# 1. AROMATIC ELECTROPHILIC SUBSTITUTION REACTIONS

**Electrophilic substitution :**

Substitution reactions which involve electrophilic reagents and called electrophilic substitutions.

Electrophilic reagents are called electrophiles. They are electron deficient species. So they attack centres which are electron rich. So they are called electrophiles (electron loving species). They may be positively charged or neutral species.

Some examples of electrophiles : (i) $NO_2^+$ (Positively charged nitronium ion) ii. $SO_3$ (Neutral) iii. $RCO^+$ (acyl cation) (v). $Cl^+$ (vi). $Br^+$ etc.

**Examples of electrophiles substituion reactions of benzene :**

i. Nitration
ii. Sulphonation
iii. Friedel Craft's acylation and alkylation etc.

**General mechanism of aromatic electrophilic substitution**

The general mechanism of aromatic electrophilic substituion consists of three steps.

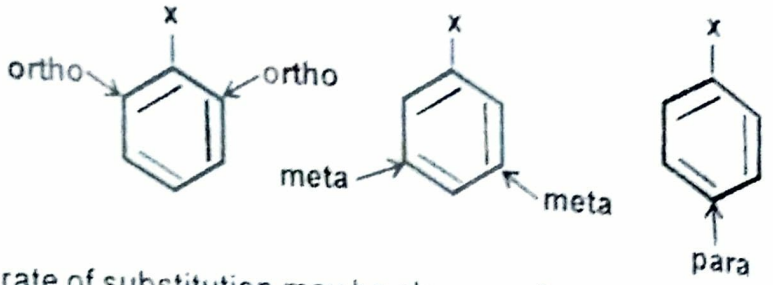
i) Generation of the electrophile
ii) Formation of carbonium ion and
iii) Proton transfer to yield the final product.

**Illustration :**

Refer Nitration, Sulphonation etc reactions which appear in subsequent pages.

**Effect of Substituents**

When one group is introduced into the benzene ring, only one product is possible, when a second group is introduced three isomers are possible, depending upon whether the incoming group goes to the ortho, meta or para position with repect to the existing group.




The rate of substitution may be slower or faster than that in benzene depending upon the nature of the substituent already present. Thus we find that substituents in benzene ring or for that matter any aromatinc compound have marked effect on substitution reactions.

## Activating and deactivating groups - directive influence - orientation

Groups which increace the electron density on the benzene ring either by the polar effects like inductive effect, mesomeric effect, electromeric effect etc., or by hyperconjugative effect are said to activate the benzene nucleus. In such cases the rate of electrophilic substituion will be more than that of the corresponding substitution reaction with unsubstituted benzene. Such groups direct the incoming electrophilic group to the ortho and para positions. On the other hand, if the group already present in the benzene ring is electron withdrawing, it will deactivate the benzene nucleus. It will direct the incoming electrophilic group to the meta position.

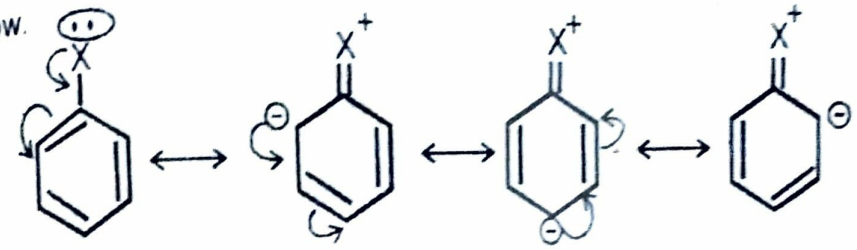
We further find that ortho and para substituion reactions are faster than meta substituion reactions. This is because activating groups increase the electron density in o - and p - positions. Thus these electrophilic substitutions are faster than those in unsubstituted benzene. Deactivating groups reduce the electron density in o-and p - positions. The m - position is only comparatively electron rich in such cases. Actually their electron density will be equal to that in unsubstituted benzene only. So m - substitution reactions will be as fast as unsubstituted benzene only. Thus we fine that o - and p - substituion reactions are faster than m-substitution reactions.

