ORGANIC CHEMISTRY

Fundamental Concepts of Organic Chemistry

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CONTENTS

INTRODUCTION

Organic chemistry started as the chemistry of life, when that was thought to be different from the chemistry in the laboratory. Then it became the **chemistry of carbon compounds**, especially those found in coal. Now it is defined as the chemistry of carbon alongwith other elements such as are found in living things and elsewhere.

Organic compounds form the basis of life, being present in proteins, carbohydrates, nucleic acids. Millions of organic compounds occur in nature on which we depend for our food, medicines, clothing, energy. In addition, several millions of organic compounds have been synthesised by man for his needs. These include plastics, rubber, medicines, fibres etc. Thus, more than 16 million organic compounds are known. What makes carbon so special that it is able to make so many compounds? We can understand the property of carbon by examining the position it occupies in the periodic table. Being at the centre of the second row of the periodic table, it neither gives up electrons readily (like the atoms Li, Be, B which are to the left of carbon) nor does it accept electrons readily (like the atoms N, O, F which are to the right of carbon). Instead, carbon has a **tendency to share electrons**. It can share electrons with several different kind of atoms as well as with its own atoms. It is this latter property, called **Catenation,** that enables the formation of a wide variety of chain - like and branched molecules of carbon.

One immediate concern that comes to mind is how to study these vast array of compounds, and how to gather all the information that makes up Organic Chemistry. The relief comes when we see that although there are innumerous organic compounds and organic reactions and the list continues, the number of guiding principles used to explain and interrelate existing facts are relatively much lesser. These principles are especially useful since they foretell the products that may be expected from the existing ones, and can forecast the outcome of changing conditions under which already known reactions are carried out. It is these **guiding principles** that constitute the **fundamental concepts of organic chemistry.**

IONIC AND COVALENT BONDS

As it is the compounds of carbon with which we deal in organic chemistry, it is important to examine **how carbon atoms form bonds with other atoms and with its ownself**. Bonds can be classified into two broad types: ionic and covalent. Underlying both types of bonding is the fact that a **completely filled outer shell of electrons**, as in the inert gases helium and neon, is a particularly stable arrangement. One way to obtain a complete shell is-transfer of electrons, giving negative or positive species called **ions**. Elements with one or two electrons in the outer shell, i.e. the metals, can lose electrons to form positively charged ions, the cations. As we move to the right of the periodic table, elements become increasingly electronegative, and have a tendency to add electrons to complete the shell, giving negatively charged ions, the **anions. An ionic bond is simply the electrostatic attraction of oppositely charged ions, as in the salt lithium fluoride.**

In the center of the periodic table, the elements boron, carbon and nitrogen have little tendency to form ions by gain or loss of electrons. A completely filled outer shell would require an ion with three or four charges, and the accumulation of like charges leads to very large electrostatic repulsion. An enormous amount of energy is required to obtain an ion such as C^{4+}. As a result, carbon completes its electron in the outer shell by forming covalent bonds. **Covalent bonds** are formed by sharing pairs of electrons between two atoms. In 1916, G. N. Lewis suggested that the tendency of carbon to form four bonds in organic compounds could be explained by completing the electron shell of carbon by sharing four electrons from other atoms.The resulting electron pairs are localized between the atoms.

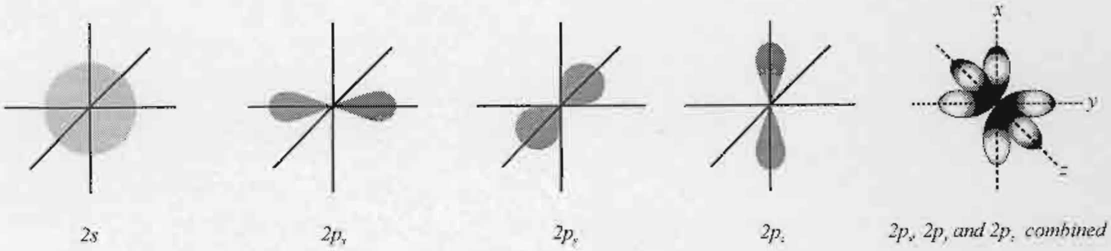
THE ORBITAL PICTURE OF COVALENT BONDING

Soon after the idea of covalent bonding had been suggested, a more detailed view of atomic structure was developed from the principles of quantum theory and wave mechanics. These concepts provided a much more complete description of chemical bonds, and paved the way to major advances in the understanding of chemical properties and reactions. According to quantum theory, electrons are arranged around the nucleus of an atom in shells and subshells, each of which has a specific energy level. The main shells are numbered 1,2,3 . . . in order of increasing energy and increasing distance from the nucleus.

The shells are made up of **orbitals**, each of which can contain a maximum of two electrons. The first shell contains one orbital, called **1s**, and the second shell, four orbitals: **2s, $2p_x$, $2p_y$** and **$2p_z$**. The three 2p orbitals are equal in energy (described as **degenerate orbitals**), and are at higher energy level than the 2s orbital.

Orbitals have definite shapes and spatial orientations. In precise terms, **orbitals represent regions of space around an atomic nucleus in which there is a high probability of finding electrons.**

The s orbitals are spherical. In contrast, p orbitals are dumbbell-shaped, with the lobes directed along three axes at right angles so that they are the maximum distance apart.



2s *$2p_x$* *$2p_y$* *$2p_z$* *$2p_x$ $2p_y$ and $2p_z$ combined*

2s and 2p orbitals

Four rules govern the order in which orbitals are filled with electrons:

1. Not more than two electrons can occupy an atomic orbital **(Pauli Exclusion principle).**
2. The two electrons in any orbital must have opposite (paired) spins.
3. Electrons occupy orbitals of lower energy first: **1s** before **2s**, and **2s** before **2p**. **(Aufbau principle).**
4. An orbital is not occupied by two electrons until all orbitals of equal energy contain one electron each **(Hund's rule).** Thus the **electronic configuration of carbon is $1s^2\ 2s^2\ 2p^1_x\ 2p^1_y$**; the superscript indicates the number of electrons in the respective orbitals.

The H_2 molecule is more stable than two separate hydrogen atoms, and there is a binding force or bond energy holding the atoms together. The bond energy in a hydrogen molecule is 104 kcal mol^{-1} (434.7 k $Jmol^{-1}$). In the formation of H_2, this amount of energy is given off, and the heat of formation is written as $\Delta H = -104$ kcal mol^{-1}(434.7 k $Jmol^{-1}$). When, however, we want to know the strength of bonding, bond energy is expressed as a positive value.

$$H\bullet + H\bullet \longrightarrow H_2 \quad \Delta H = -104 \text{ kcal/mol } (434.7 \text{ k } Jmol^{-1}).$$

VALENCE BOND THEORY AND MOLECULAR ORBITAL THEORY

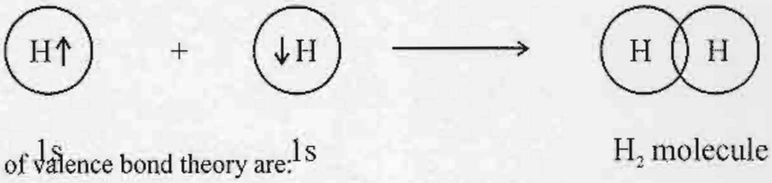
The purpose of any theory or model of chemical bonding is to provide insight into the central fact that **atoms have a strong tendency to combine into molecules.**

Two models have been developed to describe covalent bond formation: valence bond theory and molecular orbital theory. Each model has its strength and weaknesses, and chemists use them interchangeably depending on the circumstances.

Valence Bond theory

According to Valence Bond theory, a covalent bond results when two atoms approach each other closely so that a singly occupied orbital on one atoms overlap a singly occupied orbital on the other atom. The electrons are now paired in the overlapping orbitals and are attracted to the nuclei of both atoms, thus bonding the atoms together.

eg. H - H bond in H_2 molecule is formed from the overlap of two singly occupied hydrogen 1s orbital.



The key ideas of valence bond theory are:

* Covalent bonds are formed by overlap of two atomic orbitals, each of which contains one electron. The spins of the two electrons are opposite.

* Each of the bonded atoms retains its own atomic orbitals, but the electron pair in the overlapping orbitals is shared by both atoms.

* The greater the amount of orbital overlap, the stronger the bond.

The bond in the H_2 molecule has an elongated egg shape which we might get by pressing two spheres together. The H - H bond is cylindrically symmetrical, obtained by the head - on overlap of two atomic orbitals along a line drawn between the nuclei.

We must understand that there is an optimum distance required between any two nuclei forming a bond in the molecule in order to get maximum stability. Any distance between the two nuclei that is shorter or longer than this optimum distance does not favour bond formation.

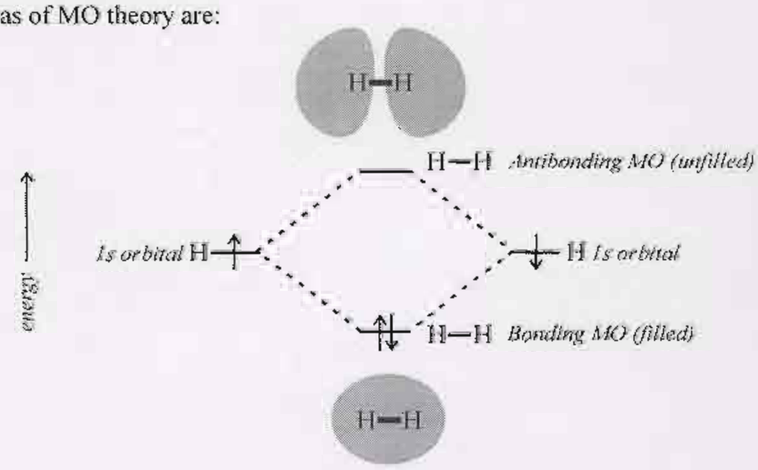
Molecular Orbital theory

MO theory describes covalent bond formation as arising from a mathematical combination of atomic orbital (in this theory, they are taken as wave functions) to form molecular orbitals. Molecular orbitals are so called because they belong to the entire molecule rather than to an individual atom and describe a region of space in a molecule where electrons are most likely to be formed. Molecular orbitals (MO), like atomic orbitals (AO) have specific size, shape and energy.

The combination of atomic orbitals always occurs in two ways - additive and subtractive.

e.g. In H_2 molecule additive combination of two 1s orbitals gives a roughly egg-shaped molecular orbital whereas subtractive combination leads to a molecular orbital that has a node between nuclei. The additive combination is lower in energy than the two atomic orbitals of the combining atoms. This combination is called **bonding MO**. Any electrons in this MO spend most of their time in the region between the two nuclei, thereby bonding the atoms together. The subtractive combination is higher in energy than the combining atomic orbitals and is called **antibonding MO**. Any electrons it contains cannot occupy the central region between the nuclei where there is a node and can not contribute to bonding. The two nuclei therefore repel each other.

The key ideas of MO theory are:



* Molecular orbitals are to molecules what atomic orbitals are to atoms. MOs describe regions of space where electrons are most likely to be found.

* MOs are formed by combining atomic orbitals. The number of MOs formed is the same as the number of atomic orbitals combined.

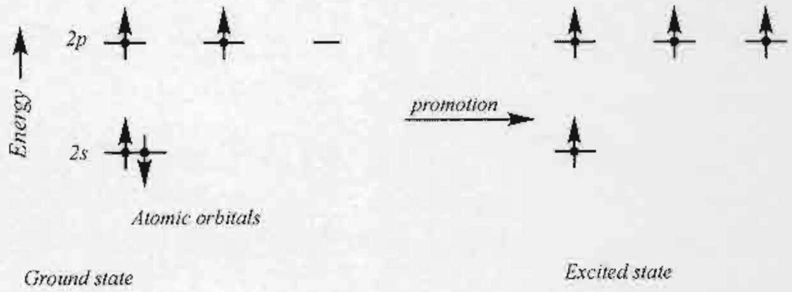
* MOs that are lower in energy than the starting atomic orbitals are **bonding**; MOs higher in energy than starting atomic orbitals are **antibonding** and MOs with same energy as the starting atomic orbitals are **nonbonding**.

HYBRIDIZATION: COVALENT BONDING OF CARBON HYBRID ORBITALS

The situation described for hydrogen extends to other elements and can be summed up in the statement that the most stable or lowest potential energy system is the one with **maximum number** of covalent bonds. For hydrogen, this number is one, since only the **1s** orbital, containing a maximum of two electrons, is available.

Of greater interest in organic compounds is bonding in carbon compounds. Since the **1s** shell is filled in all second row elements, only orbitals in the second shell are involved in bonding to other atoms. In an isolated carbon atom, two electrons occupy the **2s** orbital, and two of the **2p** orbitals each contain one electron. This arrangement would suggest that carbon can form only two covalent bonds.

This, however, is contrary to experience, for though compounds are known in which carbon is singly bonded to only two other atoms, e.g. $:CCl_2$, these are highly unstable. **In the enormous majority of its compounds carbon exhibits tetravalency**. This can be achieved by **uncoupling** the $2s^2$ electron pair and **promoting** one of them to the vacant $2p_z$ orbital. By doing this uncoupling and promotion, the carbon atom is in a higher energy (excited) state, $1s^2 2s^1 2p^1_x 2p^1_y 2p^1_z$ and so we expect the two processes not to be favoured. But as carbon now has four unpaired electrons, it is able to form four, rather than only two, bonds with other atoms or groups. The large amount of energy released by forming these two extra bonds considerably outweighs that required [≈ 97 kcal mol^{-1} (405.5 kJ mol^{-1})] for the initial $2s^2$ uncoupling, and $2s \longrightarrow 2p_z$ promotion. Thus, overall energy is released and this uncoupling and promotion is favoured.



A carbon atom combining with four other atoms clearly does not use the one 2s and the three 2p atomic orbitals as such, because this would lead to the formation of **three directed bonds** (from the three 2p orbitals), mutually at right angles , and **one different**, non-directed bond (from the spherical 2s orbital). Actually, the **four C—H bonds** in, for example, methane are known to be **identical and symmetrically disposed**.

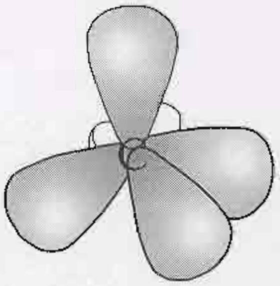
This may be accounted for by the concept of mixing orbitals, called **orbital hybridization**, proposed by Linus Pauling in 1931. The resulting orbitals are called **hybrid orbitals**. Hybridization takes place so that the concerned atom can form strong bonds and the molecule gets an overall stability. We must clearly understand that hybridization of orbitals is an operation carried out on the mathematical function that define them. It is a mathematical trick. Hybrid orbitals do not really exist. Hybridization takes place so that the atom concerned can from as strong bonds as possible, and so that the bonded atoms are kept as far apart as possible. This enables the resultant molecule to have minimum intrinsic energy.

sp^3 Hybrid Orbitals

The one 2s and three 2p orbitals of carbon are mixed together (hybridized) and then divided into four equal orbitals. The resulting hybrid orbitals are called sp^3 orbitals - where the superscript 3 means that three p orbitals were mixed with one s orbital in hybridization. Thus, four sp^3 orbitals are obtained that are all **equal in energy** (degenerate), each having 25% s character and 75% p character.

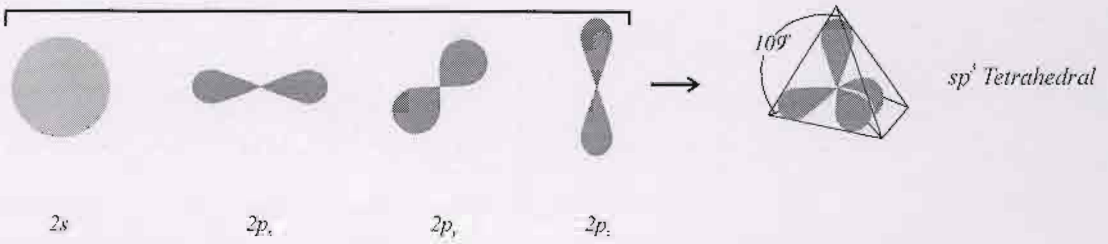
Formation of sp^3 hybrid orbitals

We can see that combining **four** atomic orbitals on the same atom gives the **same total number**, four, of hybrid orbitals. The sp^3 orbital has two lobes and a planar node through the nucleus like a p orbital. But one lobe is larger than the other because of the extra contribution of the 2s orbital, which adds to one lobe but subtracts from the other. The larger lobe is involved in covalent bond formation and hence, most of the times, only this lobe is shown for the sake of clarity.

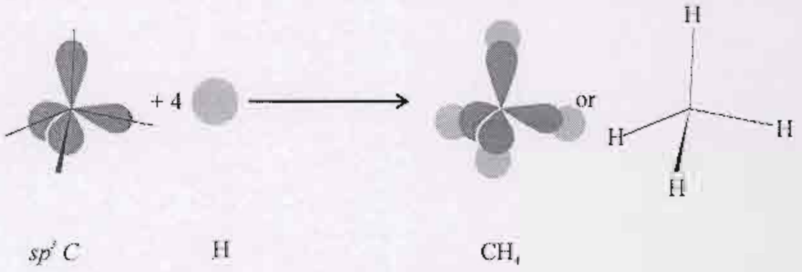


The four sp^3 orbitals arrange themselves in space in a way that allows them to get as far apart as possible.

This enables minimum repulsion of electrons. Maximum separation and hence minimum repulsion of the sp^3 bonding orbitals occur when they are directed to the corners of a **tetrahedron,** with an angle of $109^\circ 28'$ separating any two orbitals.



Consider the **case of methane, the first and the simplest member** of organic compound family. Methane is made up of four identical C—H bonds. Using the concept of hybridization, the four carbon-hydrogen bonds are formed from the overlap of the s orbital of a hydrogen with the large lobe of each sp^3 orbital of carbon. These overlaps are responsible for the identical nature of the four carbon-hydrogen bonds.



A strong bond arises from strong overlap the greater the overlap, the stronger the bond. The relative overlapping power of atomic orbitals have been calculated and found to be as follows:

s = 1.00
p = 1.72
sp = 1.93
sp^2 = 1.99
sp^3 = 2.00

The hybrid orbitals very clearly have higher overlapping powers and hence their use results in the formation of stronger bonds.

Molecular orbital description of C - H bond:

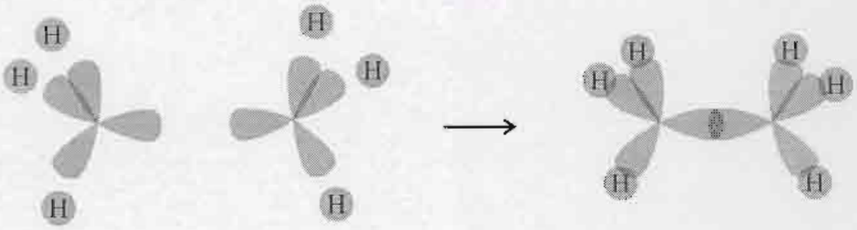
When the atoms of carbon and hydrogen have come sufficiently close (i.e. within bonding distance), overlap of their atomic orbitals gives rise to a molecular orbital (2 sp^3 + 1s). Molecular orbital contains two electrons which are distributed symmetrically around the axis between the two nucleus. This is the bonding molecular orbital, σ ,which gives rise to strong C—H sigma (σ) bond. There is also an antibonding molecular orbital σ^* (2 sp^3 - 1s) in each case, but these orbitals are empty. Thus, combination of the four sp^3 carbon orbitals and four s hydrogen orbitals with a total of eight electrons from the five atoms gives CH_4 (methane) containing four C—H bonds.

Each C—H bond in methane has a bond length of 1.10 Å and breaking any one of the bonds requires 105 kcal mol^{-1} (428.4 kJ mol^{-1}) of energy. The opposite of bond breaking i.e. formation of one C—H bond will release 105 kcal mol^{-1} (428.4 kJ mol^{-1}) of energy. Formation of four such bonds will release (105 x 4 =) 420 kcal mol^{-1} (1755.6 kJ mol^{-1}) of energy. If the atom of carbon does not undergo promotion of electrons, followed by hybridization there would have been only two bonds possible with carbon. As a result of promotion of electrons, formation of two extra bonds has been achieved. However, promotion of electrons requires the 'uncoupling' of the pair of 2s electrons and then lifting to higher energy 2p orbital. Needless to say, this requires the input of energy, calculated to be 97 kcal mol^{-1}(405.5 kJ mol^{-1}). Where is this energy being supplied from? As we can see, the energy released in the formation of the two extra C—H bonds [105 x 2 = 210 kcal/mol (877.8 kJ mol^{-1})] will more than compensate for the energy requirement for promotion of electrons [96 kcal/mol (401.3 kJ mol^{-1})] . The net result is the overall release of energy [210 - 97 = 113 kcal/mol (472.3 kJ mol^{-1})] which justifies the stability attained by the atoms in the formation of the molecule.

Carbon - Carbon Single Bonds

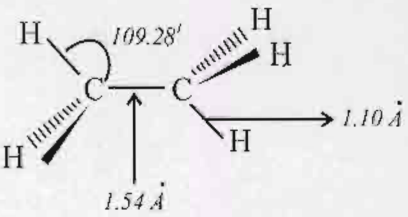
The central role of carbon in organic chemistry and in living matter depends on the fact that orbitals from two carbon atoms overlap to form strong C—C bonds. Thus a chain of virtually unlimited length can ben built up from sp^3 hybridized carbon atoms linked together by C—C σ bonds. The remaining orbitals form σ bonds to hydrogen or other atoms. The **first and the simplest member** of the family of compounds with C—C single bonds is **ethane (C_2H_6)**.

Here the combination of two carbon atoms, results from the axial overlap of two sp^3 atomic orbitals, one from each carbon atom, to form a strong σ bond between them. The remaining three sp^3 orbitals of each carbon overlaps with s orbital of hydrogen to form C—H σ bond. There are, in all, six such C—H bonds formed by the sp^3 - s overlap and one C—C bond formed by the sp^3 - sp^3 overlap.



An orbital picture of ethane

Each of the bond angles in ethane is nearly the tetrahedral bond angle of 109° 28'. In this and all other saturated compounds, the carbon - carbon bond length is 1.54 A.



The C - C bond dissociation energy is 88 kcal/mol (367.9 kJ mol^{-1}).

sp^2 Hybrid Orbitals

Hybridization of one 2s orbital of carbon can occur with two of its three 2p orbitals. This gives rise to a second type of carbon - carbon bond encountered in alkene molecules.

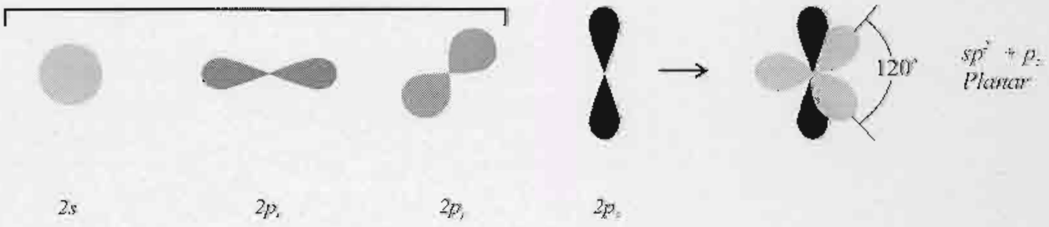
Carbon-Carbon Double Bonds

Let us take the **simplest alkene — ethene (C_2H_4)** to understand its bonding and structure.

Combination of three atomic orbitals on carbon - one 2s and two of three 2p — will give three hybrid orbitals. These orbitals are called sp^2 hybrid orbitals (superscript 2 means that two p orbitals were mixed with one s orbital in hybridization).

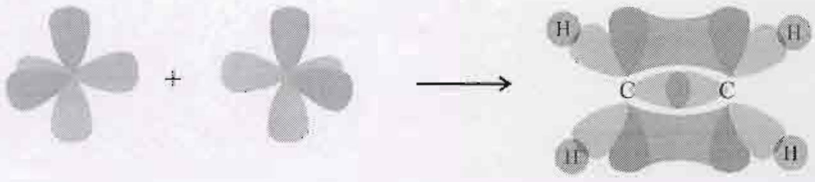
The three sp^2 orbitals are equal in energy, each having one - third s character (or 33.33% s character) and two - third p character (or 66.66% p character).

In order to get as far from each other as possible, the axes of the three sp^2 orbitals lie in a plane, directed to the corners of an equilateral triangle with the carbon nucleus in the center. This means that the bond angles are all close to 120°. Because the sp^2 hybridized carbon atom is bonded to three atoms that define a plane, it is called a **trigonal planar carbon.** The unhybridized p orbital is perpendicular to the triangular plane defined by the axes of the sp^2 orbitals.

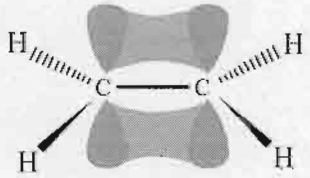


In ethene, each carbon is bonded to only **three** other atoms, two hydrogen and one carbon. Strong σ bonds are formed with these three atoms by the use of the three sp^2 orbitals. An inference drawn from this change of hybridization from sp^3 (in ethane) to sp^2 (in ethene) is that an atom normally generates **as many hybrid orbitals as it has atoms or groups to form strong σ bonds with.**

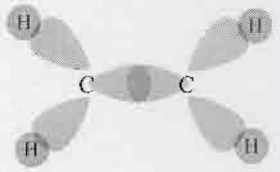
We see that there are two unhybridized $2p_z$ orbitals, one on each carbon, still left. Since p_z orbital on one carbon is perpendicular to the triangular plane containing sp^2 orbitals, it can overlap with similarly situated p_z orbital on the other carbon in a **side - to - side manner**. This overlap gives rise to what is called a pi (π) bond and is seen as the second bond between the two carbons. π bond has regions of electron density on either side of a line drawn between the nuclei but has no electron density directly between nuclei. Thus carbon atoms in ethene molecule are said to form a **double bond** with each other - one σ bond and one π bond. π bond is formed when the two p orbitals are parallel to each other to enable maximum overlap. This forces the triangle formed by one carbon and two hydrogens to lie in the same plane as the triangle formed by the other carbon and two hydrogens. Thus all the five σ bonds (one C—C and four C—H) lie in the same plane and the central π bond is formed by two $2p_z$ orbitals above and below the plane.



Bonding in ethene

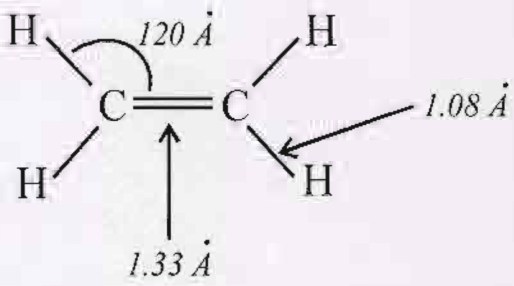


Carbon - Carbon π bond in ethene



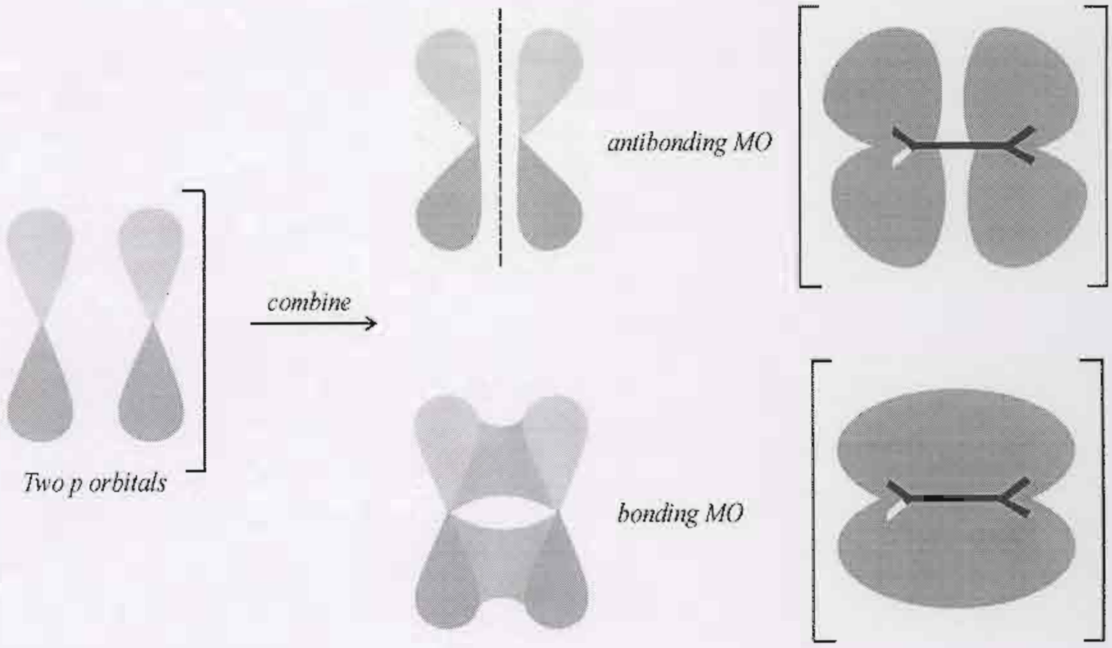
Carbon - Carbon σ bond in ethene

Because of the additional overlap and electron density (from electrons) between the two nuclei, double bond is stronger and shorter than a single σ bond (as seen in molecules with sp^3 hybridization). $C = C$ bond length is 1.33 A and the energy required to break this double bond is 145 kcal/mol (606.1 kJ mol^{-1}). The lateral overlap of the p atomic orbitals that occurs in forming a π bond is, however, less effective than the axial overlap that occurs in forming a σ bond, and the former is thus weaker than the latter. This is reflected in the fact that the energy of a carbon - carbon double bond, though more than that of a single bond is, indeed, less than twice as much. ($88 \mathrm{x} 2 \neq 145$ kcal mol^{-1})



Molecular orbital description of double bond:

Just as bonding and antibonding σ molecular orbitals result from the combination of two s atomic orbitals in H_2 (or two sp^3 orbitals / two sp^2 orbitals in ethane and ethene respectively), bonding and antibonding π molecular orbitals result from the combination of two p atomic orbitals in ethene. As before, π bonding MO has no node between nuclei and results from the combination of p orbital lobes with same algebraic sign.The π antibonding MO has a node between nuclei and results from the combination of p orbital lobes with opposite algebraic sign. Bonding MO, being lower in energy, is occupied whereas antibonding MO is vacant.



sp Hybrid Orbital

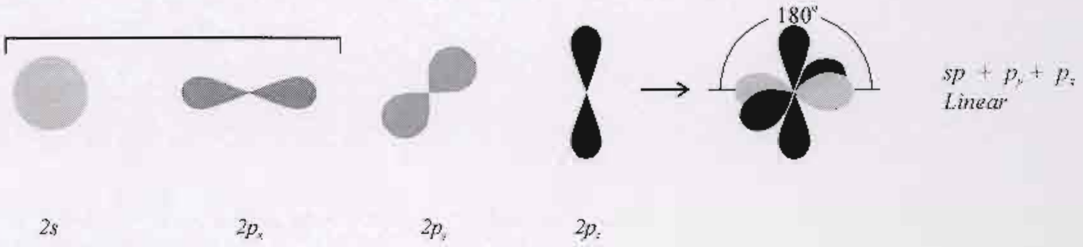
Mixing of 2s and 2p orbitals can take place in yet another manner - one 2s orbital and one 2p orbital undergo hybridization to give two sp hybrid orbitals (p carries no superscript, indicating the participation of only one p orbital).

Such hybridization gives rise to a third type of carbon - carbon bond encountered in alkynes.

Carbon-Carbon Triple Bonds

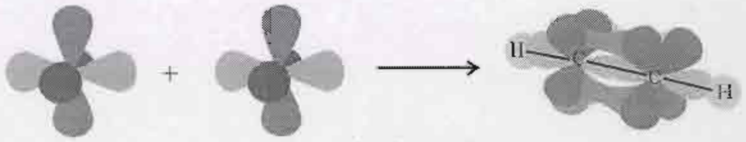
Let us take the **simplest alkyne - ethyne (C_2H_2)** to understand its bonding and structure.

The two sp orbitals are equal in energy - each having one - half s character (50% s character) and one - half p character (50% p character). The two hybrid sp orbitals will face minimum repulsion from each other when they are kept at maximum separation - 180° apart with the carbon nucleus at the centre. They are thus collinear orbitals pointing in opposite direction.

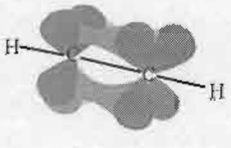


This leaves two unhybridized p_y and p_z orbitals on each carbon which are perpendicular to each other and also perpendicular to the sp orbitals.

In ethyne molecule, each carbon is bonded to only two other atoms - one carbon and one hydrogen. One of the sp orbitals on one carbon overlaps with one sp orbital of the other carbon to form carbon - carbon σ bond. The other sp orbital on each carbon formS a σ bond by overlapping with 1s orbital of hydrogen. Each of the remaining unhybridized p orbital ($2p_y$ and $2p_z$) engage in a side - to - side overlap with a parallel p orbital ($2p_y$ and $2p_z$) on other carbon to give two π molecular orbitals seen as two π bonds in - plane at right angles to each other.



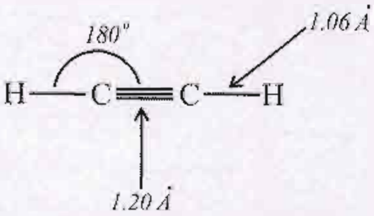
bonding in ethyne



Carbon - Carbon π bond in ethyne

Carbon - Carbon σ bond in ethyne

The carbon atoms on ethyne are said to form a triple bond with each other - one σ and two π bonds. The skeleton of the molecule is linear with three σ bonds (one C—C and two C—H) and two π bonds. Triple bond exhibits additional overlap and electron density (six electron) between the two carbon nucleus, which is even greater than that seen in double bond. It directly implies that triple bond is stronger [192 kcal/mol (802.6 kJ mol^{-1})] and shorter (1.20 A) than a double bond.

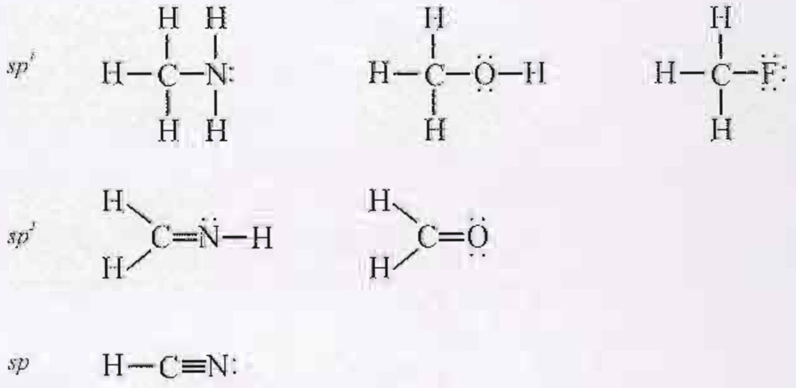


In this way, hydrocarbon skeletons are build up from tetraheral (sp^3), trigonal planar (sp^2) or linear (sp) hybridized carbon atoms. It is not necessary for us to go through the hybridization process each time we want to work out the shape of a skeleton. All we have to do is count up the single bonds at each carbon atom. If there are two, that carbon atom is linear (sp hybridized), if there are three, that carbon atom is trigonal (sp^2 hybridized), and, if there are four, that carbon atom is tetrahedral (sp^3 hybridized). We must understand that two atoms can form only **one σ bond** with each other. Any additional bond between them is a π bond.

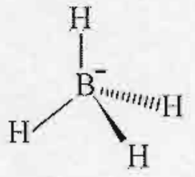
HYBRIDIZATION IN MOLECULES HAVING HETEROATOMS WITH / WITHOUT CARBON

Hybridization is a property of atomic orbitals rather than specifically of carbon. Since all atoms have atomic orbitals we can hybridize any atom. Thus covalent bonds of atoms with carbon or without carbon can be formed using the same concept of hybridization.

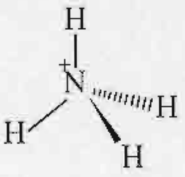
compound of carbon with N, O and F



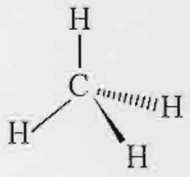
Similarly, a molecule with no carbon atom, such as the ones shown below, can also be studied on the same pattern. Both the molecules have a tetrahedral arrangement about the central atom.



borohydride anion

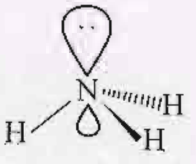


ammonuim cation

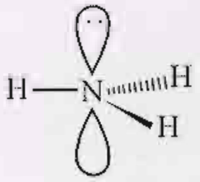


This arrangement of bonds can be rationalised by describing the central atoms as sp^3 hybridized. There are four equivalent σ bonds from the central sp^3 atoms; whether it is B or N and the same total number of bonding electrons. These molecules are said to be isoelectronic. These three elements come and after the other in the perodic table so each nucleus has one more proton than the last: B has 5, C has 6, and N has 7. This is why the charge on the central atom varies.

Take the example of a molecule with three bonds with central atom. e.g. NH_3. There are three N - H bonds bonds, each with two electrons. In addition, the central nitrogen atom also has a lone pair of electrons. We have two choices: either we could hybridize the nitrogen atom sp^2 and put the lone pair in the p orbital or we could hybridize the nitrogen sp^3 and have the lone pair in an sp^3 orbital.



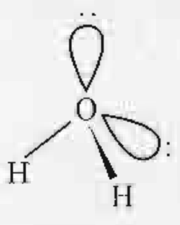
sp^3 N



sp^2 N

Since the extra pair of electrons contributes to the overall enrgy of the molecule, it should be in the lower energy orbital i.e. it should be in sp^3 rather than pure p. NH_3 therefore, has a sp^3 hybridized N with 3 N - H bonds in the three corner of a tetrahedron. The fourth corner is occupied by the lone pair of electrons. This gives NH_3 a pyramidal shape with N at apex and three H forming the triangular base.

On the same logic, in H_2O molecule the central O atom is sp^3 hybridized giving two σ bond with hydrogens. The remaining sp^3 hybrid orbitals are used to hold the two lone pair of electrons.



PARAMETERS AFFECTED BY HYBRIDIZATION

Bond Distance

An important geometric parameter associated with the shape of the molecule is bond length or bond distance i.e. the distance between atoms forming a bond. This parameter is characteristic of the kind of covalent bond and mostly remains constant from molecule to molecule without getting affected by the presence of substituents. Bond lengths to carbon depend strongly on the hybridization of the carbon involved and are little influenced by other factors. The table below gives the interatomic distances for some of the most common bonds in organic molecules.

Bond Type	Length °A	Strength	
		(kcal/mol)	(kJ/mol)
C−C			
sp^3-sp^3	1.54	88	368
sp^3-sp^2	1.51		
sp^3-sp	1.47		
sp^2-sp^2	1.48		
sp^2-sp	1.43		
$sp-sp$	1.38		
C=C			
sp^2-sp^2	1.33	152	606
sp^2-sp	1.31		
$sp-sp$	1.28		
C≡C			
$sp-sp$	1.20	200	803
C−H			
sp^3-H	1.1	101	422
sp^2-H	1.08	107	447
$sp-H$	1.06	131	548

As we can see, carbon bonds are shortened by increasing s character. This is not surprising, for an s orbital and any electrons in it are held closer to, and more tightly by the nucleus than is a p orbital and any electrons in it. This effect is carried on in the hybrid orbitals made by them with increasing contribution of s orbital. Thus, for two carbon atoms bonded together or a carbon atom bonded with a hetero atom, the nuclei are drawn severly closer together on going from $sp^3 - sp^3 \longrightarrow sp^3 - sp^2 \longrightarrow sp^3 - sp \longrightarrow sp^2 - sp^2 \longrightarrow sp^2 - sp \longrightarrow sp - sp$ and so on.

Another observation is that, more the number of bonds holding two carbon atoms together the shorter is the bond length. Shorter bond also imply them to be stronger. Thus, triple bonds are shorter and stronger than double bonds and double bonds are shorter and stronger than single bonds. However, double bond is not twice as strong as single bond, nor is the triple bond thrice as strong as the single bond. This is because the π bonds (contributing to double and triple bond) are formed by the lateral overlap of the p atomic orbitals which is less effective than the axial overlap of σ bond. Therefore, π bond is weaker than σ bond and cannot contribute the same as σ bond in bond strengthening.

The table also shows that σ bonds of carbon with hydrogen are stronger than σ bonds between two carbon atoms. This is a direct consequence of overlap of carbon with the orbital closer to the nucleus - 1s orbital of H is closer than orbitals of C (sp^3 or sp^2 or sp). The C—H bond is stronger too; due to greater electron density in the overlap region of sp^3 — s bond than of sp^3—sp^3 .(similarly higher electron density is seen in the overlap region of sp^2 — s than of sp^2 — sp^2 and so on).

The length and strength of C— H bond depends on hybridization of C atom to which H is bonded. C (50% s) More the s character in hybrid orbital, shorter and stronger is the bond. Thus, C — H bond by sp hybridized C is shorter than C — H bond by sp^2 hybridized C (33.33% s) which is shorter than sp^3 hybridized C (25% s).

Bond Angles

Like bond length, bond angles too depend on the hybridization of the atom; in these cases it depends on hybridization of carbon. Accordingly, the orbitals used by carbon will be placed as far as possible from each other. **The greater the amount of s character in the hybrid orbital, the larger is the bond angle.** Thus, tetrahedral sp^3 C disposes its orbitals at angles of $109^\circ 28'$, trigonal planar sp^2 C at angles of 120° and linear sp C at angles of 180°.

Bond angles too deviate from the normal value. These deviations occur due to:

(i) slightly different hybridization which in turn arises due to different electronegativities of bonded atoms.

(ii) presence of lone pair of electrons that has a greater steric requirement than a pair of electrons in a bond, since there is no second nucleus to draw away some of the electron density.

Bond Energy

There are two kinds of bond energies.

