This page gives you the facts and a simple, uncluttered mechanism for the electrophilic substitution reaction between benzene and chlorine or bromine in the presence of a catalyst such as aluminum chloride or iron.

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**The electrophilic substitution reaction between benzene and chlorine or bromine**

Benzene reacts with chlorine or bromine in an electrophilic substitution reaction, but only in the presence of a catalyst. The catalyst is either aluminum chloride (or aluminum bromide if you are reacting benzene with bromine) or iron. Strictly speaking iron is not a catalyst, because it gets permanently changed during the reaction. It reacts with some of the chlorine or bromine to form iron(III) chloride, \(FeCl_3\), or iron(III) bromide, \(FeBr_3\).

\[
2Fe + 3Cl_2 \rightarrow 2FeCl_3
\]

\[
2Fe + 3Br_2 \rightarrow 2FeBr_3
\]

These compounds act as the catalyst and behave exactly like aluminum chloride in these reactions.

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**The reaction with chlorine**

The reaction between benzene and chlorine in the presence of either aluminum chloride or iron gives chlorobenzene.

\[
C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl
\]

or:

![Chemical structure of chlorobenzene](image)

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**The reaction with bromine**

The reaction between benzene and bromine in the presence of either aluminum bromide or iron gives bromobenzene. Iron is usually used because it is cheaper and more readily available.

\[
C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr
\]

or:

![Chemical structure of bromobenzene](image)
The formation of the electrophile

We are going to explore the reaction using chlorine and aluminum chloride. If you want one of the other combinations, all you have to do is to replace each \(\text{Cl}\) by \(\text{Br}\), or each \(\text{Al}\) by \(\text{Fe}\). As a chlorine molecule approaches the benzene ring, the delocalized electrons in the ring repel electrons in the chlorine-chlorine bond.

![Diagram of chlorine molecule becoming polarized]

It is the slightly positive end of the chlorine molecule which acts as the electrophile. The presence of the aluminum chloride helps this polarization.

The electrophilic substitution mechanism

**Stage one**

![Diagram of stage one reaction]

**Stage two**

![Diagram of stage two reaction]

The hydrogen is removed by the \(\text{AlCl}_4^–\) ion which was formed in the first stage. The aluminum chloride catalyst is re-generated in this second stage.

Contributors

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