

# Chapter-2

## GENERAL ORGANIC CHEMISTRY

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### STRUCTURE AND PROPERTIES OF ORGANIC COMPOUNDS

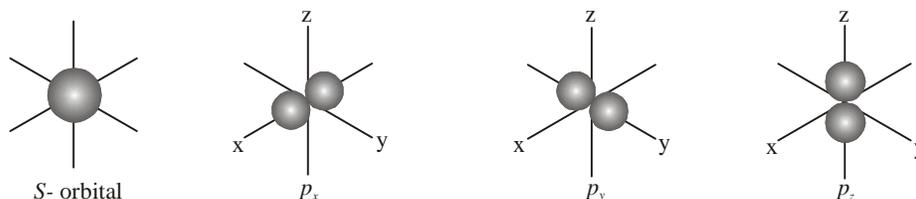
#### THEORY AFTER THE DEVELOPMENT OF QUANTUM MECHANICS

Erwin Schrodinger worked out a mathematical model for the motion of electrons in terms of wave functions. This whole model was based on the fact that electrons have dual nature, exhibit properties of both particles as well as waves. Every electron, present in an atom was assigned a wave function which ultimately led to the idea of atomic orbitals and their shapes.

#### ATOMIC ORBITAL

All wave motions are expressed by certain equations. Wave motion associated with electron is given by Schrodinger equation. Instead of talking in committed terms, this provides us a method to calculate the probability of finding the particle (electron) in an atom.

This region in space where an electron is most likely to be found is called an orbital. These orbitals are of different kinds, have different shapes and are disposed about the nucleus in specific ways. The particular kind of orbital that an electron occupies depends upon the energy of the electron. By knowing the shapes of these orbitals and their dispositions with respect to each other, we can be more precise in conveniently explaining the arrangement in space of the atoms forming the molecule and as a result determine its physical and chemical behaviour.

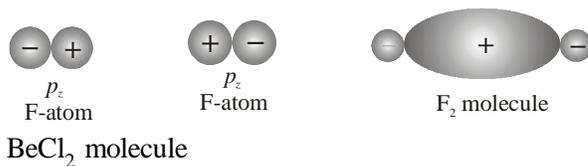
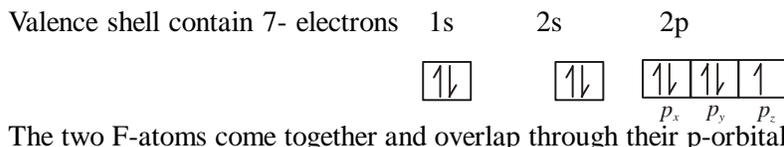


**Covalent Bonding:** The covalent bonds are typical of compounds of carbon. This bond is of chief importance in the study of organic chemistry.

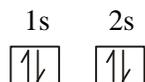
**Overlap Theory:** According to this theory for a covalent bond to be formed, the atoms must be located sufficiently close together so that an orbital of one atom overlaps with the other. Each orbital must contain single (unpaired) electron when this happens a single bond orbital is formed which is occupied by both electrons. The two electrons that occupy the orbital must have opposite spins. i.e. they must be paired. Each electron has the entire orbital (bonded) available for it and the electron may be considered to be belonging to both atomic nuclei.

This arrangement contains less energy and hence is more stable.

e.g. F atom    K        L  
                  2        7

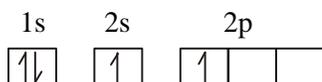


The electronic configuration of Be atom can be represented as



Be atom in order to take part in covalent bonding must have single electron orbitals.

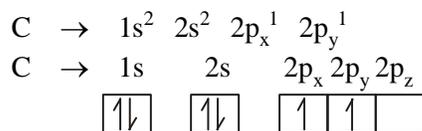
Electronic Configuration of Be atom just about to get bonded to Chlorine atoms



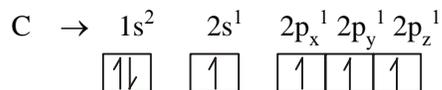
This leads to the idea that Be forms two different kinds of overlaps with every Chlorine atom i.e. one Be-Cl bond s-p overlap and other Be-Cl bond p-p overlap which would result in two different kinds of Be-Cl bonds having different bond energies and bond lengths.

But experiments have shown that both the Be-Cl bonds in BeCl<sub>2</sub> are identical. So the theory of overlap is not applicable every where.

Even if you consider the molecule of CH<sub>4</sub>. Here the central atom is Carbon. The electronic configuration of Carbon is



Just before combining with the 4 H-atoms the electronic configuration of carbon becomes

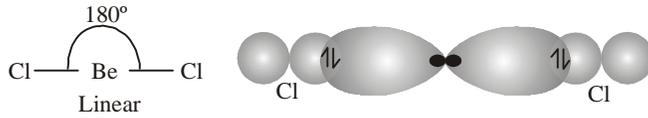
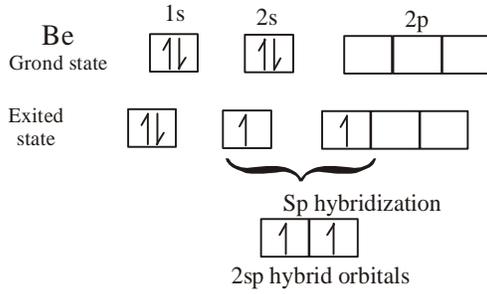


Here again we will find that according to the theory of overlap there are 3 p-s overlaps and one s-s overlap meaning there by that the bonds are not identical, but experiments have shown beyond doubt that the 4 C-H bonds are equivalent.

These anomalies are explained with the help of hybridization.

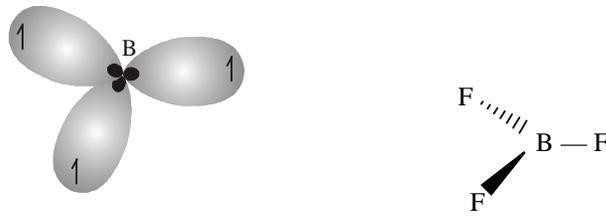
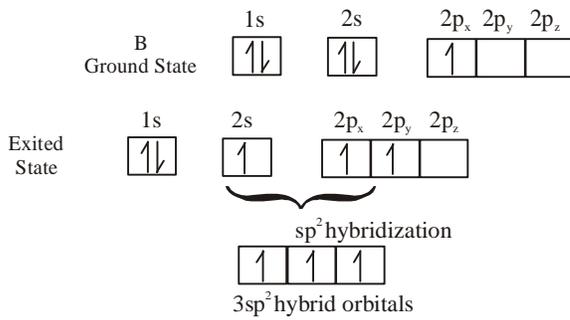
**Hybridization:** It is the mixing up of non-degenerate atomic orbitals of the atom to form degenerate orbitals called hybrid orbitals having greatest degree of directionality.

Hybrid orbitals : sp



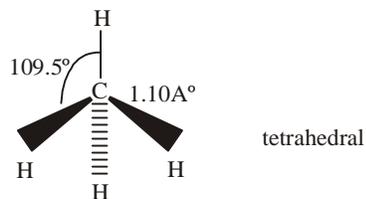
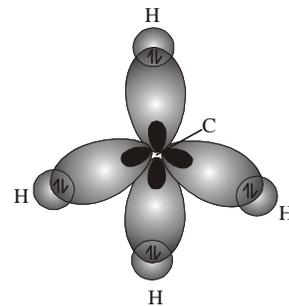
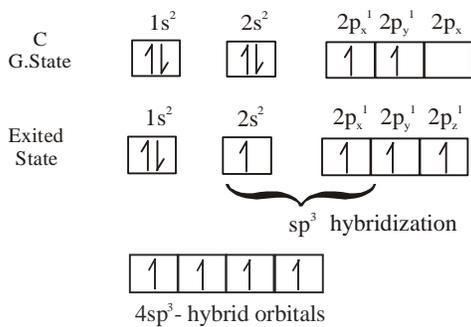
Hybrid orbitals -

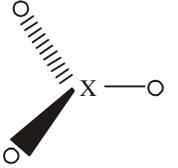
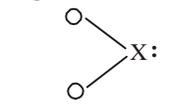
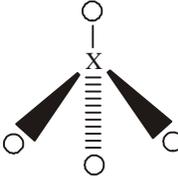
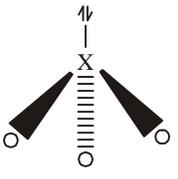
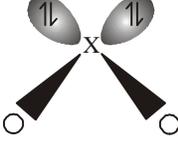
$sp^2$  in  $BF_3$



$BF_3$  hence is Trigonal planar

Hybrid Orbital -  $sp^3$  in  $CH_4$



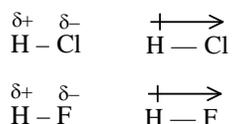
S.No.	Hybridization	Number of lone pair	Geometry	Shape and example
1.	sp	0	Linear	 $180^\circ$ $\text{BeF}_2$ , $\text{CH} \equiv \text{CH}$
2.	sp <sup>2</sup>	0	Planar Trigonal	 $\text{BF}_3$ , $\text{SO}_3$ , $\text{CH}_2 = \text{CH}_2$
3.	sp <sup>2</sup>	1	Planar Trigonal	Angular or bent  $\text{SO}_2$
4.	sp <sup>3</sup>	0	Tetrahedral	 Tetrahedral $\text{CH}_4$ , $\text{C}_2\text{H}_6$
5.	sp <sup>3</sup>	1	Tetrahedral	 Pyramidal $\text{NH}_3$ , $\text{RNH}_2$
6.	sp <sup>3</sup>	2	Tetrahedral	 Angular or bent $\text{H}_2\text{O}$

## Polarity in Molecule

- When ever covalent bonds are formed between the same atoms then the electrons are shared equally between the two atoms forming the bond e.g.  $\text{F}_2$ ,  $\text{H}_2$ , etc.

