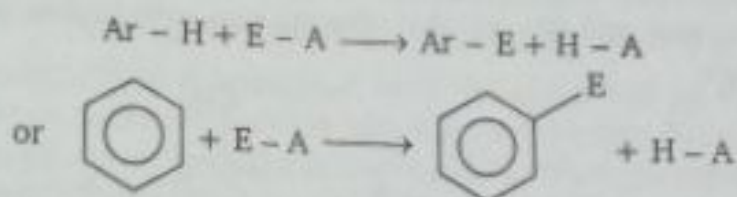


Aromatic Electrophilic Substitution

In the previous two chapters displacements by an attacking reagent on an aliphatic carbon chain have been discussed. A reagent can similarly displace an atom or group on an aromatic ring. This can be achieved principally by three processes, electrophilic, nucleophilic and free radical substitutions. The mechanism of these reactions have attracted a lot of attention. Among these the electrophilic substitution is the most widely studied. The most characteristic reaction of benzenoid arenes are substitution reaction that occur when they react with electrophilic reagents. The reactions are of the general type shown below



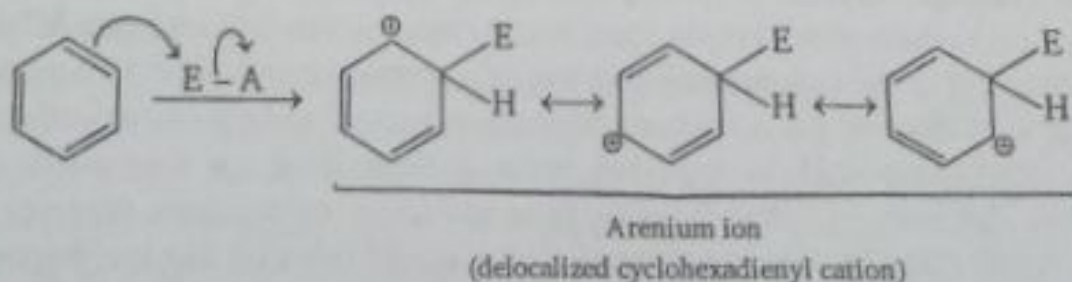
The electrophiles are either a positive ion (E^+) or some electron deficient species with a large partial positive charge. The electrophiles attack the benzene ring, replacing one of the hydrogen atoms in a reaction called as **electrophilic aromatic substitution (EAS)**.

8.1 Arenium Ion Mechanism

Benzene is susceptible to electrophilic attack primarily due to its exposed π electrons. Benzene's closed shell of six π electrons gives it a special stability. Benzene is susceptible to electrophilic attack and it undergoes substitution reactions rather than addition reactions.

Substitution reactions allow the aromatic sextet of π electrons to be regenerated after attack by the electrophile. Experimental evidence indicates that electrophiles attack the π system of benzene to form a non-aromatic **cyclohexadienyl carbocation** known as an **arenium ion**.

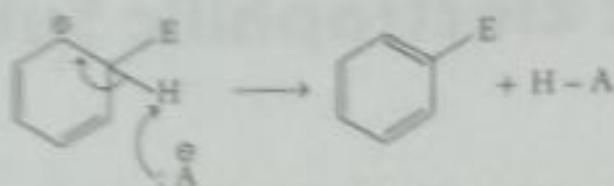
Step 1.



In step 1 the electrophile takes two electrons from the six electron π -system to form a σ bond to one carbon atom of the benzene ring. Formation of this bond interrupts the cyclic system of π electrons because in the formation of the arenium ion the carbon that forms a bond to the

electrophile becomes sp^3 hybridized and no longer has an available p orbital. Now only five carbon atoms of the ring are still sp^2 hybridized and have p orbitals. The resonance structures show the positive charge distributed in the arenium ion ring. Arenium ions are also called **Wheland intermediates** or σ complexes.

Step 2.