(i) Dissociation Energy, D

(ii) Bond Energy, E

(i) Dissociation energy is the energy required to break a particular bond in a polyatomic molecule into free radicals in the gas phase.

$$Y - Z_{(g)} \longrightarrow Y^{\cdot}_{(g)} + Z^{\cdot}_{(g)}$$

(ii) Bond energy is the **average** of the bond dissociation energies of the various bonds in the molecule. In polyatomic molecules, e.g. CH_4, the four bonds are equivalent, but the energy required to break the first bond ($CH_4 \longrightarrow \dot{C}H_3 + \dot{H}$) is not the same as that for the second bond ($\dot{C}H_3 \longrightarrow :CH_2 + \dot{H}$) etc. Each individual value is bond dissociation energy value for that particular bond. The energy of a bond depends on the nature of bond from where it is being broken. Thus bond energy is a parameter that is not independent of remainder of the molecule. In practice, an average of these values is taken and called Bond Energy.

The table below gives some bond energy values and some bond dissociation energy values of specific bonds. It is apparent that some of the bond dissociation energy values are very different from the average value or bond energy value e.g. C — H bond dissociation energy listed for tert-butane is significantly less than a C — H bond dissociation energy for methane. The reason for the relative weakness of bond in former case is the greater stability of radical produced by bond dissociation. In case of diatomic molecules, D = E.

Thus, various factors are responsible for the differences in energy of a given bond in different compounds - substituents, steric effects, angular strain.

Bond	**Energy**		**Bond**	**Energy**	
	kcal/mol	**kJ/mol**		**kcal/mol**	**kJ/mol**
CH_3-H	105	439	$C-N$	68	284
$MeCH_2-H$	97	405	$C=N$	147	614
Me_2CH-H	94	393	$C-F$	107	447
Me_3C-H	89.5	374	$C-Cl$	78	326
$C-H$ (average)	99	414	$C-Br$	68	284
$C-C$	83	347	$C-I$	51	213
$C=C$	145	606	$H-H$	103	431
$C\equiv C$	192	803	$N-N$	39	163
$C-O$	80	334	$N=N$	100	418
$C=O$	166	694	$N\equiv N$	226	945

POLAR COVALENT BONDS

We have earlier defined a covalent bond to be the one where the bonding atoms share their electrons. The electron cloud that bonds the two atoms is symmetrical i.e. if we take an imaginary plane perpendicular to the bond the electron cloud is found to be perfectly bisected or shared equally by the two atoms. However, this symmetrical distribution of electron cloud is seen only when the two atoms are identical or have the same substituents. Only in these cases, each electron spends as much time in the vicinity of one atom as in the other. An even, or nonpolar distribution of charge results. Such a bond is called a **nonpolar covalent bond.** Nonpolar covalent bond is one extreme type of chemical bonding. The other extreme is **ionic bonding** where the bond is formed by trnasfer of electrons. The transfer of electron gives rise to positive and negative charges which are held together by strong electrostatic forces of attraction.

Chemical bonding does not confine itself to these two categories. In fact, there is a continuum of possibilities of chemical bonding with these two bond types at the extremes. A great majority of chemical bonds lie between the two extremes.

In the covalent bond, the electron cloud that bonds the two atoms is, most often, unsymmetrical. The cloud, as a result migrates towards one side of the bond or towards one atom of the two bonding atoms. The atom which gets more share of the bonding electron cloud is the one which has more attraction for the cloud. Such bonds, in which the electron distribution is unsymmetrical, are called **polar covalent bonds**. Unsymmetrical distribution of electron cloud is, therefore, due to differences in attraction abilities of the bonding atoms. This intrinsic ability of an atom to attract the shared electrons in a covalent bond is called electronegativity. Electronegativity is a **fundamental characteristic of atoms** that is transferred into functional groups. Electronegativity correlates strongly with position in the periodic table. It increases in going to the right in any row of the periodic table and decreases in going down any column. Electronegativity is greatest for atoms in the upper right corner of periodic table (i.e. halogens and other reactive non metals) and lowest for atoms in the lower left corner (i.e. metals). Accordingly, fluorine is the most electronegative element and cesium the least. A number of attempts have been made to set up quantitative tables of electronegativity that indicate the direction and extent of electron - cloud distortion for a bond between any pair of atoms. The most popular of these scales, called the **Pauling scale**, is based on bond energies of diatomic molecules.

Based on the Pauling scale, carbon, the most important element in organic chemistry, has an electronegativity value of 2.5. Any element with value greater than 2.5 is more electronegative than carbon and any element with value less than 2.5 is less electronegative than carbon. The table below gives electronegativity values of some elements.

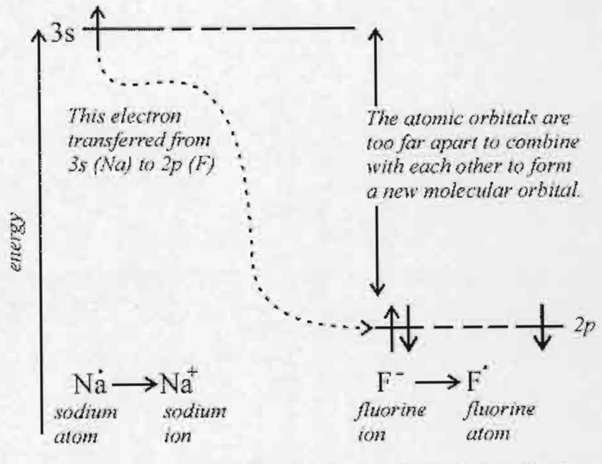
Electronegativities of Atoms

H 2.1	C 2.5	N 3.0	O 3.5	F 4.0
	Si 1.8	P 2.1	S 2.5	Cl 3.0
		As 2.0	Se 2.4	Br 2.8
Cs 0.7				I 2.5

Thus, atoms with similar electronegativities give rise to non-polar covalent bond; atoms with electronegativity difference ranging from 0.5 - 2.0 units (low to high) give rise to polar covalent bonds; atoms with a large electronegativity difference, greater than 2 units, give rise to ionic bonds.

How do the difference in electronegativities of bonding atoms give rise to the differents kind of bonds? This can be understood by looking into the energies of the atomic orbitals. The more electronegative an atom is, the more it attracts electrons i.e. the more electronegative an atom, the lower in energy are its atomic orbitals and so any electrons in them are held more tightly. This is a consequence of increasing nuclear charge on going from left to right across the periodic table.

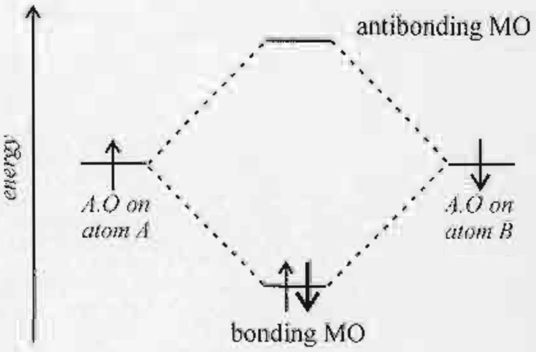
If two atoms with vastly different energy of their atomic orbitals combine, e.g. Na and F, the atomic orbitals of the atoms are too far apart in energy to form new molecular orbitals and no covalent bond is formed. As a consequence, electrons are transferred from one atom to another and ionic bonding results .



Both electron in sodium fluoride end up in fluorine's 2p orbital.

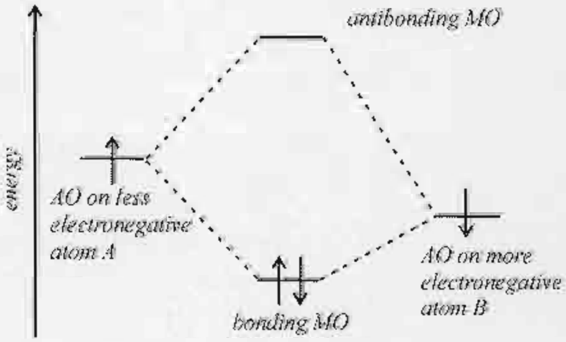
The product is the ionic salt Na$^+$F$^-$. Ionic bonding is due to the attraction between two oppositely charged ions.

When the atomic orbitals have exactly the same energy, they combine to form new molecular orbitals, one with an energy lower than the atomic orbitals, (bonding molecular orbital) and the other with an energy higher than the atomic orbitals (antibonding molecular orbital).



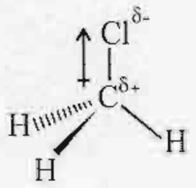
Molecular orbitals from elements of same electronegativity

When the atomic orbitals are slightly different in energy, they do combine to form new molecular orbitals, but they do so unsymmetrically. The more electronegative atom, contributes more to the bonding molecular orbital and the less electronegative element contributes more to the antibonding orbital. This applies both to σ bonds and to π bonds.

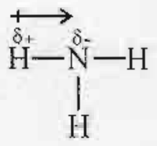


Molecular orbitals from elements of different electronegativity

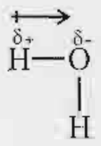
As an example, carbon - hydrogen bonds, in saturated hydrocarbons, are relatively nonpolar because carbon and hydrogen have similar electronegativities. Bonds between carbon and more electronegative elements such as oxygen, fluorine, chlorine are polar with bonding electrons drawn away from C towards the more electronegative atom. This leaves carbon with a partial positive charge, denoted by δ^+, and the electronegative atom with a partial negative charge, denoted by δ^-. Similar bond polarity is seen in N - H bond, O - H bond containing molecules (and many more).



Chlorine EN = 3.0
Carbon EN = 2.5
Difference = 0.5

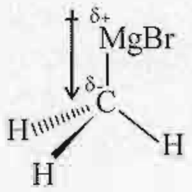


Nitrogen EN = 3.0
Hydrogen EN = 2.1
Difference = 0.9



Oxygen EN = 3.5
Hydrogen EN = 2.1
Difference = 1.4

The direction of bond polarity is indicated by a crossed arrow. By convention, the arrow indicates the direction the electrons are pulled and so the head of the arrow is at the negative end of the bond. The cross on the arrow indicates the positive end of the bond. Carbon, when combines with metals gains the δ^- charge due to its higher electronegativity. Such compounds are called organometallic compounds.



Carbon EN = 2.5
Magnesuim EN = 1.2
Difference = 1.3

Dipole Moment

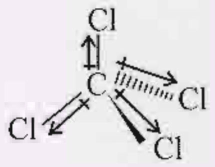
The unequal distribution of electron density in covalent bonds produces a bond dipole indicated by the dipole moment (μ). Dipole moment of a bond is defined as the magnitude of the charge (e) on the atoms (either positive or negative - magnitude of charge is same), multiplied by the distance between the two charges (d). Unit of measuring dipole moment is calle Debye, (D).

$$\mu = e \times d$$

Bonds with significant bond dipoles are described as being polar. The overall polarity of the molecule, or the dipole moment of the molecule is estimated from the vector sum of the component bond dipoles alongwith lone-pair contributions (if any). The vector summation, of bond dipoles, takes into account the geometry of the molecule. For a molecule with a single covalent bond the dipole moment of the molecule and the dipole moment of the bond is the same. For molecules with more than one covalent bond, the geometry of the molecule as well as bond moments are to be considered.

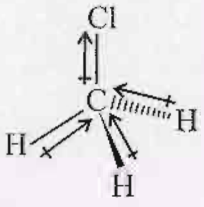
The vectorial aspect of bond dipoles can be illustrated in a relatively simple way with the carbondioxide molecule, CO_2:

$\mu = 0D$

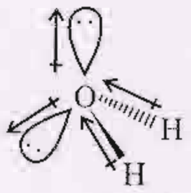


$\mu = 0D$

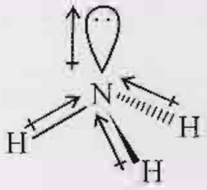
Because the CO_2 molecule is linear, the C — O bond dipoles are oriented in opposite directions. Because they have equal magnitudes, they exactly cancel. Consequently CO_2 is not a polar molecule, even though it has polar bonds. Similarly ethane, methane, CCl_4 etc. have zero dipole moments. In contrast, if a molecule contains several bond dipoles that do not cancel, the various bond dipoles add vectorially to give the overall resultant dipole moment. We can justify why dipole moment of molecules like chloromethane, ammonia, water etc. is more than the component bond moments. The dipole moments of the bonds reinforce each other and non bonding electrons contribute as well, in the overall dipole moment of the molecule.



$\mu = 1.87\ D$



$\mu = 1.85\ D$



$\mu = 1.47\ D$

Polarity is an important concept because the polarity of a molecule can significantly influence its chemical and physical properties.

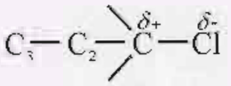
The polarity of covalent bonds between carbon and substituents is the basis of important structure - reactivity relationships in organic chemistry. The polarity of the bond, i.e. the ready availability of electrons at a particular atom, affects the reactivity of the atom (or the bond) towards a reagent.

The effect of polar bonds are generally considered to be transmitted in two ways-**Inductive effect** and **Field effect.**

POLARITY OF BONDS: INDUCTIVE EFFECT

Succesive polarization through σ bonds is called the **Inductive Effect.**

Consider the case of an alkyl halide such as alkyl chloride. Due to its higher electronegativity, the electron density tends to be greater towards chlorine than carbon. This causes chlorine to accquire a slight negative charge and C - 1 carbon to acquire a slight positive charge.



If the carbon atom joined to chlorine is itself bonded to further carbon atoms (C - 2, C - 3, etc), the effect can be transmitted further. Thus C - C bond, which is otherwise non polar, is polarised in alkyl chlorides by the presence of the electronegative chlorine atom. Thus C_1, which gets positively charged, or gets electron deficient, attracts electron pair of C_1— C_2 bond towards itself in order to nullify its electron deficiency. This causes C_2 to acquire a small positive charge, but the charge on C_2 will be smaller ($\delta\delta+$) than the charge on C_1, because the electron withdrawing effect of Cl is reaching C_2 via C_1 (and not directly). C_2 will inturn pull the electron pair of C_2— C_3 bond towards itself thereby making C_3 accquire a still smaller positive charge ($\delta\delta\delta+$). Thus the effect of C_1 on C_2 is less than the effect of Cl on C_1 and as the distance from the source increases the effect dies away rapidly. It may be ignored after the second carbon atom, for all practical purposes. **This type of electron displacement in σ bonds along a chain is called inductive effect. The electron pairs undergo permanent displacement due to the intrinsic tendencies of atoms for electron withdrawl. But there is no transfer of electron; the electrons remain in the same valency shells.**

All inductive effects are permanent polarisations in the ground state of a molecule.

Inductive effect is generally represented by an arrow head in the middle of the covalent bond pointing in the direction of the electron displacement.

Thus, in the case discussed above, inductive effect can be shown as:

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

For measurements of relative inductive effects, hydrogen is chosen as reference in the molecule CR_3—H which is taken as standard. If, when H is replaced by Z (atom or group), the electron density in the CR_3 part of the molecule is less than in CR_3---H, then Z is said to be -I group having -I effect (electron withdrawing). If electron density in the CR_3 part is greater than in CR_3—H, Z is said to be +I group with +I effect (electron releasing).

-I groups: $\overset{+}{N}R_3$, $\overset{+}{S}R_2$, $\overset{+}{N}H_3$,NO_2, SO_2R, CN, COOH, F, Cl, Br, I, OR, OH

+I groups: O^-, COO^-, $(CH_3)_3C$, $(CH_3)_2CH$, CH_3

POLARITY OF BONDS: FIELD EFFECT

Field effect is attributed to through - space interactions of the electric dipoles resulting from polar bonds i.e. the effect operates either through the space surrounding the molecule or through the molecules of solvent that surround it in case of solution.

However, due to very close similarity of operation, it is difficult to distinguish between the two effects. Reference of inductive effect normally incorporates field effect. The two effects can be collectively termed as polar effects - i.e. originating from the bond dipoles

DELOCALISED CHEMICAL BONDING

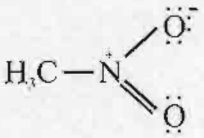
RESONANCE

Although the bonding of many compounds can be adequately described by a single structural formula, there are many other compounds wherein one structural formula is not able to satisfactorily describe the compound. This led to the idea that such compounds exist in a state which is some combination of two or more electronic structures. These structures, taken individually, are able to describe most of the properties of the compounds but none of them describe all the properties. **Taken together, the compound is described completely**. These compounds contain one or more bonding orbitals that are not restricted to two atoms, but are spread over three or more. Such bonding is said to be delocalised chemical bonding.

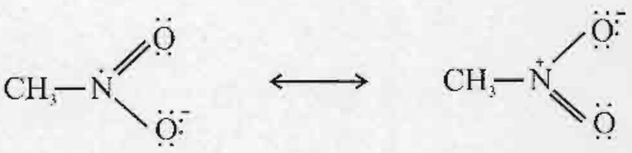
The several possible Lewis structures (electronic structures) drawn for a molecule, are called **canonical forms** or **resonance contributors**, or contributing resonance structures. This phenomenon wherein a real structure of a molecule is represented as a weighted average of two or more canonical forms is called **Resonance**. Resonance was earlier also known as mesomerism (coined by Ingold). The usefulness of the theory of resonance lies in its being a convenient way to describe delocalisation of electrons.

The canonical structures are linked by **a double headed arrow** which indicates that the real structure of the molecule is the average of these canonical structures. The real structure can also be said to be **resonance hybrid of the canonical structures**.

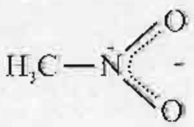
Let us understand this theory by taking the example of nitromethane. The structure of nitromethane is:



The Lewis structure shows a N - O single bond and a N = O double bond. From the earlier discussion, we expect double bonds to be shorter than single bonds. However, it is found experimentally that the two nitrogen - oxygen bonds of nitromethane have the same length, and this length is intermediate between the lengths expected for single and double bonds. To convey this idea, we represent nitromethane by these two canonical structures linked by a double headed arrow.



The actual structure can be represented in a single structure as resonance hybrid of the two canonical structures.



In this notation, the negative charge is understood to be equally shared by the atoms at the ends of the dashed semicircle - the two oxygens. The resonance hybrid structure explains the observed bond length of N - O bond. All other apparently anomalous behaviour of this compound is also addressed with this concept.

The main elements of resonance theory, which must be kept in mind in its application, are

1. Whenever alternative Lewis structures can be written for a molecule that differ only in assingment of electrons among the nuclei, and the positions of nuclei is constant in all structures, then the molecule is not adequately represented by a single Lewis structure. It has the contribution from more than one Lewis structure. Therefore, resonance permits us to draw various canonical forms by placing electrons in different ways, but keeping nuclei positions fixed.
2. The number of unpaired electrons in all canonical structures is the same. All structures are restricted to the maximum number of valence electrons appropriate for each atom e.g. two for hydrogen, eight for the second-row elements i.e. all the canonical forms must be bonafide Lewis structures.
3. All atoms taking part in the resonance or delocalisation of electrons, lie in the same plane. Planarity is required for maximum overlap of p orbitals.
4. Some individual Lewis structures are more stable than the others. Such stable structures are associated with lowest energy and make the greatest contribution to the true (hybrid) structure. The sturctures that are maximum close to the actual molecule incorporate the following features: (i) Maximum number of covalent bonds (ii) Minimum separation of unlike charges (iii) Placement of negative charge (if any) on the most electronegative atom and positive charge on the most electropositive atom (iv) Minimum distortion of bond angle. This is the reason why some structures contribute more and some contribute less towards the true structure. The structure of the molecule is, thus, the weighted average of its resonance structures. When the resonance structures are identical, they contribute equally to the actual structures.
5. Each of the resonance contributors for a compound must have the same net charge. This is because electrons are neither added nor removed from the compound when the resonance structures are drawn. Thus, if one resonance structure has net charge of +1, all other must have net charge of +1.
6. In most cases, the delocalisation of electrons, as represented by writing various structures, is associated with enhanced stability as compared to a single localized structure. The energy of these structures or the resonance hybrid is lower than that estimated for any individual contributing structure.

Types of Molecules that have Delocalised Bonds

I. **Multiple Bonds in Conjugation**

Simplest example is of 1,3-butadiene.

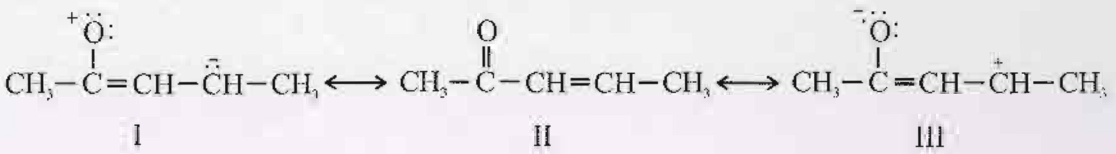
Here the two double bonds are in conjugation i.e. are separated by a single bond. Molecules containing conjugated multiple bonds are more stable than those in which they are isolated.

In resonance picture, these structures are considered to contribute as follows:

$$\overset{B}{CH_2=CH-CH=CH_2} \leftrightarrow \overset{A}{\overset{+}{C}H_2-CH=CH-\overset{-}{C}H_2} \longleftrightarrow \overset{C}{\overset{-}{C}H_2-CH=CH-\overset{+}{C}H_2}$$

These structures involve the movement of π electrons towards π bond. Contribution of B towards the resonance hybrid is maximum since there is no separation of charge and all atoms have complete octet. Structure A and C have smaller contributions due to the lack of these stabilising factors.

Similar delocalisation is found in other conjugated systems involving hetero atoms eg. $C = C — C = O$, $C = C — C = N$ as well as in longer systems with three or more multiple bonds in conjugation, and where multiple bonds are in conjugation with aromatic rings.



$$CH_3-\overset{\overset{+\ddot{O}:}{|}}{C}=CH-\overset{-}{\ddot{C}}H-CH_3 \longleftrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH=CH-CH_3 \longleftrightarrow CH_3-\overset{\overset{-\ddot{O}:}{|}}{C}=CH-\overset{+}{C}H-CH_3$$

I II III

The main contributor to the resonance hybrid is structure II with no separation of charge and complete octet of each atom. Structure III has separation of charges and incomplete octet, therefore it makes small contribution (just like structure B and C of butadiene) but structure I, with similar separation of charge and incomplete octet, is a very **unfavourable structure**. This is because, here positive charge is on more electronegative atom, oxygen. The contribution of structure I is so insignificant that it can be ignored as a resonance contributor.

II. Double or triple bonds in conjugation with p orbital on an adjacent atom

A p-orbital on an atom adjacent to a double bond results in three parallel p orbitals that overlap. The original p orbital may contain two electrons e.g. $CH_2 = CH — \bar{C}H_2$, one electron e.g. $CH_2 = CH — \dot{C}H_2$, or no electron e.g.$CH_2 = CH — \overset{+}{C}H_2$. The three species may be described as having double bonds in conjugation with , an unshared pair,an unpaired electron, and an empty orbital respectively.

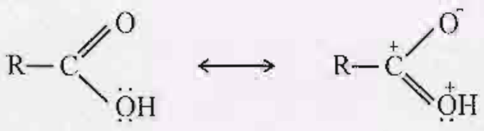
(i) $CH_2{=}CH-\overset{-}{C}H_2 \longleftrightarrow \overset{-}{C}H_2-CH{=}CH_2$

(ii) $CH_2{=}CH-\dot{C}H_2 \longleftrightarrow \dot{C}H_2-CH{=}CH_2$

(iii) $CH_2{=}CH-\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2-CH{=}CH_2$

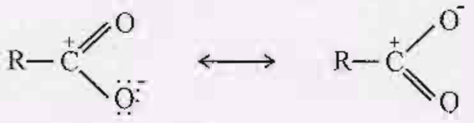
In all these cases, electrons are moving towards sp^2C. These electrons could be π electrons, non bonding electron or unpaired electrons. sp^2 Carbon can have a π bond that can break, as in (i) a positive charge as in (iii) or an unpaired electron as in (ii) and so it can accept electrons without violating the octet rule. Movement of electrons does not take place to a sp^3 C which has four σ bonds and according to octet rule it cannot bear any more electrons.

Any system containing such an arrangement of multiply bonded atoms and unshared, unpaired or no electron can show this type of delocalisation.



I II

Here the non bonding electrons are moving towards π bond. Contribution of II is much lesser than I due to its instablity arising from the separation of charge.



III IV

Both III and IV are of equal stability and so contribute equally to the resonance hybrid.

As mentioned before, the energetically favourable resonance contributors are obtained by movement of electrons towards electronegative atoms. Structures with movement of electron away from the electronegative atom make such insignificant contribution that they are not included as resonance contributors. However, if this is the only way movement of electrons can be shown in the molecule, then such structures are definitely included. In other words, **movement of electron away from the electronegative atom is better than no movement at all.**

e.g.

$$CH_2{=}CH{-}\overset{..}{\underset{..}{O}}{-}CH_3 \qquad\qquad \overset{-}{C}H_2{-}CH{=}\overset{+}{\underset{..}{O}}{-}CH_3$$

I II

It is obvious that between the two structures, structure I has major contribution; yet II is also the other contributor.

Resonance always results in **a redistribution of electron density taking place** in unsaturated, and especially conjugated systems via their π orbitals. There is decrease in electron density at one position and corresponding increase elsewhere which is termed as resonance effect or mesomeric effect. The effect is caused by the fact that the electrons are in a different place from that we would expect if there was no resonance.

III. Hyperconjugation

This type of delocalisation will be dealt with in a separate section.

Applications of Inductive Effect and Resonance Effect

Some fundamental structure-stability relationships can be employed to illustrate the use of inductive effect and resonance effect.

I. Acids and their strengths

An acid is a species having a tendency to lose a proton (**Bronsted Definition**).

An organic compound AH is an acid, if it ionizes in a solvent and as follows:

$$\text{AH (solvent)} \rightleftharpoons \text{A}^- \text{(solvent)} + \text{H}^+\text{(solvent)}$$

The strength of the acid i.e. the extert to which it is dissociated is determined from its equilibruim constant, ka.

$$K_a = \frac{[\text{H}^+\text{(solvent)}]\,[\text{A}^-\text{(solvent)}]}{[\text{HA (solvent)}]}$$

K_a is called the acidity constant of the acid in the sovent. Acidity constant series as a guide to compare streingths of various acids. Instead of giving strength in terms of K_a which is in negative powers of 10, K_a is converted to pK_a.

$$pK_a = -\log_{10} K_a$$

The **smaller** the numerical value of pK_a, the **stronger** tha acid.

The factors that influence the ionization, and hence the strength of the acid are:

(i) The strength of the A — H bond - clearly, the easier it is to break this bonded, the stronger the acid.

(ii) The electronegativity of A - More the electronegative atom to which H is bond, more is the ionization.

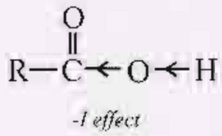
(iii) Intrinsic stability of the conjugate base, anion A^- - The more stable the conjugate base, A^-, the less basic it will be and so the stronger will the acid be.

(iv) The solvent - The better the solvent is at stabilizing the ions, the easier it is for the reaction to occur.

Let us study the acidity of organic compounds in various categories keeping these factors in mind:

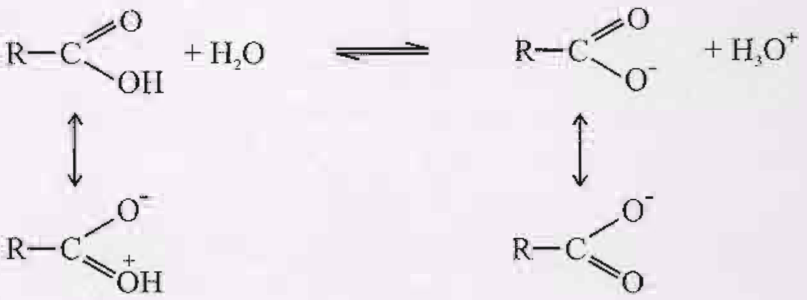
A. Acidity of Carboxylic Acids

In carboxylic acids, the electronegative O atom exerts a -I effect to pull the electron pair of O - H bond towards itself. This makes O - H bond polar, weak and therefore, prone to cleavage.Hence, factor (i).



$$R-\overset{\overset{\displaystyle O}{\|}}{C}\leftarrow O\leftarrow H$$

Carboxyl carbon attached to electronegative oxygen makes the O - H bond further weak. Hence, factor (ii). But the main factor is (iii).



Carboxylic acids have the same number of resonance structures for both undissociated and dissociated acids. However, carboxylate anion shows a much more effective delocalisation than carboxylic acid because of the two resonance structures being identical and hence of identical energy. This is not the case with carboxylic acid where the major contribution is from the structure with no charge separation. The other structure has much lesser contribution due to separation of charge. Thus the effective delocalisation of charge and hence stabilization of the conjugate base, the carboxylate anion, is much more, making the equilibrium shift more towards the right.

B. Acidity of alcohols vs. aliphatic carboxylic acids

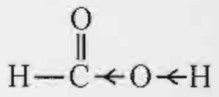
CH_3OH is a stronger acid (pK_a ~ 16) than $CH_3 — H$ (pK_a - 43). This is attributed to the large difference in electronegativity of O and C. Oxygen, being much more electronegative (-I effect), pulls the electron pair of O — H bond much more towards itself than C does for the electron pair of C — H bond. In fact, C — H bond in methane is non-polar and, therefore, methane does not exhibit inductive effect. This makes the hydrogen of O — H σ bond more devoid of electron cloud and is more easily removable or is more acidic.

$$H_3C\overset{\delta-}{O}\leftarrow\overset{\delta+}{H} \qquad H_3C—H$$

Now, if we compare methanol with methanoic acid, pKa of methanol is much higher (pK_a ~16) than methanoic acid ($pK_a = 3.77$), or methanol is a much weaker acid than methanoic acid.

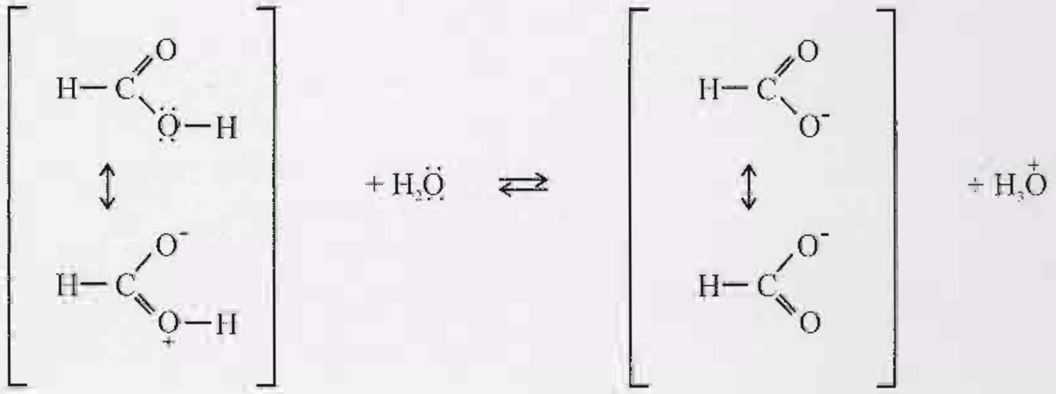
Here both compounds have the same atom (oxygen) to which acidic hydrogen is bonded. Therefore, factor (i) is of no importance here. Factor (ii) does play a role here. Electronegativity and hence -I effect of oxygen attached to the incipient proton is enhanced by the electron withdrawing carbonyl group of methanoic acid whereas the electron releasing CH_3 group reduces the electronegativity and hence -I effect of oxygen in methanol.

$CH_3 \rightarrow O \leftarrow H$



$H-\overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$

But the more important factor is (iii) i.e. the conjugate base of methanoic acid is much more stable than the undissociated methanoic acid molecule.



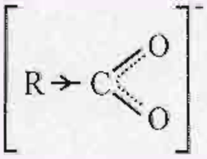
The delocalisation is very effective in the methanoate ion, since both form are of equal energy. The anion is, therefore, very much stabilized in comparison to methanoic acid where the delocalisation occurs with the same two structures but different energies. Charge separation in one structure makes its contribution less effective. In case of methanol, the conjugate base CH_3O^-, does not experience any stabilising effect by such factors, relative to methanol. Thus methanol, or alcohols in general, are much less acidic than carboxylic acids.

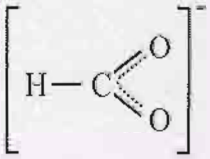
C. Acidity of alkyl substituted acetic acids

The pK_a values of some simple aliphatic acids is given below.

	pK_a
$(CH_3)_3$ C COOH	5.0
$(CH_3)_2$ CH COOH	4.9
CH_3CH_2 COOH	4.9
CH_3 COOH	4.8
H COOH	3.8

The replacement of the non acidic H of formic acid by alkyl groups results in weaker acids. This is due to the +I effect of alkyl groups which reduces the electron affinity of the oxygen atom carrying the incipient proton, and so reduces the strength of the acid. The conjugate anion base is also less stabilized due to electron releasing effect of alkyl groups as compared to the formic acid / formate ion system.





Apart from this, factor (iv) - the effect of solvent - also plays an important role. Solvation is more in smaller formate anion that stabilizes it and hence makes formic acid stronger.

Further substitution by alkyl groups at α C has lesser effect on the acid strength than the first introduction. This is because of several other factors.

D. Acidity of unsaturated carboxylic acids.

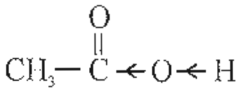
If the carbon adjacent to COOH group is unsaturated, the -I effect of sp^2 C (for a doubly bonded hydrocarbon group) or sp C (for a triply bonded hydrocarbon group) stabilizes the anionic conjugate base much more than its saturated counterpart, making such acids stronger than saturated acids. sp C being more electronegative than sp^2 C renders the acid containing alkynyl groups stronger than the acids containing alkenyl groups.

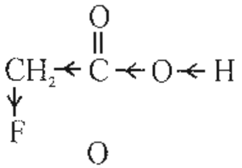
	pK_a
$CH_3CH_2\ COOH$	4.88
$CH_2 = CH\ COOH$	4.25
$CH \equiv C\ COOH$	1.84

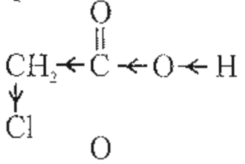
E. Acidity of substituted aliphatic acids.

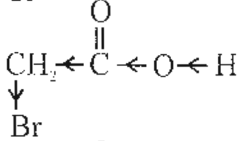
Substitution of hydrogen at α -C of acetic acid by a halogen (-I group) increases the equilibrium constant for ionization i.e. makes the acid stronger. The highly electronegative fluorine atom pulls the electrons of the O — H bond more away from the proton than does the less electronegative chlorine atom. Also, electron withdrawl by fluorine stabilizes the conjugate base much more than the stabilization done by chlorine atom. Bromine and iodine follow chlorine in this order for the same reason.

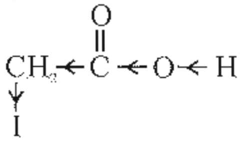
pK$_a$


$CH_3-\overset{O}{\overset{\|}{C}}\leftarrow O\leftarrow H$ 4.8


$\underset{F}{\underset{\downarrow}{CH_2}}\leftarrow\overset{O}{\overset{\|}{C}}\leftarrow O\leftarrow H$ 2.7


$\underset{Cl}{\underset{\downarrow}{CH_2}}\leftarrow\overset{O}{\overset{\|}{C}}\leftarrow O\leftarrow H$ 2.8


$\underset{Br}{\underset{\downarrow}{CH_2}}\leftarrow\overset{O}{\overset{\|}{C}}\leftarrow O\leftarrow H$ 2.9


$\underset{I}{\underset{\downarrow}{CH_2}}\leftarrow\overset{O}{\overset{\|}{C}}\leftarrow O\leftarrow H$ 3.2

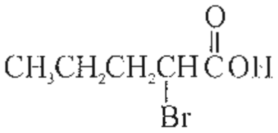
As the number of electron withdrawing -I groups on the α - C increase, the O — H bonding electrons experience more and more pull away from the proton thereby making the acid increasingly stronger.

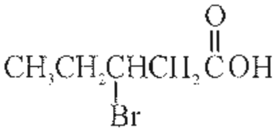
pK$_a$

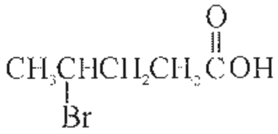
$Cl_3\,C\,COOH$ 0.7

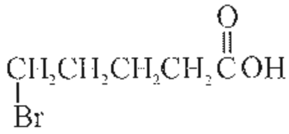
As the substituent -I group is moved farther away from the O — H bond, its effect on the acidity of the compound decreases because it becomes lesser effective at withdrawing eletrons from the O — H bond. As a result the acid becomes weaker.

pK$_a$


$CH_3CH_2CH_2\underset{Br}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}OH$ 3.0


$CH_3CH_2\underset{Br}{\underset{|}{CH}}CH_2\overset{O}{\overset{\|}{C}}OH$ 4.0

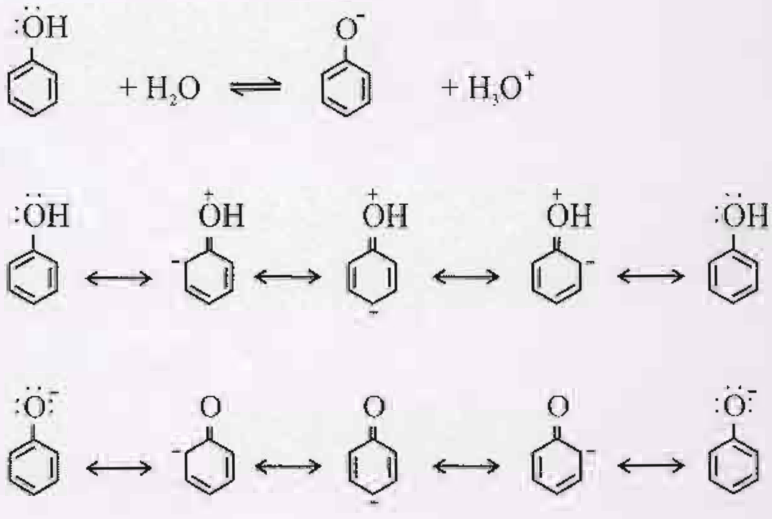

$CH_3\underset{Br}{\underset{|}{CH}}CH_2CH_2\overset{O}{\overset{\|}{C}}OH$ 4.5


$\underset{Br}{\underset{|}{CH_2}}CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}OH$ 4.7

Other -I groups that increase the strength of carboxylic acids are R_3N^+, CN^-, NO_2, CO etc. Hydroxyl and methoxyl groups, with electronegative O at α - C, also have an acid strengthening effect.

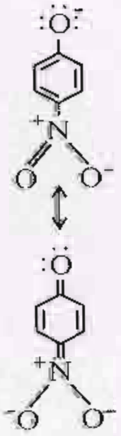
F Acidity of phenols

Phenol as well as phenoxide ion, obtained by dissociation of phenol, show delocalisation.



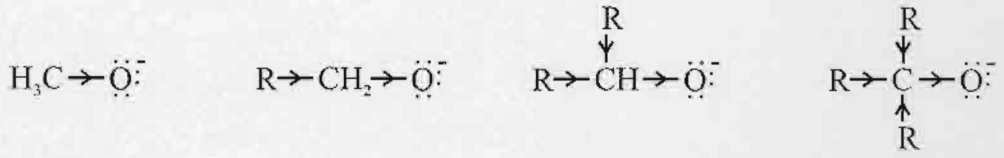
In phenol, the unshared electron pair is in conjugation with the ring double bond. Delocalisation of the unshared electron pair results in the separation of charge, whereas in phenoxide ion the already existing negative charge gets delocalised and there is no separation of charge. The phenoxide ion is thus more stable inspite of having the same number of resonance structures as phenol. This makes the equilibrium shift more towards the right and hence makes phenol acidic. Phenoxide ion is reluctant to recombine with a proton to give phenol. Any substituent on phenol that can further stabilize the negative charge of phenoxide ion will increase the acidity of phenol.

e.g.



Among other resonance structures, there is an additional resonance structure due to the N = O group in conjugation with phenyl ring. This makes an extended dispersal of negative charge and hence greater stabilization, which in turn imparts greater acidity to phenol.

Phenols, due to the resonance stabilization of phenoxide ion, are much more acidic than alcohols. In alcohols, the alkoxide ion has a localized negative charge which gets further destabilized by +I effect of alkyl group substituents. There is no possibility of the negative charge to undergo delocalisation since O carrying negative charge is bonded to sp^3 carbon. The alkoxide ion does not get stabilized relative to the alcohols.



$$H_3C \rightarrow \ddot{\underset{..}{O}}{:}^{-} \qquad R \rightarrow CH_2 \rightarrow \ddot{\underset{..}{O}}{:}^{-} \qquad R \rightarrow \overset{\overset{R}{\downarrow}}{C}H \rightarrow \ddot{\underset{..}{O}}{:}^{-} \qquad R \rightarrow \underset{\underset{R}{\uparrow}}{\overset{\overset{R}{\downarrow}}{C}} \rightarrow \ddot{\underset{..}{O}}{:}^{-}$$

Acidity of Phenols vs. Carboxylic acids

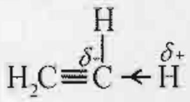
Between phenol and carboxylic acid, it is carboxylic acid which is more acidic. To understand this difference, we again assess the relative stabilization of the two conjugate anions, this time not with respect to their corresponding acids, but with respect to each other.

We can see that although the phenoxide ion has 5 resonance structures, each of these have different energy and so each has contribution different from the other. On the other hand, carboxylate anion with only two resonance structures, has equal contribution from both structures due to their identical energy.

Moreover, the negative charge is equally shared by the more electronegative atoms - the two oxygen atoms; which is not the case in phenoxide ion where there is only one oxygen atom and the negative charge is not with it in 3 out of 5 structures. Three of the structures are drawn with negative charge on the less electronegative carbon atoms. The net result of these two facts is that there is more effective delocalisation and hence stabilization in carboxylate anion relative to carboxylic acid as compared to stabilization of phenoxide ion relative to phenol. Thus, carboxylic acids are more acidic than phenols.