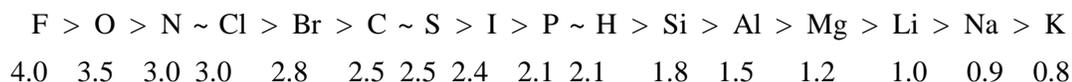
However, when the covalent bond is formed between two dissimilar atoms then there is unequal sharing of electrons resulting in the electron of the covalent bond being drawn closer to the more electronegative atom resulting in a bond dipole e.g.  $\text{HCl}$ ,  $\text{HBr}$  etc.

The polarised covalent bond may be shown as



The polarity in a bond arises from the difference in electronegativities of the two atoms participating in the bond formation.

The greater the difference in the electronegativity between the atoms bonded, the greater will be the polarity of the bond. Electronegativity order of some elements is as follows



Electronegativities of Carbon and Hydrogen are close enough hence C-H bonds do not have much polarity. Bonds of high polarity are given below :

H-O

H-F

H-Cl

H-N

Even C-X, C-O and C-N bonds are also polar.

Dipole moment = charge  $\times$  distance (Bond length)

Bond polarity contributes greatly to the physical and chemical properties of molecules.

### DIPOLE MOMENTS OF COVALENT MOLECULE

- For a diatomic molecule with different atoms the bond dipole is also the dipole moment.



$$\mu = 1.98 \text{ D}$$



$$\mu = 1.03 \text{ D}$$



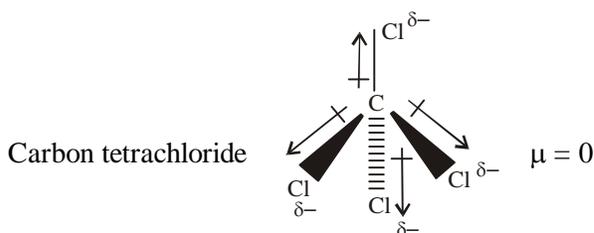
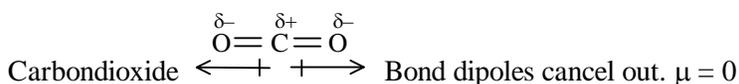
$$\mu = 0.78 \text{ D}$$



$$\mu = 0.38 \text{ D}$$

- For diatomic molecule with same atom there is no bond dipole e.g. H-H and I-I
- The overall dipole moment of a molecule containing more than two atoms is vector quantity of some of the individual bond dipole moments.

A molecule may contain polar bonds but have no overall dipole moment if the shape of the molecule is such that the individual bond moments cancel out.



### MOLECULAR INTERACTIONS

It is observed that covalent compounds exist as solids, liquids and gases.

This immediately puts to mind a question as to what forces hold neutral molecules together.

Like interionic forces, these forces seem to be electrostatic in nature involving attraction of +ve charge for negative charge.

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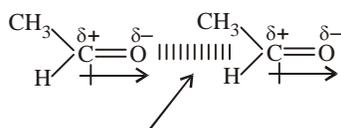
These are of two types

- a. Dipole - Dipole interactions                      b. van der Waal's forces.

### Dipole - Dipole Interaction

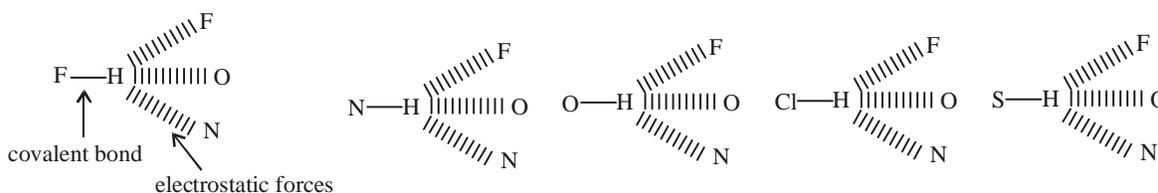
1. This exists mainly in polar molecules. Here there is attraction of the +ve end of one polar molecule for the negative end of another polar molecule.

In Acetaldehyde the relatively -ve Oxygen end is attracted to the relatively +ve Carbon atoms.



Dipole-Dipole Interaction

2. **H-Bonding** [Special kind of Dipole-Dipole Interaction]. Here the H-atom seems as a bridge between two electronegative atoms, holding one by a covalent bond and other by purely electrostatic forces.



Also the strength of hydrogen bonding order is



### NON - POLAR FORCES

It is found that even non polar molecules solidify and hence there must be some forces which exist in such solids. Such attractive forces are called van der Waal's forces.

The existence of forces can be accounted by quantum mechanics which says that the average distribution of charge about *e.g.* CH<sub>4</sub> molecule is symmetrical, so that there is no net dipole moment. However the electron move about, so that at any instant the distributions become distorted leading to a small dipole. This momentary dipole induces another small dipole moment to another molecule and so on.

Though the momentary dipole and induced dipoles are constantly changing, the net result is attraction between the two molecules.

van der Waal's forces have a very short range and they act only between the portions of different molecules that are in close contact, that is between surfaces of molecule.

- (a) van der Waal's forces are directly proportional to molecular mass  
(b) van der Waal's forces are directly proportional to surface area.

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The molecular forces of attraction are very useful in comparing the rates of evaporation, vapour pressures, boiling point, melting point, viscosity etc.

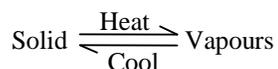
## PURIFICATION AND CHARACTERISATION OF ORGANIC COMPOUNDS

**Purification of Organic Compounds :** The methods which are generally employed for the purification of organic compounds are

(i) Crystallisation (ii) Sublimation (iii) Distillation (iv) Fractional distillation (v) Distillation under reduced pressure (vi) Steam distillation (vii) Azeotropic distillation (viii) Differential extraction (ix) Chromatography.

These are briefly discussed as follows :-

- (i) **Crystallisation :** It is used to purify organic solids which dissolve in a particular solvent either as such or on heating while the impurities do not dissolve in it. A hot concentrated solution of the compound is prepared and this upon filtration and cooling gives the crystals of the pure compound.
- (ii) **Sublimation :** Sublimation is the process employed for those solids which directly pass to the vapour state upon heating without passing through the liquid state and the vapours upon cooling give back the solid state.



Impure samples of Naphthalene, Anthracene, camphor, Benzoic acid,  $\text{NH}_4\text{Cl}$ ,  $\text{HgCl}_2$ , dry ice, Salicylic acid, Iodine etc. can be purified by this method provided the impurities are non-volatile.

- (iii) **Distillation :** The method is applied if the organic liquid which is stable at its boiling point, and contains a non-volatile impurity. When the given liquid is heated to its boiling point, it is converted into vapours and the vapours on cooling condense to give back the original liquid in its pure form. The liquid so obtained is called as distillate and the process is called distillation. It can be applied only if the two liquids differ in their boiling point by 30-50 K. e.g. (a) Ether and Toluene, (b) Benzene and Aniline
- (iv) **Fractional distillation :** Sometimes we come across the mixture of two liquids which differ in their boiling temperatures by about 10 K to 15 K e.g., a mixture of Acetone (boiling point 329 K) and Methyl alcohol (boiling point 338 K). The process of simple distillation can not be used to separate them, because vapours of both the liquids will be formed simultaneously and the distillate will also contain both of them. In such a case the process of fractional distillation is used which utilizes specially designed columns called fractionating columns.
- (v) **Distillation under reduced pressure :** Certain liquids have a tendency to decompose at temperature below their boiling point. Such liquids can not be purified by simple distillation and can be distilled under reduced pressure. Under reduced pressure the liquid will boil at lower temperature and temperature of decomposition will not be reached and thus escaped. e.g. the boiling point of Glycerol is 563 K but it decomposes much before this temperature. However if the pressure is reduced to 12 mm, Glycerol boils at 453 K without decomposition. Other examples are  $\text{H}_2\text{O}_2$ , concentration of sugar cane juice in sugar industry.

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- (vi) **Steam distillation** : This process is used to purify the substances which are (a) volatile in steam but are not miscible with water (b) possess sufficiently high vapour pressure at the boiling point of water (373 K) (c) contain non-volatile impurities.

*Principle* : In this process, pressure inside the distillation flask is reduced and the liquid gets distilled at a temperature below its boiling point. This can be explained with the help of Dalton's law of partial pressures as follows :

The law states that the pressure exerted by the gaseous mixture in a container is the sum of partial pressures of the constituent gases provided they do not react chemically.

Where  $P$  ( $P = P_1 + P_2$ ) is the total pressure while  $P_1$  and  $P_2$  are the partial pressures of the constituent gases.

The distillation flask contains the vapours of water (vapour pressure =  $P_1$ ) and of the liquid to be purified (vapour pressure =  $P_2$ ). Since the vapour of each is less than the atmospheric pressure therefore the liquid gets distilled under reduced pressure by applying this process.

The process of steam distillation can also be used to separate a mixture of two organic substances one of which is steam volatile while the other is not e.g. when steam is passed through a mixture of orthonitrophenol and p-nitrophenol, the vapours of steam carry the vapours of o-Nitrophenol along with them which gets condensed in the receiver. p-Nitrophenol is left behind in the distillation flask. e.g. Aniline, Nitrobenzene, Sandal, wood oil, Turpentine oil etc.