Thus we find that a substituent group in bezene affects both the reactivity and orientation in electronic aromatic substitution.

We can divide the groups present in the benzene nucleus into the following two categories.

**Electron donating groups and their polar effects in substitution:**

These are groups which can donate a pair of electrons to the benzene ring. e.g.,–O–, $-NR_2$, –NHR, –, $-NH_2$, –OH, –OR, –NHCOR, –OCOR and halogens. In all these cases a pair of electrons present on the atom (N or O or halogens) flows into the ring. That is +M effect occurs. Due to the mesomeric effect, the electrons go to the ortho and para positions of the ring. Thus the ortho and para positions become rich in electron density. The +M effect in substituted benzene is shown below.

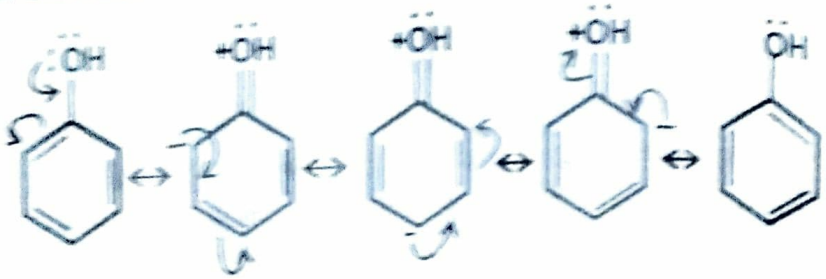


When we consider the electrophilic substitution, the incoming group is electron loving. That is the incoming group will go to the position of high electron density, i.e., the incoming group will go to the ortho and the para positions. Thus when an electron donating group is present in the benzene ring, it directs the incoming electrophilic groups ($\overset{+}{N}O_2$, $\overset{+}{S}O_3H$, $\overset{+}{C}OCH_3$ etc.) to the ortho and para position.

It is interesting to note that although the halogen (Cl, Br, I) are electronegative they are ortho para directing. Since the halogens are electronegative one would expect a decrease of electron density in the ring due to inductive (-I) effect. Consequently it must orient an entering electrophilic group to the metaposition. But in practice it is ortho-para directing. So some other effect also operates in halobenzene. Mesomeric (+M) effect operates in the ring. It operates in a direction opposite to that of inductive effect. Since the +M effect predominates the -I effect, the halobenzene becomes ortho-para directing. However, the ring is deactvated by the inductive effect of halogen hence the rate of substitution is lower than in benzene.

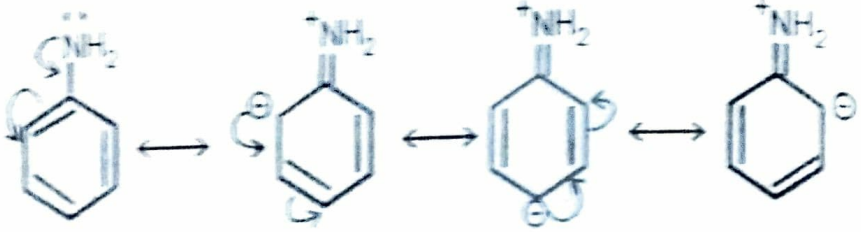
When OH is present in benzene, i.e., in phenol, due to resonance effect (+R) the benzene ring is activated. So phenol under goes electrophilic substitutions more easily than benzene. For example, phenol is easily nitrated than benzene. For the same reason phenol is easily nitrated than benzene. For the same reason phenol is nitrated even by dilute nitric acid.