Aromatic carboxylic acids are more acidic than their aliphatic counterparts. The carboxylate anion of the former experiences the -I effect of phenyl group (due to sp^2C) to get further stabilized whereas the alkylgroup exerts a +I effect to destabilize the aliphatic carboxylate anion. Substituents on the aromatic ring may increase or decrease the acidity depending on their nature and position in the ring. If there are groups with multiple bonds to atoms more electronegative than carbon and if these bonds are at ortho or para positions to the carboxylic acid group, then there is a net stabilization of the carboxylate anion due to the electron withdrawing resonance effect (-R effect).

$HC\equiv\overset{\delta-}{C}\leftarrow\overset{\delta+}{H}$



$H_2\overset{\delta-}{C}\equiv\overset{H}{C}\leftarrow\overset{\delta+}{H}$

II. **Bases and their strengths**.

A base is a species that can accept a proton by donating a pair of electrons. e.g. ammonia, water, methyl anion etc.

The strength of a base B:, in water may be determined by considering the equilibrium.

$$B: + HOH \rightleftharpoons B\overset{+}{H} + \overset{-}{O}H$$

and the equilibriumconstant K_b is given by

$$K_b = \frac{[B\overset{+}{H}]\,[\overset{-}{O}H]}{[B:]}$$

H_2O concentration has been ignored due to its large excess

Therefore, strength of bases is measured by its pK_b values. Lower pK_b indicates a stronger base. However, it is a usual practice to express strength of bases in terms of their pK_a values rather than their pK_b values. This gives the convenience of having a single continuous scale for both acids and bases. To express in terms of pK_a, the reference reaction taken is:

$$B\overset{+}{H} + H_2O \rightleftharpoons B: + H_3O^+$$

$$\therefore\ K_a = \frac{[B:]\,[H_3O]}{[BH^+]}$$

K_a (or pK_a) is a measure of the acid strength of the conjugate acid BH^+ of the base B: This gives a measure of the ease of the acid BH^+ to give a proton or the lack of ease of the base B: to accept a proton. Thus the **smaller** the pK_a the **weaker** the base.

A. **Neutral Nitrogen bases**

Ammonia is the simplest nitrogen base with pK_a 9.24. Any substituent that increases the electron density on nitrogen, therefore, raises the energy of the lone pair thus making it more available for protonation and increasing the basicity of the amine. Conversely, any substituent that withdraws electron density from the nitrogen makes it less basic.

Electron density on nitrogen can be increased by attaching an electron releasing +I group. Another way is to conjugate the nitrogen with an electron donating group. The latter approach is understood on the basis of another electron displacement effect - mesomeric effect which we shall discuss later. We will discuss the effect of attaching +I groups on the base strength here. The simplest example of an electron releasing (+I group) group is an alkyl group. If we successively substitute each hydrogen in ammonia by an electron releasing alkyl group, we should increase the amine's basicity. Table below shows the pK_a values of primary, secondary and tertiary amines.

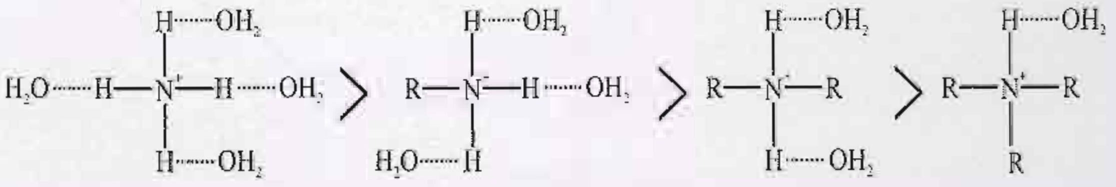
pK_a

R	RNH_2	R_2NH	R_3N
Me	10.6	10.8	9.8
Et	10.7	11.0	10.8
n-Pr	10.7	11.0	10.3
n-Bu	10.7	11.3	9.9

From the table, the following information is noteworthy

* All the amines have pK_a greater than that of ammonia (9.24).
* All primary amines have approximately the same pK_a (about 10.7).
* All the secondary amines have pK_a slightly higher than the corresponding primary amine.
* The increase in strength of base in going from primary to secondary amine is very little in comparison to increase in base strength in going from ammonia to primary amine.
* Most of the tertiary amines have pK_a lower than those of the primary amines.

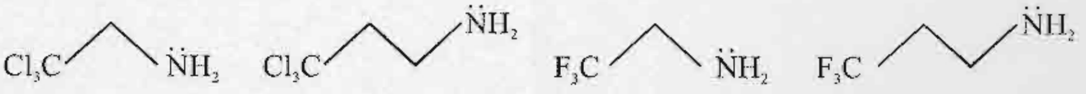
The first point needs no clarification. The alkyl group, due to its +I effect, increases the electron density on N and makes it a stronger base. Substituting one H of NH_3 by alkyl group increases basicity by a factor of 10 (one pK_a unit) but the increase in basicity on a second substitution is much lesser and in the trisubstituted amine, pK_a is actually lower. We expected to see an increase in base strength in going from $NH_3 \longrightarrow RNH_2 \longrightarrow R_2NH \longrightarrow R_3N$, due to the increasing inductive effect (+ I effect) of successive alkyl group making the nitrogen atom more electron donating. The actual result is different. The reason is that the cause of basicity is not just the availability of lone pair. The stabilization of the resultant positively charged protonated ion is also important. Each successive alkyl group does stabilize the positive charge on nitrogen by its electron releasing effect but there is another stabilizing effect - stabilization by the solvent (solvation). Each hydrogen attached directly to nitrogen will be hydrogen bonded with solvent water and this also helps in stabilization of charge of cation formed; the more hydrogen bonding, the more stabilization. As we increase the alkyl substitution, we decrease the number of hydrogens directly bonded to nitrogen and hence decrease the stabilization of the ammonuim ion via H-bonding with solvent. Thus, on going along the series $NH_3 \longrightarrow RNH_2 \longrightarrow R_2NH \longrightarrow R_3N$, the +I effect will tend to increase the basicity, but progressively less stabilization of the cation by hydration will occur, which will tend to decrease the basicity. The net effect of introducing successive alkyl groups becomes smaller and an actual change over takes place on going from secondary to tertiary amine.



In the absence of solvents capable of hydrogen bonding e.g. in hydrocarbon solvent or in gas phase, only Inductive effect operates and not the opposing cation stabilization effect. Therefore, in such cases the original base strength order is retained

i.e. $R_3N > R_2NH > RNH_2 > NH_3$

Electron withdrawing groups attached directly or indirectly to nitrogen will decrease the base strength. This is due to their -I effect.

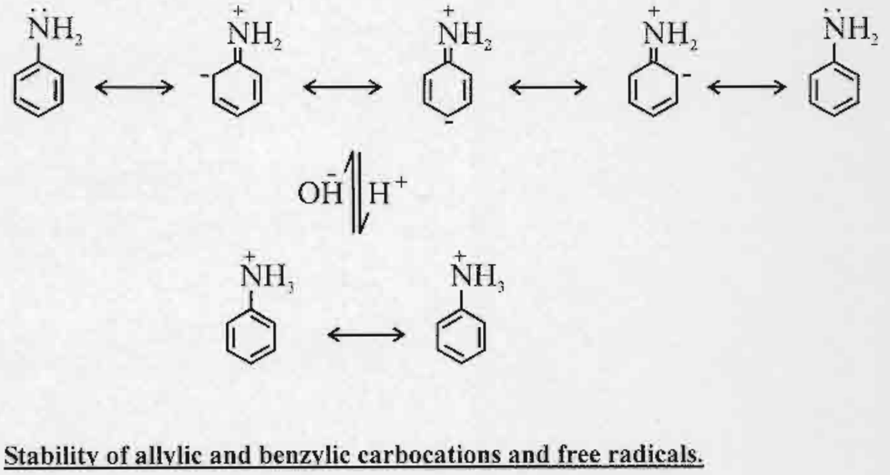


pK_a 5.5 9.7 5.7 8.7

As before, the greater the distance between the substituent and the source, the lesser is the influence of the substituent on the basicity i.e. inductive effect falls off rapidly with distance.

B. **Aromatic vs. Alicyclic amines**

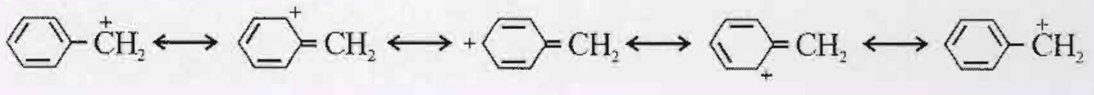
If we compare aniline with its saturated counterpart (cyclohexyl amine), we find that NH_2 group is attached to more electron withdrawing phenyl sp^2C (-I effect) which, due to its electron affinity, will not encourage the donation of unshared pair of electrons of on nitrogen easily to a proton. In contrast, cyclohexyl amine with its sp^3C (+I effect) enables easy donation of unshared electron pair of nitrogen. Apart from this reason, electron delocalisation also plays an important role. The unshared electron pair on nitrogen is in conjugation with benzene ring and, therefore, enters into delocalisation in the π electron system of the ring. This makes the electron pair not readily available for donation, or in other words aniline is a poor base. Also, on protonation the anilinium ion so obtained has used up its non bonding electrons. Therefore, no more delocalisation of these electrons is possible. Thus, in comparison to anilinium ion, aniline is more stable and makes the equilibrium shift to left side (i.e. towards aniline).



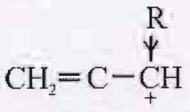
III. **Stability of allylic and benzylic carbocations and free radicals.**

The allylic and benzylic cations are known to be particularly table carbocations in comparison to the similarly substituted carbocations with localized electrons. The stability can be understood by recognising that the positive charge in allyl cation is delocalized between two carbon atoms as represented by the two equivalent resonance structures. The p orbitals of three carbons are aligned in the same direction to permit electron delocalization. Similarly, benzyl cation has the positive charge delocalized between four carbon atoms for which there are seven p orbitals of carbon involved in electron delocalization. Five resonance structures contribute to the stability of benzyl cation.

$$CH_2{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH_2$$

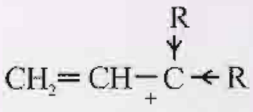


The above two carbocations are primary carbocations (positive charge on primary carbon). Secondary and tertiary carbocations are more stable than primary carbocation; tertiary more than secondary. Here, there is an additional stabilizing effect of positive charge by the electron releasing (+I) alkyl groups.



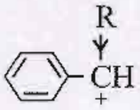
$$CH_2{=}C{-}\underset{+}{\overset{\overset{R}{\downarrow}}{C}}H$$

2° allylic carbocation
(+I effect of one R group)

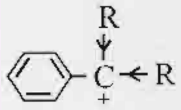


$$CH_2{=}CH{-}\underset{+}{\overset{\overset{R}{\downarrow}}{C}}\leftarrow R$$

3° allylic carbocation
(+I effect of 2 R groups)



2° benzylic carbocation

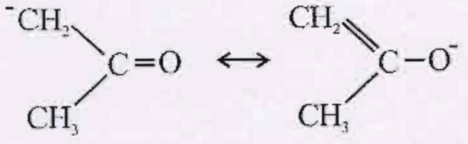


3° benzylic carbocation

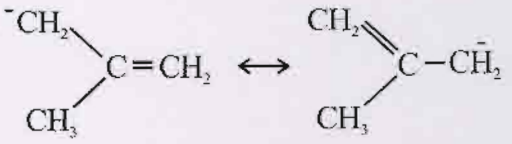
Just like carbocation, **allylic free radical**, with an unpaired electron, **shows two resonance structures** while **benzylic free radical** shows **five resonance structures**. The delocalisation of this unpaired electron accounts for the stability of the radical intermediate.

IV. Stability of the enolate anion

Enolate anions are formed by the deprotonation of carbonyl compounds and get stabilized by the delocalisation of negative charge. This can be illustrated by comparing the relative acidities of 2-methyl propene (isobutene) and 2-propanone (acetone). 2-propanone is far more acidic than isobutene. Thus, it is much easier for a proton to be removed from acetone than from isobutene. One of the main reasons for the difference in acidity is the difference in stability of the two conjugate bases. A resonance stabilized anion is generated in each case, but the anion from acetone is far more stabilized due to the negative charge on oxygen in one of the contributing structures. In both contributing structures for the isobutene anion, the negative charge is on carbon. Oxygen being more electronegative than carbon, resonance theory leads to the conclusions that acetone anion is more stable then isobutene anion which makes acetone more acidic.



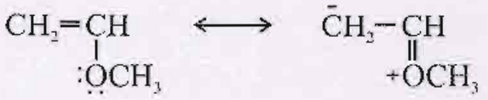
anion from acetone



anion from isobutene

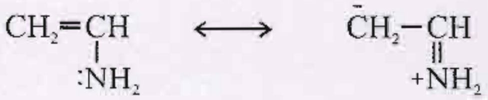
V. Reactivity of vinyl ethers and enamines

Vinyl ethers and enamines have double bonds in conjugation with alkoxy and amino groups respectively. Thus, although the electronegative O and N (in alkoxy and amino group respectively) exert a -I effect, the delocalisation of conjugated unshared electrons into the π electron system of C = C (+R effect) is more effective. Structure II in both cases, is responsible for the reaction of these compounds with electron deficient species.



$$\underset{:\ddot{O}CH_3}{CH_2{=}CH} \longleftrightarrow \underset{+\ddot{O}CH_3}{\bar{C}H_2{-}CH}$$

I II

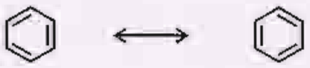


$$\underset{:NH_2}{CH_2{=}CH} \longleftrightarrow \underset{+NH_2}{\bar{C}H_2{-}CH}$$

I II

VI. Benzene

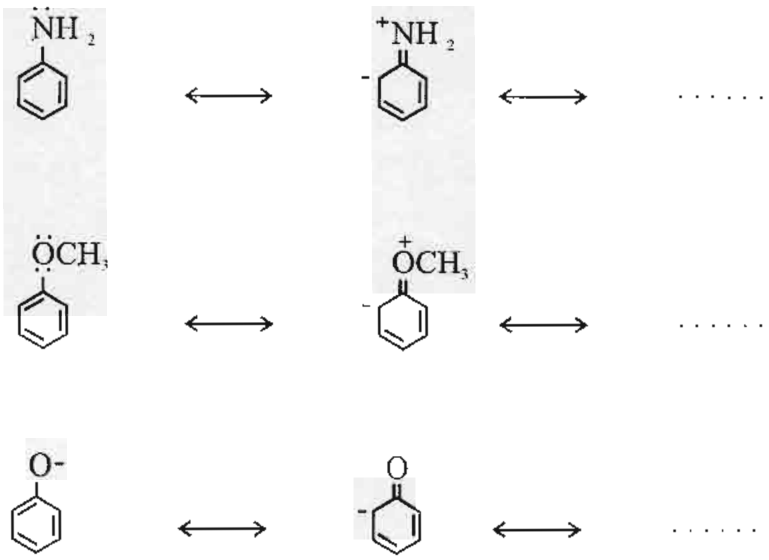
The most impressive example of resonance stabilization is benzene wherein delocalisation gives an exceptionally stable molecule. It is this delocalisation that gives benzene an **'aromatic'** character



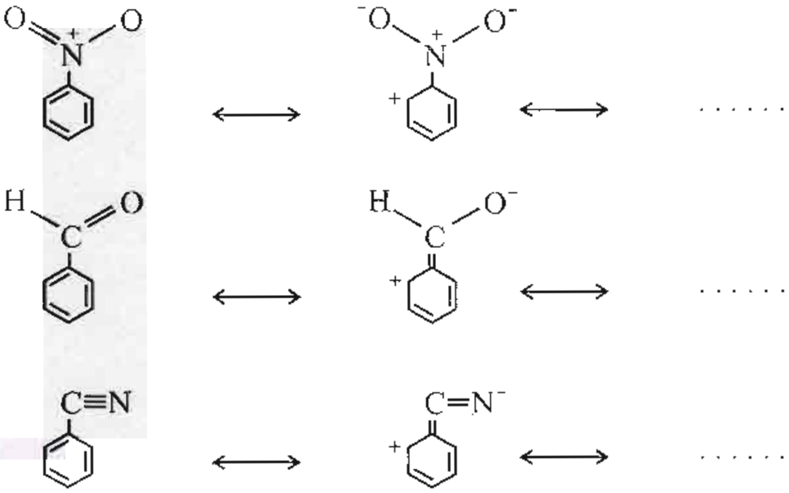
Several compounds like benzene are termed aromatic because they have one structural feature in common - conjugated double bonds in the ring that enable delocalisation.

Details of benzene and its stability is discussed separately under the heading of **'aromaticity'**.

Substituted benzenes provide examples of how proper use of the resonance concept can be valuable in predicting reactivity. Certain substituents donate electrons into the π electron system of the ring and are considered as electron donating groups and are shown as +M or +R groups. Others that accept electrons from π electron system of the ring are considered as electron withdrawing groups and shown as -M or -



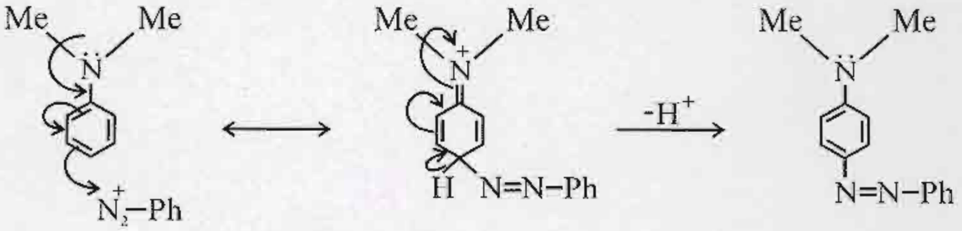
+M/+R groups: NH_2, -O CH_3, -O^- etc. These groups have at least one unshared pair of electrons (lone pair or negative charge) on the atom directly attached to the phenyl ring.



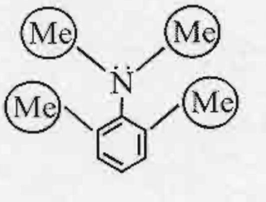
-M/R groups: -NO_2, -CHO, -CN etc. These groups have a multiply bonded atom directly attached to the phenyl ring.

VII. Steric Effect of Resonance

One of the important rules of resonance requires the atoms involved in electron delocalisation to be all in one plane. This is essential, since only then the p or π orbitals on the atoms are parallel to effectively overlap laterally and consequently enable effective delocalisation. But if due to steric reasons, the atoms are forced out of planarity, resonance is reduced severely or even prevented. This is reflected in the properties exhibited by the compound. For example, N, N- dimethyl aniline has a strongly electron releasing dimethyl amino group due to two +I alkyl groups. The methyl groups enhance the delocalisation of nitrogen lone pair in the ring. This enables the molecule to have a significant negative charge at para position suited for certain reactions with electrophiles, such as diazonium cation.



If there are more electron releasing alkyl groups on the benzene ring at ortho and para position, one expects the above reaction to be even more feasible due to increased electron dencity in the ring. However, it is found that now the diazonium cation does not react at all. This unexpected result is attributed to the steric hindrance of Me groups at 2 and 6 positions with the methyl groups on nitrogen. This disables the Me groups on nitrogen to be in-plane with benzene nucleus. The p orbitals on nitrogen and ring carbons are prevented from being parallel to each other and their overlapping is inhibited. Thus, electron density is not increased at para position of benzene ring.



Resonance Energy

Delocalisation of electrons results in a compound with more stability than it would have, had the electrons been localized. **This extra stability that a compound gains due to the electron redistribution via delocalization is called resonance energy or delocalisation energy.** Resonance energy is the energy by which a compound gets stabilized; it is therefore an energy that the compound 'does not have'. This energy which the compound 'does not have', makes it stable.

The concept of resonance energy can be better understood by looking at the unusual stability of benzene. Structure of benzene has three conjugated double bonds which enable the delocalization of π electrons. Let us compare the stability of such a delocalized system with the hypothetical cyclic structure containing three localized double bonds at alternate positions. This hypothetical structure is of cyclohexatriene.

The heat of hydrogenation of cyclohexene (one double bond) was found to be 28.6 kcal/mol (119.6 kJ mol^{-1}). With another double bond in conjugation, i.e. cyclohexadiene, the heat of hydrogenation would become double[28.6 x 2 = 57.2 kcal/mol (418 kJ mol^{-1})]. The experimental result is close to the calculated values. Accordingly, cyclohexatriene (a hypothetical molecule), with three localized π bonds at alternate carbons, can be calculated to have a heat of hydrogenation triple in comparison to cyclohexene [28.6 x 3 = 85.8 kcal/mol (358.6 kJ mol^{-1})]. However, the molecule of benzene does not release this amount of heat on hydrogenation (fig. A). In fact, heat of hydrogenation was experimentally found to be 49.8 kcal/mol (208.2 kJ mol^{-1}) (The difference between calculated and experimental values of heats of hydrogenation is 85.8 - 49.8 = 36 kcal/mol [150.5 kJ mol^{-1}]). Both compounds give the same product of hydrogenation - cyclohexane. Thus, the only way one can rationalise the difference of heat of hydrogenation of the two compounds is their different stabilities. In other words, benzene - the real molecule - is already very stable and at a lower energy level than the imaginary cyclohexatriene. Consequently the heat released on its hydrogenation will not be as much as for the hypothetical cyclohexatriene (Heat of hydrogenation is inversely related to the stability of the alkene). This energy difference signifies the extent to which benzene is stable as compared to cyclohexatriene. The difference in heats of hydrogenation which is due to difference in stability is in turn **due to difference in the distribution of electrons**. The difference in energy between experimental and calculated heats of hydrogenation, which is a measure of stability, is the **resonance energy of benzene**.

What, then, is the actual structure of benzene that can account for such high stability?

Several structures were proposed for benzene.

A B

Kekule structure

D

Claus structure

E

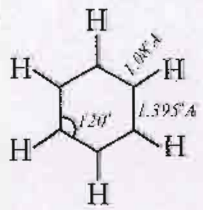
Dewar structure

F

Armstrong-Bayer structure

Amongst these, the most accepted structure was the one given by Kekule. According to him, benzene molecule actually oscillates between the two structures, each molecule spending half its time in form A and the other half in form B.

However, even this explanation could not completely justify the following facts about the structure viz. All C-C bond lengths are equal, 1.395A, which is a value intermediate between sp^2-sp^2 single bonds (1.48A) and double bonds (1.33 A). All atoms in the benzene molecule lie in one plane.



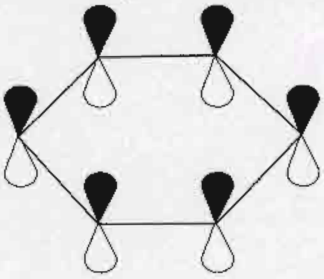
Kekule's description of the benzene structure shows two types of carbon-carbon bonds: single bond and double bond

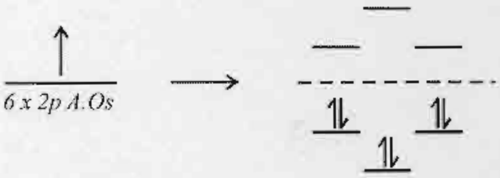
This inadequacy of the Kekule structure can be remedied, by depicting benzene as the hybrid of two equally contributing resonance structures

Benzene is an average of these structures; it is **one** compound with **one** type of carbon-carbon bond that is neither a single bond nor a double bond, but something in between.

The π bonds of benzene are different from the hypothetical cyclohexatrine (where the π bonds are localised).

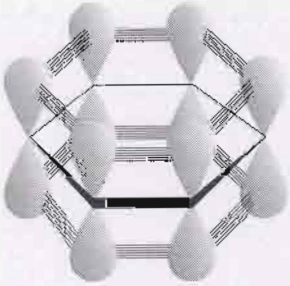
The Kekule structure for benzene suggests that each carbon atom should be trigonal, and therefore sp^2 hybridised. This means that each carbon atom has an unhybridized 2p orbital. Because the benzene molecule is planar, and the axes of all six 2p orbitals of benzene are parallal, these 2p orbitals can overlap to form π molecular orbitals. The six 2p orbitals overlap giving rise to six new molecular orbitals (MOs) - three bonding MOs and three antibonding MOs, with there energy destribution as shown.





The six available π electrons completely fill the bonding levels, leading to an enhanced stability of the π system.

The lowest energy π molecular orbital is the one where π-electron density lies in a doughnut shaped region above and below the plane of the benzene ring. This overlap is symbolized by the resonance structure of benzene.



Resonance hybrid can be represented as

Let us summarise a few important points about resonance effect which make it different from inductive effect.

* Resonance effect is a **permanent polarisation** in the ground state of the molecule, just like

inductive effect. However, unlike Inductive effect, it does not diminish on transmission.

* As a result of resonance effect the polarity at adjacent atoms alternates. Polarity at adjacent atom remains same in inductive effect although the intensity changes.

* Resonance effect operates only in unsaturated systems in conjugation (with π bonds, positive charge, unpaired electron, negative charge). It involves the π electrons and π orbitals only. Inductive effect operates in both saturated and unsaturated systems and involves σ bond electrons only.

Aromaticity

We have learned that benzene is unusually stable and that this stability has been correlated with the overlap of the 2p orbitals of the six carbon atoms to form π molecular orbitals.

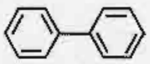
In 1931, Erich Hückel used similar molecular orbital approach to lay down the criterea for the sort of stability of benzene seen in other molecules which has come to be called **Aromaticity**. Aromaticity is thus a term that has evolved out of the deeper understanding of special properties of benzene and other related compounds. A compound is said to be aromatic when it meets **all** of the following criterea:

1. Structures with one or more rings and a cyclic arrangement of p orbitals leading to stable π molecular orbitals are called aromatic. Thus, **aromaticity** requires the compounds to be **cyclic**.
2. Every atom of the aromatic ring has a p orbital.
3. Aromatic rings are planar.
4. The planar cyclic arrangement of p orbitals will be aromatic only when there are $(4n + 2)\pi$ electrons (n is any positive integer such as 0, 1, 2, 3, ...) in the ring. Thus, an aromatic ring must contain 2, 6, 10, ... π electrons.

These criteria are often called collectively the **Hückel 4n + 2 rule** or simply the **4n + 2 rule**. Hückel rule can be reasoned if we look into the MO description of structures of such compounds. According to MO theory of cyclic π -electron systems, continuous cycles of p orbitals are a must for aromatic stability - this justifies criteria 1 and 2. The theory also requires that the p orbitals must overlap to form π molecular orbitals. For this, the aromatic ring must be planar. In non-planar rings overlap of p orbitals is ineffective - thus criterion 3. Finally, the number of π electrons should be 4n + 2. This can be understood from the number of π molecular orbitals and the number of electrons they contain. The number of molecular orbitals is equal to the number of overlapping p orbitals. Quantum mechanical calculations show that bonding molecular orbital of aromatic π -electron system have particularly **low energies.** Each electron in a bonding molecular orbital lowers the energy of a molecule. Thus a compound has the lowest energy when all its bonding molecular orbitals are filled. MO theory shows that in aromatic compounds it always takes 4n + 2 electrons to fill exactly the bonding molecular orbitals of their π electron system - thus criterion 4.

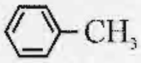
Applications of Hückel Rule of Aromaticity.

1. **Cyclic hydrocarbons.**



Biphenyl - aromatic

Each ring is separately planar, with 6π -electrons contributed by six p orbitals of their respective carbon. Therefore there are 2 aromatic rings each of which is separately aromatic.

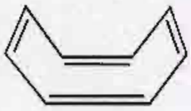


Toluene - aromatic

Although CH$_3$ group is not aromatic, it is a substituent on the ring and not a part of the ring system.

1, 3, 5, - cycloheptatriene - not aromatic

Although satisfies criterion 1, 3, 4 i.e. ring is planar with 6 electrons, it does not have p orbital on all carbons of ring (creterion 2). Therefore, not aromatic.



Cyclooctatetraene - not aromatic

Criterion 3 - planarity of ring is not obeyed. It is a tub shaped molecule and not planar. It is therefore not aromatic.

2. **Aromatic heterocycles.**

Cyclic structures containing heteroatoms can also be aromatic if they meet all the criterea of Hückel rule.

Pyridine-aromatic

Planar ring. Each atom has one p orbital and contributes one π - electron. 4n + 2 rule satisfied (6 π electron). Lone pair on this doubly bonded N is not included in the π - electron count. It resides in an sp^2 orbital in the plane of ring. Such pair of vinylic electrons (electrons on doubly bonded atom) are not counted as π electrons.

Pyridine-aromatic

Planar ring. N is not doubly bonded here (allylic N). 2p orbital on N bears its lone pair of electrons, therefore, contributes 2 electrons to the π -electron system. The other four atoms which are doubly bonded to each other, give one π electron each. Ring is planar and 4n + 2 rule is satisfied. In general, allylic electrons are counted as π electrons when they reside in orbitals that are properly situated for overlap with other p orbitals in the molecule.

Thiophene-aromatic

Each doubly bonded carbon contributes one π -electron. S is not doubly bonded. One of its two lone pairs is contributing to the π -electron system of the planar ring.

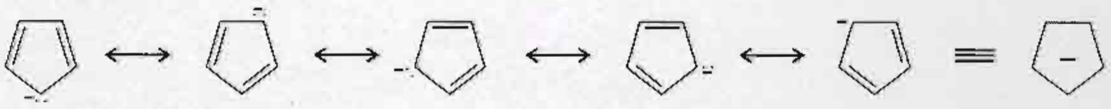
3. Aromatic Ions

Aromaticity is not restricted to neutral molecules; a number of cyclic ions are aromatic.

Aromatic Anions

Cyclopentadienyl/cyclopentadien-1-ide anion-aromatic. Unshared electron on C is analoguos to lone pair on N in pyrrole and hence is considered as a part of π electron system. Therefore, 4n + 2 rule is satisfied. Ring is planar and therefore, the ion is aromatic.

Cyclopentadienide anion is a highly stable anion and its resonance structures are:



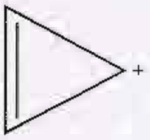
All five structures are equivalent. Each carbon gets the negative charge. Equivalence of the resonance structures imparts them identical energies which in turn gives the cyclopentadienide anion very high stability, not found even in pyrrole, furan etc. As a result, the conjugate acid of cyclopentadienyl anion viz cyclopentadiene, is an unusually **strong hydrocarbon acid** - 10^{10} times more acidic than 1-alkyne and about as acidic as water.

On the same basis, Hückel rule predicts aromatic stability for cyclononatetraenide anion.

If we look at cycloheptatrienide anion, it is not aromatic inspite of having double bonds conjugated with negative charge. This is because the 4n + 2 electron rule is not followed.

Aromatic Cations

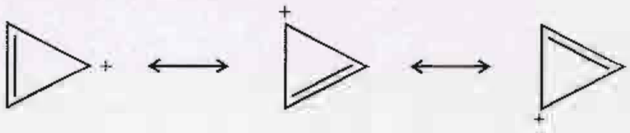
A cyclic cation can also be aromatic when the positive charge is in conjugation with π -electron system in a planar ring and 4n + 2 rule is being completely followed. The positive charge signifies an empty p orbital which is also a part of the π electron system. Due to lack of electrons, it does not contribute in the π -electron count.



Cyclopropenyl cation-aromatic

Ring is planar, 4n + 2 rule satisfied (here n=0). All carbons have one p orbital each, which overlap amongst themselves.

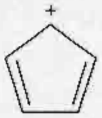
The resonance stabilization structures for cyclopropenyl cation are:



All three structures are equivalent in energy and hence contribute equally. The stabilization via resonance is, therefore, very effective.

On the same basis, Hückel rule predicts aromatic stability for cycloheptatrienyl cation (also called tropylium ion).

The cyclopentadienyl cation is not aromatic due to the 4n + 2 rule being not satisfied.



Number of π electrons = 4

Counting π electron accurately is, therefore, crucial for the successful application of 4n + 2 rule. π -electrons in the ring are counted by keeping the following points in mind:

* Each atom forming a double bond contributes one π -electron.

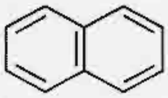
* Vinylic electron pair, i.e. unshared **electron pair on doubly bonded atom** does not contribute to the π -electron count.

* Allylic electron pair i.e. unshared **electron pair on an atom conjugated to double bond** contributes to π -electron count provided it is in an orbital parallel to other p orbitals in the molecule.

* An atom with positive charge has an empty p orbital that can be part of a continuous aromatic π -electron system without any π electron contribution.

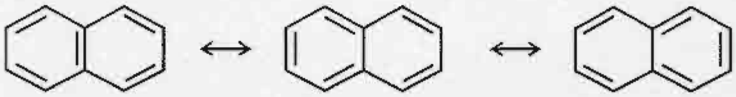
4. Aromatic Polycyclic Compounds

The Hückel 4n + 2 rule applies strictly to single rings i.e. to monocyclic compounds. However, a number of well-known fused bicyclic and polycyclic compounds are also aromatic e.g. naphthalene, anthracene, phenanthrene, pyrene. These molecules have two or more benzene rings fused together. They are therefore, also called **benzenoid compounds.**



naphthalene

Stabilization of naphthalene occurs via the following three resonance structures :

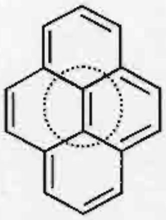


However, all the structures are not equivalent. One of them has a central double bond. (i.e. at the fused bond). Also, in this structuret the p orbitals overlap around the periphery of both rings and across the points of ring fusion.

Anthracene

Phenanthrene and anthracene are isomers. In anthracene, the three rings are fused in a linear way and in phenanthrene they are fused so as to produce an angular molecule.

Pyrene is also aromatic. The total number of π electrons in pyrene is 16 (8 double bonds). Sixteen is a non-Hückel number, but Hückel rule is intended to be applied only to monocyclic compounds and pyrene is tetracyclic. If we disregard the internal double bond of pyrene and look only at the periphery we see that



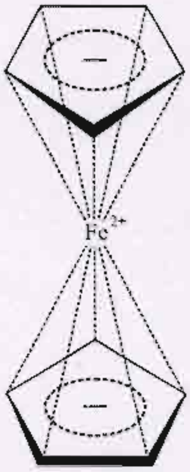
pyrene

the periphery is a planar monocyclic ring with 14 π electons. 14 is a Hückel number (4n + 2, n=3) and based on the periphery, pyrene would be aromatic. Ignoring the internal double bond, pyrene will be very much like [14] annulene about which we discuss shortly.

5. Aromatic Organometallic Compounds

Some organometallic compounds also exhibit aromatic character.

Cyclopentadienide anion forms stable complexes with a number of transition-metal cations. One of the best known of these complexes is ferrocene. It is a molecular sandwich wherein a ferrous ion is embedded between two cyclopentadienide anions.

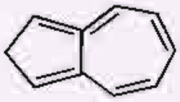


6. Nonbenzenoid Aromatics

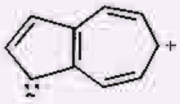
Members of this class of compounds include some carbocyclic compounds, which, in contrast to benzene, have rings containing odd number of ring atoms. Yet, despite this, they appear to have aromatic character. They exist either as cations or anions or as dipolar compounds. Here also we find six π electrons. eg. cyclopentadienide anion, cycloheptatrienium cation, aromatic annulenes (except [6] annulene).

Another example is the compounds azulene.

This deep blue coloured hydrocarbon is an isomer of naphlthalene - being isoelectronic with naphthalene.



Another feature of azulene is that it is found to have a substantial dipole moment (1.0 D). However, naphthalene has zero dipole moment. This may be attributed to resonance structures wherein charge separation occurs. One such structure is shown below. Such charge separated resonance structures give rise to a five membered ring very much like aromatic cyclopentadienide anion and a seven membered righ very much like aromatic cycloheptatrienium cation both of which are especially stable.

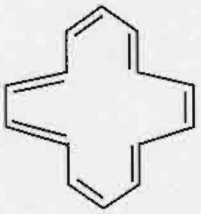


7. Annulenes

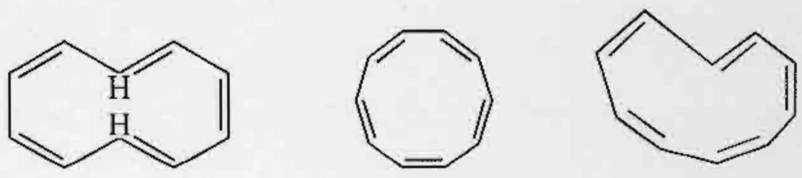
The term 'annulene' was coined to refer to the completely conjugated monocyclic polyenes. The ring size of an annulene is indicated by a number which is placed in brackets. Thus, benzene is [6] annulene and cyclooctatetraene is [8] annulene. As before, annulenes will be aromatic if they obey all the 4n + 2 Hückel rules.

Accordingly [6], [14], [18] annulenes [n = 1, 2, 3 ....] have been found to be aromatic while [16], [20] annulenes are not aromatic due to absence of (4n + 2) π electrons.

[10] annulenes, although have 4n + 2 electrons (n=1), are not aromatic due to absence of planarity of ring. The [10] annulene A has two trans bonds with bond angles of 120°. However, carbon atoms of the ring are not in one plane and so the overlap of their p orbitals is not effective. Structure B has cis double bonds and is planar but has severe angle strain. Similarly structure C has only one trans double bond and is planar but experiences severe amg;e strain.



[14] Annulene



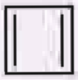
A B C

[10] Annulene

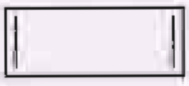
8. Anti Aromatic Compounds and Non Aromatic Compounds

Compounds that have **planar continuous rings of p orbital** bearing atoms contributing to **4n π electrons** are found to be especially unstable. If the stability of such compounds is compared with their open chain counterpart, the ring has greater π -electron energy or lesser stability than the open chain. Such compounds are called **anti aromatic compounds.**

1, 3 cyclobutadiene or [4] annulene, the first member of this series of annulene, is such a compound.



Although the double bonds are conjugated and ring is planar, resonance in such compounds causes destabilization i.e. overlap of p orbitals in molecules with cyclic rings of 4n π electrons is a destabilizing effect. Therefore, it is anti aromatic. Consequently, antiaromatic molecules are distorted so that this destabilizing overlap is minimized. Cyclobutadiene, therefore instead of having all bond lengths equal, has a rectangular geometry with longer single bonds separating double bonds so that their interaction is minimized.



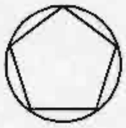
Cyclobutadiene has effectively got localized double bonds. This distortion, makes the overlap minimum but introduces even more strain in the molecule.

On the same basis, cyclooctatetraene, if considered as a planar ring, will be highly unstable than its open chain compound. Hence it would be antiaromatic. Actually, for this reason cyclooctatetraene is not planar and behaves like a simple cyclic polyene. Due to non planar tub-shape, it avoids antiaromaticity and becomes non aromatic.

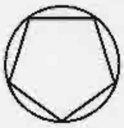
Non aromatic compounds too are **carbocyclic planar rings** with conjugated double bonds, but the π - electron energy and hence their stability is comparable to their open chain analogs. eg. cycloheptatriene. One of the carbons is sp^3 hybridized there by preventing a completly cyclic overlapping π system.

The order of decreasing resonance energy and hence stability of aromatic, anti aromatic and non aromatic compounds is: **Aromatic > Non Aromatic > Anti Aromatic**

A simple method has been devised to get a picture of the relative energies of the π -molecular orbitals of conjugated monocyclic systems from where one can understand why a compound is aromatic or antiaromatic. The method is called **polygon-and-circle method**. We inscribe the polygon, corresponding to the ring of the compound, in a circle in a way that one vertex of the polygon is at the bottom.



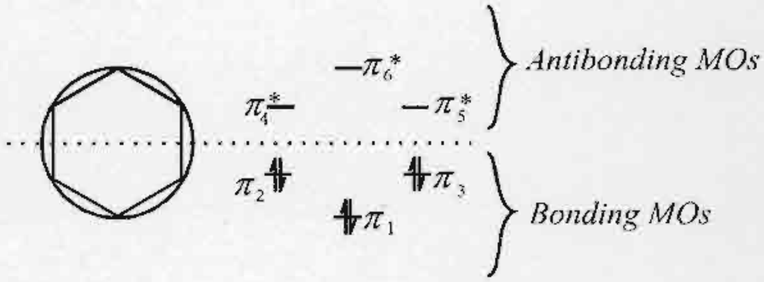
*2 vertices at the bottom, **incorrect***



*one vertex at the bottom, **correct***

With this placement of polygon in a circle, we note the position occupied by the rest of the vertices of the polygon. The vertices represent relative energies of the MOs (molecular orbitals) with energies increasing from the bottom to the top of the circle. The vertices below the horizantal diameter are bonding MOs, those above are antibonding MOs and those on the diameter are non bonding MOs.

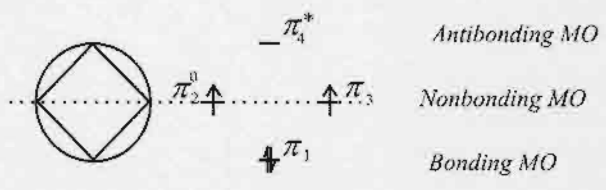
Consider the molecule of benzene. The hexagon of benzene furnishes six MOs. Keeping one vertex at the bottom, there will be three MOs below and three MOs above the horizontal diameter.



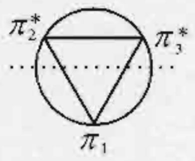
Aromaticity is observed when all the bonding MOs are completely filled and non bonding MOs, if present, are empty or completely filled. If, on the other hand, there are electrons in the antibonding MOs, or if it has half filled bonding MOs or non bonding MOs, the molecule is antiaromatic.

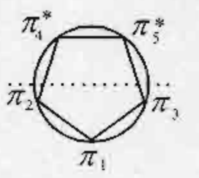
In benzene there are 6 π electrons completely filling the three bonding MOs. This lowers the π - electron energy much more than its open chain analog. Therefore, benzene is aromatic.

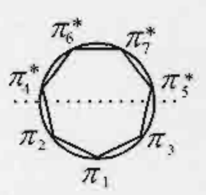
In cyclobutadiene (4 π electron system), there is one bonding MO, two nonbonding MOs and one antibonding MO. The 4 π electron completely fill bonding MO but can only half-fill the degenaerate non bonding MOs. This raises the π electron energy more than its open chain analog. Therefore, cyclobutadiene is antiaromatic.

