

2.

BASIC CONCEPTS

2.1 ATOMIC ORBITALS

An **atomic orbital** (A O) is a region in space around the nucleus of an atom in which the probability of finding an electron is maximum. Each orbital has a definite energy associated with it. An atomic orbital surrounds a single nucleus. *s*, *p*, *d* and *f* are atomic orbitals. An orbital can contain maximum of two electrons and only if they have opposite spins (Pauli exclusion principle).

According to the modern theory, electron is believed to have wave properties as well as properties of a particle. Due to this dual nature of electron, it is impossible to determine accurately both the momentum and the position of an electron simultaneously (Heisenberg uncertainty principle). Thus we must use a statistical approach and speak of the probability of finding an electron within specified regions in space.

With the emergence of wave mechanics, the idea of an electron particle is replaced by the concept of the electron wave. In 1926 Erwin Schrodinger developed a **wave equation** which relates the energy of a system to the wave motion. For a one-electron system, the equation is written as;

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

Where *m* is the mass of the electron, *E* is its total energy, *h* is Planck's constant and Ψ is its wave function of the spatial coordinates, *x*, *y* and *z*. The wave function, ψ (Greek letter "psi") is such that $\psi(x, y, z)$ represents the amplitude of the electron wave at various points in space. When the value of a wave function, Ψ is calculated for a particular point in space relative to the nucleus, its value may be a positive number or a negative number (or zero). The wave function Ψ is plus (+) in crests and minus (-) in troughs. At the nucleus it is zero; these places are called **nodes**. The signs are sometimes called **phase signs**.

The wave function, Ψ , by itself has no physical significance. The position of the electron cannot be precisely located at any instant but the probability distribution for its location can be calculated from the wave function, Ψ , by squaring it. The probability that the electron is found in a given small volume element *dV* at the position (*x*, *y*, *z*) is equal to the square of the wave function multiplied by the magnitude of the volume element.

$$\text{Probability} = \psi^2(x, y, z) dV$$

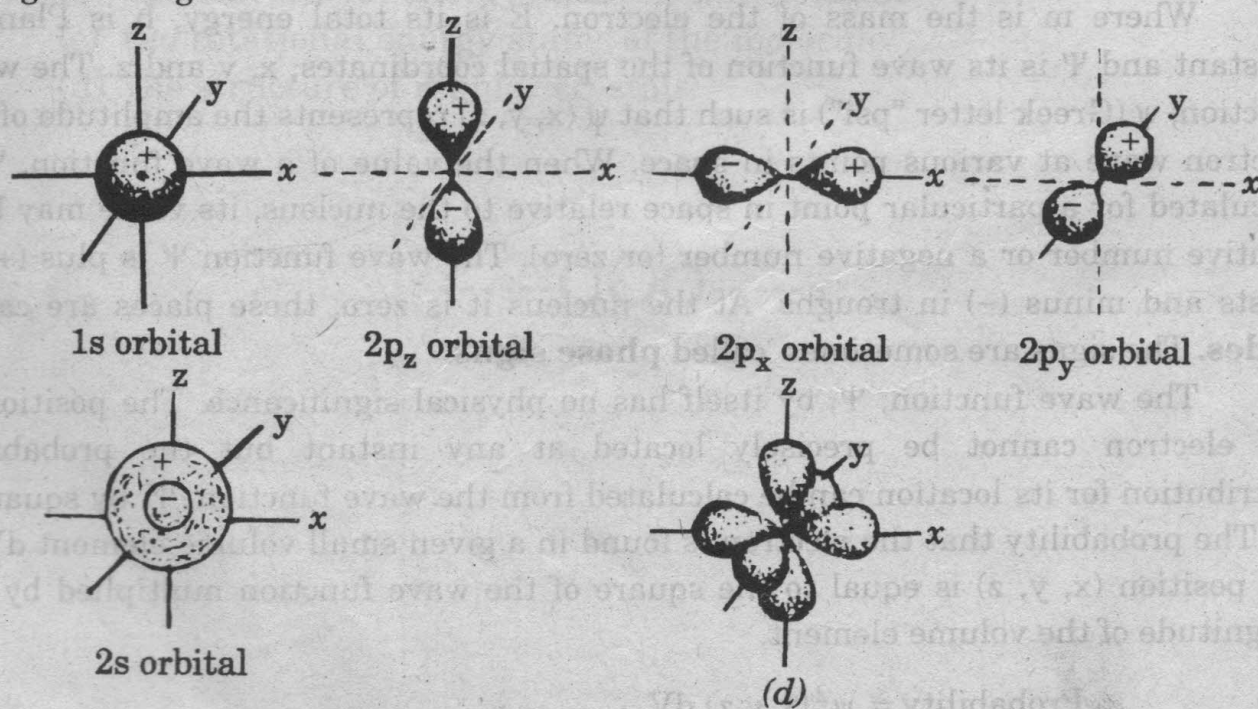
The greater the value of ψ^2 in a unit volume of space, the greater the probability of finding the electron in that volume.

The Schrodinger wave equation is a second order differential equation

and therefore, has a large number of possible solutions. Each of these solutions is associated with a set of numbers, called **quantum numbers**, that describe the energies of electrons in atoms. Solutions of the Schrodinger wave equation also give information about the shapes and orientations of the atomic orbitals, which are directly related to the quantum numbers. These quantum numbers can be used to define the allowed orbitals and to describe the behaviour of an electron in an orbital.

Shape of the atomic orbitals

The *s* orbital is a sphere around the nucleus. In other words, *s* orbital is spherically symmetrical about the nucleus. Both 1*s* and 2*s* orbitals are spheres, but 2*s* orbital is bigger in size and has a spherical node, since 1*s* orbital is present between the nucleus and the 2*s* orbital. In the inner portion of the 2*s* orbital, ψ_{2s} is negative. A *p* orbital is dumb-bell shaped. Each *p* orbital consists of two lobes touching on opposite sides of the nucleus. There are three *p* orbitals of equal energies which are mutually perpendicular and are labeled p_x , p_y and p_z , because they are oriented along the *x*-, *y*- and *z*-axes, respectively. In a *p* orbital there is no chance of finding an electron at the nucleus and thus the nucleus is called a **node point**. The phase sign of the wave function, ψ_{2p} , is positive in one lobe and negative in the other. The 3*s* and 3*p* orbitals are similar in shape to the 2*s* and 2*p* orbitals but of higher energies.



Assemblage of three mutually perpendicular 2*p* orbitals.

Fig. 2.1 Shapes of some *s* and *p* orbitals.

The 3*d*, 4*d* and 5*f* orbitals have still higher energies and quite different

shapes and are not important for bond making in organic compounds.

Filling up of the Orbitals with Electrons

The orbitals are filled with electrons successively according to the following rules,

1. The Aufbau Principle. The orbitals are filled with electrons in the order of increasing energy; the orbitals of lowest energy are filled first. The lowest energy orbital is that which has lowest value of $n + l$. If two orbitals have the same value of $n + l$, then the lowest energy orbital is that which has the lower n value. The order of increasing energy orbitals in most neutral atoms is:

$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7d$ etc.

2. Pauli Exclusion Principle; An orbital can have a maximum of two electrons when their spins are opposite. This principle states, "No two electrons in an atom can have the same set of four identical quantum numbers".

3. Hund's Rule. When orbitals of equal energy are available, electrons occupy these singly and have parallel spins rather than in pairs. As a result, an atom tends to have as many unpaired electrons as possible. The arrangement of electrons in various atoms is shown below:

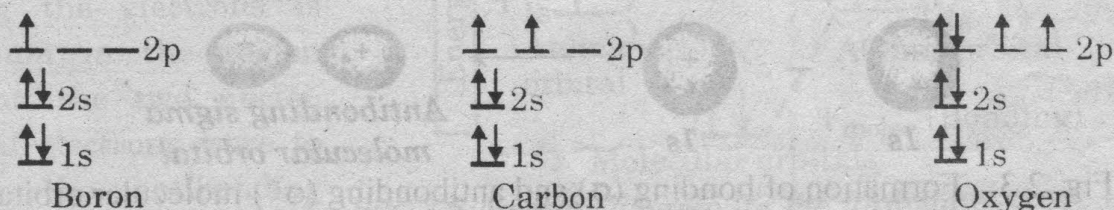


Fig. 2.2 Electronic configuration of some elements

According to Hund's rule, the number of unpaired electrons in the atom of an element is the valency of that element. Carbon has two unpaired electrons and should be divalent, but carbon is tetravalent in most of its compounds. This discrepancy had been resolved by the concept of orbital hybridization.

2.2 MOLECULAR ORBITALS (COVALENT BOND FORMATION)

A covalent bond forms by overlap of two partially filled atomic orbitals, one from each atom, is called a **molecular orbital** (MO), which embraces both atoms. The interaction of two atomic orbitals actually creates two molecular orbitals.

When atomic orbitals combine to form molecular orbitals, **the number of molecular orbitals that result always equals the number of atomic orbitals that combine**. Like an atomic orbital, a molecular orbital can contain a maximum of two spin paired electrons.

A covalent bond is formed between two atoms, when the two atoms come so close that a partially filled atomic orbital of one overlaps with a partially filled atomic orbital of the other. The two overlapping atomic orbitals lose their identities and linearly combine to produce two molecular orbitals. *Orbitals which have buried in them two or more atomic nuclei are called molecular orbitals.*

A molecular orbital which is formed by the atomic orbitals of the same phase sign overlap, and has a lower energy (greater stability) than the individual atomic orbitals is called a **bonding molecular orbital**, whereas a molecular orbital which is formed by the atomic orbitals of opposite sign overlap and has a higher energy (less stability) than the individual atomic orbitals is called an **antibonding molecular orbital**. A bonding orbital which is symmetrical about a line joining the two atomic nuclei is called a **sigma (σ) orbital** and the bond is called σ bond. The corresponding antibonding molecular orbital is called a sigma star (σ^*) orbital. The imaginary line joining the nuclei of the bonding atoms is the **bond axis, whose length is the bond length**. These molecular orbitals are filled with available electrons according to the same principles which are applied for filling atomic orbitals.

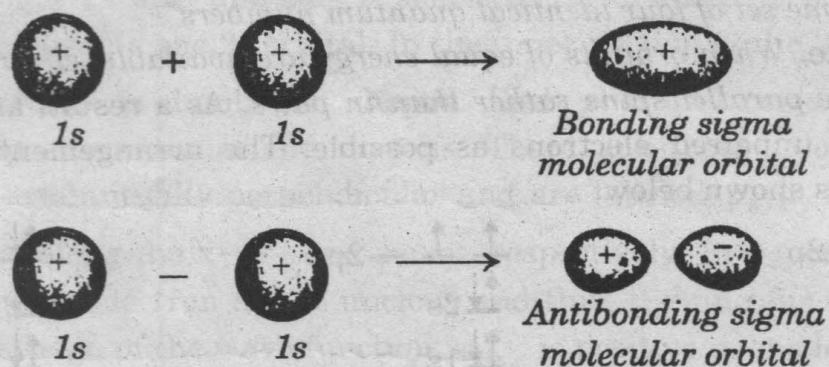


Fig. 2.3 Formation of bonding (σ) and antibonding (σ^*) molecular orbitals.

"A molecular orbital which is symmetrical about a line joining the two nuclei and is occupied by a pair of electrons is called a sigma (σ) molecular orbital and the linkage thus established is called **sigma bond**."

Consider the **formation of hydrogen molecule** from two hydrogen atoms. When two hydrogen atoms come close enough so that their $1s$ orbitals overlap, the two overlapping atomic orbitals linearly combine to form two molecular orbitals; a σ orbital and a σ^* orbital (fig. 2.4) (Two plus signs means that the two orbitals are in the same phase and can overlap, while plus and minus signs show that the two orbitals are out of phase and therefore cannot overlap).

The two $1s$ electrons from the hydrogen atoms fill the low energy σ

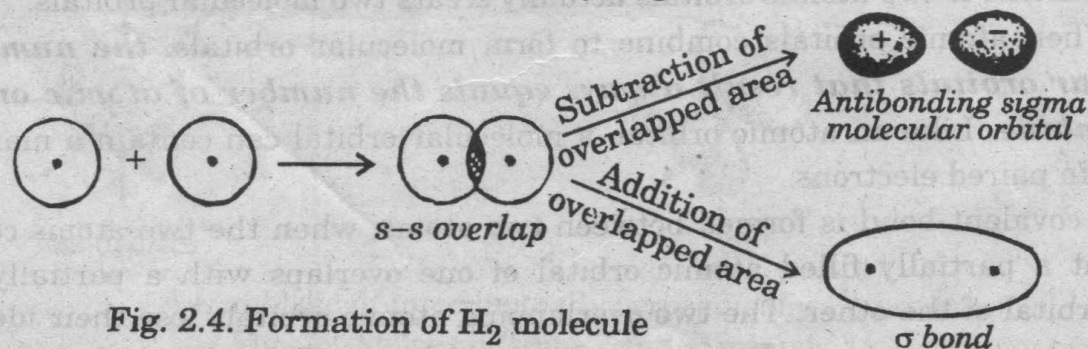


Fig. 2.4. Formation of H_2 molecule

orbital and have paired spins ($\downarrow\uparrow$). The high energy σ^* remains empty. In the σ orbital the probability of finding the electron pair is maximum in the region between

the two nuclei. Each of the two electrons occupying the σ orbital is attracted by both the atomic nuclei. Before the formation of H_2 molecule, each electron was attracted by only one nucleus.

The attractive force of the two nuclei for the two electrons in the σ orbital is more than offsets the repulsive force acting between the two nuclei and between the two electrons. This extra attractive force lowers the energy of the system (H_2 molecule). Thus 436 kJ/mol of energy is released when two hydrogen atoms combine to form a hydrogen molecule. This 436 kJ/mol is called the bond energy of H-H bond.



The two atomic nuclei are therefore held together by the electron pair of the σ orbital. The two electrons in the σ orbital are called σ electrons and the resulting bond is called σ bond.

In an antibonding molecular orbital, i.e., σ^* orbital, the probability of finding the electrons is minimum in the region between the two nuclei. Thus if electrons were to occupy the antibonding orbital, the electron would

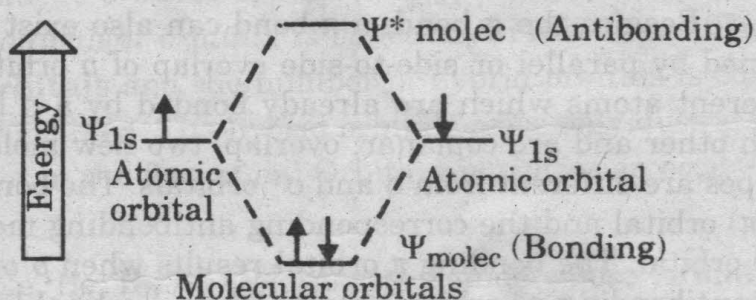


Fig. 2.5 Energy diagram for the formation of H_2 molecule

avoid the region between the nuclei. Since the repulsive forces (between the two nuclei and between the two electrons) would be greater than the attractive forces of the two nuclei for the two electrons and thus the molecule would be unstable.

When two atoms approach each other, the nuclei of two approaching orbitals must be at an optimum or equilibrium distance to form the lowest energy (stable) molecule. In the H_2 molecule, the two nuclei are 0.074 nm apart. This distance is called the bond length.

From the above discussion it is obvious why a two electron covalent bond is specially stable. If there are three or four electrons available, the extra electrons will occupy the antibonding σ^* orbital which will make the system unstable. Similarly, a one electron σ bond (i.e., a single electron in the σ orbital) will not be as strong as a two electron σ bond because the electron bond will be relatively weaker in the former case.

A σ bond is also formed between two atoms when a p orbital of one atom overlaps with s orbital of the other ($s - p$ overlap) or when a p orbital of one atom overlaps with a p orbital of the other ($p - p$ overlap), provided the axes of the two overlapping atomic orbitals form a straight line and have the same phase signs.

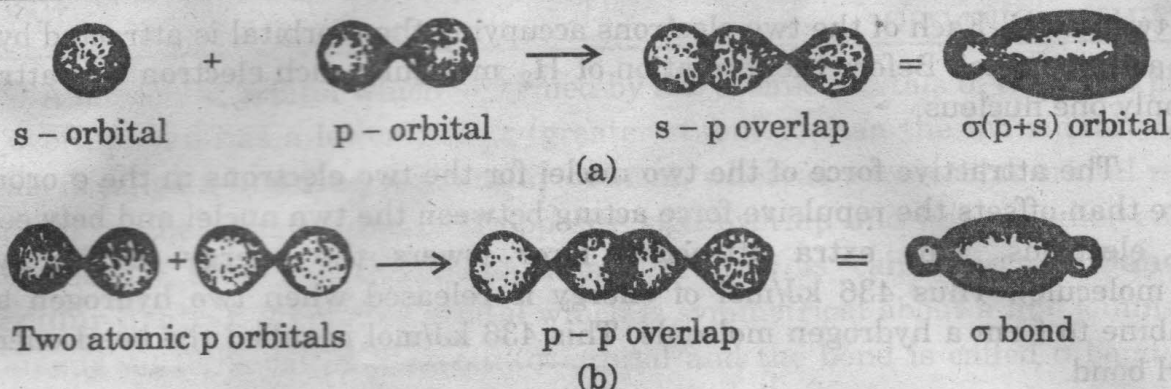


Fig. 2.6. (a) s - p overlap (b) p - p overlap

Molecular orbitals may be formed by the overlap of any kind of atomic orbitals (s , p or d) whether they are same or different, but the two lobes that overlap must have the same sign. However the extent of overlap depends upon the atomic orbitals involved.

Pi (π) Bond

Besides the σ bond, a π bond can also exist between two atoms. A π bond is formed by parallel or side-to-side overlap of p orbitals. When two p orbitals on two different atoms which are already bonded by a σ bond, have their axes parallel to each other and are coplanar, overlap, two new molecular orbitals are formed whose shapes are different from σ and σ^* orbitals. The bonding molecular orbital is called a pi (π) orbital and the corresponding antibonding molecular orbital is called a pi star (π^*) orbital. The bonding π orbital results when p orbital lobes of same sign overlap; the antibonding π^* orbital results when p orbital lobes of opposite sign overlap. The π orbital has two regions of electrons density above and below the plane containing the two nuclei and this plane is a nodal plane (plane of no electron density) for π orbitals. The two electrons from the two overlapping p orbitals fill the low energy π orbital and are called π electrons. The resultant bond is called a π bond. The π bond is not as strong as the σ bond, because of a relatively small overlap in the former case. This is why, whenever possible, the orbitals will overlap in the σ manner to allow for maximum overlap of atomic orbital. The antibonding π^* orbital is of higher energy and it is not occupied by electrons when the molecule is in the ground state. A π^* orbital has two nodal planes, one passing between two atoms and the other perpendicular to it.

"A molecular orbital formed by the side-wise overlap of two half-filled orbitals and having one and only one nodal plane containing the nuclear axis is called π molecular orbital (π MO)."

