

# General Organic Chemistry

## 1.1 Introduction:

Organic reaction involve the breaking and making of covalent bonds. The breaking and making of covalent bonds usually occurs in several discrete steps before transformation into product. The detailed sequential description of all steps of the transformation into products is called the mechanism of a reaction.

Complete information regarding all the steps is seldom obtained. However, a good deal of data can be gathered from the following

- study of kinetics of the reactions
- isolation of intermediate, if isolable.
- study of reactions in the presence of other similar substrate.
- study of the isotopically labelled atom in the reactants.
- trapping of free radicals
- crossover experiments
- stereochemical aspects etc.

Reaction mechanism containing following tools

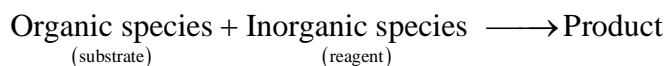


### (i) Reactant :

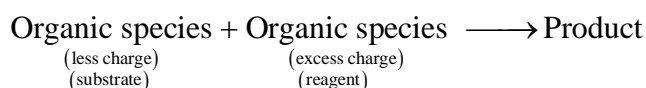
Reactant are classified into substrate and reagent

- substrate  $\Rightarrow$  species at which reagent attack.
- Reagent  $\Rightarrow$  attacking species (more reactive species)

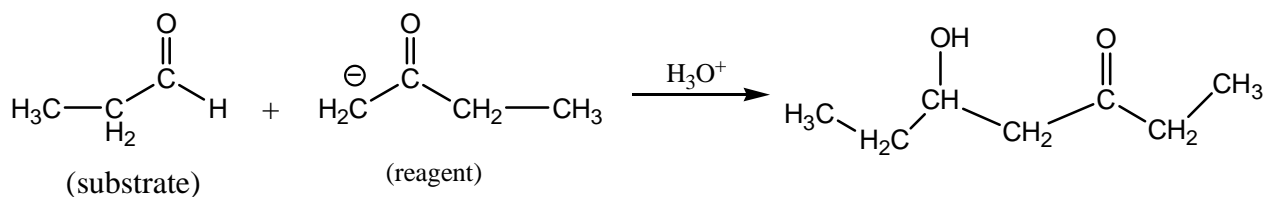
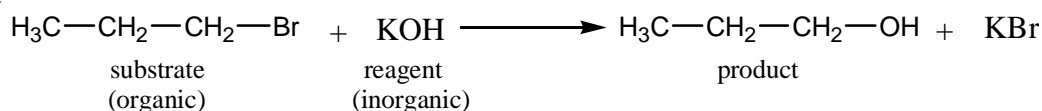
**Case-I:** If reaction occurs between organic and inorganic species, organic species act as substrate and inorganic species act as reagent.



**Case-II:** If reaction takes place between organic species then usually higher charge species act as reagent, other species act as substrate.



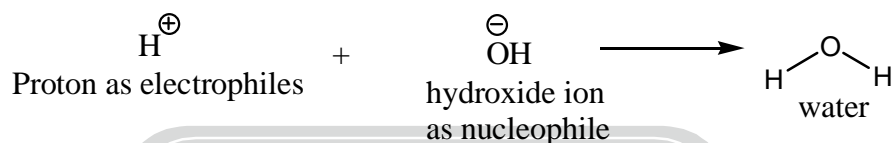
Reactant are the species whose change gives the product. Reagent are the species which helps reagents to change its state to get converted to the products.

**Example:**

In this case both are substrate and reagent is that species which helps the ketone to form the anion or enol.

**1.2. Electrophiles :**

(Electron loving species) electrophiles are electrons-deficient species and tend to attack the substrate at a site of high electron density. They may be neutral species as exemplified by Lewis acid (such as  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{ZnCl}_2$ ), carbene and carbocations.

**Classification of electrophiles:**

(a) Species having positive charge

Example :  $\text{H}^+$ ,  $\text{R}^+$ ,  $\text{Cl}^+$ ,  $\text{NO}^+$ ,  $\text{NO}_2^+$ ,  $\text{C}_6\text{H}_5-\text{N}^+$ ,  $\text{CH}_3-\text{C}^+=\text{O}$  etc.

(b) Neutral species having vacant p-orbitals

Example :  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{BBr}_3$ , carbene, etc., all are octate deficient species.

(c) Species having vacant d-orbital

Example :  $\text{FeCl}_3$ ,  $\text{FeCl}_2$  etc.

(d) Species having low lying  $\sigma$ -antibonding molecular orbital.

Example :  $\text{Br}_2$ ,  $\text{Cl}_2$ ,  $\text{I}_2$  etc.

(e)  $\pi$ -bonding molecule:



All are octate filled but electrophilic because the negative charge is stabilised by delocalization or electron withdrawing atom.