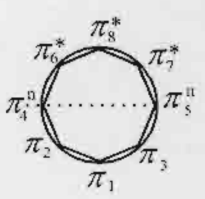


Polygon - and - circle rule can be shown for other systems (such as 3 carbon, 5 carbon, 7 carbon, 8 carbon system) as well.







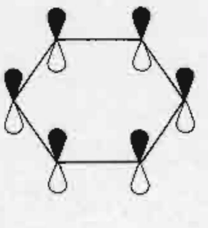


Mobius Array

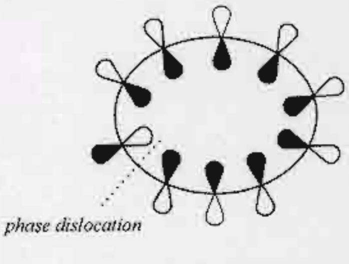
Hückels rule, which states that a cyclic system of electrons is aromatic when it consists of 4n + 2 electrons, applies to molecules in their ground states. In understanding the feasibility of certain reactions (viz. pericylic reactions), a quick way of assessment is by examiningg the cyclic array of relevant orbitals at the transition state of the reaction. If this array has no nodes or has even number of nodes (i.e. phase change) between atoms then the reaction is allowed provided the number of π electrons is (4n + 2). Such an array of orbitals is called Hückels array. If, on the other hand, it has an odd number of nodes between atoms, then there should be 4n π electrons to make the reaction allowed. This array of orbitals is called Möbius array. In a Hückels system, one can arrange the constituent atomic orbitals so that they overlap in - phase. A Mobius system is one is which the set of atomic orbitals, called the basis set, cannot be arranged without involving any phase dislocation at some point in the ring system. If a planar linear polyene is twisted so that one end is turned 180° relative to the other, and the ends of the polyene are then joined, the top portion of the π-system will overlap with what was the bottom, and the cyclic system will be a so-called Mobius polyene. Such polyenes are **unknown** in the **ground state** but can exist in the **transition states** of pericyclic reactions.

The term Mobius is derived from the Mobius strip. Such a strip is formed when the two ends of a strip of paper is joined by giving the strip a half twist (180^0).

The mobius strip is remarkable in that it has a single continuous ring instead of two separate rings of the normal cyclic π-systems.



Huckel system



Mobius system

Based to the Huckel or Mobius systems, cyclic concerted reaction can be classified as aromatic or antiaromatic.

For thermal pericyclic reactions, the predictions are.

Number of electron	Hückel type	Mobius type
0, 4, 8, ..., 4n	unfavourable (antiaromatic)	favourable (aromatic)
2, 6, 10, ..., (4n + 2)	favourable (aromatic)	unfavourable (antiaromatic)

For photochemical pericyclic reactions, the rules are reversed.

HYPERCONJUGATION

All of the delocalization discussed so far involves π electrons. One of the assumption in Hückel approximations is the non interaction of the π -orbital system with the σ molecular framework. In planar systems, this assumption is reasonable. However, there is another type of delocalisation, which describes interaction involving σ electrons. Such special type of resonance is known as hyperconjugation which although does not involve a double bond, does nevertheless **involve a kind of conjugation.**

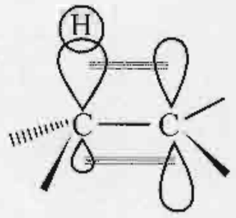
When a carbon possessing at least one hydrogen is attached to another carbon bearing an unshared orbital or to an unsaturated carbon there are more than one structures (canonical forms) that can be drawn for the molecule. These canonical forms result from the overlap of bonding electrons of the C — H σ bond with the 2p orbital of adjacent carbon or with π orbital. As a result, in these structures the bond between carbon and hydrogen does not exist anymore. The shared pair of electrons is now borne by carbon alone and hydrogen is in its close proximity as a proton. The negative charge developed on the carbon then gets delocalised by overlap with adjacent p orbital. Hyperconjugation can help understand the stability and reactivity of several compounds and intermediates.

Applications of Hyperconjugation

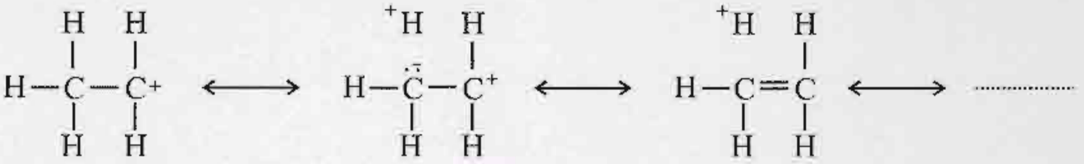
Let us see the cases where such special type of resonance phenomenon operates.

1. Alkyl cations and their relative stability

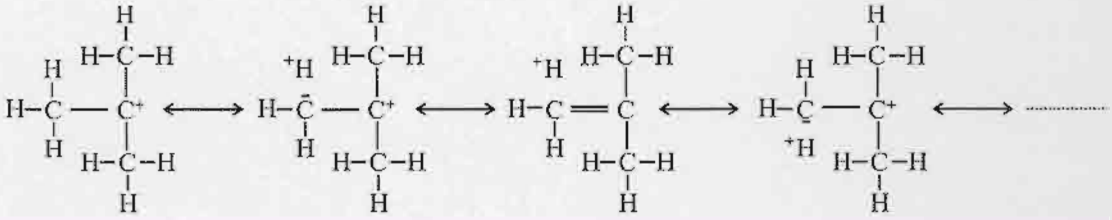
Alkyl cations, or carbocations, have an electron deficient (positively charged) carbon. The p orbital on this sp^2 carbon is empty. This empty p orbital of a carbocation can overlap with σ orbitals of C - H bond of adjacent alkyl groups (α C - H bonds). σ bond provides the bonding orbitals for the overlap.



This overlap permits individual electrons to help bind together three nuclues, two carbons and one hydrogen. Therefore, positive charge is no longer localized but gets dispersed over a larger volume of space and is consequently stabilized. In resonance language, we say that there is no bond at all between carbon and hydrogen, which results in structures of the kind shown.



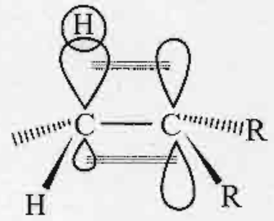
In these structures, double bond joins the two carbon and positive charge is carried by a hydrogen. In ethyl cation having three α C-H bonds, positive charge is borne by three hydrogens. Thus, ethyl cation is represented by seven structures. **The more alkyl groups there are on the carbocation, the more number of α C - H σ bonds and hence more possibilities there are for hyperconjugation which makes the carbocation more stable.** Isoproppropyl cation is stabilized by thirteen structures and tertiary butyl cation is stabilized by nineteen structures caused by the positive charge over six hydrogens and nine hydrogens respectively.



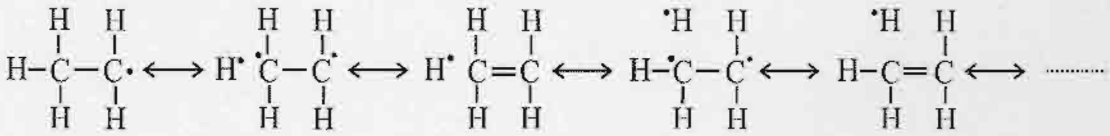
As a result, the order of stability of carbocation is t-alkyl carbocation > sec-alkyl carbocation > primary alkyl carbocation. Hyperconjugation is also called **'no-bond resonance'** due to the 'no-bond' between C and H in its canonical forms.

2. Alkyl radicals and their relative stability

The relative stability of tertiary, secondary and primary alkyl radicals is accounted for on exactly the same basis as done for carbocations. Radicals have a *p*-orbital on carbon occupied by an odd electron which gets delocalized over three nuclei (2 carbon and one hydrogen) by the overlap with σ orbital of C - H bond of adjacent alkyl group.



Thus ethyl radical can be represented as the hybrid of the seven 4 no-bond resonance structures. A double bond is formed between 2 carbons and odd electron is held by a hydrogen atom.



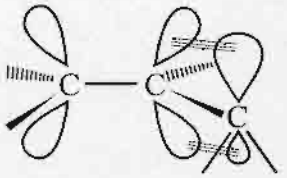
Isopropyl radical is a hybrid of thirteen no-bond resonance structures. t-butylradical is a hybrid of nineteen no-bond resonance structures.

The order of stability depends on the extent of delocalisation. The greater the delocalisation the more is the stability.

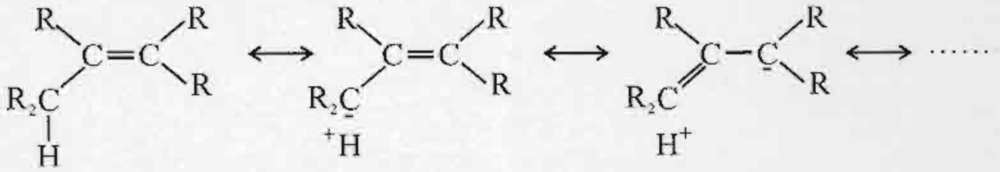
t-butyl radical > isopropyl radical > ethyl radical > methyl radical.

3. Alkenes and their stability

Stability of alkenes, substituted by alkyl groups, can be understood on the basis of hyperconjugation. Overlap of σ orbital of C - H bond and π orbital of the adjacent C - C bond gives rise to canonical structures. Delocalisation of electrons occurs over three nuclei and stabilizes the alkene.



An alkene with α C-H containing alkyl groups, such as the one shown, will be able to get stabilized by the following kind of hyperconjugative structures:



α C-H possesses partial ionic character and its electrons get delocalised into the adjacent π-system. The more the substituents more is the oppurtunity for hyperconjugation and the more stable the alkene. Thus, alkyl groups on the unsaturated carbon system exert an electron releasing effect, by a different mechanism (hyperconjugative effect), to stabilize the alkene.

Stability of alkenes will increase with increase with number of hydrogens α to unsaturated system.

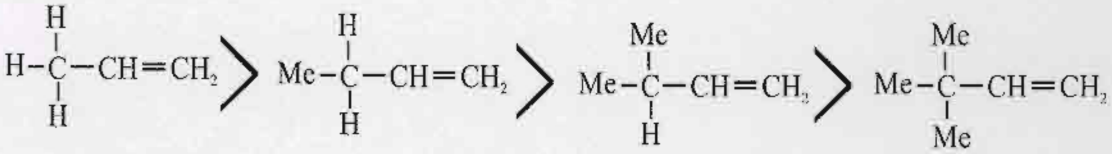
$$CH_2 = CH_2 < (CH_3)CH = CH_2 < (CH_3)_2C = CH_2 \approx (CH_3)CH = CH(CH_3) <$$

1 structure *7 no-bond resonance structure (3 αC - H bonds)* *13 no-bond resonance structures (6 αC - H bonds)*

$$(CH_3)_2C = CH(CH_3) < (CH_3)_2C = C(CH_3)_2$$

19 no-bond resonance structures (9αC - H bonds) *25 no-bond resonance structures (12αC - H bonds)*

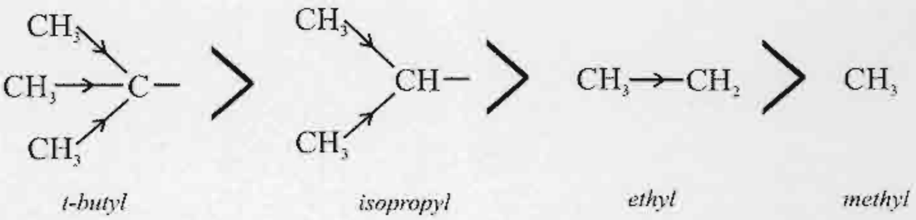
On the same basis, lack of the α C - H bonds in the susbtituents accounts for lesser electron donation by alkyl groups in the following series $CH_3 > MeCH_2 > Me_2CH > Me_3C$ which is reflected in their stability of the alkenes:



$$H-\underset{H}{\overset{H}{C}}-CH=CH_2 > Me-\underset{H}{\overset{H}{C}}-CH=CH_2 > Me-\underset{H}{\overset{Me}{C}}-CH=CH_2 > Me-\underset{Me}{\overset{Me}{C}}-CH=CH_2$$

4. **Alkyl Substituted Benzenes**

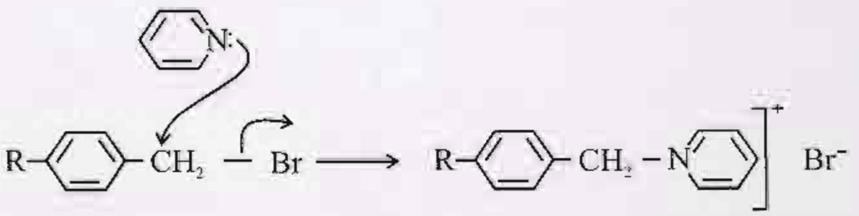
We are aware that inductive effect (rather, field effect) gives the relative order of electron release in alkyl groups as:



This order is observed in many phenomenon and satisfactorily explains several physical data.

However, when these groups are substituents in benzene rings and other unsaturated systems, order of electron release gets reversed in explaining certain reactions in aromatic compounds. In other words, alkyl groups exert an electron releasing effect on the benzene ring in an order reverse of that expected from inductive effect. This can explained on the basis of hyperconjugation.

Baker and Nathan examined the reaction between p-substituted benzyl bromides and pyridine. The reaction is a substitution reaction (S_N2), typical of alkyl halides, wherein the bromo group is replaced by pyridine.

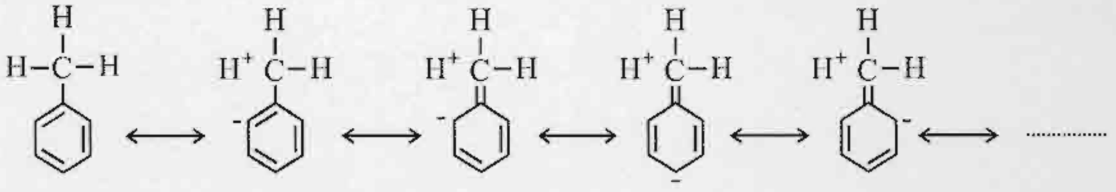


The greater the electron release (+I effect) by the R group faster would be the reaction. However, it was found that the order of the rate of reaction for the R groups was:

Me > Et > iso pr > t - but

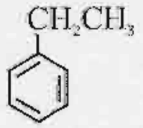
This order, opposite to the order of electron release by +I effect, could be explained only on the basis of hyperconjugation, and come to be known as **Baker-Nathan effect.**

A methyl substituent on benzene ring, i.e. toluene molecule, will have 3 α -hydrogen capable of undergoing an overlap of their σ bonds with the π orbital of the conjugated double bonds of benzene ring. This possibility of stabilisation decreases as the number of hyperconjugable α - hydrogen decreases. In other words, branching at α - C reduces the delocalisation by hyperconjugation due to reduction in the number of α C - H bonds.

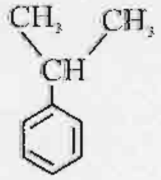


(Four canonical structures showing cleavage of C - H bond and delocalisation of negative charge in the benzene ring will exist from each α - H).

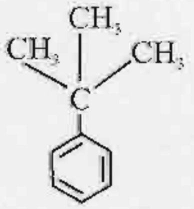
Total number of canonical forms = 14 structures. (12 structures showing hyperconjugation and 2 structures showing the two kekule forms of benzene).



number of C - H bonds = 2
number of canonical forms = 10



number of C - H bonds = 1
number of canonical forms = 6



number of C - H bonds = 0
number of canonical forms = 2

Methyl group, therefore, is the **strongest electron donor** and so gives the fastest of reaction while t-butyl group is the weakest electron donor group and give the slowest rate of reaction.

A few points are required to be noted while studying hyperconjugation.

1. While making 'no-bond resonance' structure, we must understand that the hydrogen atoms, of the 'no-bond' between carbon and hydrogen, are not free. They are shown as protons in the same position

as occupied by them when there is a formal bond between carbon and hydrogen. The effect of the 'no-bond' is to increase the ionic character of the C - H bond, the electrons of which get delocalised through conjugation. If the proton is moved from its original position one of the conditions necessary for delocalisation to occur would be contradicted.

2. Hyperconjugation results in the σ-electrons of the C-H bond to be less localised by entering into conjugation with attached unsaturated system or p orbital with no or one eletron. i.e. there is a σ - π conjugation or a σ -p conjugation.

3. It is a permanent effect which increases the ionic character of C-H bond.

4. Hyperconjugation of the kind described to understand the stability of alkenes is called **sacrificial hyperconjugation**. This is because the canonical forms have one bond less than the main form. Also, the canonical forms have charge separation not seen in main form.

Hyperconjugation in free radicals and carbocation involves no 'sacrifice'; the canonical forms show no more charge separation than the main form. Hence, it is called **isovalent hyperconjugation**. These name were coined by **Muller and Mulliken.**

INTERMOLECULAR FORCES

The forces that act between neutral molecues to hold them together are called **Intermolecular forces or intermolecular non-bonding interactions**. These forces are responsible for the physical state in which the covalent compounds, (gases / liquids / solids) under the given conditions of temperature and pressure. Compounds which have low molecular masses and no dipole moments, such as methane and carbon dioxide, are gases at ordinary temperatures and pressures. This is due to their weak forces of attraction. These interaction increases significantly as the molecular mass, and hence the size of the molecules, increases. The interactions also increase with increasing polarity of molecules. **Three types of intermolecular forces are important.**

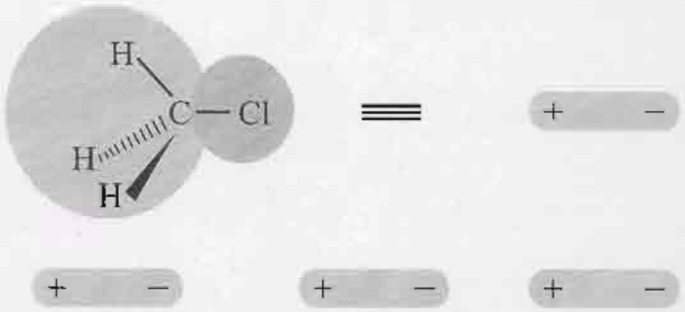
(1) Dipole - Dipole Interactions
(2) Van der Waals Interactions
(3) Hydrogen Bonding.

DIPOLE - DIPOLE INTERACTION

Molecules with dipole moments tend to orient themselves in a way that negative end of one molecule faces the positive end of the other molecules.

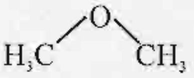
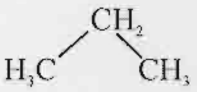
This interaction is between molecules with permanent dipoles which makes them hold each other more strongly.

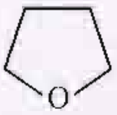
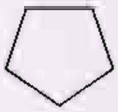
eg. CH_3Cl has a dipole moment of 1.86 D lying along the carbon - chlorine bond. Chloromethane molecules orient themselves so that the positive end of one dipole is pointed towards the negative end of another dipole. Strength of such attractive forces is about 3 kcal mol^{-1} (12.5 kJ mol^{-1}) as against 30 - 130 kcal mol^{-1} (120.5-543.4 kJ mol^{-1})for covalent bond.



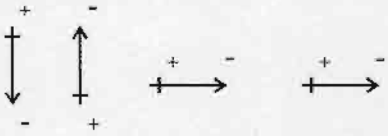
The polarity of a compound influences the attractive forces between its molecules which affects its physical properties, for example boiling points.

Below is given the comparison of boiling points of two molecules with same shape and molecular mass but diferent polarity.

		
dipole moment	1.31 D	≈0D
boiling point	- 23.7°	- 42.1°

		
dipole moment	1.7 D	0D
boiling point	66°	49.1°

We can see that the more polar molecules exhibit higher boiling points. This is a direct consequence of greater attraction between more polar molecules which align in a way that negative end of one dipole is attracted to the positive end of the other.



two ways in which dipoles can align attractively.

When a polar molecule contains a non polar hydrocarbon portion of even moderate size, its polarity has little effect on its physical properties; it behaves more like a non polar molecule with comparable molecular mass (i.e. alkane)

	$H_3C-O-CH_2CH_2CH_2CH_2CH_3$	$H_3C-CH_2-CH_2CH_2CH_2CH_2CH_3$
boiling point	99°	98°

Thus, larger intermolecular attractions translate into higher boiling points and similarly higher solubility etc.

VAN DER WAALS INTERACTIONS

Intermolecular forces attract even nonpolar molecules to each other, as is evident from the fact that even nonpolar molecules can solidify.

In non polar molecules, the average distribution of charge over a period of time is uniform. However, at any given instant, because electrons move, the shape of electron clouds can be altered by external forces. Thus, the charge may not be uniformly distributed. One such external force is the electric field of the electrons in the nearby molecules. When two molecules approach each other closely,the electron clouds of one molecule repel the electron clouds of the other. As a result , both molecules temporarily acquire small localized separation of charge called **induced dipole**. In other words, molecules acquire a temporary dipole moment. The deficiency of electrons (positive charge) in part of one molecule is attracted by the excess of electrons (negative charge) in part of another molecule i.e. the temporary dipole in one molecule induces opposite (attractive) dipole, in surrounding molecule. These temporary dipoles change constantly, but the net result of their existence is to produce attractive forces between non polar molecules. This attraction between induced dipole is called **Van der Waal force** or **dispersion force** of **London force**.

In small molecules, like methane, the interactions are very weak so that such compounds are gases at room temperatures. As the molecular mass increase, in hexane for example, the molecules get larger and attractive forces increase to make them exist as liquids at room temperature.

This is the cohesive force that must be overcome in order to vaporize liquid hydrocarbons. Because of this, we can understand why ionic organic compound often decompose before they boil. The thermal energy required to completely separate (vaporize) the ions is so great that chemical reaction (decomposition) occurs first.

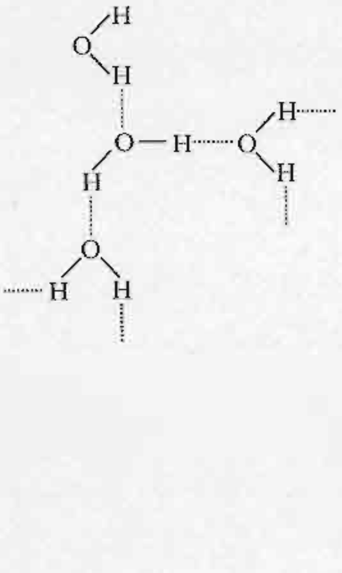
Van der Waal forces help us to understand why larger molecules have higher boiling points. With increase in number of carbon and hydrogen atoms the additive effect of these weak intermolecular forces become more significant. Larger, heavier molecules require greater thermal energy in order to acquire velocities sufficiently higher to escape the liquid surface which is reflected in the increase in their boiling points / melting points. Van der Waals interactions can act only through the parts of different molecules that are within a certain distance of each other. i.e. they are short ranged or between the surfaces of molecules. The strength of these interactions is strongly related to surface area of the interacting electron clouds, i.e. the larger the interacting surfaces, the greater the magnitude of the induced dipoles. A larger molecule has a greater surface of electron clouds and therefore, greater Van der Waals interactions with other molecules. It therefore, implies that larger molecules have higher boiling points.

The shape of a molecule is also important in determining its boiling points. For example, a comparison of the boiling point of the highly branched alkane, neopentane (9.4°C) and its unbranched isomer n-pentane (36.1°C) is particularly striking. Neopentane has four methyl groups disposed in a tetrahedral arrangement about a central carbon so that overall it gets a more compact spherical shape whereas pentane is rather extended with more of ellipsoidal shape (it would, therefore, not fit into the same sphere as neopentane). The more a molecule approaches spherical proportions, the less surface area it presents to other molecules (a sphere is the three - dimentional object with the minimum surface - to - volume ratio) giving rise to fewer cohesive interaction. As a result, neopentane will have lower boiling point than pentane.

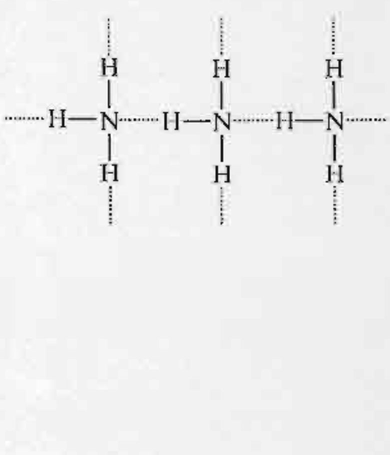
In this context, fluorocarbon (compounds with only carbon and fluorine) have extraordinarily low boiling points when compared to hydrocarbons of the same molecular mass or with the same number of carbon atoms. A straight chain fluorocarbon has a slightly lower boiling point than a straight chain hydrocarbon even though the former has a far higher molecular mass. This behaviour is understood on the basis of low polarizability of fluorine atoms, resulting in very small Van der Waals forces.

HYDROGEN BONDING

An especially strong kind of dipole - dipole interaction is hydrogen bonding. Here the polarity in bond arises **when a hydrogen atom is covalently bonded to strongly electronegative atoms, such as oxygen, fluorine or nitrogen**. In such a situation, electron cloud is severely distorted towards the electronegative atom, exposing the hydrogen nucleus. The positive charge of hydrogen nucleus is, in turn, attracted by the negative charge of the electronegative atom of second molecule. Hydrogen atom, thus, acts as a bridge between two electronegative atoms - one held by covalent bond and other by purely electrostatic forces. The strength of such bonds is about 3 - 10 kcal mol^{-1} (12.5 - 40.2 kJ mol^{-1}), making them the **strongest of intermolecular interactions**. The attractive forces of hydrogen bonding are indicated by a dashed line. Water is the best example of molecules exhibiting H-bonding. Other examples are NH_3, HF etc.



$H{-}F\cdots H{-}F\cdots H{-}F$

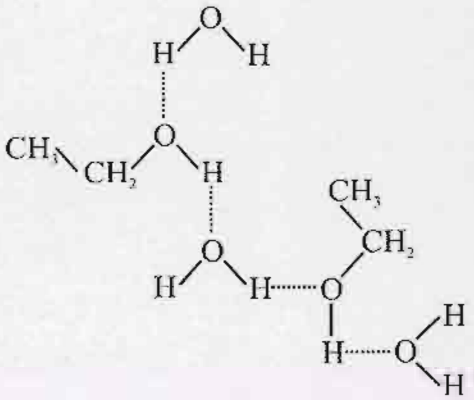


Only hydrogen bonded to one of the three electronegative atoms - F, O, N- is positive enough and only these three elements are negative enough for these attractions to exist.

eg. Chlorine atoms are not involved in hydrogen bonding. This is due to their larger size than fluorine, oxygen or nitrogen. The partial negative charge on Cl atom in a covalent bond is more diffused and does not attract the hydrogen atoms. Similarly hydrogen atom bonded to carbon are not usually involved in the formation of hydrogen bonds.

The effect of hydrogen bonding is seen in physical properties like boiling points, solubility etc. For example, the boiling points of ethanol and its isomer dimethyl ether, are dramatically different (78°C and -24°C respectively). This striking difference is attributed to the existence of hydrogen bonding in ethanol and lack of the same in dimethyl ether. In latter case, the only dipole - dipole interaction exist (H is not linked directly to O, OH bond is not polar, thus, no possibility of H- bonding).

Similarly, molecules that can participate in formation of hydrogen bonds with water, will disolve in water. This solubility is very good if non polar portion of molecule is not too large (portion containing only carbon and hydrogen). Thus, with increase in non-polar portion, as we go from ethanol 1-butanol 1-hexanol, the solubility in water decreases.



STEREOCHEMISTRY

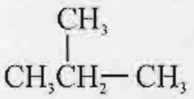
Compounds with identical molecular formula (same number and kind of atoms) but different from each other are called isomers and the phenomenon called **Isomerism.**

Structural isomers

Molecules having the same molecular formula, but different sequence of their atom connectivity are called Structural Isomers. Structural isomers are alco called constitutional isomers. The term constitution connotes the number, kind and connectivity of the atom in a molecule. This constitution of a molecule is represented by a two - dimensional graph in which atoms linked to each other are connected by single, double and triple bonds (lewis structures) .constitutional isomers are again classified an.

(a) Chain isomers: differing in the length of C - chain.

$CH_3CH_2CH_2CH_3$ and

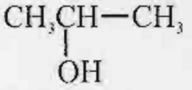


$$CH_3\overset{\overset{CH_3}{|}}{C}H_2-CH_3$$

n-butane isobutane

(b) Position isomers: differing in the position of functional group.

$CH_3CH_2CH_2OH$ and



$$CH_3\underset{\underset{OH}{|}}{C}H-CH_3$$

propan-1-ol propan-2-ol

(c) Functional isomers: differing in the functional group.

CH_3CH_2OH and CH_3-O-CH_3

ethanol *dimethylether*

(d) Metamerism: differing in distribution of carbon atoms on either side of functional group.

$CH_3CH_2OCH_2CH_3$ and $CH_3OCH_2CH_2CH_3$

diethylether *methylpropylether*

(e) Tautomerism: a case of dynamic structural isomerism.

Stereoisomers

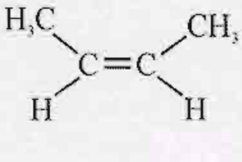
Molecules having the same connectivity of atoms but differing in the relative three - dimensional arrangement of their atoms are known as stereoisomers. Since there is difference in configuration, stereoisomers are also called **configurational isomers.**

Earlier, Stereoisomers were classified as :

(i) Optical isomers: Stereoisomers capable of rotating plane of plane polarized light.

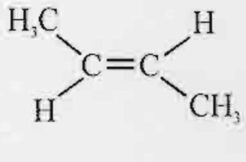
eg. Lactic acid oxists as a pair of stereoisomers that can rotate plane of plane polarized lights.

(ii) Geometrical isomers: Stereoisomers arising from the restriction in rotation in doubly bonded systems and cyclic systems. Such stereoisomers are also called cis-trans isomers.



cis

similar groups on same side of double bond



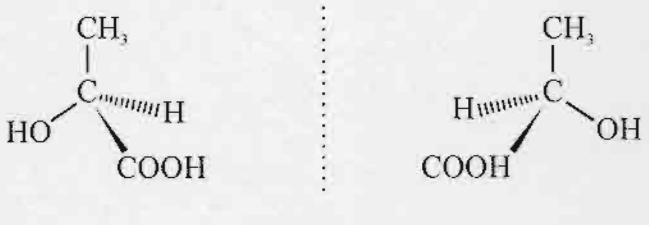
trans

similar groups on opposite side of double bond

Present classification is based on symmetry of molecules and recognises two types of stereoisomers.

(I) Enantiomers: If two stereoisomers are related to each other as object and minor image which are not superimposable, they are called enantiomers. Enantiomers always exists as pair of stereoisomers and are optically active i.e. they rotate the plane of plane polarized light to an equal degree but in opposite directions.

Enantiomers necessarily exist due to chirality of molecules. Chirality is the condition when molecules form non-superimposable mirror images of each other.



a pair of enantiomers
non superimposable mirror images
hence, chiral.

(II) Diastereomers: Stereoisomers which are not related to each other as object and minor image are said to be diastereomers.

Geometrical isomers, due to the symmetry of molecule, do not show optical activity. If they are optically active there has to be some other structural feature in them that is responsible for the optical activity.

ORGANIC REACTIONS

If we take a pure compound, all the molecules of this compound retain their identity even on standing for years, without any change in the chemical composition of the molecules e.g. a bottle of acetone remains unchanged. Yet, when we add chemical reagents such as sodium cyanide, chemical reactions occur. How does the reaction occur? Why does the reaction occur with sodium cyanide; why not with water (for example). Such questions and many more are dealt with in the study of organic reactions.

To, understand organic chemistry, we must be familiar with two languages - (i) the description of structure of molecule (ii) the description of the way the molecule undergoes a reaction (mechanism).

(a) What happens in the reaction; (b) Why does the reaction occur; (c) How does the reaction take place? Underlying the three questions is the fact that: Molecules react because they are in constant motion. There is internal motion: stretching of bonds, bending of bonds, vibrations etc. Apart from this, molecules as a whole move in space, collide with each other, into the vessel wall and into the solvent if they are in solution. Collisions between two different molecules is the first requirement for a reaction to materialise. However, all collisions do not always result in a reaction. For the reaction to occur, the colliding molecules must be given enough energy for overcoming the repulsion between them so that they get close enough to each other. This repulsion exists between their outermost electrons.

Inorganic reactions occur by the electrostatic forces of attraction between oppositely charged species (cations and anions) which overcome the repulsive forces. Organic reactions, however, do not mostly involve such cations and anions (i.e. with formal charges). A more common sight is the attraction between a charged reagent (cation or anion) and a neutral organic compound possessing a dipole. Furthermore, the reagent may not even be charged but may have a dipole.

When these molecules with complementary dipoles (or dipole and charges) collide and have required energy (activation energy) to overcome the electronic repulsion, chemical reaction can occur.
Apart from this, organic reactions also take place between completely uncharged molecules with no dipole moments. The details of the energetics of the reaction will be taken up shortly.

Whatever the interaction between organic molecules, reactions involve electrons moving from one place to another. The details of this process is called mechanism of the reaction. **Mechanism of a reaction may broadly be defined as the events that take place at molecular level as reactants become products.** Certain terms used frequently need to be introduced and explained before we go into the details of mechanisms of reactions.

NUCLEOPHILES AND ELECTROPHILES

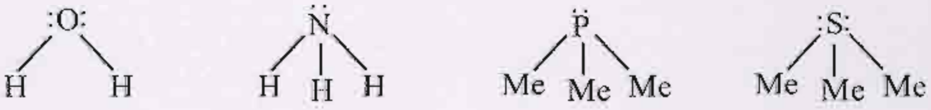
We have just now said that electron flow is responsible for reactivity. This means, electrons flow from one molecule to another as the reaction proceeds. The electron donor is called a nucleophile (nucleus loving) while the electron acceptor is called the electrophile (electron loving). Nucleophile likes nuclei because latter are positively charged and electrophile likes electrons because latter are negatively charged. Let us see which species acts as nucleophiles and which species act as electrophiles.

Nucleophiles

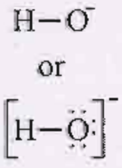
Nucleophiles are electron rich species which are capable of forming a bond by donating electrons to electron deficient species (or electrophile). That is why they are said to be nucleus bonding.

Nucleophiles are either negatively charged or neutral species with non bonding pair of electrons. This pair of electrons is in their high energy filled orbital that they can donate to an electrophile. Neutral nucleophiles usually have the non bonding electron pair on a hetero atom such as O, N, S, P.

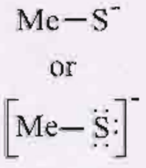
e.g.



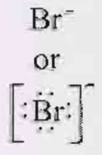
These four neutral molecules ammonia, water, trimethylphosphide, dimethylsulphide all have one pair of electrons in sp^3 orbitals and this is the donor or the nucleophilic orbital. Nucleophilic anions have their negative charge on hetero atoms such as O, S or halogen.



hydroxide



methanethiolate



bromide

Lewis bases are also defined as species that are electron donors. This means that this definition of lewis base is also the definition of nucleophile. In fact, nucleophiles are lewis bases - they are electron-pair donors.

A number of common nucleophiles are listed below:

$$H^-, BH_4^-, HSO_3^-, HO^-, RO^-, RS^-, \bar{C}N, RCOO^-, RC\equiv C^-$$

$$\bar{C}H(COOEt)_2, \ddot{O}, \ddot{N}, \ddot{S}, R^-\overset{+}{M}gBr, R^-Li^+$$

Carbanions, or carbon anions, are usually strong bases and strong nucleophiles.

Carbon nucleophiles with lone pair of electrons, are few in number; the most famous being the cyanide ion. Though cyanide ion has one lone pair of electrons on nitrogen and one on carbon, the nucleophilic tom is usually anionic carbon rather than neutral nitrogen as the sp orbital on carbon has a higher energy than that on the more electronegative nitrogen.

$$^{-}C\equiv N$$

or

$$\left[:C\equiv\dot{N}\right]^{-}$$

Apart from the nucleophilic centres, π bonds between two carbon atoms can act as nucleophilic portion of the molecule. Also, σ bonds in certain reactions can act as nucleophilic bonds.

Such nucleophiles having more than one - generally two - suitable atoms through which they can attack the electron deficient species are called **ambident nucleophiles**.

$$^{-}\underset{..}{C}\equiv\dot{N} \longleftrightarrow \underset{..}{C}\equiv\underset{..}{\dot{N}}^{-}$$

$$^{-}ON{=}O \longleftrightarrow {}^{-}NO_2$$

Electrophiles

Electrophiles are electron deficient species and can form a bond by accepting a pair of electrons from an electron rich species (or nucleophiles). These species attack the substrate at a position of high electron density, hence the name. Electrophiles can be either neutral or positively charged species. Such species have an empty atomic orbital or a low energy antibonding orbital.

The simplest electrophile is proton, H^+, a species without any electrons at all and a vacant 1s orbital. It is so reactive that it is hardly ever found as such since almost any nucleophile will react with it.

Lewis acids also are species that are electron deficient and hence accept electrons. This is also the definition of electrophiles. Thus, electrophiles are lewis acids - electron pair acceptors.

Proton is normally said to be acidic rather than electrophilic. In fact, acid is just a special kind of electrophile. Some common electrophiles are:

$$H^+,\ H_3O^+,\ \overset{+}{N}O_2,\ {}^{+}NO,\ PhN_2^+,\ R_3C^+,\ SO_3,\ CO_2,\ BF_3,$$

$$AlCl_3,\ Br_2,\ ICl,\ O_3.$$

Carbenes and carbon radicals are also electrophiles. Carbonyl functional group is one of the most important electrophiles - a partial positive charge on carbon and a low energy antibonding π orbital ready to accept electrons.

Some σ bond are electrophilic even though they have no dipole at all. e.g. Br_2 molecule with a weak Br - Br bond is strongly electrophilic.

Since nucleophiles and electrophiles are also Lewis bases and Lewis acids respectively, organic chemistry is explainable is terms of acid - base reactions. The main difference is that the terms nucleophile and electrophile are used when bonds to carbon are involved.

RELATIVE STRENGTHS OF NUCLEOPHILES AND ELECTROPHILES

Nucleophiles

The relative nucleophilic strength (or nucleophilicity) of an anion, or a nucleophilic site within a neutral molecule, depends on the availability of the two electrons. The more electronegative the atom, the less nucleophilic the atom will be, because the electrons are held tighter to the nucleus.

A nucleophile with a negative charge is always a more powerful nucleophile than its conjugate acid (which is neutral).

e.g.

Nucleophilic strength $HO^{\ominus} > H_2\ddot{O}$

The nucleophilic strength of anions, within the same row of the periodic table, follows the same order as basicity: the more electronegative the atom bearing the negative charge, the weaker the nucleophile and the weaker the base.

Nucleophilic strength (or basicity) $R_3C^{\ominus} > R_3N^{\ominus} > RO^{\ominus} > F^{\ominus}$

Electronegativity $C < N < O < F$

Nucleophilic strength (or basicity) $R{-}\ddot{N}H_2 > R{-}\ddot{O}H > R{-}\ddot{F}$

The pK_a values can, therefore, be used to estimate the nucleophilicity of atoms within the same row. It is not exact because the nucleophilicity is strongly affected by steric factors which is not so for, the basicity. The nucleophilic strength of anions and neutral atoms increases on going down a group of the periodic table. The electrons are held less tightly to the nucleus as the atom size increases, and hence they are more available for forming bonds. Larger atoms, with more loosely held electrons than smaller atoms, are said to have a higher **polarisability**.

Nucleophilic strength $H_2\ddot{S} > H_2\ddot{O}$

$I^- > Br^- > Cl^- > F^-$

The nucleophilic strength of anions depends on the solvents.

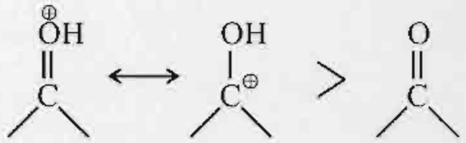
* Anions are generally more nucleophilic in aprotic solvents (these contain polar groups but no O - H or N - H bonds), such as dimethyl sulfoxide (Me_2SO), than in protic solvents.

* In protic solvents (these contain polar groups and O - H or N - H bonds), such as methanol (MeOH), the solvent can form hydrogen bonds to the anion. This lowers the nucleophilicity because a solvent shell surrounds the anion, and this hinders attack on the electrophile. Large anions are less solvated and hence are stronger nucleophiles than small anions in protic solvents. For example, the smaller F^- ion is more heavily solvated than I^- and hence is a weaker nucleophile.

Electrophiles

An electrophile with a positive charge is always a more powerful electrophile than its conjugate base (which is neutral).

Electrophilic strength

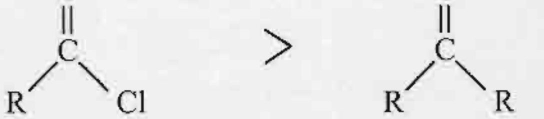


The relative electrophile strength (or electrophilicity) of a cation depends on the stability of the positive charge. Inductive (+I), mesomeric (+ M) and / or steric effects can all lower the reactivity of the cation. The relative electrophilic strength of an electrophilic site within a neutral molecule depends on the size of the partial positive charge (δ +). Hydrogen or carbon atoms are electrophilic when attached to electronegative atoms (- I groups). The more electronegative the atom(s), the more electrophilic the hydrogen or carbon atom.