- (vii) **Azeotropic distillation** : The liquid mixtures which have constant boiling point and distills with unchanged composition are called azeotropes. These mixtures behave as pure liquids and can not be separated by simple distillation. A solvent (such as  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$  etc.) is added to form a new azeotrope with one of the component and is then removed and subsequently separated in a second column. An example of the use of azeotropic distillation is the dehydration of 96% ethanol to absolute alcohol using Benzene.
- (viii) **Differential extraction** : This process is used to separate a given organic compound present in an aqueous solution by shaking with a suitable organic solvent in which compound is more soluble as compared to water. However the organic solvent and water must not be miscible with each other.
- (ix) **Chromatography** : It is the modern technique used for the separation and purification of organic compounds. This method was discovered by Tswett, a Russian botanist in 1906 for the separation of coloured pigments from a plant. But now this method is widely used for the separation and purification of a number of mixtures, whether coloured or colourless.

**Principle of Chromatography**: It is based upon the principle of distributing the components of a given organic mixture between two phases; one of which is stationary and the other is mobile. The stationary phase can either be solid or a liquid supported over a solid and the mobile phase may be liquid or gas. Over the years, the number of techniques such as column or adsorption chromatography, paper chromatography, thin layer chromatography and gas liquid chromatography have been developed.

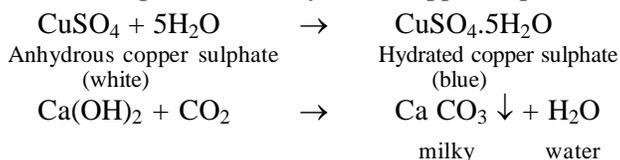
Types of chromatography	Mobile/Stationary Phase	Uses
1. Adsorption or Column	Liquid/solid	Large scale separations
2. Thin layer chromatography (TLC)	Liquid/solid	Qualitative analysis
3. High Performance Liquid Chromatography (HPLC)	Liquid/solid	Qualitative and Quantitative analysis
4. Gas liquid chromatography (GLC)	Gas/liquid	Qualitative and Quantitative analysis
5. Paper or Partition chromatography	liquid/liquid	Qualitative and Quantitative analysis

**Qualitative Analysis:** The qualitative analysis of an organic compound implies the detection of all the major elements which can be present in it with the help of suitable chemical test. Carbon and Hydrogen are the essential constituents of all the organic compounds. These are therefore, normally not detected. Apart from that the organic compounds may contain Nitrogen, Sulphur, Halogens, Phosphorous and Oxygen.

- Detection of Carbon and Hydrogen :** These are detected with the Copper oxide test. A small quantity of the organic compound is mixed with double the amount of pure and dry Copper oxide. The mixture is heated in a hard glass test tube and the gas evolved is passed through bulb containing anhydrous Copper sulphate and then through a bulb containing lime water. On heating, the organic compound undergoes combustion and is oxidised to carbon di-oxide and water vapours according to the following reaction :



Now water vapour turns anhydrous Copper sulphate, blue, and Carbon dioxide turns lime water milky.



## 2. Detection of Nitrogen

- Soda-lime test :** A pinch of an organic compound is heated strongly with soda-lime (NaOH + CaO) in a test tube. The evolution of Ammonia gives the indication of Nitrogen. For example :

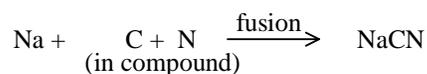


**Limitations :** A large number of organic compounds such as Nitro and diazo compounds do not liberate Ammonia under these conditions.

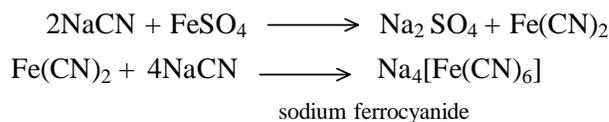
- Lassaigues's Test :**

- Preparation of Lassaigues's extract :** A small piece of dry Sodium metal is heated gently in a fusion tube till it melts to a shiny globule. At this stage a small amount of organic substance is added and the tube is heated strongly. The red hot tube is plunged into distilled water contained in a china dish. The contents of dish are boiled for couple of minutes, cooled and filtered. The filtered liquid is called as Sodium extract (S.E.) or Lassaigues's extract (L.E.).

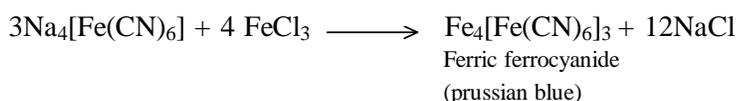
- (b) **Test for Nitrogen** : The Lassaigne's extract is usually alkaline. If not it may be made alkaline by the addition of few drops of a dilute sodium hydroxide. To a part of extract a small amount of freshly prepared ferrous sulphate solution is added and the contents are warmed. A few drops of ferric chloride solution are then added to the contents and the resulting solution is acidified with conc. hydrochloric acid. The appearance of a bluish green or a Prussian blue colouration confirms the presence of Nitrogen in the organic compound.
- (c) **Chemistry of the test** : During fusion, carbon and Nitrogen present in the organic compound combine with Sodium to form Sodium cyanide.



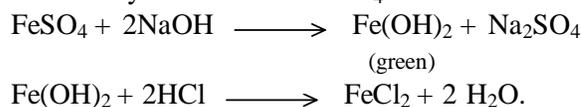
Upon heating the extract with ferrous sulphate Sodium ferrocyanide is formed as follows :



The treatment with ferric chloride yield ferric ferro cyanide which has bluish green or Prussian blue colouration.

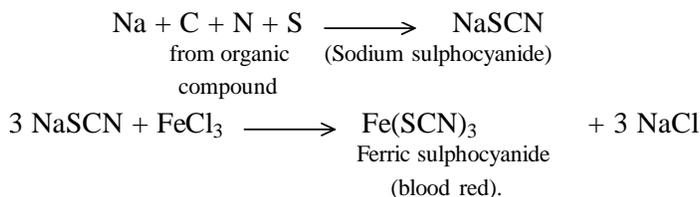


The reason for adding concentrated Hydrochloric acid is to destroy any  $\text{Fe(OH)}_2$  which might have been formed by the action of  $\text{FeSO}_4$  with  $\text{NaOH}$ .

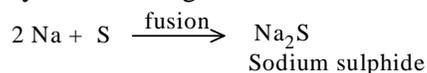


If this is not done, the green colour of ferrous hydroxide will interfere with the detection of Nitrogen.

- (d) If the organic substance contains Nitrogen and Sulphur together, Sodium sulphocyanide is formed in the sodium extract which gives blood red colouration with  $\text{FeCl}_3$  due to the formation of ferric sulphocyanide.



3. **Detection of sulphur**: The presence of Sulphur in an organic compound which does not contain Nitrogen is detected by the following tests :

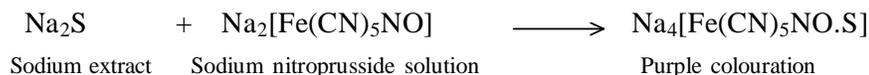


The extract is divided into two parts as follows :-

- (i) **Lead acetate test** : One part of the extract is acidified with Acetic acid and then Lead acetate solution is added. Formation of black precipitate confirms the presence of Sulphur in the organic compound.



(ii) **Sodium nitroprusside test** : A few drops of Sodium nitroprusside solution are added to the other part of the Lassaigne's extract. The appearance of purple colouration confirms the presence of Sulphur.

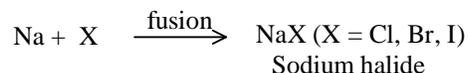


4. **Detection of halogens** The presence of halogens in the organic compound is detected by the following tests :-

(i) **Beilsteins test** : A copper wire flattened at one end is heated in the oxidising flame of Bunsen burner. The heating is continued till it does not impart blue or green colour to the flame. The hot end of copper wire is now touched with the organic substance and is once again kept in the flame. The appearance of blue or green colour indicates the presence of halogens in the organic compound.

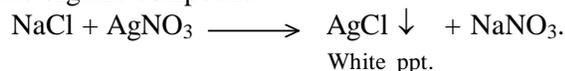
*Limitations* : (a) Substances, such as Urea, Thiourea etc. do not contain halogens (Cl, Br, I) but gives this test.

(ii) **Lassaigne's test** : This is very reliable test for the detection of the halogens [Cl, Br, I] in an organic compound. The procedure for the formation of extract is same as in Nitrogen. During fusion, Sodium will combine with the halogen to form Sodium halide.



The Lassaigne's extract is boiled with conc.  $\text{HNO}_3$  to expel the gases. It is then cooled and treated with  $\text{AgNO}_3$  solution.

(a) A white precipitate soluble in Ammonium hydroxide solution indicates the presence of Chlorine in the organic compound.



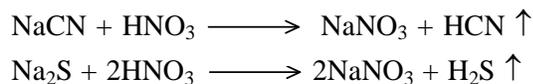
(b) A pale yellow precipitate partially soluble in  $\text{NH}_4\text{OH}$  solution indicates the presence of Bromine in the organic compound.



(c) A yellow precipitate, insoluble in  $\text{NH}_4\text{OH}$  indicates the presence of Iodine



**Function of  $\text{HNO}_3$**  : In case Nitrogen and Sulphur are present along with the halogens in the organic compound, Lassaigne's test will also contain Sodium sulphide ( $\text{Na}_2\text{S}$ ) and Sodium cyanide ( $\text{NaCN}$ ) along with the sodium halide. Nitric acid decomposes Sodium cyanide and sodium sulphide, which otherwise form black ppt. with  $\text{AgNO}_3$ .



(iii) **Special tests for Bromine and Iodine** : The presence of Bromine and Iodine can also be detected by performing carbon disulphide test with the Lassaigne's extract. The extract is treated with a few drops of carbon di-sulphide (or Chloroform) and then with excess of freshly prepared Chlorine water. The contents are shaken and the tube is allowed to stand.

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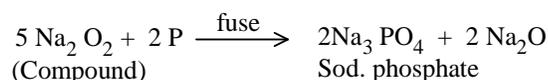
(a) An orange colour in carbon disulphide layer confirms Bromine

(b) A violet colour in carbon disulphide layer confirms Iodine.