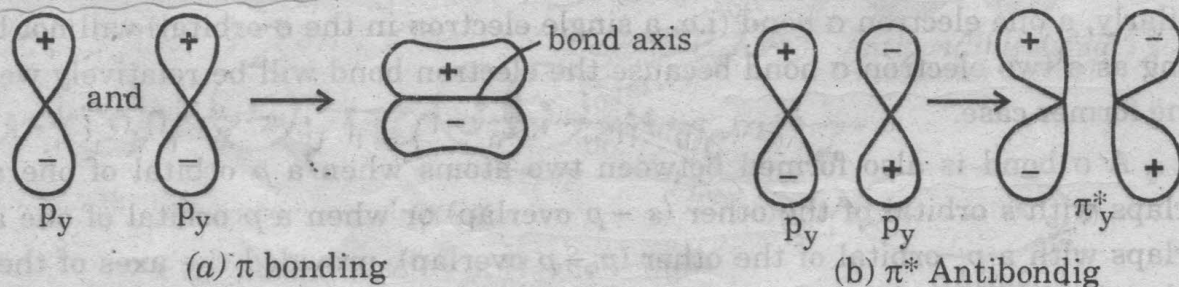


Fig. 2.7. The interaction of p orbitals to form π and π^* orbitals

Difference between sigma and pi bonds

Sigma bond	Pi bond
1. It is formed by head - to head overlap of atomic orbitals.	1. It is formed by lateral (sidewise) overlap of p orbitals (or p or d orbitals).
2. It has a single region of electron density between the two nuclei.	2. It has two regions of electron density above and below the nuclei.
3. Rotation of atoms about a σ bond occurs freely.	3. Rotation of atoms is not possible around a π bond.
4. It has lower energy.	4. It has higher energy.
5. Only one bond can exist between two atoms.	5. One or two bonds can exist between two atoms.
6. The overlap is more effective.	6. The overlap is not as effective as in σ bond overlap.

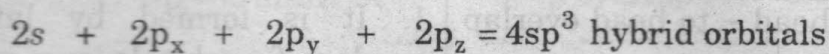
2.3 Hybridization of Atomic Orbitals.

The process of mixing of atomic orbitals of different types (*s, p, d, etc*) of the same atom to give a set of new equivalent orbitals is called **hybridization**. These new orbitals are called **hybrid orbitals** and the number of hybrid orbitals is equal to the number of atomic orbitals combined. The hybrid orbitals arise only during the process of bonding and do not exist in the free atom. Orbital hybridization occurs in the excited state.

Many elements, for example, Be, B and C, form compounds whose formation cannot be explained on the basis of the configuration of the elements in the ground state. However, a satisfactory description of compounds of these elements can be obtained through an orbital hybridization approach. The atomic orbitals of carbon can be hybridized in three different ways depending upon the number of atoms bonded to the carbon atom.

The electronic configuration of carbon in its ground or atomic state is $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$. It has only two unpaired electrons (partially filled orbitals) which can form only two covalent bonds, but carbon forms four bonds in the majority of its compounds. Its tetravalency can be explained by assuming that an electron from the $2s$ orbital is promoted to an empty $2p_z$ orbital giving the excited state a configuration $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$. In its excited state, carbon can form four bonds but these would not be equivalent. Three *p*-orbitals would form the bonds along the three mutually perpendicular axes, whereas the fourth bond arising from $2s$ orbital would be non-directional because *s* orbitals are spherically symmetrical. This shows that two different types of C-H bonds are involved in the formation of CH_4 molecule. In actual practice, all the four bonds in CH_4 are equivalent with a bond angle of 109.5° . This has been explained by the process of hybridization in which $2s$

and three $2p$ orbitals (p_x, p_y and p_z) in the excited state are mixed to form a set of four equivalent hybrid orbitals.



The process of combining the s and the three p orbitals to get four sp^3 orbitals is called **sp^3 hybridization**. The symbol sp^3 signifies that each sp^3 orbital is made up of s and p orbitals in the ratio of 1:3. The sp^3 orbitals are directed from the center of a regular tetrahedron to its four corners, making an angle of 109.5° with each other. The sp^3 hybridization is therefore, also called **tetrahedral hybridization**. These sp^3 orbitals are non-coplanar (do not lie in the same plane). The small lobe is often omitted when depicting hybrid orbitals.

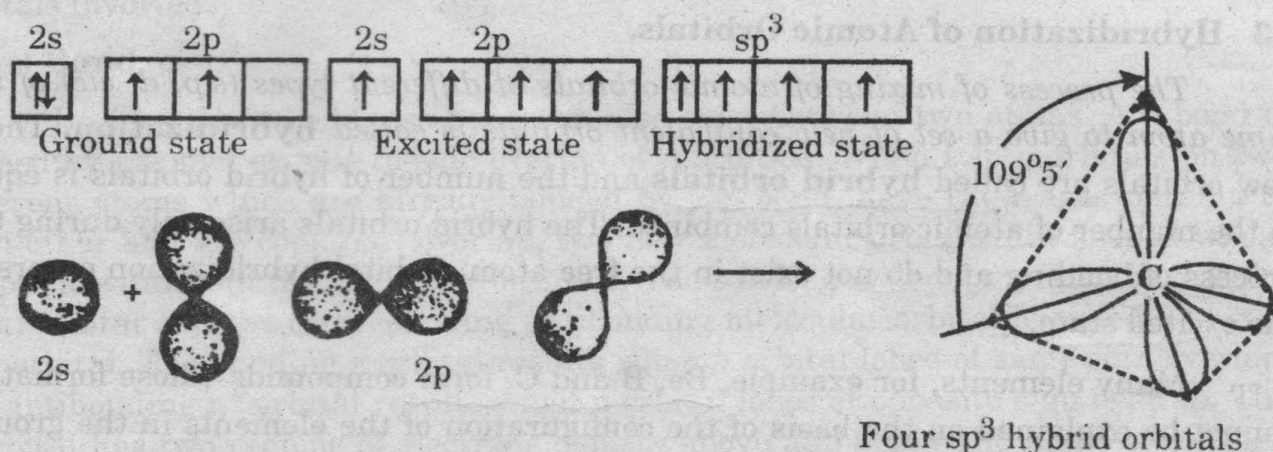


Fig. 2.8 Hybridization of s and three p orbitals to form $4sp^3$ hybrid orbitals.

The methane molecule is formed by the overlap of four sp^3 orbitals of carbon with $1s$ orbitals of four hydrogen atoms. The methane molecule contains four σ bonds, each due to sp^3-s overlap and each H-C-H bond angle = 109.5° (tetrahedral). The sp^3 hybridization occurs when carbon is bonded to four other atoms.

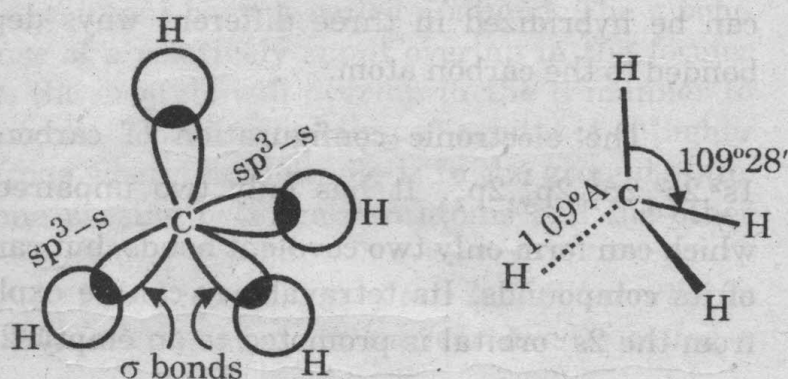


Fig. 2.9 Bonding in methane

The promotion of an electron from the $2s$ to a $2p$ orbital requires energy 406 kJ mol^{-1} , but by doing this carbon forms four covalent bonds instead of two bonds and releases energy 887 kJ mol^{-1} . The formation of two additional bonds releases energy more than compensate for that required to excite the electron.

2.4 Multiple (localized) Bond: Trigonal and digonal Hybridization

Trigonal or sp^2 Hybridization. When carbon is bonded to only three other atoms as in ethene, C_2H_4 (one carbon and two H atoms), the $2s$ and two of the three $2p$

orbitals of each carbon atom are hybridized to give three equivalent sp^2 hybrid orbitals of each carbon, leaving the remaining $2p$ orbital unhybridized. Each sp^2 orbital is composed of s and p orbitals in a ratio of 1:2. These three sp^2

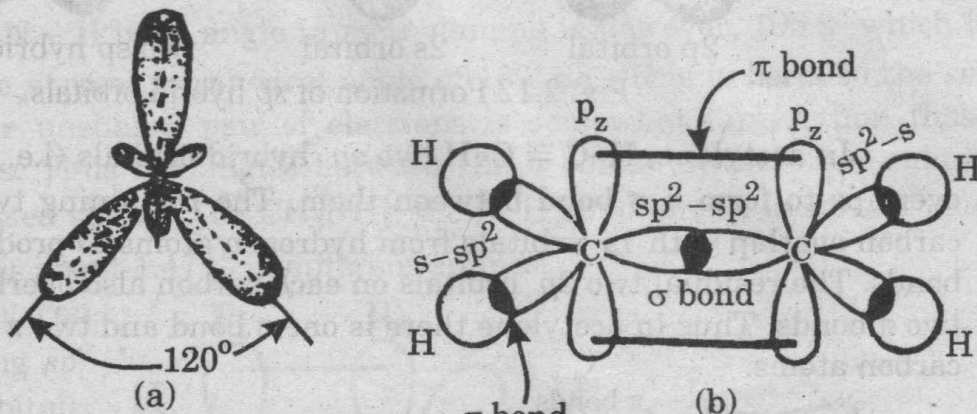


Fig. 2.10 (a) The $3sp^2$ orbitals (b) Bonding in ethene

orbitals lie in the same plane and make an angle 120° with each other, the unhybridized $2p$ orbital is perpendicular to this plane. The sp^2 hybridization is, therefore, also called trigonal hybridization.

In ethene, two sp^2 hybridized carbon atoms form a σ bond between them by the overlap of one sp^2 orbital from each carbon, the remaining two sp^2 orbitals of each carbon form σ bonds to four hydrogen through overlap with the $1s$ orbitals of the hydrogen atoms.

The two unhybridized p orbitals one on each carbon are perpendicular to the axis joining the two carbon nuclei and their axes are parallel. These two p orbitals are in a perfect position to overlap laterally (side-to-side) to

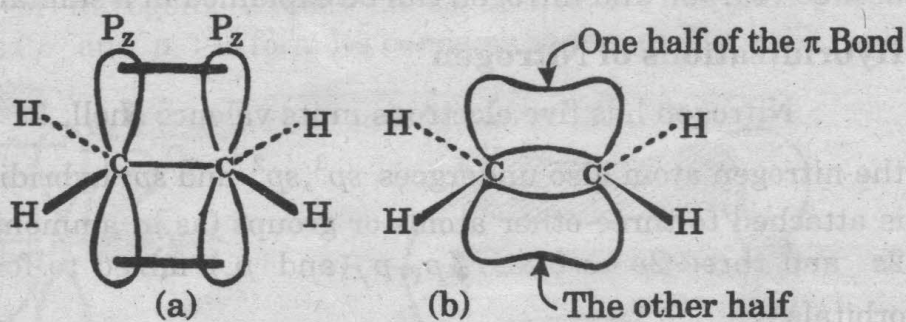


Fig. 2.11. Formation of π bond in ethene

generate two new molecular orbitals, i.e., a bonding π orbital and an antibonding π^* orbital. The electrons fill the low energy bonding π orbital leaving the high energy antibonding π^* orbital empty. This sidewise overlap of p orbitals results a pi (π) bond. Thus carbon - carbon double bond consists of two different kinds of bonds, a σ bond and a π bond. The π bond is more diffused and is weaker than that of σ bond.

sp hybridization

When each carbon atom (as in acetylene) is bonded to only two other atoms, the $2s$ orbital and one $2p$ orbital of carbon are hybridized to form $2sp$ hybrid orbitals, leaving two $2p$ orbitals as unhybridized. The axes of the two sp orbitals form a straight line. The angle between the two sp orbitals is thus 180° . The sp hybridization is, therefore, called linear or diagonal hybridization. The two

unhybridized $2p$ orbitals are perpendicular to the axis that passes through the centre of the $2sp$ orbitals.



Fig. 2.12 Formation of sp hybrid orbitals.

In acetylene, $\text{H}-\text{C}\equiv\text{C}-\text{H}$ two sp hybrid orbitals (i.e., one from each carbon) overlaps to form a σ bond between them. The remaining two sp orbitals at each carbon overlap with $1s$ orbitals from hydrogen atoms to produce two sigma (σ) C-H bonds. The residual two $2p$ orbitals on each carbon also overlap side-to-side to form two π bonds. Thus in acetylene there is one σ bond and two π bonds between the two carbon atoms.

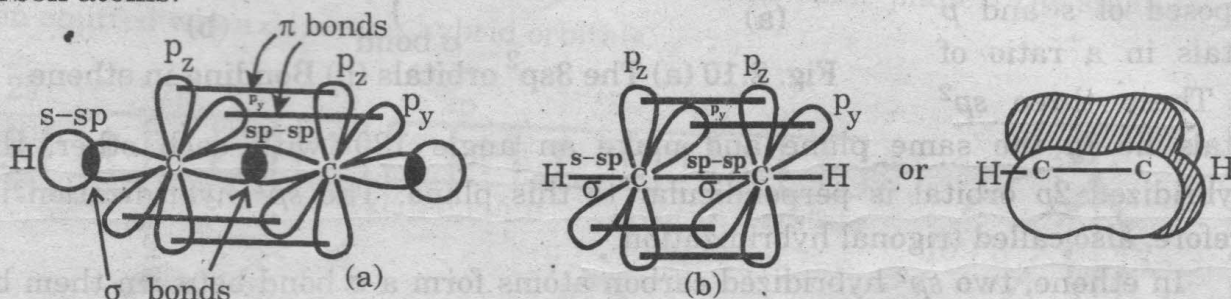
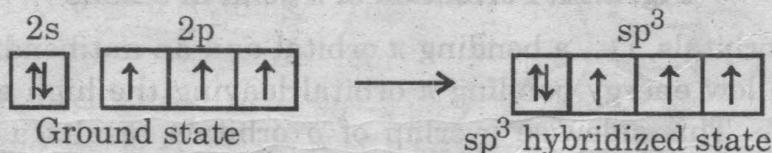


Fig. 2.13. (a) bonding in acetylene (b) Formation of two π bonds in acetylene

The formation of a double bond between carbon and oxygen and a triple bond between carbon and nitrogen can be explained in a similar manner.

Hybridizations of Nitrogen

Nitrogen has five electrons in its valence shell; $2s^2, 2p_x^1, 2p_y^1, 2p_z^1$. Like carbon, the nitrogen atom also undergoes sp^3, sp^2 and sp hybridization. Whenever nitrogen is attached to three other atoms or groups (as in ammonia and methylamine), then $2s$ and three $2p$ orbitals (p_x, p_y and p_z) mixed to form four equivalent hybrid orbitals.



The four sp^3 orbitals of nitrogen are directed towards the corners of a regular tetrahedron, just as the sp^3 orbitals of carbon do. Consider the formation of methylamine. In methylamine both nitrogen and carbon are sp^3 hybridized. One of the sp^3 orbitals of nitrogen is completely filled and cannot take part in bond formation. The C - N σ bond in CH_3NH_2 is formed by overlap of an sp^3 orbital of

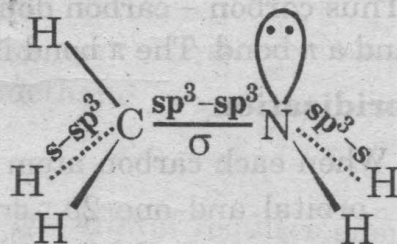


Fig. 2.14 Structure of methylamine

nitrogen and sp^3 orbital of carbon. Each N - H σ bond is formed by the overlap of an sp^3 orbital of N and s orbital of hydrogen. Each C - H σ bond is formed by overlap of an sp^3 orbital of carbon and s orbital of hydrogen. All bond angles are approximately tetrahedral. The H - N - H bond angle in methylamine is however, 105.9° which is slightly less than the normal tetrahedral angle of $109^\circ 28'$. This is because the sp^3 orbital containing the unshared pair of electrons is somewhat larger than those containing bond pairs. Thus the angles between the σ bonds on the other side of molecule are compressed slightly. In CH_3NH_2 the N-H bond length is 1.011\AA and the C-N bond length is about 1.47\AA in different amines.

Also, nitrogen can form compounds using sp^2 and sp hybrid orbitals. Whenever nitrogen is bonded to two other atoms or groups (as in imines or azo compounds), it uses two sp^2 hybrid orbitals plus the unhybridized p_z orbital to form its bonds.

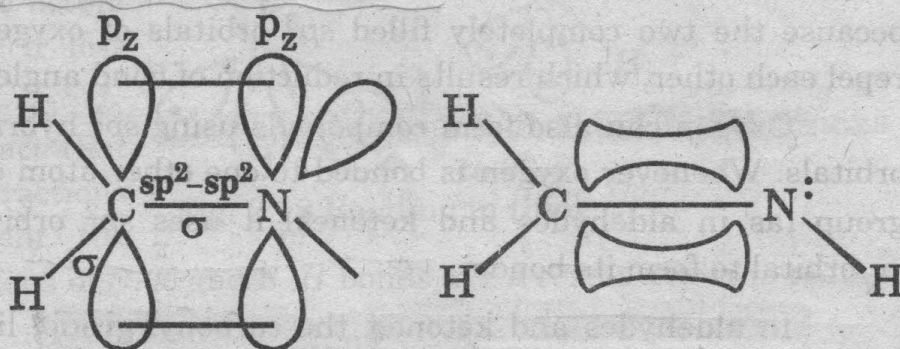


Fig. 2.15. Bonding in $\text{CH}_2 = \text{NH}$. Both C and N are sp^2 hybridized

Whenever nitrogen is bonded to only one other atom or group of atoms (as in H-CN, methyl cyanide, or nitrogen), it uses an sp hybrid orbital plus the two unhybridized $2p$ orbitals (p_y and p_z) to form its bonds as shown in Fig. 2.17.

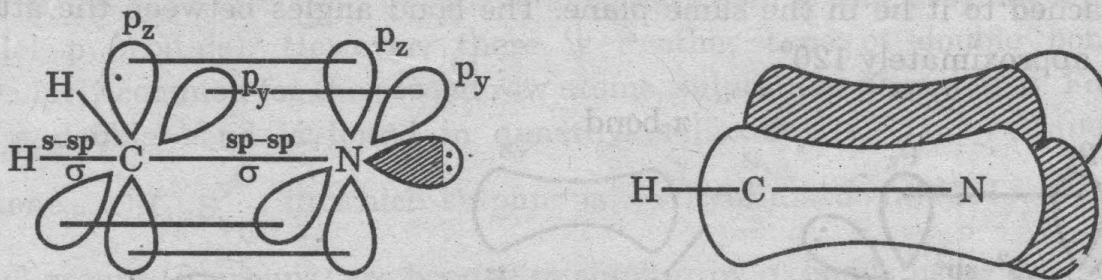
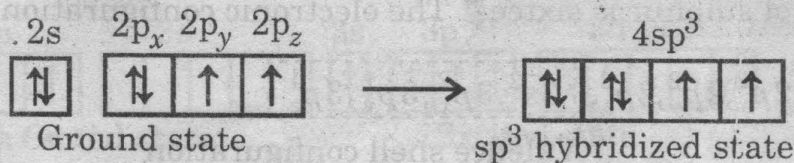


Fig. 2.16 Bonding in hydrogen cyanide, $\text{H}-\text{C} \equiv \text{N}$

Hybridizations of Oxygen

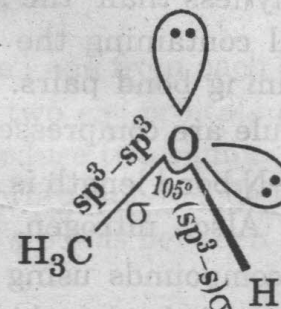
Oxygen has six electrons in its valence shell; $2s^2, 2p_x^2, 2p_y^1, 2p_z^1$. Like carbon or nitrogen, the oxygen undergoes sp^3 and sp^2 hybridizations. Whenever oxygen is bonded to two other atoms or groups (as in water, ethers, or alcohols or phenols), then $2s$ and three $2p$ orbitals (p_x, p_y and p_z) mix to form $4sp^3$ equivalent hybrid orbitals.



