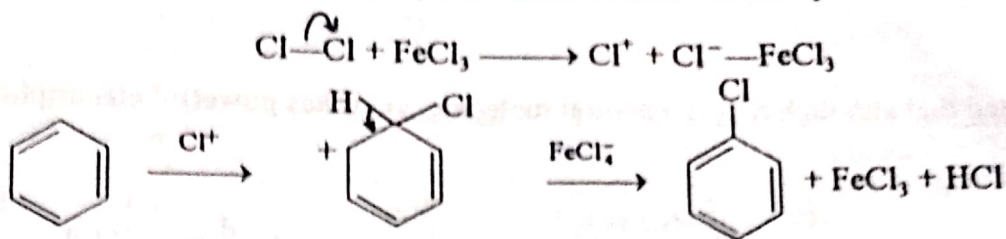


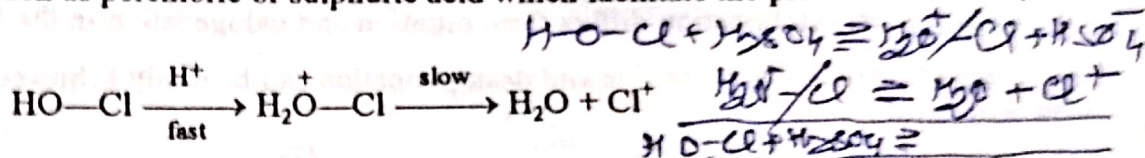
... by NO_2^+ ions also takes place simultaneously.

2. Halogenation : Halogenation¹ of benzene takes place in the presence of a catalyst² (a halogen carrier) such as FeCl_3 , ZnCl_2 , AlBr_3 , iodine, pyridine, etc. The function of the catalyst is to facilitate the formation of the electrophile, *halonium ion*. The rest of the process is same as that of nitration.



The formation of halonium ion and hence, the ionic nature of the reaction (halogenation) is supported by the following points.

✓(i) Halogenation may also be brought about with the aqueous hypohalous acid (HOX) but only in presence of strong acids, such as perchloric or sulphuric acid which facilitate the production of Cl^+ , the real chlorinating agent.



✓(ii) Interhalogen compounds such as BrCl and ICl cause bromination and iodination (but not chlorination) respectively which indicate clearly that the positively charged halonium ion is the active halogenating agent.

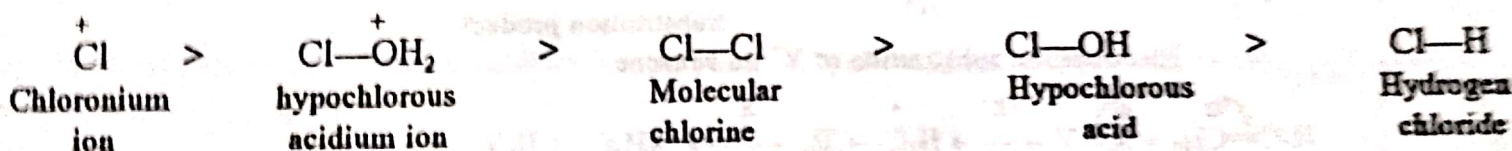


Since the order of electron attracting power among the halogens is $\text{Cl} > \text{Br} > \text{I}$; the interhalogen compounds will undergo the inductive effect as shown above.

✓(iii) Bromination and iodination of benzene are catalysed by the presence of silver salts because here again the halonium ion is formed as follows.



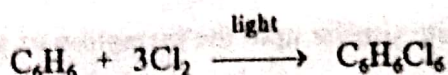
So if halonium ion is the actual halogenating agent then that halogenating agent will be more reactive which is capable of forming a halonium ion and indeed it is found so, e.g.,

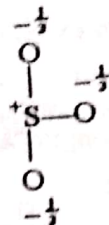
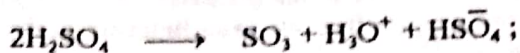


3. Sulphonation : The details of sulphonation are less well known and there has been a good deal of discussion regarding the nature of the electrophilic reagent, *i.e.*, whether electrophilic attacking species is the bisulphite ion, SO_3H^- or free sulphur trioxide, SO_3 . However, there are more evidences in favour of free SO_3 (Cowdry and Davis; 1949) which is produced in the following manner.