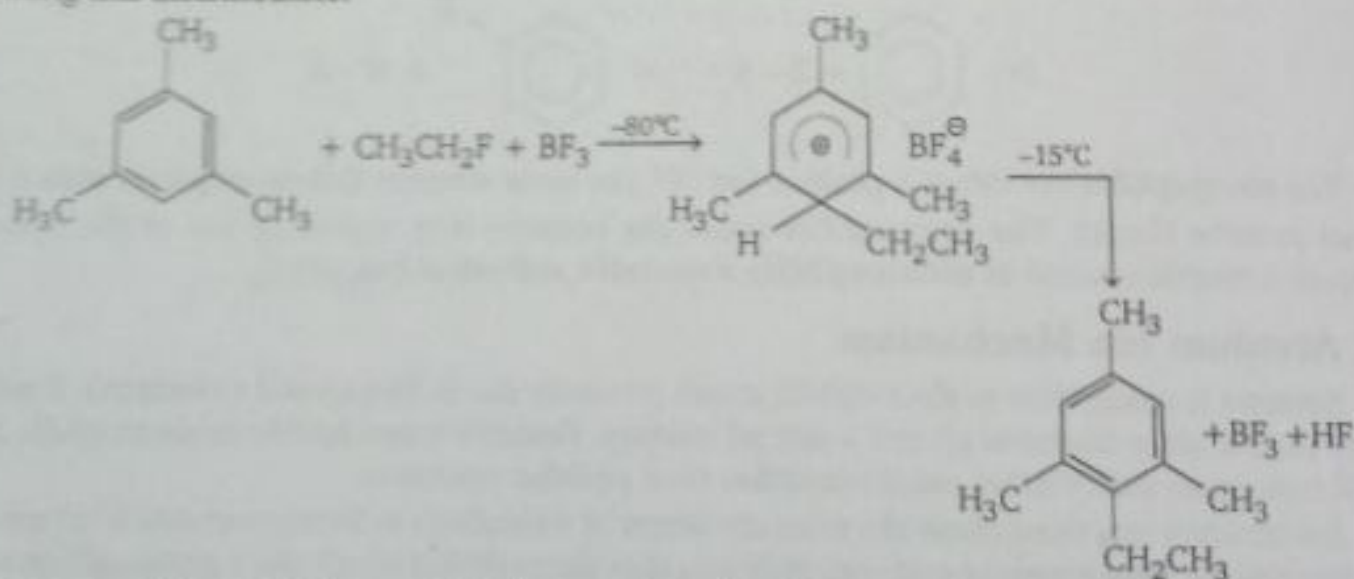


In step 2, a proton is removed by any base present in the reaction mixture from the carbon atom of the arenium ion that bears the electrophile. The two protons that bonded the proton to carbon become a part of the π system. The carbon atom that bears the electrophile becomes again sp^2 hybridized and a benzene derivative with delocalized 6π electrons is formed.