The four sp^3 hybrid orbitals of oxygen are directed towards the corners of a regular tetrahedron, just as the sp^3 orbitals of carbon or nitrogen.

In methanol both carbon and oxygen are sp^3 hybridized. Two of the sp^3 orbitals, are completely filled and cannot take part in bond formation.

The C–O bond in methanol is formed by overlap of an sp^3 orbital of carbon and an sp^3 orbital of oxygen. The O–H bond is formed by overlap of an sp^3 orbital of oxygen and s orbital of hydrogen. The C–O–H bond angle is 105° , which is less than the normal tetrahedron angle. This is because the two completely filled sp^3 orbitals of oxygen repel each other, which results in reduction of bond angle.



Structure of methanol

Oxygen can also form compounds using sp^2 hybrid orbitals. Whenever oxygen is bonded to one other atom or group (as in aldehydes and ketones) it uses sp^2 orbitals plus the unhybridized p_x orbital to form its bonds.

In aldehydes and ketones, the carbonyl group, like the C–C double bond of alkenes, is composed of one σ bond and one π bond. Both the carbon and oxygen are sp^2 hybridized. The σ bond is formed by the overlap of an sp^2 orbital of carbon and an sp^2 orbital of oxygen. The π bond is formed by the overlap of unhybridized p orbitals of the two atoms. The two unshared electrons pairs of oxygen occupy the sp^2 hybrid orbitals of oxygen. Because the carbonyl carbon is sp^2 hybridized, the three atoms attached to it lie in the same plane. The bond angles between the attached atoms are approximately 120° .

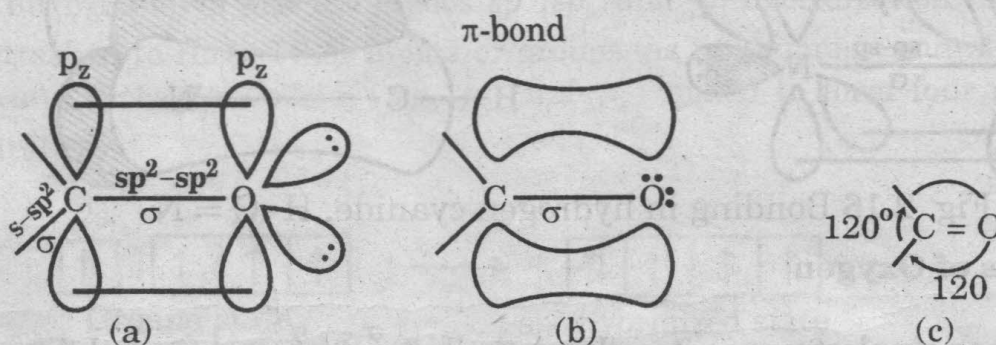
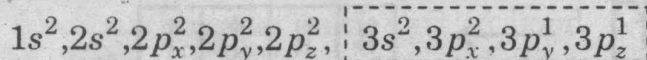


Fig. 2.17 Bonding in aldehydes and Ketones

Oxygen does not undergo sp hybridization.

Hybridization of Sulphur

Atomic number of sulphur is sixteen. The electronic configuration of sulphur is



Valence shell configuration

The sulphur undergoes sp^3 , sp^2 and sp^3d^2 hybridizations. In sp^3 hybridization, $3s$, $3p_x$, $3p_y$, $3p_z$ atomic orbitals of the valence shell of sulphur combine to form four sp^3 hybridized orbitals. Two of these hybridized orbitals contain two electrons each (the lone-pair electrons), while the other two are singly occupied. In the formation of thiol molecule RSH, one singly occupied sp^3 orbital of S-atom overlaps with the sp^3 orbital of R group to form a σ (sigma) bond. The second singly occupied sp^3 orbital of S overlaps with $1s$ orbital of H atom to form another σ bond.

Since in thiols sulphur is sp^3 hybridized, the $\angle R-S-H$ should be normally 109.5° . But the actual $\angle RSH$ is shrink to a much less value; 99.4° in case of CH_3SH . This is attributed to the fact that the lone pair-lone pair interactions overshadow to some extent the bond pair-bond pair repulsions of $S-R$ and $S-H$ bonds. As a result $\angle RSH$ is reduced considerably.

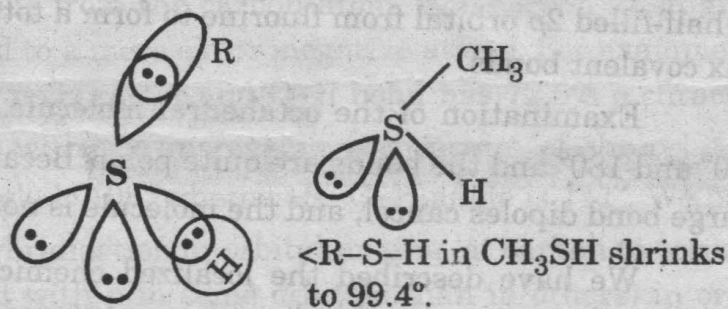


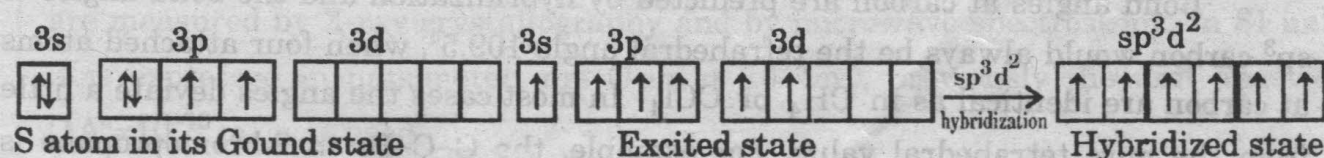
Fig. 2.18 Bonding in thiol

In dimethyl sulphide, $(CH_3)_2S$, sulphur is also sp^3 hybridized, two sp^3 orbitals are occupied by bonding pair of electrons and two by lone pairs.

π - $d\pi$ bonding (π_{d-p} bond)

In general, atoms of the second row of the periodic table do not form stable bonds of the type discussed in ethene and acetylene (π bonds formed by overlap of parallel p orbitals). However, there is another type of double bond that is particularly common for the second row atoms, sulphur and phosphorus. For example, such a double bond is found in dimethyl sulfoxide, $(CH_3)_2S=O$, and dimethyl sulphone, $(CH_3)_2S(=O)_2$, in which sulphur is sp^3 hybridized. In $(CH_3)_2S=O$, the two methyl groups (R groups) are bonded to sulphur by σ bonds using two sp^3 orbitals; the O atom is bonded to S by a σ bonds using third sp^3 orbital and a π_{d-p} bond (one of the sulphur electron is promoted to 3d orbital), a lone pair occupies the fourth sp^3 orbital of sulphur. In sulphones, there are four σ bonds to four sp^3 orbitals of sulphur and two π_{d-p} bonds, one to each oxygen atom.

When sulphur is bonded to six other atoms as in SF_6 , then S atom uses all the six valence shell electrons in forming six S-F σ bonds.



One s ($3s$), three p ($3p_x, 3p_y$ and $3p_z$) and two d ($3d$) orbitals of sulphur undergo sp^3d^2 hybridization to form six equal energy hybrid orbitals which are directed toward the corners of regular octahedron. Each hybrid orbital contain one electron. Each sp^3d^2 hybrid orbital is overlapped by a half-filled $2p$ orbital from fluorine to form a total of six covalent bonds.

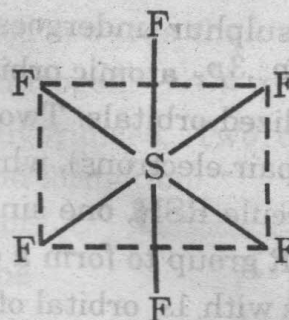


Fig. 2.19 Octahedral shape of SF_6 molecule

Examination of the octahedral molecule shows that $F-S-F$ bond angles are 90° and 180° and the bonds are quite polar. Because the molecule is symmetrical, the large bond dipoles cancel, and the molecule is nonpolar.

We have described the localized chemical bonds that are constituted from overlap of two atomic orbitals and are centered around two nuclei. *Bonds in which the bonding electrons are shared by only two nuclei in a molecule* are called **localized bonds**. A single covalent bond is called sigma (σ) bond. In multiple localized bonds both the σ and π electrons are confined between only two atoms (i.e; nuclei). In other words the electron density is concentrated between only two atoms. Compounds which have localized bonds can be described by a single Lewis structure. Also the predicted bond lengths, bond energies and dipole moments agree fairly with the experimentally observed values. Their chemical reactivity and spectral behaviour is also predictable.

Difference between an AO, a hybrid AO, a MO and a localized MO.

An atomic orbital is a region of space in an atom in which an electron may exist. A hybrid atomic orbital is mathematically fabricated (made up) from some number of atomic orbitals to explain equivalency of bonds. A molecular orbital is a region of space about the *entire molecule* capable of accommodating electrons. A localized molecular orbital is a region of space between a pair of bonded atoms in which the bonding electrons are assumed to be present.

2.5 Properties of Chemical Bonds

(i) Bond Angles

Bond angle is the mean angle formed by the two imaginary lines that connect the central atom with the two atoms on either side of it. For example, in the water molecule $H-O-H$, the bond angle is the angle formed by the lines representing the two $O-H$ bonds, and $H-O-H$ bond angle is 104.5° .

Bond angles at carbon are predicted by hybridization and the bond angles of sp^3 carbon would always be the tetrahedral angle 109.5° , when four attached atoms at carbon are identical as in CH_4 or CCl_4 . In most cases the angles deviate a little from the pure tetrahedral value. For example, the $C-C-Br$ in 2-bromopropane is

114.2° and $C-CH_2-C$ is 112° . Similarly, slight variations are generally found from the ideal values of 120° and 180° for sp^2 and sp carbon respectively. These deviations occur because of slightly different hybridization, i.e., a carbon bonded to four other atoms hybridizes one s and three p orbitals, but the $4sp^3$ hybrid orbitals thus formed are generally non-equivalent, each sp^3 orbital does not contain exactly 25% s and 75% p character. Because the four atoms have different electronegativities, each makes its own demand for electrons from the carbon atom. The carbon atom gives more p character when it is bonded to a more electronegative atoms. For example, in CH_3Cl , the $C-Cl$ bond has 77.5% p character and $C-H$ bond has 72.5% p character. The inter-orbital angle decreases with the increasing p characters of the orbitals. Therefore, in CH_3Cl , $H-C-Cl$ angle is 108° whereas $H-C-H$ angle is 111° . We have seen above, it is possible for the hybridization or orbital mixing, at carbon to occur in asymmetric fashion (more s mixed with p in some orbitals than in others) in order best to accommodate different substituents.

Atoms with unshared pairs of electrons follow the same hybridization pattern as asymmetrically substituted carbon. For example, an sp^3 hybridization scheme produces good agreement for the bond angles in H_2O and NH_3 . In these compounds, oxygen and nitrogen hybridize their $2s$ and $2p$ to form four sp^3 hybrid orbitals and then use only two (or three) of these for bonding with hydrogen, the others remaining occupied by unshared pairs. As we have seen above, an atom supplies more p character when it is bonded to more electronegative atoms. An unshared electron pair may be considered to be an "atom" of the lowest possible electronegativity. Consequently, the orbitals with the unshared pairs of electrons have more s character and the $O-H$ (or $H-N-H$) bond orbitals have more p character than pure sp^3 orbitals and the angles $H-O-H$ (or $H-N-H$) are slightly smaller than tetrahedral angle 109.5° . The observed $H-O-H$ bond angle in water is 104.5° and $H-N-H$ bond angle in ammonia is 107.2° . The oxygen with two lone pairs in water supplies more p character than the nitrogen with one lone pair in NH_3 , therefore, the bond angle in water is still smaller than in ammonia.

(ii) Bond Lengths

The mean distance between the centres of the nuclei of two bonded atoms is called bond length. The distance between the atoms of a bond does not remain constant since the atoms are always vibrating with respect to each other in a molecule; the measured bond distance is therefore an average value. Bond lengths are measured by X-ray crystallography and by microwave spectroscopy. In SI units it is expressed in nanometer, nm ($1nm = 10^{-9}m$), previously the unit angstrom ($1\text{\AA} = 10^{-10}m$) was used.

The bond length between two given atoms remains constant fairly in different molecules, the variation is less than 1%. In most of the compounds, the C-C single bond length is about 0.154 nm and C-H bond length is 0.108 nm. The C-C bond distance in $\text{H}_3\text{C}-\text{CH}_3$, $\text{CH}_3-\text{CH}_2-\text{CH}_3$, $\text{CH}_3-\text{CH}_2\text{Cl}$ are 0.154 nm, 0.154 nm and 0.155 nm respectively. Similarly, the C-Cl bond length is 0.175 nm in CCl_4 and 0.177 nm in CH_3-Cl . Deviations from the normal bond lengths give important information about the structure of compounds.

“One half of the bond length between two similar atoms is called the covalent radius of that atom.” For example, the covalent radius of carbon is 0.077 nm which is one half of the C-C bond length (0.154 nm). Similarly the covalent radii of chlorine (0.099 nm) and hydrogen (0.037 nm) are one-half respectively of the Cl-Cl (0.199 nm) and H-H (0.074 nm) bond lengths. *The covalent radii can be used to calculate the bond lengths between the unlike atoms which, in some cases, the bond lengths between unlike atoms are not equal to the sum of the covalent radii of the two bonded atoms. For example, the C-Cl bond length in $\text{H}_3\text{C}-\text{Cl}$ is 0.176 nm which is equal to the sum of the bond radii of carbon (0.077 nm) and chlorine (0.099 nm). Similarly the C-H bond distance in ethane is 0.109 nm. However in most cases, the bond lengths between unlike atoms are not equal to the sum of the covalent radii of the two bonded atoms. For example, the observed C-N bond length (in CH_3NH_2) is 0.147 nm, whereas the sum of the covalent radii of carbon and nitrogen is 0.151 nm. Similarly, the observed C-O bond length in ethanol is 0.141 nm, although the sum of the covalent radii carbon and oxygen is 0.150 nm. In general, the shrinkage in bond length becomes more and more marked as the difference between the electronegativities of the two bonded atoms increase.*

Bond length is also affected by nature of hybridization of the bonded atoms. A large fraction of s character means a shorter bond. The hybridization effect can be seen in a series of C-H bonds. The C-H bond lengths in C_2H_6 (C atom is sp^3), C_2H_4 (the C is sp^2) and C_2H_2 (the C is sp) are 0.110 nm, 0.107 nm and 0.106 nm respectively. This is because the hybrid orbital with increased s character is held more strongly by the nucleus.

A single bond is longer than a double bond, and a double bond is longer than a triple bond between the same two atoms. For example, the C-C bond length in C_2H_6 is 0.154 nm, while the C=C bond length in C_2H_4 is 0.134 nm and the $\text{C}\equiv\text{C}$ bond length in C_2H_2 is 0.120 nm. The shrinkage of the multiple bonds is due to the presence of extra π electrons between the two nuclei which exert additional attraction on the nuclei and thus nuclei come closer to each other.

Table 2.1 Bond lengths and Bond Energies

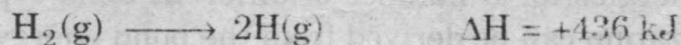
Bond	Bond length (nm)	Bond energy kJ/mole	Bond	Bond length (nm)	Bond energy kJ/mole
H - H	0.074	436	C - O	0.143	358
C - H	0.108	414	C = O	0.122	740
C - C	0.154	345	C - N	0.147	305
C = C	0.134	610	C = N	0.128	615
C \equiv C	0.120	835	C \equiv N	0.116	891
C - F	0.138	450	N - H	0.101	391
C - Cl	0.177	326	N - N	0.145	163
C - Br	0.194	276	N \equiv N	0.110	945
C - I	0.214	240	O - H	0.096	464
O - O	0.148	146	H - Cl	0.127	431
O = O	0.121	498	H - Br	0.141	365

(iii) Bond Energies

The energies required to break one mole of bonds in a substance in the gaseous state into atoms in the gaseous state is called bond energy. Energy is always required to break a chemical bond and is released when a bond is formed. The net energy that is released or absorbed in chemical reactions is due to the difference between the energies associated with the chemical bonds of the reactants and the products. The energy involved in a chemical reaction is known as *heat of reaction* and is measured in terms of enthalpy change, ΔH .

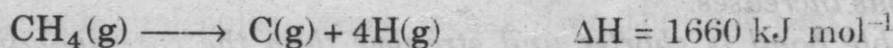
$$\Delta H_{\text{reaction}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

The bond energy is defined as enthalpy change (ΔH) when one mole of bonds is broken in the gaseous state". The SI units for bond energies are kilojoules per mole of bond (kJ/mol). Bond energies can be measured by calorimetry and spectroscopic methods. For example, for the reaction,

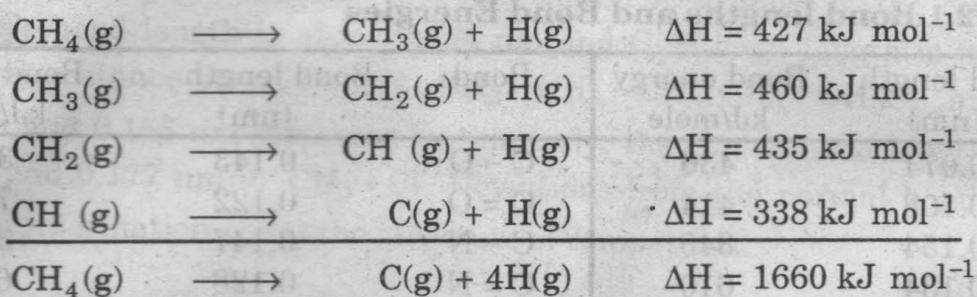


the bond energy of the H - H bond is 436 kJ/mole of bonds, which is called the bond **dissociation energy**.

Let us consider more complex molecules. For the reaction

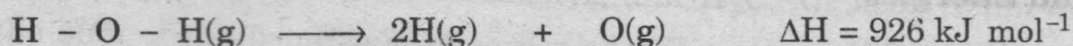


Since the four hydrogen atoms are identical, all the C - H bonds are identical in bond length and strength in methane molecule. However, the energies required to break the individual C-H bonds differ for successively broken bonds, as shown below.



$$\text{Average C - H bond energy} = \frac{\Delta\text{H}}{4} = \frac{1660}{4} = 415 \text{ kJ mol}^{-1}$$

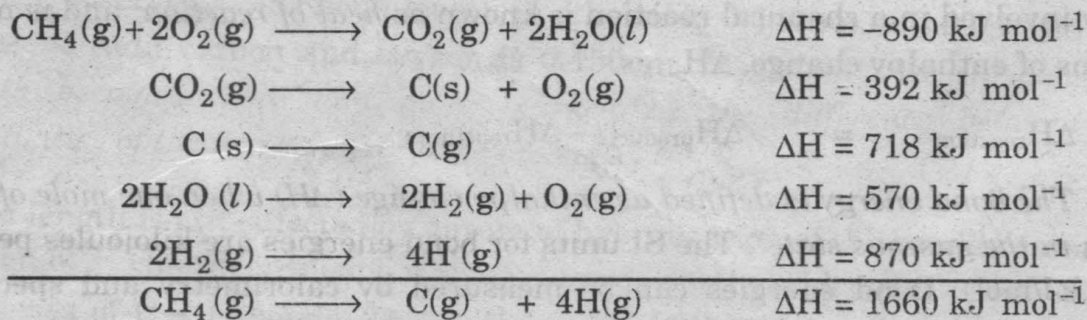
The average bond energy in methane is one fourth of the energy required to dissociate one mole of CH_4 into carbon and four hydrogen atoms. We do not try to measure the heat needed to break just one bond in a molecule with a number of bonds. Instead, we find the energy needed to break all of the bonds in the molecule and then divided by the number of bonds. This procedure gives us the average bond energy. We can define the average bond energy of the O - H bond in H_2O as follows:



Since there are two O - H bonds, the average bond energy is

$$\Delta\text{H}/2 = 926/2 = 463 \text{ kJ/mol.}$$

The ΔH values may be determined from the heats of atomization of compounds. More commonly ΔH values are calculated from the heats of combustion, making use of the Hess's law, as shown below:



The average C - H bond energy is therefore $1660/4 = 415 \text{ kJ/mol}$ at 25°C . Average values of bond energies for a number of different bond types are listed in table 2.1. Certain generalization can be derived from the bond energy data.

