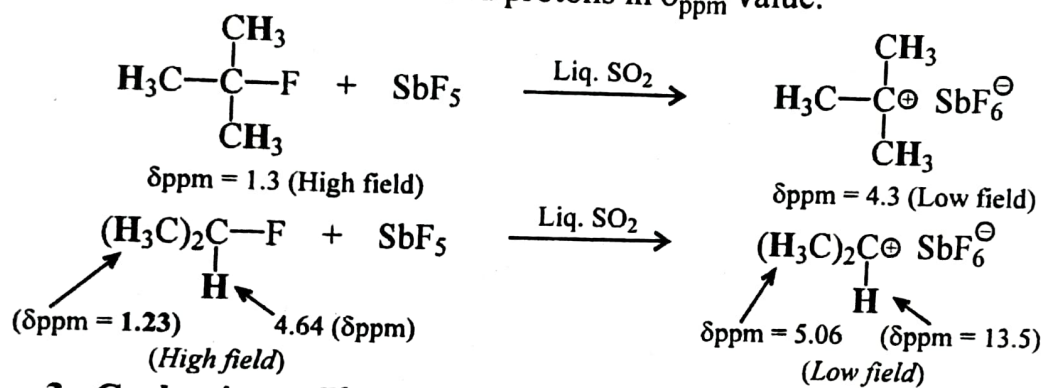
The new carbocation may combine with an anionic species to form a stable product or it may add to yet another molecule of the alkene to form a still larger carbocation (see **vinyl polymerisation**).

(v) **Abstraction of a hydride ion from another molecule.** A carbocation

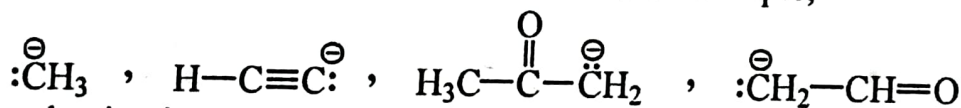
may abstract a hydride ion from another molecule. For example,



(f) **Detection.** The formation of carbocations can be detected directly by *NMR spectroscopy. For example, *tert*-butyl fluoride in liquid SO_2 gives a *singlet* of nine equivalent protons at higher magnetic field ($\delta_{\text{ppm}} = 1.3$). But the same compound when treated with SbF_5 and converted to *tert*-butyl antimony hexafluoride (carbocation) the NMR peak shifts to lower magnetic field ($\delta_{\text{ppm}} = 4.35$) due to *deshielding* of electrons caused by **carbocation** formation. Similar changes in chemical shifts can be observed in other alkyl fluorides also on treatment with antimony penta fluoride in liq. SO_2 . See equations given below with chemical shifts of concerned protons in δ_{ppm} value.



3. Carbanions. The anionic species containing a trivalent carbon with a lone pair of electrons is called a **carbanion**. For example,



A carbanion is necessarily a base (Lewis base) and also a nucleophile.

(a) **Structure.** It is likely that the central carbon in a carbanion is sp^3 -hybridised. The unshared pair of electrons occupies one of four sp^3 orbitals, the other three are involved in the formation of three bonds. Thus, carbanions would have *tetrahedral* structures (Fig. 9).

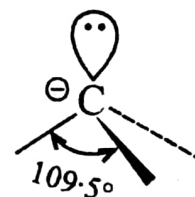


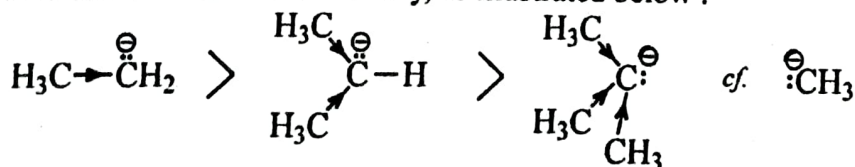
Fig. 9. Structure of a carbanion

(b) **Stability.** The stability of a carbanion is determined by its structures, as illustrated below :

(i) **Simple alkyl carbanion.** The order of stability of alkyl carbanions is :



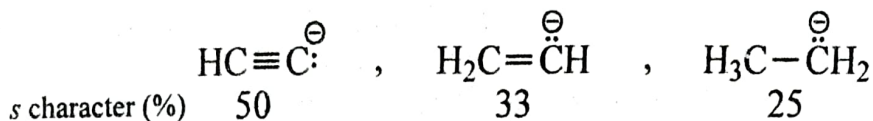
Explanation. The increasing number of electron-releasing alkyl groups in the above series increases the negative charge density at the central carbon atom of the carbanion, and thereby decreases the carbanion stability, as illustrated below :



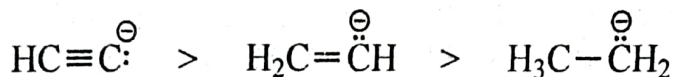
Decreasing stabilities of 1° , 2° and 3° carbanions

*These techniques shall be discussed in greater details in the chapter on 'Spectroscopy'

(ii) **Carbanions derived from alkynes, alkenes, and alkanes.** Consider the following series of carbanions and also their relative *s* characters :

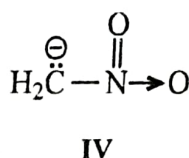
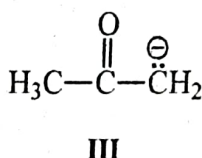
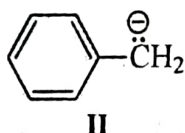
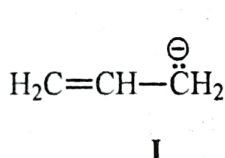


The higher the *s* character, the closer the electrons are to the nucleus and hence of lower energy. Therefore, the stability order in the above series of carbanions should be, and actually is, as follows :

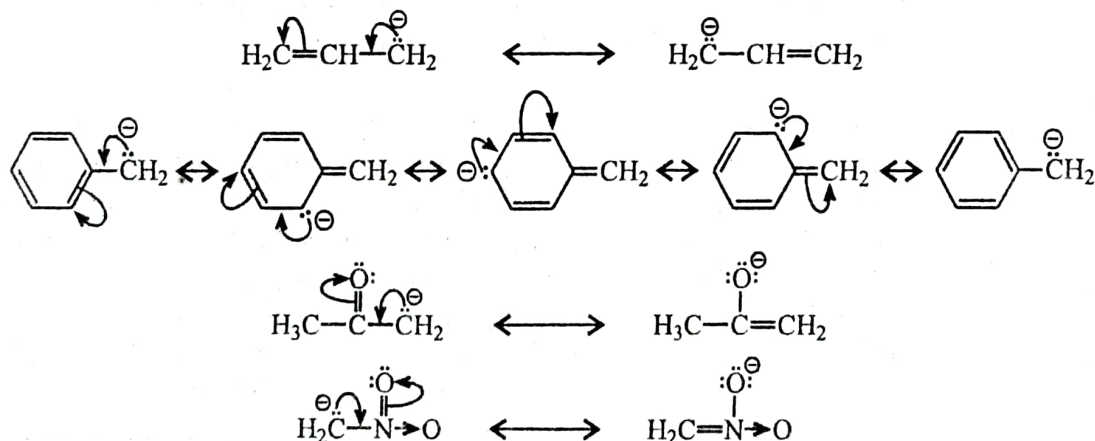


In general, stability of carbanions increases with increase in the amount of 's' character at the carbanionic carbon.

(iii) **Carbanions in which the unshared electron pair is conjugated with an unsaturated bond.** Consider the following carbanions (I to IV) in which the unsaturated bond is situated α to the carbanionic carbon :

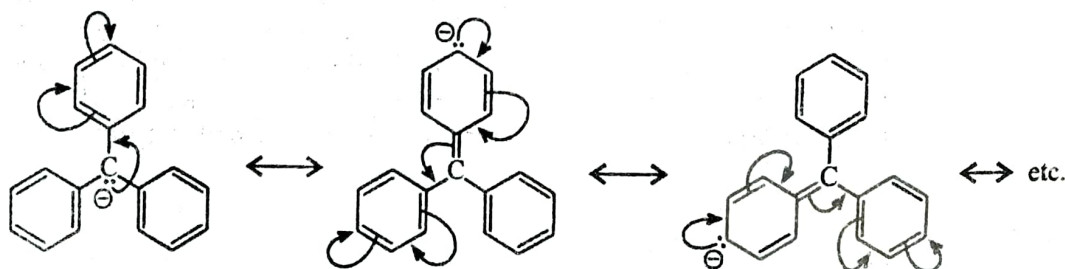


Each of these carbanions is stabilised by resonance, as shown below :



Therefore, these **carbanions** should be *more stable* than simple alkyl carbanions.

In diphenylmethyl and triphenylmethyl carbanions, resonance-stabilisation would be even more pronounced than in benzyl carbanion (II), as illustrated below in the case of **triphenylmethyl carbanion**.



Resonance stabilisation of triphenylmethyl carbanion

Obviously, the stability order among these carbanions should be as follows :



Actually, diphenyl and triphenylmethyl carbanions can be kept in solution indefinitely if water is excluded rigorously.

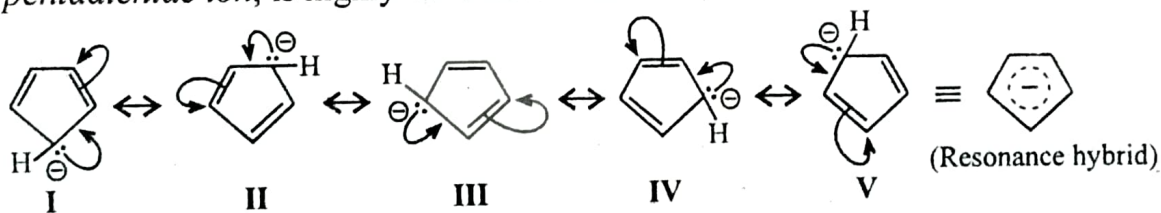
As a natural corollary, the decreasing acidity of the corresponding hydrocarbons should be, and actually is, as follows :



Compared with allyl and benzyl carbanions (I and II above) III and IV should show greater stability because the electronegative atoms oxygen and nitrogen in these are more capable of bearing a negative charge than carbon. Actually, the carbanions III and IV are more stable than even triphenylmethyl carbanion.