> Evidence for Arenium Ion Mechanism

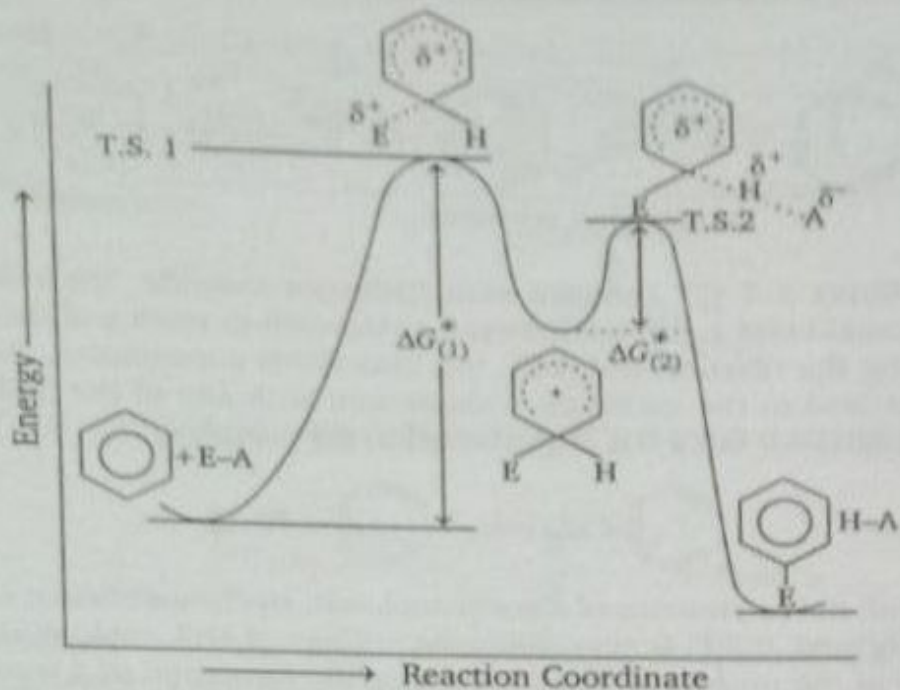
There is considerable evidence that the arenium ion is a true intermediate in electrophilic aromatic substitution reactions. It is not a transition state.

(a) Isolation of arenium ion intermediate: Arenium ion has been isolated by the treatment of mesitylene with ethyl fluoride and BF_3 at -80° . The normal substitution product was obtained on warming this intermediate.

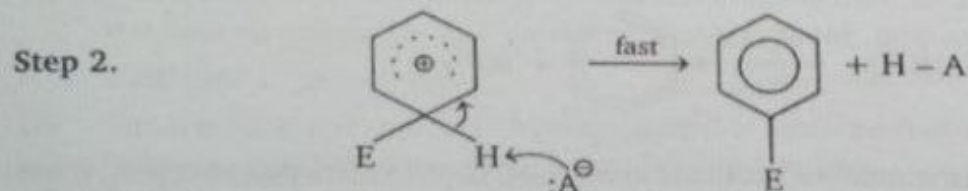
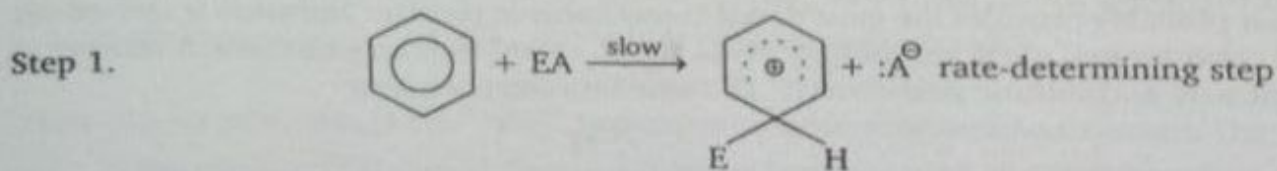


(b) Isotope Effects: A difference in the rate of reaction due to a difference in the isotope present is called the **isotope effect**. A carbon-hydrogen bond breaks more readily than a bond between carbon and deuterium which breaks more readily than carbon-tritium bond. It follows that whenever a hydrogen is lost in the rate determining step of a reaction it will show an isotope effect on replacing the hydrogen by deuterium. A deuterated substance must undergo substitution more slowly than a non-deuterated compound. As expected, isotope effects have not been observed in most aromatic substitution. The rates of nitration of deuterio and tritio-benzenes for example are the same as the rate for benzene. This shows that aromatic electrophilic substitutions involve two steps and that the loss of proton is not the rate-determining step.

As the arenium ion is not a transition state, it means that in free-energy diagram the arenium ion lies in the energy valley between two transition states.

