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(4) Halogenation:

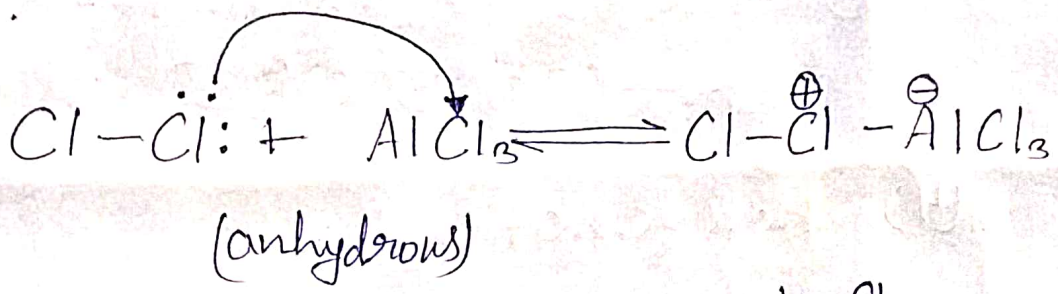
Halogenation of an aromatic ring is a synthetically important reaction. It takes place in the presence of varied reaction condition depending on reactivity of the aromatic ring. For very reactive aromatic compounds in polar solvents, the molecular halogens themselves may acts as electrophiles. In the case of nonpolar solvents, halogenation is catalysed by a Lewis acid like $AlCl_3$, or $FeCl_3$. Reactivity of halogens has the following order:,

$$I_2 < Br_2 < Cl_2$$

Let us take chlorination as a representative reaction to understand the mechanism of halogenation. Chlorine, in the presence of $AlCl_3$ or $FeCl_3$ forms a complex, $Cl_2-AlCl_3$.

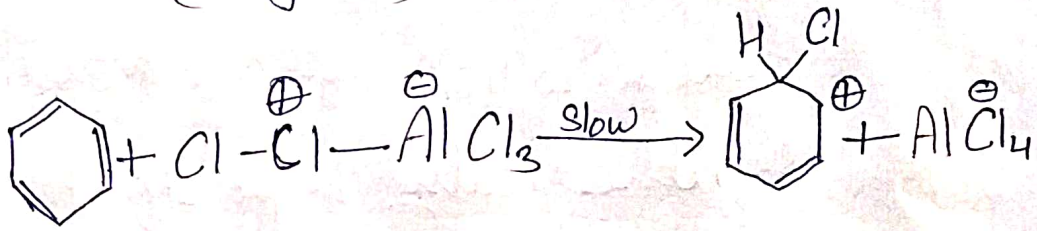
This complex can itself be the reactive electrophile or it may dissociate to give $Cl^+$.

Step 1:

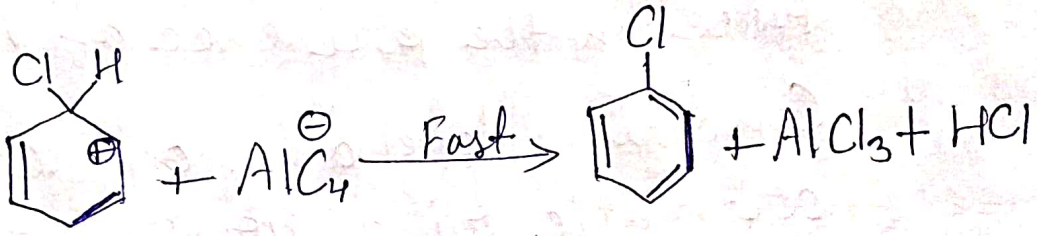



(anhydrous)

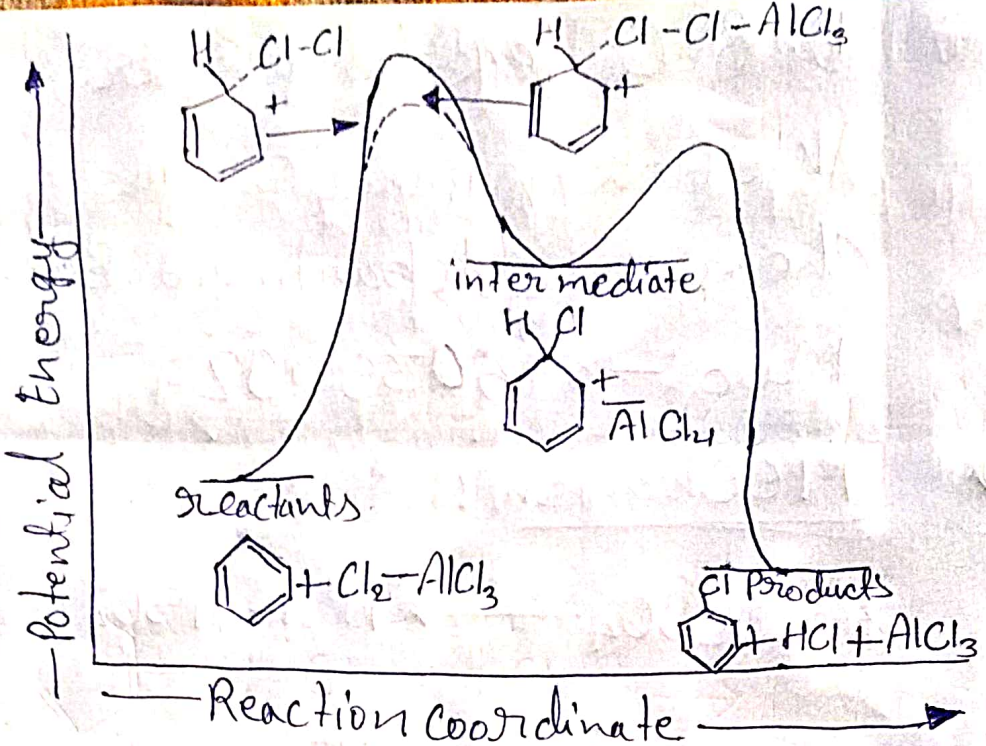
Step 2:




Step 3:




However, there is no significant evidence for the involvement of $Cl^+$ as an electrophile and it is likely that the complex itself attacks the substrate. In the $Cl_2$–$AlCl_3$ complex, role of the Lewis acid is to polarize the halogen molecule and weaken the Cl–Cl bond. This lowers the activation energy for the formation of σ-complex.




Schematic potential ~~energy~~ energy diagram for chlorination of benzene with $Cl_2$ (-) and $Cl_2AlCl_3$ (+) as the electrophile

Bromination follows a similar mechanism. As said above, iodine is weakest of the three halogens and even in the presence of a Lewis acid, it can halogenate reactive aromatics only. Therefore, in most of the cases iodine-monochloride is used in the presence of Lewis acid, $ZnCl_2$.