(f) Element in their atomic state :

Example : O, S etc.

**1.3. Nucleophiles:**

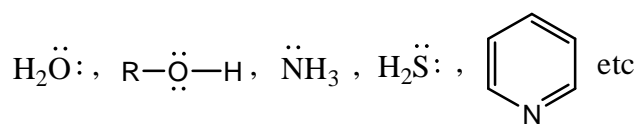
(Nucleus-loving species) Nucleophiles are electron donar species. Nucleophilic reagents tend to attack the electron deficient species (electrophiles).

**Classification of Nucleophiles:**

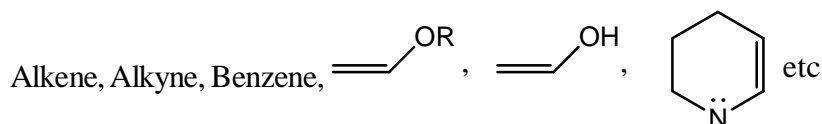
(a) Negative charge species:  $\text{OH}^-$ ,  $\text{OR}^-$ ,  $\text{SH}^-$ ,  $\text{SR}^-$ ,  $\text{R}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  etc

(b) Organometallic reagent:  $\text{R}^-\text{MgX}$ ,  $\text{R}^-\text{Li}$ ,  $\text{R}_2^-\text{CuLi}$ ,  $\text{R}_2^-\text{Cd}$ ,  $\text{R}_2^-\text{Zn}$  etc

(c) Lone pair containing species:



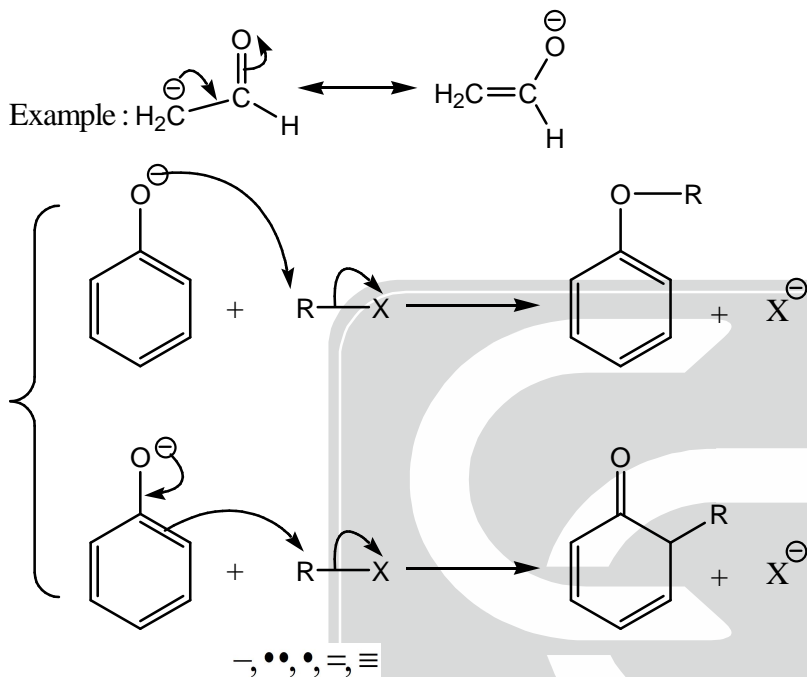
(d)  $\pi$ -bonded molecules:



**Note:** Some species behave as the electrophiles as well as nucleophiles

Example :  $\text{Br}_2$ ,  $\text{Cl}_2$ ,  $\text{I}_2$ , etc.

**Ambidentated nucleophile :** Those nucleophile which possess more than one site for  $\text{E}^+$  attack but at the same time only one site is used to form bond with electrophile. It is called ambidentated nucleophile, such type of ambidentated nucleophile are regioselective.