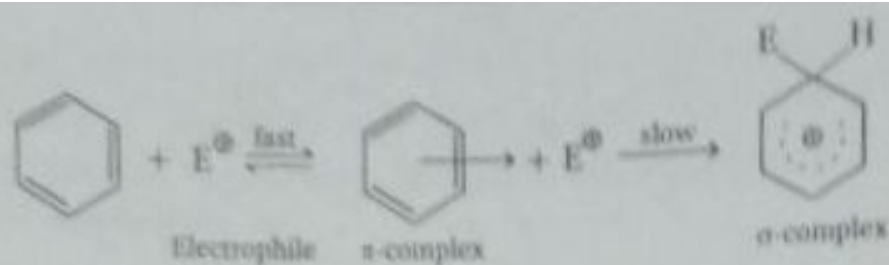


The free energy of activation $\Delta G_{(1)}^{\ddagger}$, for the reaction leading from benzene and the electrophile, E^{\oplus} , to the arenium ion is much greater than the free energy of activation $\Delta G_{(2)}^{\ddagger}$, leading from arenium ion to the product. This is consistent with the expectation as the reaction leading from benzene and an electrophile to the arenium ion is highly endothermic, because the benzene ring loses its resonance energy. On the other hand, the reaction leading from the arenium ion to the substituted benzene is highly exothermic as the benzene ring regains its resonance energy. Of the two-steps, the formation of the arenium ion, is the rate determining step in electrophilic aromatic substitution.

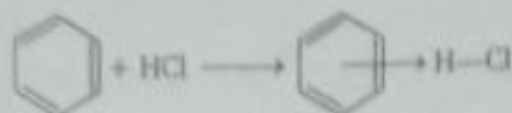


➤ σ - and π -complexes

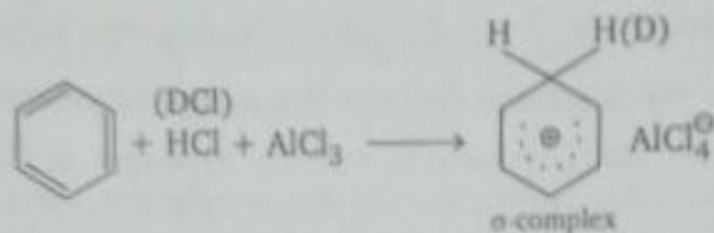
The intermediates of aromatic substitution discussed so far are referred to as σ -complexes. In these complexes there is actual bonding of the electrophile with the ring carbon atom and as the π orbitals now involve only five carbon atoms, there is loss of aromaticity. Experimental evidence suggests that the formation of the above type of σ -complex follows the initial formation of a complex known as π -complex in which the electrophile is loosely held near the π -electron cloud of the aromatic ring. In most of the aromatic substitutions formation of a π -complex is found to be reversible and rapid step, which is followed by the slow (rate determining) and irreversible step of a σ -complex formation.



Thus, benzene forms a 1 : 1 complex with hydrogen chloride, the reaction being readily reversible. That no actual bond is formed between a ring-carbon atom and the proton from HCl is confirmed by repeating the reaction with DCl; this also yields a π complex, but its formation and decomposition do not lead to the exchange of deuterium with any of the hydrogen atoms of the nucleus showing that no C—D bond has been formed in the complex.

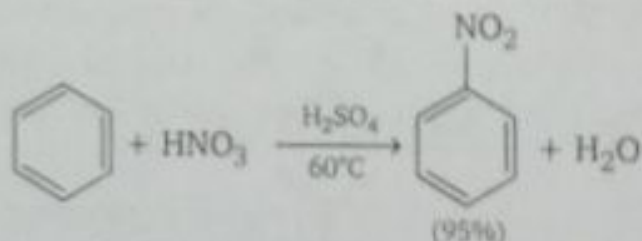


On the other hand, in the presence of a compound with electron-deficient orbital *e.g.*, AlCl_3 , a different complex is formed. If DCl is now employed in place of HCl, rapid exchange of deuterium with hydrogen atoms of the nucleus is found indicating the formation of a σ complex or Wheland intermediate.