To sum up, carbanions in which the unshared pair of electrons is conjugated with an unsaturated bond show enhanced stability due to resonance.

(iv) **Cyclopentadienyl anion.** This carbanion, also known as *cyclopentadienide ion*, is highly resonance-stabilised, as shown below :



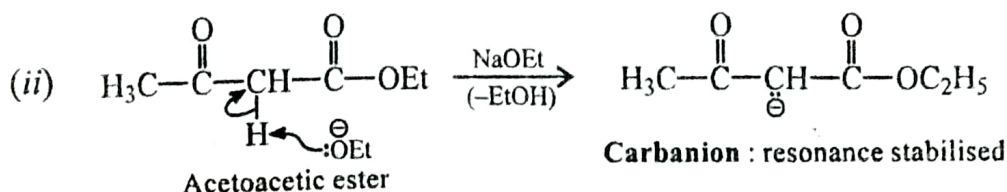
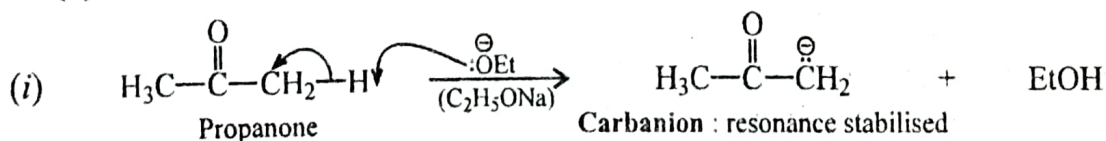
Resonance stabilisation in Cyclopentadienide ion

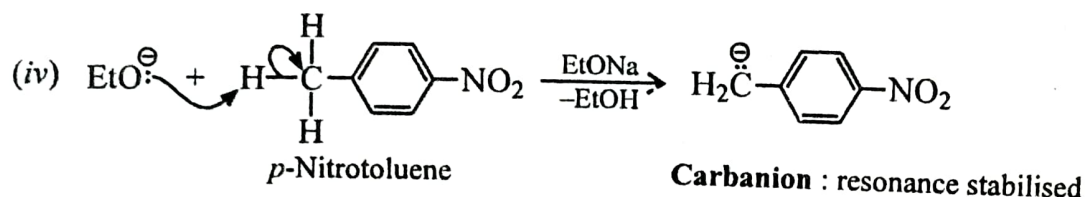
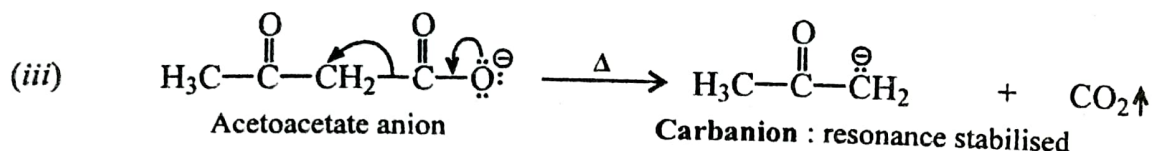
Since, all the five contributing structures (I to V) are equivalent, this carbanion should show remarkable stability (*cf.* aromatics) and is usually represented as a resonance hybrid.

The calculated resonance energy of cyclopentadienide ion is 175 kJ/mole (*cf.* benzene with resonance energy of about 151 kJ/mole). Thus, cyclopentadienide ion represents an aromatic system and it should exhibit aromatic character. Actually, the typical aromatic substitution reactions have been successfully performed on this carbanion.

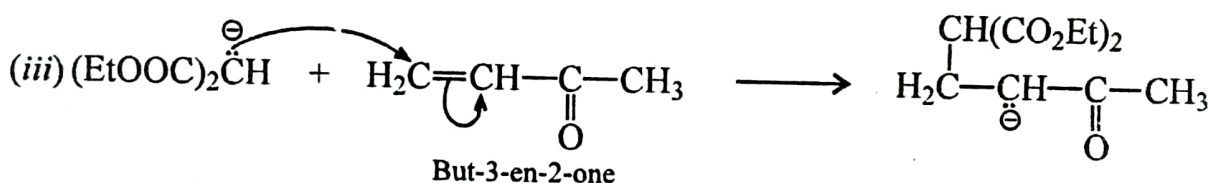
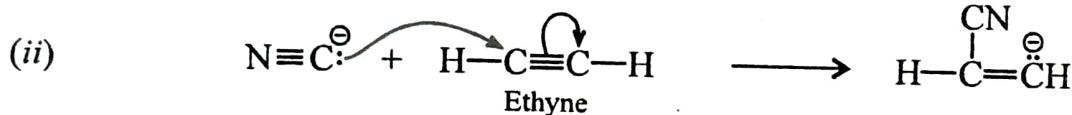
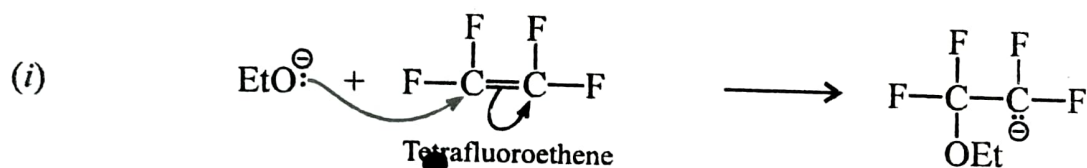
(c) **Formation.** Carbanions are formed in the following reactions, although they are generally too unstable to be isolated as such.

(1) **Direct heterolysis.** For example,



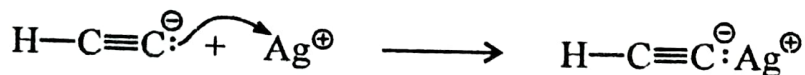


(2) Nucleophilic attack at a carbon-carbon multiple bond. For example,

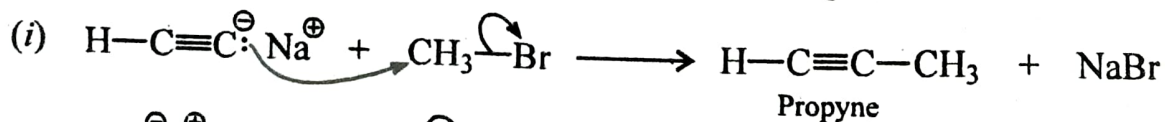


(d) Reaction. Some representative reactions of carbanions are outlined below :

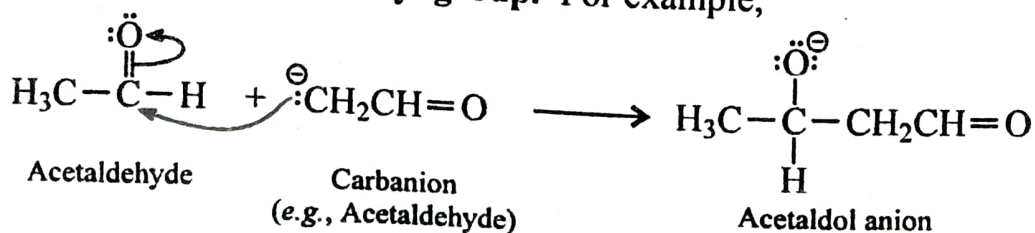
(1) Combination with a cationic species or electron-deficient species/ Lewis acids. For example,



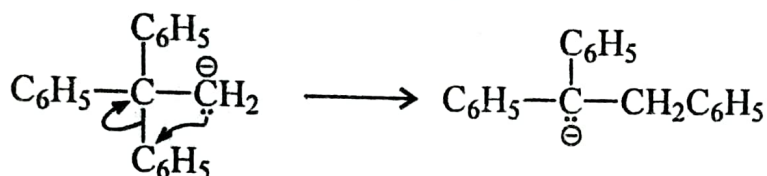
(2) Substitution at saturated carbon. For example,



(3) Addition to carbonyl group. For example,



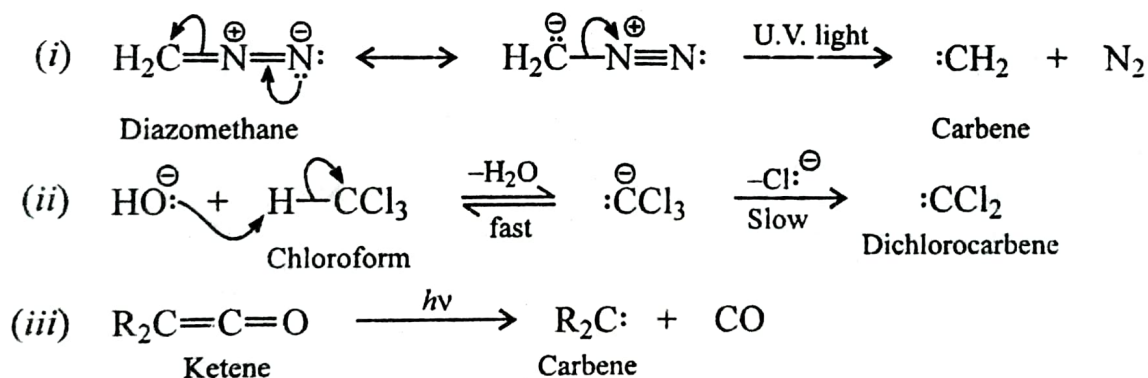
(4) **Rearrangement.** Carbanions undergo rearrangement to other carbanions, though only occasionally. For example,



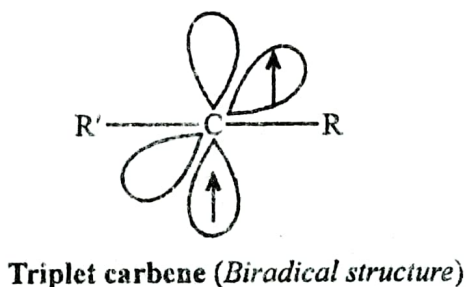
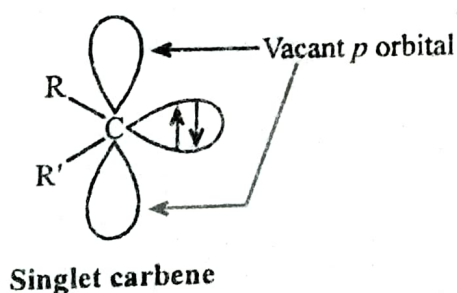
Reactions involved carbanion intermediates can be seen in condensation reactions (e.g., Aldol condensation, Knoevenagel reaction, Claisen condensation, Perkin reaction, Stobbe condensation, etc.), **Michael addition** reaction and substitution reactions utilising active methylene compounds, G.R. and acetylene. The mechanism of these reactions will be discussed in detail at proper places.