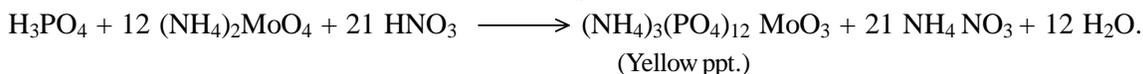
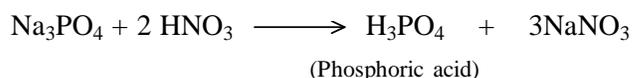
Actually chlorine being more reactive than bromine and iodine displaces these halogens from their respective halides.



5. **Detection of Phosphorus:** In order to detect Phosphorus, the organic compound is fused with Sodium peroxide, when Phosphorus is converted into Sodium phosphate.



The fused mass is extracted with water and the water extract is boiled with conc.  $\text{HNO}_3$ . Upon cooling a few drops of Ammonium molybdate solution are added. A yellow ppt. confirms Phosphorus.



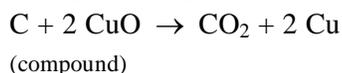
6. **Detection of Oxygen:** There is no direct method to detect oxygen in an organic compound. It is present in the form of functional groups such as  $-\text{OH}$ ,  $-\text{CHO}$ ,  $-\text{COOH}$ ,  $-\text{NO}_2$  etc. and is detected by testing for these groups.

## Estimations in Organic Compounds

### (1) Estimation of Carbon and Hydrogen :

The presence of C and H in an organic compound can be estimated by Liebig method.

A known weight of given dry organic compound, is taken in a small platinum cup and is heated strongly with dry cupric oxide in an atmosphere of dry oxygen (or air) free from  $\text{CO}_2$ . The carbon and hydrogen present in the organic compound are oxidised to  $\text{CO}_2$  and water vapours respectively.



These vapours are passed through previously weighed potash bulb and V-shaped Calcium chloride tube. The former absorbs  $\text{CO}_2$  while the latter will take up moisture or water vapours. The increase in weight of potash bulb will correspond to the weight of  $\text{CO}_2$  while that of  $\text{CaCl}_2$  tube will yield the weight of water formed. From the respective weights the percentage of Carbon and Hydrogen can be determined, by the formula

$$\% \text{ of Carbon} = \frac{12 \times \text{Mass of CO}_2 \times 100}{44 \times \text{Mass of organic compound}}$$

$$\% \text{ of Hydrogen} = \frac{2 \times \text{Mass of H}_2\text{O} \times 100}{18 \times \text{Mass of organic compound}}$$

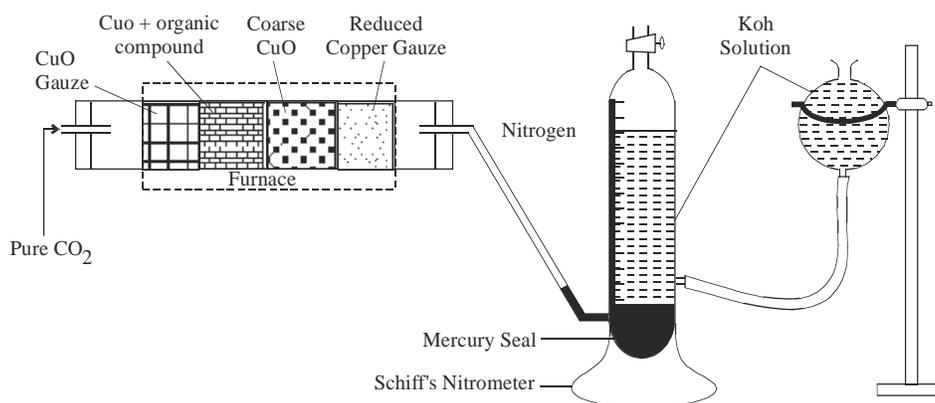
### 2. Estimation of Nitrogen :

Estimation of Nitrogen in an organic compound can be done by two ways :

(a) Duma's method      (b) Kjeldahl's method.

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- (a) **Duma's method** : A known mass of the given organic compound is heated with dry cupric oxide in a combustion tube in an atmosphere of  $\text{CO}_2$ . The gas is obtained by heating sodium bicarbonate and is bubbled through conc.  $\text{H}_2\text{SO}_4$  to remove moisture. A roll of oxidised copper gauze placed in the combustion tube which prevents the backward diffusion of the gases evolved in the combustion. A layer of coarse copper oxide that fills about 2/3 of the combustion tube helps in the oxidation of the compound. Upon heating Carbon and Hydrogen present in the organic compound are oxidised to  $\text{CO}_2$  and water vapours respectively, while  $\text{N}_2$  is set free. A small amount of Nitrogen might be oxidised to its oxides but they are reduced back to Nitrogen with the help of reduced copper placed at the end of the combustion tube.



The gaseous vapours are then passed into Schiff's nitrometer tube which contains in it about 40% KOH solution. It is provided with mercury seal at the bottom to check the backward flow of the liquid. The reservoir attached to the tube is used to record the volume of the Nitrogen at the atmospheric pressure. Both  $\text{CO}_2$  and water vapours are absorbed by KOH solution, and  $\text{N}_2$  gets collected over it. Its volume is recorded after careful levelling (the aqueous tension of the water vapours corresponding to this temperature is recorded from the tables).

$$\% \text{ age of Nitrogen} = \frac{28 V \times 1000}{22,400 \times W}$$

where  $V$  = Volume of  $\text{N}_2$  evolved

$W$  = Weight of organic compound taken

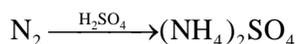
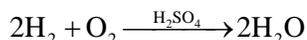
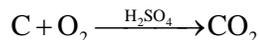
- (b) **Kjeldahl's method** : This method is convenient as compared to Duma's method and is largely used to estimate Nitrogen in food, fertilizers and drugs etc. However this method is not applicable to the compounds having a nitro ( $-\text{NO}_2$ ) or a diazo group ( $-\text{N} \equiv \text{N}-$ )

*Principle* : This method is based on the principle that when the nitrogenous compound is heated with conc.  $\text{H}_2\text{SO}_4$  in the presence of Potassium sulphate, the nitrogen present in the compound is converted into Ammonium sulphate. The Ammonium sulphate so formed is decomposed with excess of alkali and the Ammonia evolved is estimated volumetrically. The percentage of Nitrogen is then calculated from the amount of Ammonia.

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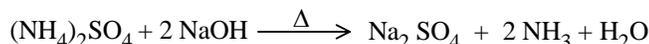
**Procedure :**

**Step I :** A known weight of the given organic compound is heated with conc.  $\text{H}_2\text{SO}_4$  in Kjeldhal's flask which is a round bottomed flask having a long neck provided with loose stopper. A small amount of  $\text{K}_2\text{SO}_4$  is added to raise the boiling point of  $\text{H}_2\text{SO}_4$ . Traces of  $\text{CuSO}_4$  or  $\text{Hg}$  is generally added to catalyse the reaction. The heating is done for two to three hours when Carbon and Hydrogen present in the compound are oxidised to  $\text{CO}_2$  and water vapour respectively, while Nitrogen is converted into Ammonium sulphate.



$\text{CO}_2$  and  $\text{H}_2\text{O}$  vapour escape through the loose stopper while  $\text{NH}_4^+$  is left behind in the flask.

**Step-II:** The contents of flask after cooling are transferred to a round bottomed flask. These are diluted with water and a few drops of methyl orange indicator are added. The indicator will impart pink colour to the solution which is acidic in nature. The flask is provided with a dropping funnel which contains about 40%  $\text{NaOH}$  solution. It is also connected to a water condenser through a Kjeldhal's trap.  $\text{NaOH}$  solution is dropped in the flask from the dropping funnel till the colour of the solution in the flask changes to yellow which indicates an alkaline medium. It is now heated and  $\text{NaOH}$  decomposes  $(\text{NH}_4)_2\text{SO}_4$  to evolve  $\text{NH}_3$ .



Vapours of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  will evolve through the trap which retains water. The  $\text{NH}_3$  vapours are condensed by a water condenser. The liquid  $\text{NH}_3$  formed is then absorbed in excess of standard acid (dil.  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ ) taken in a conical flask.  $\text{NH}_3$  is neutralized by the acid.



The excess of the acid is diluted with water and its volume is determined by titrating it against standard solution. By subtracting it from the total volume, the amount of acid used against  $\text{NH}_3$  can be determined. With the help of calculations the amount of  $\text{NH}_3$  absorbed by the acid and thus, the amount of Nitrogen is determined.

The % of Nitrogen in a compound is given by =  $\frac{1.4\text{NV}}{W}$  or  $\frac{1.4 \times (N_1V_1 - N_2V_2)}{W}$

### 3. Estimation of Halogens :

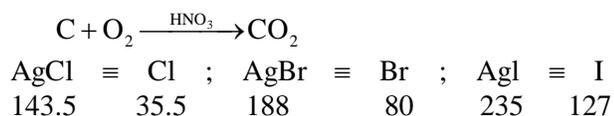
#### **Carius method**

*Principle :* A known mass of the organic substance is heated with fuming  $\text{HNO}_3$  in a Carius tube. The silver halide so obtained is separated, washed, dried and weighed. From the weight of silver halide formed, the percentage of halogen can be calculated.