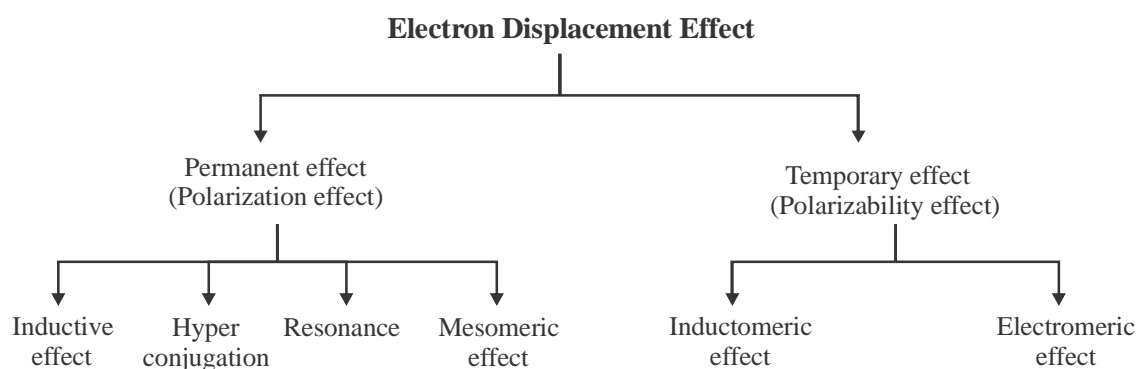


**Note:**  $\text{—}, \bullet\bullet, \bullet, =, \equiv$   
Decreasing order of nucleophilicity  
[Electronegativity  $\propto$  % of s-character]

**Note : Electron Displacement Effects:**

Effect occurring due to displacement of electron in organic compound is called *Electron Displacement Effect* or electron delocalisation effect.

Electron displacement effect is of mainly two types.

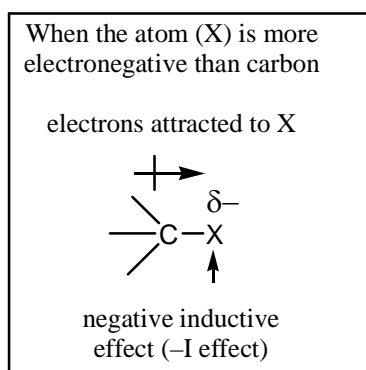


**Other Effect:**

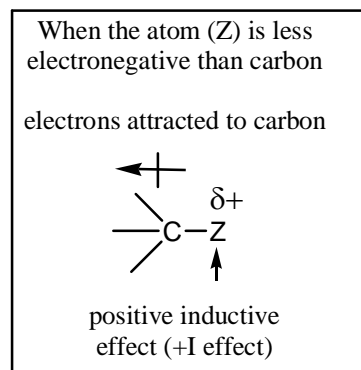
(a) Steric inhibition of resonance      (b) Ortho effect.

### 1.4. Inductive effects:

In a covalent bond between two different atoms, the electrons in the  $\sigma$  – bond are not shared equally. The electrons are attracted towards the most electronegative atom. An arrow drawn above the line representing the covalently bonded electrons shifts towards higher electronegative atom can show this. Electrons are pulled in the direction of the arrow.



**-I groups**



**+I groups**

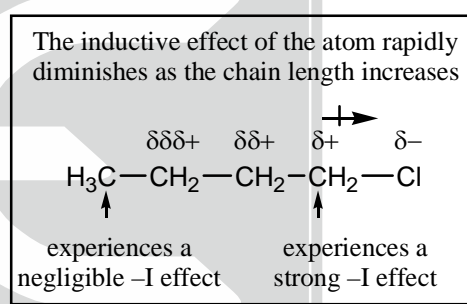
X=Br, Cl, NO<sub>2</sub>, OH, OR, SH,  
SR, NH<sub>2</sub>, NHR, NR<sub>2</sub>, CN, CO<sub>2</sub>H,  
CHO, COR

Z=R(alkyl or aryl),  
metals (e.g. Li or Mg) and anions

The more electronegative the atom(X),  
the stronger the -I effect

The more electropositive the atom (Z),  
the stronger the +I effect.

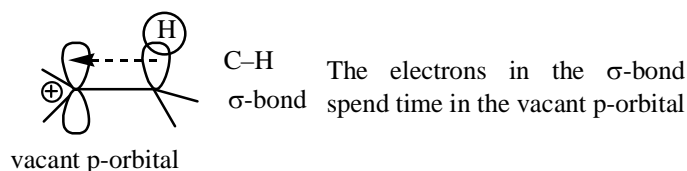
Pauling electronegativity scale	
K = 0.8	I = 2.5
C = 2.5	Br = 2.8
N = 3.0	Cl = 3.0
O = 3.5	F = 4.0
Higher the value, more electronegative will be atom	



The overall polarity of a molecule is determined by the individual bond polarities, formal charges and lone pair contributions, and this can be measured by the dipole moment ( $\mu$ ). Higher the dipole moment (measured in debyes (D)), more polar will be compound.

### 1.5. Hyperconjugation:

A  $\sigma$  – bond can stabilise a neighbouring carbocation (or positively charged carbon) by donating electrons to the vacant p-orbital. The positive charge is delocalised or ‘spread out’, and this stabilising effect is known as “no-bond resonance”.



#### Points to Remember :

Number of  $\alpha$  hydrogen  $\propto$  number of hyperconjugating structure  $\propto$  stability

$$\propto \frac{1}{\text{Heat of hydrogenation}} \propto \text{Polarity} \propto \text{dipole moment} \propto \frac{1}{\text{bond length}}$$