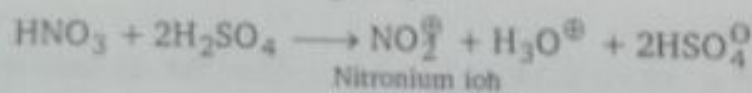


8.2 Nitration

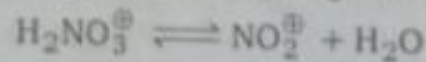
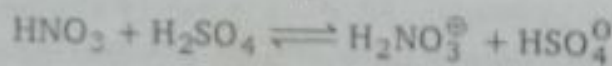
The aromatic substitution reaction that has received by far the closest study in nitration and as a result, it is one that probably provides the most detailed mechanistic picture. Nitration is carried out with a mixture of concentrated nitric and sulfuric acids, the so-called nitrating mixture. A mixture of concentrated nitric acid and sulfuric acid converts benzene into nitrobenzene



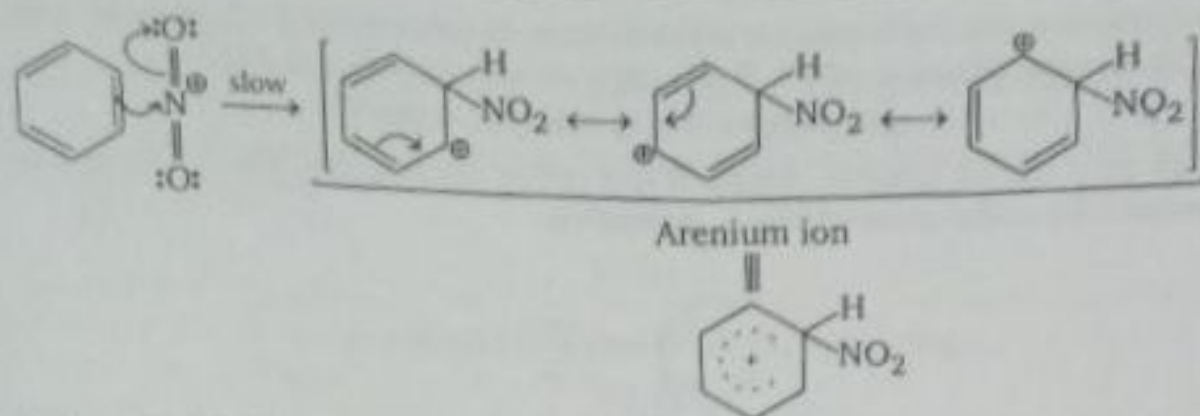
In the mixture of concentrated nitric acid and sulfuric acid, used for the nitration reaction, it has been shown that a positive nitronium ion (NO_2^{\oplus}) is present.



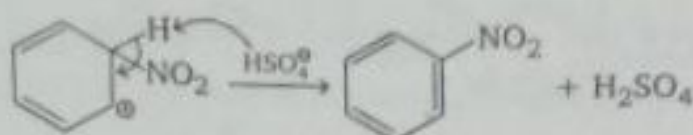
or



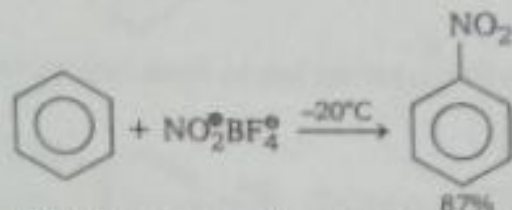
This is an acid base reaction in which nitric acid is the base. The nitronium ion formed above represents a powerful electrophile. It reacts with benzene to form a resonance stabilized arenium ion



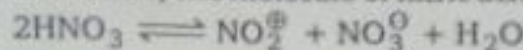
Finally the removal of proton (by a base) from the arenium ion and formation of the substitution product occurs:



The salts of nitronium ion such as $\text{NO}_2^{\oplus} \text{ClO}_4^{\ominus}$ (nitronium perchlorate) and $\text{NO}_2^{\oplus} \text{BF}_4^{\ominus}$ (nitronium fluoroborate) are also effective nitrating agents.

