

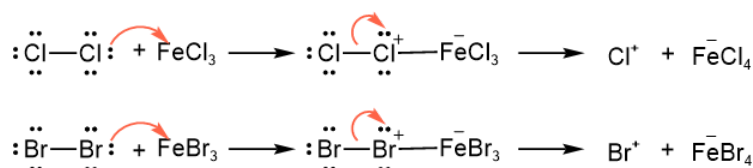
4.8: Electrophilic aromatic substitution reactions

Learning Objectives

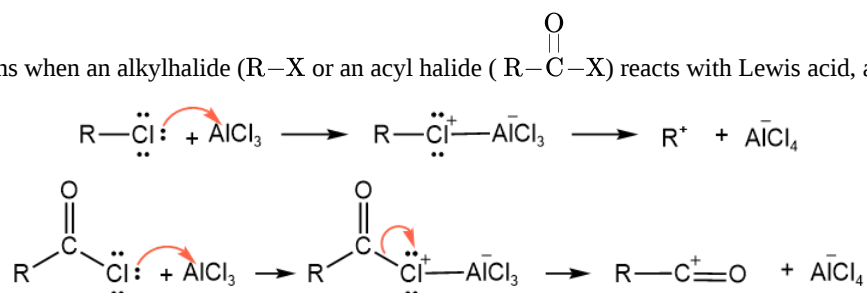
- Understand the difference in the electrophilicity of π -bond of benzene and alkenes.
- Draw the electrophilic aromatic substitution mechanism with curly arrows showing the flow of electrons.
- Apply the electrophilic aromatic substitution to some reactions of benzene, including halogenation, nitration, sulfonation, alkylation, and acylation reactions.

Which electrophiles can react with an aromatic substrate?

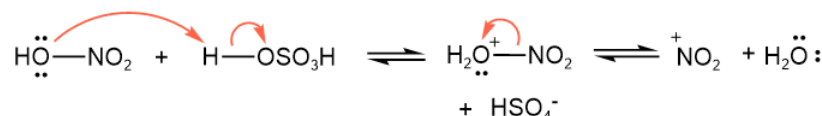
The π -bonds in a benzene ring of aromatic compounds are weaker nucleophiles than the π -bonds in alkenes. This is because breaking a π -bond of alkene costs about 260 kJ/mole energy, but breaking a π -bond in an aromatic substrate costs an additional 208 kJ/mol because the aromatic stabilization is lost. Unlike alkenes, the aromatic substrates do not react with partial positive (δ^+ δ^- $A-B$) electrophiles. The aromatic substrates react with electrophiles in their most reactive cation E^+ form. The cation electrophiles are generated in situ by acid-base or Lewis acid-Lewis base reactions. For example, halogens ($X-X$ react as Lewis bases with Lewis acids like AlX_3 or FeX_3 , where X is a halogen atom (Cl or Br). The Lewis acid receives a lone pair from one halogen atom causing a heterolytic breaking of $X-X$. The other halogen leaves as X^+ , as shown below.



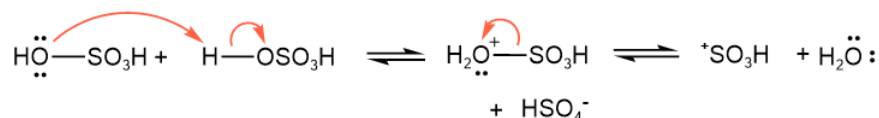
Similar reaction happens when an alkylhalide ($R-X$ or an acyl halide ($R-\overset{O}{\parallel}C-X$) reacts with Lewis acid, as shown below.



An $-OH$ bonded with a potential electrophile E^+ can be converted into a better leaving $-\overset{+}{O}H_2$ group by adding a stronger acid to the substrate. The $-\overset{+}{O}H_2$ leaves as neutral nucleophile H_2O , leaving behind the E^+ . For example, protonation of nitric acid with sulfuric acid generated nitronium ion ($\overset{+}{N}O_2$), as shown below.

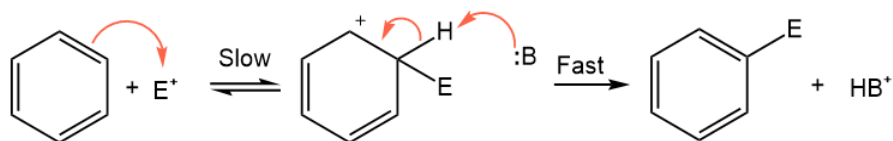


Like the auto-ionization of water, the autoionization of sulfuric acid followed by elimination of H_2O generates protonated sulfur trioxide ($\overset{+}{S}O_3H$), as shown below.



Electrophilic aromatic substitution mechanism

The nucleophilic π -bond of an aromatic compound attacks the cation electrophile (E^+), as shown in step#1 in the mechanism illustrated below. Any base group in the medium removes the acidic proton that re-establishes the π -bond in Step#2.

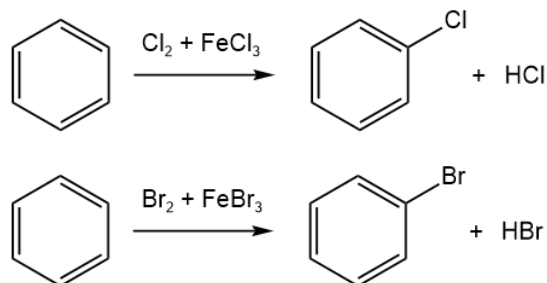


Removal of the proton by a base is preferred over electrophile attacking the carbonation intermediate in step#2, because aromatic stabilization decreases the energy barrier for the former. It is called **electrophilic aromatic substitution reaction** because an electrophile E^+ substitutes another electrophile H^+ from an aromatic substrate.

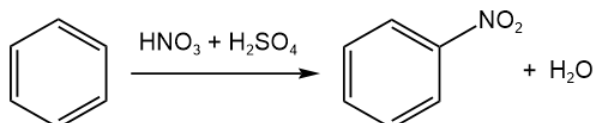
Examples of electrophilic aromatic substitution reactions

Some of the important electrophilic aromatic substitution reactions of benzene are listed below.

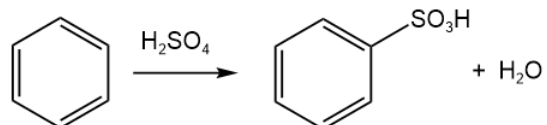
- Halogenation of benzene** substitutes a $-H$ with a halogen ($-Cl$ or $-Br$), as shown below.



- Nitration of benzene** substitutes a $-H$ with nitro group ($-NO_2$) by the following reaction.



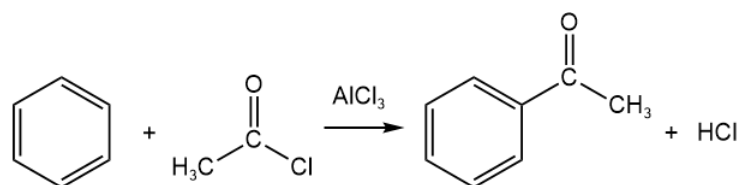
- Sulfonation of benzene** substitutes a $-H$ with sulfonic acid group ($-SO_3H$) by the following reaction.



- Alkylation of benzene** substitutes a $-H$ with alkyl acid group ($-R$), e.g.,:



- Acylation of benzene** substitutes a $-H$ with acyl group ($-\overset{O}{\parallel}C-R$), e.g.,:



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