Halogen

Carbon, Hydrogen or Sulphur present in the compound will be oxidised to CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> respectively.



$$(a) \quad \% \text{ of Cl} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl} \times 100}{\text{Mass of organic compound}}$$

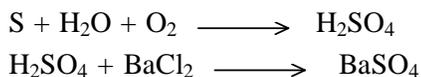
$$(b) \quad \% \text{ of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr} \times 100}{\text{Mass of organic compound}}$$

$$(c) \quad \% \text{ of I} = \frac{127}{235} \times \frac{\text{Mass of AgI} \times 100}{\text{Mass of organic compound}}$$

#### 4. Estimation of Sulphur :

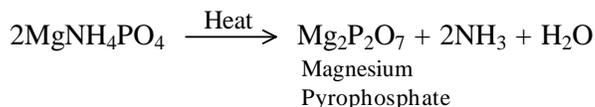
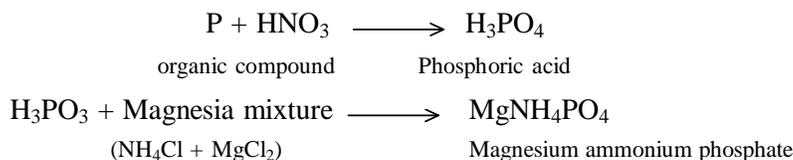
##### **Carius method**

*Principle* : A known mass of the organic compound is heated with fuming HNO<sub>3</sub> in a sealed tube when sulphur is quantitatively converted into sulphuric acid. It is then precipitated with barium chloride as barium sulphate. The precipitate is filtered, washed, dried and weighed. From the weight of BaSO<sub>4</sub> formed, the percentage of sulphur can be calculated. The main reactions are :



$$\% \text{ of sulphur} = \frac{32 \times \text{Mass of BaSO}_4 \times 100}{233 \times \text{Mass of organic compound}}$$

5. Estimation of Phosphorus : For the estimation of Phosphorus, the given organic compound is heated strongly with fuming nitric acid. The phosphorus in the compound is oxidised to phosphoric acid. It is treated with magnesia mixture (a solution containing magnesium chloride, ammonium chloride and a little of ammonia). A precipitate of magnesium ammonium phosphate MgNH<sub>4</sub>PO<sub>4</sub> is formed. This is filtered, washed, dried and then ignited to give Magnesium pyrophosphate (Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>). From the weight of Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, Phosphorus can be estimated.



$$\% \text{ of Phosphorus} = \frac{62 \times \text{Mass of Mg}_2\text{P}_2\text{O}_7}{222 \times \text{Mass of organic compound}} \times 100$$

6. Estimation of Oxygen : There is no direct method for the estimation of Oxygen in a given organic compound. It is estimated by subtracting the sum of the percentages of all other elements in the compound from 100.  
Percentage of oxygen = 100 – (sum % of all other element.)

**Determination of Molecular Mass:** After the percentage of the various elements present in an organic compound have been determined, the next step in finding the molecular structure of the compounds, is to determine its molecular mass.

Victor Meyer's method : It is a convenient method for the determination of molecular masses of volatile substances. It works on the following principle.

*Principle* : A known mass of a volatile substances is heated in Victor Meyer's tube. As a result, the substance changes into vapours. The vapours, in turn, displace an equal volume of air which is collected over water. The volume of air thus collected is measured at laboratory temperature and pressure. This volume is then converted into volume at STP by applying, the general gas equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

### Calculation

First Method :

Suppose the mass of the substance taken =  $w$  g

Volume of air displaced =  $V$  cm<sup>3</sup>

Experimental pressure (read from the barometer) =  $P$  mm

Room temperature =  $t^\circ$  C

Aq. Tension of  $t^\circ$  C (read from tables) =  $p$  mm

Pressure of the dry air =  $(P - p)$  mm

Step - I : To convert the volume at the experimental conditions to the volume at STP.

Experimental Conditions

At STP

$$P_1 = (P - p) \text{ mm}$$

$$P_2 = 760 \text{ mm}$$

$$V_1 = V \text{ cm}^3$$

$$V_2 = ?$$

$$T_1 = (273 + t) \text{ K}$$

$$T_2 = 273 \text{ K}$$

$$\text{Now, } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{ Or } \frac{(P - p) \times V}{(273 + t)} = \frac{760 \times V_2}{273}$$

So ' $V_2$ ' can be calculated.

Here, volume of air displaced at STP = Volume of liquid vapours =  $V_2$  cm<sup>3</sup>

Step - I : *i.e.* Molecular Mass =  $\frac{\text{Mass of substance taken}}{\text{Vol. of displaced air at STP}} \times 22400$

Second Method (Alternatively) : Using the Ideal gas equation. we calculate the number of moles of the vapour collected.

$$\Rightarrow (P - p) \text{ mm} = \frac{P - p}{760} \text{ atm}$$

$$\text{Volume} = V \text{ ml} = \frac{V}{1000} \text{ litre}$$

$$T = (273 + t) \text{ K} \Rightarrow n = \frac{P_1 V_1}{RT} = \frac{\left(\frac{P - p}{760}\right) \frac{V}{1000}}{RT}$$

Number of moles  $\times$  mol. wt = amount of substance

$$n \times M_0 = w$$

$$\Rightarrow M_0 = \frac{w}{n}$$

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Third Method (Alternatively) :

$$\text{vapour density of substance} = \frac{\text{Mass of } V_2 \text{ ml of vapour at STP}}{\text{Mass of } V_2 \text{ ml of } H_2 \text{ at STP}} = \frac{w \times 22400}{V_2 \times 2} = \text{Vapour density}$$

$$\text{Mol. wt.} = 2 \times \text{vapour Density.}$$

## ELECTRONIC EFFECTS

It is often observed that most of the attacking reagents always possess either a positive or negative charge, therefore a reaction takes place on a covalent bond, which possesses oppositely charged centres. This is made possible by the displacement (partial or complete) of bonding electrons.

These displacements of bonding electrons both partial or complete are called Electronic effects.

These electronic effects may be

- (a) Permanent effects
- (b) Temporary effects

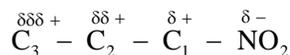
**Permanent Electronic Effects:** Here the displacement in the electron cloud is permanent as in R-X, R-OH, etc. These are also called polarisation effects.

The different permanent electronic effects in molecules are

- (a) Inductive Effect
- (b) Resonance Effect

**Temporary or Impermanent:** These are brought about in a molecule in the presence of attacking reagent and as soon as the attacking reagent is removed the electronic effect disappears such effects are termed as polarisability effects. Some of these are, electromeric effect, inductomeric effect and hyperconjugation effect.

**Inductive Effect:** This is introduced in the Carbon chain when an atom/group of atoms (X) of different electronegativity is attached to its one end. This results in the electron pairs of the chains displaced towards X (if more electronegative) or away from X (if less electronegative) and thereby a polarity gets introduced in the chain permanently *e.g.* let us consider a Carbon chain with a NO<sub>2</sub> group, having more electronegative than Carbon.



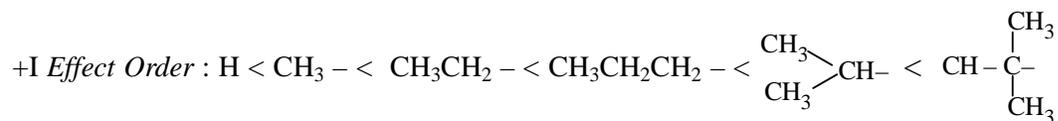
NO<sub>2</sub> group being more electronegative attracts the shared electron pair towards itself. C<sub>1</sub> thus acquires a small +ve charge. The NO<sub>2</sub> group will also influence the C<sub>2</sub> Carbon but the C<sub>2</sub> Carbon will acquire a less positive charge than C<sub>1</sub>. This transmission is passed on to C<sub>3</sub> and C<sub>4</sub> but to a lesser intensity. We can therefore say that the NO<sub>2</sub> group exerts inductive effect only till a certain length of Carbon chain, depending on the electronegativity of atom/group of atoms. Beyond this Carbon atom, the effect disappears. For all practical purposes Inductive effect is ignored beyond, third Carbon atoms.

**Types of Inductive Effects:** It is of two types

**+I Effect:** If the inductive effect of an atom or group of atoms is less than that of H-atom, it is called +I effect. These are electron releasing groups or pumping groups.

**-I Effect:** If the inductive effect of the atom or group of atoms is more than H-atom it is called -I Effect.

These are electron attracting or withdrawing groups.



-I Effect Order :  $NO_2 > CN > SO_3H > F > COOH > \text{Acid derivative} > \text{aldehyde} > \text{Ketones} > Cl > Br$

$> I > OH > OCH_3 > NH_2 > NHR > \text{C}_6\text{H}_5 > H.$

## Applications

### 1. Stability of Reaction Intermediate

(a) **Carbocations** : The Carbon atoms carrying +ve charge is called carbocation. e.g.  $CH_3^+$ ,  $CH_3CH_2^+$ , etc.

(i) The stability of a carbocation would be maximum if the charge density is least.

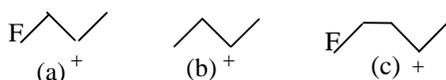
[Any charged species is most stable if its charge density is least.]

Hence  $CH_3CH_2^+$  is more stable than  $CH_3^+$

This is because the  $CH_3$  group in  $CH_3CH_2^+$  being a +I group pushes  $e^-$ s and decreases the +ve charge density.

(ii)  $CH_3CH_2^+$ ,  $(CH_3)_2CH^+$ ,  $(CH_3)_3C^+$

Here stability in decreasing order is  $(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3 - CH_2^+$

(iii)  Here the stability order is  $b > c > a$ .

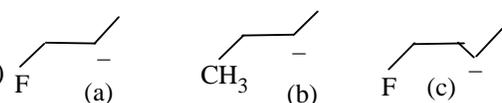
This is because F group is a -I group and  $CH_3$  is a +I group. Hence F group destabilized the cation whereas  $CH_3$  group stabilizes the cation.