1. *There is a correlation between bond energy and bond distance. The stronger a chemical bond, the shorter the bond distance.*
2. *Bonds become weaker as we go down the periodic table, since bond distance increases as we go down the periodic table because the number of inner shells electrons increases.*
3. *A double bond is shorter and stronger than the corresponding single bond, and a triple bond, in turn, is shorter and stronger than the double bond.*

2.6 Ionic Character of Covalent Bonds (Polar and Nonpolar Covalent Bonds)

Covalent bonds are described as being either **polar** or **nonpolar** bonds. "A covalent bond between two identical atoms like H-H or Cl-Cl, in which the bonding

electron pair is equally attracted by both the bonded atoms is called a **Nonpolar Covalent Bond**". In other words, in nonpolar covalent bonds the electron density is symmetrically distributed around the two nuclei in the molecular orbital. Thus, we can generalize, that the covalent bonds in all *homonuclear diatomic molecules* must be nonpolar. However, when a covalent bond exists between two atoms of different electronegativities, the atom with higher electronegativity attracts the bonding electron pair more strongly than the less electronegative atom. As a result, the atom with higher electronegativity acquires a partial negative charge (δ^-) and the less electronegative atom acquires a partial positive charge (δ^+). Such a bond which appears to have positive end and a negative end is called a **polar covalent bond** or **partially ionic covalent bond**. e.g., $\text{H}^{\delta+} - \text{Cl}^{\delta-}$, $\text{H}_3\text{C}^{\delta+} - \text{Cl}^{\delta-}$ "A covalent bond between two unlike atoms in which there is an unsymmetrical distribution of electron density is called a **polar bond**." Consider, for example, the H - Cl bond. Since chlorine is more electronegative than hydrogen, the electron density in the molecular orbital would be higher around chlorine atom than around the hydrogen atom. Thus in the H - Cl molecule there will be a partial negative charge on chlorine and a partial positive charge on hydrogen. "The power of an atom in a molecule to attract electrons to itself is called *electronegativity*."

Polar covalent bonds may be thought of as being intermediate between pure (nonpolar) covalent bonds and pure ionic bonds. In fact, bond polarity is sometimes described in terms of *partial ionic character*, which usually increases with increasing difference in electronegativity between two bonded atoms. The amount of charge transferred from one atom to the other is a measure of the ionic character of the bond, and depends on the difference Δx between the electronegativity of the two atoms. If Δx is greater than about 2.0, the bond may be assumed to be almost ionic, e.g., Na^+Cl^- . If the electronegativity difference is less than 0.5, the amount of charge transferred is small and the bonding electrons are shared approximately equally between the two atoms. For intermediate values (0.5 to 2.0) of Δx , somewhat less than a full electronic charge is transferred, e.g., $\text{H}^{\delta+} - \text{Cl}^{\delta-}$, $\text{H}^{\delta+} - \text{Br}^{\delta-}$. The covalent bonds between H and Cl, H and Br are partially ionic covalent bonds.

The polarity of a bond tells us what kind of reactions can occur at the bond. Further the polarity of bond can make a molecule polar and thus affects its melting point, boiling point and solubility.

The electronegativity is related to ionization energy and electron affinity. The most widely used electronegative scale has been devised by Linus Pauling from bond energies of diatomic molecules, which is based on the fact that the bond energy $E_{\text{A-B}}$ between unlike atoms A-B is always greater than the arithmetic mean of the bond energies $E_{\text{A-A}}$ and $E_{\text{B-B}}$, because of the opposite partial charges on the two atoms of A-B bond, which attract each other and make the bond stronger, therefore, extra energy is required to break this A-B bond. The "extra" bond energy is directly

proportional to the difference in electronegativities of the two bonded atoms, which is related to the ionic character of the bond. If the value of electronegativity of one element is arbitrarily fixed (which is assigned 4.0 to fluorine, the most electronegative element), the electronegativity of another element can be obtained by using the formula

$$X_A - X_B = \sqrt{\frac{\Delta}{96.5}}$$

Where X_A and X_B are the electronegativities of the elements A and B respectively, Δ is the difference between the bond energy E_{A-B} and the mean energies E_{A-A} and E_{B-B} , and 96.5 is an arbitrary constant. For example, Δ for H - Cl is

$$\begin{aligned}\Delta \text{ for HCl} &= H_{\text{H-Cl}} - \frac{1}{2} (E_{\text{H-H}} + E_{\text{Cl-Cl}}) \\ &= 431 - \frac{1}{2} (435 + 243) = 92 \text{ kJ/mol}\end{aligned}$$

$$X_{\text{Cl}} - X_{\text{H}} = \sqrt{\frac{92}{96.5}} = 0.988 = 0.99$$

$$X_{\text{Cl}} = X_{\text{H}} + 0.99 = 2.1 + 0.99 = 3.09$$

Electronegativities values of some elements are given in table 2.2

Table 2.2 Electronegativity of some elements on the pauling Scale

Elements	Electronegativity	Elements	Electronegativity
Na	0.9	N	3.0
K	0.8	P	2.1
Si	1.9	F	4.0
C	2.5	Cl	3.1
S	2.5	Br	2.8
H	2.1	I	2.5
O	3.5	Mg	1.2

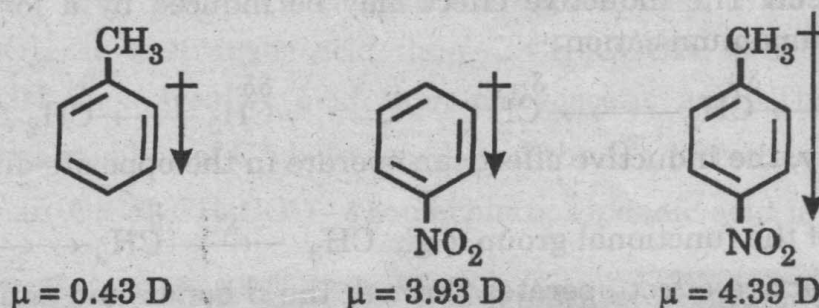
2.7 Dipole Moment

The separation of charge in a polar covalent bond creates a **dipole**. The word dipole means "two poles" and refers to the positive and negative poles or ends, that result from the separation of charge within the molecule. The polarity of a molecule is expressed quantitatively by its **dipole moment**, μ (Greek letter mu), which is a measure of the magnitude of the separated charges and the distance between them. The **dipole moment**, μ , is defined as the product of the magnitude of the charge, q , (at either end) and the distance, d , between the centres of gravity of the positive and negative charges.

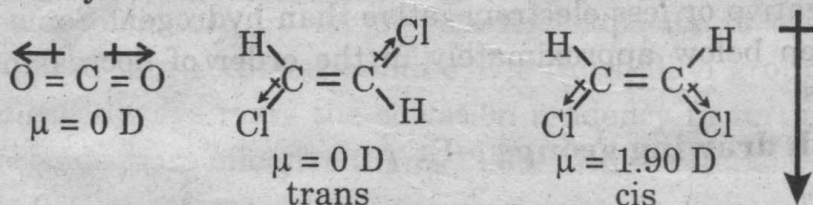
$$\mu = q \times d$$

The charges are of the order of 10^{-10} esu and distances are of the order of 10^{-8} cm; therefore, the usual magnitude of the dipole moment is of the order of

10^{-18} esu cm. For convenience this unit, 1×10^{-18} esu cm is defined as one **debye** and is abbreviated D. In SI units, dipole moments are measured in coulomb-meter (C.m). $1D = 3.34 \times 10^{-30}$ C.m. However, commonly unit used is Debye, D. Thus CH_3Cl which has a dipole moment = 1.87D. It is not possible to determine the individual bond moments within a molecule; we can only measure the *net dipole moment of the molecule, which is a vectorial sum of the individual bond moments which are directional*. The direction of the dipole moment is indicated by an arrow over a molecule pointing towards the negative pole. The values of the individual bond moments are roughly the same in all molecules, and therefore, can be used to calculate the expected dipole moments of the molecules. For example, the dipole moment of toluene is 0.43D and that of the nitrobenzene is 3.93D; the dipole moment of *p*-nitrotoluene is therefore expected to be 4.36 D. The actual value is 4.39D which is very close to the expected value.



Many molecules which have polar bonds do not exhibit dipole moment because the individual bond moments are so oriented that they cancel out one another. Any molecule that has a centre of symmetry do not exhibit dipole moment. For example, the bonds in the CO_2 molecule are polar, with dipoles directed towards the more electronegative O atoms. However, $\mu = 0$ for CO_2 molecule because the molecule is linear and the two bond moments which are equal and in opposite direction cancel out each other. Similarly, *trans*-1, 2-dichloroethylene does not exhibit any dipole moment although its *cis*-isomer has a dipole moment of 1.90D, since in *cis*-isomer the bond moments are so oriented so as to provide overall electrical dissymmetry.



Similarly, the dipole moment of CCl_4 , CH_4 , *p*-dinitrobenzene, etc., is zero and these molecules are nonpolar. In general, the dipole moment is the measure of the polarity of the molecule. *The greater the value of the dipole moment, the greater the polarity of the molecule.*

2.8 Inductive Effect (I Effect)

The inductive effect of a group of atoms is the change in the electron density at

a nearby atom caused by differences in electronegativity. The inductive effect can be "electron-releasing" or "electron-withdrawing," meaning that the electron density at the nearby site is either increased or decreased, respectively.

Chlorine being more electronegative than carbon atom makes C-Cl bond in chloroethane polar, decreasing the electron density of the α -carbon atom and producing a partial positive charge on it. The α -carbon will attract the bonding electron pair between it and the β -carbon more to itself and thus creates a partial positive charge on the β -carbon, but the charge will be smaller than on C_α because the effect of Cl atom has been transmitted through C_α to C_β . The β -carbon, in turn, will attract the bonding electron pair between it and a β -hydrogen atom more to itself, creating a partial positive charge on the β -hydrogen. Thus a polar bond between two unlike atoms induces charge separation in an adjacent bond and even further along a chain. This permanent dipole induced by another is called the **inductive effect**. The inductive effect may be induced by a formal charge as in ethyltrialkyl ammonium cation.



Similarly, the inductive effect can operate in the opposite direction depending on the nature of the functional group, e.g., $\overset{\delta}{\text{CH}_3} \overset{\delta-}{\text{---}} \overset{\delta-}{\text{CH}_2} \overset{-}{\text{---}} \text{O}^-$.

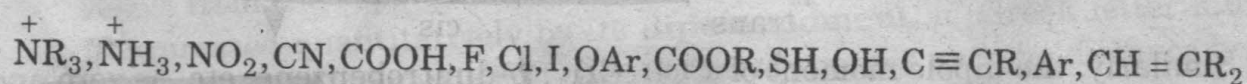
The inductive effect operates through the σ bonds and can be considered as dipole-dipole and charge-dipole interactions. It is not confined to the polarization of one bond. It is transmitted through a chain of bond and the effect decreases with increasing chain length.

The polarization of a bond induced by an adjacent polar bond through movement of σ electrons is called inductive effect.

The inductive effect refers to the polarity produced in a molecule as a result of higher electronegativity of one atom compared to another.

The functional groups responsible for producing inductive effect can be classified as with an electron-withdrawing inductive effect (-I) or with an electron-donating inductive effect (+I), relative to hydrogen depending on whether they are more electronegative or less electronegative than hydrogen. Some of the common -I and +I are given below approximately in the order of decreasing strength of the inductive effects.

Electron - with drawing groups (-I):



Electron - donating (electron-releasing) group (+I):



Alkyl groups have usually been regarded as electron-donating, but in recent years many examples have been found, and their behaviour in some cases is best explained by +I and -I in relative to hydrogen, depending on the situation.

The inductive effect changes the electron density at the atoms involved and, therefore, their reactivity is affected. **Chloroacetic acid is about 100 times more acidic than acetic acid.** This can be explained by the fact that chlorine is electronegative and therefore exerts an electron-withdrawing inductive effect to disperse the electron density from the oxygens of COO^- . The anion $\text{ClCH}_2\text{COO}^-$ is therefore a weaker base than CH_3COO^- , and thus chloroacetic acid is a stronger acid than acetic acid since. The stronger the acid, the weaker is its conjugate base.



Acid

Base

Base

Acid

Fluoroacetic acid is more stronger than chloroacetic acid: F is more electronegative than Cl and more effectively with draws electron density from the oxygens of COO^- . FCH_2COO^- is therefore a weaker base than $\text{ClCH}_2\text{COO}^-$ and, thus FCH_2COOH is a stronger acid than ClCH_2COOH . 3-chloropropanoic acid, $\text{ClCH}_2\text{CH}_2\text{COOH}$ is a weaker acid than chloroacetic acid; The inductive effect diminishes as the number of C's between Cl and the O's increases. $\text{ClCH}_2\text{COO}^-$ is a weaker base than $\text{ClCH}_2\text{CH}_2\text{COO}^-$. Thus chloropropanoic acid is weaker acid than chloroacetic acid.

On the other hand, the electron-donating group (+I) destabilizes the carboxylate anion relative to the carboxylic acid and thus decreases its acidity. Acetic acid is 10 times less acidic than formic acid due to presence of methyl group which is regarded as electron-donating as compared to hydrogen.

Since basicity of the amines depends upon the availability of the unshared pair of electrons on the nitrogen, the electron repelling inductive effect of alkyl groups makes the primary and secondary amines more basic than ammonia. Although tertiary amines are more basic than ammonia, they are less basic than secondary (trimethyl amine, a tertiary amine, is the weakest unsubstituted aliphatic amine). This anomaly has been explained on the basis of solvation and the consequent stabilization of the conjugate acids of amines by water through hydrogen bonding. The conjugate acid of a tertiary amine has less capacity to enter into hydrogen bonding as compared to a secondary amine. The third alkyl group, though increase the inductive effect, always mars the solvation tendency in tertiary amines. Since, the solvation becomes more effective than +I effect when comparing the pK_a values of conjugate acids of secondary and tertiary amines, the former are always stronger.

Conjugate acids	NH_4^+	CH_3NH_3^+	$(\text{CH}_3)_2\text{NH}_2^+$	$(\text{CH}_3)_3\text{NH}^+$
pK_a values	9.27	10.62	10.77	9.80

Another closely related effect to the inductive effect is known as the field effect. The inductive effect operates through the sigma (σ) bonds. Whereas the field effect operates directly through space or solvent molecules. Generally, the field effect

depends on the geometry of the molecule but the inductive effect depends only on the nature of the bonds. It is very difficult to separate the inductive and field effects, they are frequently grouped together under the name of **field effect**.

2.9 Delocalized Chemical Bonding

A multiple covalent bond is formed by sharing of two or even three electron pairs between two atoms. A *covalent bond in which the electron density is concentrated between only two nuclei of the combining atoms is called localized bond and the bonding electrons are called localized electrons*. The compounds containing localized bonds are fully described by a single lewis structure. There are, however, many organic compounds in which one or more bonding orbitals are spread out more than two nuclei (i.e., atoms), the resulting bonds are called **delocalized bonds**. *Systems that have a p-orbital on an atom adjacent to a double bond (i.e., molecules with delocalized π bonds) are called conjugated unsaturated systems*. This phenomenon is called **conjugation**. In simple words, *the alternation of single and double (or triple) bonds in a molecule is referred to as conjugation*. The *p* orbital may be one that contains a single electron as in allyl radical, $\text{CH}_2 = \dot{\text{C}}\text{HCH}_2$, it may be vacant *p* orbital as in allyl cation $\text{CH}_2 = \overset{+}{\text{C}}\text{HCH}_2$, or it may be the *p* orbital of another double bond as in 1,3-butadiene, $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$. A conjugated system is not fully described by a single lewis structure. Conjugation gives these systems special properties. For example, conjugated radicals, ions, or molecules are more stable than nonconjugated ones. Conjugation also allows molecules to undergo unusual reactions.

The conjugated systems can be described either by the molecular orbital method or resonance method.

The Molecular orbital Method

In molecular orbital theory, the delocalized bond in conjugated systems are described in terms of delocalized molecular orbitals (*p* orbitals which are spread out more than two atoms). We shall demonstrate this with the allylic system and 1,3-butadiene.

1. Double bond in conjugation with a *p* orbital; Allylic System

The allylic system includes allyl radical, allyl cation. In the allyl radical, $\text{CH}_2 = \dot{\text{C}}\text{HCH}_2$, each carbon is sp^2 hybridized (since each carbon is bonded to only three other atoms). The C - C σ bonds result from $sp^2 - sp^2$ overlaps and the C-H σ bonds result from $sp^2 - s$ overlap. This leaves a *p* orbital on each carbon atom, each containing one electron. All carbon and hydrogen atoms lie in one plane and the *p* orbitals are parallel to each other and perpendicular to the plane of σ bonds. The central *p* orbital is in a position to overlap equally with both the terminal *p* orbitals. The three *p* orbitals of the allyl radical linearly combine to form three π molecular orbitals, i.e., a bonding, a nonbonding and an antibonding molecular orbitals (Fig. 2.25).