Electrophilic strength $\quad \text{H—OH} > \text{H—NH}_2$

The hydrogen atom in water is more electrophilic as oxygen is more electronegative than nitrogen

Electrophilic strength



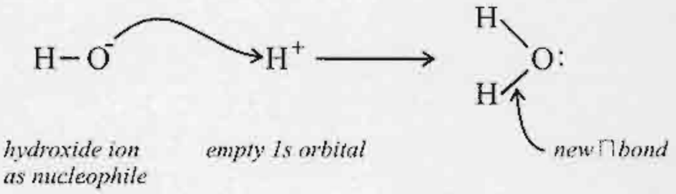
The (carbonyl) carbon atom of the acid chloride is more electrophilic because both oxygen and chlorine atoms are electronegative

USE OF CURLY ARROWS IN REACTION MECHANISM

Organic reaction mechanisms are represented by the means of curly or curved arrows. A curved arrow represents an actual movement of electron (i.e. the direction of electron flow) from filled orbital to empty orbital. The curved arrow does not show the movement of atoms. The atoms follow the flow of electrons. This enables the chemist to understand the mechanisms of reactions.

This method of notation of electron movement is useful only when exact position of the curly arrow is drawn accurately. The arrow always starts with its tail on the source of the moving electrons, representing the filled orbital involved in the reaction. The head of the arrow indicates the find destination of the pair of electrons. Let us understand the movement of electrons in various reactions using curly arrows.

1. In the simplest cases, movement of electrons results in the formation of a bond between two atoms - one belonging to electron donor species and other to electron acceptor species. e.g. transfer of lone pair of electrons from filled atomic orbital (of nucleophile) to empty atomic orbital (of electrophile).



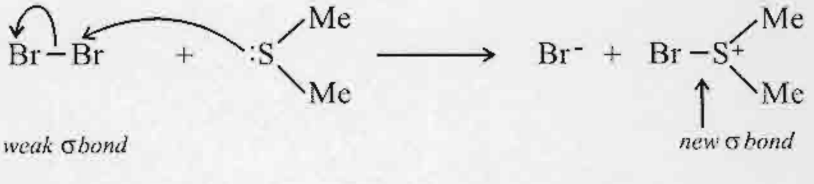
Nucleophile can be negatively charged or neutral. Electrophile can be positively charged or neutral.

A negatively charged or a neutral nucleophile on reaction with neutral electrophile make the latter negatively charged, whereas a negatively charged or neutral nucleophile on reaction with positively charged electrophile makes the latter neutral.

In these reactions, a negatively charged nucleophile itself becomes neutral and a neutral nucleophile itself becomes positively charged.

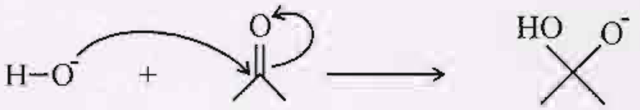
2. If a nucleophile attacks a species with a weak σ bond between its atoms, we need two curly arrows - one to make a new bond and other to break the old bond.

e.g.



The bond making arrow is the same as before but the bond - breaking arrow is new. The latter shows the transfer of two bonding electrons to one atom (bromine) which results in the formation of an anion. The transfer of shared electron pair is shown by keeping the tail of the curly arrow in the centre of the σ bond and the head pointing on the atom at the end of the bond.

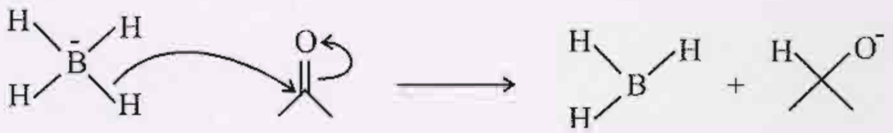
3. Movement of electrons from an electron rich centre to a π bond is also possible.



Carbonyl π bond has an electrophilic carbon which gets the electrons from nucleophilic hydroxide ion. The curved arrow shows electron movement from lone pair to the eletrophilic centre of π bond (carbon in this case). A second arrow is drawn in the middle of π bond ending at the atom that gets the π bond electron pair (more electronegative atom, oxygen, in this case) and gets converted into an anion. In this transfer of electron, σ bond is not touched at all.

4. A curved arrow can begin with a covalent bond (instead of unshared electron) made of bonding electron pair. The covalent bond itself can be of two types: σ bond and π bond. When the movement of electrons is from a π bond to an electrophile, it effectively means that π bond is being cleaved - in such a situation σ bond should be left in place and π bond is broken. The first curved arrow is started in the middle of π bond and ended by pointing the arrowhead into the gap between the two atoms that will form the new σ bond. The second arrow takes the electron pair out of the old σ bond and puts it on one atom to make it an anion.

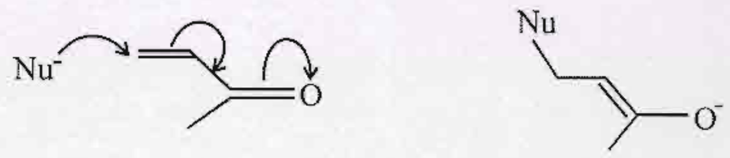
When the movement of electrons is from σ bond, the electrons also have to go to one end of the σ bond, as they form a new bond to the electrophile.



The arrow on the nucleophile should again start in the middle of the σ bond that breaks and should show which atom is transferred to the electrophile. The arrow head should point to the electron deficient centre that recieves the electron pair of the σ bond. The second arrow is the one that has been explained before.

5. There is no limit to the number of arrows that might be involved to represent the mechanism. Movement of electrons within the molecule is also shown by curved arrows.

e.g.

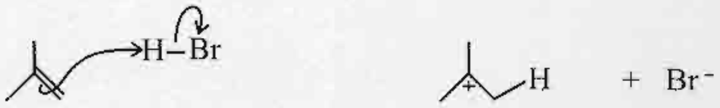


Nu-nucleophile

Last arrow is breaking the π bond to convert oxygen into its anion. Middle arrow shows the transfer of π electrons. First arrow is the one showing a new σ bond formation between atoms of 2 molecules.

Thus, from the curly arrow one can know what is happening in the reaction. The curvature of curly arrow is of no consequence. Also, it does not matter if we draw the arrow above or below the bonds or on same side of the bonds.

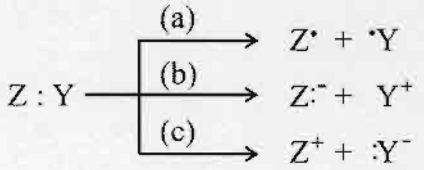
Some chemists prefer to draw atom - specific curly arrow i.e. the arrow, which represents movement of electrons, is drawn in a way that it passes through the atoms that react.



The curly arrow is indicating the carbon atom of the double bond that is involved in the new σ bond formation with the hydrogen atoms.

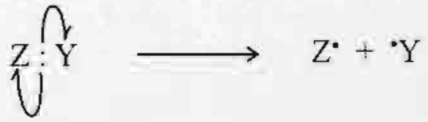
HOMOLYSIS AND HETEROLYSIS OF COVALENT BONDS

Reactions of organic compounds almost inevitably involve the making and breaking of covalent bonds. Consider a hypothetical molecule Z : Y. Its covalent bond may break in three possible ways :



In (a) the covalent bond has cleaved in such a way that each of the bonding atoms, Z and Y, retains the electron it has shared for making the bond. The two species are neutral with one electron short to attain its octet. Such fragments are represented as Z˙ and Y˙, indicating the odd electron (unpaired electron) on the atom, and are called free radicals. This type of bond breaking, resulting in two species - of the same charge (neutral) is called **homolytic bond fission or homolysis.** (Greek : homo or same, lysis - loosening or cleavage).

The homolytic bond cleavage can be represented by two single - headed curly arrows, called **fish hook arrows**, to indicate that only one electron is moving.



In (b) and (c), the covalent bond has cleaved in such a way that both the electrons, involved in bond formation, have moved to one of the fragments.

This, therefore, results in the formation of charged species - one species bearing the electron pair of the covalent bond will be negatively charged and the one which has even lost its own electron to the other species will be positively charged.

$$Z:Y \longrightarrow Z:^{-} + Y^{+}$$

Z takes both the electrons of covalent bond

$$Z:Y \longrightarrow Z^{+} + :Y^{-}$$

Y takes both the electrons of covalent bond

Such a bond cleavage resulting in charged fragments or ions is called **heterolytic bond fission or heterolysis** (Greek : hetero - different; lysis - loosening or cleavage).

TYPES OF ORGANIC REACTIONS

Although the number and type of organic reactions is enormous, they can be fitted into the following **categories**.

Substitution Reaction

When two reactants exchange parts to give two new products.

$$A-B + C-D \longrightarrow A-C + B-D$$

Thus A - B and C - D bonds are broken and new bonds, A - C and the B - D, are formed. If the substitution reaction occurs via homolytic bond cleavage, the reaction is called **free radical substitution reaction**.

$$A-B + D^{\bullet} \longrightarrow A-D + B^{\bullet}$$

If the bonds are broken heterolytically, the substitution reactions are classified as **nucleophilic substitution and electrophilic substitution**. In the former, the nucleophile displaces a part or group of the reactant (called substrate) and in latter, electrophile displaces a part or group of the reactant.

nucleophilic substitution

electrophilic substitution

Addition Reaction

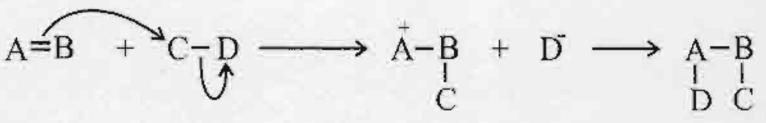
When two reactants add together to give a new product with all atoms in the product. Since a single product is obtained, one of the reactant to which the other reactant adds, must have structural features

$$A + B \longrightarrow C$$

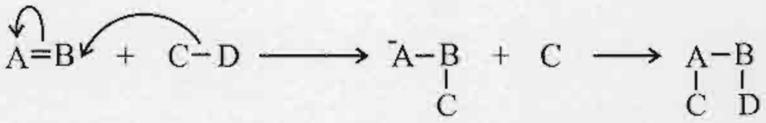
that are able to accommodate the other reactant. In other words, addition takes place on double or triple bonds.

Like substitution reaction, addition reactions are also of three types

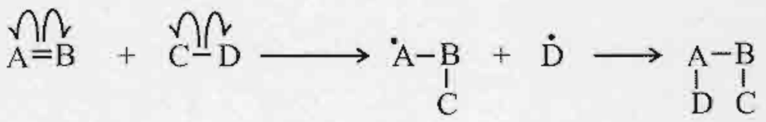
Electrophilic addition (heterolytic)



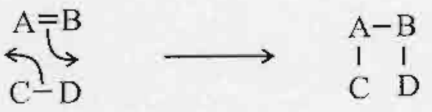
Nucleophilic addition (heterolytic)



Free radical addition (homolytic)

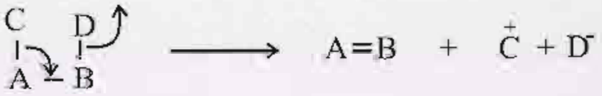


Simultaneous (concerted)



Elimination Reaction

When a single reactant splits into two reactants by the removal of simple molecules. This is just the opposite of addition reactions.



Rearrangement Reaction

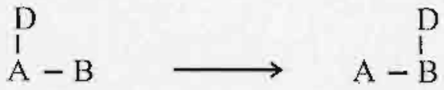
When a single reactant undergoes a rearrangements of bonds and atoms to give an isomeric product. The group or atom that leaves an atom and bonds to another atom of the same molecule is called migrating group.

$$A \longrightarrow B$$

(isomer of A)

There are three types of rearrangements, depending on how many electrons the migrating group or atom carries with it.

Migration with electron pair



$$\overset{D}{\overset{|}{A}} - B \longrightarrow A - \overset{D}{\overset{|}{B}}$$

Migration with one electron

$$\overset{D}{\overset{|}{A}} - B^{\bullet} \longrightarrow \dot{A} - \overset{D}{\overset{|}{B}}$$

Migration without electron

$$\overset{D}{\overset{|}{A}} - B^{-} \longrightarrow {}^{-}A - \overset{D}{\overset{|}{B}}$$

Migration shown here are to adjacent atoms. Migrations to other atoms of the molecules are also possible.

Oxidation and Reduction

Many oxidation and reduction reactions fall naturally into one of the four types of reaction given above, but many others do not.

Pericyclic Reaction

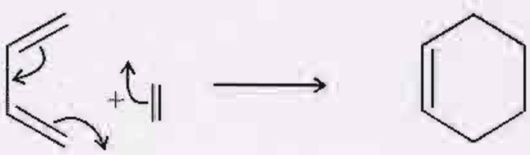
A pericyclic reaction is one involving a concerted bond reorganization in which the essential bonding changes occur within a cyclic array of the participating atomic centres. Such reactions do not involve ions or radicals as intermediates, are not affected by solvent polarity or catalyst.

Pericyclic reactions are further subdivided into three types:

(a) Cycloaddition (b) Electrocyclic reaction

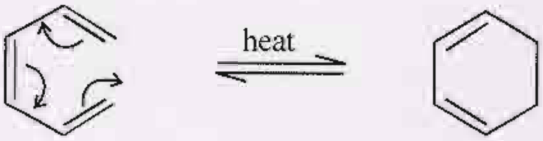
(c) Sigmatropic reaction

(a) Cycloadditon



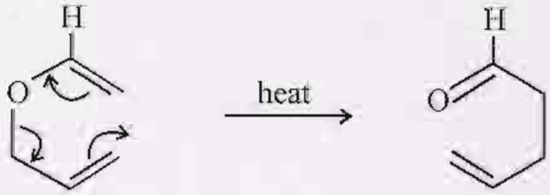
(b) Electrocyclic Reaction

These are intramolecular pericyclic reactions which involve the formation of a ring by the generation of a new σ-bond and consumption of one π-bond or the converse of it.



(c) Sigmatropic Reaction

In these, an atom or group migrates within a π-electron system without change in the number of σ or π-bonds.



ENERGETICS OF REACTION

If a chemical reaction takes place, there is always a reason why? In addition, we are concerned with how far or to what extent the reaction takes place and how fast the reaction takes place. All this is explained by looking into the **thermodynamics and kinetics of a reaction.**

THERMODYNAMICS OF REACTION

A chemical reaction will take place if it leads to a decrease in free energy. Free energy changes are the thermodynamic driving forces behind all chemical reactions. In fact, a decrease in energy is the driving forces behind all physical processes as well. For example, a ball when thrown up comes down, water rushes down a hill, fruits fall down a tree - all these do so because they move to a position of lower gravitational energy in this way.

Free energy (G) is made up of two components, enthalpy (H) and entropy (S) and are related as shown:

$$G = H - TS$$

T is the absolute temperature.

It is of more interest to chemists to know the change in free energy occuring in a reaction (ΔG) rather than to know G, the absolute free energy of a substance. ΔG is related to change in enthalpy (ΔH) and change in entropy (ΔS) in an analogous way.

i.e.

$$\Delta G = \Delta H - T\Delta S$$

For a reaction taking place in standard conditions - all species at 1M concentration, temperature at 25°C and pressure at 1atm - free energy change is called standard free energy change (ΔG°).

Again, $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$

Every chemical reaction, in principle, can go in either forward or backward direction or in other words every chemical reaction is reversible. A reaction in a particular direction is favourable if ΔG° of that direction is negative i.e. the system will have lost energy. This is what happens in a spontaneous thermodynamic process. **ΔG° will be negative if ΔH° is negative and ΔS° is positive.** Such a reaction that proceeds with a negative free - energy change is said to be **exergonic**. Because the free energy change is negative, we can say that in energy terms the reaction goes downhill. **The products of the reaction are at lower level of free energy than the reactants**. Conversely, **a positive ΔH° and a negative ΔS° will result in a positive ΔG° and an unfavourable reaction**. Such a reaction that proceeds with a positive free energy change is said to be **endergonic**. **The products of the reaction are at higher level of free energy than the reactants.** If ΔH° and ΔS° are of same sign, the reaction may or may not be favourable depending on the relative sizes of the terms and the temperature.

The enthalpy change of a reaction, **ΔH°, is** also known as the **heat of reaction**. A reaction with negative ΔH° gives out heat and is said to be **exothermic**. Reactions with positive ΔH° absorb heat from their surroundings; these are **endothermic**. ΔH° is mostly determined by the bond strengths of the reactants and products. ΔH° can be calculated by totalling the bond energies of all the bonds broken, subtracting from this the total of bond energies of all the bonds formed. The formation of strong bonds in the product at the expense of weaker bonds in the reactants will lead to a negative ΔH° or an exothermic reaction; this is a common driving force for reactions. Other factors can also influence ΔH°, such as ring strain, resonance energy, solvation energy.

Entropy is a measure of the **degree of disorder** in a system. The less order in a system the more positive its ΔS° which is favourable for a spontaneous reaction (negative ΔG°).

1) A common way in which entropy might increase is if the total number of molecules increases such as cleavage of a reactant molecule to give more than one product molecule.

2) Reaction which liberate gases show increase is entropy due to much more freedom and randomnes. In general, solids have lowest entropy followed by liquids and gases.

3) An acyclic molecule has more entropy than cyclic molecule because there are more conformations for the former.

Equilibrium Constants

As stated before, all chemical reactions can go in forward and reverse direction. The extent to which the reaction is reversible can be quantified with the equilibrium constant, K_{eq}. For a reaction,

$$aA + bB \rightleftharpoons cC + dD$$

the equilibuim constant is defined by the formula :

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{[\text{products}]}{[\text{reactants}]}$$

Where [A], [B], are concentration of the reactants and [C], [D] are concentration of products after the reaction has attained equilibrium. Thus, equilibrium constant is equal to the product concentrations multiplied together divided by the reactant concentrations multiplied together, with each concentration raised to the power of its stoichometric co-efficient in the balanced equation.

The value of K_{eq} tells which direction of the reaction is energetically favoured. If K_{eq} is greater than 1, it means the product concentration terms is larger than the reactant concentration term or the **forward reaction is favoured.** In other words, products are more stable than reactants. **If K_{eq} is less than 1, then the reverse reaction is favoured.**

There is a simple relationship between the standard free energy change for a reaction, ΔG° and its equilibrium constant K_{eq}.

$$\Delta G^\circ = -RT \ln K_{eq} \qquad R = \text{gas constant}$$

If $\Delta G^\circ = O$, it implies $K = 1$ or reactants and products are present in equal concentrations.

If ΔG° = positive, it implies $K < 1$ or concentration of reactants is more than products.

If ΔG° = negative, it implies $K > 1$ or concentration of products is more than reactants.

The last condition is what we think of as a favourable reaction. An equilibrium constant of greater than 10^3 means that the amount of reactant left over is barely detectable.

KINETICS OF REACTION

Although a negative ΔG° is a necessary condition for a reaction to take place it is not sufficient. This is because ΔG° of a reaction tells us only the different between the stability of the reactants and the stability of the products. If we are to observe a reaction, it must be fast i.e. at a measurable rate. The rate of a reaction is the number of reactant molecules converted into products in a given time. Many reactions with negative ΔG° are also fast. But many others which are favourable thermodynanically (i.e. possessing negative ΔG°) take place so slowly that we consider them to not happen at all. For example, conversion of diamond to graphite is

thermodynamically favourable, but the rate is so slow that it is not considered to occur at all.
If a reaction is fast it is said to be kinetically favourable.
Thus, **rate of a reaction is a kinetic factor of the reaction that tells us how fast or slow the reaction is whereas equilibruim constant and free energy change is a thermodynamic factor of reaction which gives the direction in which the reaction proceeds.**

REACTION PROFILES

It is useful to plot the absolute free energy of a reaction against the course of a reaction. This gives a graph called a **reaction profile** (fig. B). The energy of the components of the reaction (reactants and products) is plotted on the vertical axis, and the reaction coordinate is plotted along the horizontal axis. The reaction coordinate is a measure of the progress of the reaction, which is related to the time course of the reaction. It represents the changes in bond orders and bond distances that must take place when the reactants are coverted to products.

We plot the free energy of the reactants on the left area of the graph, and that of the products on the right side. The difference between these two free energies is ΔG°. What is the shape of the line joining the reactants and products? The first thought that comes to mind is a straight line, but actually this does not happen. The general shape of this line joining energy level of reactants and products is that of a hill called **energy hill**. In other words, the line rises to a maximum somewhere between the two ends. The precise shape of the hill varies according to the nature of the reaction. **The kinetics of a reaction are dependent on this maximum of the energy hill which is the energy barrier that exists between the reactants and the products. The higher this energy maximum, the slower the reaction. The difference in energy between the reactant and the energy maximum is called the free energy of activation $\Delta G^{\#}$.** The difference in free energy between the reactant and products is the free - energy change for the reaction, ΔG°. Thus, **ΔG° relates to the equilibrium constant of the reaction, whereas $\Delta G^{\#}$ relates to the rate of the reaction. Conversion of reactants to products, despite a negative ΔG°, is a barrier to be overcome.**

Where do reactant molecules get the energy to cross the energy barrier and form products? In general, molecules obtain the energy, required to react, from their thermal motion leading to collision. At a given termperature, a collection of molecules may be characterized by an average energy. The rate of reaction is directly related to (i) the number of collisions between reacting molecules, (ii) the fraction of collision that have enough energy to cross the energy barrier in a given amount of time, (iii) fraction of collisions that occur with the proper orientation.

rate of a reaction = (number of collisions per unit time) X *(fraction with sufficient energy)* X *(fraction with proper orientation)*

If free energy of activation, $\Delta G^{\#}$, is small, it will not be difficult for the reactant molecules to overcome this energy barrier since most molecules will possess enough energy to cross the barrier and the reaction will proceed quickly. If, on the other hand, the activation energy is large, it will be more difficult for majority of reactants to find this amount of energy, and the reaction will be correspondingly slower. Fig. C illustrates some possibilities of reaction profiles.

For a given reaction under a given set of conditions, we cannot control the size of the energy barrier; it is a natural property of the reaction. Some reactions are intrinsically slow and some are intrinsically fast. What we can sometimes control is the fraction of molecules with enough energy to cross the energy barrier.

Effect of Concentration and Temperature on Rate of Reaction

Increasing concentration of reactants will increase the number of collisions per unittime which will in turn increase the rate of the reaction .

Increasing temperature will increase the frequency of collisions and thenumber of collisions with sufficient energy to cross the energy barrier. Hence, increasing temperature will increase the rate of the reaction.

For a reaction with single reactant molecule (A) getting converted into a product molecule (B), the rate of the reaction is proportional to the concentration of A. Change in concentration of A will proportionately chage the rate of reaction, i.e. if concentration of A is doubled , the rate of reaction will also get doubled and so on.Such a reaction whose rate is proportional to concentration of only one reactantis called **first-order reaction.**

$$A \longrightarrow B$$

$$\text{rate} \;\alpha\; [A]$$

$$\text{rate} = k\,[A]$$

Here k is called rate constant of the reaction. For a first order reactionk is the first order rate constant. Similarly, when rate of reaction is proportional to concentration of two reactantsor two molecules of same reactan, the reaction is said to be **second- order reaction.**

Rate constant tells us how easy it is to cross the energy barrier. Low energy barrier implies large rate constants and vice versa. Rate of reaction tells us the measure of product formed per unit time. Rate of reaction is the product of rate constant and concentration(s) of reactant(s).Thus, while rate of reaction is dependent on concentration, rate constant is independent of concentration.

Rate constant, however, does depend on temperatur.Arrhenius equation gives the relationship of rate constant with temperature and experimental energy of activaton, E_a

$$k = A\,e^{-Ea/RT}$$

Here, T is the absolute temerature, R is the gas constant and A is the frequency factorwhich is determined experimentally for each reaction.; it accounts for the fraction of collisions that occur with the proper orientation. The factor $e^{-Ea/RT}$ corresponds to the fraction of collisions that have the minimum energy (E_a)

The physical significance of dependence of rate of reaction on temperature is that at any temperature, the reaction mixture has a wide distribution of energies , as shown for two tmeperatures, T_1 and T_2.From the shapes of the curves, we can understand that a slight increase in temperature brings a large increase in number of molecules with large energies.in fig. D, the minimum free energy of activation is also marked. The number of collisions having sufficient energy to allow reaction to take place at a given temperature is proportional to the areas under the portion of the curve thatrepresent free energies greater than or equal to $\Delta G^{\#}$. At lower teperatureT_1, this number is relatively small while it is much higher at higher temperature T_2.Thus, a slight increase in temperature produces a large increase in number of collisions with energy sufficient energy to lead to a reaction and cosequently rate of reaction increases significantly.

There is another important relationship between the rate constant k and $\Delta G^{\#}$.

$$k = k_0 e^{-\Delta G\#/RT}$$

Here, k_0 is the absolute rate constant. Because of this exponential relationship, a reaction with a lower free energy of activation will occur very much faster than a reaction with a higher one.

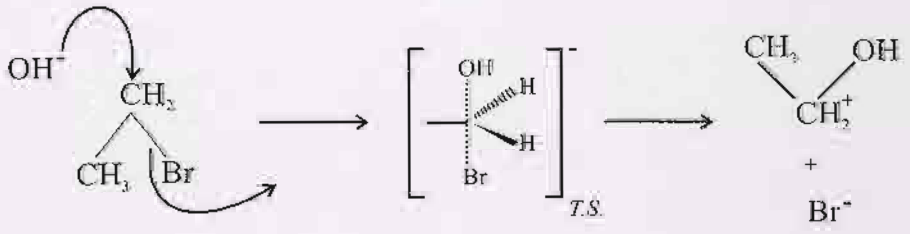
Intermediates and Transition State

While discussing the pathway of a reaction, the structures of entities between the two ends, i.e. the reactants and the products, is often drawn. They fall in two categories: intermediates and transition state.

Transition State

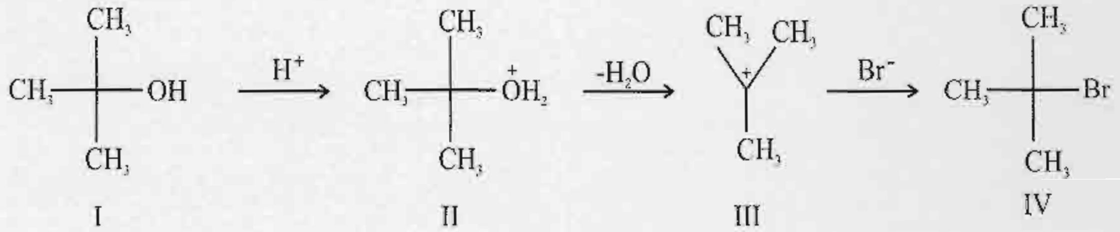
The position of maximum free energy in the energy hill of reaction profile corresponds to the least stable configuration through which the reactants pass during their conversion into products. It is referred to as an activated complex or transition state. Since transtion state (abbreviated as T.S.) has higher energy than reactants or products it represents the energy barrier to their interconversion, irrespective of ΔG of the reaction. Thus the free energy of activation, $\Delta G^{\#}$, is the difference between the free energies of T.S. and reactants. It should be clearly understood that T.S. is a highly unstable state that is passed through transiently, during the course of the reaction. It does not represent any discrete molecular species.

An example of T. S. formation is seen in the substitution of ethyl bromide by hydroxide ion. The reaction profile consists of a hill with the peak maximum corresponding to the T.S. for the reaction (fig. E).



Intermediates

There are many chemical reactions that take place with formation of reactive intermediates. An intermediate is a **genuine chemical entity** which has a **finite existence**, even though this may be very short. When intermediates exist in a reaction, then what we commonly express as one reaction, is actually a sequence of two or more reactions. Such reactions are termed as **multistep reactions**. For example, the substitution reaction of t-butyl alcohol with HBr to give t-butyl bromide. The reaction proceeds through protonation of the hydroxyl oxygen and cleavage of the C - O bond. In this reaction, both the protonated alcohol (II) and the carbocation (III) are intermediates. The formation of (II) and (III) corresponds to the steps of the reaction.



Each step of this multistep reaction has its own characteristic rate and therefore its own transition state. The energy changes in such a reaction can also be depicted in a reaction profile. (fig. F) There are two local energy minima in this profile; these are the **intermediates**. This is the characterizing feature of an intermediate: **intermediates** corresponds to **local energy minima** although they are considerably higher in energy than the reactants or products. Each free energy maximum between reactant and products represents a T.S. - there are three T.S. in this reaction. The overall Δ G of this reaction (or in general, any reaction), regardless of its complexity is the energy difference between initial reactants and final products. Generally, the rate of a multistep reaction depends on the rates of its various steps. However, one step of a multistep reaction is significantly slower than the others. This slowest step of the reaction is called **rate determining** or **rate limiting step** of the reaction. Rate of overall reaction is, in such cases, the same as the rate of the rate - limiting step.

Let us understand this fact.

Consider a multistep reaction such as:

Step 1 $\quad A \xrightarrow{slow}$ *intermediate-1*

Step 2 $\quad$ *intermediate-1* $\xrightarrow{fast}$ *intermediate-2*

Step 3 $\quad$ *intermediate-2* $\xrightarrow{fast}$ *product*

Step 1 is intrincically slow which implies that the rate constant for this step is much smaller than that for step 2 and step 3. If k_1, k_2, k_3, are the rate constant for step 1, step2, step 3 respectively, then

$$k_1 << k_2 \text{ or } k_3$$

Since rate constants of step 2 and step 3 are very high, these steps coule take place very fast if ever the concentration of the two intermediates becomes large. But because step 1 is slow, intermediate-1 concentration can never become large which in turn will restrict the formation of intermediate-2. Thus, because step 1 is slow, step 2 and step 3 will have to occur at the same rate as step 1. Thus, overall reaction will happen at a rate equal to the rate of step 1. In other words, step 1 is the rate limiting step.

In terms of the reaction profile, the **rate limiting step is the step with the T.S. of highest free energy** (fig. G).

An important feature of the rate limiting step is that any factor that effects the rate of this step,affects the rate of overall reaction. Conversely, if the rate of overall reaction has been affected by a change in reaction conditions, it is the effect on the rate - limiting step that is observed.

Effect of Catalyst

The effect of a catalyst is to increase the rate at which a reaction will take place: this is done by making available an alternative path of less energetic demand (fig. H). This is often done through the formation of a new, and more stable intermediate.

Hammonds Postulate

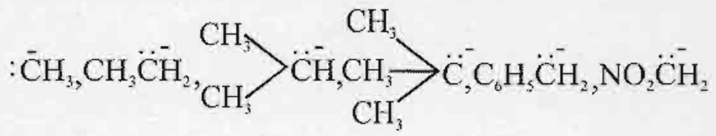
Although we cannot observe transition states directly due to their zero lifetimes, we can draw inferences about them from high energy intermediates. In this regard, we are greatly aided by the **Hammond-Leffler Postulate** - popularly called **Hammond Postulate** which states that for any single reaction step, the structure of the transition state for that step resembles the side (or species) to which it is closer in energy. Let us understand the postulate. Consider a highly exothermic reaction (fig. I). It is clearly visible that the energy levels of T.S. and reactants are closer to each other than that of T.S. and products in such an exothermic reaction. Since T.S. is closer to reactant energetically, we make the assumption that T.S. resembles the reactants structurally as well, more than products. On the same basis for an endothermic reaction, the energy levels and hence the structure of T.S. resembles products more than reactants (fig. J). This postulate is most useful in multistep reactions dealing with intermediates. In the reaction shown in (fig. K) the first step has lower activation energy than second step ($\Delta G^{\#}_{1} < \Delta G^{\#}_{2}$). The T.S. of the first step is closer in energy to the local energy minimum corresponding to its intermediate rather than reactants. Therefore, T.S. resembles intermediate. In the second step, again T.S. of step two is closer in energy to the local energy minimum (the intermediate) more than the product. Therefore, T.S. again resembles the intermediate more than the product. So, both T.S. resemble the intermediates more than the reactant or product. This is generally the case when reaction involves very reactive intermediates. Fig. L shows reaction profile where the first peak is higher than the second peak. However, here also the two T.S. resemble their respective intermediate more than the reactant or the product.

REACTIVE INTERMEDIATES

Several intermediates based on carbon, take part in organic reactions. We shall discuss these first. Apart from the intermediates based on carbon, intermediates of nitrogen will also be discussed.

CARBANIONS

A carbanion is a molecule in which a negative charge resides on a carbon atom.



$$:\bar{C}H_3,\ CH_3\ddot{\bar{C}}H_2,\ (CH_3)_2\ddot{\bar{C}}H,\ CH_3-(CH_3)_2\bar{C},\ C_6H_5\bar{C}H_2,\ NO_2\bar{C}H_2$$

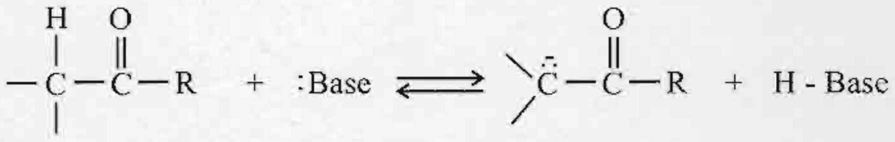
Since carbanion bears a negative charge it must exist with a positively charged counter ion. The two ions may be independent of each other, thereby retaining their respective identities and for this reason the most common counter ion is a metal ion. It may, as well, be associated via various degress of covalent bonding with the positive counter-ion i.e. the bonding may be negligible to considerable. e.g. Grignard reagents have carbanion - like molecule in which the carbon metal bond has significant covalent character whereas potassium salts of highly bulky carbanions are negligibly bonded.

$$R^- \ M^+ \quad \xleftrightarrow{\overset{-}{R}-\overset{+}{M}} \quad R-M$$

dissociated
carbanion-metal pair

covalent
organometallic compound

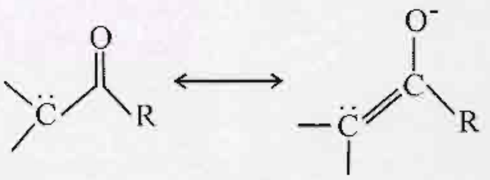
Enolate anions their are the conjugate - base anions of carbonyl compounds formed by removal of one of α -hydrogens.



$$-\overset{H}{\overset{|}{\underset{|}{C}}}-\overset{O}{\overset{\|}{C}}-R \ + \ :Base \ \rightleftharpoons \ \ddot{\bar{C}}-\overset{O}{\overset{\|}{C}}-R \ + \ H-Base$$

enolate anion

The negative charge is spread throughout the delocalized molecular orbital, some of the charge residing on carbon and some on oxygen. However, the distribution of charge, unlike allyl anion, is not symmetrical due to the presence of heteroatom, oxygen in the anion. Oxygen gets a larger share of the negative charge due to its higher electronegativity. In that sense, some people prefer to call enolate anion as oxyanion. Yet, because the negative charge does reside over carbon for some time and there are reactions where carbon is the site of bond formation, therefore, enolate anions can be comfortably studied under the heading of carbanion.



Structure

A carbanion with a localized negatively charged carbon, as in the alkyl carbanions, makes three covalent σ bonds to atoms (Hs or alkyl groups) and has a fourth orbital that occupies the non - bonding electron pair. Although only three σ bonds are formed (and so we expect it to be sp^2C) the carbon atom is sp^3

hybridized, since in this hybridization there is maximum separation of bonds and lone pair. The shape is not a true tetrahedron - the shape is **pyramidal** - because the lone pair bearing orbital is not exactly equivalent to the three C - H bonds, just as ammonia is not a perfect tetrahedron.

If the negative charge can be delocalized, the carbon that bears the negative charge will normally change from sp^3 to sp^2 hybridization. This is essential so that lone pair resides in unhybridized p orbital and enables interaction with the conjugated π system. The negative charge spreads over more atoms in the molecule.

carbanion

The stabilization imparted from the resonance delocalization more than compensates for the destabilisation brought about by a change in hybridization form sp^3 to sterically unfavourable sp^2 state.

e.g. allyl anion

The two terminal carbon atoms are equivalent. Charge distribution is symmetrical. Both canonical forms being equivalent, have identical energy and therefore equal contribution to the resonance hybrid. The delocalization is very effective.

Factors affecting the stability of carbanions

(i) Increasing alkyl substituents at the carbanionic carbon decreases the stability of the carbanion through the increasing +I effect. Thus, tertiary carbanions are less stable than secondary carbanions which are in turn less stable than primary carbanions.

$$R_3-\bar{C} < R_2C\bar{H} < RC\bar{H} < C\bar{H}_3$$

least stable ——— order of increasing stability ———→ most stable

(ii) The hybridization of carbon affects the stability, the most stable carbanion being sp hybridized and the least stable sp^3 hybridized. This order is due to the decreasing electronegativity of carbon as the hybridization state goes from sp to sp^2 to sp^3. Due to highest s character (50%) in sp hybrid state, the electrons are held most tightly by the carbon atom or the electronegativity is maximum, which enables the most effective dispersal and stabilization of negative charge in the carbanion. In fact, it is this highest s character in sp hybrid orbital that the formation of carbanion is easiest in terminal alkynes by the cleavage of C-H bond. As the s character decreases, the electronegativity decreases and hence stabilization of carbanion decreases.

$$CH\equiv C^- > CH_2=C\bar{H} > CH_3C\bar{H}_2$$

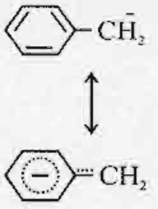
order of stability

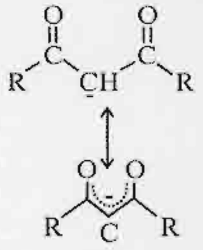
(iii) An electron withdrawing group sufficiently close to the carbanion will help stabilize it. Electron withdrawl can be exerted owing to the -I effect of the group or both -I and -R effect of the group. Thus groups like -F, -Cl, -Br, -N$^+$R$_3$, -P$^+$Ph$_3$ etc. help in dispersal of negative charge through -I effect and groups like -NO$_2$, -C≡N, etc. exert both -I and -R effect to stabilize the carbanion.

$$\bar{C}H_2-C\equiv N \longleftrightarrow CH_2=C=\bar{N}$$

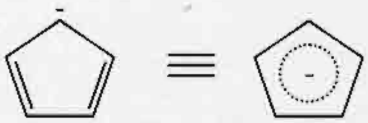
-I, -R effect

(iv) If deprotonation of the molecule (i.e. formation of carbanion) creates a conjugated π system of carbon atoms or carbon and hetero atoms, this will help to stabilize the carbanion as is seen in enolate anions and benzyl anions etc.





A conjugated π system could be created to the extent of formation of aromatic ring which makes the carbanion especially stable.



Formation of carbanions

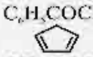
(i) Treatment of alkanes with a strong base. Examples of bases include NaOEt, Na_2CO_3, BuLi, $NaNH_2$ etc. All carbanions may, in fact, be thought of as the conjugate bases of carbon acids. The latter is a very weak acid so that **carbanions are very strong bases.**

$$R_3C-H \quad + \quad B: \quad \rightleftharpoons \quad R_3C^- \quad + \quad BH^+$$

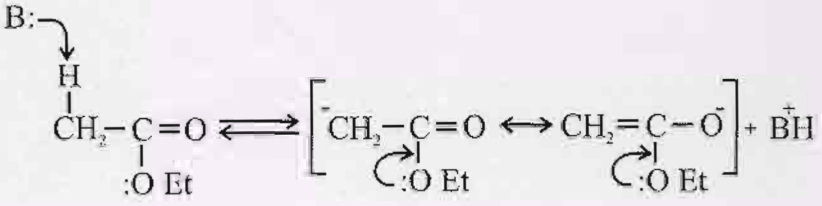
B - base

Depending on the acidity of the proton to be removed for formation of carbanion, the conditions of the reaction are varied.

Alkanes are, in fact, the weakest acids with pK_a 43. Alkenes are slightly stronger than alkanes but the alkynes are the strongest acids among the three. Introduction of electron withdrawing groups increases the acidity of hydrogen atoms on carbon. This makes the pK_a values of haloalkanes such as haloforms, HCF_3 etc. very low (≈28) so that the carbanion, $^-CF_3$, is a very stable base(and hence weak base). Even stronger than these, are the carbon acids that have the structural facility to withdraw and delocalise the negative charge e.g. CH_3CN, CH_3COCH_3, CH_3NO_2 have pK_a values between 25 to 11. Table below gives the pK_a values of some carbon acids and typical bases used to generate carbanions from them.

Compound		*pKa*	*Typical base used for deprotonation*
alkane	CH_4	43	BuLi
alkene	$CH_2=CH_2$	37	BuLi
triphenyl methane	Ph_3CH	33	$NaNH_2$ / Liq NH_3
halogen	CF_3-H	28	$\bar{O}H$
nitrile	$CH_3C\equiv N$	25	NaOEt
ketone	CH_3COCH_3	20	NaOEt
aromatic ketone	$C_6H_5COCH_3$	19	NaOEt
cyclopentadiene		14	$Bu^t\bar{O}\overset{+}{K}$, NaOEt
malonic ester	$CH_2(COOEt)_2$	13.3	NaOEt
ethylacetoacetate	CH_3COCH_2COOEt	10.7	NaOEt
nitro alkane	CH_3NO_2	10.2	Na_2CO_3,NaOEt
diketone	$CH_3COCH_2COCH_3$	8.8	Na_2CO_3,NaOEt

The carboxylate group is less effective in carbanion stabilisation than C = O group in simple aldehydes and ketones. This is clear from the sequence of pK_a values of $CH_2(COOEt)_2$, 13.3, CH_3COCH_2COOEt, 10.7 and $CH_2(COMe)_2$, 8.8. This is due to the electron - donating conjugative ability of the lone pair of electrons on the oxygen atom of the OEt group.



$$B{:} + H{-}CH_2{-}\underset{:OEt}{C}{=}O \rightleftharpoons \left[{}^{-}CH_2{-}\underset{:OEt}{C}{=}O \longleftrightarrow CH_2{=}\underset{:OEt}{C}{-}O^{-} \right] + B\overset{+}{H}$$

(ii) Removal of halogens, without their bonding electron pair, in alkyl and aryl halides on treatment with certain metals produces carbanions in the form of organometallic compounds.

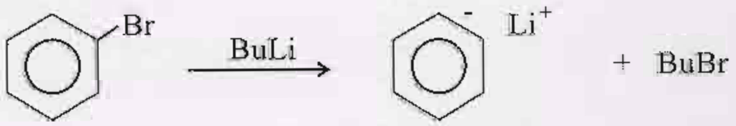
$$R{-}X + Mg \xrightarrow{ether} R^{-}\overset{+}{M}gX$$

Grignard reagent

$$R{-}X + 2Li \xrightarrow{ether} RLi + LiX$$

alkyl lithium

When an organic halide is treated with an organo metallic compound, a halogen - metal exchange occurs to create carbanion.

