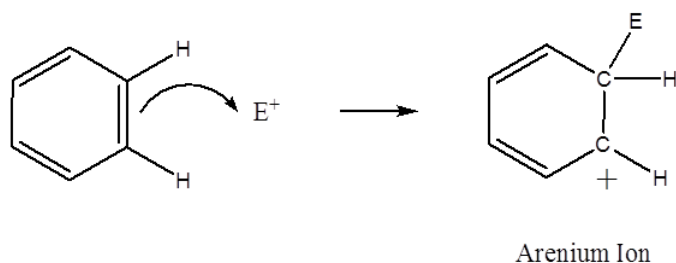


16.8: The General Mechanism

The General Mechanism

Step 1 (Slow)



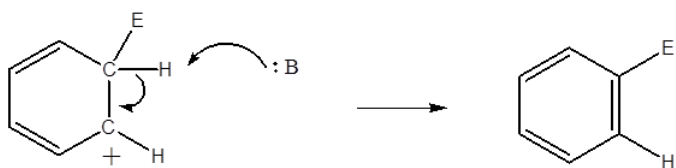
The e⁻ in the pi bond attacks the electrophile

One carbon gets a positive charge the other forms a C-E bond

This forms the arenium ion.

The arenium ion is conjugated but not aromatic.

Step 2 (Fast)

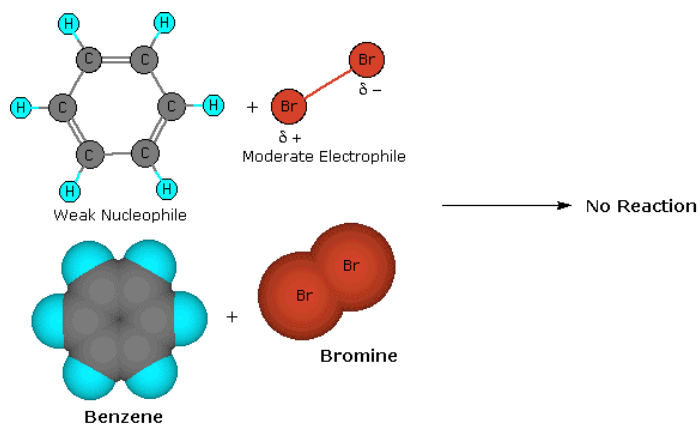


The LPE on a base attacks the hydrogen.

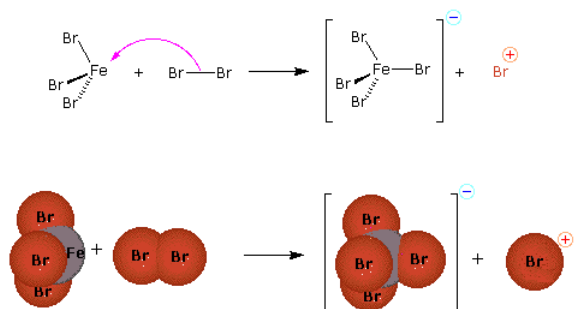
This causes the e⁻ in the C-H bond to form a C-C double bond and aromaticity is reformed

A Detailed discussion of the 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.

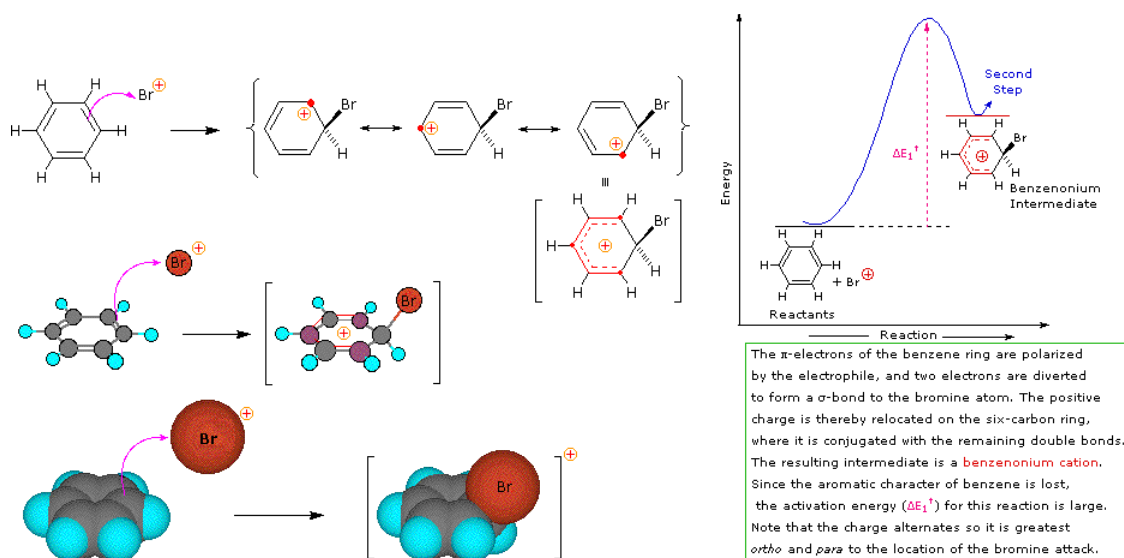


The bromine molecule is polarized so that one end is electrophilic and the other nucleophilic. Although the electrophilic end reacts easily with simple alkenes and dienes, it fails to react with the more stable and weaker nucleophilic π -electron system of benzene.