Because of +R effect of OH group electron densities in o and p position increase

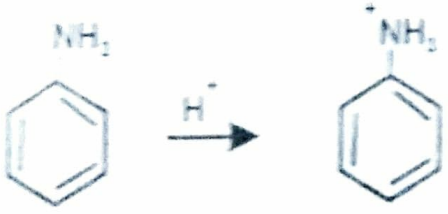


Thus substitution with electrophilic reagents takes place in o,and p - positions. Thus nitration of phenol yields o and p - nitrophenols.

The amino group in aniline is o, p–orienting due to +R effect of amino group

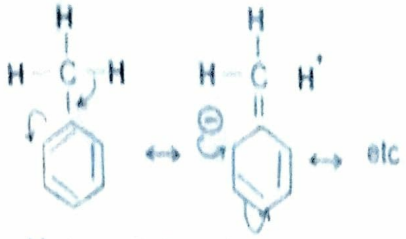


Thus nitration with dilute nitric acid produces a mixtures of o and p-nitroanilines. On the other hand the nitration of aniline in 98% conc. sulphuric acid gives m-nitroaniline as the major product (62%). This is because in this case aniline gets protonated to give $[C_6H_5NH_3]^+$



Thus +R effect disappears and strong – I effect of $NH_3^+$ group largely controls the orientations. Thus m-nitroaniline is formed as a major product.

Directive effect of methyl group is another interesting case. Since methyl group is electron repelling, due to (+I) inductive effect the o, p -positions of benzene become rich in electron density. In addition to inductive effect, another effect called *hyper conjugative effect* also operates to activate the o, p - positions. The hyper conjugation in toluene is shown above.



Hyper conjugation in touene

Thus we find that in toluene the benzene ring is activated by the +I and hyper conjugative effects of $CH_3$ group. This makes the o and p-positions electron rich. Further, because the benzene itself

In general the order of increasing inductive effect of alkyl groups is methyl < ethyl < propyl < isoprophyl < t-butyl, then the activating effect of an R group, if entirely due the +I effect would be in the same order. Actually in a number of cases the order is the reverse. One explanation offered for this reversal is hyper conjugation. We know that hyper conjugation is greatest in the methyl group and least in the t-butyl group.

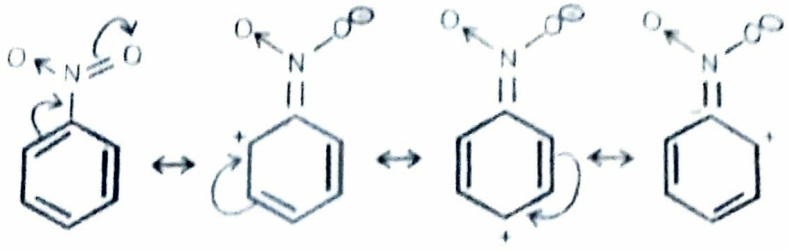
In this connection, it is found that isopropyl benzene can be more easily solphonated than toluene. This can be explained as follows. Sulphonation is electrophilic substitution. Toluene and isopropyl benzene activate the ring though +I effect as well as hyper conjugation. As for as +I effect is concerned isopropyl benzene activates the bezene ring to a greater extent than toluene. But with respect to hyper conjugative effect, toluene activitates the benzene right to a greater extent than isopropye benzene. So we find that in this case inductive effect predominates the hyper conjugative effect. That is why isopropyl benzene is more easily sulphonated than toluene.

Now we can compare toluene and chloro benzene. Which will react faster? Toluene will react faster because in toluene both +I and hyper conjugative effect are operating making the benzene ring highly activated. In chloro benzene –I and +M effects are operating. In effect, here also the benzene right is activated because +M effect predominates. But the activation of benzene ring in chloro benzene will be less than that in toluene. So toluene will react faster.