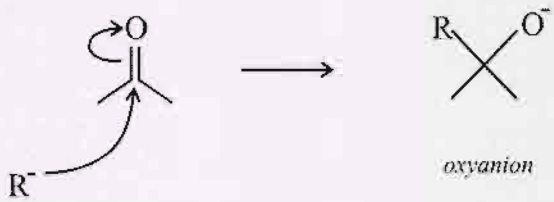


(iii) Addition of a nucleophile to an unsaturated C-C bond generates a carbanion.

Reactivity of Carbanions

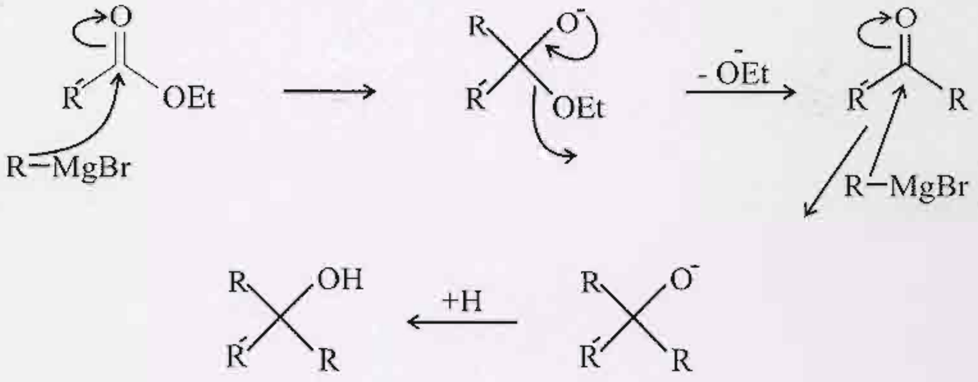
1. All carbanions are bases, and so may react with proton sources to give the corresponding alkanes. This is also the reason for generating carbanions in anhydrous conditions using aprotic solvents (i.e. with no acidic hydrogen). Since alkanes themselves are deprotonated to give carbanions, the protonation of carbanions is hardly any useful method to prepare alkanes. It is commonly used to introduce deuterium isotope into a molecule which may be necessary for biological or mechanistic study.

2. Carbanions are potential nucleophiles. They take part in a range of reactions such as displacements and additions. e.g. One common reaction is the nucleophilic addition on a carbonyl group.

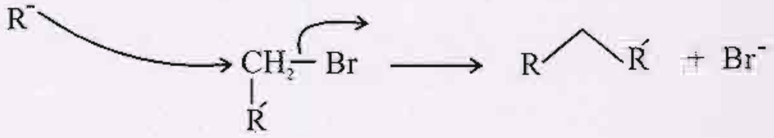


Oxyanion formed may get protonated to give an alcohol or may be involved in some other reaction depending on the nature of R. Such reactions which involve addition of carbanions are Aldol condensation, Perkin reaction, Claisen condensation, Michael addition etc.

The example shown below is a commonly used reaction with Grignard reagent and ester molecule. The intermediate oxyanion breaks down to form a ketone by loss of an alkoxide anion. This can then react further with another molecule of Grignard reagent to produce the tertiary alcohol.



3. Carbanions react with alkyl halides in substitution reactions.



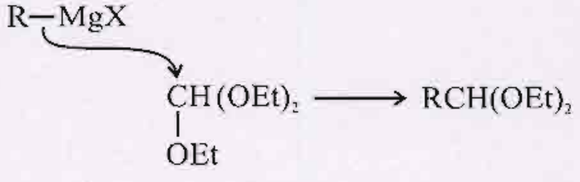
$$R^{-} \quad \underset{R'}{CH_2}-Br \longrightarrow R\diagup\!\diagdown R' + Br^{-}$$

Particularly useful carbanions, for preparation of several compounds, are those derived from β keto esters, malonic ester, 1, 3 - diketones etc.

Grignard reagents are an exception to this reaction i.e. if this reaction were to take place with Grignard reagent, which are themselves prepared from alkyl halide, it would not have been possible to produce them and isolate them.

However, Grignard reagents can act as nucleophile for substitution in other substrates.

e.g.

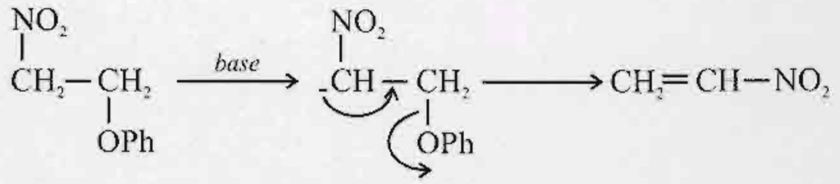


$$R-MgX \quad \underset{OEt}{CH(OEt)_2} \longrightarrow RCH(OEt)_2$$

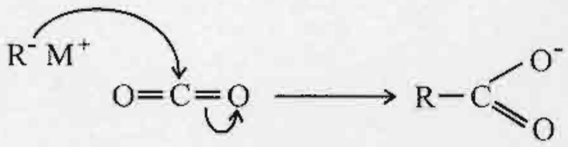
When we use more electropositive metals like sodium metal, alkyl halides react to generate the carbanion which subsequently reacts with alkyl halides to give higher alkanes (Wurtz Reaction).

$$R-CH_2CH_2-Cl \xrightarrow{2Na} RCH_2\overset{-}{C}H_2\overset{+}{Na} \xrightarrow{R'Br} RCH_2CH_2R'$$

4. Carbanions may also undergo elimination reactions. This is known as the E_1cB mechanism (elimination unimolecular conjugate base). This is however, not a common mechanism.

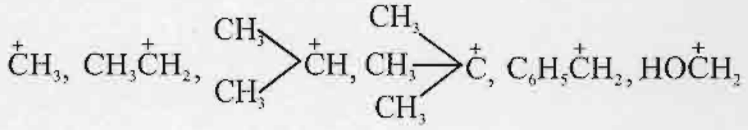


5. Carbanions and negatively charged carbon species from Grignard reagents can add to the weak electrophile CO_2 to form the corresponding carboxylate anion - this reaction is termed as **carbonation**.



CARBOCATIONS

A carbocation is a molecule in which a positive charge resides on a carbon atom.

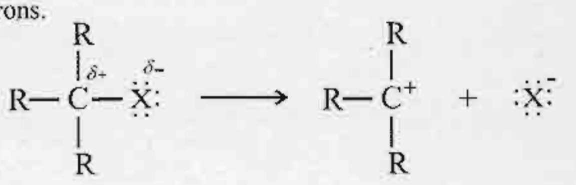


The positive charge indicates the incomplete octet on the carbon atom i.e. its hypovalent nature (or its valency is less than the usual). Carbocations, being positively charged, are associated with counter ions which are negatively charged. Yet, unlike carbanions, carbocations have a definite independent identity so that these are purely ionic species.

Structure

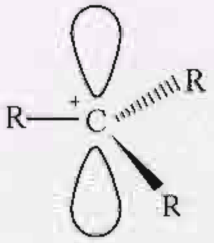
The term **Carbocation** includes two classes of ions: **Carbenuim ions** and **Carbonuim ions**.

Carbenuim ions: If the carbon atom is bonded to a more electronegative element, the latter can separate together with the bonding electrons, and the carbon atom is left as a **three-coordinate carbenuim ion** with six valence electrons.



carbenuim ion

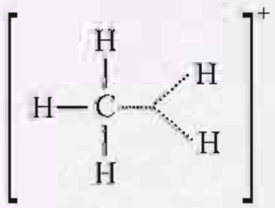
Carbenium ions have only three substituents and are therefore **sp^2 hybridised**. A typical structure is of methyl cation where the three sp^2 orbitals form three σ bonds with 1s orbital of three hydrogens, separated at an angle of 120° from each other in the same plane. The empty unhybridized p orbital is perpendicular to the trigonal planar molecule. This orbital, being vacant, is of higher energy. In all reactions of carbenium ions, this vacant p orbital interacts with filled orbital of another molecule.



Carbenium ions are the more important of carbocations and hence one studies mainly carbenium ions when we talk of carbocations.

Carbonuim ions: Olah has described compounds with five-coordinate carbon, of the type CH_5^+, as carbonuim ions, by analogy to ammonuim ions from ammonia.

Using standard structural formulae, it is not possible to denote the bonding of five hydrogens to the carbon atom, with only eight electrons available. The octet principle can be preserved by formulating three-centre bonds. These are represented by dotted lines drawn from the atoms concerned and meeting at a point. The point where the lines meet does not represent any extra atom.



carbonium ion

Factors affecting the stability of carbocations

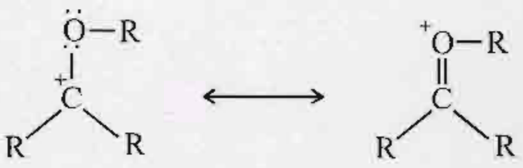
1. Increasing the number of electron releasing alkyl substituents (+I groups) on the carbon carrying positive charge will increase the dispersal of charge and hence stability of carbocation. Thus, tertiary carbocations are more stable than secondary which are in turn more stable than primary carbocations.

$$R_3C^+ > R_2\overset{+}{C}H > R\overset{+}{C}H_2 > \overset{+}{C}H_3$$

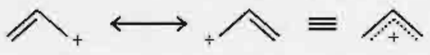
most stable ——— *decreasing order of stability* ———→ *least stable*
of carbocations

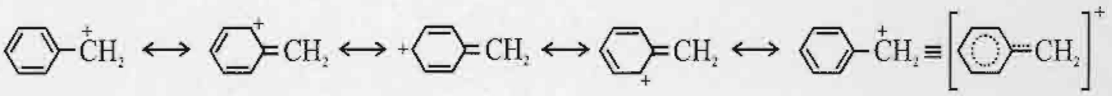
The stability conferred by alkyl substituents is due mainly to two factors - hyperconjugation and inductive effect of alkyl groups.

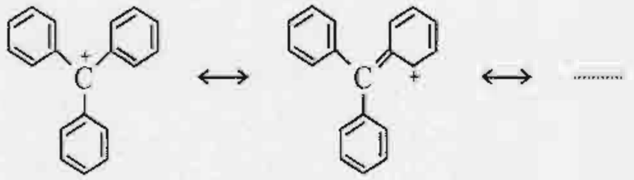
2. Presence of an adjacent heteroatom with lone pair of electrons stabilizes the positive charge by its +R effect.

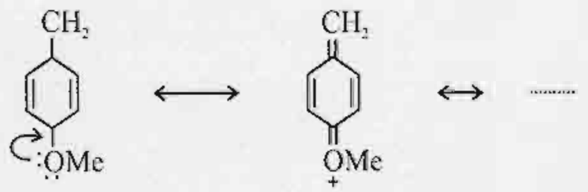


3. Presence of conjugated π system will also stabilize the positive charge by delocalisation over larger number of atoms. Thus, the allyl cation is more stable than primary alkyl cation and the benzyl cation is even more so. The trityl cation (with three phenyl rings) has even more extensive delocalisation and so is much more stable. The stability of such cations is further increased if electron donating substituents are present.

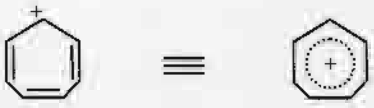




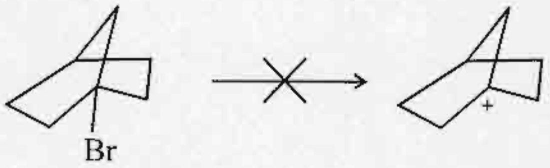




4. As wtih carbanion, formation of an aromatic species helps to stabilize a carbocation e.g. Tropylium cation is aromatic and very stable.



5. An essential requirement for formation of carbocation is that it should be planar, for it is only in this configuration that effective stabilisation can occur. For example, it is not possible to form a carbocation from norbornyl bromide, since the bridgehead carbon cannot be planar.

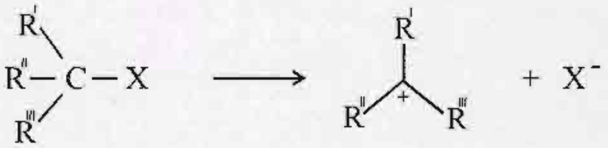


this bond can never be in plane with the other bonds.

Formation of Carbocations

1. **Heterolytic fission of a neutral species**

Cleavage of a bond between carbon and another atom, which leaves with its lone pair.



This reaction is favoured if the resulting carbocation is stable and if the leaving group is a good leaving group. Compounds are more likely to dissociate in this way in a **polar solvent** as this stabilizes the charges formed.

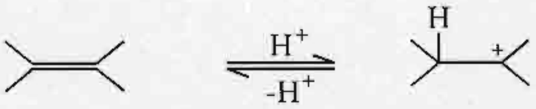
Ionization may also be induced by lewis acids e.g. BF_3, $AlCl_3$.

$$R{-}X + AlCl_3 \longrightarrow R{-}\overset{+}{X}Al\overset{-}{Cl}_3 \longrightarrow \overset{+}{R} + X\overset{-}{A}lCl_3$$

Super acids such as SbF_5 / FSO_3H (work done by Olah) are also used. **With the use of latter, even alkanes can be ionized to give alkyl cation.**

2. **Addition of cations to neutral species**

A positively charged species can add to a carbon - carbon double bond to give a carbocation. Most often, this positively charged species is a proton. When, the electrophile is proton, the reaction (protonation) is reversible.



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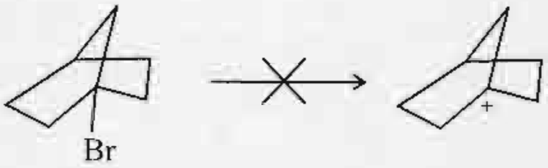

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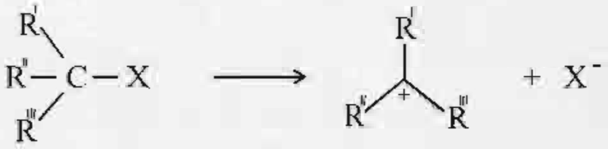
Formation of Carbocations

1. **Heterolytic fission of a neutral species**

Cleavage of a bond between carbon and another atom, which leaves with its lone pair.



This reaction is favoured if the resulting carbocation is stable and if the leaving group is a good leaving group. Compounds are more likely to dissociate in this way in a **polar solvent** as this stabilizes the charges formed.

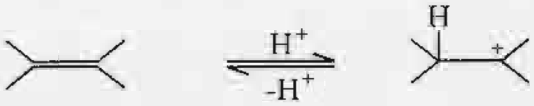
Ionization may also be induced by lewis acids e.g. BF_3, $AlCl_3$.

$$R{-}X + AlCl_3 \longrightarrow R{-}\overset{+}{X}Al\overset{-}{Cl_3} \longrightarrow \overset{+}{R} + X\overset{-}{Al}Cl_3$$

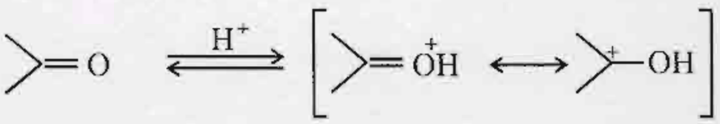
Super acids such as SbF_5 / FSO_3H (work done by Olah) are also used. **With the use of latter, even alkanes can be ionized to give alkyl cation.**

2. **Addition of cations to neutral species**

A positively charged species can add to a carbon - carbon double bond to give a carbocation. Most often, this positively charged species is a proton. When, the electrophile is proton, the reaction (protonation) is reversible.



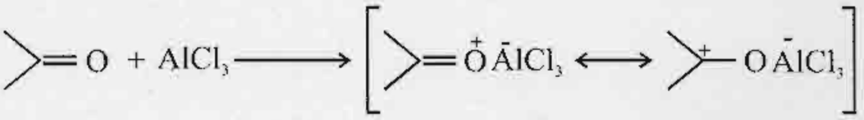
Protonation can also occur on oxygen in a carbon - oxygen double bond, thus providing a more positive carbon atom.



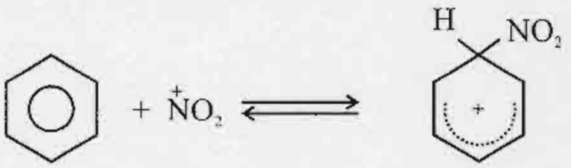
Protonation of a heteroatom to convert it into a better leaving group, also helps in the formation of carbocation.

$$Ph_3C-OH \xrightleftharpoons{H^+} Ph_3C-\overset{+}{O}H_2 \longrightarrow Ph_3C^+ + H_2O$$

Addition of lewis to double bonds, between carbon and heteroatom, gives carbocations.



Similarly other cations can add to double bond to produce cabocations.



The carbocation so formed is a resonance stabilized intermediate.

Carbocation, itself, can add to the carbon - carbon double bond in which case a chain reaction can take place leading to polymersation.

3. **From Other Cations**

Decomposition of other cations e.g. diazonium cations.

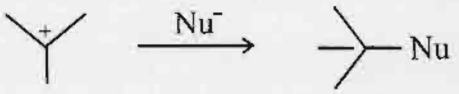
$$\left[R-\overset{+}{N}\equiv\ddot{N} \longleftrightarrow R-\ddot{N}=\overset{+}{\ddot{N}}\right] \longrightarrow R^+ + N_2\uparrow$$

Reactivity of Carbocations

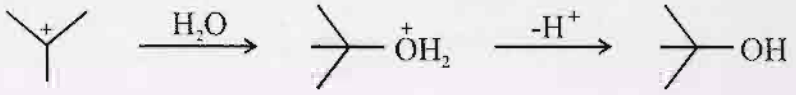
We know that carbocations are just a type of electrophile and hence they show the same properties as shown by typical electrophiles.

1. **Combination with a nucleophile**

If the nucleophile is negatively charged, combination with carbocation gives a neutral species.



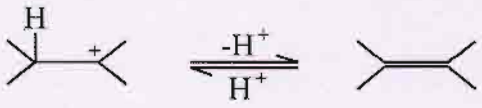
If the nucleophile is neutral, a positively charged product is formed first. For example, with water a protonated alcohol is formed. This readily loses a proton to give neutral alcohol.



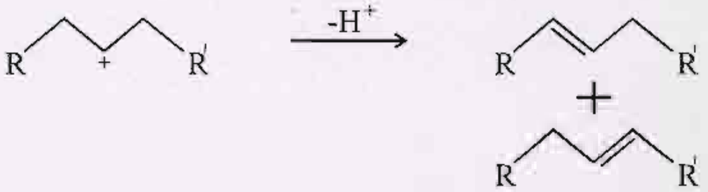
2. Elimination of proton or other electrophilic leaving group.

Elimination of a proton or any other leaving group without the bonding electron pair from the position adjacent to the positively charged carbon, results in an alkene. This is the reverese of their formation from protonation of double bonds.

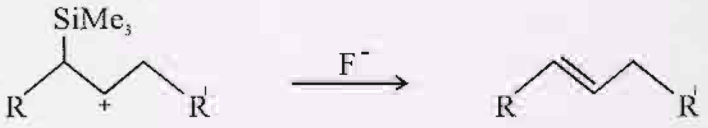
Most often, it is a proton that is eliminated. A base facililates the removal of proton.



If more than one α - proton is there, the position of double bond varies and a mixture of products often results.

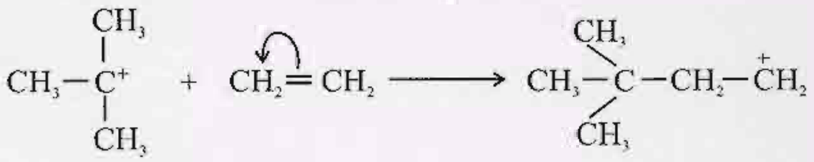


Other groups may also be eliminated from the carbocation e.g. trimethyl silyl group (TMS) is able to leave this way. It is a better leaving group than proton.



3. Addition Reactions

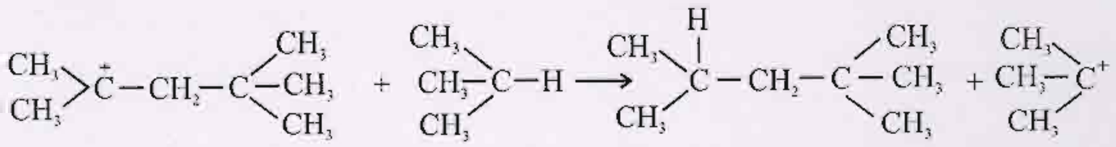
Addition of carbocations at double bond causes the formation of another carbocation. This addition occurs mostly in the absense of other effective nucleophiles.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C^+}} + CH_2=CH_2 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{+}{C}H_2$$

4. Abstraction of a hydride ion

A carbocation can abstract a hydride ion from an alkane which results in the generation of the carbocation of the latter.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\overset{+}{C}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 + CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>\overset{H}{C}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 + CH_3-\overset{CH_3}{\underset{CH_3}{C^+}}$$

Rearrangement of Carbocations

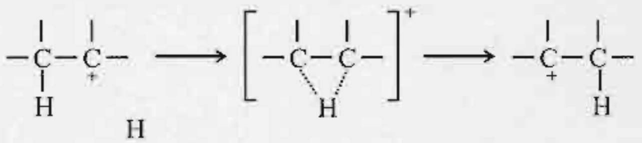
Carbocations commonly react by intra molecular rearrangement. This takes place so that a more stable carbocation is formed, such as a tertiary carbocation instead of a secondary carbocation.

(The order of stability of carbocations is 3° > 2° > 1°)

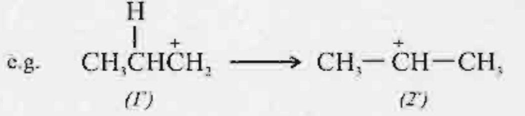
Rearrangements involving carbocation takes place by the migration of a hydrogen atom or alkyl group with a pair of electrons from an adjacent carbon to the carbon bearing the positive charge. The carbon that loses the migrating group now itself becomes positively charged. A migration of hydrogen with electron pair is called **hydride shift** and that of **alkyl group** is called alkyl shift. Another interpretation of these migrations is that rearrangement of carbocations may be divided into those in which an actual change in carbon skeleton takes place and those in which change in carbon skeleton does not take place.

(i) Without change in carbon skeleton.

1,2-hydride shift falls in this category.

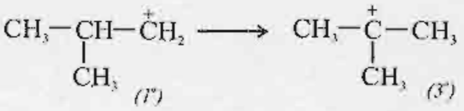


$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{+}{C}}- \longrightarrow \left[-\overset{|}{C}-\overset{|}{C}-\right]^{+} \longrightarrow -\overset{|}{\underset{+}{C}}-\underset{H}{\overset{|}{\underset{|}{C}}}-$$



$$\text{e.g.}\quad CH_3\overset{H}{\overset{|}{C}}H\overset{+}{C}H_2 \longrightarrow CH_3-\overset{+}{C}H-CH_3$$

(1°) *(2°)*

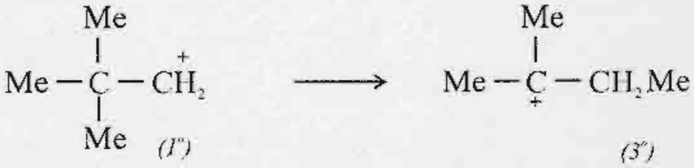


$$CH_3-\underset{CH_3}{\underset{|}{C}}H-\overset{+}{C}H_2 \longrightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{+}{C}}}-CH_3$$

(1°) *(3°)*

(ii) With change in carbon skeleton

1,2-methyl shift falls in this category.



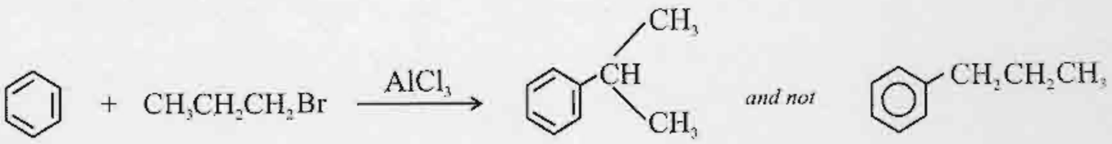
$$Me-\underset{Me}{\underset{|}{\overset{Me}{\overset{|}{C}}}}-\overset{+}{C}H_2 \longrightarrow Me-\underset{+}{\overset{Me}{\overset{|}{C}}}-CH_2Me$$

(1°) *(3°)*

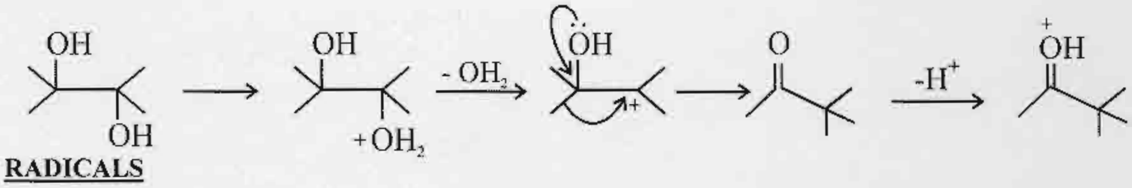
neopentyl cation *tertiary carbocation*

This rearrangement has both merits and demerits. Demerit is that it is not possible to get straight chain substituents using carbocation mechanism.

e.g. Friedel crafts reaction is a very efficient method to produce alkyl benzene however straight chain alkyl groups do not get connected to benzene ring is this form. They instead undergo rearrangement and give branched alkyl benzene.

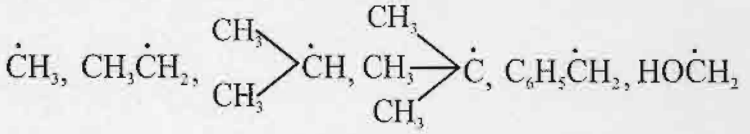


Sometimes rearrangement can lead to useful reactions. One such is the pinacol rearrangement in which 1,2-diol is treated with an acid. A tertiary carbocation is formed which rearranges to even more stable cation.



RADICALS

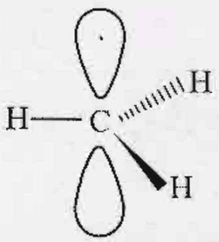
Free radicals, normally referred to simply as radicals, are species containing an unpaired electron (denoted by a dot adjacent to the relevant atom). These are electrically neutral species.



$$\dot{C}H_3,\ CH_3\dot{C}H_2,\ (CH_3)_2\dot{C}H,\ (CH_3)_3\dot{C},\ C_6H_5\dot{C}H_2,\ HO\dot{C}H_2$$

Most carbon free radicals are very reactive and hence short lived (fleeting existence). However, certain other radicals e.g. $NO^{\cdot}$, are stable. Due to the odd electron, free radicals show paramagnetic character.

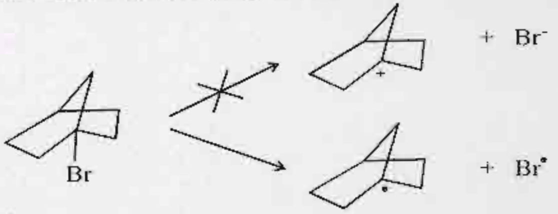
Structure: Radicals have an sp^2 hybrid carbon forming 3 σ bonds with three substituents and the unhybridized p orbital bearing an odd electron. Thus it has a trigonal planar geometry, like the carbocations. This geometry allows the odd electron to get delocalized if the structure permits. Structure of methyl radical is shown here.



The **s character** of the **half-filled orbital** is found to increase across the series.

$$\dot{C}H_3 < \dot{C}H_2F < \dot{C}HF_2 < \dot{C}F_3$$

$\dot{C}F_3$ is essentially sp^3 so that it has a pyramidal shape. Thus, depending on the substituents the hybridization in radicals various from sp^2 to sp^3 and correspondingly shape varies from planar to pyramidal. Another example that proves the sp^3 configuration is radicals is that form norbornyl bromide. Which the impossibility of forming the sp^2 configuration precludes the formation of a cation from the bridged alkyl bromide, it is perfectly possible to form a radical. This radical must have sp^3 configuration because of the shape of the molecule.



Factors Affecting Stability of Radicals

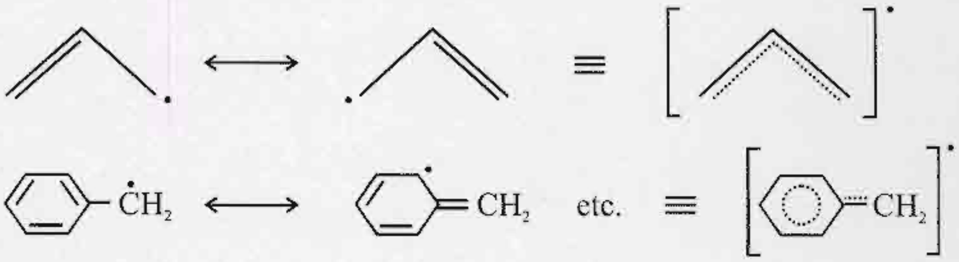
The qualitative difference between cation, anion and radical is in the number of electrons in the non bonding orbital : none in cation, one in the radical and two in the anion. A half filled non bonding orbital in the radical is treated like the vacant nonbonding orbital of cation. Hence it will also be stabilized by interaction with filled orbital. Radicals are, infact, stabilized by many of the factors that stabilize cation and also by those that stabilize anions.

1. The order of stability of simple alkyl radicals is the same as that of carbocations, viz.

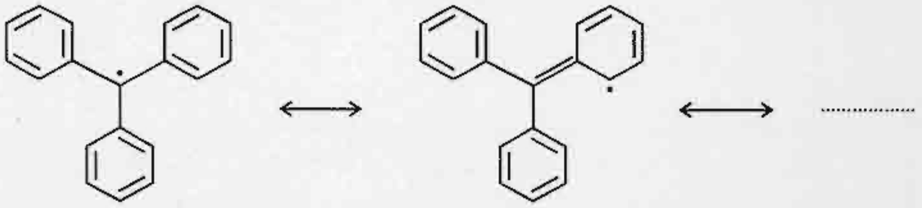
tertiary > secondary > primary > methyl.

Hyperconjugation explains this order. There is also a decreasing relief in strain on going from sp^3 hybridized precursor to essentially sp^2 hybridized radical as the series is traversed.

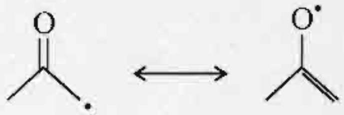
2. The most important factor contributing to the stability of radicals is conjugation.Conjugated double bonds, as in allyl radical and benzyl radical, are more stable than simple alkyl radicals due to delocalisation of odd electron over more number of atoms.



Trityl radical (triphenylmethyl radical) is still more stable.



3. Radicals adjacent to double bond with hetero atoms, such as ketone groups, are also stabilized via resonance.



4. A lone pair of electrons on an atom adjacent to carbon carrying odd electron, stabilizes the molecule, again via delocalisation. Hence such radicals are more stable than simple alkyl radicals.

$$CH_3-\ddot{\underset{\cdot\cdot}{O}}-\dot{C}H_2 \longleftrightarrow CH_3-\dot{\underset{\cdot\cdot}{O}}=CH_2$$

Formation of Radicals

As radicals are reactive interemediates, they are not present at the start of a reaction. Methods of formation include:

1. **Homolysis of a paired - electron molecule**

Homolytic cleavage of bond of carbon with heteroatom takes place easily in gas phase. Radicals are also formed in solution particularly when non - polar solvents are used. Radicals, once formed, are usually very reactive.

Homolytic fission can occur in a number of ways:

(i) **Photolysis**

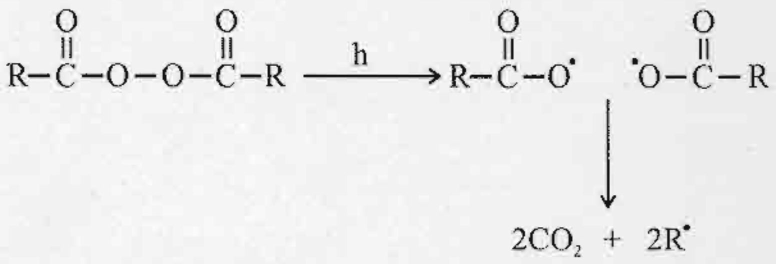
In this method, the molecule absorbs light in visible or U.V. range, which leads to its photochemical decomposition to give a pair of radicals. Species that undergo ready photolysis are halogens (Cl_2, Br_2), alkyl hypochlorite, alkylnitrites, diacyl peroxides.

$$Cl-Cl \xrightarrow{h\nu} Cl^{\bullet} + Cl^{\bullet}$$

$$Br-Br \xrightarrow{h\nu} Br^{\bullet} + Br^{\bullet}$$

$$RO-Cl \xrightarrow{h\nu} RO^{\bullet} + Cl^{\bullet}$$

$$RO{-}N{=}O \xrightarrow{h} RO^{\bullet} + NO^{\bullet}$$



$$R{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}R \xrightarrow{h} R{-}\overset{O}{\overset{\|}{C}}{-}O^{\bullet}\quad {}^{\bullet}O{-}\overset{O}{\overset{\|}{C}}{-}R \longrightarrow 2CO_2 + 2R^{\bullet}$$

The advantages of photolysis are (a) strong bonds get cleaved by this method which are not easy to break otherwise.

e.g.

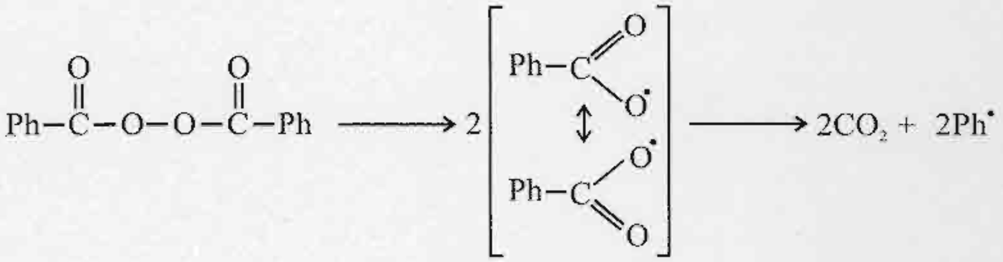
$$R{-}N{=}N{-}R \xrightarrow{h} R^{\bullet} + N{\equiv}N + {}^{\bullet}R$$

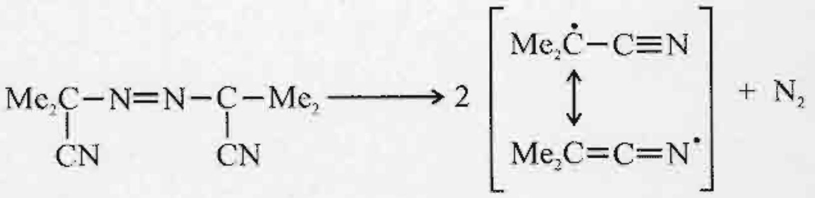
(b) The photolytic cleavage is specific for a bond type in the molecule. This is due to the different absorption frequencies of different bond types. This makes the homolytic cleavage more useful.

Other methods of effecting photolysis include irradiation of neutral molecules with X - rays or γ - rays.

(ii) **Thermolysis**

Thermal decomposition of molecules in gas phase and solution phase can generate radicals. The bonds that are susceptible to thermal cleavage are formed from atoms other than carbon e.g. peroxides and azo compounds where cleavage of O - O and C - N bonds occur respectively. With the use of proper substituents that can stabilize the radical well, the ease of thermal decomposition is increased.





(iii) **Redox reactions**

Redox reactions involve one - electron transfer in generating the radical.

Cu^+ ions accelerate the decomposition of acyl peroxides without its further decompostion to alkyl radical. This is a reduction reaction.

$$Ar\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-Ar + Cu^{+} \longrightarrow Ar\overset{O}{\overset{\|}{C}}-O^{\bullet} + {}^{-}O-\overset{O}{\overset{\|}{C}}-Ar + Cu^{2+}$$

Similarly diazonuim salts give the aryl radical transiently in presence of Cu^{+}.

$$Ar\,N_2^{+} + Cu^{+} \longrightarrow Ar^{\bullet} + N_2 + Cu^{2+}$$

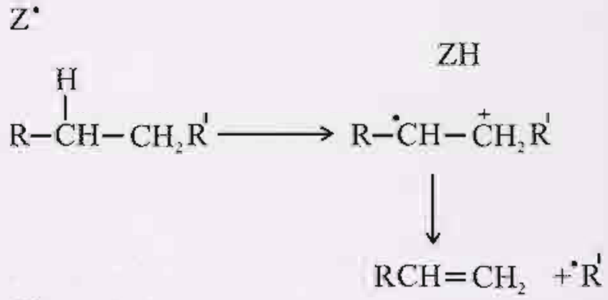
Oxidative reaction can also give radicals.

$$HO-OH + Fe^{2+} \longrightarrow HO^{\bullet} + {}^{-}OH + Fe^{3+}$$

Here the oxidising agent is hydroxyl radical. This mixture is called Fenton's reagent.

2) **Reaction of radical with a paired - electron molecule.**

This is the commonest way of formation of carbon radicals. The compounds which are used to generate radicals for the reaction are called **Radical Initiators**. This substance readily undergoes homolytic cleavage to supply a source of radicals which can then react with paired electron molecule to produce the radicals of interest. Benzoyl peroxide and 2,2-azobisisobutyronitrile (AIBN) are the commonly used radical initiators which give radicals on heating. Carbon-carbon bond fission is seen in the radical induced 'cracking' at 600° C of long chain alkanes. A radical abstracts a hydrogen atom from in between the chain to generate a non-terminal radical which then undergoes fission β to the radical carbon to yield a lower alkene and a further radical. This radical continues the chain reaction.



$$\overset{Z^{\bullet}}{R-\overset{H}{\overset{|}{C}}H-CH_2R'} \xrightarrow{\hspace{1em}} \overset{ZH}{R-\dot{C}H-\overset{+}{C}H_2R'}$$

$$\downarrow$$

$$RCH=CH_2 \quad + {}^{\bullet}R'$$

$Z^{\bullet} =$ *radical species*

Reactivity of Radicals

Many radical reactions are chain reactions, in which new radicals are constantly being formed. The steps in a radical chain reaction can be divided into three types :

(i) Initiation

The initial formation of radical, by the homolytic fission

$$X-Y \longrightarrow X^{\bullet} + {}^{\bullet}Y$$

(ii) Propagation

The step in which a radical reacts with a paired - electron molecule, giving rise to a further radical. This reaction may be abstraction of a hydrogen or other group, or addition to a multiple bond.

$$X^\bullet + H-R \longrightarrow X-H + R^\bullet$$

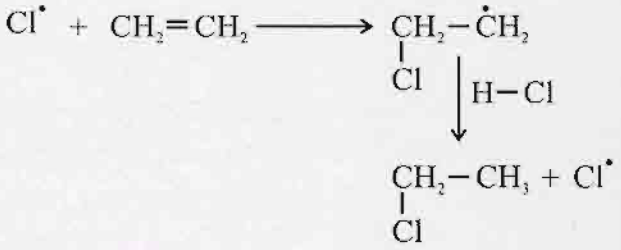
$$X^\bullet + A=B \longrightarrow X-A-B^\bullet$$

Abstraction of hydrogen is seen in the free radical halogenation of alkanes e.g. chlorination of alkane. Here chlorine radical, formed in the initiation step by photolysis of chlorine molecule, abstracts a hydrogen atom from an alkane to produce a carbon radical. This carbon radical reacts with chlorine molecule.

$$Cl^\bullet + H-R \longrightarrow R^\bullet + HCl$$

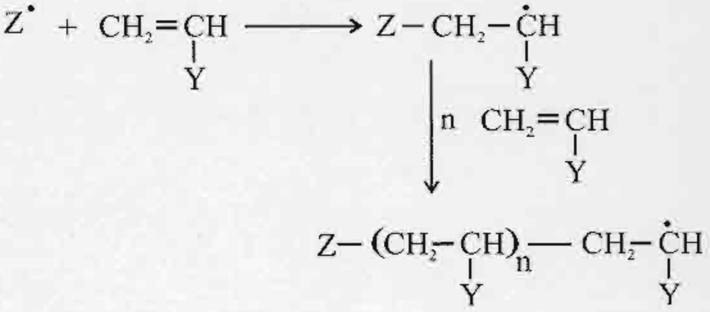
$$R^\bullet + Cl-Cl \longrightarrow RCl + {}^\bullet Cl$$

Similarly addition to C = C (or C ≡ C) is seen in free radical addition of halogens and halogen acids,



$$Cl^\bullet + CH_2=CH_2 \longrightarrow \underset{Cl}{CH_2}-\dot{C}H_2 \xrightarrow{H-Cl} \underset{Cl}{CH_2}-CH_3 + Cl^\bullet$$

Vinyl polymerisation is also an example of radical addition to multiple bonds.



$$Z^\bullet + CH_2=\underset{Y}{CH} \longrightarrow Z-CH_2-\underset{Y}{\dot{C}H} \xrightarrow{n\ CH_2=\underset{Y}{CH}} Z-(CH_2-\underset{Y}{CH})_n-CH_2-\underset{Y}{\dot{C}H}$$

3. Termination

The step in which two radicals combine to form a paired - electron molecule.

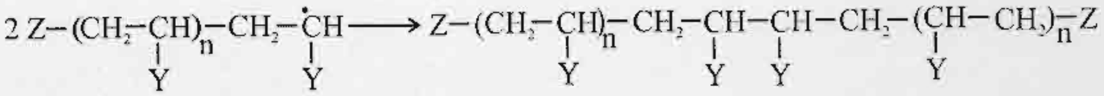
$$X^\bullet + R^\bullet \longrightarrow X-R$$

e.g.

$$Cl^\bullet + Cl^\bullet \longrightarrow Cl_2$$

$${}^\bullet CH_3 + {}^\bullet CH_3 \longrightarrow CH_3-CH_3$$

$${}^\bullet CH_2Cl + {}^\bullet CH_2Cl \longrightarrow ClCH_2-CH_2Cl$$



$$2\,Z-(CH_2-\underset{Y}{CH})_n-CH_2-\underset{Y}{\dot{C}H} \longrightarrow Z-(CH_2-\underset{Y}{CH})_n-CH_2-\underset{Y}{CH}-\underset{Y}{CH}-CH_2-(\underset{Y}{CH}-CH_2)_n-Z$$

When two identical radicals combine, the process is called **dimerisation**.