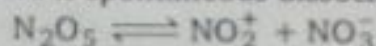


In case of concentrated nitric acid alone, one molecule of nitric acid is the acid and another the base



The equilibrium lies to the left but enough NO_2^{\oplus} is formed for nitration to occur.

In the case of N_2O_5 in CCl_4 , there is spontaneous dissociation

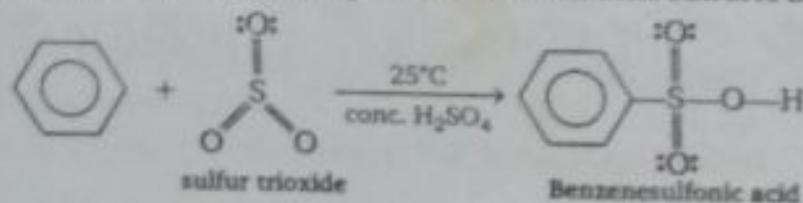


There is a lot of evidence that NO_2^{\oplus} is present in most nitrations and that it is the attacking entity.

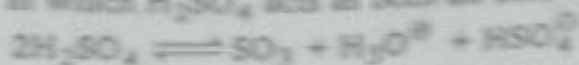
- When nitric acid is dissolved in concentrated sulfuric acid, the peak for nitric acid disappears in the Raman spectrum and two new peaks appear, one at 1400 cm^{-1} due to NO_2^{\oplus} and one at 1050 cm^{-1} due to HSO_4^{\ominus} .
- The freezing point of 100% sulfuric acid is lowered four times the expected value by HNO_3 , it indicates the presence of four ions in the solution.
- By the actual isolation of the crystalline nitronium salts i. e., nitronium perchlorate ($\text{NO}_2^{\oplus} \text{ClO}_4^{\ominus}$) and nitronium nitrate ($\text{NO}_2^{\oplus} \text{NO}_3^{\ominus}$).

8.3 Sulfonation

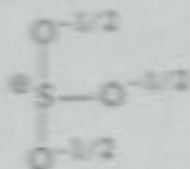
The details of sulfonation are less well known. Benzene reacts with fuming sulfuric acid at room temperature to produce benzenesulfonic acid. Fuming sulfuric acid is sulfuric acid that contains added sulfur trioxide (SO_3). Sulfonation takes place in concentrated sulfuric acid alone, but slowly.



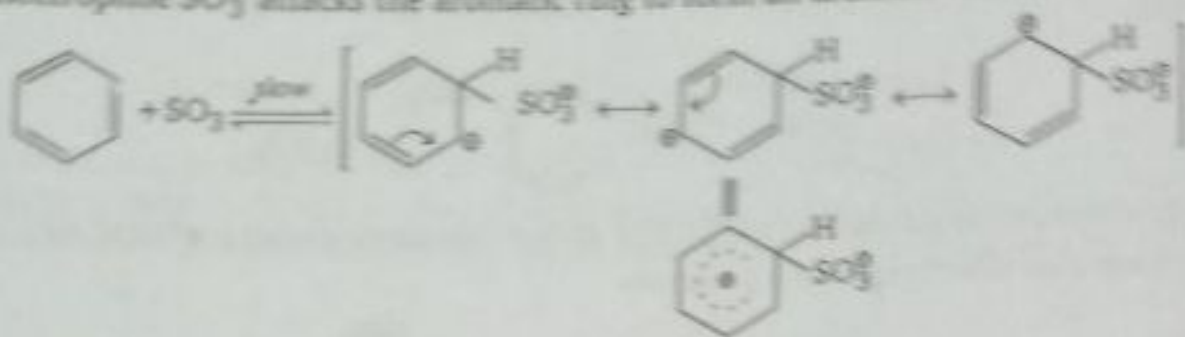
In either reaction, the electrophile is sulfur trioxide. In concentrated sulfuric acid, sulfur trioxide is produced in an equilibrium in which H_2SO_4 acts as both an acid and a base.