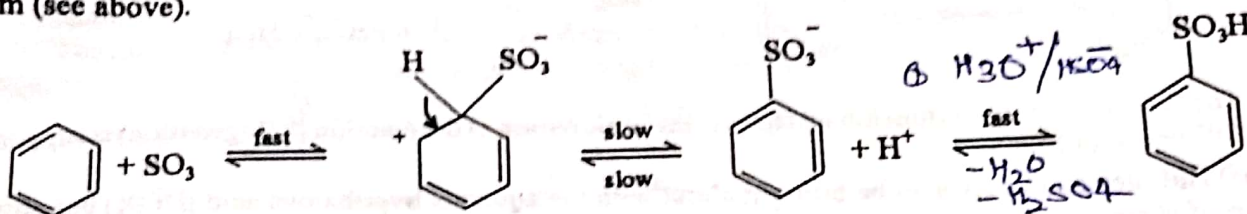
¹ The order of reactivity of halogens is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$; fluoroine is too reactive and hence, it is of little synthetic use; iodine is usually unreactive in most cases.

² It must be remembered that in the absence of a catalyst and in the presence of light, benzene undergoes addition reaction with chlorine by a free radical mechanism.



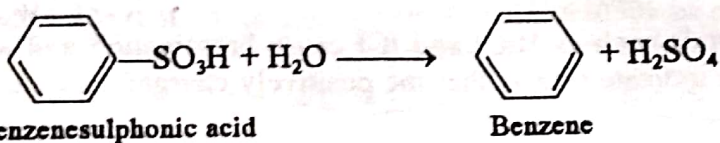


It must be noted that although SO_3 is a neutral molecule, yet it has powerful electrophilic sulphur atom (see above).



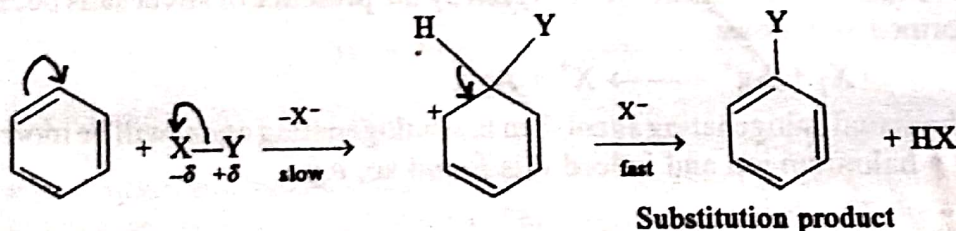
However, sulphonation differs from nitration and halogenation in the following two respects.

(i) The process is reversible and desulphonation can be easily achieved by treating the sulphonic acid with steam.

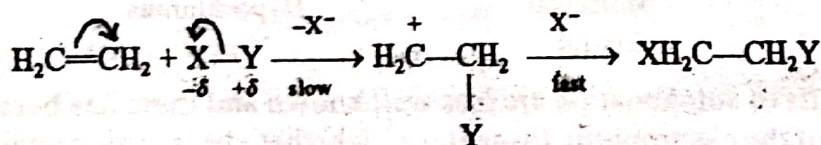


(ii) Not first, but second step is the rate-determining step of the process.

Note: From the above discussion we see that there are certain similarities between the electrophilic aromatic substitution reactions of benzene and electrophilic addition reactions of olefins. Before we summarise the various points of similarities, let us draw our attention to the mechanism of both the reactions.



Electrophilic substitution of Y^+ on benzene



Addition product

Electrophilic addition of $X-Y$ on ethylene

Now let us summarise the similarities between the two reactions.

(i) Many of the reagents that commonly add to the alkenes also substitute an aromatic nucleus, viz $Cl_2, Br_2, H_2SO_4, HO-Cl$, etc.

(ii) Both types of reactions are polar, stepwise processes and involve the attack of electrophilic reagents.

(iii) In both cases the rate determining step is the attack of an electrophile at carbon (first step) to form a cationic intermediate.

So we see that the two reactions are quite similar upto the formation of cationic intermediate but after this the