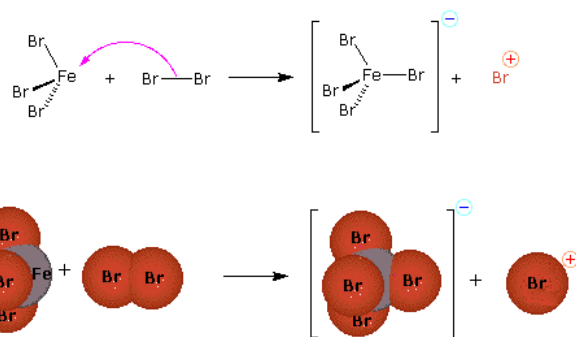


## 18.2: HALOGENATION OF BENZENE (AN EAS REACTION)

### A MECHANISM FOR HALOGENATION OF BENZENE

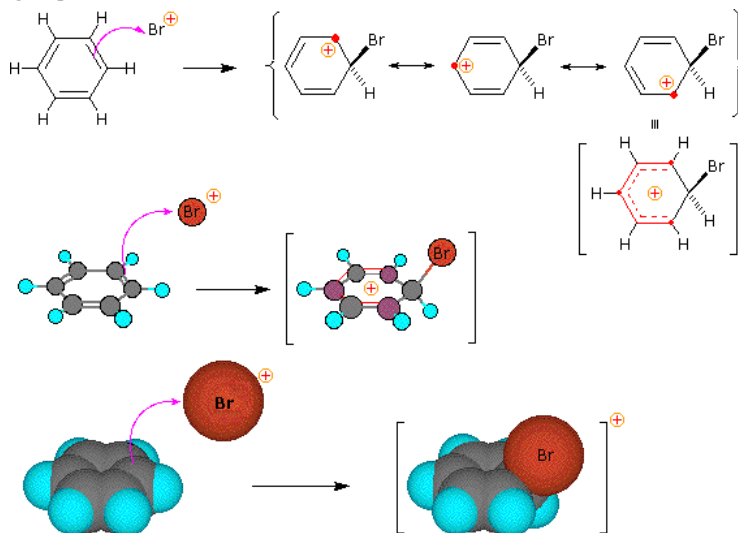
A three-step mechanism is common for many electrophilic aromatic substitution reactions. In the first step, a strong electrophile is created to entice the pi electrons of the aromatic ring to react. In the second, slow or rate-determining step a pair of pi electrons from the benzene form a sigma-bond with the electrophile generating a positively charged sigma complex (**the benzenonium intermediate for halogenation**). In the third, fast step, a proton is removed from the sigma complex producing a halogenated benzene ring. The steps are illustrated below.

**Step 1:** Formation of a strong electrophile, in this case an electrophilic bromine cation.

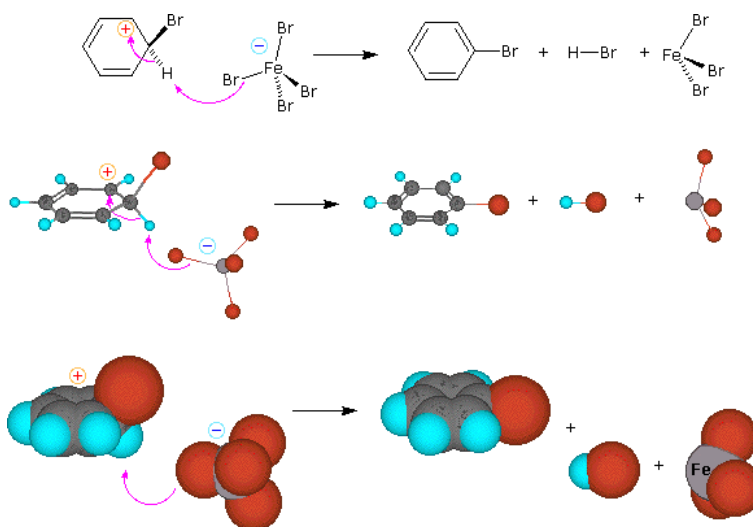


Ferric bromide and other Lewis acids enhance the electrophilic strength of bromine by forming a complex anion, in this case  $\text{FeBr}_4^-$ . At the same time, this complexation creates the strongly electrophilic bromine cation, which reacts with nucleophiles.