(b) **Carbanions** : The Carbon atom carrying the -ve charge is called carbanion e.g.  $CH_3^-$ ,  $CH_3CH_2^-$

(i) As the +I effect increases the negative charge density increases, the stability decreases, in

$CH_3 - CH_2^-$  there is a  $CH_3$  group which pushes  $e^-$ s to  $-CH_2^-$  group and thereby destabilizes it.

So  $CH_3^-$  is more stable than  $CH_3 - CH_2^-$

(ii) 

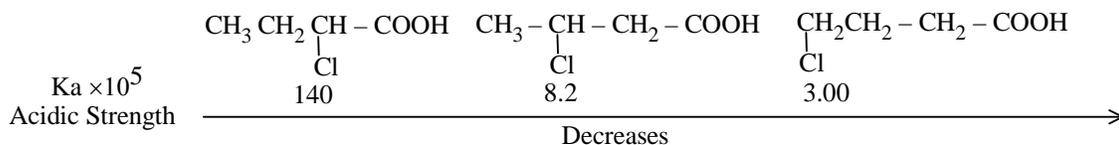
Here the -I group F pulls the  $e^-$ s whereas the +I group  $CH_3$  pushes the  $e^-$ s.

Due to the -I effect of F the -ve charge density decreases and thereby stability increases so  $a > c > b$ .

**Acidic strength:** The acidic strength of the substances may be compared based on the stability of conjugate base.



Also since the inductive effect (-I) decreases as the group responsible for the effect moves farther from functional acidic group the acidic strength decreases.



	$K_a$		$K_a$
HCOOH	$17.7 \times 10^{-5}$	$\text{CH}_3\text{CHClCH}_2\text{COOH}$	$8.9 \times 10^{-5}$
$\text{CH}_3\text{COOH}$	$1.75 \times 10^{-5}$	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$	$2.96 \times 10^{-5}$
$\text{ClCH}_2\text{COOH}$	$136 \times 10^{-5}$	$\text{FCH}_2\text{COOH}$	$260 \times 10^{-5}$
$\text{Cl}_2\text{CHCOOH}$	$5530 \times 10^{-5}$	$\text{BrCH}_2\text{COOH}$	$125 \times 10^{-5}$
$\text{Cl}_3\text{CCOOH}$	$23200 \times 10^{-5}$	$\text{ICH}_2\text{COOH}$	$67 \times 10^{-5}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	$1.52 \times 10^{-5}$	$\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$	$4.9 \times 10^{-5}$
$\text{CH}_3\text{CH}_2\text{CHClCOOH}$	$139 \times 10^{-5}$	$p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{COOH}$	$14.1 \times 10^{-5}$

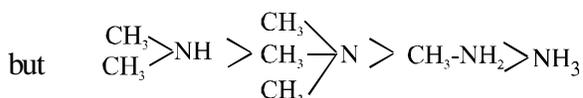
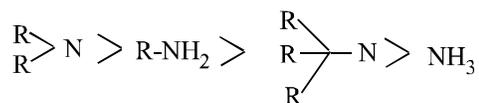
**Basic Strength of Amines:** The basic strength of amines is due to the presence of unpaired electron on Nitrogen atom which accepts a proton.

The reactivity with which the lone pair of electrons is available for proton determines the relative basic strength.

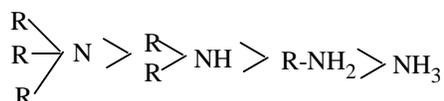
This reactivity depends upon *solvent effect* and *structural effects*.

When R = CH<sub>3</sub> group then

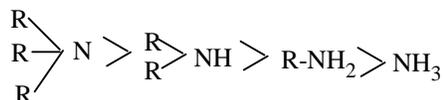
(a) In Polar protic solvents the decreasing order of basic strength is



(b) In Polar aprotic solvents the decreasing order of basicity is

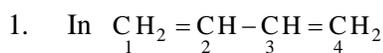


(c) In air



## RESONANCE AND RESONANCE EFFECT

**Resonance:** It is often observed that sometimes a single structure of a compound cannot explain satisfactorily all its properties e.g.



2. Benzene ordinarily is represented as either I or II has two types of Carbon-Carbon



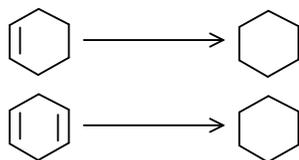
I



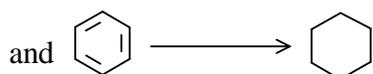
II

bonds; thus C–C (bond length 1.54 Å) and three C = C (bond length 1.34 Å), but experimentally all the Carbon-Carbon bonds in Benzene are found to be identical in all respects e.g. their bond length is 1.39 Å. Also in spite of the presence of double bonds, Benzene does not take part in electrophilic addition reactions,

3. It is found that the heat of hydrogenation for  $\text{CH}_2 = \text{CH}_2 \rightarrow \text{CH}_3\text{-CH}_3$



determined experimentally is equal to the heat of hydrogenation determined by bond energy values which means that their structures are adequate to explain the experimental values. Whereas the heat of hydrogenation for  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \longrightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$



as determined experimentally are less than the heats of hydrogenation obtained with the help B.E. values.

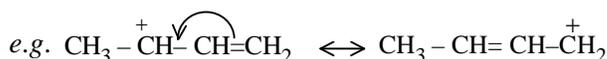
4. Such and other allied properties of Benzene and several other compounds can only be explained if we consider that the Benzene and other molecules are a hybrid of different structures.

This phenomenon in which two or more structures can be written for the true structures of a molecule, but none of these can be said to represent it uniquely, is referred to as resonance. The true structure of the molecule is said to be a resonance hybrid of the various possible alternative structure which themselves do not exist (resonating structure or canonical structure).

The resonance hybrid may be defined as the actual structure of all possible structures that can be written for the molecule without changing the relative positions of its atoms and without violating the rules of covalence maxima for the atoms.

### Rules for writing resonating structures

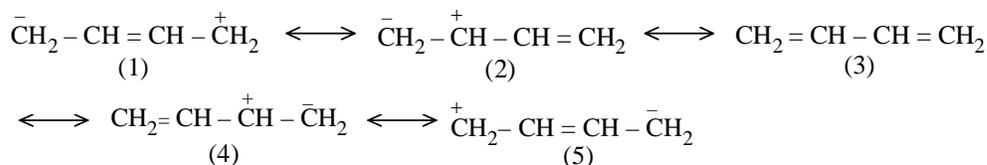
1. The position of atoms in the molecule should not change.



2. Every resonating structure must have the same number of (Bond pair + lone pairs) of electrons. In the above structure, the sum of electrons in lone pairs and bond pair are same i.e. 22.
3. The atoms like C, N, O, F if involved in resonance must follow the octet rule. i.e. they can have a maximum of eight electrons in the valence shell. But atoms like Cl, Br, I, S, P if involved in resonance can have more than 8-electrons in the valence shell.
4. The energies of the various limiting structures must be same or nearly the same.
5. All the resonating structure must be planar.

### Example : Resonating Structure

#### 1,3-Butadiene



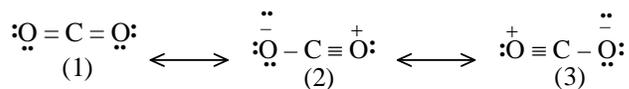
- (a) If one counts the sum of electrons in lone pair and bond pair, it is the same which is 22 in all resonating structures.
- (b) Each Carbon atom satisfies the octet rule.
- (c) All atoms are in the same plane.
- (d) The stability order of the different structures is:  $3 > 2 = 4 > 1 = 5$
6. All resonating structures do not have real existence. The structure which only contribute to the real structure is the resonance hybrid.

All the resonating structures do not contribute equally to the resonance hybrid.

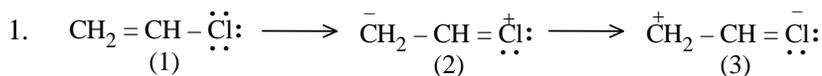
The more stable form contributes to the maximum extent and the least stable form to the least extent.

- (a) A neutral form is more stable than a dipolar ion.
- (b) That structural form is most stable which has maximum number of covalent bonds.
- (c) As the charge separation increases stability decreases.
- (d) If all structures have formal charge, the most stable one is that in which the negative and the +ve charges reside on the most electronegative and most electropositive atom respectively.
- (e) Though it is better to have a negative charge on a more electronegative atom and the charge on a more electro positive atom that structure will not be stable which follows octet rule.

#### Resonating Structures of $\text{CO}_2$

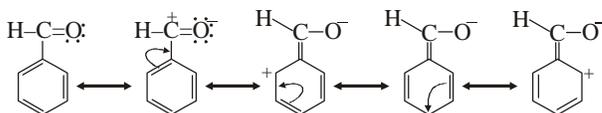
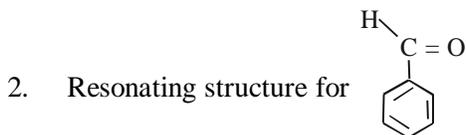


#### Resonating Structures of Vinyl Chloride



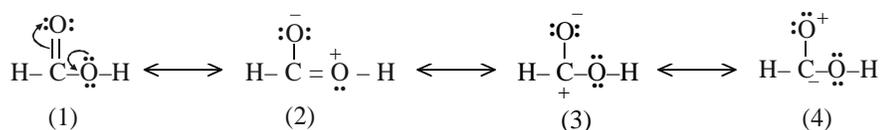
If you observe you will find that

- (a) Sum of the electrons in lone pair and bond pair is equal to 18 in all the three resonating structures written above.
- (b) The chlorine atom in structure (3) contains 10 electrons in the valency shell which is possible for chlorine atom.
- (c) All the atoms are in the same plane.



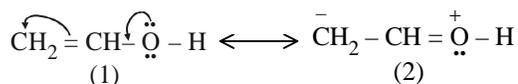
Here again all the resonating structure satisfy the conditions for resonance.