**2. Electron withdrawing groups and their polar effects in substitution :**

These are groups which are electron withdrawing from the benzene ring e.g., $-NR_3$, $-NO_2$, $-CN$, $-SO_3H$, $-CHO$, $-COOH$, $-COOR$, $-CCl_3$, –

$NH_3$, all these groups have got – I effect. Due to this inductive effect they withdraw electrons from the ring. Thus the ring is deactivated. In addition to inductive effect there is mesomeric (–M) effect. Due to the M effect there is actual flow of electrons from the right to the group attached to the ring. When we consider nitrobenzene, the nitro group withdraws the electrons from the ring. The electron density in the ortho and para positions decreases. Thus comparatively the meta position is rich in electron density. When the incoming group is electrophilic (like $NO_2^+$, $SO_2H^+$, $Cl^+$ etc.) it goes to the meta position.

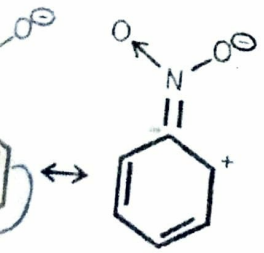


Thus when an electron withdrawing group is present in the benzene ring, it directs the incoming electrophilic group to the meta position. Since the entire ring is deactivated, the rate of electrophilic substitution will be lower than benzene itself. Thus nitrobenzene on further nitration yields m-dinitrobenzene, but only slowly. That is why, nitro benzene is further nitrated by fuming nitric acid and sulphuric acid to get m-dinitro benzene. Thus in general meta directing effect of $-NO_2$ group is due to the combined inductive and mesomeric effects. The meta orientation and a lower rate of reaction go together.

In some cases electrophilic substitution can not take place in nitro benzene. For example, nitro benzene can not be acetylated. This is because nitro group is highly deactivating through –I and –M effects. So, if at all acetylation is to take place, it should take place in m-position only. Acetyl group is a weak electrophile. It requires strong activated centres. The m-position is not activated. So it can not be acetylated. In other words nitro group which is an electron withdrawing group hinders or inhibits acetylation reaction.

Similarly when $-SO_3H$ group is present in the benzene rign, it directs the incoming electrophilic group to meta position because it is an electron withdrawing group i.e., it is a deactivating group. Thus when benzene sulphonic acid is sulphonated we get benzene-m-disulphonic acid.

Due to this inductive effect they
ring is deactivated. In addition
M) effect. Due to the M effect
right to the group attached to
the nitro group withdraws the
nsity in the ortho and para
the meta position is rich in
p is electrophilic (like $NO_2^+$,



is present in the benzene
up to the meta position.
electrophilic substitution
zene on further nitration
is why, nitro benzene is
ric acid to get m-dinitro
of $-NO_2$ group is due to
The meta orientation

not take place in nitro
e acetylated. This is
h –I and –M effects.
e place in m-position
ires strong activated
not be acetylated. In
awing group hinders

nzene rign, it directs
because it is an
group. Thus when
ene-m-disulphonic

## ISOTOPIC EFFECT

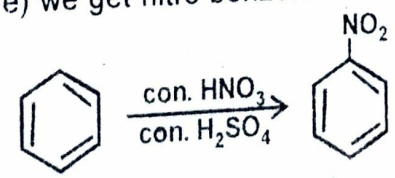
We know that isotopes are chemically similar. So chemical properties of compounds are not qualititatively changed when an isotope is substituted for an atom. However the isotopes are not exactly identical. So the rate at which chemical reactions occur varies from isotope to isotope. Thie variation in the rate of a reaction due to difference in the isotope present in the molecule is called isotopic effect. The $K_H/K_D$ value is nearly 7 at 25°C. This is means that the rate of reaction involving the breaking of a C–H bond is seven times faster than the breaking of a C–D bond. The reason for this is that the bond dissociation energy of a C–D bond is more than of a C–H bond. Thus the activation energy of the deuterium compound would be more than that of the hydrogen compound.

The isotopic effect is used to elucidate the mechanism of reactions. For example benzene, $C_6H_6$ and the hexa deutero benzene $C_6D_6$ are found to undergo nitration at the **same rate.** This proved the fact C–H bond breaking is not **involved** in the rate determining step of the nitration reaction.