(e) **Detection.** Carbanions cannot be detected by NMR or ESR spectroscopy but the existence of carbanion is provided by the base catalysed **racemisation** of optically active ketones (e.g., phenyl *sec.* butyl ketone).

4. **Carbenes.** These are *highly reactive neutral species in which the carbon atom has six electrons in the valency shell of which two are unshared*. Carbenes are formed as intermediates in many organic reactions, as illustrated below :



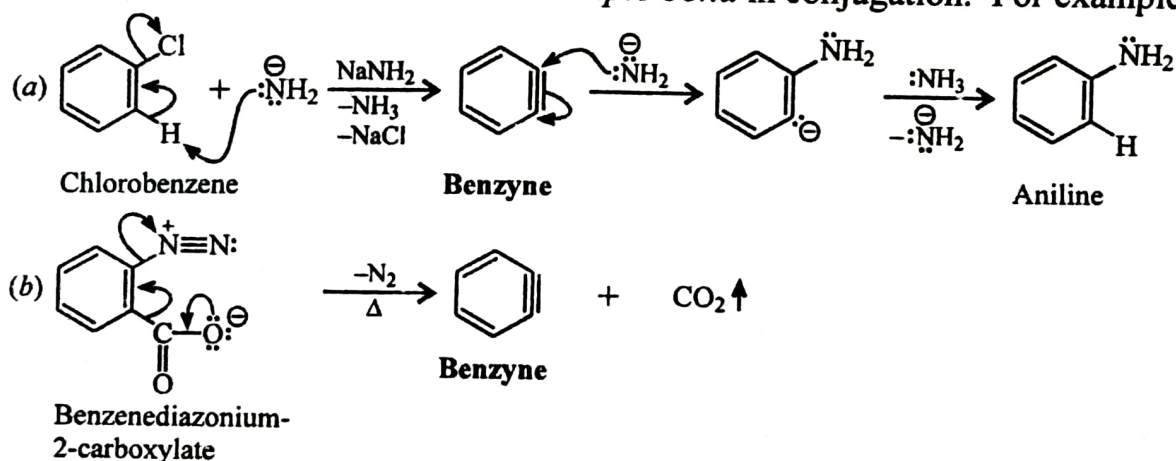
(a) **Structure.** Carbenes have two possible structures namely *singlet* and *triplet* carbenes. In singlet state carbon atom is believed to be sp^2 hybridised in which one of the sp^2 hybrid orbital contains the unshared pair of electrons with opposite spins and two sp^2 hybrid orbitals form two covalent bonds. The remaining p orbitals are vacant. The carbon atom in *triplet* carbene is believed to be sp hybridised with nearly *linear* shape. The two sp hybrid orbitals are utilised in two covalent bond formation and remaining two electrons with parallel spins occupy mutually perpendicular p_y and p_z orbitals. See structures given below :



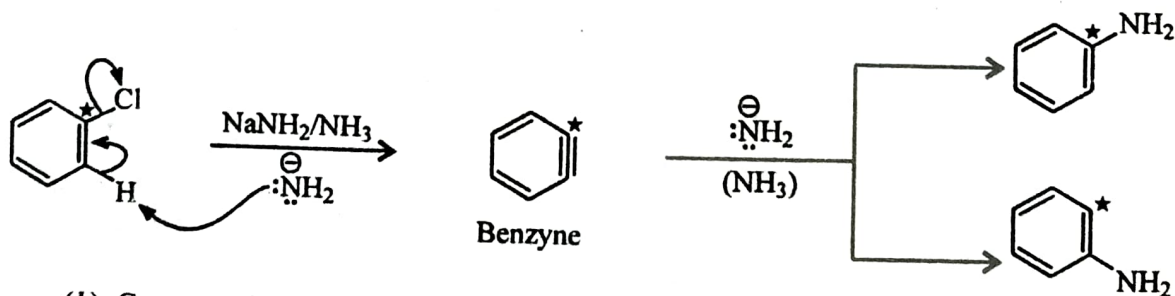
(b) **Reactions.** Reactions like **Reimer-Tiemann reaction**, **carbylamine reaction**, α -**elimination reaction**, **cycloaddition to alkene** etc. involve carbene as intermediates will be discussed in detail with their *mechanism* in concerned chapters.

(c) **Detection.** Triplet carbene bearing odd electron in two separate orbitals can be detected by electron spin resonance (ESR) spectroscopy*.

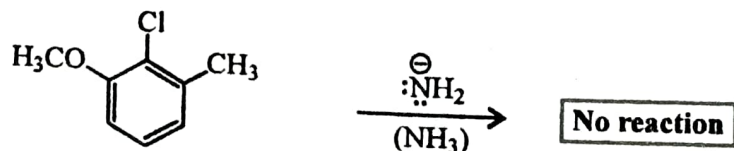
5. Benzyne/Arynes. These are the reaction intermediates formed during the reaction of aryl halides with strong bases like sodamide (NaNH_2) or pot. *tert*-butoxide. These may be considered as 1,2-dehydrobenzenes having *two* double bonds and *one* carbon-carbon *triple bond* in conjugation. For example,



Evidence in support of benzyne/aryne formation. (a) **Tracer experiments.** When chlorobenzene in which chlorine is attached to C^{14} isotope (C^*) is treated with sodamide (NaNH_2) in liq. ammonia, two types of aniline, one in which $-\text{NH}_2$ group is attached to isotopic carbon (C^*) and other in which $-\text{NH}_2$ group is borne by ortho carbon to it results. This result can be rationalised by the following reaction sequence involving benzyne intermediate.



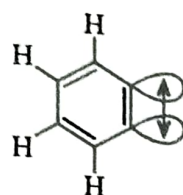
(b) Compounds containing two other substituents *ortho*-to halogen atom in benzene nucleus do not react with $\text{NaNH}_2\text{-NH}_3$, as intermediate benzyne formation is not feasible in this case due to lack of *o*-hydrogen.



Structure. The triple bond in benzyne/aryne is not like acetylenic triple bond which utilises *sp*-orbitals of two carbon atoms for a σ -bond formation

*Singlet carbenes with paired electrons in the same orbital cannot be detected by ESR spectroscopy.

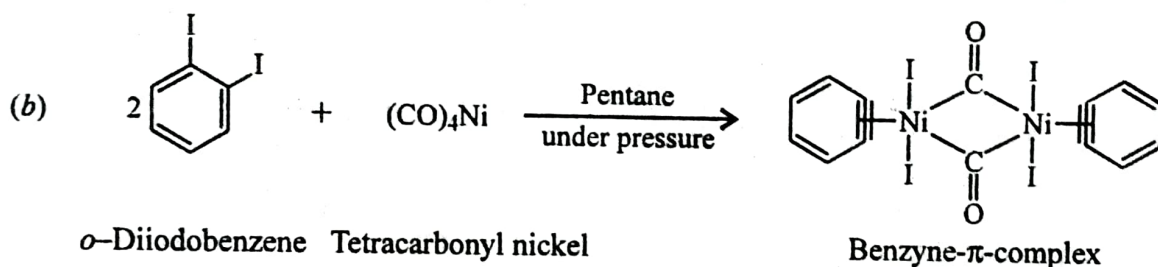
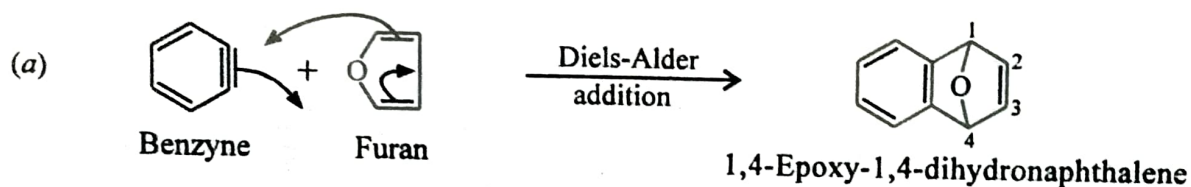
and remaining p -orbitals for π -bond formation. Such acetylenic structure is not feasible in benzyne because of **hexagonal geometry** associated with benzene ring system. Therefore, it is obvious that the new bond of benzyne/aryne must be formed by the sideways overlapping of sp^2 orbitals of two neighbouring carbon atoms as shown in structure.



Benzyne molecule :
showing sideways overlapping

Since such sideways overlapping is *not* efficient, the new bond is very weak and therefore such species are *highly* reactive.

Detection. (1) **By trapping.** These intermediates can be trapped by cycloaddition with *furan*, formation of π -complex with tetracarbonyl nickel and dimerisations (as shown below).