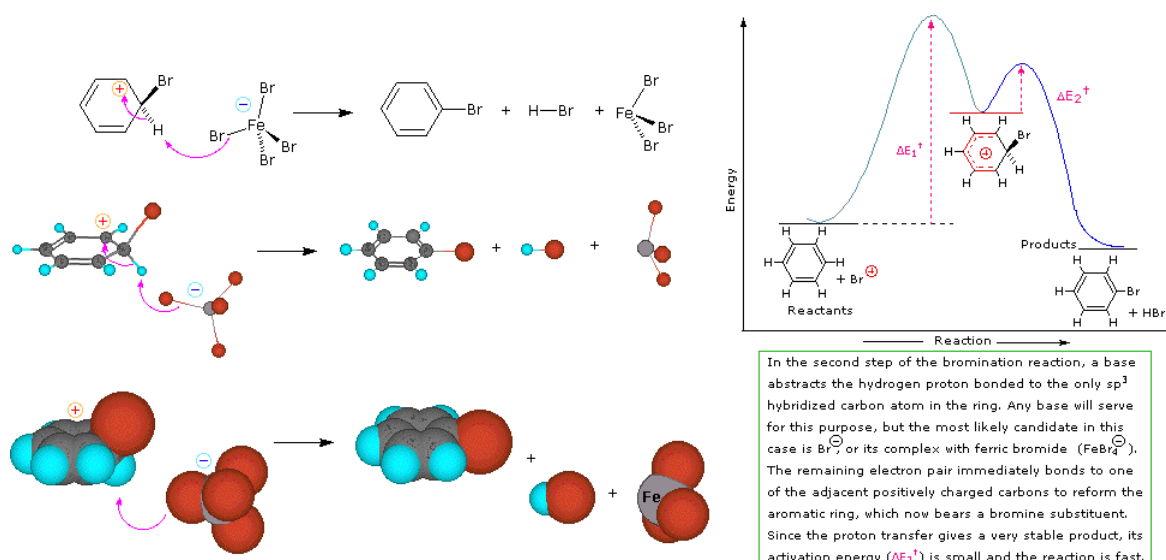


Ferric bromide and other Lewis acids enhance the electrophilic strength of bromine by forming a complex anion, in this case FeBr_4^- . At the same time, this complexation creates the strongly electrophilic bromine cation, which reacts with nucleophiles.

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



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 S_N1 and E1 reactions of alkyl halides, and Brønsted 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:

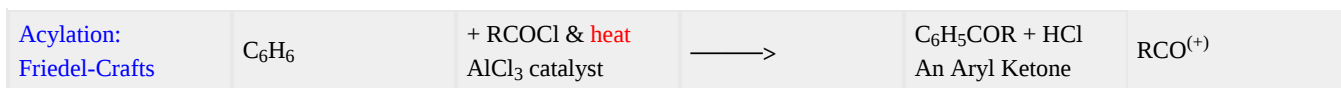
1. The cation may bond to a nucleophile to give a substitution or addition product.
2. The cation may transfer a proton to a base, giving a double bond product.
3. The cation may rearrange to a more stable carbocation, and then react by mode #1 or #2.

S_N1 and E1 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 (*ie.* proton loss).

Other Examples of Electrophilic Aromatic Substitution

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.

Reaction Type	Typical Equation			Electrophile E ⁽⁺⁾	
Halogenation:	C ₆ H ₆	+ Cl ₂ & heat FeCl ₃ catalyst	→	C ₆ H ₅ Cl + HCl Chlorobenzene	Cl ⁽⁺⁾ or Br ⁽⁺⁾
Nitration:	C ₆ H ₆	+ HNO ₃ & heat H ₂ SO ₄ catalyst	→	C ₆ H ₅ NO ₂ + H ₂ O Nitrobenzene	NO ₂ ⁽⁺⁾
Sulfonation:	C ₆ H ₆	+ H ₂ SO ₄ + SO ₃ & heat	→	C ₆ H ₅ SO ₃ H + H ₂ O Benzenesulfonic acid	SO ₃ H ⁽⁺⁾
Alkylation: Friedel-Crafts	C ₆ H ₆	+ R-Cl & heat AlCl ₃ catalyst	→	C ₆ H ₅ -R + HCl An Arene	R ⁽⁺⁾



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