## Resonating Structure of Formic Acid



Here the stability order is  $1 > 2 > 3 > 4$

Resonating structures in vinyl alcohol.

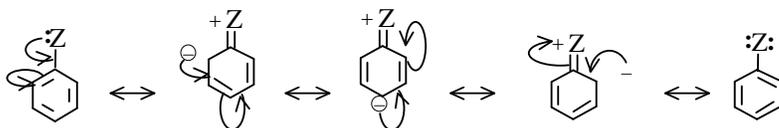


The stability order of vinyl alcohol is  $1 > 2$ .

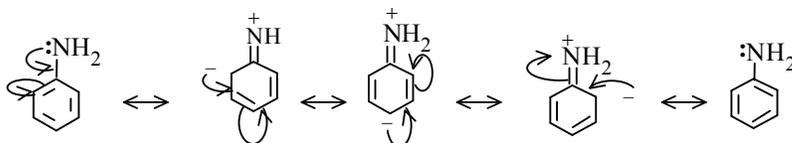
**Resonance Effect:** The transfer of electrons from one part of conjugated  $\pi$  system to the other due to the phenomenon of resonance is called resonance effect.

The resonance effect is of two types,

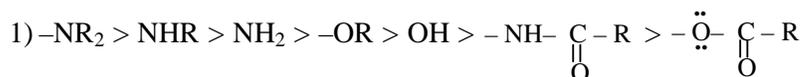
- (a) When the electrons displacement is away from the atom or group attached to the given molecule, it is called +R or +M effect.



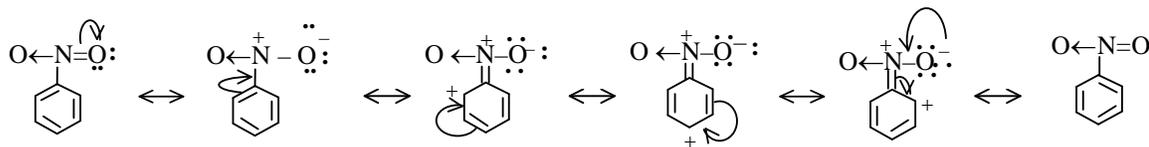
**Ex.**



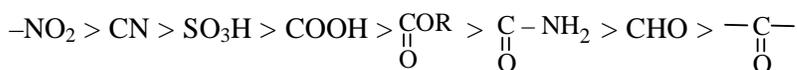
Groups with the Z can be (+M or +R groups) are



- (b) When electron displacement is towards the atom or group attached to the given molecule it is called -R or -M effect.



Examples of such groups are (-R or -M groups)

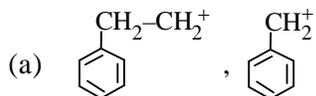


These (+M and the -M) effects like inductive +I and the -I effect, affect both the physical as well as the chemical reactivities (viz acidic, basic strength, etc) of a molecule.

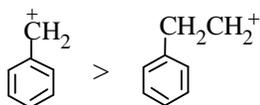
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## Applications

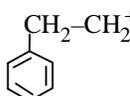
### 1. Stability of ions

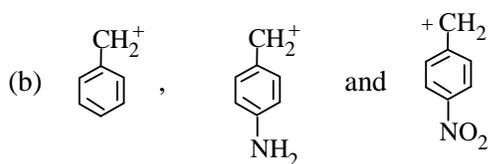


Here the stability order of carbocations is

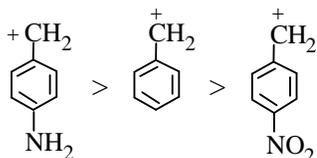


In  we have resonance stabilization due to delocalization of the charge.

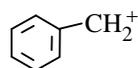
In the structure  the phenyl group offers a -I effect thereby destabilizing the systems.



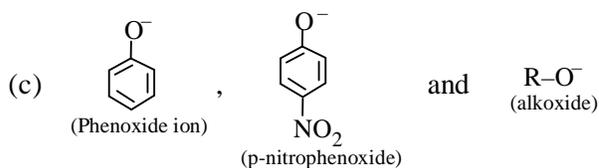
Here the stability order of the carbocation is

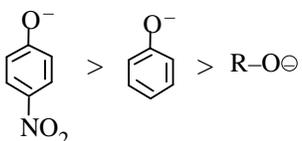


Here the -NH<sub>2</sub> group being a +R group pushes electrons and helps resonance stabilization of

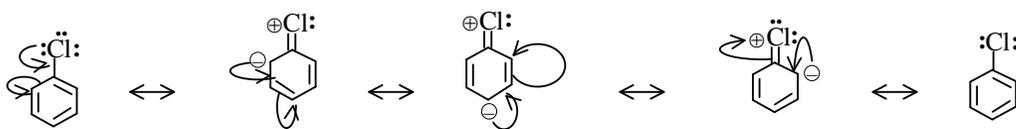
 group while -NO<sub>2</sub> group being a (-R) group pulls electron thereby deactivating the

 group further.



The stability order is 

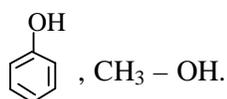
2. Chlorobenzene is deactivating but o-, p-, directing towards electrophilic substitution reaction. In chlorobenzene though conjugation takes place as



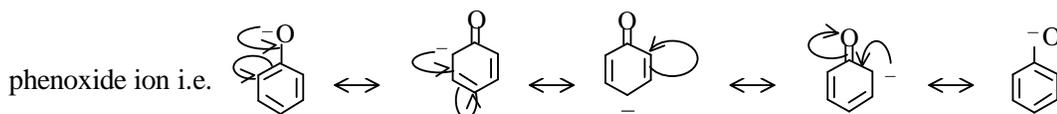
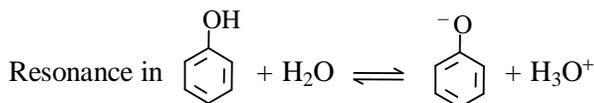
So one would expect the benzene ring to be highly activated. Still due to the strong -I character of -Cl group the electron pushing tendency gets reduced. Hence due to its -I character it is strongly deactivating but during chemical reactions (electrophilic substitution) enough energy is given in the form of heat where by the resonance pushing, becomes a dominant effect and it becomes ortho and para directing.

### Acidic Character

3. (a) Phenol is a stronger acid than methanol.



Phenol in water dissociates to form phenoxide ion which is resonance stabilized,



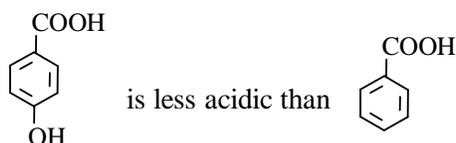
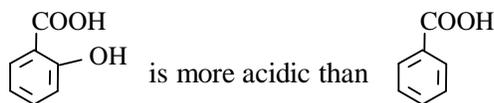
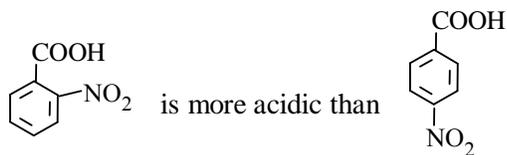
where as Methanol gives methoxide ion



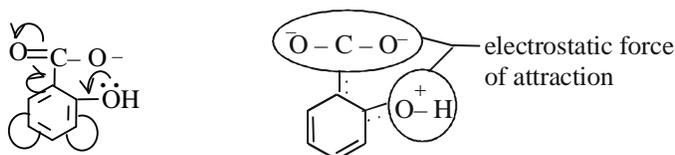
The methoxide ions is unstable due to the strong +I effect of Methyl group.

Hence Phenol is a stronger acid than methanol.

- (b) The Acidic strength of Phenol or Benzoic acid generally increase on introducing a strong electron withdrawing groups while acidic strength decreases on introducing a electron releasing groups e.g.
- Nitrobenzoic acid is more acidic than Benzoic acid
  - Toluic acid is less acidic than Benzoic acid.
- (c) Most of the times but not always acidic strength increases many fold when a + R group or -R group is introduced at ortho position, this is called ortho effect e.g.



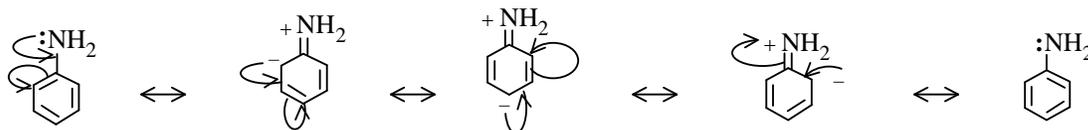
- (d) Reason for being more acidic than all hydroxy benzoic acid inspite of the fact that  $-OH$  group is  $+R$  group and should destabilize the conjugate base, is that the conjugate base of *o*-hydroxy benzoic acid is highly stable due to electrostatic force of attraction between the negatively charged  $\text{-C(=O)O}^-$  and  $+ve$  charged  $-OH$  group. This is because after pushing the electrons  $-OH$  group becomes  $+vely$  charged.



4. *Aniline is a weaker base than aliphatic amine.*

The basic strength of Amines depend upon the protonating power of the Amine on the Nitrogen atom. This would greatly depend upon the electron availability on Nitrogen.

In Aniline, the lone pairs of electron on Nitrogen is in conjugation with the Benzene ring



This results in the non-availability of electrons on the Nitrogen thereby decreasing the protonating

power where as in  $R-NH_2$ ,  $R \rightarrow \begin{array}{c} H \\ | \\ N \\ | \\ H \end{array}$  due to the electron pushing ( $+I$ ) nature of alkyl group it increases

the basic strength of any amines.

