The mechanism of electrophilic aromatic substitution follows two elementary steps. First, donation of a pair of \( \pi \) electrons to the electrophile results in a loss of aromaticity and formation of a cation. Second, removal of a proton from that cation restores aromaticity.

How does the electrophile form in the first place? The details of that part of the reaction vary from case to case. With the catalysed bromine reaction, the Lewis acid activates the halogen to render it more electrophilic. The activation may even go so far as to form a bromine cation, as suggested earlier. Otherwise, the positive charge on the bromine atom that ligates the Lewis acid can be nullified, indirectly, when the arene donates to the terminal bromine atom.

The appearance of a bromide ion to deprotonate the cation simply results from the equilibrium of the Lewis acid-base complex.

Problem AR3.1.

Show the mechanism for chlorination of benzene in the presence of ferric chloride.

The reactions of alkyl and acyl halides also involve Lewis acid catalysts; frequently, aluminum chloride (\( \text{AlCl}_3 \)) is employed. These two reactions are called Friedel-Crafts reactions after the French and American co-discoverers of the reaction. Typically, Friedel-Crafts reactions are believed to occur through initial formation of cationic electrophiles, which then react with aromatics in the same way as halogen electrophiles.

Because Friedel-Crafts alkylations occur via alkyl cations, the reactions of primary alkyl halides are generally pretty slow. Also, in some cases, multiple products may result via rearrangements. These observations provide additional evidence for the cationic nature of the intermediate.

Problem AR3.2.

Show the mechanism for the Friedel-Crafts alkylation of benzene with 2-chloropropane in the presence of aluminum chloride.

Problem AR3.3.

Why is the Friedel-Crafts reaction of 1-chloropropane so much slower than the reaction of 2-chloropropane? Explain using a mechanism and intermediates.
Problem AR3.4.
Show why Friedel-Crafts alkylation of benzene with 2-chloropentane results in the formation of two different products.

Problem AR3.5.
Show the mechanism for the Friedel-Crafts acylation of benzene with ethanoyl chloride (acetyl chloride) in the presence of aluminum chloride.

Problem AR3.6.
Show why the Friedel-Crafts acylation of benzene with pentanoyl chloride results in only one product, with no rearrangement.

Nitration and sulfonation reactions differ from the other substitutions that we have seen because they do not utilize Lewis acid catalysis. These reactions depend on equilibria that occur in strongly acidic media. When nitric acid is dissolved in sulfuric acid, there is spectroscopic evidence than NO$_2^+$ forms, providing an electrophile. Similarly, when sulfuric acid is concentrated by boiling off residual water, sulfur trioxide results. The latter probably forms via SO$_3$H$, the electrophile in sulfonation.

Problem AR3.7.
Provide a mechanism for the formation of NO$^+$ from nitric and sulfuric acid.

Problem AR3.8.
Provide a mechanism for the formation of SO$_3$H$^+$ from sulfuric acid.

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