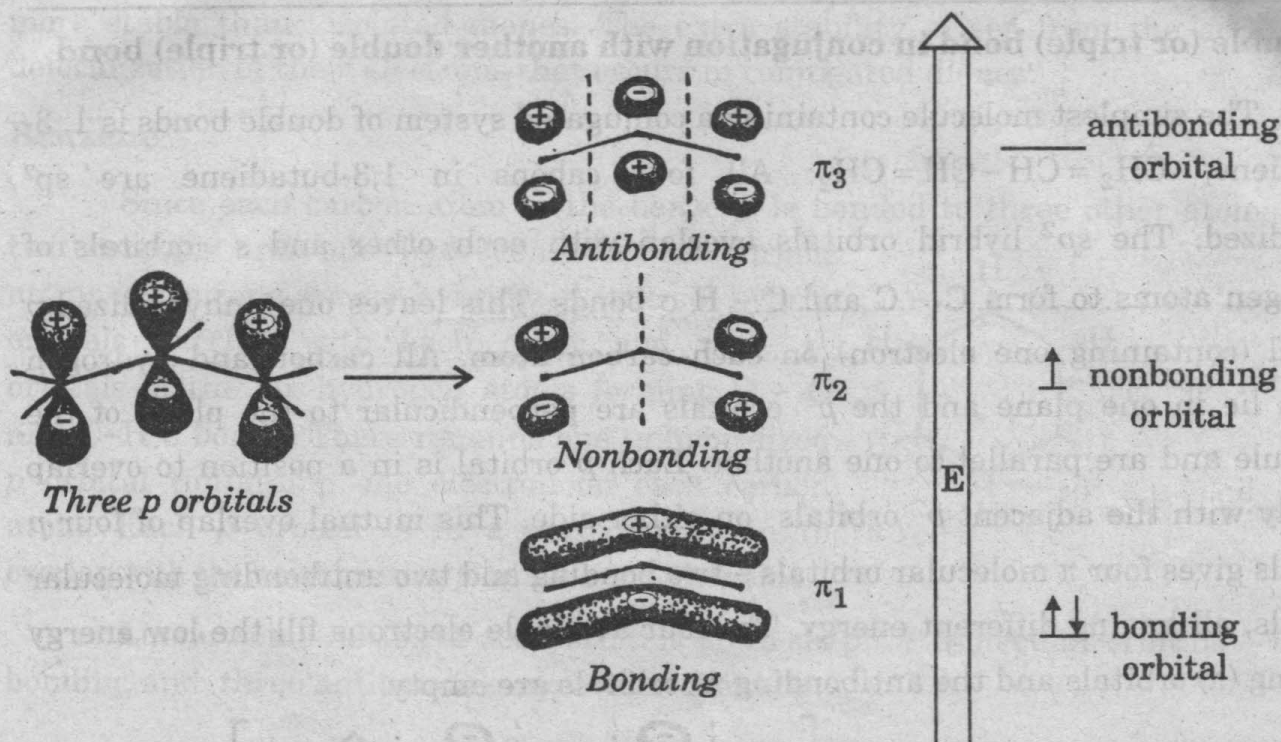


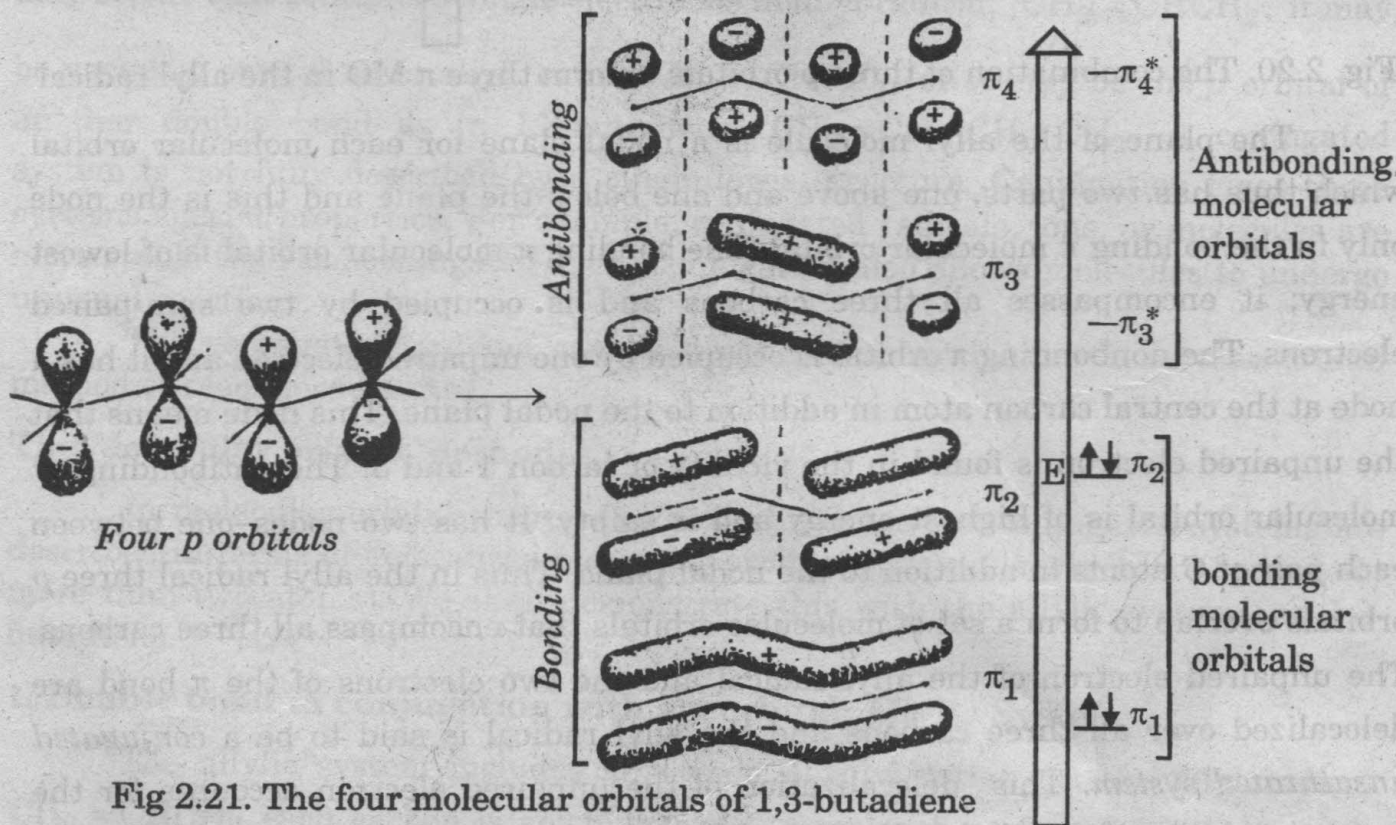
Fig. 2.20. The combination of three p orbitals to form three π MO in the allyl radical

The plane of the allyl molecule is a nodal plane for each molecular orbital which thus has two parts, one above and one below the plane and this is the node only in the bonding π molecular orbital. The bonding π molecular orbital is of lowest energy; it encompasses all three carbons and is occupied by two spin-paired electrons. The nonbonding π orbital is occupied by one unpaired electron and it has a node at the central carbon atom in addition to the nodal plane. This node means that the unpaired electron is found in the vicinity of carbon 1 and 3. The antibonding π^* molecular orbital is of highest energy and is empty. It has two nodes—one between each pair of C atoms in addition to the nodal plane. Thus in the allyl radical three p orbitals overlap to form a set of molecular orbitals that encompass all three carbons. The unpaired electron of the allyl radical and the two electrons of the π bond are delocalized over all three carbons and the allyl radical is said to be a *conjugated unsaturated system*. This delocalization of the unpaired electron accounts for the greater stability of the allyl radical as compared to primary, secondary, and tertiary radicals.

The **allyl cation**, $\text{CH}_2 = \overset{+}{\text{C}}\text{HCH}_2$ has molecular picture similar to allyl radical, but only two p electrons are available and these will occupy the lowest energy bonding molecular orbital. The nonbonding and antibonding π^* molecular orbitals will remain empty. Since the π electrons are attracted by three nuclei rather than only two (as in the case of localized π orbital), the allylic carbocation has special stability.

2. Double (or triple) bond in conjugation with another double (or triple) bond

The simplest molecule containing a conjugated system of double bonds is 1, 3-butadiene, $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$. All four carbons in 1,3-butadiene are sp^2 hybridized. The sp^2 hybrid orbitals overlap with each other and s orbitals of hydrogen atoms to form $\text{C} - \text{C}$ and $\text{C} - \text{H}$ σ bonds. This leaves one unhybridized p orbital (containing one electron) on each carbon atom. All carbon and hydrogen atoms lie in one plane and the p orbitals are perpendicular to the plane of the molecule and are parallel to one another. Each p orbital is in a position to overlap equally with the adjacent p orbitals on either side. This mutual overlap of four p orbitals gives four π molecular orbitals – two bonding and two antibonding molecular orbitals, all having different energy. The four available electrons fill the low energy bonding (π) orbitals and the antibonding π^* orbitals are empty.

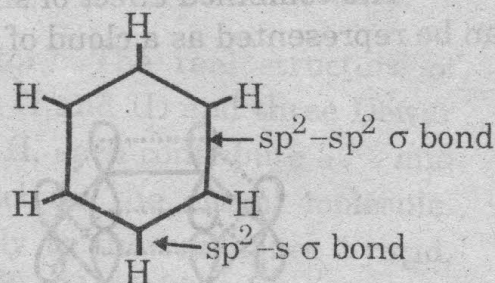


The plane of the molecule is a nodal plane for each molecular orbital. Note that as we go from π_1 , (bonding) to π_4^* (antibonding), each orbital has one more node than the one of next lower energy. In general, when p orbitals overlap, as in butadiene, they do so in such a way as to produce one molecular orbital having no node, a second molecular orbital with one node, a third with two nodes, and a fourth with three nodes. These nodes are in addition to the nodal plane. The relative energy of the molecular orbitals depends on the number of nodes; the greater the number of nodes, the higher the energy of the molecular orbital. The conjugated dienes are

more stable than isolated dienes. The extra stability arises from the additional delocalization of the π electrons that occurs in conjugated dienes.

Benzene

Since each carbon atom in the benzene is bonded to three other atoms, i.e., two carbons and one hydrogen, the six carbon atoms in benzene are sp^2 hybridized. The sp^2 hybrid orbitals overlap with each other and with $1s$ orbitals of the six hydrogen atoms forming C - C and C-H σ bonds. There remains one unhybridized p orbital containing one electron on each carbon atom. Each p orbital is in a perfect position to overlap with the neighbouring p orbitals on either side.



Linear combination of six p orbitals gives six pi (π) molecular orbitals – three bonding and three antibonding molecular orbitals.

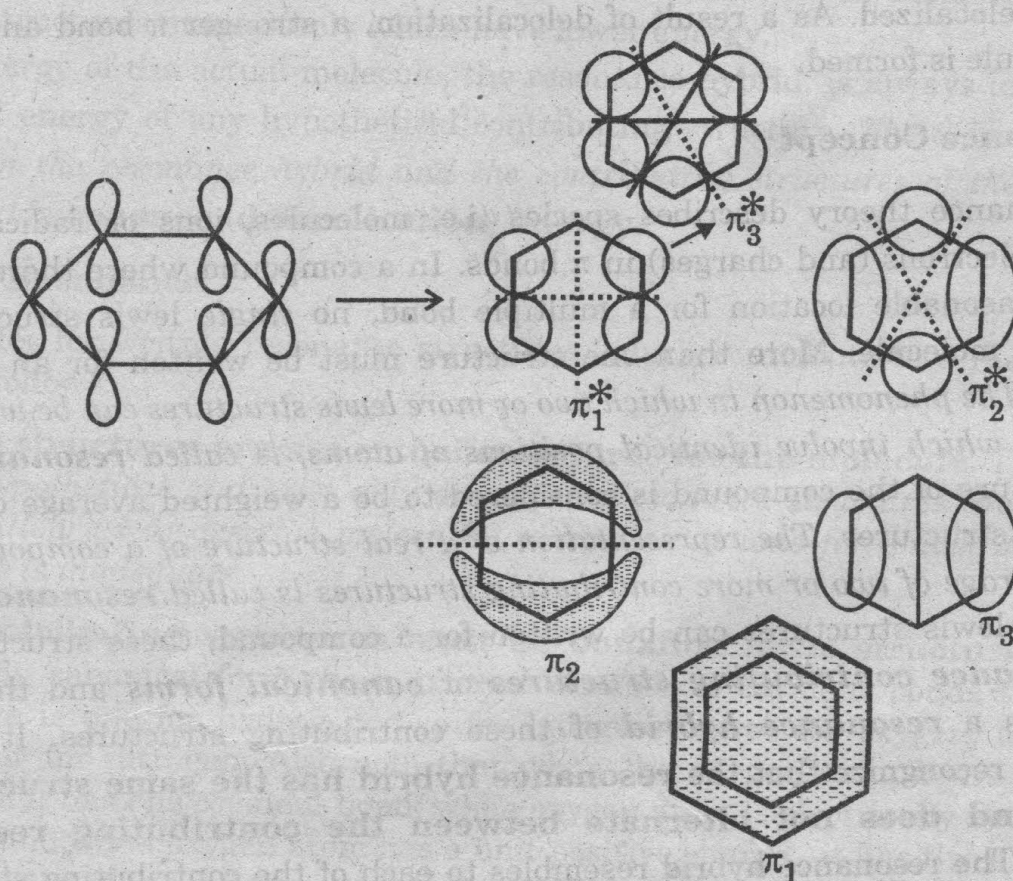


Fig. 2.22. Six π molecular orbitals of benzene, formed by the overlap of six $2p$ orbital

The six available electrons fill the three lowest energy bonding orbitals, π_1 , π_2 and π_3 , while the three antibonding orbitals, π_1^* , π_2^* and π_3^* remain empty when the benzene is in the ground state (most stable state).

The most stable bonding orbitals, π_1 has no node. It concentrates electron

density between each pair of nuclei. The bonding orbitals π_2 and π_3 are of equal energy, each having one node. Similarly, the two antibonding orbitals π_1^* and π_2^* are of equal energy each having two nodes. The least stable antibonding orbital, π_3^* has three nodes between the nuclei.

The combined effect of six electrons in π_1, π_2 and π_3 orbitals in benzene ring can be represented as a cloud of electrons above and below the ring as shown in Fig.

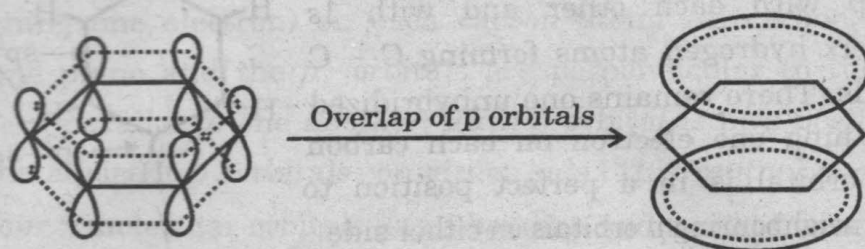
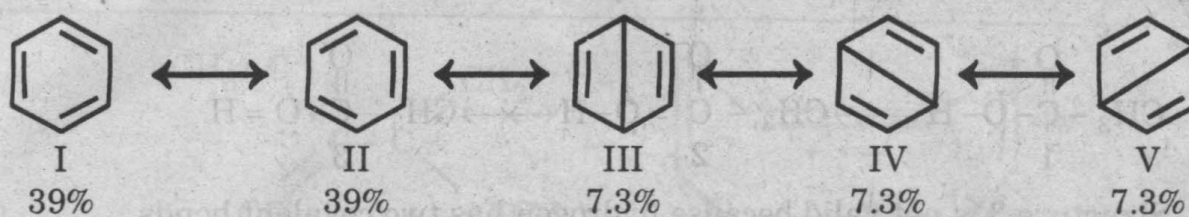


Fig. 2.23 Combined effect of bonding orbitals in benzene

The six electrons of the p orbitals now cover all the six carbon atoms and are said to be delocalized. As a result of delocalization, a stronger π bond and a more stable molecule is formed.

2.10 Resonance Concept

Resonance theory describes species (i.e. molecules, ions or radicals) with delocalized electrons (and charges) in π bonds. In a compound where there is more than one reasonable location for a multiple bond, no *single* lewis structure can describe the molecule. More than one structure must be written for an accurate description. *The phenomenon in which two or more lewis structures can be written for a compound which involve identical positions of atoms, is called resonance.* The actual structure of the compound is considered to be a weighted average of all the contributing structures. *The representation of a real structure of a compound as a weighted average of two or more contributing structures is called resonance.* When two or more lewis structures can be written for a compound, these structures are called **resonance contributing structures** or **canonical forms** and the actual structure is a **resonance hybrid** of these contributing structures. It is very important to recognize that the **resonance hybrid has the same structure all the time and does not alternate between the contributing resonance structures.** The resonance hybrid resembles to each of the contributing structures but identical non of them. A double headed arrow (\longleftrightarrow) is placed between each pair of contributing structures to represent the resonance hybrid. The double headed arrow does not mean the oscillation of molecule from one lewis structure to another. Rather, it means that the real structure is a blend of the contributing structures, which are imaginary. For example, the various contributing structures of benzene are:



None of these structures represent benzene satisfactorily. The real structure of benzene is a resonance hybrid of two Kekulé structures (I and II) and three Dewar structures (III, IV and V). The Kekulé structures I and II, each contribute 39% and Dewar structures, III, IV and V, contribute 7.3% each to the actual molecule. Obviously, the two Kekulé structures contribute largely to the resonance hybrid, hence benzene is a resonance hybrid, principally, of two Kekulé structures.

We have seen, it is not necessary that the actual molecule should resemble each contributing structure to the same extent. The actual molecule (hybrid) may resemble one contributing structure more than it does another, since the hybrid has lower energy than any of the contributing structures, and it will resemble those contributing structures more closely which have lower energy.

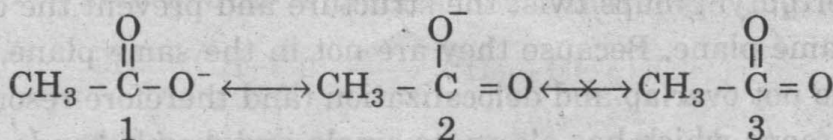
The energy of the actual molecule, the resonance hybrid, is always less than the calculated energy of any hypothetical contributing structure. *The difference in energy between the resonance hybrid and the contributing structures of the lowest energy is called resonance (delocalization) energy.*

The Rules of Resonance

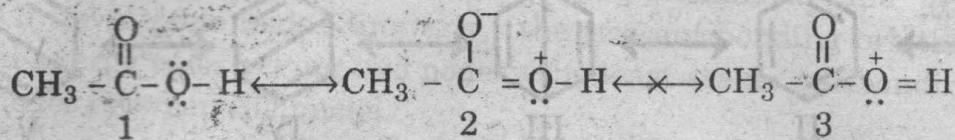
The rules for writing resonance structures, which contribute to a resonance hybrid are as follows:

1. Resonance structures are not actual structures for the molecule. They are nonexistent, hypothetical and exist only on paper. Resonance structures are useful because they allow us to describe molecules, radicals and ions for which a single Lewis structure is inadequate.

2. All the contributing structures must be bonafide Lewis structures. For instance, in any canonical form the maximum number of covalent bonds that an atom may have is one for hydrogen, two for halogens, three for oxygen, four for carbon and four for nitrogen. Also note that when the oxygen atom bears a unit negative charge it has one covalent bond, when oxygen atom is electrically neutral it has two bonds and when oxygen atom has a unit positive charge, it has three bonds. For example,

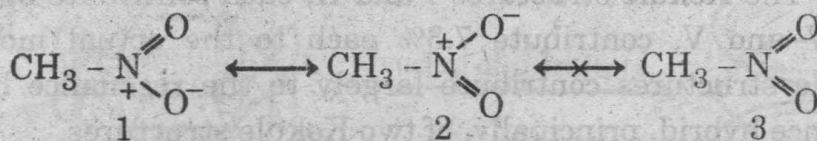


Structure 3 is not a proper resonance structure because carbon has five covalent bonds.

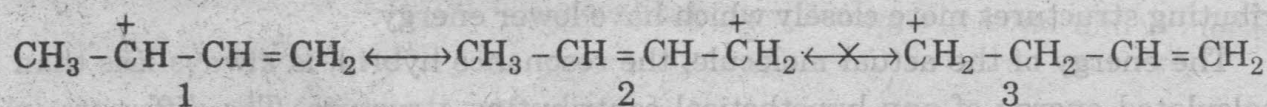


Structure 3 is not valid because hydrogen has two covalent bonds.

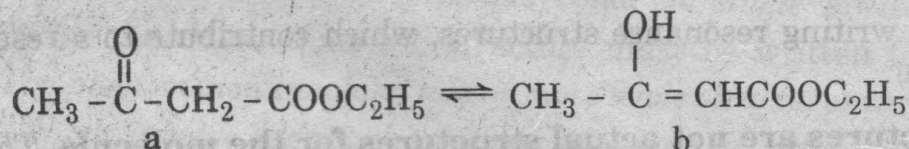
Again consider the resonance picture of a nitro compound: Here structure 3 is not valid because nitrogen has five covalent bonds. Note that when nitrogen bears a unit positive charge, it has four covalent bonds.



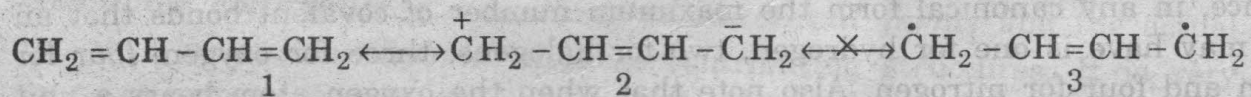
3. In writing resonance structures we are only allowed to move electrons. The atomic nuclei must have the same positions in all the canonical forms. Structure 3 below is not a resonance structure for the allylic cation because the position of hydrogen atom has been changed (moved).