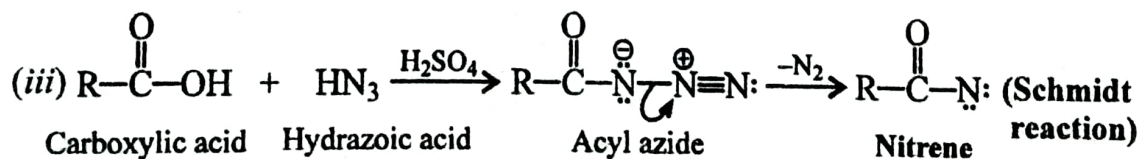
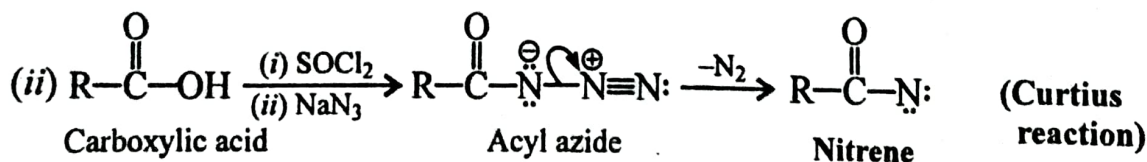
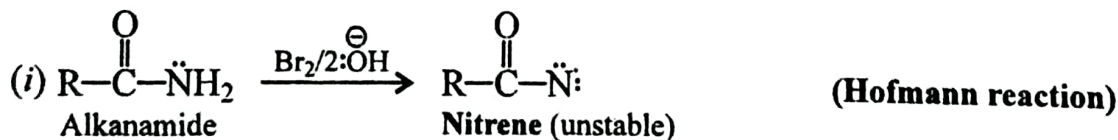
o-Diiodobenzene Tetracarbonyl nickel

Benzyne- π -complex

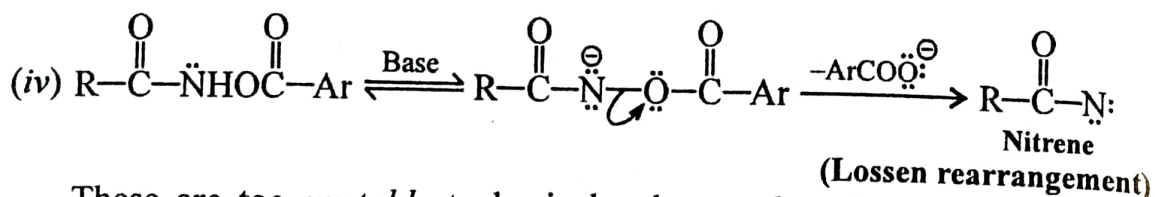
(2) These can also be detected by the combination of flash photolysis and mass spectroscopy ($m/e = 76$ for benzyne)*.

Reactions. For reactions see Ch. 30 on Aryl halides.

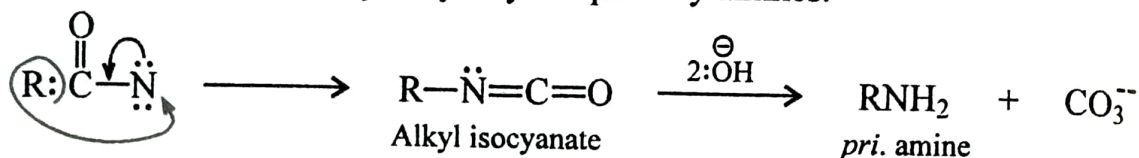
6. Nitrenes. These are *neutral, monovalent*, electron deficient nitrogen containing species, formed as intermediates in **Hofmann**, **Curtius**, **Schmidt** and **Lossen** rearrangements.



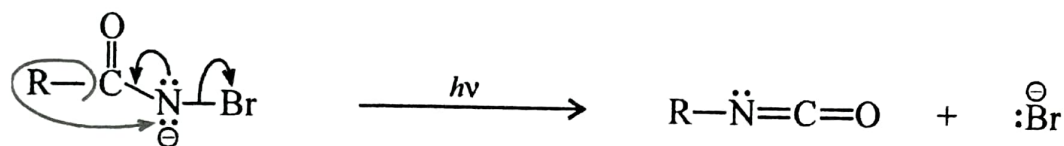
*These techniques shall be discussed in greater details in the chapter "spectroscopy".



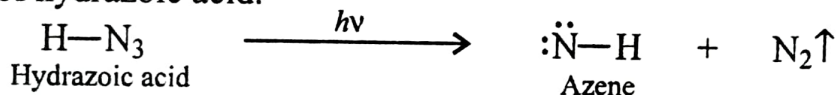
These are too *unstable* to be isolated as such and rearrange to **stable isocyanates**, which on hydrolysis yield primary amines.



Since nitrenes are too *unstable* to be isolated, it is believed that reactions like Hofmann bromamide reaction proceeds in a concerted manner to form isocyanate as shown below :



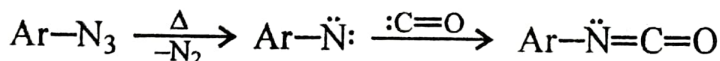
The parent nitrene $:\ddot{\text{N}}-\text{H}$, called as **azene** or **imene** is formed by the photolysis of hydrazoic acid.



(a) **Structure.** Nitrenes may be considered as nitrogen analogues of carbene in which nitrogen atom has sextet of electron in its outer shell. Similar to **carbenes** two electrons in nitrogen atom can exist either in pair as **singlet** or in different orbitals as **triplet** as shown below :

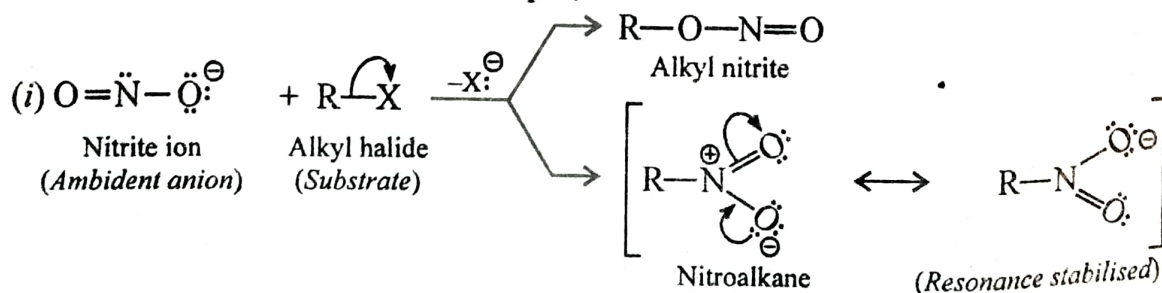


(b) **Detection.** Due to triplet structure, they can be detected by electron spin resonance spectroscopy (ESR). Occasionally, a nitrene can be trapped by its reaction with carbon monoxide to form isocyanate. For example,

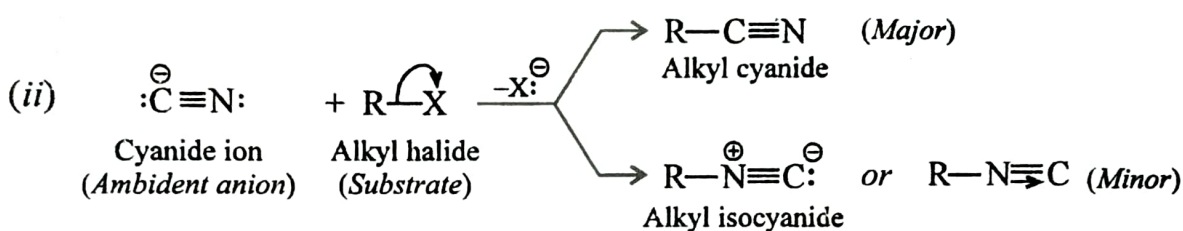
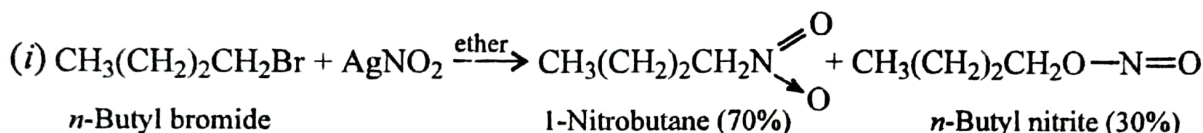


(c) **Reactions.** For detailed reactions see chapter 14 and 16.

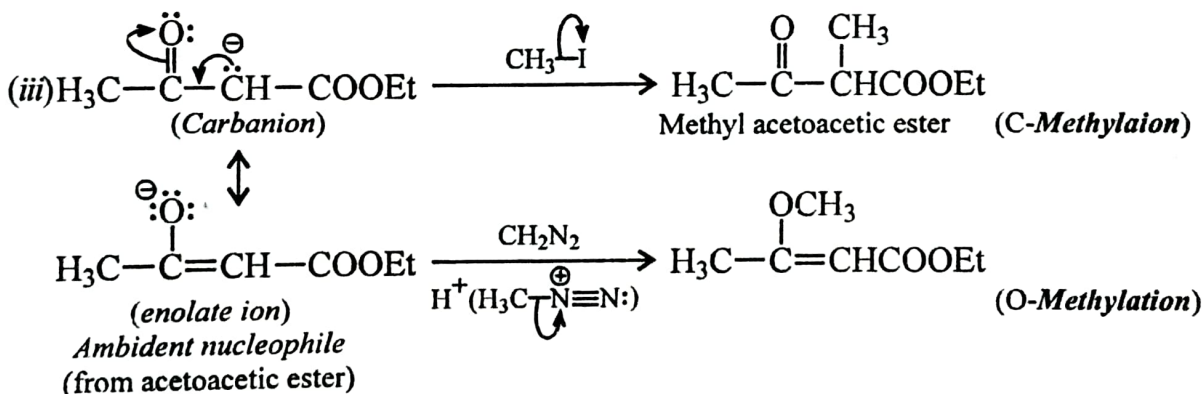
AMBIDENT IONS. Ions (anions and cations) which can react with the substrate from two *different positions* are called **ambident ion** (*ambo*, L., both ; *dentis*, L., tooth). For example,



In this example, both nitrogen and oxygen are first row elements of V and VI group and have comparable *nucleophilic* character and can attack from either site (*i.e.*, nitrogen or oxygen). The formation of these two products (alkyl nitrite and nitroalkane) depends on the reaction conditions used. For example, silver nitrite reacts with *n*-butyl bromide to give 1-nitrobutane (70%) and *n*-butyl nitrite in 30% yield.



