Many other substitution reactions of benzene have been observed, the five most useful are listed below (chlorination and bromination are the most common halogenation reactions). Since the reagents and conditions employed in these reactions are electrophilic, these reactions are commonly referred to as **Electrophilic Aromatic Substitution**. The catalysts and co-reagents serve to generate the strong electrophilic species needed to effect the initial step of the substitution. The specific electrophile believed to function in each type of reaction is listed in the right hand column.

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Typical Equation</th>
<th>Electrophile E(+)</th>
</tr>
</thead>
</table>
| **Halogenation:**   | $\text{C}_6\text{H}_6 + \text{Cl}_2 \text{ & heat}$  \(\text{FeCl}_3\) catalyst | $\text{C}_6\text{H}_5\text{Cl} + \text{HCl}$ Chlorobenzene  
Cl(+) or Br(+) |
| **Nitration:**      | $\text{C}_6\text{H}_6 + \text{HNO}_3 \text{ & heat}$  \(\text{H}_2\text{SO}_4\) catalyst | $\text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$ Nitrobenzene  
NO$_2$(+) |
| **Sulfonation:**    | $\text{C}_6\text{H}_6 + \text{H}_2\text{SO}_4 + \text{SO}_3$  \& heat | $\text{C}_6\text{H}_5\text{SO}_3\text{H} + \text{H}_2\text{O}$ Benzenesulfonic acid  
SO$_3$H(+) |
| **Alkylation:**     | $\text{C}_6\text{H}_6 + \text{R-Cl} \text{ & heat}$  \(\text{AlCl}_3\) catalyst | $\text{C}_6\text{H}_5\text{R} + \text{HCl}$ An Arene  
R(+) |
| **Acylation:**      | $\text{C}_6\text{H}_6 + \text{RCOCl} \text{ & heat}$  \(\text{AlCl}_3\) catalyst | $\text{C}_6\text{H}_5\text{COR} + \text{HCl}$ An Aryl Ketone  
RCO(+) |

### A Mechanism for Electrophilic Substitution Reactions of Benzene

A two-step mechanism has been proposed for these electrophilic substitution reactions. In the first, slow or rate-determining, step the electrophile forms a sigma-bond to the benzene ring, generating a positively charged **benzenonium intermediate**. In the second, fast step, a proton is removed from this intermediate, yielding a substituted benzene ring. The following four-part illustration shows this mechanism for the bromination reaction. Also, an animated diagram may be viewed.

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The bromine molecule is polarized so that one end is electrophilic and the other nucleophilic. Although the electrophilic end reacts easily with simple alkynes and alkenes, it fails to react with the more stable and weaker nucleophilic σ-electron system of benzene.
Ferric bromide and other Lewis acids enhance the electrophilic strength of bromine by forming a complex anion, in this case FeBr₆⁻. At the same time, this complexation creates the strongly electrophilic bromine cation, which reacts with nucleophiles.

**Preliminary step: Formation of the strongly electrophilic bromine cation**
Step 1: The electrophile forms a sigma-bond to the benzene ring, generating a positively charged benzenonium intermediate.

The π-electrons of the benzene ring are polarized by the electrophile, and two electrons are divered to form a σ-bond to the bromine atom. The positive charge is thereby relocated on the six-carbon ring, where it is conjugated with the remaining double bonds. The resulting intermediate is a benzenonium cation. Since the aromatic character of benzene is lost, the activation energy ($\Delta G^\ddagger$) for this reaction is large. Note that the charge alternates so it is greatest ortho and para to the location of the bromine attack.
Step 2: A proton is removed from this intermediate, yielding a substituted benzene ring

This mechanism for electrophilic aromatic substitution should be considered in context with other mechanisms involving carbocation intermediates. These include $\text{SN}_1$ and $\text{E}_1$ reactions of alkyl halides, and Bronsted acid addition reactions of alkenes.

To summarize, when carbocation intermediates are formed one can expect them to react further by one or more of the following modes:

1. The cation may bond to a nucleophile to give a substitution or addition product.
2. The cation may transfer a proton to a base, giving a double bond product.
3. The cation may rearrange to a more stable carbocation, and then react by mode #1 or #2.

$\text{SN}_1$ and $\text{E}_1$ reactions are respective examples of the first two modes of reaction. The second step of alkene addition reactions proceeds by the first mode, and any of these three reactions may exhibit molecular rearrangement if an initial unstable carbocation is formed. The carbocation intermediate in electrophilic aromatic substitution (the benzenonium ion) is stabilized by charge delocalization (resonance) so it is not subject to rearrangement. In principle it could react by either mode 1 or 2, but the energetic advantage of reforming an aromatic ring leads to exclusive reaction by mode 2 (i.e. proton loss).
Contributors