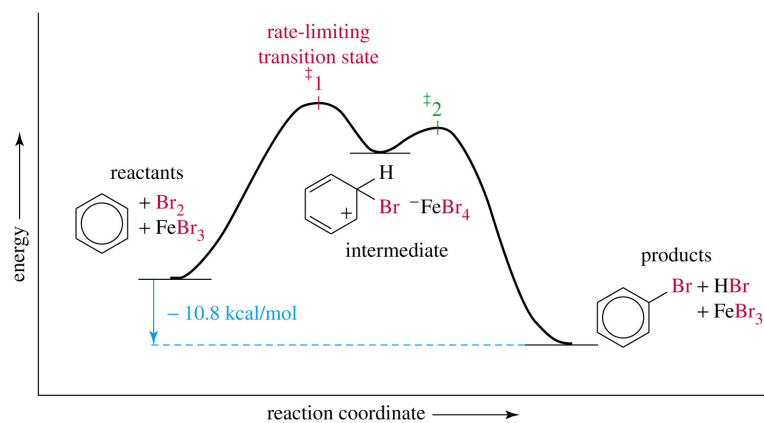
**Step 2:** Pi electrons of benzene react with the bromine cation to form the sigma complex, resonance stabilized benzenonium intermediate. This step is the rate determining step.



**Step 3:** Deprotonation of the benzenonium intermediate (sigma complex) to restore aromaticity.

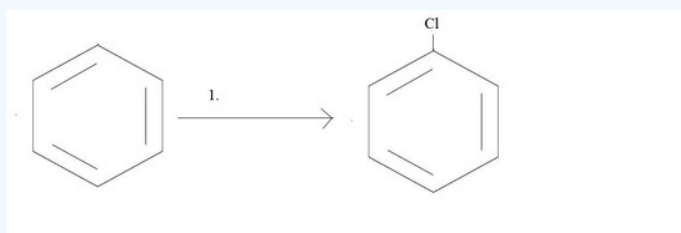


The reaction energy diagram below shows Steps 2 and 3 of the mechanism since these steps involve benzene.

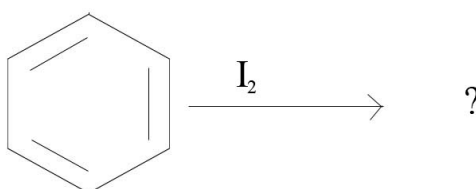


### Exercises

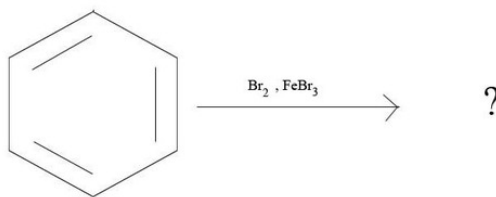
1. What reagents would you need to get the given product?



2. What product would result from the given reagents?



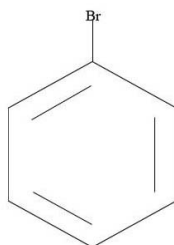
3. What is the major product given the reagents below?



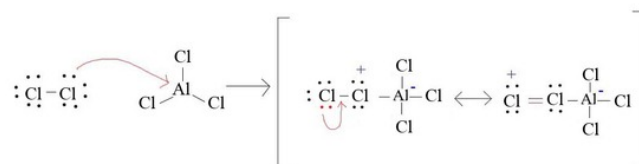
4. Draw the formation of  $\text{Cl}^+$  from  $\text{AlCl}_3$  and  $\text{Cl}_2$
5. Draw the mechanism of the reaction between  $\text{Cl}^+$  and a benzene.

**Answer**

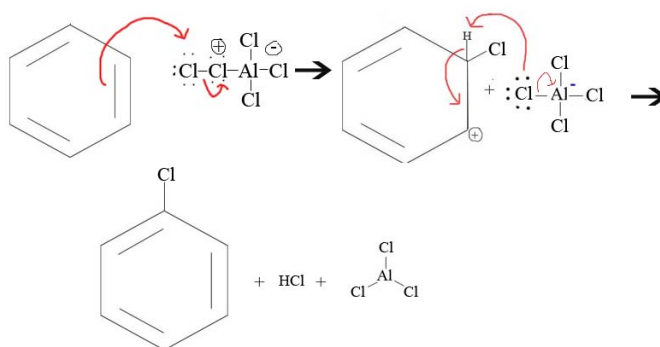
1.  $\text{Cl}_2$  and  $\text{AlCl}_3$  or  $\text{Cl}_2$  and  $\text{FeCl}_3$
2. No Reaction
- 3.



4.



5.



## CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- Catherine Nguyen

- William Reusch, Professor Emeritus ([Michigan State U.](#)), Virtual Textbook of Organic Chemistry

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