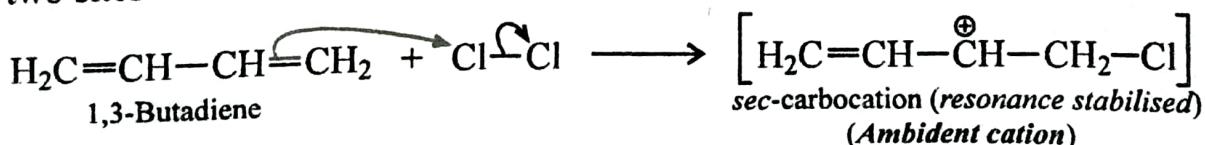
In this case both *carbanion* and *nitrogen* (part of CN) with unshared pair of electrons can attack as *nucleophile* on alkyl carbon of the halide to form *alkyl cyanide* and *isocyanide*. The amount of these products also depends on the reaction conditions and reagent used. For example, when NaCN is used alkyl cyanide is the *major* product with the formation of minor alkyl isocyanide also. A reverse order is seen if AgCN is used.

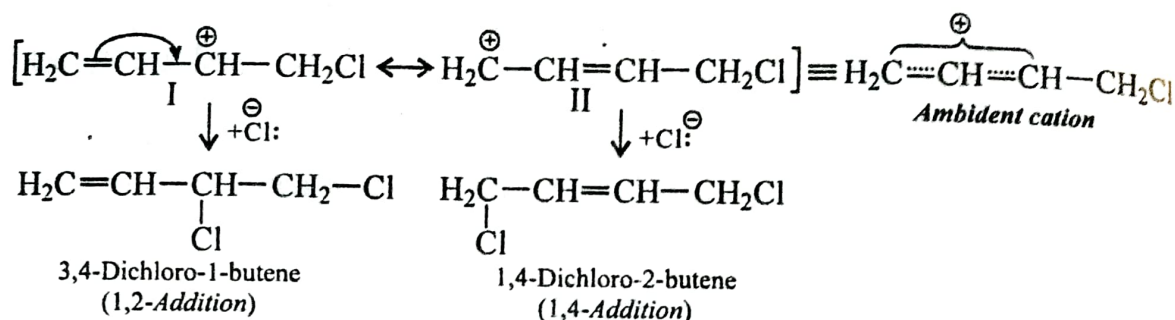


In this example, a *carbanion* (nucleophile) generated from the active methylene compound (acetoacetic ester) by sodium ethoxide (base) can undergo enolisation to give enolate ion (*nucleophile*). This provides *ambident* nucleophile from active methylene compound to form two centres of attack to form two series of products as *C-alkylated* or *O-alkylated*, as shown above.

The ambident ions cited above (i) to (iii) are all *nucleophiles* and are therefore referred to as **ambident nucleophiles**.

Now, we will consider an example of **ambident cation** which provides two sites to be attacked by a nucleophile. For example,





In this example, 1,3-butadiene when treated with chlorine gives 1,2- and 1,4-addition products. At first chlorine adds in *electrophilic* manner to yield a *sec.* carbocation intermediate. This carbocation (an ambident cation) then adds Cl^\ominus in two ways (see above) to form 1,2- and 1,4-adducts.

In due course you will find several examples of organic compounds which possess such **ambident** characteristics.

BOND DISSOCIATION ENERGY. Organic reactions involve essentially rupture and formation of covalent bonds and these processes consume/release energy. *The amount of energy taken up or liberated when a covalent bond is broken or formed is known as the bond dissociation energy (D) of that bond.* Each bond has a characteristic value of this energy and it is a measure of the strength of that bond. *The greater the bond dissociation energy, the stronger the bond is.* Table 1 lists the bond dissociation energies of some typical covalent bonds.

Table 1. Bond dissociation energies of covalent bonds in kJ mol^{-1} *

Bond	Bond dissociation energy (D) kJ mol^{-1}	Bond	Bond dissociation energy (D) kJ mol^{-1}
C-H	414	H-Cl	427
C-H (Ar)	412	H-Br	364
C-C	348	H-I	297
C-F	448	F-F	151
C-Cl	330	Cl-Cl	242
C-Br	285	Br-Br	188
C-I	212	I-I	151
C-O	356	O=O	496
O-H	464	N≡N	948
N-H	390	C=C	610
H-H	432	C≡C	834
H-F	560	C=O(CO ₂)	802
C=O (aldehydes)	736	C=O (ketones)	823

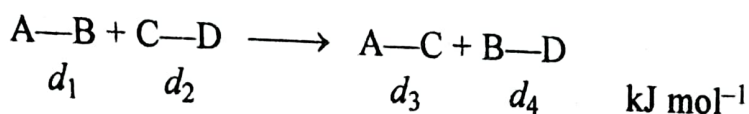
It is important to note that D is not always identical even when apparently

*Bond dissociation energies have also been expressed as kcal. If necessary corresponding values in kcal can be calculated from the relationship $1 \text{ kcal} = 4.184 \text{ kJoule}$ (often shortened to kJ).

equivalent bonds dissociate. When the four C—H bonds in methane, for example, dissociate successively, the four values of D are slightly different*. The average value of the C—H bond energy in methane would be 414 kJ mol^{-1} and such average values of **bond energies** are often denoted by the letter E to distinguish them from bond dissociation energies (D).

HEAT OR ENTHALPY OF A REACTION. *The total energy accompanying the conversion of a definite number of moles of reactions into products as per stoichiometry of the reaction is called Heat or Enthalpy (ΔH) of a reaction.*

Consider the general reaction :



(d_1, d_2, d_3, d_4 are the bond dissociation energies of the respective bonds)

$$\left. \begin{array}{l} \text{Energy required to break the bonds} \\ \text{A—B and C—D} \end{array} \right\} = (d_1 + d_2) \text{ kJ}$$

$$\left. \begin{array}{l} \text{Energy required during formation} \\ \text{bonds A—C and B—D} \end{array} \right\} = (d_3 + d_4) \text{ kJ}$$

$$\therefore \left. \begin{array}{l} \text{Total energy change during the} \\ \text{reaction} \end{array} \right\} = (d_1 + d_2) - (d_3 + d_4) \text{ kJ}$$

$$\text{or Heat of the reaction} = (d_1 + d_2) - (d_3 + d_4)$$

$$\begin{array}{l} \text{If energy consumed} > \text{energy released,} \\ (d_1 + d_2) > (d_3 + d_4) \end{array}$$

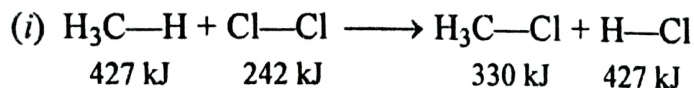
there would be over-all consumption of energy *i.e.*, the reaction would be **endothermic** and ΔH would have a +ve value.

However, if energy consumed < energy released,

$$(d_1 + d_2) < (d_3 + d_4)$$

there would be a net release of energy, *i.e.*, the reaction would be **exothermic** and ΔH would have a negative value.

Examples : (For values of bond dissociation energies, refer to Table 1)



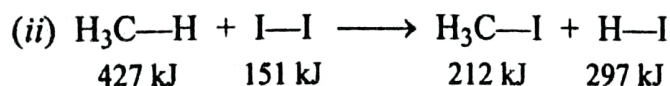
$$\begin{array}{cccc} 427 \text{ kJ} & 242 \text{ kJ} & 330 \text{ kJ} & 427 \text{ kJ} \end{array}$$

$$d_1 + d_2 = (427 + 242) \text{ kJ} = 669 \text{ kJ}$$

$$d_3 + d_4 = (330 + 427) \text{ kJ} = 757 \text{ kJ}$$

$$\text{or } (d_1 + d_2) - (d_3 + d_4) = (669 - 757) \text{ kJ} = -88 \text{ kJ}$$

Therefore, the above reaction is an exothermic reaction ($\Delta H -88 \text{ kJ mol}^{-1}$).



$$\begin{array}{cccc} 427 \text{ kJ} & 151 \text{ kJ} & 212 \text{ kJ} & 297 \text{ kJ} \end{array}$$

*The average C—H bond energy is about 414 kJ mol^{-1} .

$$\begin{aligned} \text{or } (d_1 + d_2) - (d_3 + d_4) &= (427 + 151) - (212 + 297) \text{ kJ} \\ &= 578 - 509 \text{ kJ} = 69 \text{ kJ} \end{aligned}$$

\therefore The above reaction is endothermic ($\Delta H = + 69 \text{ kJ mol}^{-1}$)

ENERGY PROFILES. Organic reactions are generally slow and they require energy in the form of heat, light, electricity, etc., to start them. Usually, the potential energy of products in a reaction is lower than that of the reactants. If we plot the progress of a reaction against the energy content of the reaction system, we get the **energy profiles** of that reaction. Fig. 10 depicts the energy profile of a single-step reaction. Apparently, the reactants have to be energised to a state, known as the **transition state** of the reaction, before they can be transformed into the products. Speaking figuratively, reactants and products of a reaction can be imagined as lying in the two valleys separated by

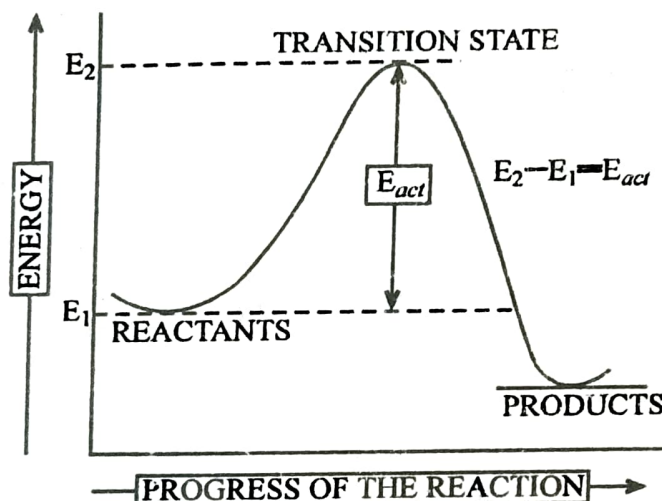


Fig. 10. Energy profile of a single-step reaction.

a steep hill. In order that reactants can move to the valley of products lying at a lower energy level, they have to *climb up* the hill separating the two valleys. The steepness of the hill corresponds to the **energy barrier** between the reactants and products which has to be crossed before the reaction can be accomplished. If E_2 represents the energy of the transition state and E_1 that of the reactants, $E_2 - E_1$ represents the amount of energy that is needed to transform the reactants into products. This energy difference is called the **energy of activation** often represented by the symbol E_{act} . It also follows that *the transition state of reaction is the state of highest potential energy acquired by the reactants during their transformation into products*. The transition state, due to its high energy content, is too *unstable* to be isolated.