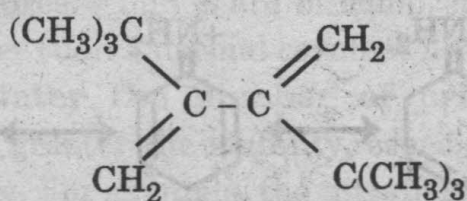
The two forms of acetoacetic ester represent two different compounds which are in equilibrium with each other; they are not the canonical forms of the same compound as the position of a hydrogen has changed in going from a to b.



4. All canonical forms must have the same number of unpaired electrons. The structure 3 below is not a resonance structure for the 1,3-butadiene because it has two unpaired electrons while the canonical forms of butadiene have no unpaired electrons.



5. All atoms involved in resonance must lie in a plane. The reason for planarity is to allow maximum overlap of the *p* orbitals for the delocalization of the electrons. For example, 2, 3-di-tert-butylbutadiene behaves like a *nonconjugated diene* because the large tertbutyl groups twist the structure and prevent the double bonds from lying in the same plane. Because they are not in the same plane, the *p* orbitals at C-2 and C-3 do not overlap and delocalization (and therefore resonance) is prevented. Cyclooctatetraene which has alternate single and double bonds, but it does not show resonance because its molecule is not planar but tub-shaped as shown below.

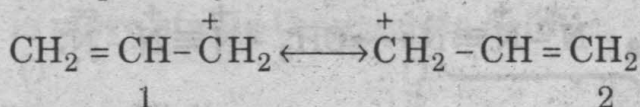


2,3-di-tert-butylbutadiene



Cyclooctatetraene

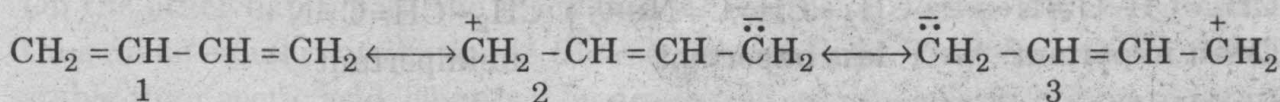
6. The actual molecule, i.e. the resonance hybrid, is always more stable than any of its canonical forms. This is because in any one canonical form each pair of bonding electrons is localized only between two atoms, whereas in the resonance hybrid the π electrons are delocalized over three or more atoms. The delocalization of π electrons accounts for the extra stability of the hybrid. Resonance, therefore, is a stabilizing phenomenon and the hybrid is said to be resonance stabilized. The actual allyl cation, for example, is more stable than either canonical form 1 or 2 taken separately would indicate.



Contribution of resonance structures:

7. All resonance structures do not contribute equally to the actual molecule. Each structure contributes in proportion to its stability. The more the stability of a resonance structure, the more is its contribution. It is not always easy to decide the relative stabilities of resonance structures. However, the following rules may be helpful in making decision about the relative stabilities of resonance structures.

(a) Structures with more covalent bonds are generally more stable than with fewer. Consider the structures for 1,3-butadiene.

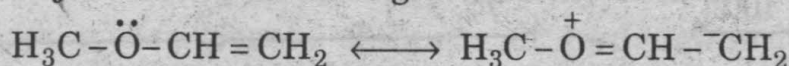


The structure 1 is the most stable and the most important contributor because it contains more covalent bonds.

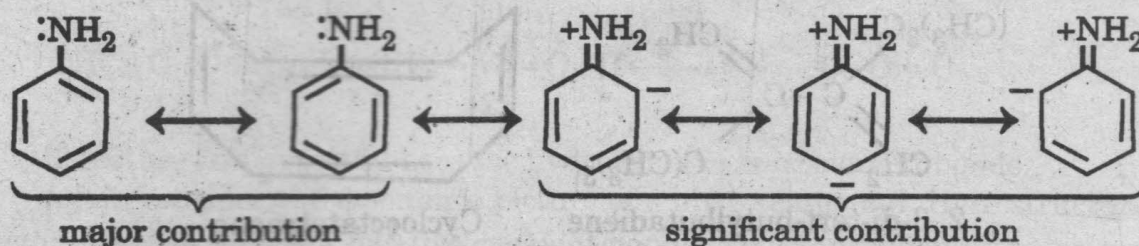
(b) Structures without a charge are more stable than those with charge separation. Separating opposite charges require energy. Charge separation decreases stability, especially, if charge separation leads to reduction in the number of covalent bonds. If structures with separated charges have the same number of covalent bonds as those without a charge, their contribution is significant. For example, for vinyl chloride below structure 1 makes a larger contribution because it does not have separated charges and structure 2 makes a significant contribution because it has separated charges. A structure without charges means that there is no charge separation.



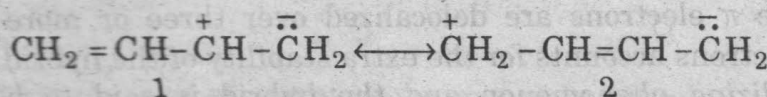
major contribution significant contribution



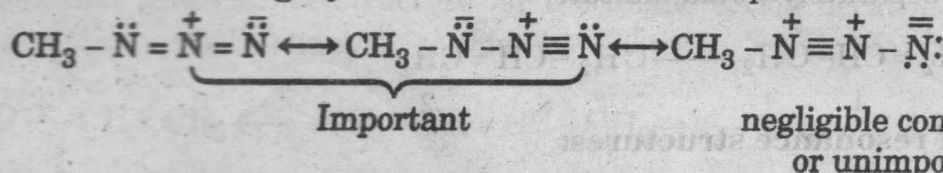
major contribution significant contribution



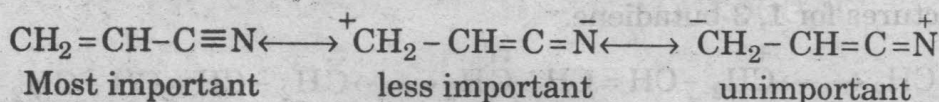
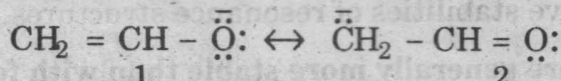
(c) The greater the charge separation, the less the stability. Structure 2 is less stable than 1.



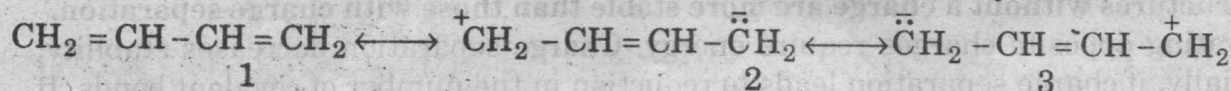
(d) Resonance structures with like charges on the same atom or on adjacent atoms are highly unstable and hence unimportant.



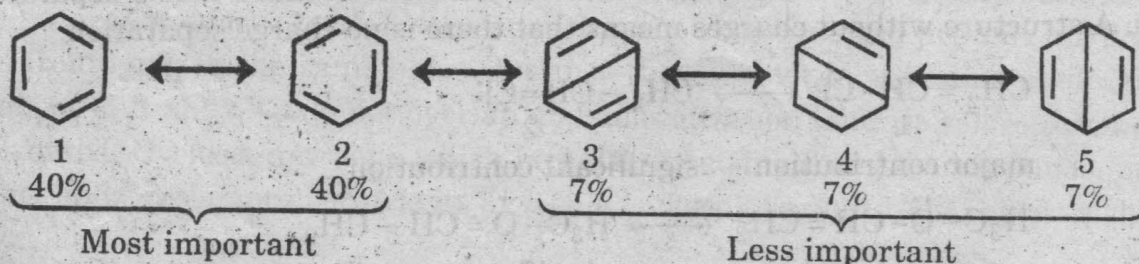
(e) Structure with a negative charge on a more electronegative atom are more stable than those in which the negative charge is on a less electronegative atom. Thus structure 1 is more stable than 2. Similarly, positive charges are best carried on atoms of low electronegativity.



(f) Equivalent resonance structures make equal contribution to the resonance hybrid, and the system described by them have a large resonance stabilization. Structures 2 and 3 make equal contribution to the hybrid.

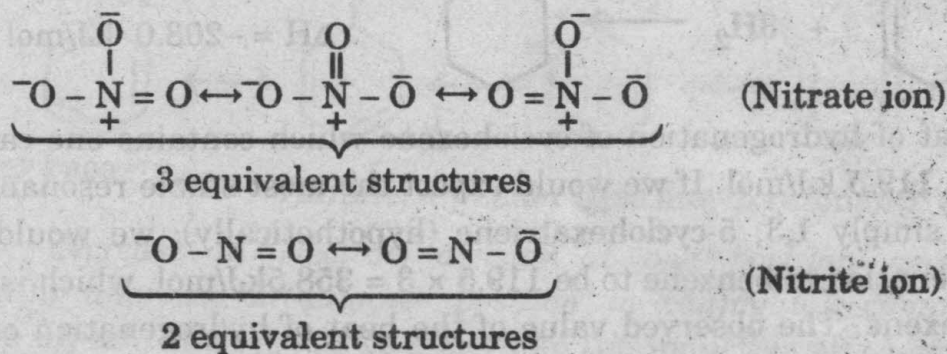


(g) Structures in which bond angles and bond length resemble closely with the resonance hybrid are more stable than those with distorted bond angles and bond lengths, e.g.,

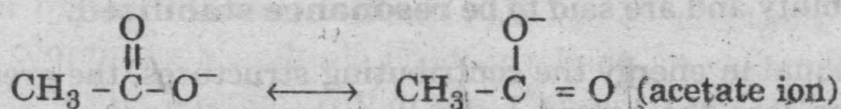
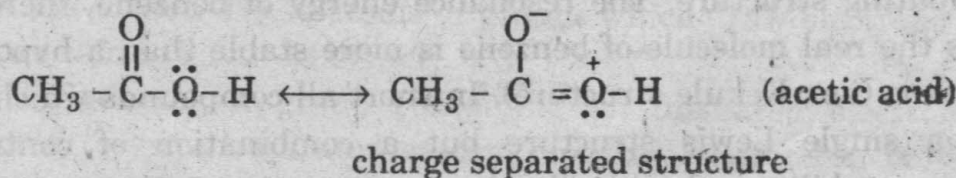


Structures 1 and 2 are of equal energy but 3, 4 and 5 have one bond each which is longer than a normal covalent bond and therefore, are less important.

(h) The greater the number of principal contributing structures of a molecule the greater the stability, especially if the contributing structures are of equal energy. For example, the nitrate ion is more stable than the nitrite ion:



Acetate ion is more stable than acetic acid



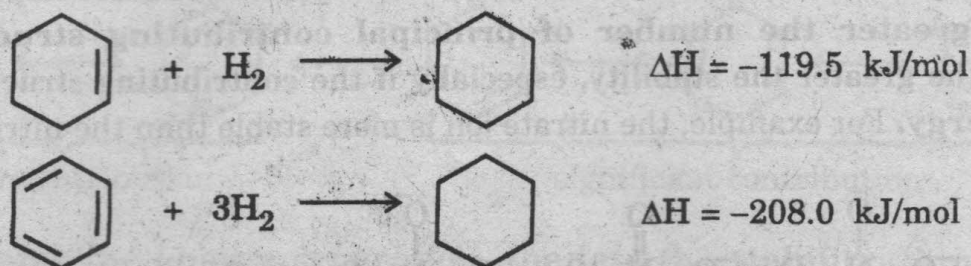
Two equivalent structures without charge separation.

In acetic acid, one resonance structure is with charge separation and makes less contribution to the resonance hybrid than the other without charge separation. On the other hand, both the resonance structures of acetate ion are equivalent and thus make equal contribution to the resonance hybrid. Therefore, acetate ion is more stable than acetic acid. That is why acetic acid readily loses a proton to form a more stable anion and thus behaves as an acid.

2.11 RESONANCE ENERGY

The energy of the actual molecule (hybrid) is always less than the calculated energy of any hypothetical contributing structure. *The difference in energy between the most stable contributing structure and the actual molecule (the hybrid) is called the resonance energy* (sometimes called the **stabilization energy** or **delocalization energy**). The resonance energy can never be measured, only estimated, since we can measure the energy of the actual molecule practically but the energy of the contributing structure can only be estimated from its bond energies by comparison with an arbitrarily chosen model compounds, since contributing structure does not exist. One method frequently used for estimation of resonance energy involves measurements of **heats of hydrogenation**. For example, the resonance energy of benzene can be estimated by comparing heats of hydrogenation

of benzene with that of cyclohexene. In both the cases the same product, cyclohexane is obtained.



The heat of hydrogenation of cyclohexene which contains one carbon-carbon double bond is 119.5 kJ/mol. If we would expect the most stable resonance structure of benzene is simply 1,3, 5-cyclohexatriene (hypothetically), we would expect the heat of hydrogenation of benzene to be $119.5 \times 3 = 358.5 \text{ kJ/mol}$, which is three times that of cyclohexene. The observed value of the heat of hydrogenation of benzene is 208 kJ/mol, which is less ($358.5 - 208 = 150.5 \text{ kJ/mol}$) than the expected value of the most stable contributing structure. The resonance energy of benzene, therefore, is 150.5 kJ/mol. Thus the real molecule of benzene is more stable than a hypothetical 1, 3, 5-cyclohexatriene (i.e., Kekule structure). In short all compounds which cannot be described by a single Lewis structure but a combination of contributing structures have extra stability and are said to be **resonance stabilized**.

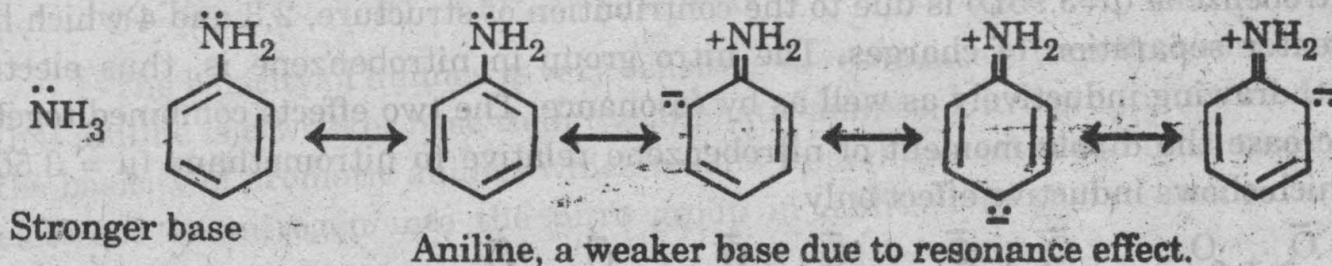
The more nearly equal in energy the contributing structures, the greater the resonance energy and the less the hybrid looks like the contributing structures. When contributing structures have dissimilar energies, the hybrid looks like the lowest-energy structure. The resonance energy increases as the number of the principal contributing structures increases. For example the resonance energy of benzene, naphthalene, anthracene and phenanthrene, for which we can draw two, three, four and five principal contributing structures, respectively, is 150.0, 255.0, 351.0 and 384.5 kJ/mol.

2.12 Resonance Effect

The resonance (or mesomeric) effect refers to the polarity produced in a molecule as a result of interaction between two π bonds or a π bond and lone pair of electrons. This effect operates through π electrons of double and triple bonds and is transmitted along a chain of carbon atoms. The resonance effect is of great importance in conjugated compounds. In such systems, the π electrons get delocalized as a result of resonance effect giving a number of resonance structures of the molecule.

The distribution of electron density in a system involving resonance is not the same as it would be if there were no resonance. For example, *aniline*, $\text{C}_6\text{H}_5\text{NH}_2$, an aromatic amine, is a weaker base than ammonia or aliphatic amine, because in aniline the electrons density due to unshared electron pair of nitrogen is delocalized over to the ring, resulting in the decrease of electron density on the nitrogen atom

and the corresponding increase of electron density on the ring due to resonance effect while in ammonia or aliphatic amines, where the resonance is absent, the unshared electrons pair resides entirely on the nitrogen atom. The decreased electron density on the nitrogen atom of aniline relative to ammonia or aliphatic amines explains why aniline is a weaker base than ammonia.



The decrease in electron density at one position accompanied by a corresponding increase at another position in conjugated compounds is called **resonance effect**. The resonance effect like the inductive effect may be positive or negative. Atoms or groups which donate electrons towards a carbon atom are said to have a **+M effect**. Those atoms or groups which draw electrons away from a carbon atom are said to have **-M effect**.

In general, a group containing an unshared electron pair on an atom connected to an unsaturated system, donates an electron pair to the unsaturated system by the resonance effect is said to be **electron-donating (+M group)**. A group containing a multiple bond, involving an electronegative atom, connected to an unsaturated system, withdraws electrons from the unsaturated system by the resonance effect is said to be **electron-withdrawing (-M group)**. Some common atoms or groups which cause +M or -M effect are listed below:

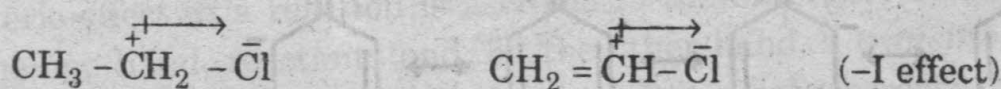
Electron-donating groups (+M effect groups):

-Cl, -Br, -I, -NH₂, -OH, -OR, -OCOR, O⁻, Ar

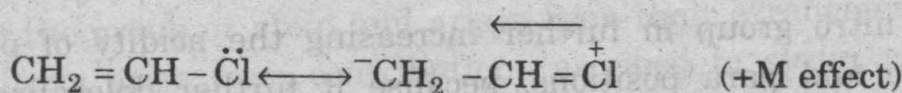
Electron-withdrawing groups (-M groups):

-NO₂, -CN, -COOH, -COOR, -CONH₂, -CHO, -COR, -CONHR, Ar

The group Ar is capable of both kinds of effect. The resonance effect has an appreciable influence on the physical characteristics and chemical reactivities of resonance hybrids relative to molecule with no resonance. Consider, for example, **the dipole moment of vinyl chloride is smaller than that of ethyl chloride**. The C - Cl bond is polarized because the chlorine atom is electron withdrawing due to the inductive effect both in vinyl chloride and ethyl chloride.