## 1. NITRATION

**Reaction :**

When benzene is nitrated with concentrated nitric acid and concentrated nitric acid and concentrated sulphuric acid mixture (called nitrating mixture) we get nitro benzene.




benzene nitro benzene

**Mechanism :**

The commonly accepted mechanism for nitration involves the following steps.

1. Formation of nitronium ion.

$$HONO_2 + 2H_2SO_4 \rightleftharpoons H_3O^+ + 2HSO_4^- + \overset{+}{N}O_2$$

2. Reaction of nitronium ion with benzene.

$$\overset{+}{N}O_2 + C_6H_6 \xrightarrow{\text{Slow}} \overset{+}{C}_6H_5NO_2$$

3. Loss of a proton

$$\overset{+}{C}_6H_6NO_2 + HSO_4^- \xrightarrow{\text{Fast}} C_6H_5NO_2 + H_2SO_4$$

**1. Formation of nitronium ion :**

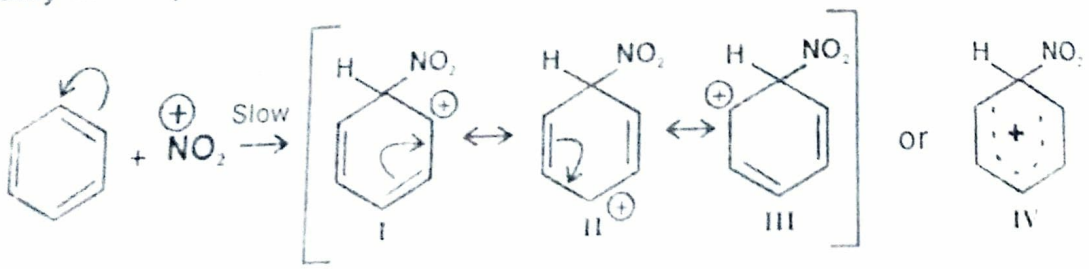
When only nitric acid is used the nitration is very slow. It suggests that $H_2SO_4$ is reacting with nitric acid rather than with benzene. The reaction of $HNO_3$ and $H_2SO_4$ can be written as

$$HONO_2 + 2H_2SO_4 \rightleftharpoons \underset{\text{Nitronium ion}}{\overset{+}{N}O_2} + \overset{+}{H}_3O + 2HSO_4^-$$

The nitronium ion is well known, existing in salts such as nitronium perchlorate $NO^+_2$, $ClO_4$ and nitronium fluorate $NO^+_2$, $BF_4$. Solutions of those nitronium salts (in solvents like nitromethane or acetic acid) have been found to nitrate aromatic compountds smoothly. The yield was also good at room temperature. This confirms that nitronium ion is responsible for nitration. Instead of $H_2SO_4$ other strong acids like $HClO_4$, HF and $FB_3$ have also been found to liberate $NO_2^+$ ion from nitric acid.

**2. Reaction of nitronium ion with benzene :**

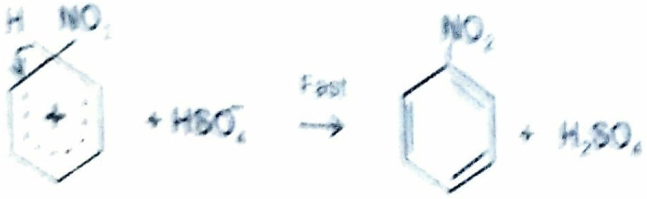
$NO_2^+$ ion, which is the electrophilic particle actually attacks the benzene ring. This reaction is simply an acid-base reaction. A σ complex is formed. It is a carbonium ion. We find that the carbonium ion can be represented by three resonating structures I, II and III. These differ only in the position of double bonds and positive charge.