Many organic reactions are multi-step reactions in which certain *stable* substances are *isolated* during the course of the reaction and these substances called **intermediates** then change into the products when they are allowed to stay in the reaction conditions. Fig. 11 depicts the energy profile of a two-step reaction, with a stable intermediate which could be isolated.

Apparently, such a reaction involves two separate transition states, the first representing the state through which the reactants pass into the intermediate

and the second representing the state through which the intermediate is transformed into the products. It is important to note that the terms **transition state** and **intermediate** are quite distinct and should not be confused as synonymous species. Intermediates are generally stable enough to be isolated, whereas transition states are species too unstable to be isolated.

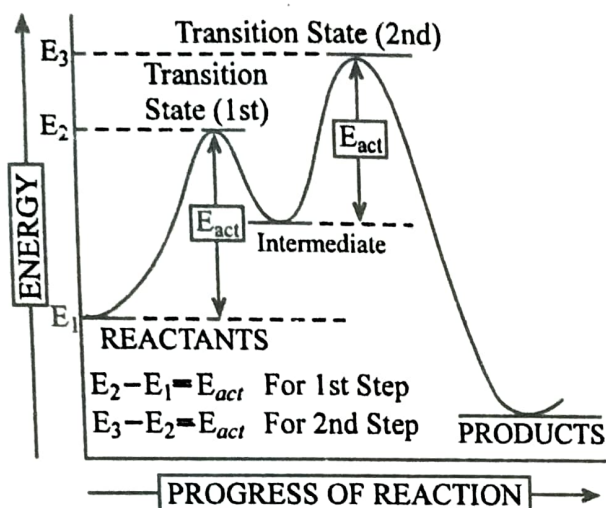
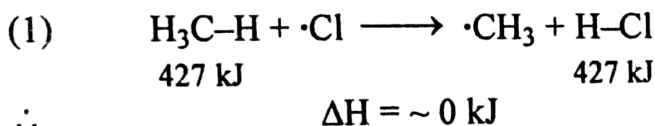
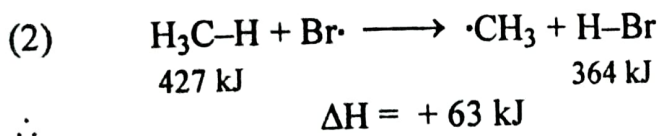


Fig. 11. Energy profile of a two-step reaction.

It is important to note that reactions, endothermic or exothermic, take place *only* when energy is supplied to reactants. This energy, commonly referred to as *energy of activation* (E_{act}), may be small or large depending on the nature of the reaction. For example,



However, it has been actually observed that energy to the extent of about 17 kJ has to be supplied for this reaction to take place. In other words, the E_{act} of this reaction is 17 kJ mol⁻¹.

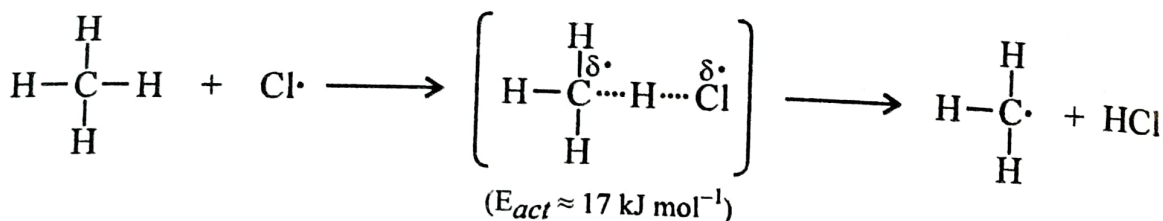


By definition, E_{act} of this reaction must be at least as large as the ΔH of the reaction.

However, actually E_{act} of this reaction is about 75 kJ mol⁻¹.

It will be seen that even exothermic reactions (ΔH is negative) would have positive E_{act} , however small, and such reactions also proceed only when some energy is supplied in the first instance to break the bonds of the reactants. Thus, *energy of activation* (E_{act}) is an important requirement of most reactions.

The term '*transition*' has been explained above in a general way and also depicted in Figs. 10 and 11. To show how this term is usually expressed in writing, consider a specific reaction sequence relevant to halogenation of alkanes.

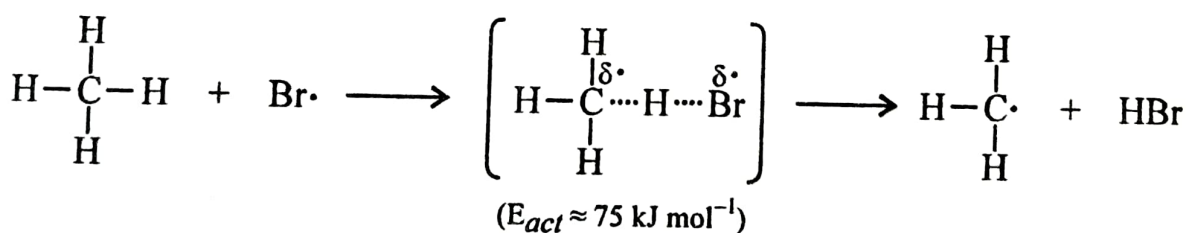


The carbon atom in methane is in tetrahedral (sp^3) state while in methyl radical it is in trigonal (sp^2) state. At the transition state, C—H bond is partly (but not completely) broken and a new C—Cl bond has begun to be formed. The carbon in the transition state is somewhere between sp^2 and sp^3 states of hybridisation. The odd electron in the transition state is equally divided between carbon and chlorine, and it is generally depicted by the symbol $\delta\cdot$ on each atom as shown above. It must be pointed out that *the transition state does not represent any substance which can be isolated or even detected*. As soon as the transition state is reached, there is a sudden fall in potential energy and products ($\cdot\text{CH}_3$ and $\text{H}-\text{Cl}$) are formed.

It may be noted that the E_{act} of the above reaction is rather low and the transition state is reached quite early. At that stage, the arrangement of atoms and electrons is almost the same as it was in the reactants. In other words, carbon is still nearly tetrahedral and the methyl group has developed very little free radical character. In such reactions, transition state tends to resemble reactants.

The relative stability of transition state is important in determining chemical reactivity. *The greater the stability of the transition state relative to the reactants, the greater the ease with which the reaction will proceed.*

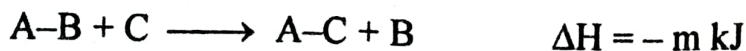
Consider now the reaction between methane and bromine atoms :



Here, the E_{act} is high and the transition state is reached rather late. At that time, C—H bond is almost completely broken and the arrangement of atoms and electrons approaches that of products. The carbon atom becomes almost trigonal and the methyl part has developed a large free radical character. In other words, transition state in such reactions tends to resemble the products.

ENERGY CHANGES DURING REACTIONS. These can be considered in general terms under the following sub-heads :

(a) **When the reaction is exothermic.** Consider the reaction :



As the reaction proceeds, there are changes in the potential energy and

these changes are depicted in Fig. 12.

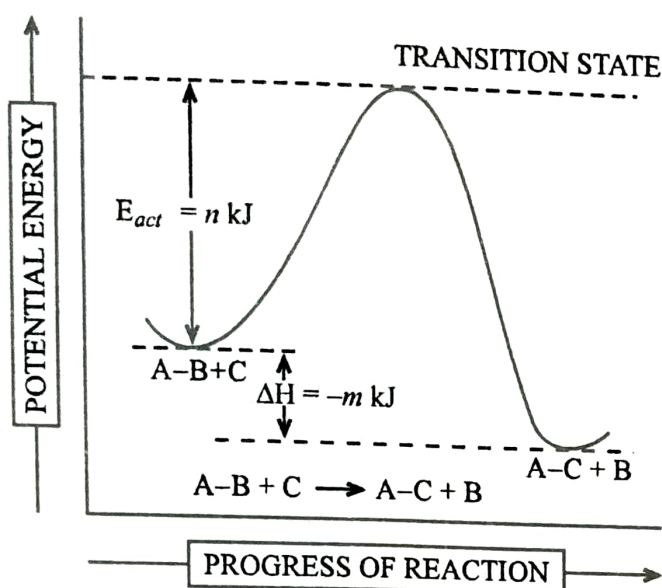
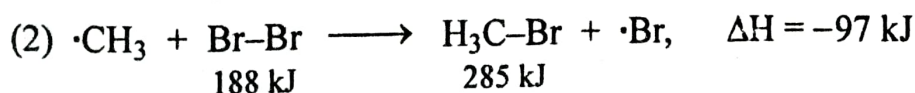
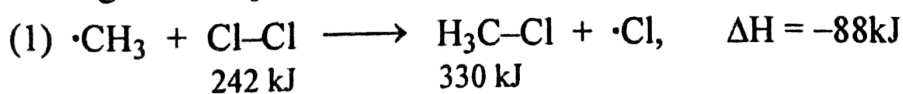


Fig. 12. Energy changes during the progress of an exothermic reaction.