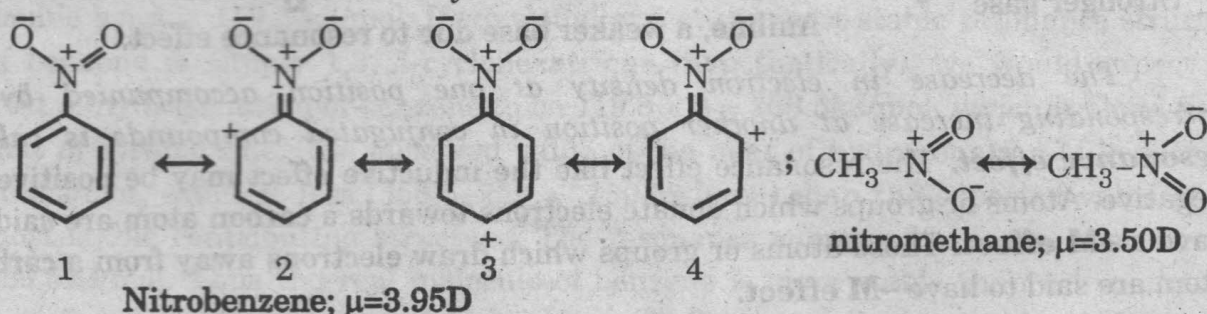


However, the molecule of vinyl chloride is a hybrid of resonance structures such as

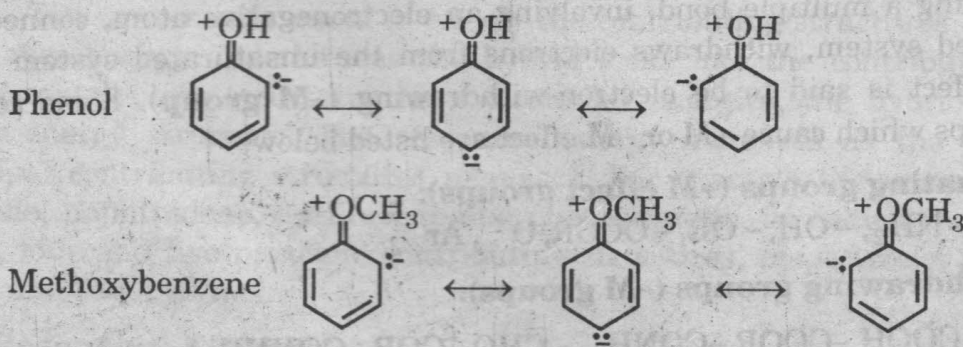


The chlorine atom is electron-donating due to resonance effect in the

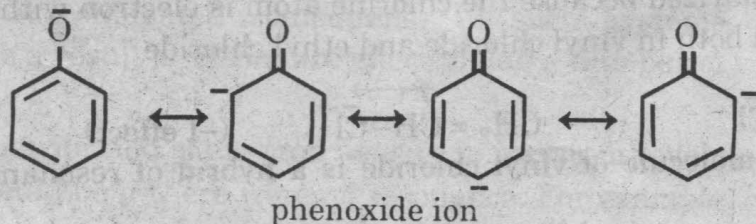
opposite direction in the contributing structure $^{-}\text{CH}_2 - \text{CH} = \overset{+}{\text{Cl}}$ to the inductive effect. The resonance effect is absent in ethyl chloride. Since the resonance effect is opposed to the inductive effect in this case, therefore, the observed dipole moment of vinyl chloride is smaller than that ethyl chloride. The larger dipole moment of nitrobenzene ($\mu=3.95\text{D}$) is due to the contribution of structure, 2,3 and 4 which have greater separation of charges. The nitro group in nitrobenzene is, thus electron-withdrawing inductively as well as by resonance. The two effects combined together increase the dipole moment of nitrobenzene relative to nitromethane ($\mu = 3.50\text{ D}$) which shows inductive effect only.



Similarly the dipole moments of aniline, phenol, chlorobenzene and methoxy benzene are smaller than those of their aliphatic analogues due to significant contributions of their resonance contributing structures.

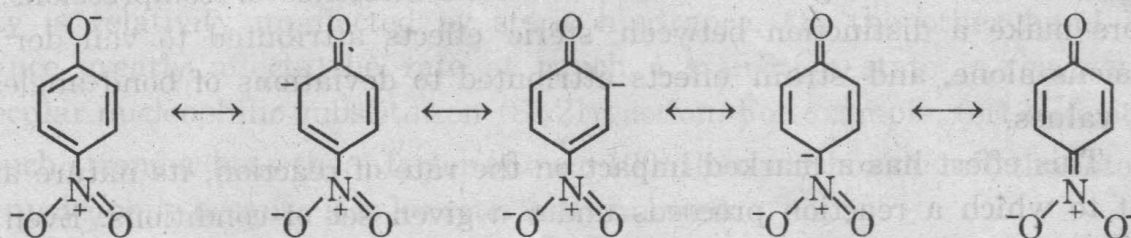


The greater acidity of phenols relative to alcohols can be attributed to resonance stabilization through delocalization of the negative charge of phenolate anion over the benzene ring, while the negative charge on the alkoxides anion, RO^{-} cannot be delocalized. Phenoxide ion is therefore a weaker base than RO^{-} , and phenol is a stronger acid.



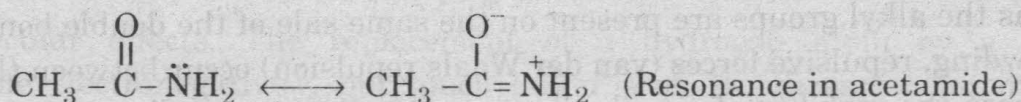
The influence of nitro group in further increasing the acidity of phenol, particularly in the ortho and para positions, because it further delocalizes the negative charge over to the nitro group, increasing the number of resonance

contributing structures.



The basicity of amines is very sensitive to resonance effects as is shown above that aniline is a weaker base than the aliphatic amines. Nitro group further reduces the basicity of aromatic amines which results from dispersal of the unshared pair of electrons on nitrogen into the nitro group in addition to the resonance seen in aniline.

Amides are much less basic than amines, largely because of delocalization of electrons of nitrogen, into carbonyl as shown below:



The C-Cl bond length in vinyl chloride is shorter than that in $\text{CH}_3\text{CH}_2\text{Cl}$ (ethyl chloride) due to resonance effect. The contribution of the structure $\bar{\text{C}}\text{H}_2 - \text{CH} = \overset{+}{\text{C}}\text{l}$ shows greater electron density between carbon and Cl than expected from one bonding electron pair only (as in $\text{CH}_3 - \text{CH}_2 - \text{Cl}$). The increased electron density between C and Cl atoms in vinyl chloride enables them to come closer, therefore the observed C-Cl bond length in vinyl chloride is shorter than that in $\text{CH}_3 - \text{CH}_2 - \text{Cl}$.

Mostly the resonance effect is observed alongwith the field effect. The field effect operates through space or solvent molecules and depend on the geometry of the molecule, and it is difficult to separate the two effects. These are, therefore, frequently grouped together under the heading of **electrical effect**.

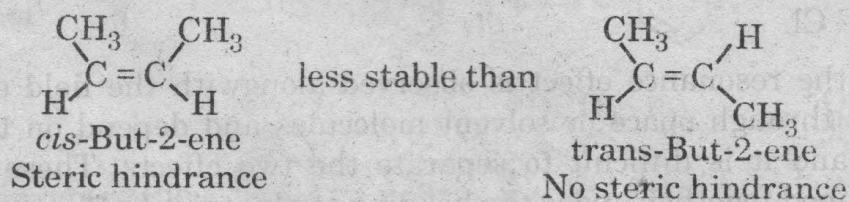
2.13 Steric Effect and its Applications

Destabilization resulting from van der Waals repulsion of groups that are close to each other is referred to as a **steric effect**. In other words, the presence of group or atoms in close proximity of each other causes van der Waal repulsions and the phenomenon is called **steric effect** (also known as **steric hindrance**). The steric effect in a reaction is ascribed to the difference in steric energy between, on the one hand, reactants and, on the other hand, a *transition state* (or products). A steric effect on a rate process may result in a rate increase ('steric acceleration') or a decrease ('steric retardation'). Steric effect largely depends upon the size (bulkiness) of the group or atom and arises from their arrangement in reacting species. Steric effects arise from contributions ascribed to *strain* as the sum of (i) non-bonded

repulsions, (ii) bond angle strain and (iii) bond stretches or compressions. Some authors make a distinction between 'steric' effects attributed to van der Waals repulsions alone, and 'strain' effects attributed to deviations of bond angles from 'ideal' values.

This effect has a marked impact on the rate of reaction, its nature and the extent to which a reaction proceeds under a given set of conditions. Even if the reaction conditions are favourable there may be a change or inhibition of reaction due to steric effect. The stability of molecules, their chemical reactivity and few of the physical properties (like acidity and basicity) are greatly influenced by steric effect.

Stability of two geometric isomers. The relative stability of two geometric isomers is usually determined simply by considerations of **steric hindrance**. Trans-alkene is more stable than isomeric cis-alkene. In cis-alkenes, steric hindrance is present, as the alkyl groups are present on the same side of the double bond. Due to steric crowding, repulsive forces (van der Waals repulsion) occur between the groups and decrease the stability of cis-alkene as compared to trans-alkene. On the other hand, in trans-alkene, the alkyl groups are present on opposite sides of the double bond and repulsion does not occur. Thus *cis*-2-butene is slightly less stable than *trans*-2-butene, while with the bulkier phenyl groups the difference in energy between *cis*- and *trans*-stilbene (1,2-diphenylethylene) is so great that an equilibrium mixture contains 10^4 times as much trans as cis isomer at room temperature.



Because of higher stability, the heat of hydrogenation of trans-alkene is lesser than that of cis-alkene.

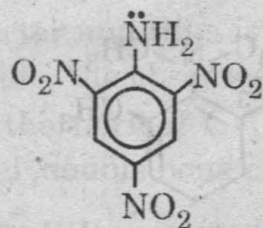
Hydrolysis of a haloalkane. Hydrolysis of a haloalkane is a nucleophilic substitution reaction that results in the formation of alcohol. In general, 1° haloalkanes follow S_N2 reactions whereas 3° haloalkanes follow S_N1 mechanism. Neopentyl bromide is a 1° haloalkane but the tert butyl group causes steric hindrance in the transition state of S_N2 mechanism and inhibits it from following a S_N2 mechanism during hydrolysis. However, the reaction may follow S_N1 mechanism during which it undergoes a carbocation rearrangement (1,2-methyl shift) to form more stable 3° carbocation that undergoes nucleophilic attack of water to form a 3° alcohol. Thus, although neopentyl bromide is a primary haloalkane but its hydrolysis does not follow S_N2 mechanism.

Effect of steric hindrance on Nucleophilicity. Because a proton is very small, basicity is relatively unaffected by steric hindrance. On the other hand, steric hindrance greatly affects the rate at which a transition state is reached in a bimolecular nucleophilic substitution (S_N2) reaction. For example, tert-butoxide ion is a much stronger base (by a factor of over 100) than methoxide ion, the latter is a better nucleophile because it is less sterically hindered.

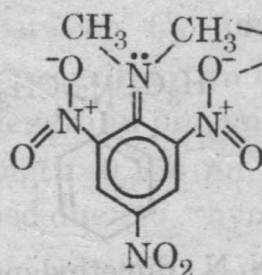
Acidity of Alcohols. The acidity of alcohols decreases as the degree of substitution of the carbinol carbon increases. Thus, in the solution-phase, acidities of methanol, ethanol, 2-propanol, and tert-butanol decrease by more than two pK_a units as the carbon bearing the OH group becomes more fully alkylated. However, the order of acidity in solution ($CH_3OH > C_2H_5OH > 2$ -propanol $>$ tert-butanol), where solvation and intermolecular association are important, is reversed in the gas phase, where isolated molecules are observed. The pK_a in solution must therefore be sensitive to intermolecular effects. The replacement of a hydrogen atom by a group of comparable electronegativity, but much larger size, stabilizes an ion in the gas phase but induces a permanent destabilizing steric effect on the solvation of the same anion (conjugate base). The presence of alkyl substituents on the carbinol carbon pushes the solvent molecules away from the negatively charged oxygen atom of the alkoxide and thus inhibits the stabilizing interaction of the solvent with the anion.

Basicity of Amines. The presence of three alkyl groups (+ I effect) in 3° amines increases the electron density on nitrogen but the crowding due to the presence of three bulkier groups hinders the ability of nitrogen to make these electrons available to other species (like solvent molecules). Thus the steric hindrance in 3° amines makes them less basic compared to 2° amines. Thus in aqueous solution the order of basicity is $(CH_3)_2NH > CH_3NH_2 < (CH_3)_3N$.

In general, the steric hindrance in 3° amines reduces the basicity as compared to 1° and 2° amines. However, in some cases, the steric hindrance enhances the basicity. For example, despite of steric crowding, N, N-dimethyl-2,4,6-trinitroaniline is a much stronger base compared to 2,4,6-trinitroaniline.



2,4,6-trinitroaniline



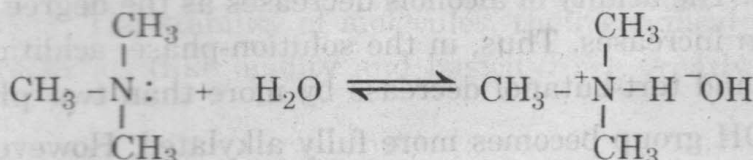
N,N-Dimethyl 2,4,6-trinitroaniline

Steric hindrance inhibits the coplanarity thus, -R effect due to nitro groups at ortho' position is not observed.

Steric Effects on Solvation. Steric hindrance to solvation caused by the bulk of the acid or of the solvent can inhibit solvent stabilization of the conjugate base.

Acidity is thereby lowered.

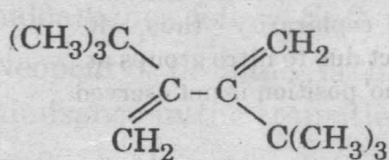
Amines exhibit a similar steric inhibition of solvation. The order of base strength for methylamines in water is : $(\text{CH}_3)_2\ddot{\text{N}}\text{H} > \text{CH}_3\ddot{\text{N}}\text{H}_2 > (\text{CH}_3)_3\ddot{\text{N}}$. In this series, solvent stabilization is more important for the conjugate acids, the charged species, than for the amines. Trimethylammonium ion is sterically the most hindered conjugate acid and therefore its stabilization by solvent is least effective.



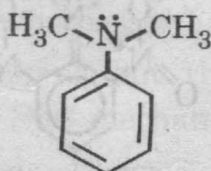
$(\text{CH}_3)_2\ddot{\text{N}}\text{H}$ and $\text{CH}_3\ddot{\text{N}}\text{H}_2$ in the series are opposite in order to what would be predicted from steric considerations. Here both steric and inductive effects play a role. Inductive electron donation by methyl groups enhances electron density on the N atom and thus increases basicity. The basicity of dimethyl amine benefits more from the electron donating effect of two methyl groups than it loses from steric inhibition of solvation, thus it is more basic than methylamine. However, the order of the same series of amines in the gas phase is $(\text{CH}_3)_3\ddot{\text{N}} > (\text{CH}_3)_2\ddot{\text{N}}\text{H} > \text{CH}_3\ddot{\text{N}}\text{H}_2$, that would be predicted from inductive effects in the absence of solvation.

Steric Inhibition of Resonance

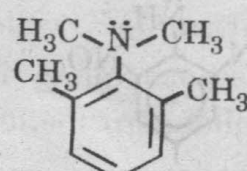
According to one of the rules of resonance *all the atoms involved in resonance must lie in the same plane to facilitate delocalization of electrons*. The reason for planarity is maximum overlap of the *p* orbitals. Any structural feature that destroys this coplanarity of the conjugated system inhibits resonance. Many examples are known where resonance is prevented or reduced because the atoms are sterically forced out of planarity. For example, 2,3-di-tert-butylbutadiene behaves like a *nonconjugated* diene because the large tert-butyl groups twist the structure and prevent the double bonds from lying in the same plane. Because the double bonds are not in the same plane, the *p* orbitals at C-2 and C-3 do not overlap and delocalization (and therefore resonance) is prevented. This phenomenon is **called steric inhibition of resonance**.



2, 3- di - tert - butylbutadiene



N, N - dimethylaniline



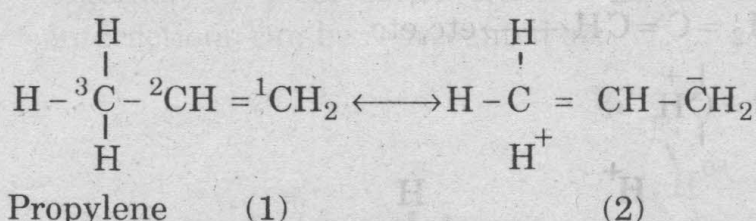
2, 6, N, N - tetramethylaniline

Consider, the effect of ortho substituents on the basicity of N, N-dimethylaniline which is less basic than aliphatic amines due to the delocalization of nonbonding electrons of the amino nitrogen atom over to the benzene ring mainly to

the ortho and para positions, dimethylamino group being coplanar with the benzene ring. However, substitution of methyl groups at the ortho positions pushes the dimethylamino out of the plane of the ring, making resonance delocalization of nonbonding electrons of the amino nitrogen atom impossible (difficult) and results in the increased basicity of 2, 6, N, N-tetramethylaniline as compared to N, N-dimethylaniline. This hindrance to delocalization by the methyl groups in the ortho position by pushing the dimethylamino group out of the plane of the ring is called **steric inhibition of resonance**.

2.14 Hyperconjugation

We have discussed so far the delocalization of π electrons. There is another type of delocalization, called **hyperconjugation**, which involves σ electrons. *Hyperconjugation may be regarded as a $\sigma - \pi$ orbital overlap, analogous to the $\pi - \pi$ orbital overlap.* In hyperconjugation the sigma C-H bond on the alpha C is delocalized with the empty p orbital of a C = C or a carbocation. The resulting H^+ does not change its position. For compounds which have a CH, a CH_2 , or a CH_3 group attached to an unsaturated carbon atom, canonical forms such as (2) can be written:

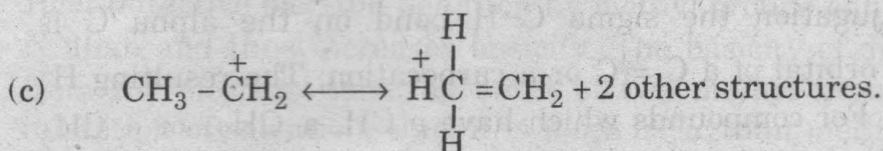
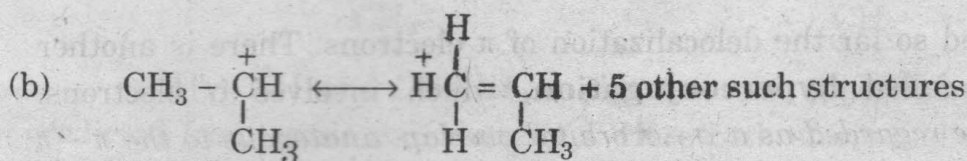
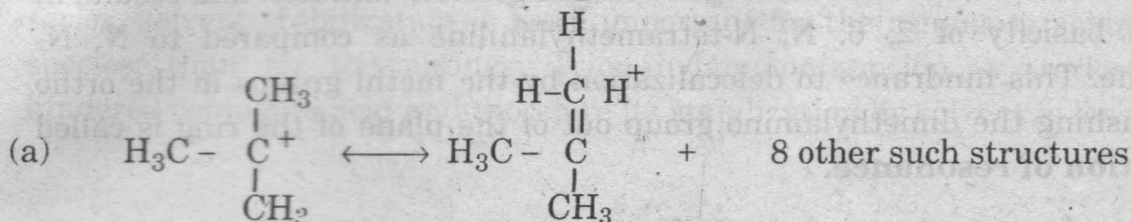
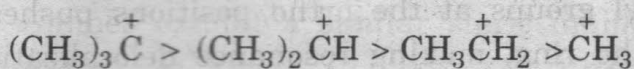


In the canonical form (2) there is no bond between the carbon and the hydrogen atoms. *This type of resonance is called **no bond resonance***, and this system of conjugation where the σ electrons of a C-H bond are in conjugation with π electrons of the unsaturated system or with p orbital, is known as **hyperconjugation**.