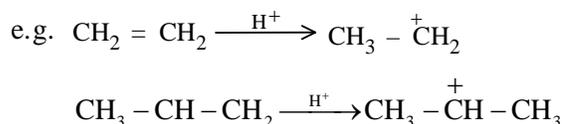
$K_a$ of Benzoic acid = $6.3 \times 10^{-5}$					
	$K_a$		$K_a$		$K_a$
<i>p</i> -NO <sub>2</sub>	$36 \times 10^{-5}$	<i>m</i> -NO <sub>2</sub>	$32 \times 10^{-5}$	<i>o</i> -NO <sub>2</sub>	$670 \times 10^{-5}$
<i>p</i> -Cl	$10.3 \times 10^{-5}$	<i>m</i> -Cl	$15.1 \times 10^{-5}$	<i>o</i> -Cl	$120 \times 10^{-5}$
<i>p</i> -CH <sub>3</sub>	$4.2 \times 10^{-5}$	<i>m</i> -CH <sub>3</sub>	$5.4 \times 10^{-5}$	<i>o</i> -CH <sub>3</sub>	$12.4 \times 10^{-5}$
<i>p</i> -OCH <sub>3</sub>	$3.3 \times 10^{-5}$	<i>m</i> -OCH <sub>3</sub>	$8.2 \times 10^{-5}$	<i>o</i> -OCH <sub>3</sub>	$8.2 \times 10^{-5}$
<i>p</i> -OH	$2.6 \times 10^{-5}$	<i>m</i> -OH	$8.3 \times 10^{-5}$	<i>o</i> -OH	$105 \times 10^{-5}$
<i>p</i> -NH <sub>2</sub>	$1.4 \times 10^{-5}$	<i>m</i> -NH <sub>2</sub>	$1.9 \times 10^{-5}$	<i>o</i> -NH <sub>2</sub>	$1.6 \times 10^{-5}$

Generally electron releasing groups increases the basic strength of Aniline and electron withdrawing groups decreases basic strength of Aniline also whether electron releasing or electron withstanding groups if present at the ortho-position with respect to NH<sub>2</sub> group will always decrease basic strength of Aniline.

$K_b$ of Aniline = $4.2 \times 10^{-10}$					
	$K_b$		$K_b$		$K_b$
<i>p</i> -NH <sub>2</sub>	$140 \times 10^{-10}$	<i>m</i> -NH <sub>2</sub>	$10 \times 10^{-10}$	<i>o</i> -NH <sub>2</sub>	$3 \times 10^{-10}$
<i>p</i> -OCH <sub>3</sub>	$20 \times 10^{-10}$	<i>m</i> -OCH <sub>3</sub>	$2 \times 10^{-10}$	<i>o</i> -OCH <sub>3</sub>	$3 \times 10^{-10}$
<i>p</i> -CH <sub>3</sub>	$12 \times 10^{-10}$	<i>m</i> -CH <sub>3</sub>	$5 \times 10^{-10}$	<i>o</i> -CH <sub>3</sub>	$2.6 \times 10^{-10}$
<i>p</i> -Cl	$1 \times 10^{-10}$	<i>m</i> -Cl	$0.3 \times 10^{-10}$	<i>o</i> -Cl	$0.05 \times 10^{-10}$
<i>p</i> -NO <sub>2</sub>	$0.001 \times 10^{-105}$	<i>m</i> -NO <sub>2</sub>	$0.029 \times 10^{-10}$	<i>o</i> -NO <sub>2</sub>	$0.00006 \times 10^{-10}$

### Temporary Displacements

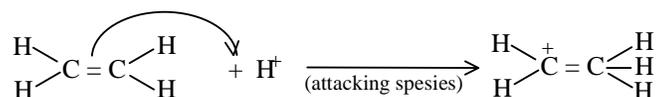
**Electromeric effect** : This is a temporary effect which involves the complete transference of shared pair of  $\pi$ -electrons to either of the two atoms involved in multiple bond in the presence of attacking reagent.



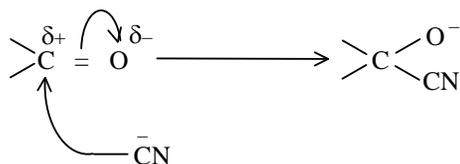
Here electromeric effect will be formal in the direction of stable carbocation.

*Types of Effects* : These are the two types

(i) **+E-Effect** : When the electron transfer takes place towards the attacking reagent it is called +E effect.

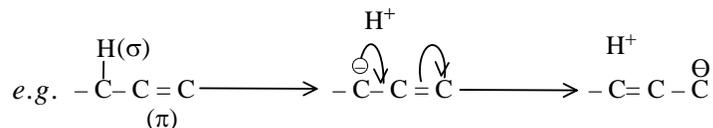


(ii) **-E-Effect** :- when electron transfer takes place away from attacking reagent.



Here electron movement arrow specifies that it is against the attacking species.

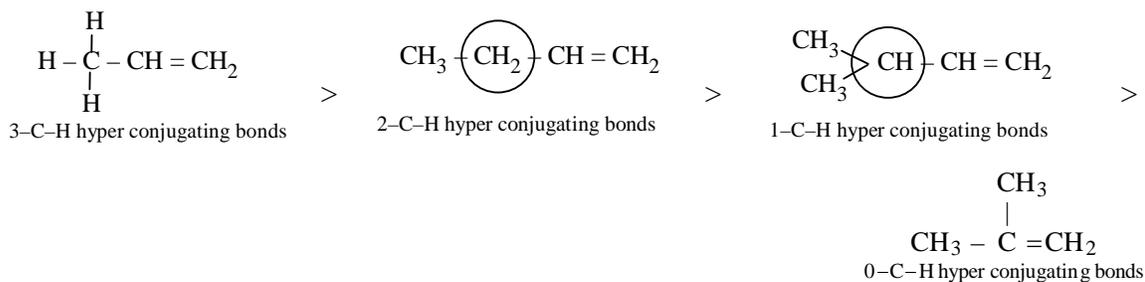
**Hyperconjugation:** It is the delocalization of electrons through overlap between  $\pi$ -orbitals and  $\sigma$ -orbital of alkyl group. This was suggested by Baker and Nathan. It was suggested that alkyl groups with at least one Hydrogen atom on the  $\alpha$ -Carbon atom, attached to an unsaturated Carbon atom, are able to release electrons by a mechanism similar to that of electromeric effect.



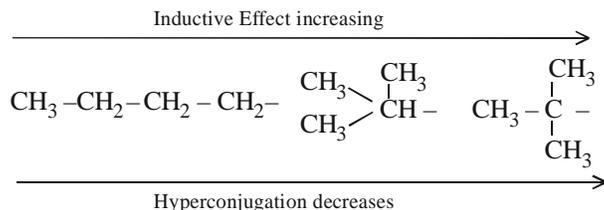
This is also known as  $\sigma$ - $\pi$  conjugation or no bond resonance.

More the number of H-C bonds attached to unsaturated carbon atoms more will be the probability of electron release mechanism.

Hence the electron release by this mechanism will be greater in methyl, than in ethyl group.



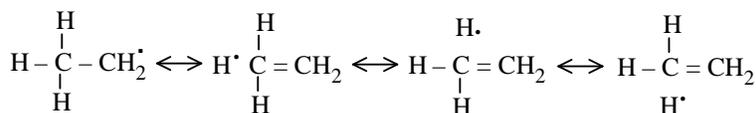
It is important to note that although hyperconjugation is like inductive effect, the two effect may reinforce or oppose each other.



Number of hyperconjugating structures = number of hyperconjugating H-atoms +1.

### Applications :

#### 1. Stability of Free Radical



More the hyperconjugation more is the stability.

For  $\text{CH}_3\dot{\text{C}}\text{H}_2$  number of hyperconjugation = 4

$(\text{CH}_3)_2\dot{\text{C}}\text{H}$  number of hyperconjugation = 7

$(\text{CH}_3)_3\dot{\text{C}}$  number of hyperconjugation = 10.

The stability order : t-alkyl > s-alkyl > p-alkyl >  $\text{CH}_3$

#### 2. Stability of $\text{CH}_3\text{CH}=\text{CH}_2$ and $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_3$

2-Butene is more stable than Propene.

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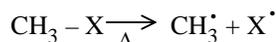
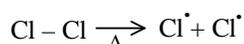
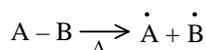
## Organic Reaction

Here we shall study a chemical reaction by means of actual (not HYPOTHETICAL) series of discrete steps which are involved in the transformation of reactants to products.

In organic reactions since covalent bonds are involved they therefore involve

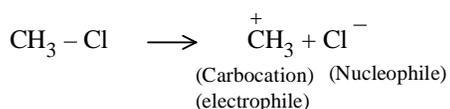
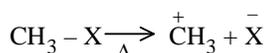
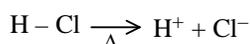
- (a) breaking of old covalent bonds.
  - (b) making of new covalent bonds
1. Whenever energy is made available to a covalent bond it will break in two ways
- (a) *Homolytically* – Leads to the formation of free radicals.
  - (b) *Heterolytically* – Leads to the formation of ions.

**Homolytic Cleavage:** When cleavage of bonds takes place symmetrically i.e. one electron is taken by each atom forming the bond then it is called homolytic cleavage which leads to the formation of free radical.



Many a times homolytic fission involves bonds where the atoms forming them are similar or have no electronegativity difference between them..

**Heterolytic Cleavage:** When on supply of energy to bond the cleavage takes place in such a manner that the shared pair of electrons are taken up by only one which is more electronegative, then the cleavage is called heterolytic cleavage.



## The Attacking Reagents

The attacking reagents are classified into two main groups.

1. **Electrophiles :** The species which carry +ve charge or are electron deficient are called electrophiles.

These attack regions of high electron density in a molecule.

- (a) Positively charged electrophiles.



- (b) Neutral electrophiles