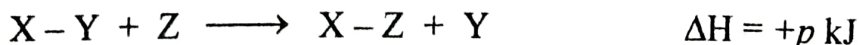
The potential energy of reactants A-B and C is shown on the left and that of the products A-C and B on the right (Fig. 12). As the reaction begins, the kinetic energy of the reactants (due to their motion) is converted into potential energy and there is an increase in the over-all potential energy. More and more kinetic energy is converted into potential energy as a result of collisions and we reach the peak level of potential energy. As the reaction proceeds further the potential energy is gradually converted back into kinetic energy till we reach the potential energy level of products. As the potential energy of products is *less* than that of reactants (Fig. 12), there must be a corresponding increase in kinetic energy. In other words, the molecules of the products (A-C and B) would be moving faster than the molecules of the reactants (A-B and C), and there would be a *rise* in temperature or heat will be evolved. ΔH , the difference in the energy contents of the reactants and products, is $-m$ kJ and E_{act} , the difference in the energy contents of the reactants and the transition state, is n kJ in this general example. In an exothermic reaction, the potential energy of the product is *less* than that of the reactants. Consequently, the E_{act} of such a reaction can be high, low or even nil. That it is actually so is evident from the following example of exothermic reactions.

As the reaction proceeds, there are changes in the potential energy and these changes are depicted in Fig. 12.



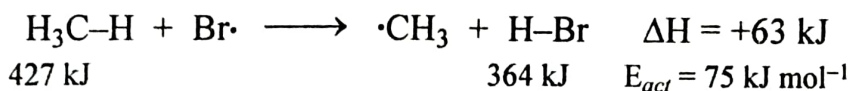
These exothermic reactions/steps should be, and actually are, quite facile. These reactions (1) and (2) are involved in the halogenation of alkanes and are very facile as expected.

(b) When the reaction is endothermic. Fig. 13 shows energy changes during the progress of the endothermic reaction :



Here, the products contain more potential energy than the reactants. Alternatively, the kinetic energy of the products is less than that of reactants (lowering of temperature) and heat will be *absorbed* from the surroundings.

ΔH , the difference in the energy contents of reactants and products is $+p$ kJ and E_{act} , the difference between the energy levels of reactants and the transition state is q kJ. It is evident from Fig. 13 that in an endothermic reaction, E_{act} should be at least as large as its ΔH (cf. an exothermic reaction). This is actually illustrated by the energy data of the following endothermic reaction :



Thus we see that *in an endothermic reaction*, E_{act} has to be at least as large as its ΔH .

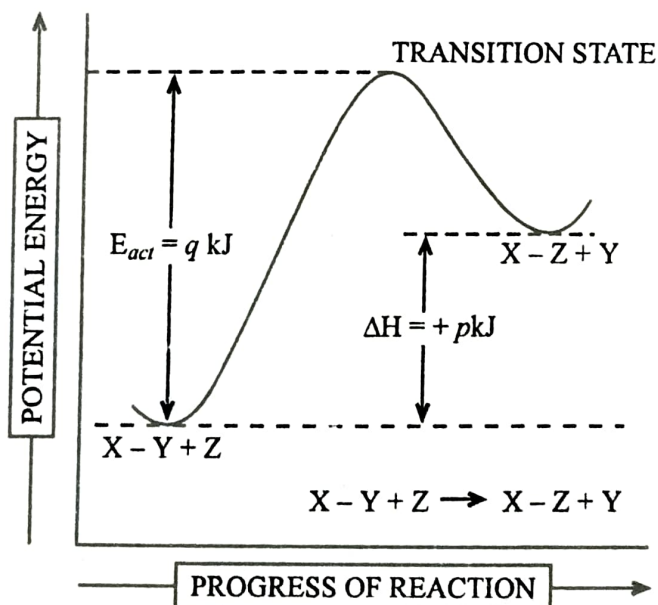
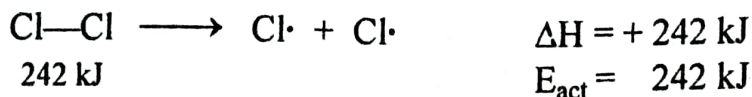


Fig. 13. Energy changes during the progress of an endothermic reaction.

(c) When it is a dissociation reaction. Consider the dissociation reaction :



Energy changes during this dissociation reaction are depicted in Fig. 14. Such a reaction involves only bond-cleavage and no bond formation. Consequently, there would only be climbing, but no descent of the slope (Fig. 14) in such cases. In other words, the E_{act} of such reactions must be equal to ΔH (i.e., m kJ). This is actually confirmed by the following dissociation reaction :



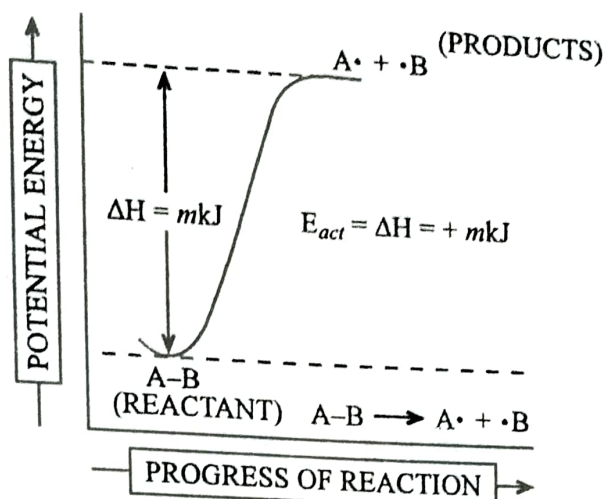


Fig. 14. Energy changes during the progress of a reaction involving simple dissociation only.

Conversely, the union of radicals ($A\cdot$ and $B\cdot$) would involve no bond cleavage and there would just be *descent* of the slope. In other words, union of radicals would require no E_{act} and it should take place almost spontaneously, as shown in Fig. 15. This is generally true for all reactions involving union or

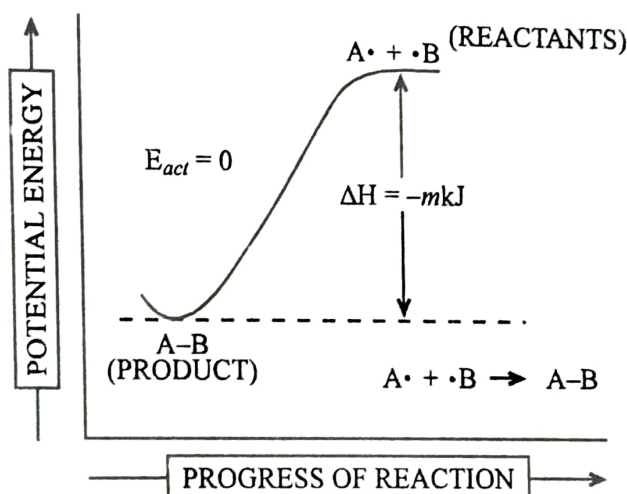
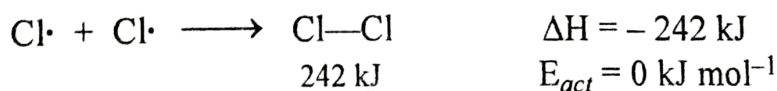


Fig. 15. Energy changes during the progress of a reaction involving bond formation only.

coupling of two free radicals. For example,



To sum up, we have learnt that

(i) E_{act} of a reaction is crucial in determining the progress of that reaction.

(ii) E_{act} of an exothermic reaction may be very high or very low or even nil, but in an endothermic reaction, E_{act} must be at least as large as ΔH .

(iii) E_{act} of a simple dissociation reaction is equal to ΔH .

(iv) E_{act} of reactions involving union of free radicals is 0.

REACTION RATE. Consider the general reaction :



In order that this reaction occurs, the reactant molecules/atoms $A-B$ and C must come close and *collide* together. However, all such collisions may not lead to the formation of products, $A-C$ and B . For a collision to be *effective* in bringing about the reaction, it must fulfil the following two conditions also :

(i) The collision must take place between really fast moving molecules/atoms so that it provides a certain minimum amount of energy required for the reaction to occur. In other words, *the collision must be sufficiently energetic*.

(ii) The collision must be head-on collision to have full impact. In other words, *the colliding molecules/atoms must have proper orientation with respect to each other*.

It is understandable that the number of sufficiently energetic collisions in a reaction would be small as compared with the total number of collisions, and those between molecules/atoms with proper orientation would be still less. In other words, the number of *effective* collision in a reaction are usually quite small except in extremely favourable experimental conditions (see below).

We have seen above that a reaction takes place as a result of *effective* collisions between reactants, *i.e.*, collisions with sufficient energy and proper orientation. It, therefore, follows that the rate of a reaction is determined by the rate at which these effective collisions occur. Mathematically, it can be expressed as follows :

Rate of a reaction = Rate of 'effective' collisions

or Rate of a reaction = The number of 'effective' collisions per c.c. per sec.

Now, the rate of 'effective' collisions depends on three factors, *viz.*, total number of collisions per c.c. per sec. (*collision frequency*), fraction of collisions of sufficient energy (*energy factor*) and fraction of collisions of proper orientation (*orientation factor*). This can be expressed mathematically as follows :

$$\text{Rate of reaction} = \left(\begin{array}{c} \text{No. of collisions} \\ \text{per c.c. per sec.} \\ \text{(Collision frequency} \\ \text{factor } N) \end{array} \right) \times \left(\begin{array}{c} \text{No. of collisions} \\ \text{with sufficient energy} \\ \text{(Energy factor } E) \end{array} \right) \times \left(\begin{array}{c} \text{No. of collisions with} \\ \text{proper orientation} \\ \text{(Orientation factor } P) \end{array} \right)$$

The rate of a reaction will naturally be influenced by changes in one or more of these three factors. Let us, therefore, consider the changes which can take place in these three factors.