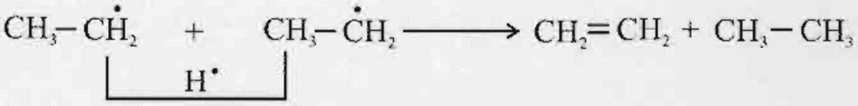
Because the concentration of radicals is usually low as compared to paired-electron molecule, the collision of two radicals to terminate the reaction will be less frequent than the collision of a radical with a paired - electron molecule. Thus, there will normally be many propagation reactions for every termination reaction. This gives rise to the chain reaction.

Other reactions of radicals include:

(a) Fragmentation: The radical breaks down to give a radical fragment and a neutral molecule.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\bullet} \longrightarrow R^{\bullet} + CO_2$$

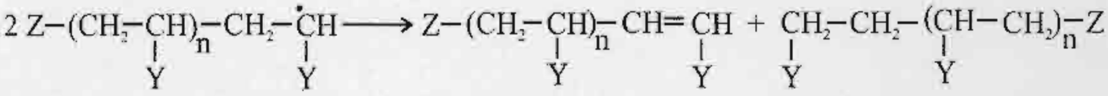
(b) Disproportionation: Two radicals react in such a manner that one transfers its hydrogen atom to the other one, producing a saturated and unsaturated compound.



$$CH_3-\dot{C}H_2 + CH_3-\dot{C}H_2 \longrightarrow CH_2=CH_2 + CH_3-CH_3$$

$$H^{\bullet}$$

This is the most common method of termination in polymerization chain reactions.



$$2\,Z-(CH_2-\underset{Y}{CH})_n-CH_2-\underset{Y}{\dot{C}H} \longrightarrow Z-(CH_2-\underset{Y}{CH})_n-CH=\underset{Y}{CH} + \underset{Y}{CH_2}-CH_2-(\underset{Y}{CH}-CH_2)_n-Z$$

CARBENES

Structure and stability of carbenes

A carbene is a divalent carbon species. It has no electric charge and only six electrons in the valence shell. Carbenes are extremely reactive and short-lived, and never exist as stable species. They can be trapped using frozen inert gas, otherwise their existence is only fleeting.

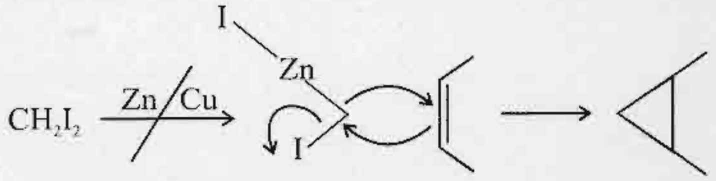
The simplest and one of the most common carbenes is methylene, CH_2. Another common carbene is dichlorocarbene, CCl_2.

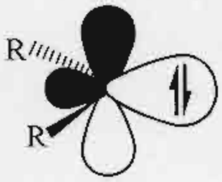
Carbenes can exist in either of two electronic states: singlet or triplet. These terms refer to the magnetic properties of the species; in the triplet state, the nuclear magnetic resonance (NMR) signal of the carbon nucleus is split into three lines by interaction with the electrons, whereas in the singlet state this splitting is not present. In the singlet state, the two electrons are paired and occupy one orbital, and the fourth orbital is vacant, whereas in the triplet state there are two unpaired electrons in two separate orbitals. Thus a singlet carbene can be regarded as being both a carbanion and a carbocation combined (with the charges cancelling out) and a triplet carbene can be regarded as a diradical. The triplet state is the ground state for simple alkyl carbenes such as methylene. However, for dihalocarbenes, the singlet state is the one of lower energy.

In singlet state of carbene, the carbon atom is considered to be sp^2 hybridized. Two of the sp^2 hybrid orbitals are bonded to two groups (H/R/X) and third contains lone pair of electrons. The unhybridized p orbital is unoccupied. Bond angle is 103°.

In triplet state, carbon atom can be considered to be sp hybridized with two groups bonded with its two sp orbitals. Each of the two unhybridized p-orbital contain one electron. The triplet state of carbene is also C bent molecule with an angle of about 136°. A singlet carbene is diamagentic, while the triplet carbene is paramagnetic.

Because carbenes are so reactive and short-lived, it is not always possible to tell whether a free carbene is present in a reaction, or whether the reaction passes through an intermediate which has proportion similar to carbene. Such intermediates are termed as **carbenoids** which have reactivity similar to carbenes but are not true carbenes. For example, in the Simmon-Smith reaction, an alkene is treated with diiodomethane and a zinc-copper couple. The organozinc compound is an intermediate in this reaction, and behaves like a carbene, although the free carbene is not present at any stage. This intermediate can be called a carbenoid.





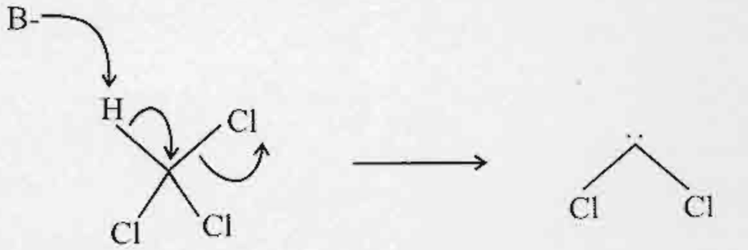
singlet carbene

triplet carbene

Formation of Carbenes

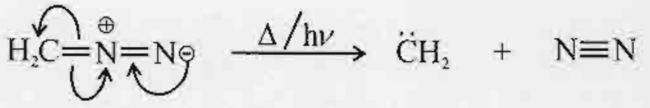
(i) α **- Elimination reaction**

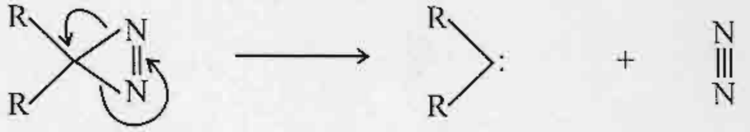
The most common α - elimination reaction used to form carbenes is the elimination of HCl from chloroform by treatment with base to form dichlorocarbene. Other carbenes may also be formed in this manner, for example dichloromethane may be treated with base to form chlorocarbene, CHCl.



(ii) **Thermal or photolytic cleavage**

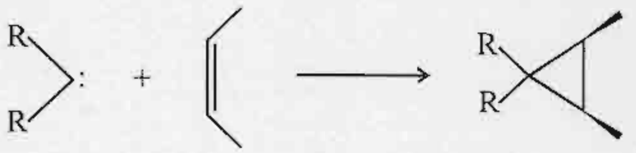
breakdown of compounds with double bonds, such as diazomethane. The decomposition of diazirines is similar, although here two single bonds are broken instead of one double bond.





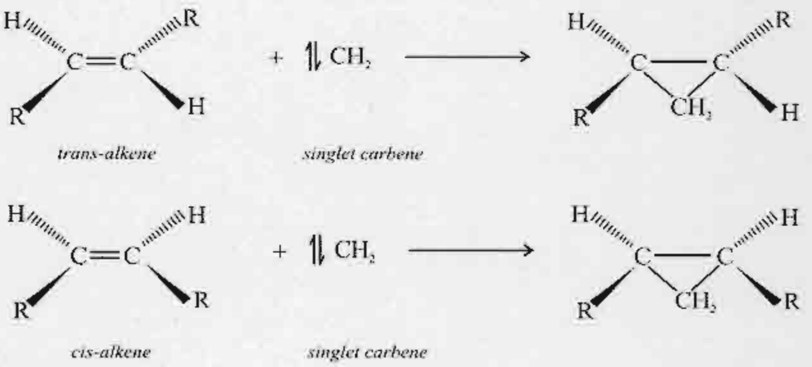
Reactivity of carbenes

(i) The most useful reaction of carbenes is their **insertion** into double bonds ie. **Cycloaddition.**

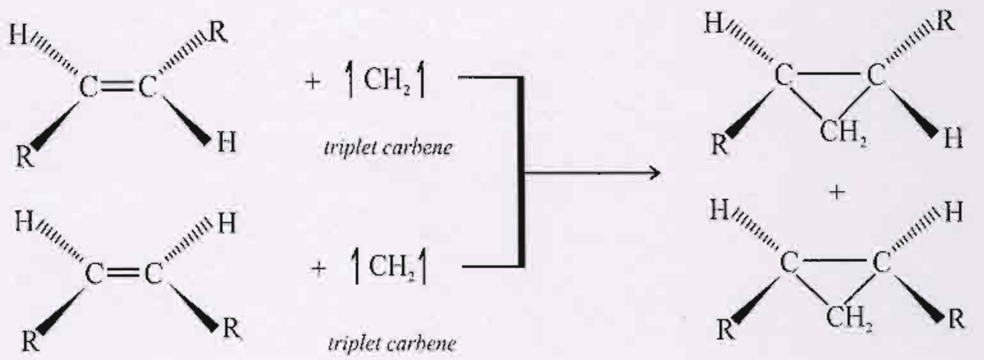


This is the most common way of preparing cyclopropanes. It is a very efficient reaction, and takes place even with electron-poor double bonds such as tetracyanoethylene, (having four electron withdrawing -I groups on the double bond) compound inert to many of the reactions of olefins.

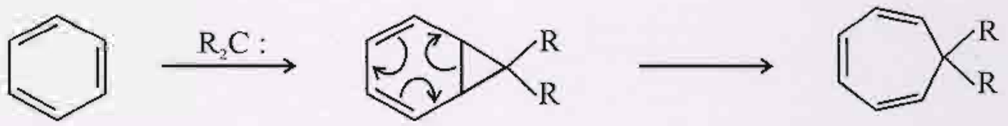
When the addition of carbene to double bond is done in liquid medium, it is the singlet carbene that adds. This addition takes place in a concerted manner and hence is a stereospecific addition. Thus, cis-alkene gives cis-cyclopropane and trans-alkene gives trans cyclopropane.



In gaseous medium, the attacking species is triplet carbene, which has the unpaired electrons with parallel spin. Therefore, addition takes places step wise that causes loss of stereospecificity of reaction. Electrons must have opposing spin to form bonds, so when the first carbene electron has formed a bond with one of the electrons of the olefin, the remaining electron must have the same spin as the second carbene electron. The second bond therefore cannot form until one of the electrons is able to flip by interaction with its surroundings. This interaction will in general be a slower process than rotation about a single bond, so the stereochemistry of the olefin will be lost and a mixture of cis and trans product will result.

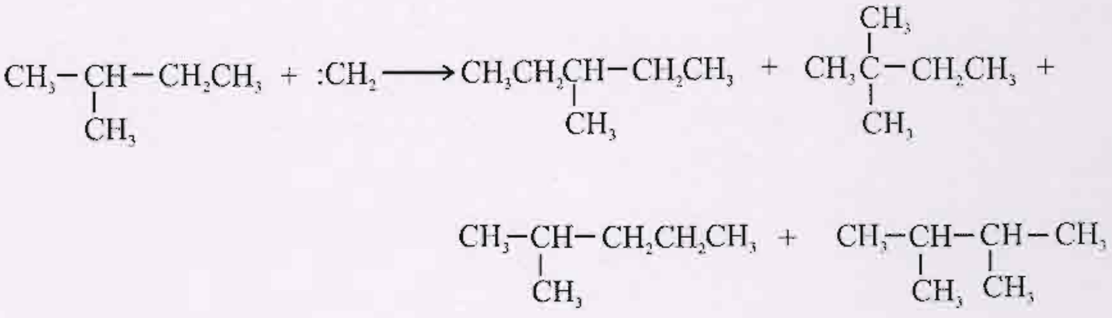


The insertion can also take place into the double bonds of aromatic compounds. The products of reactions in such cases rearrange to give a ring-expanded product.



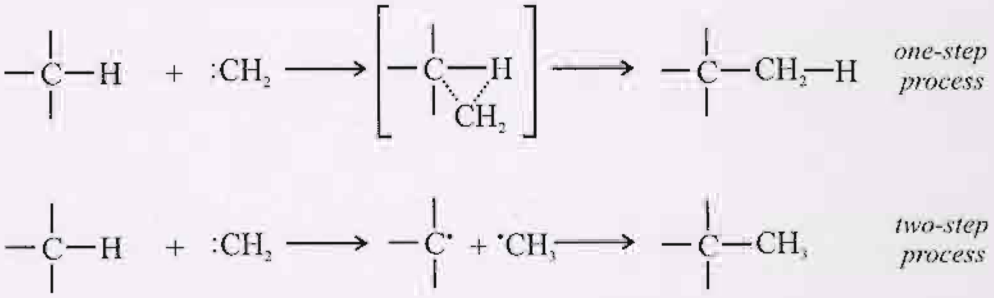
(ii) Carbenes can also insert into single bonds such as C - H, C - N, C - Cl, C - O, O - H, C - C etc. These reactions are seldom of any use preparatively, as they are not selective. These reactions can take place with singlet and triplet carbenes both intra and inter moleculalry.

$$-\overset{|}{\underset{|}{C}}-H + :CH_2 \longrightarrow -\overset{|}{\underset{|}{C}}-CH_3$$



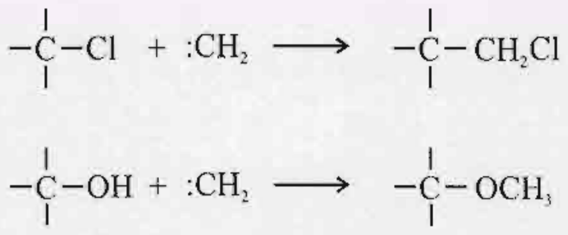
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3 + :CH_2 \longrightarrow CH_3CH_2\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3 + CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3 + CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_2CH_3 + CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

The reaction can occur in one step or two steps.



$$-\overset{|}{\underset{|}{C}}-H + :CH_2 \longrightarrow \left[-\overset{|}{\underset{|}{C}}\overset{H}{\underset{CH_2}{\triangleleft}}\right] \longrightarrow -\overset{|}{\underset{|}{C}}-CH_2-H \quad \text{one-step process}$$

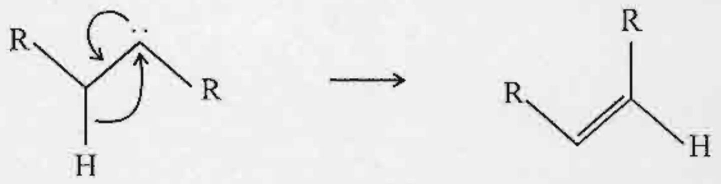
$$-\overset{|}{\underset{|}{C}}-H + :CH_2 \longrightarrow -\overset{|}{\underset{|}{C}}\cdot + \cdot CH_3 \longrightarrow -\overset{|}{\underset{|}{C}}-CH_3 \quad \text{two-step process}$$



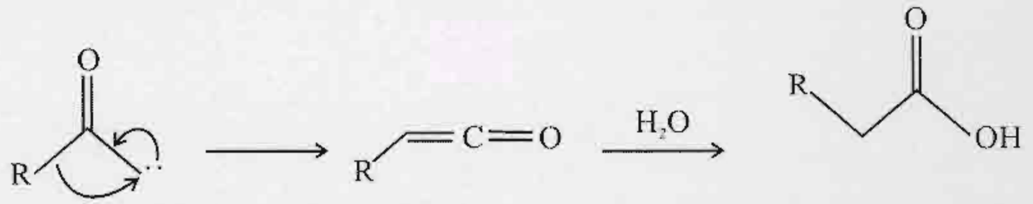
$$-\overset{|}{\underset{|}{C}}-Cl + :CH_2 \longrightarrow -\overset{|}{\underset{|}{C}}-CH_2Cl$$

$$-\overset{|}{\underset{|}{C}}-OH + :CH_2 \longrightarrow -\overset{|}{\underset{|}{C}}-OCH_3$$

(iii) Carbenes can rearrange to give stable products. Any carbene with an α - hydrogen rearranges rapidly to give an olefin. This rearrangement is so rapid that it is not generally possible to use these carbenes for any other purpose, which is one of the reasons why the carbenes most often encountered have such simple structures.



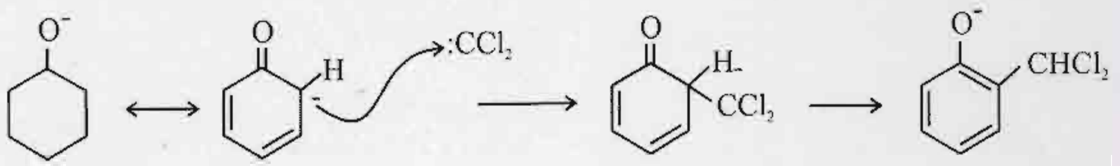
A similar reaction is the rearrangement of α - carbonylcarbenes, which is known as the **Wolff rearrangment**. The initial product is a ketene, but this is readily hydrolysed to a carboxylic acid in the presence of water.



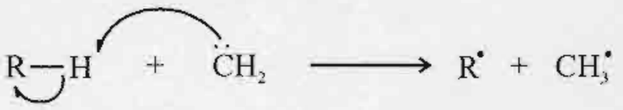
It can also be converted to other acid derivatives if suitable alternatives to water are present; for example, esters are produced if alcohols are used as the solvent. This reaction is an important step in the **Arndt - Eistert synthesis**, used for extending the carbon chain of a carboxylic acid by one unit.

(iv) With carbanions.

In Reimer Tiemann reaction, dichlorocarbene reacts with aryl carbanion (phenoxide ion) to give an intermediate:



(v) Carbenes can also abstract radicals, leading to the formation of two radicals. This reaction is not unexpected for triplet carbenes, as these are a kind of free radical. However, under some circumstances singlet carbenes can also react in this way. In fact, radical abstraction and recombination is the postulated mechanism for the insertion of carbenes into single bonds.



(vi) Carbenes can couples with one another forming alkenes.

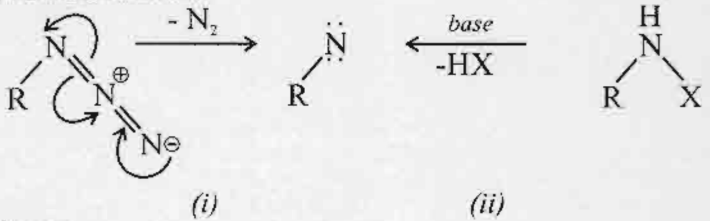
$$2R_2C: \longrightarrow R_2C = CR_2$$

NITRENES

Nitrenes are the nitrogen equivalents of carbenes. Like carbenes, they are unstable intermediates with only a fleeting existence.

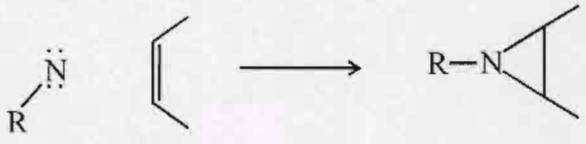
Formation of Nitrenes

There are two common ways in which they are formed: (i) decomposition of azides and (ii) α -elimination of appropriately substituted amines.

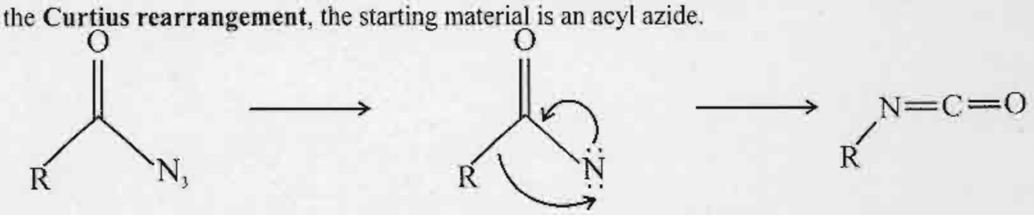


Reactivity of Nitrenes

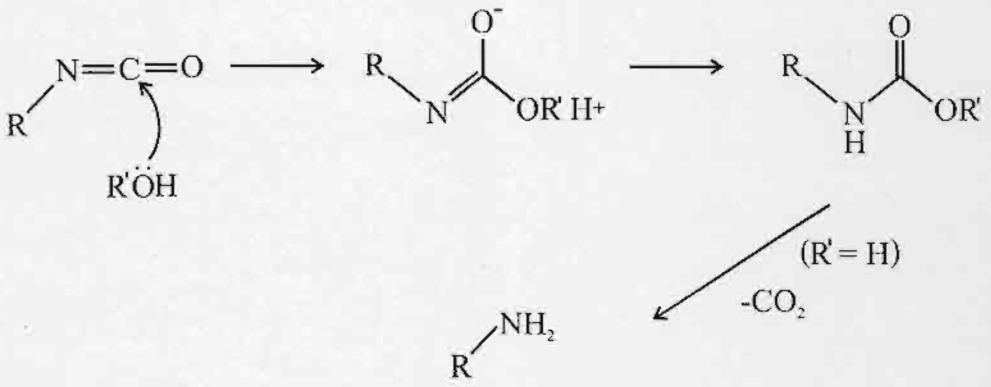
Nitrenes undergo much the same reactions as carbenes. They may insert into single bonds, add to double bonds, or rearrange. They may also dimerize to give azo compounds, in contrast to carbenes, which rarely dimerize.



One nitrene rearrangement is worth mentioning. This goes by four different names, depending on how the nitrene is formed, but the rearrangement is always the same, an acyl nitrene rearranging to an isocyanate. In the **Curtius rearrangement**, the starting material is an acyl azide.

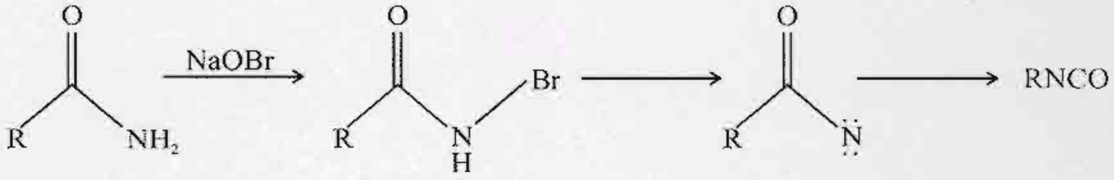


This decomposes therimally to give the nitrene, which then rearranges to the isocyanate. Isocyanates can react futher by hydrolysis to the amine (via a carbamic acid, which decarboxylates) or by alcoholysis to a carbamate).

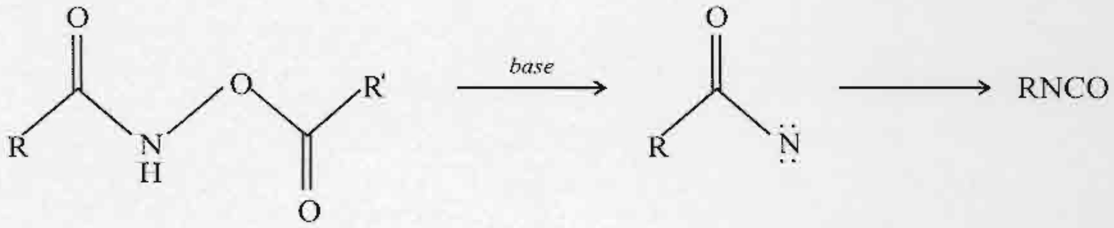


The **Schmidt reaction** is similar, here the starting material is a carboxylic acid. This reacts under rather harsh conditions with hydrazoic acid (NH_3) to form the azide, which then reacts further as in the Curtius reaction. Here, however, the conditions used are such that the final product is almost always the amine.

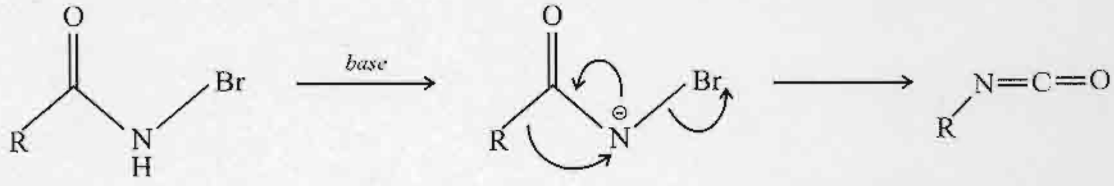
In the **Hofmann rearrangement**, a primary amide is treated with bromine and sodium hydroxide (or sodium hypobromite). This initially forms and N-bromo amide which then undergoes α -elimination to give the nitrene, which reacts as before.



The **Lossen rearrangement** is similar; here the starting material is an O-acyl hydroxamic acid. This is treated with base to give the nitrene.



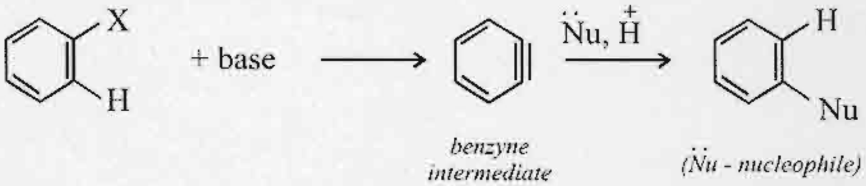
These reactions have all been described as proceeding via free nitrenes, although this has not been proved experimentally. It has been proposed that these reactions may be concerted, the rearrangement taking place at the same time as the other groups leave the nitrogen.



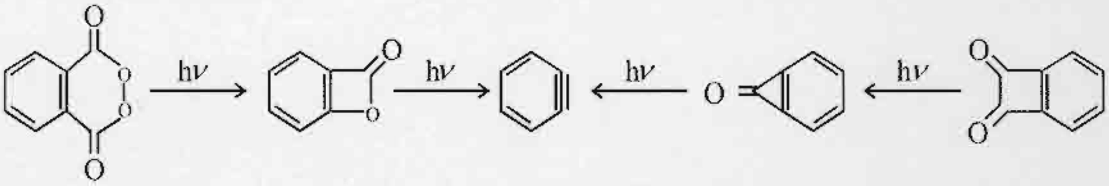
ARYNES

Arynes is the general name given to the **highly unstable or reactive intermediates** formed in certain aromatic nucleophilic substitution reaction. Benzyne is a specific example of such aryines. It is also known as **dehydrobenzene**. The mechanism that involves the formation of benzyne intermediate is called **elimination - addition mechanism.**

This reaction is usually seen in aryl halides when they are treated with strong bases.



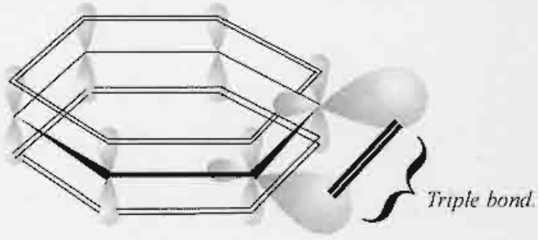
Benzynes differ from carbocations, carbanions , carbenes and other reactive intermediates discussed so far in that each carbon has a valency of 4 i.e. each carbon has a complete octet. Nevertheless, the species is extremely reactive. Neither benzene nor any other aryne has yet been isolated under ordinary conditions but stable benzyne has been isolated in an inert (argon) matrix at very low temperatures (8 K) where it is observed spectroscopically (I R spectrum). For these studies, the molecule is generated photolytically.



Structure

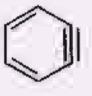
Benzynes, or arynes in general, cannot be acetylinic in the usual sense as this would require enormous deformation of the benzene ring in order to accomodate the 180^0 bond angle required by the sp hybridized carbons in an alkyne.

The most generally used pictures of benzynes gives it a structure similar to benzene but with an additional weak bond in the plane of the ring, formed by the overlap of the two sp^2 orbitals. Studies indicate that conjugation is maintained and that benzyne is a strained but aromatic moleule. This implies that the extra electron pair does not affect aromaticity, the two electrons are accomodated in the orginal sp^2 hybrid orbitals forming an additional π bond restricted between two carbons. This bond is weak due to the nature of the overlapping orbitals.

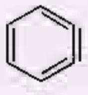


orbital picture of benzyne

Benzynes do not have a formal triple bond. This is because two canonical form (I) and (II) contribute to the hybrid. Contribution of (I) bas been found to be more than II.



I



II

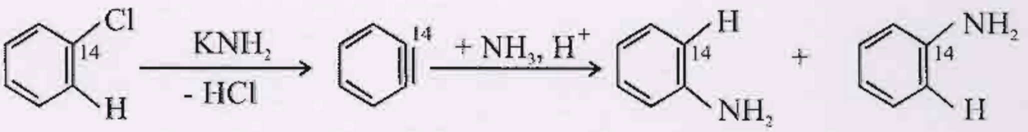
Other aromatic rings and even non aromatic rings can react via such an intermediate.

Formation of Arynes

(i) **Base catalysed elimination of hydrogen halide from a halobenzene.**

e.g. Chlorobenzene reacts with liquid ammonia in presence of strong base, potasium amide, to give aniline. The substitution of -Cl group by -NH_2 group is brought about via benzyne mechanism.

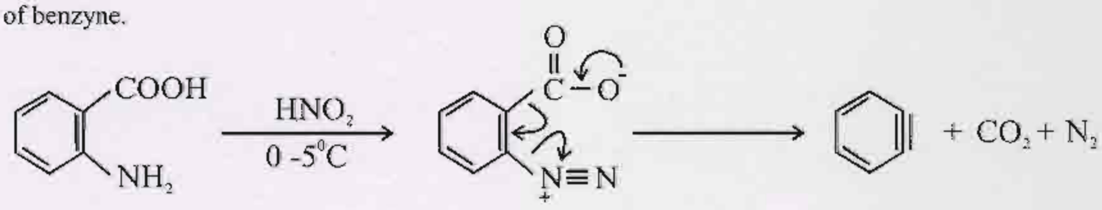
This type of reaction was used by J.D. Roberts to prove the benzyne intermediate formation. He took chlorobenzene labelled with ^{14}C at C - 1and showed that such a labelled reactant gives two aniline products on reaction with potassium amide - one with NH_2 linked to ^{14}C and the other with NH_2 linked to unlabelled carbon ortho to ^{14}C. Such pattern of product formation was possible only with the involvement of benzyne intermediate.



Thus, with benzyne as th eintermediate, nucleophilic substitution on the ring need not always be at the carbon to which the leaving groups was bound.

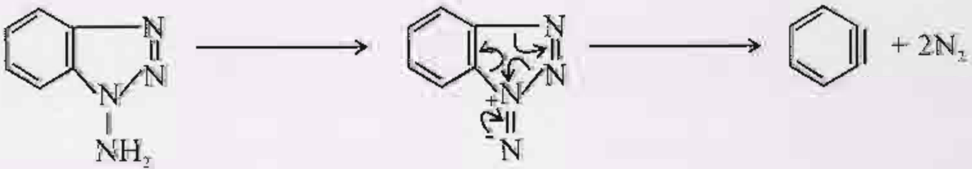
(ii) **Diazotization of o-amino benzoic acid**

When o-aminobenzoic acid (anthranilic acid) is subjected to diazotisation (i.e. treated with HNO_2, which is in turn prepared in - situ by $NaNO_2$ and HCl at low temperatures), the product undergoes photolytic or thermal decomposition and there is a concerted loss of nitrogen and carbon dioxide leading to generation of benzyne.



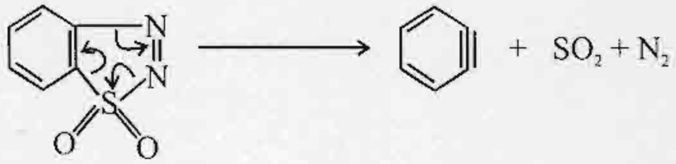
The zwitterion decomposes to give benzyne. Other derivatives of anthranilic acid also undergo such reactions.

(iii) **Oxidation of 1-aminobenztriazole**



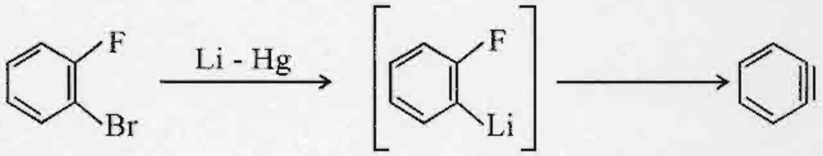
The oxidized intermediate decomposes with loss of two molecules of nitrogen.

(iv) Decomposition of Benzothiadiazole



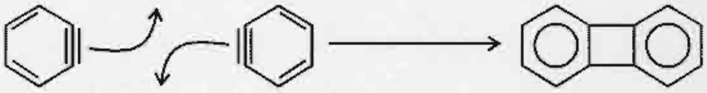
(v) From o-Dihaloaromatics

o-Dihalobenzene on reaction with lithium or magnesium amalgam results in the formation of a transient organometallic compound that decomposes with elimination of lithium halide. 1-Bromo-2-fluorobenzene is the usual starting material in this procedure.

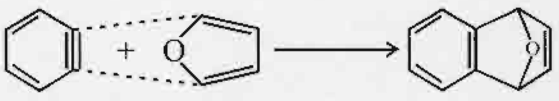


Reactivity of Benzyne

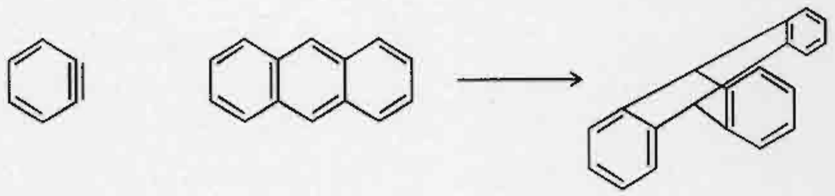
i) If benzyne is produced under conditions where there is no suitable species for it to react with, then it dimerises very rapidly to the stable biphenylene.



ii) When benzyne is generated is the presence of potential dienes, such as furan, addition at the highly strained 'trible bond' occur.



Such additions can take place on other dienes like cyclopentadienones and anthracene.



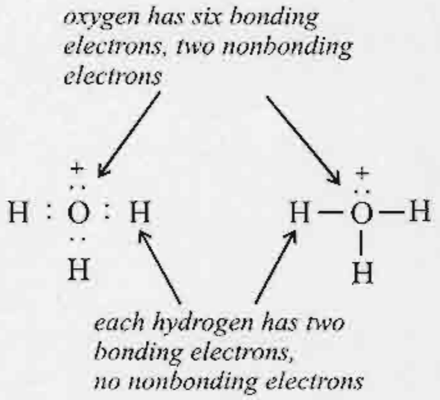
FORMAL CHARGE

Organic chemists are not satisfied with the simple statement that an ion, such as the hydronium ion, H_3O^+, is positively charged. They find it useful to locate the charge on a particular atom in the ion. The hydronium ion is shown with the positive charge next to the oxygen atom. The decision as to where to put the charge is made by calculating the formal charge for each atom in an ion, or a molecule.

The formal charge for an atom may be calculated using this formula:

Formal charge = (number of valence electrons)-(number of nonbonding electrons)-½ (number of bonding electrons)

To locate the formal charge in the hydronium ion, all of the electrons in the valence shell of each atom are counted.



Each hydrogen atom in the hydronium ion has no formal charge because each has one valence electron, no nonbonding electrons, and two bonding electrons.

Formal charge for hydrogen = 1 - 0 - ½ (2) = 0

In the hydronium ion, oxygen shares six electrons with the hydrogen atoms and therefore has six bonding electrons. It has two nonbonding electrons. Because it is in Group 16 of the periodic table, it has six valence electrons. (For elements in groups 13 - 18, the number of valence electrons equals the group number minus ten.)

Formal charge for oxygen = 6 - 2 - ½ (6) = 6 - 5 = + 1

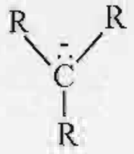
Calculating a formal charge is essentially the same as asking whether an atom in a molecule or ion has in its valence shell more electrons or fewer electrons than are necessary to balance its nuclear charge, the number of protons in the nucleus. An uncharged oxygen atom has to have six electrons in its valence shell. In the hydronium ion, oxygen bonds with three hydrogen atoms, so only five electrons effectively belong to oxygen, which is one fewer than it needs; therefore it bears a formal charge of + 1.

The sum of the formal charges on the atoms in an uncharged molecule is zero. For an ion, the sum of the formal charges on different atoms should add up to the charge on the ion.

Carbon forms four covalent bonds. When only three covalent bonds are present, the carbon atom can have either a formal negative charge or a formal positive charge.

* Carbanions - three covalent bonds to carbon and a formal negative charge.

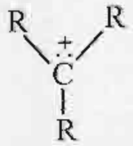
Formal charge on C:
4 - 2 - 3 = -1



The negative charge is used to show the 2 non-bonding electrons

* Carbocations - three covalent bonds to carbon and a formal positive charge.

Formal charge on C:
4 - 0 - 3 = +1



The positive charge is used to show the 2 non-bonding electrons

INVESTIGATING REACTION MECHANISM BY VARIOUS TECHNIQUES

Mechanism of reactions are presented to us as established truths. Although all mechanisms are not known with certainity, they are generally thought to be accurate.

To specify the mechanism of a reaction, we should ideally know the precise position of all atoms and the energy of all interemediates at every stage of the mechanism. However, practically this is impossible to achieve and so conclusively we cannot prove a mechanism to be correct. In fact, we often prove mechanisms to be incorrect, and prove a mechanism by ruling out other mechanisms.

To establish a mechanism with reasonable certainity we take the aid of several experiments and quantum mechanical calculation. Latter are best left to theoretical chemists. We will talk of **experimental techniques** used to establish a mechanism.

CLUES FROM PRODUCTS

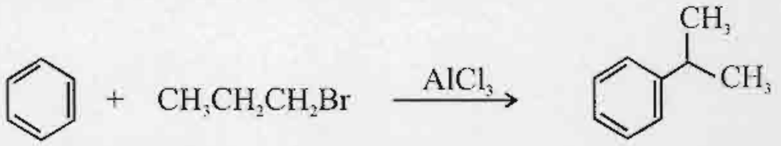
Product analysis is the most fundamental information for understanding the course of a reaction. In this, it is important to establish the following facts.

(i) Structure and nature of product or products and relating this information to the structure of the reactant.

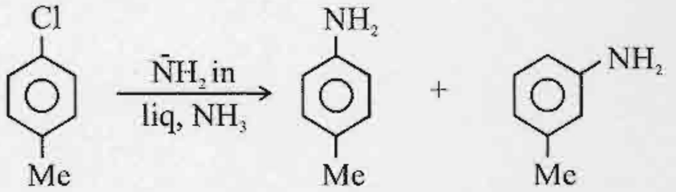
(ii) Relative proportions of the products formed.

It is most essential to be absolutely certain about what the product of the reaction actually is. This may sound obvious, but the following points will make us realise the importance.

(a) Some reaction may give unexpected products. In the Friedel Crafts reaction of 1-bromopropane with benzene, the major product is isopropyl benzene and not the expected n-propyl benzene. This rearrangement provides an important piece of evidence for the intermediacy of the carbocations, since the 1-propyl cation is known to rearrange easily to the more stable 2-propyl cation.



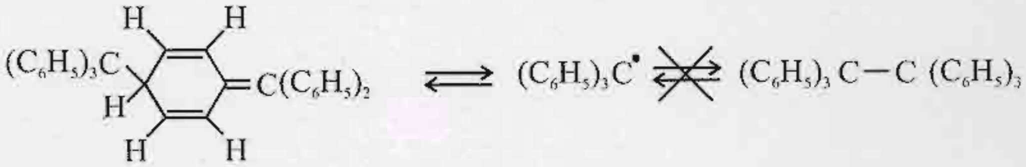
Reaction of p-chlorotoluene with amide ion $(\bar{N}H_2)$ in liquid ammonia is found to lead not only to the expected p-toluidine but also to the quite unexpected m-toluidine which is in fact the major product.



expected (minor) *unexpected (major)*

The formation of the unexpected product in major proportion indicates that a simple substitutes of -Cl by $-NH_2$ is not the pathway of this reaction. There has to be a different pathway or a common intermediate leading to these products.

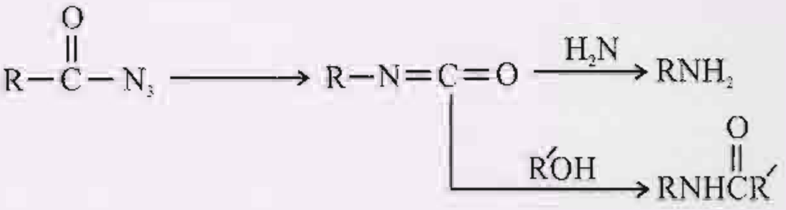
(b) If the structure is not correct, it can lead to a lot of confusions e.g. Triphenyl methyl radical is a coloured species which readily undergoes dimerisation to give colouless dimer. Till 1900, this dimer was, quite reasonably, thought to be hexaphenylethane with thirty aromatic hydrogen atoms. Only after seventy years, with the help of NMR spectroscopy, was it fond that the dimer had only twenty five aromatic Hs, four 'dienic' Hs and one saturated H. This finding did not match with the proviously proposed structure (II). Instead, the correct structure was (I)



(I) *(II)*

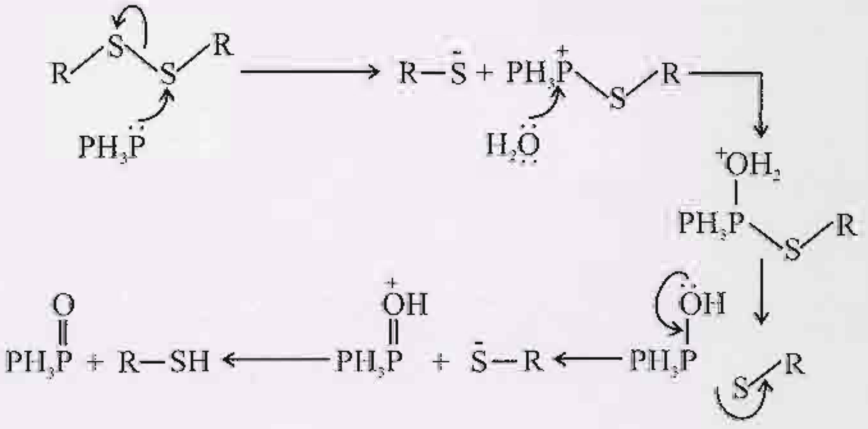
It was only after the correct elucidation of structure, that several seemingly anomalous properties of the dimer were understand

(c) Some reactions give different products depending on the conditions e.g. in the Curtius rearrangement, if water is used as solvent the product is an amine and if alcohol is used, the product is a carbamate.