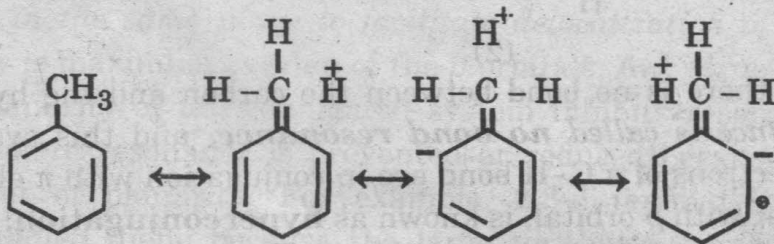
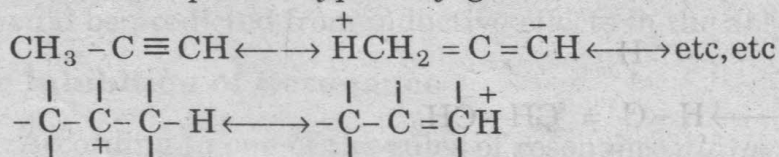
The hydrogen atom does not leave the molecule (because 2 does not exist but is only a canonical form that contributes to the actual structure of the molecule). The effect of 2 is that in the resonance hybrid (actual molecule) the C-H bond under consideration is weaker than a normal C-H bond or it has character between a single and no bond and the bond between C_2 and C_3 has some double bond character and thus is expected to be shorter than an ordinary C-C single bond. For example, the observed $CH_3 - C$ bond length in propyne is 0.147 nm which is shorter than the normal C-C single bond length (0.154 nm). This can be explained by a partial double bond character developed due to hyperconjugation as shown in canonical form 2. $CH_3 - C \equiv CH \longleftrightarrow \overset{+}{H}CH_2 = C = \bar{C}H$

The more hyperconjugation structures that can be written for a species, the more stable is the species. Thus tertiary carbonium ion is more stable than a secondary carbonium ion which is more stable than a primary carbonium ion as

shown below.



Other examples of hyperconjugation are as follows:



Toluene has a dipole moment due to hyperconjugation.

2.15 Hydrogen Bonding

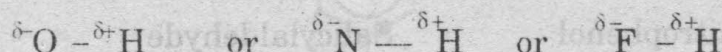
"The electrostatic attraction between a hydrogen atom covalently bonded to a small, highly electronegative atom and a lone pair of electrons on highly electronegative atom in another molecule, is called **hydrogen bonding**". Hydrogen bond is represented by a dotted or dashed line. It is much weaker than a covalent or ionic bond but it is much stronger than the van der Waals attractive forces, i.e., the forces between the molecules of nonpolar compounds. It should be noted that:

- (i) A hydrogen atom can participate in hydrogen bonding if it is bonded to O, N or F which have highly electronegativity and small atomic size.
- (ii) Hydrogen bond is longer and much weaker than a normal covalent bond. The energies (strengths) of the hydrogen bonds are in the range 8 - 42 kJ/mol, while the O - H covalent bond dissociation energy in water is 464 kJ/mol.

- (iii) Hydrogen bonding results in long chains or clusters of a large number of associated molecules like many tiny magnets.
- (iv) Like a covalent bond, hydrogen bond has a preferred bonding direction. This is attributed to the fact that hydrogen bonding occurs through p orbital which contain the lone pair of electrons on O, N or F atom.

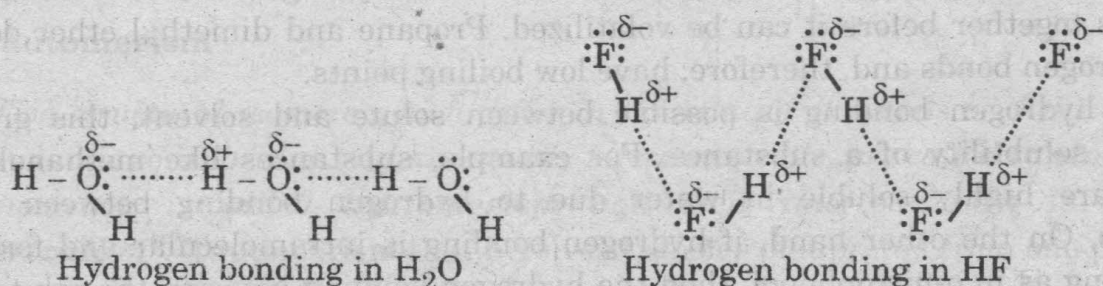
Conditions for Formation of Hydrogen Bonding

- (i) H atom is covalently bonded to O, N or F, i.e., the molecule must contain a polar bond.



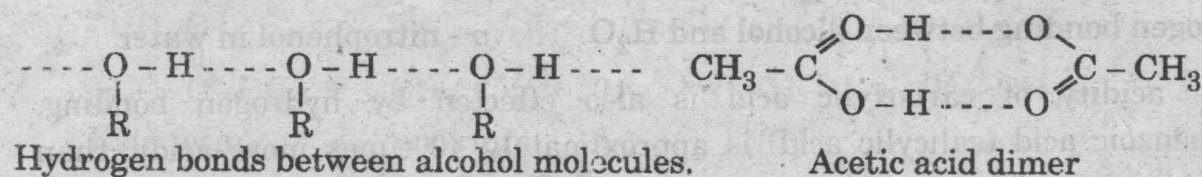
- (ii) The electronegative atom O, N or F in the polar bonds must have unshared electron pair.

When hydrogen atom is covalently bonded to highly electronegative atom such as N, O or F, it carries partial positive charge and interacts with the lone pair of highly electronegative atom of another molecule near by. In general whenever polar molecules come near to one another, the positive end (δ^+) of one molecule interacts with the negative end (δ^-) of another because of electrostatic attraction between them and thus these molecules will associate together to form large clusters of molecules. In water and HF these interactions can be represented as:



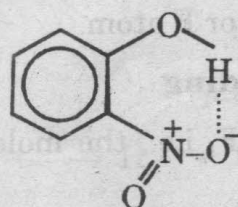
Types of hydrogen bond. There are two types of hydrogen bonds.

(i) **Intermolecular H - bonding (Association).** This type of hydrogen bonding is between two or more similar or different molecules. As a result of this type of bonding two or more molecules are associated together. Ammonia, water, hydrogen fluoride, alcohols, carboxylic acids etc are the examples containing intermolecular H- bonds.

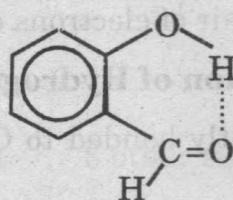


Intramolecular H - bonding (Chelation). In some cases a hydrogen bonding can occur within a single molecule. This types of H - bonding is between two functional groups of the same molecule and thus leads to the formation of a ring structure. This

type of hydrogen bonding is therefore, a kind of chelation. *o*-hydroxybenzaldehyde (i.e., salicylaldehyde), *o*-nitrophenol, *o*-chlorophenol are the examples containing intramolecular hydrogen bonding.



o - nitrophenol



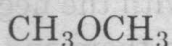
Salicylaldehyde

Effects of Hydrogen bonding on various properties of organic compounds

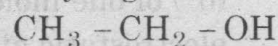
Hydrogen bonding has a significant effect on the physical properties (boiling points, solubility) of organic compounds. It is understandable that substances having nearly the same molecular masses have the same boiling point. The boiling points of alkanes and ethers of comparable molecular masses are not far apart, but the boiling points of alcohols having the same molecular masses are considerably higher.



propane (b.p; -45°C)



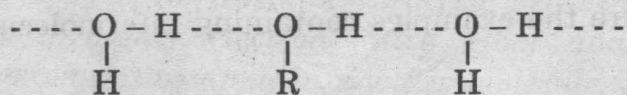
Dimethyl ether; b.p. -25°C



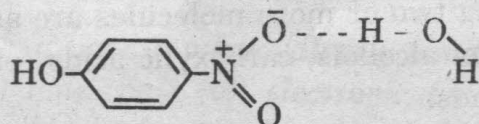
Ethanol; b.p. 78°C

This can be explained on the basis of hydrogen bonding. Ethanol forms hydrogen bonds and extra energy is required to break the hydrogen bonds holding the molecules together before it can be volatilized. Propane and dimethyl ether do not form hydrogen bonds and, therefore, have low boiling points.

If hydrogen bonding is possible between solute and solvent, this greatly increases solubility of a substance. For example, substances like methanol and ethanol are highly soluble in water due to hydrogen bonding between their molecules. On the other hand, if hydrogen bonding is intramolecular and forms a chelate ring as in *o*-nitrophenol, then the hydrogen bonding between the solute and solvent is restricted and reduces solubility in H_2O . Thus solubility of *o*-nitrophenol in water is lower as compared to its *p*-isomer (*p*-nitrophenol) which is free to form hydrogen bonding with water.

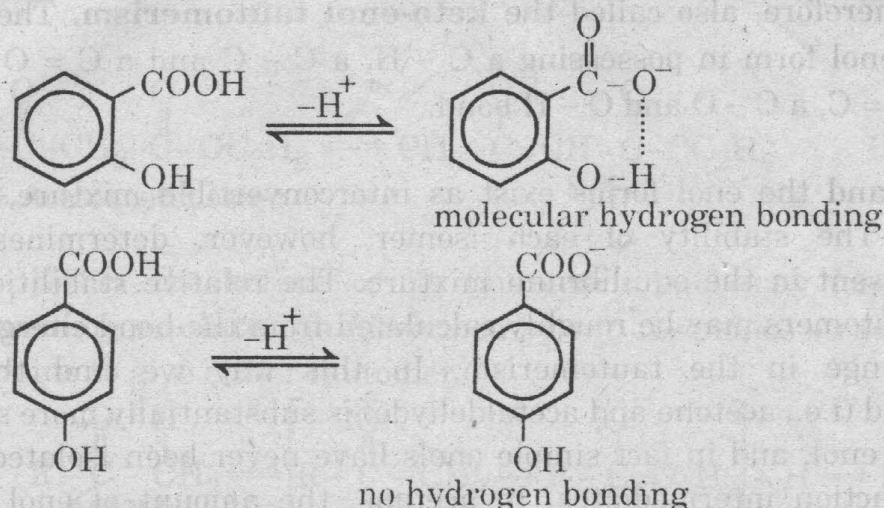


Hydrogen bonding between alcohol and H_2O

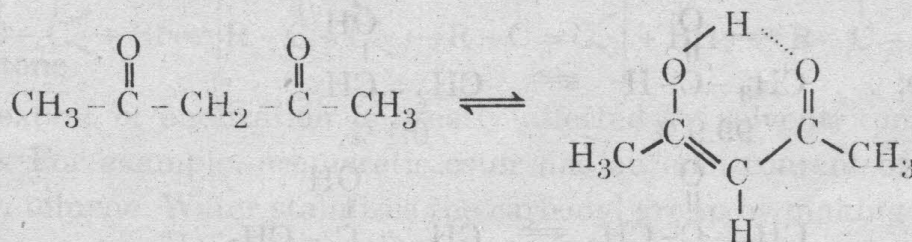


p - nitrophenol in water

The acidity of carboxylic acid is also effected by hydrogen bonding. *o*-hydroxybenzoic acid (salicylic acid) is approximately 40 times more acidic than *p*-hydroxybenzoic acid, because the anion produced after ionization of salicylic acid is stabilized through intramolecular hydrogen bonding, by chelation, whereas the anion of *p*-hydroxybenzoic acid has no intramolecular hydrogen bonding since the hydroxy group is far away from the carboxylate ion.

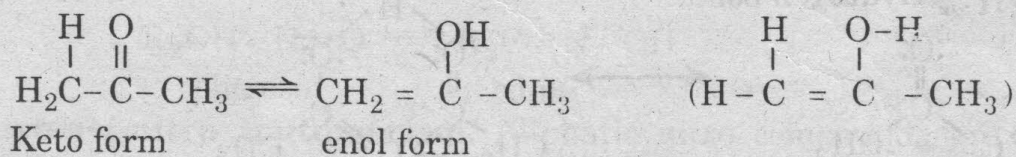


Intramolecular hydrogen bonding is also responsible for the large amount of enol present in certain tautomeric equilibria. The larger enol content (76.4%) in the equilibrium mixture of acetylacetone may be described to intramolecular hydrogen bonding.



2.16 Tautomerism

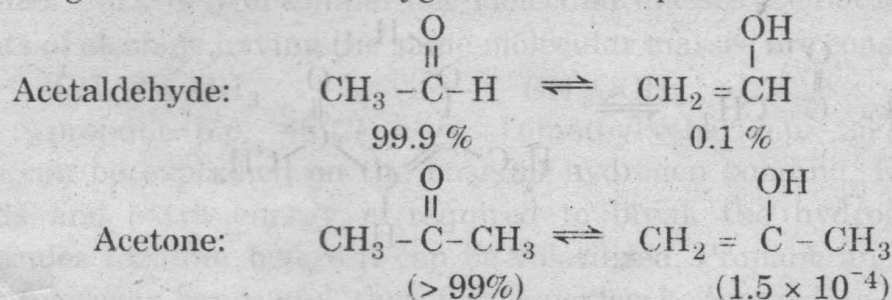
"Two structural isomers which differ in the relative positions of their atoms, exist in dynamic equilibrium, and are readily interconvertible, are called **tautomers**, the phenomenon is called **tautomerism** and their interconversion is called **tautomerization**". Tautomerism that involves transfer of a proton from one part of the molecule to another is called **proton tautomerism**. The most common examples of proton tautomerism are provided by the carbonyl compounds containing α -hydrogen, in which the proton from the α -carbon atom shifts to the carbonyl oxygen, and a pair of electron shifts from the C-H bond to C - C bond, to form an enol (from ene + ol, i.e., unsaturated alcohol). This process is called **enolization**. The proton then moves back to convert the enol form into the keto form.



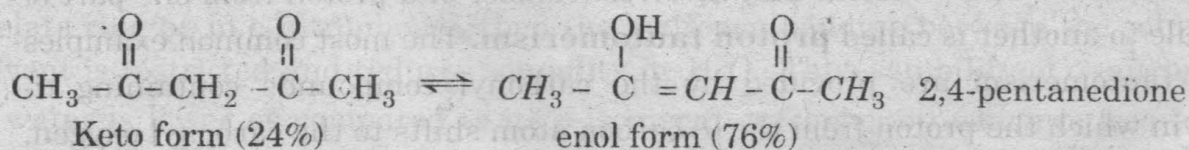
The tautomers containing the carbonyl group ($\text{C}=\text{O}$) is designated as the keto form. The other one containing a hydroxyl group attached to a doubly bonded carbon is called **enol form**. Since, there is a rapid equilibrium between the keto and

the enol forms, it is therefore, also called the **keto-enol tautomerism**. The keto form differs from the enol form in possessing a C - H, a C - C and a C = O bond where the enol has a C = C, a C - O and O - H bond.

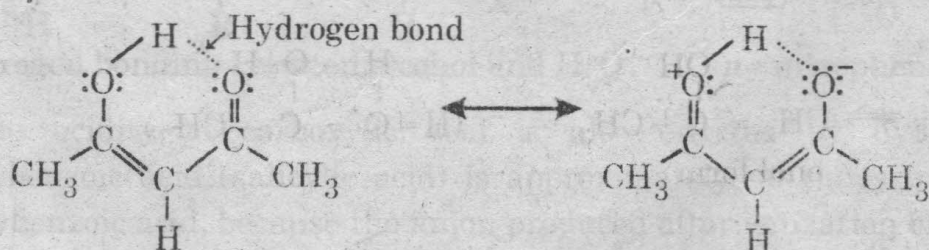
Since the keto and the enol forms exist as interconvertible mixture, their isolation is difficult. The stability of each isomer, however, determines the percentage of each present in the equilibrium mixture. The relative stabilities (or energies) of the two tautomers may be roughly calculated from the bond energies of the bonds which change in the tautomerism. In this way we find that a monocarbonyl compound (i.e., acetone and acetaldehyde) is substantially more stable than its corresponding enol, and in fact simple enols have never been isolated and are known only as reaction intermediates. In acetone, the amount of enol form present at equilibrium is much less than 1% ; in acetaldehyde the enol content is too small to be detected. The keto form is more stable by about 69 kJ/mol. The greater stability of the keto forms of monocarbonyl compounds can be related to the greater strength of the carbon - oxygen π bond compared to the carbon - carbon bond.



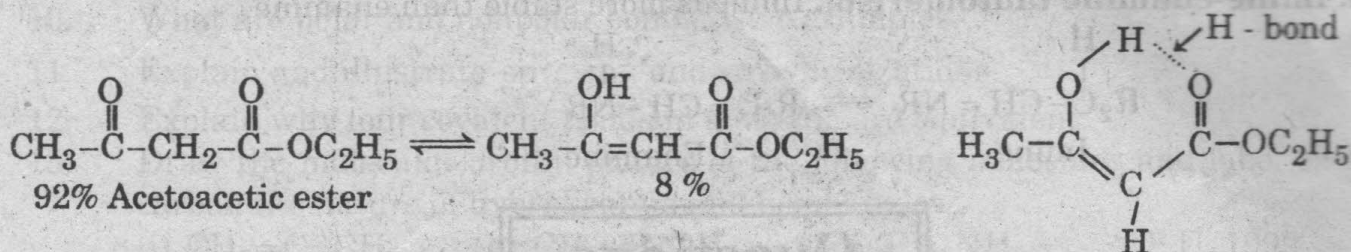
In compounds whose molecules have two carbonyl groups separated by a methylene group ($-\text{CH}_2-$), (called β -dicarbonyl compounds), the amount of enol present at equilibrium is far higher. For example, 2,4-pentanedione exists in the enol form to an extent of 76%.



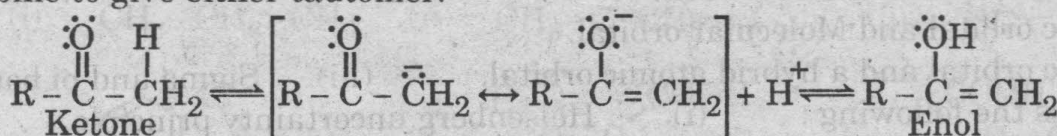
The greater stability of the enol form of β -dicarbonyl compounds can be attributed to stability gained through hydrogen bonding in a cyclic form and to resonance.



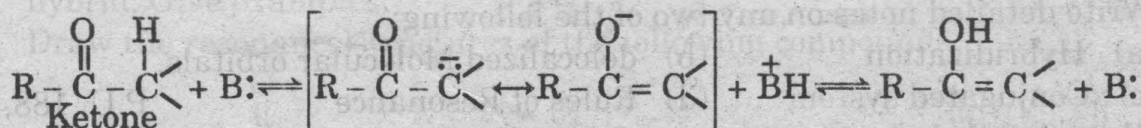
Similarly, in acetoacetic ester, the enol is also stabilized by internal hydrogen bonding, which is unavailable to keto form.



Either the ketone or its tautomeric enol may lose a proton to form an intermediate **enolate ion** (described by two resonance structures), which may then recombine to give either tautomer.



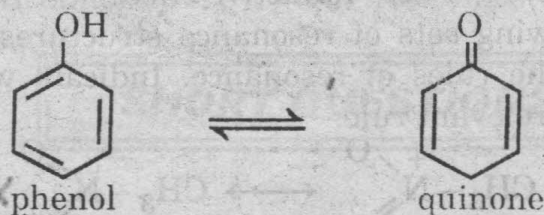
Since tautomerization involves the transfer of a proton, it is catalysed by both acids and bases.



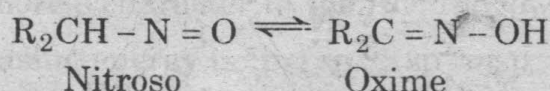
The extent of enolization is greatly affected by solvent, concentration and temperature. For example, acetoacetic ester has an enol content of 0.4% in water and 19.8% in toluene. Water stabilizes the carbonyl group by making hydrogen bond with it, making this group less available for internal hydrogen bonding.

There are other types of tautomerism which also involve a rapid shift of proton, similar to the keto-enol tautomerism.

1. Phenol - keto tautomerism. For simple phenols equilibrium lies well on the side of phenol, since aromaticity is on the side of phenol. For phenol itself there is no evidence for the existence of the keto form.



2. Nitroso-oxime tautomerism. Oximes are more stable than the nitro compounds. As a rule nitro compounds are stable only when there is no α -hydrogen.



3. Nitro-aci-nitro tautomerism. Aliphatic nitro compounds are in equilibrium with aci forms. The nitro form is more stable than aci form.