The actual ion must then be a resonance hybrid of these three structures. This means that the positive charge is not localised on one carbon atom. It is distributed over the molecule. Sometimes the hybrid carbonium ion is represented as IV.

**3. Loss of a proton :**

The formation of the carbonium ion (step 2) is more difficult a step. Once the carbonium ion is formed, it loses a hydrogen ion (porton) to form the products. This is a fast step.



The rate determining step is the initial attack of the nitronium ion ($NO_2^+$). The removal of proton is very fast and does not affect the rate. This has been confirmed by the fact that the rate of nitration remains unaffected when the hydrogens of the benzene ring are replaced by the heavier isotope deuterium.

## 2. SULPHONATION

The sulphonation of benzene and other aromatic compounds is brought about by the action of sulphuric acid or oleum. The commonly accepted mechanism for sulphonation of aromatic compounds involves the following steps.

### 1. Generation of electrophile

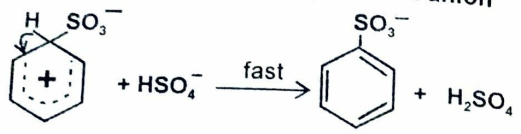
$$HO\text{-}SO_2\text{-}OH + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- + HSO_4^- + SO_3$$

In this step the electrophile namely sulphur trioxide is generated. $SO_3$ formed in this step is the attacking reagent. The concentration of $SO_3$ is decreased by the addition of water because the equilibrium will be shifted towards left. Therefore sulphonation must be carried out in the absence of water. The sulphur atom of $SO_3$ acquires a positive charge as shown below which makes it the electrophilic centre.

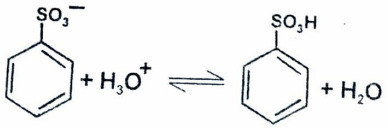
### 2. Formation of σ - complex

(As the carbonium ion formed during nitration gives three resonating structures, this carbonium ion also gives three resonating structures. The hybrid carbonium ion is represented with brokenlines.

**3. Transfer of proton from the sulphonic acid anion**




**4. Reaction between sulphonic acid anion and hydronium ion to yield the final product.**




## 3. HALOGENATION

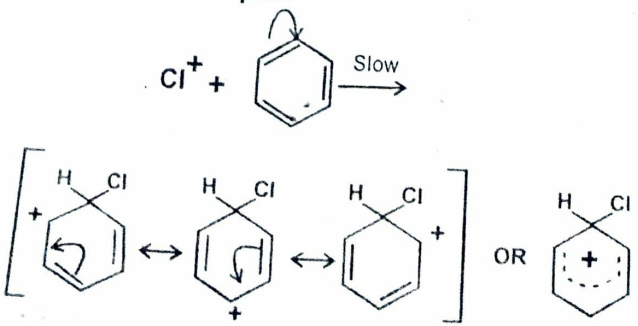
Halogenation (chlorination and bromination) takes place in the presence of Lewis acids such as $ZnCl_2$, $FeCl_3$, $FeBr_3$, $AlCl_3$, $AlBr_3$, etc. Chlorination can be taken as an illustration for halogenation. The usual practise is to add to the reaction mixture some iron filings which are converted by chlorine into ferric chloride. Ferric chloride acts as catalyst. The function of the catalyst is to induce a small degree of polarization in the halogen molecule. The sequence of reaction is illustrated below:

**1. Generation of electrophile**

$$Cl_2 + FeCl_3 \rightleftharpoons FeCl_4^- + Cl^+$$

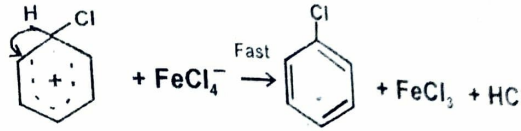
This step is an acid-base equilibrium. The ferric chloride (or any other catalyst) attaches itself to a chlorine molecule to from the $FeCl_4^-$ ion and a positive chlorine ion.