(a) **Collision frequency.** It depends on (i) the concentration per c.c. or pressure in case of gaseous reactions, (ii) size of the colliding molecules/atoms, and (iii) mobility of reactants which in turn, would depend on their weight and temperature. As the size and weight of reactants are practically constant in a reaction, the collision frequency in a reaction can be varied by changing concentration per c.c. (or pressure in the case of gaseous reactants) and the temperature of the reaction.

(b) **Orientation factor.** This factor, also known as *probability factor*, depends on the shape or geometry of reactant in a reaction. As each molecule/atom has a characteristic shape, this factor does not vary much in closely related reactions.

(c) **Energy factor.** This is the most important factor affecting a reaction rate. It depends on (i) temperature and (ii) energy of activation (E_{act}) of a reaction. The E_{act} , which is characteristic of a reaction, is related to the fraction of collisions having energy greater than E_{act} by the following mathematical expression :

$$\text{Fraction of collisions with energy greater than } E_{act} = e^{-E_{act}/RT}$$

where $e = 2.718$ (base of natural logarithms)

$R = 1.986$ (gas constant)

and $T = \text{Temperature on absolute scale}$

It follows from the above exponential relationship that at a given temperature, the fraction of collisions with energy greater than E_{act} would be influenced by even a small difference in E_{act} . *The greater the value of E_{act} , the smaller the fraction of collisions possessing that energy is.*

It has been stated above that

$$\text{Rate of reaction} = \text{Collision frequency (N)} \times \text{Probability frequency (P)} \times \text{Energy factor (E)}$$

At a given temperature, the energy factor will be determined only by the fraction of collisions with energy greater than E_{act} . Therefore, at a given temperature,

$$\text{Rate of reaction} = N \times P \times e^{-E_{act}/RT}$$

Evidently, even a small difference in E_{act} will have a large effect on the effect of sufficiently energetic collisions in a reaction, and hence the rate of reaction. Other things being equal, a reaction with $E_{act} = 21$ kJ will proceed 100 times faster than the one with $E_{act} = 42$ kJ. If the energy of activation were 63 kJ, the reaction will be slower by 10,000 times.

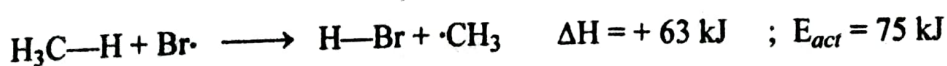
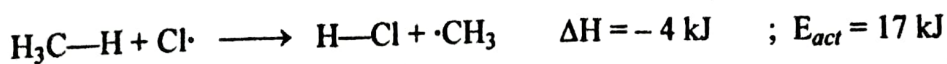
Temperature also has a marked influence on the rate of a reaction. As the temperature rises, the average kinetic energy and the average velocities of molecules/atoms taking part in a reaction increase. This in turn will lead to an increase in the fraction of sufficiently energetic collisions and hence in the reaction rate. For a given E_{act} , a rise in temperature, therefore, increases the rate of a reaction. Further, since the above mathematical expression has an exponential relationship, for a given E_{act} the reaction rate will increase considerably even by a small rise in temperature. It also follows from the above exponential relationship that *the greater the E_{act} , the greater is the effect of a given change with temperature.*

To sum up, the rate of reaction can be enhanced by (i) raising the temperature, (ii) increasing the concentration (or pressure, if reactants are gaseous) of reactants and (iii) lowering E_{act} if possible.

RELATIVE REACTION RATES. We have seen above that the rate of a reaction depends on three factors, namely collision frequency (N), orientation or probability (P) and energy (E) as expressed by the following relationship :

$$\text{Rate of a reaction} = N \times P \times E$$

Difference in the rates of two reactions will naturally depend on the difference in one or more of these factors. Let us consider two closely related reactions, say the action of chlorine and bromine atoms on methane, and see how these three factors operate to determine their relative rates. The energy data of these two reactions can be summarised as follows :



To reduce the number of variables, it may be assumed that these reactions proceed under the same conditions of temperature and concentration.

Bromine atom is no doubt heavier than chlorine atom, but it is larger too. Obviously, the effects of these two attributes tend to cancel out and there should be little difference in the **collision frequency** of these two reactions carried out at a given temperature and concentration. This is actually so in these reactions. Therefore, it can be stated that *for the same temperature and concentration, two closely related reactions do not differ much in their collision frequency and as such the collision frequency factor cannot contribute much to the difference in their reaction rates.*

Although the **probability factor** is not completely understood, it is reasonable to assume that these two closely related reactions would have similar probability factors. This is actually confirmed by the experimental data of these two reactions. In general, it can be stated that *for related reactions, a difference in their probability factor is not likely to be responsible for the large differences in their reaction rates.*

Let us now consider the role of the **energy factor** in the relative rates of these two reactions. At a given temperature, the fractions of *effective* collisions in the two reactions will naturally depend on their E_{act} . We have already seen that even a small difference in the E_{act} can cause a large difference in the reaction rate. In the two closely related examples given above the E_{act} is of the order of 17 and 75 kJ in the two reactions. The difference in the E_{act} is indeed large and it can cause an enormous difference in the energy factor, and hence the rates, of the reactions. Actually, also chlorine atoms are 250,000 times as reactive as bromine atoms in their reactivity towards methane. In general, it can be stated that *for closely related reactions carried out under the same conditions, the difference in their reaction rates are mostly due to the differences in the E_{act} .*

To sum up, *differences in the rates of closely related reactions are largely due to difference in E_{act} . The smaller the E_{act} , the faster the reaction rate.*

QUESTIONS

1. Define and illustrate the term hybridisation, as used in Organic Chemistry.
2. Why is it necessary to invoke sp^2 hybridization to explain the bonding in C_2H_4 ?
3. What are hydrogen bonds ? What type of compounds form hydrogen bonds ? How does the strength of hydrogen bonds compare with other types of bonds ? Explain why water boils at $100^\circ C/760$ mm, whereas analogous hydrogen sulphide of much higher molecular weight boils only at $-62^\circ C/760$ mm.
4. Explain why HF has a higher boiling point than HCl ?
5. Write a short note on Mesomeric effect.
6. What are the essential conditions for resonance ? Explain.
7. How has the concept of resonance been used to explain the aromatic character of benzene and naphthalene ?
8. What are (i) Carbanions (ii) Carbonium ions (carbocations) ? How are they generated ? Mention a few reactions involving carbanions and carbonium ions. Illustrate your answer with suitable examples.
9. Which do you expect to have the higher boiling point :
 o -Chlorophenol or m -Chlorophenol ? Why ?
10. Dimethyl ether and ethanol have the same molecular weight but ethanol has a much higher boiling point. Why ?
11. Select compounds from the following which have (i) sp^3 , (ii) sp^2 and (iii) sp hybridisation :
 NH_3 , H_2O , $HC\equiv CH$, CH_4 , C_6H_6
12. Indicate the type of hybridisation on each carbon atom in the following molecules :
 (a) $CH_3-CH=CH-CH_3$ (b) $CH_3-C\equiv C-CH_3$
 (c) $HC\equiv C-C\equiv CH$ (d) $CH_3-CH_2-C\equiv CH$

13. What is the significance of hybridised orbitals with types of hybridised orbitals are involved in the molecules having the following geometry :

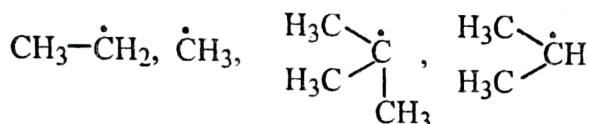
(i) Tetrahedral (ii) Planar and (iii) Collinear.

14. Explain the term "hyperconjugation" with special reference to toluene.

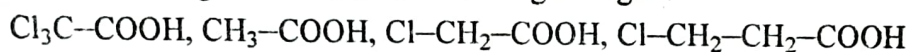
15. Write a critical note on factors affecting the strength of organic acids.

16. Discuss resonance as applied to benzene and carbon dioxide.

17. Arrange the following in the increasing order of stability :—



18. Arrange the following in the order of increasing strength :—



19. Why the carbanion, $:\ddot{\text{C}}\text{H}_2\text{CH}=\text{O}$ is stable ?

20. Make neat diagrams showing the main features of the structures of methyl free radical and ethyl carbonium ion.

21. Differentiate between Electromeric effect and Inductive effect.

22. Write a note on "Energy of activation and the transition state."

23. What are carbonium ions ? How do you account for the relative stability of primary, secondary and tertiary carbonium ions ?

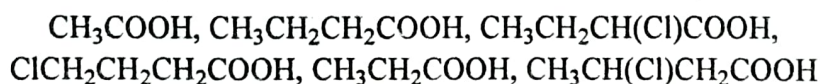
24. Discuss the stability and ease of formation of free radicals.

25. How do you account for the relative stability of primary, secondary and tertiary alkyl carbocations ?

26. Why is acetic acid a weaker acid than formic acid ?

27. Between bromoacetic acid and chloroacetic acid, which is stronger and why ?

28. Arrange the following in the decreasing order of their acid strengths :

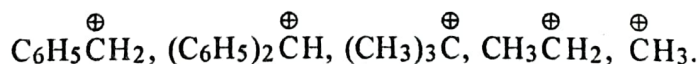


29. Between methylamine and ammonia, which is a stronger base and why ?

30. Explain the terms "Sacrificial hyperconjugation" and "Isovalent hyperconjugation", giving examples.

31. Explain with suitable examples the role of NMR spectroscopy in the detection of carbocation.

Arrange the following in order of increasing stability :



32. What are arynes ? Discuss the reactions involving aryne intermediates.

33. What are nitrenes ? Discuss the various reactions involving nitrene intermediates.

34. Define ambident ion. Discuss the reactions involving ambident *anions* and *cations*.