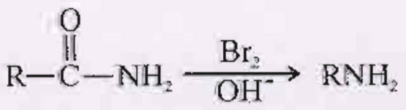
In both cases there is formation of an isocyanate which reacts further to give various products.

(d) Not only are the desired products of interest, but the side products of a reaction can also provide important clues. e.g. Disulphides can be cleaved to thiols by treatment with triphenylphosphine in a solvent that contains water. An important clue to the mechanism of this reaction is that the triphenylphosphine is converted into triphenyl phosphine oxide. This shows that the triphenylphosphine acts as a reducing agent and allows us to postulate the mechanism as shown.



STUDY OF INTERMEDIATES

For reaction that proceed in more than one step, isolation of the intermediates may provide invaluable evidence about the course of the reaction e.g. In the Hofmann rearrangement, an acid amide is converted into an amine.



$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[OH^-]{Br_2} RNH_2$$

In this reaction, it has been possible to isolate several intermediates that have enable to elucidate the overall mechanism. These intermediate are:

N-bromoamide, $RCONHBr$, its anion $RCO\bar{N}Br$, and an isocyanate $RN = C = O$.

Firstly, we must be sure that the compounds isolated during the course of a reaction are true intermediates.

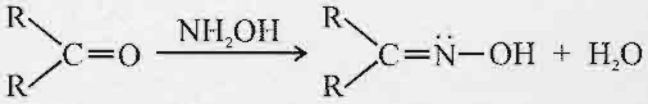
This is because a compound may look like an intermediate but it may as well be just a side product. Conersely, if a proposed intermediate cannot be isolated from a reaction, this does not mean that it is not present; it may be that it is very short-lived.

An important test to show that a compound is an intermediate is to show that can be converted to the normal products under the conditions of the reaction.

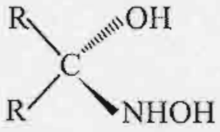
e.g. isocyanate is surely an intermediate in the Hofmann rearrangement since it does give the expected amine when treated with water under the condition of the reaction. Of course, it still does not prove that it is the only intermediate, the reaction could go via another pathway with the isocyanate on a minor route to the product.

Nevertheless, if a suspected intermediate is shown not to be converted to the products, this provides a sure proof that it is not an intermediate.

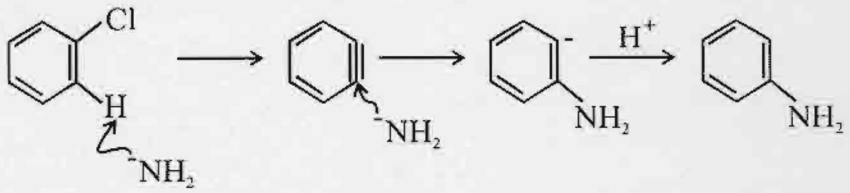
The failure to isolate a postulated intermediate does not necessarily mean that we cannot obtain some evidence of its existence. Their occurence may often be inferred from physical, particularly, spectroscopic measurements made on the system. e.g. In the reaction of carbonyl compounds with hydroxylamine to get oximes, the infrared absorption band characteristic of C = O in the starting material disappears rapidly.

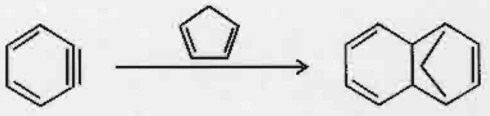


It goes off completely before the I.R. absorption band characteristic of C = N appears. This clearly shows that an intermediate must be formed. Further evidence suggests that it is the carbanolamine which forms rapidly and then breaks down only slowly to yeild the products, the oxime and water.

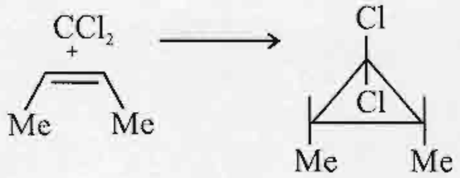


Another evidence for intermediates can be provided by trapping experiment. Here, a reagent that would be expected to react rapidly with the postulated intermediate is added to the reaction. This diverts the labile intermediate from the main reaction pathway and isolates a stable species into which it is unequivocally incorporated. Thus, an important piece of evidence for the benzyne mechanism is that addition of cyclopentadiene to the reaction medium gives the product shown. This product presumably arises from a Diels-Alder reaction between cyclopemtadiene and benzyne.





Similarly in the hydrolysis of trichloromethane with strong bases, the highly electron deficient dichloncarberoe, CCl_2, which is considered a labile intermediate, is 'trapped' by introducing an electron-rich species, cis-2-butene, into the reaction mixture and then isolating the resultant stable cyclopropane derivative.



KINETIC STUDIES

Kinetics of the reaction give a lot of useful information about the reaction pathway. Kinetic investigation can be divided into two types:

(i) Those which discover the rate law for a reaction.

(ii) Those which measure change is the rate when various condition of reaction are charged.

Rates can be measured by various methods.

e.g. By measuring rate of disappearance of starting material or appearance of product. This can be done by the help of spectroscopic techniques.

e.g. U.V. or NMR or IR absorption band characteristic of the reactant or product can be continuously monitored to follow the course of reaction. Depending on the nature of reaction, continuous measurement of pH, conductance, optical activity etc. can prove to be very informative.

Another widely used, though laborious, method is to quench the reaction at various intervals and to analyse the reaction mixture.

The goal of a kinetic study is to establish the quantitative relationship between the concentration of reactants and catalyst and the rate of the reaction. Such a study involves rate measurements at several different concentration of each reactant so that the kinetic order with respect to each reactant can be assessed. A complete investigation allows the reaction to be described by a rate law, which is an algebraic expresion containing one or more rate constants as well as the concentrations of all reactants that are involved in the rate determining step and the steps prior to the rate determining step. Each concentration has an exponent, which is the order of the reaction with respect to that component. The overall kinetic order of the reaction is the sum of all the exponents in the rate expresion.

For example, consider the reaction sequence:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \xrightarrow{k_2} D \xrightarrow{k_3} E + F$$

the rates for the successive steps are:

$$\text{step 1:} \quad \frac{d[C]}{dt} = k_1\ [A][B] - k_{-1}\ [C]$$

$$\text{step 2:}\quad \frac{d[D]}{dt} = k_2\ [C]$$

$$\text{step 3:}\quad \frac{d[E]}{dt} = \frac{d[F]}{dt} = d[D]$$

Every single step has a rate expresion where concentration terms for each reacting species is written. If first step has been specified to be a rapid, unfavourable equilibrium and $K_2 << K_3$, then second step will govern the overall rate of reaction. Therefore, step 2 is the rate determining step. Kinetic data does not allow K_3 to appear in the overall rate expresion because it corresponds to step 3 that comes after step 2. The rate of overall reaction is governed by the second step which is the bottleneck in the proces. Therefore, rate of step 2 (= rate of overall reaction) is given by:

$$\frac{d[D]}{dt} = k_2\ [C]$$

Now, concentration of C may not be directly measureable. However, [C] is related to [A] and [B] by an equilibrium constant:

$$K = \frac{[C]}{[A][B]}$$

K is related to k_1 and k_{-1}, by the requirement that no net change in composition occurs at equilibrium.

$$k_{-1}\ [C] = k_1\ [A][B]$$

$$\text{therefore}\quad [C] = \frac{k_1}{k_{-1}}\ [A][B]$$

$$\text{therefore}\quad \frac{d(D)}{dt} = k_2\ [C] = k_2\ \frac{k_1}{k_{-1}}\ [A][B]$$

$$= k_{obs}\ [A][B]$$

Experimentally, it would be observed that the reaction rate would be proportional to concentration of both reactants A and B or rate of reaction is proportional to the concentration of A times the concentration of B. It will be first order in both reactants. It is therefore having second - order kinetics. An example is S_N2 displacement reaction. Here, rate is proportional to concentration of substrate multiplied by concentration of nucleophile, reflecting the participation of both of these in the rates determining step (here, this is the only step).

A reaction with a rate proportional to the square of concentration of one reagent would also be send to have second - order kinetics. On the other hand, a reaction like S_N2 reaction has rate proportional to concentration of only one reactant; therefore, has first order kinetics. Here, substrate is the only molecule that appear in the rate equation, because it is the only molecule taking part in the rate determining step.

First order and second order reactions are most common, but third - order reactions are also sometimes

[illegible]

we should not confuse between order of reaction and molecularity. Molecularity is the number of molecules

[illegible]

determining step is same as order of reaction.

[illegible]

participate in rate determining step but does not appear in rate equation since it is present in such large

[illegible]

compare the observed rate law with the various mechanisms and postulate the likely mechanisms by

[illegible]

mechanisms.

[illegible]

Mechanism B has the distinctive feature that it is zero - order in the reactant benzene, because the rate determining step occurs prior to the involvement of benzene. Mechanism B has been established for nitration of benzene in several organic solvents and in each case benzene concentration is absent for the rate law giving more evidence for this mechanism to be correct. Mechanism A and C, on the other hand, provide kinetic expressions that are similar in form, differing only in the inclusion of water in the expression for mechanism C.

This is not a conspicuous difference. If the concentration of water is several times larger than that of benzene, its overall concentration will change little during the course of the reaction. In this circumstance, the term for the concentration of water would disappear, so that the form of kinetic expression alone would not distinguish between mechanisms A and C.

A reaction that is found to proceed unexpectedly faster or slown than the apparently similar reaction, suggests the operation of a different or modified pathway from the one that might have been assumed for the series.

e.g. Hydrolysis of chloromethanes with strong bases varies as follows:

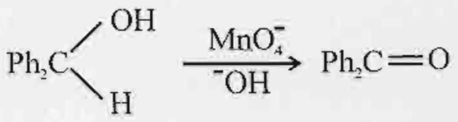
$$CH_3Cl >> CH_2Cl_2 << CHCl_3 >> CCl_4$$

This clearly suggests that trichloromethane (showing unexpected behaviour) hydrolyses in a different manner from other compounds.

ISOTOPIC STUDIES

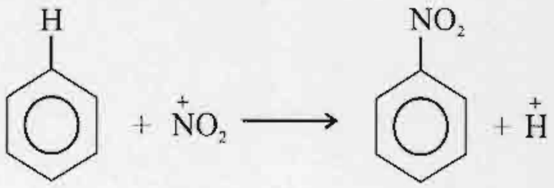
Compounds that differ only in their isotopic composition are often described as being chemically identical, but this is not stricly true. Quantum mechanical calculations show that a carbon - deuterium bond has a lower zero-point energy than a corresponding carbon-hydrogen bond, this being the residual vibrational energy of the bond when it has the minimum vibrational energy allowed by the laws of quantum mechanics (which cannot be exactly zero). Because of this difference in the zero-point energies, the carbon-deuterium bond is slightly stronger than the carbon-hydrogen bond. This is a general finding, applicable to bonds between hydrogen/deuterium and other atoms, or in fact to any pair of isotopes; thus a C - ^{18}O bond is stronger than a C - ^{16}O bond. This is an interesting finding since **isotopic labelling can be used to change the condition of the reaction and consequently obtain information about rate laws and mechanisms.** The difference in bond strengths of C - H and C - D bond means that when a C - H bond is broken in the RDS of a reaction, the reaction will be slower where the starting material contains a C - D bond at this position instead. This is known as a **primary kinetic isotope effect**. An example is E2 elimination, in which there is a primary kinetic isotope effect for the β-hydrogens with $k_H/k_D = 3\text{-}5$, or in other words the reaction is 3-5 times faster when the reaction is carried out with hydrogen than when it is carried out with deuterium.

Similarly, in the oxidation



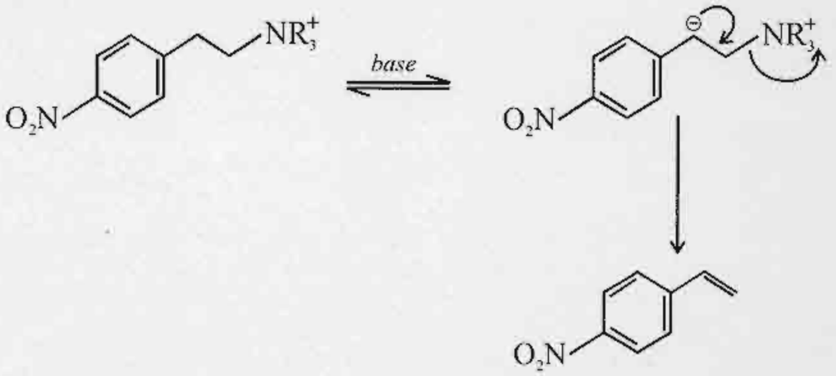
$$Ph_2C(OH)H \xrightarrow[^{-}OH]{MnO_4^-} Ph_2C{=}O$$

It is found that Ph_2CHOH is oxidised 6.7 times as rapidly as Ph_2CDOH; the reaction exhibits a primary kinetic isotope effect, and breaking of the C - H bond must clearly be involved in the rate-limiting step of the reaction. By contrast benzene, C_6H_6 amd hexadeuterobenzene, C_6D_6, are found to undergo nitration at essentially the same rate. Therefore, C - H bond-breaking, that must occur at some stage in the overall process, thus cannot be involved in the rate-limiting step.



Primary kinetic isotope effects typically range from 1 (no isotope effect) to about 7 or 8, depending on the extent of C - H bond breaking in the RDS.

Inverse isotope effects are also known, in which k_H/k_D is less than 1. An example is in the base catalysted elimination of the amine constituent in the quaternary ammonium compound shown below, where $k_H/k_D = 0.13$ for the water used solvent.



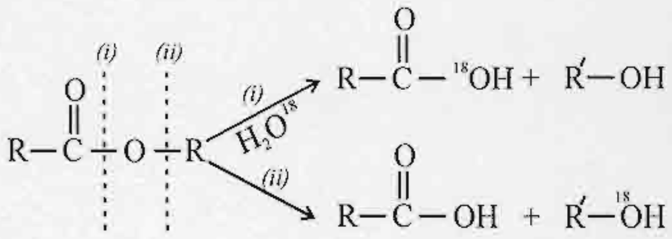
This is consistent with an E1cB mechanism (elimination, conjugate base). When the carbanion intermediate is formed, it may eliminate the amine or it may revert to the starting material. If the reaction is carried out in D_2O, the return to the starting material will be slower, as an O - D bond must be broken instead of an O - H bond. This increases the concentration of the intermediate, which in turn increases the overall rate of desired reaction.

Primary kinetic isotope effects may be measured for isopotes other than hydrogen and deuterium, but more sensitive measurements are required because the differences are much smaller. A C^{12}/C^{13} isotopes effect, for example, will typically be of the order of 1.02-1.10.

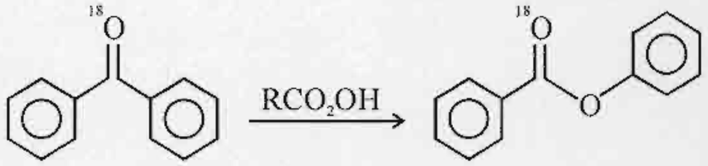
Isotope effect may be observed even when the bond to the hydrogen showing the effect is not itself broken during the reaction. These are known as **secondary kinetic isotope effects**. They are generally smaller than primary isotope effects, and are more difficult to interpret, so they are less useful in providing information about a reaction. In general, knowledge of a reaction mechanism is necessary to rationalize a secondary isotope effect, rather than the isotope effect providing useful information about the reaction mechanism. An example of a secondary isotope effect is found in the S_N1 hydrolysis of isopropyl bromide, which is marginally faster for the protonated compound. This is thought to be because of the less effective hyperconjugation in the transition state for the deuteriated compound.

Isotopes can be used to solve mechanistic problems that are non-kinetic. For example, aqueous hydrolysis of esters leads to an acid and an alcohol. The mechanism could proceed by cleavage of (i) acyl - oxygen bond or (ii) alkyl - oxygen bond. In such cases, isotopic labelling proves to be very usful.

If the reaction was carried out in water enriched in ^{18}O, the acid so produced was found to be rich in ^{18}O thereby showing that the ester hydrolysis occurs via cleavage of acyl - oxygen bond.



Mechanism of Baeyer Villiger rearrangement has been elucidated with the help of isotopic labelling. When benzophenore labled with ^{18}O was subjected to the rearrangement, the product of the reaction was labelled with ^{18}O entirely in the carbonyl position. This ruled out a carboxylate intermediate in which the label could become scrambled between the carbonyl oxygen and the alkoxy oxygen. This led to strong evidence for concerted mechanism.



A wide range of isotopes, both radioactive and stable, may be used in mechanistic investigations. Some of the more commonly used radiosotopes are ^{3}H (tritium, T), ^{14}C, ^{32}P, ^{35}S, and ^{131}I. Stable isotopes that may be used for labelling include ^{2}H (deuterium, D), ^{13}C, ^{15}N, ^{17}O and ^{18}O.

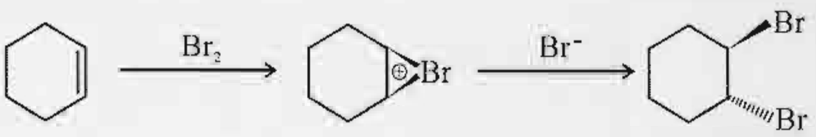
The presence of radiosotopes may easily be detected by measuring their radioactivity. This is a sensitive method, requiring only minute amounts of sample, but suffers from the disadvantage of revealing nothing about the position of the radioactive label within a molecule.

All the stable isotopes may be detected by mass spectrometry. Again, this is a sensitive method, but also does not give definitive information about the location of the label. However, the fragmentation patterns in the spectrum may give useful clues.

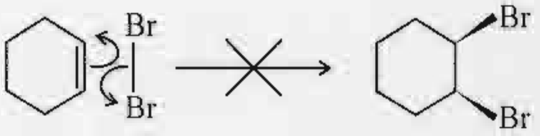
Some isotopes can be detected by NMR, such as deuterium, ^{13}C, ^{15}N, and ^{17}O (but not ^{18}O). This method is less sensitive, but has the advantage of telling us the position of the label within the molecule.

STEREOCHEMICAL EVIDENCE

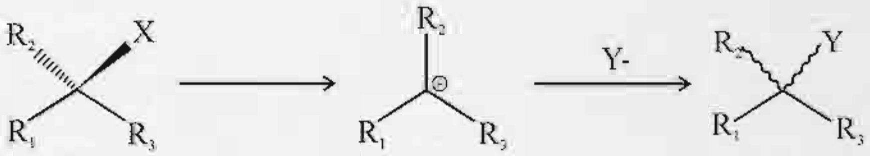
The stereochemistry of products can provide important clues to the mechanism. Addition of bromine to olefins proceeds through a bromonium ion. An important peice of evidence for this mechanism is the addition of the two bromine atoms to opposite sides of the double bond, as can be seen in the bromination of cyclohexene.



This rules out a mechanism in which the bromine adds directly to the bond in a simultaneous mechanism, as this would give syn addition.

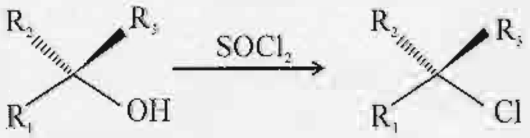


If optically active compounds are used, we can often derive useful information from the stereochemistry of the product. If the product of the reaction is racemic, then this shows that it must proceed through a planar intermediate. The classic example of this is S_N1 substitution. The racemization observed in this reaction is a strong piece of evidence for the intermediate carbocation.

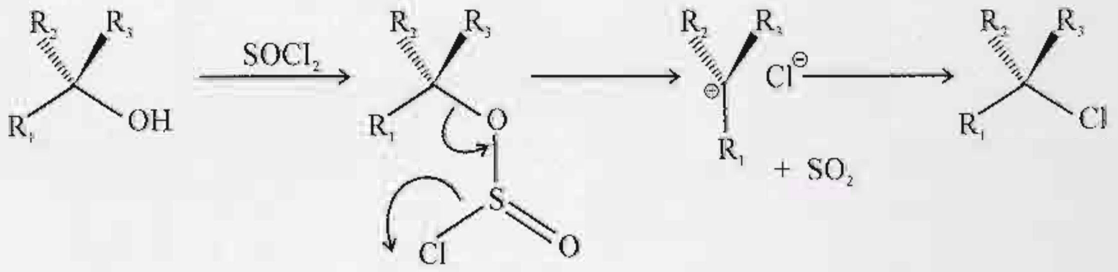


(actually, S_N1 reaction proceeds with partial racemization due to formation of intimate ion pair with carbocation).

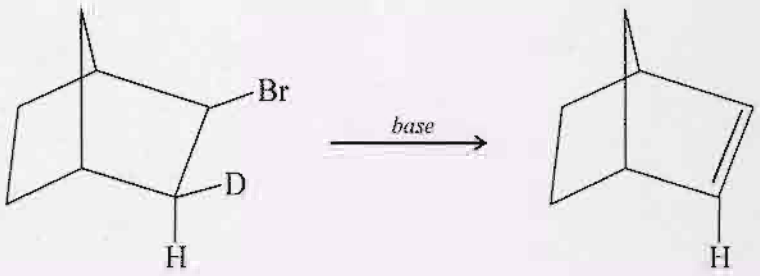
Clearly, a mechanism that proceeds with inversion of configuration at a chiral centre is not the same as one proceeding with retention. Retention of configuration in the reaction of alcohols with thionyl chloride shows us that this reaction is not a normal S_N2 inversion, and leads to the postulation of the S_Ni mechanism.



S_Ni mechanism



e.g. Isotopic labeling contributes in support of stereochemical evidence. Elimination of HBr from the norbornyl bromide. Without labelling, it is impossible to tell whether the elimination is syn or anti. However, deuterium labelling shows that this is a syn elimination; if the elimination were anti, the product would contain deuterium.



Elimination are usually anti, but the reaction here is different because the rigidity of the molecule prevents the bromine adopting an antiperiplanar congormation to a hydrogen, but allows a synperiplanar conformation.

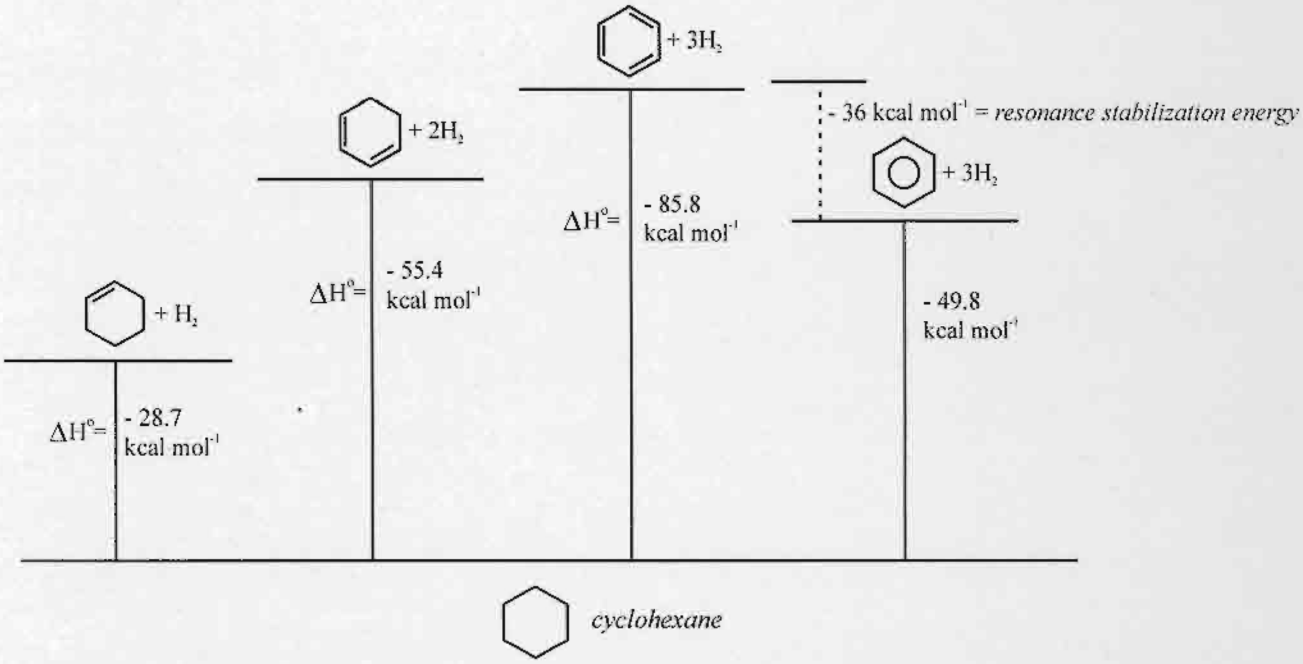


Fig A: Comparison of heat of hydrogenation of cyclohexene, cyclohexadiene, cyclohexatriene (hypothetical) and benzene. (All give same product-cyclohexane, on hydrogenation)

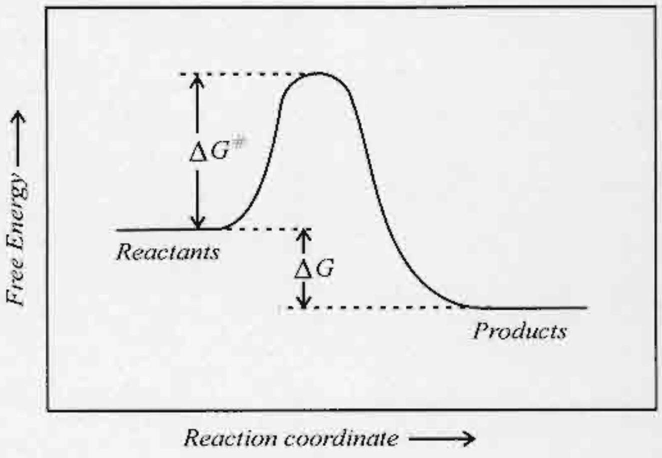


Fig B: A typical reaction profile

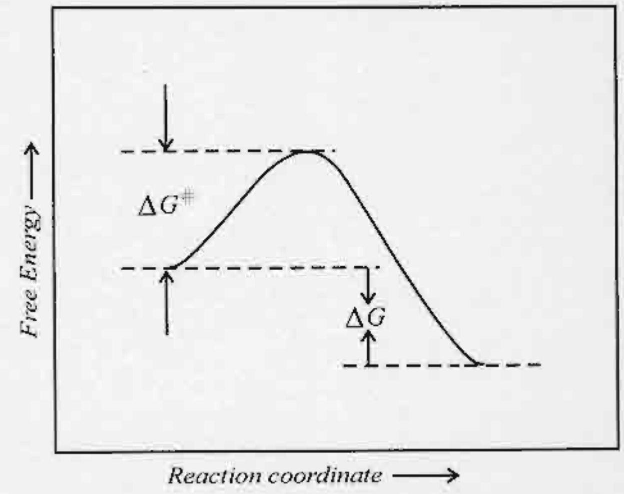


Fig C(i): A fast exergonic reaction

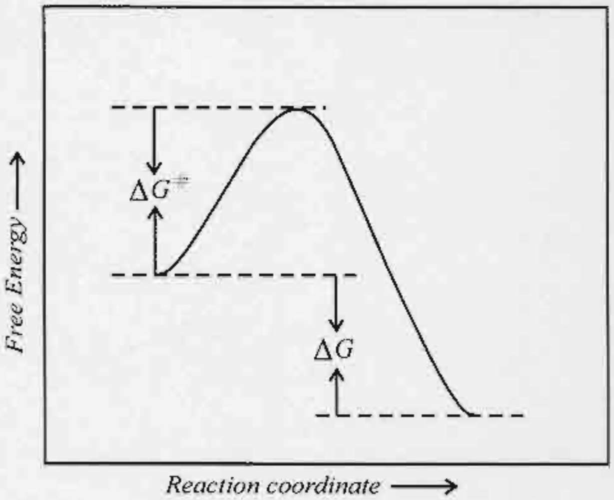


Fig C(ii): A slow exergonic reaction

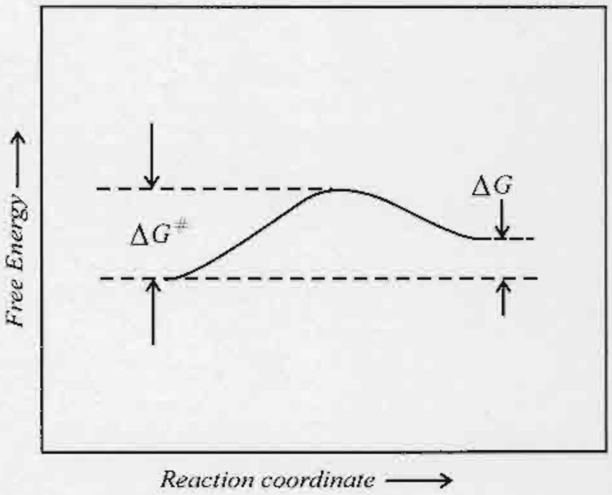


Fig C(iii): A fast endergonic reaction

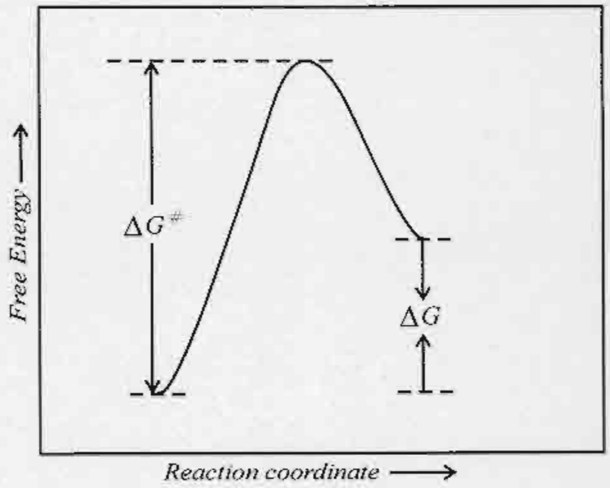


Fig C(iv): A slow endergonic reaction

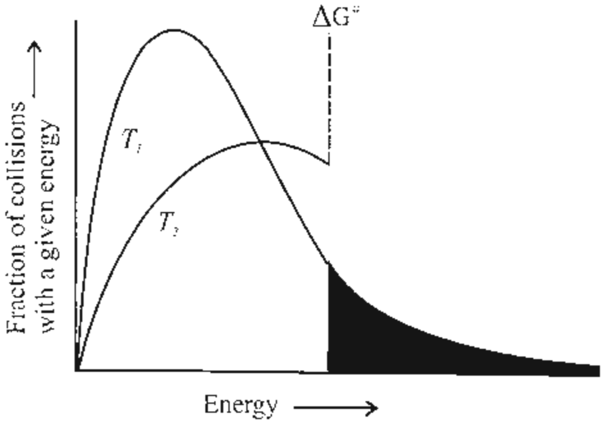


Fig D: Distribution of energy among molecules at temperature T_1 and T_2.

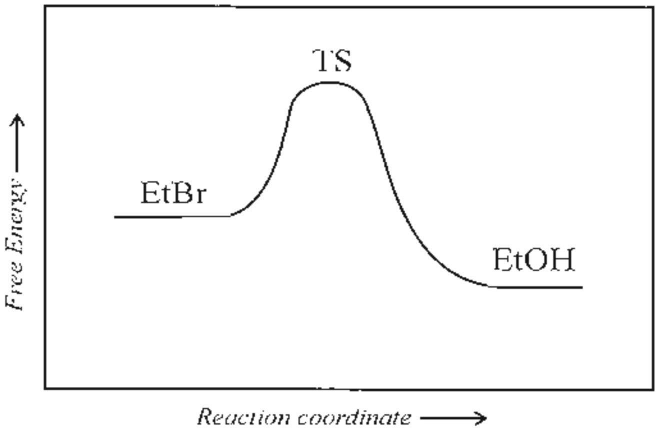


Fig E: Reaction profile of substitution reaction of ethyl bromide by hydroxide ion.

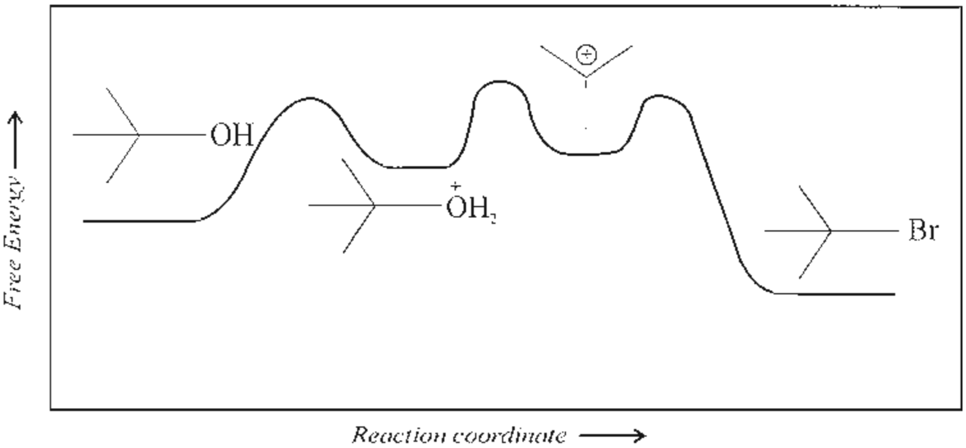


Fig F: Reaction profile of a multi step reaction: reaction of t-butyne alcohol with HBr. Each local energy minimum corresponds to an intermediate

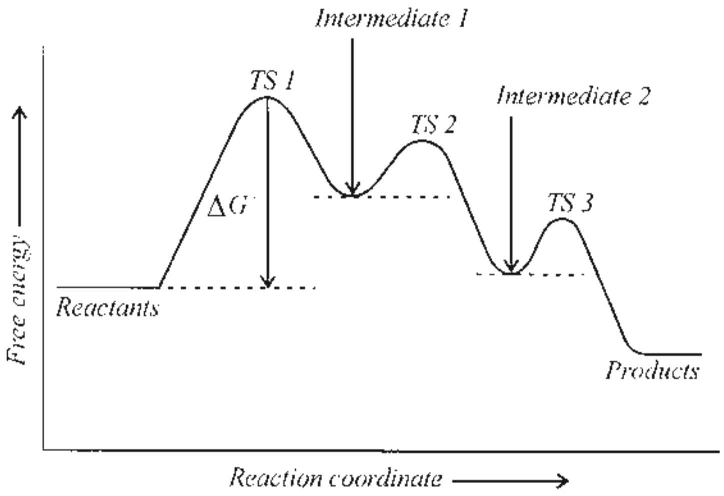


Fig.G: Multistep reaction involving T.S. of varying energies

The conversion of the reactants to Intermediate 1 is the rate-determining step

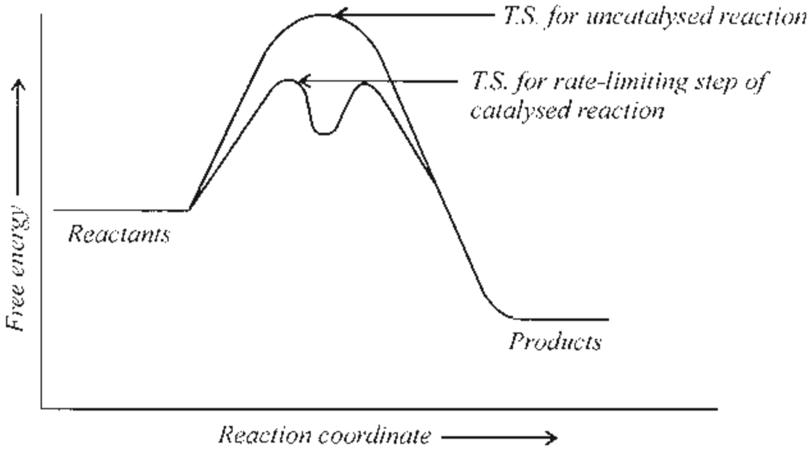


Fig. H: Effect of catalyst on rate of reaction

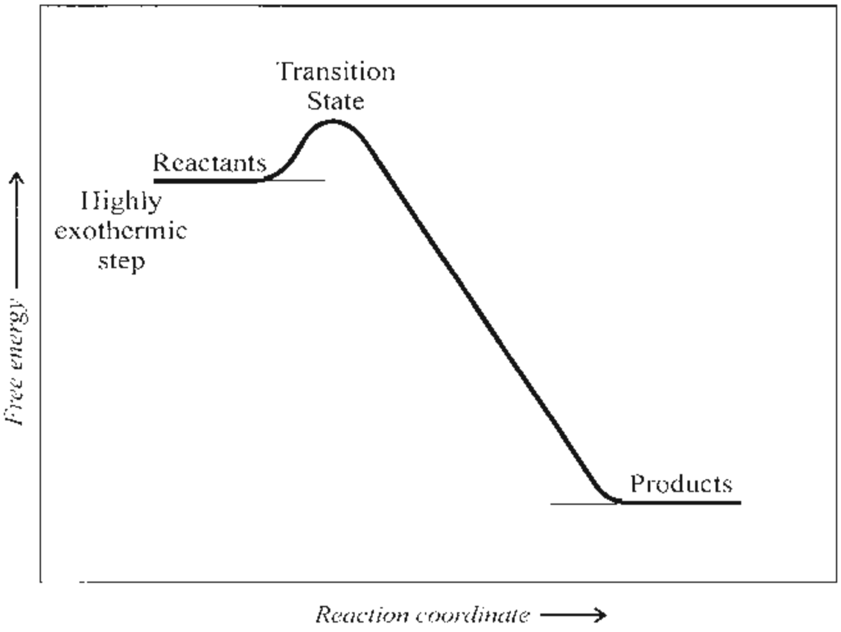


Fig. I: Energy diagram for highly exothermic step of reaction

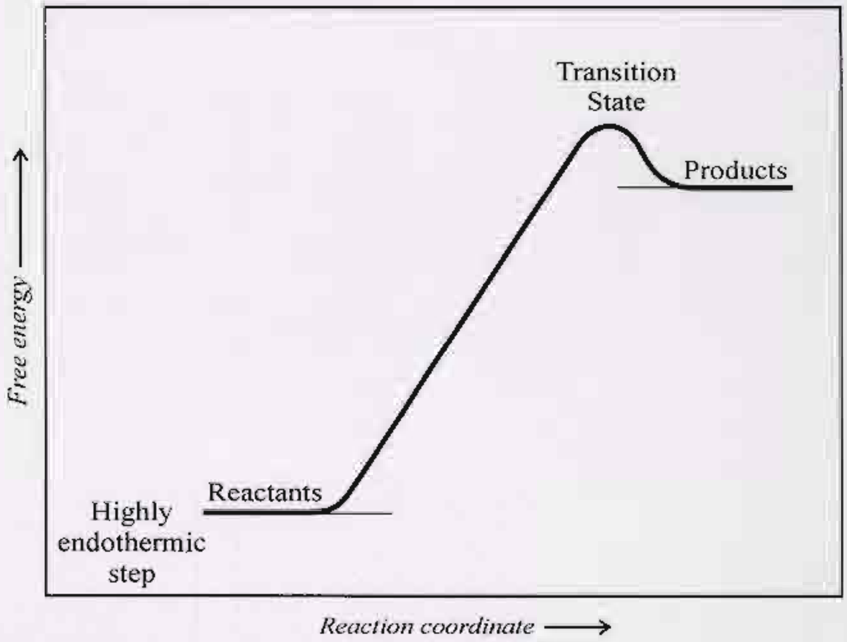


Fig. J: Energy diagram for highly endothermic step of reaction

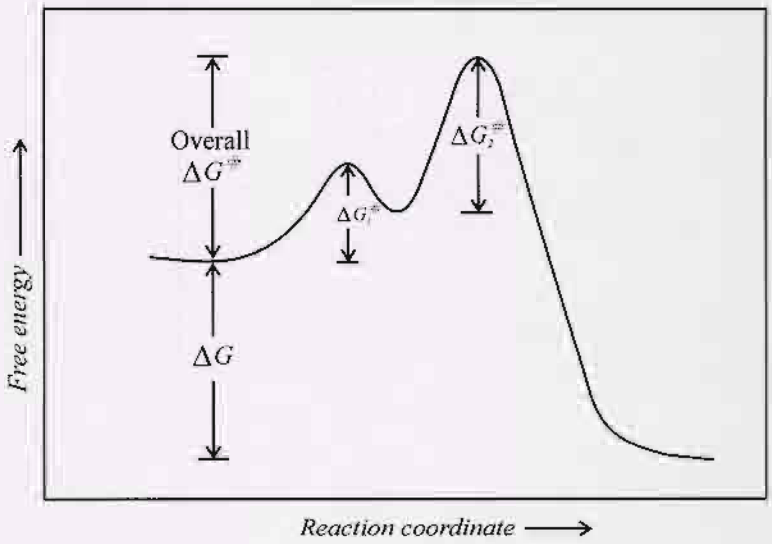


Fig. K: Reaction profile for a two step reaction. $\Delta G_1^{\ddagger}$ *and* $\Delta G_2^{\ddagger}$ *are free energy of activation for first and second step respectively.* $\Delta G_1^{\ddagger} < \Delta G_2^{\ddagger}$

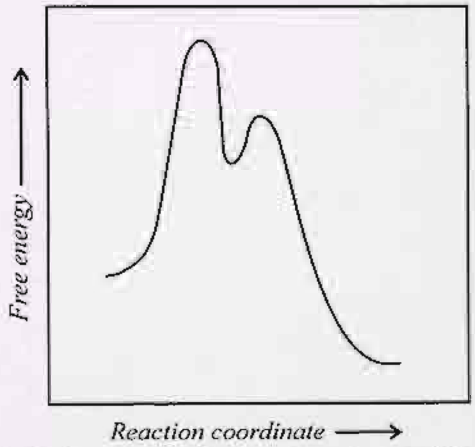


Fig. L: Reaction profile for a two step reaction with fist peak higher than second peak