**2. Formation of σ - complex**






**3. Proton transfer to yield the final product**




## 4. FRIEDEL - CRAFT'S ALKYLATION

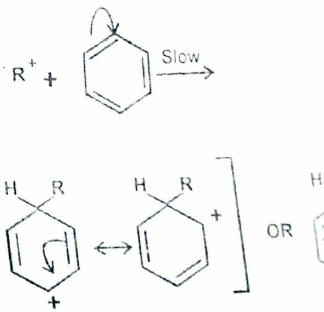
This reaction involves the introduction of an alkyl grou the benzene ring by using an alkyl chloride (RCl) and a Le catalyst. The usual catalyst is anhydrous aluminium chl Friedel-Crafts' alkylation is complicated affair. It can proc mechanisms. We shall discuss the mechanisam which wi pattern of elctrophilic aromatic substitution.

**1. Generation of electrophile**

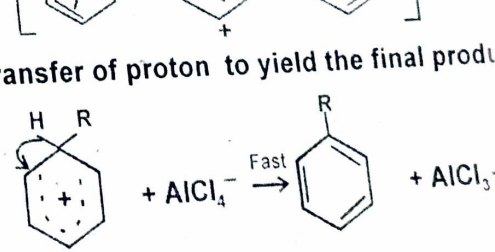
$$R - Cl + AlCl_3 \rightleftharpoons \underset{\text{Alkyl carbonium ion}}{R^+} + AlCl_4^-$$

Alkyl halides, alchohols, esters, olefins, aldehydes may be used as alkylating agents.

**2. Formation of carbonium ion (σ – complex)**



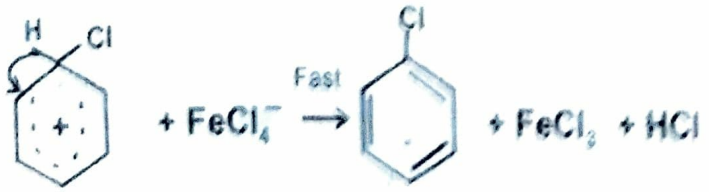

**3. Transfer of proton to yield the final produ**




**Alternate mechanism :**

In certain cases, the actual attacking reage alkyl carbonium ion. On the other hand, the a

3. Proton transfer to yield the final product




## 4. FRIEDEL - CRAFT'S ALKYLATION

This reaction involves the introduction of an alkyl group ($R^+$) into the benzene ring by using an alkyl chloride (RCl) and a Lewis acid as catalyst. The usual catalyst is anhydrous aluminium chloride. The Friedel-Crafts' alkylation is complicated affair. It can proceed by two mechanisms. We shall discuss the mechanisam which will fit into the pattern of elctrophilic aromatic substitution.

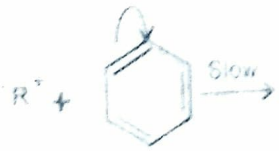
### 1. Generation of electrophile

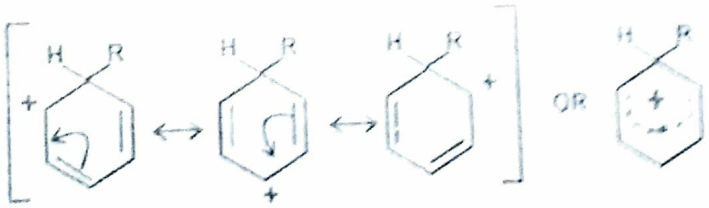
$$R - Cl + AlCl_3 \rightleftharpoons R^+ + AlCl_4^-$$

Alkyl carbonium ion

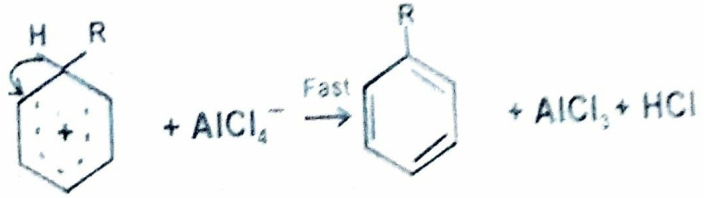
Alkyl halides, alchohols, esters, olefins, aldehydes and ketones may be used as alkylating agents.