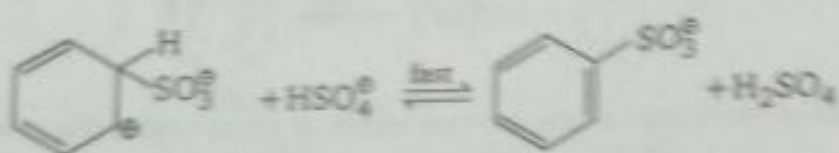
Although SO_3 has no positive charge, it is a strong electrophile. This is because the extent of electron around the sulfur atom of SO_3 is incomplete.



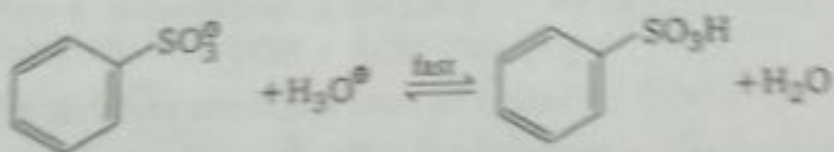
The electrophile SO_3 attacks the aromatic ring to form an arenium ion.



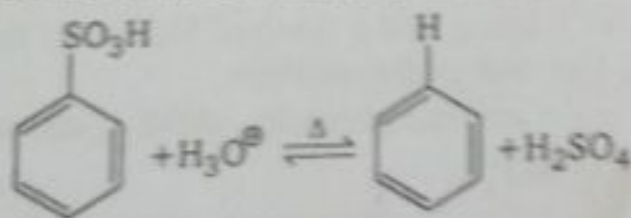
The proton is removed from the arenium ion to form benzenesulfonate ion.



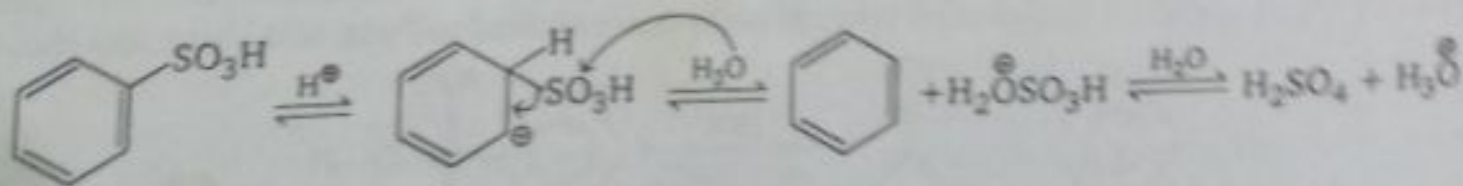
The benzenesulfonate ion accepts a proton to become benzenesulfonic acid



Sulfonation is a reversible process, especially at high temperatures. However, high yields of sulfonic acids are obtained when a solution of sulfur trioxide in sulfuric acid is used.

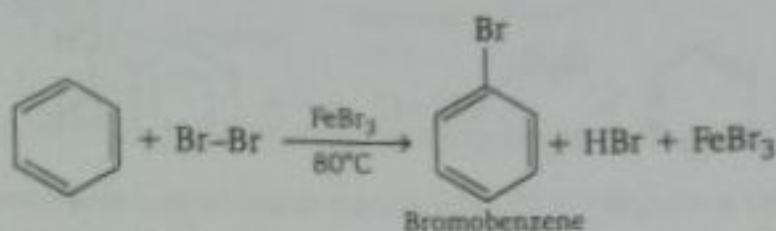


When benzenesulfonic acid is heated with aqueous sulfuric acid, the sulfonic acid group is removed. The mechanism of desulfonation is just reverse of the sulfonation process.