### 2. Formation of carbonium ion ($\sigma$ – complex)



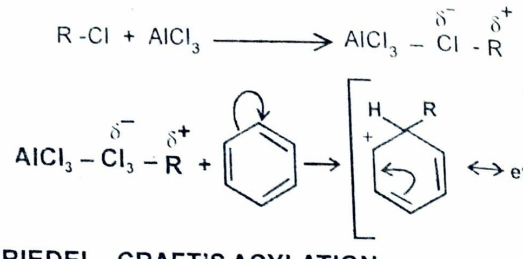

### 3. Transfer of proton to yield the final product




**Alternate mechanism :**

In certain cases, the actual attacking reagent may not be a free alkyl carbonium ion. On the other hand the attack may be brought

about by the positive end of a polar complex formed between alkyl halide and aluminium chloride.



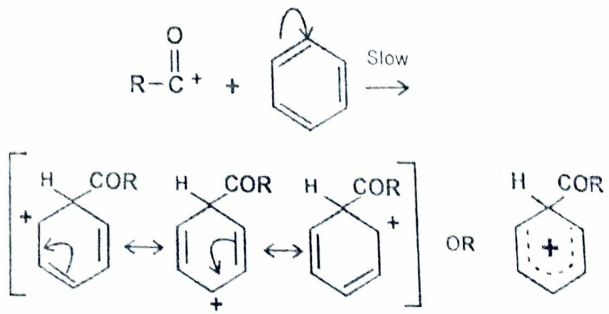
## 5. FRIEDEL - CRAFT'S ACYLATION

This reaction involves the introduction of an acyl group ($RCO^-$) into benzene ring by using an acid chloride (RCOCl) and a Lewis acid as catalyst. The usual catalyst is anhydrous aluminium chloride. The mechanisum is as follows:

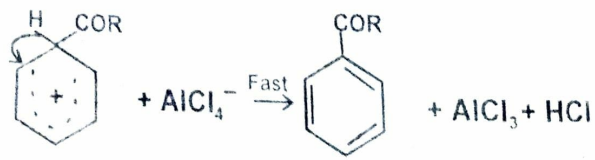
### 1. Generation of electrophile

Acyl carbonium ion

### 2. Formation of σ - complex



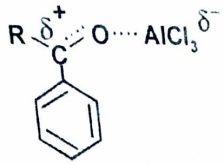
### 3. Proton transfer to yield the final product





**Note :**

There is a difference between acylation and alkylation. In acylation more catalyst (Lewis acid) is required than for alkylation. This it because the Lewis acid forms a complex with the product of acylation, viz., the ketone. This complex thus removes some catalyst. To compensate such loss of catalyst molecule's more catalyst is required.



## ENERGY PROFILE DIAGRAMS

**What are they?** These are graphs obtained by plotting the poten energy of a system against the reaction co-ordinate i.e., the vari distances between the reacting nuclei.

**Explanation :**

Let as consider a approaching BC along the bonding line form the opposite side in which C is located as shown below :

A.....→.....B – C

A will be forced against the repulsion of BC. Simultaneou bond B–C stretches unitll A and C compete for B on equal terms point is reached when the distances A–B and B–C are such forces between AB and BC are the same. This condition is c transition state (T.S) or activated complex. In this state, ne molecule AB or BC exists independently. The system can nov in either direction to from A and BC or AB and C. This se events is given below ;

A + BC → A...B....C (T.S.) → AB + C

When these events are represented as a graph by potential energy of the reacting system against the reacti we get an **energy profile diagram.** Figure a is the energy on an exothermic reaction while Figure b is that of reaction.