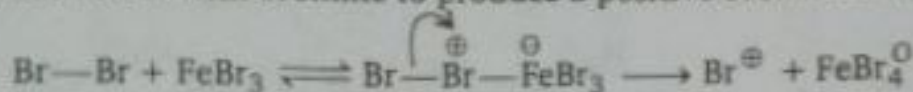


8.4 Halogenation

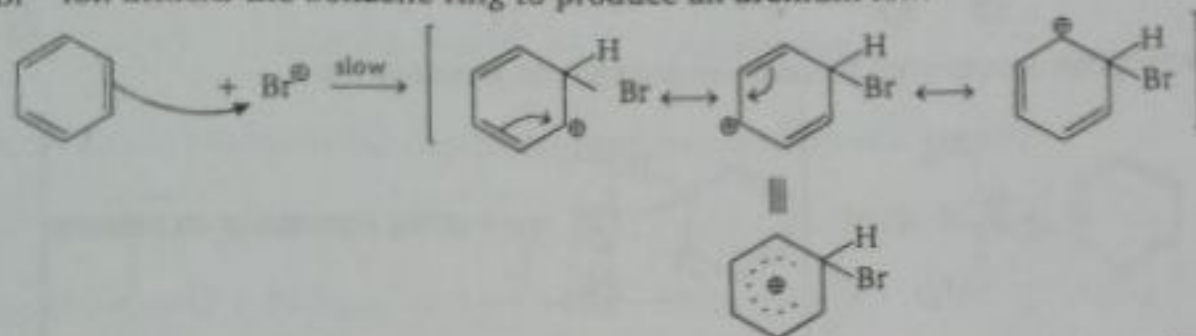
Benzene can be halogenated with chlorine and bromine in the presence of a Lewis acid catalyst such as FeBr_3 , FeCl_3 , AlCl_3 etc. Lewis acid assists polarization of the attacking halogen molecule, thereby making it more reactive. For example, bromine reacts with benzene in presence of FeBr_3 at 80°C to form bromobenzene.



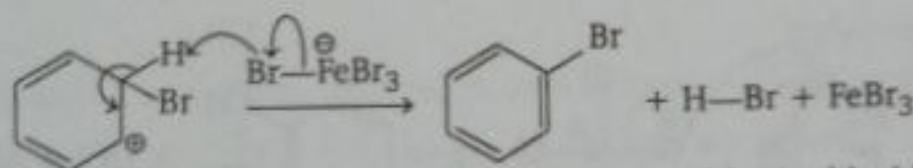
The ferric bromide reacts with bromine to produce a positive bromine ion, Br^\oplus (and FeBr_4^\ominus).



This Br^\oplus ion attacks the benzene ring to produce an arenium ion.

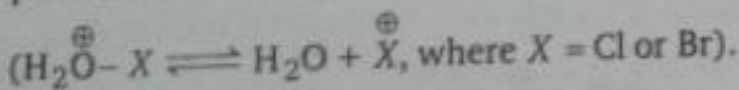


Finally a proton is removed from the arenium ion by FeBr_4^\ominus . This results in the formation of bromobenzene, hydrogen bromide and the catalyst FeBr_3 is regenerated



The mechanism of chlorination of benzene in the presence of ferric chloride is analogous to the one for bromination. Fluorine reacts vigorously with aromatic hydrocarbons even in the absence of catalyst. However, iodine is very unreactive even in the presence of catalyst.

Similar mechanism operates when halogenation is carried out with HOCl or HOBr in the presence of a strong acid. The active electrophile in this case is either $\text{H}_2\text{O}^\oplus - \text{X}$ or positive halogen



8.5 Friedel-Crafts Reaction

The introduction of an alkyl or acyl group into one aromatic compound in the presence of Lewis acid catalysts is called Friedel Crafts reaction. These reactions are particularly important as they allow the construction of larger organic molecules by adding alkyl or acyl side chains to an aromatic ring.

8.5.1 Friedel-Crafts Alkylation

The carbon atom of alkyl halides $\overset{\delta^+}{\text{R}}-\overset{\delta^-}{\text{X}}$, is electrophilic but rarely it is sufficient to effect the substitution of aromatic species and hence the presence of a Lewis acid catalyst is required. The order of effectiveness of Lewis acid catalysts is

