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.

### 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, \( \text{FeCl}_3 \), or iron(III) bromide, \( \text{FeBr}_3 \).

\[
\begin{align*}
2 \text{Fe} + 3\text{Cl}_2 & \rightarrow 2\text{FeCl}_3 \\
2 \text{Fe} + 3\text{Br}_2 & \rightarrow 2\text{FeBr}_3
\end{align*}
\]

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

#### The reaction with chlorine

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

\[
\begin{align*}
\text{C}_6\text{H}_6 + \text{Cl}_2 & \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{HCl}
\end{align*}
\]

or:

![Chemical structure of chlorobenzene]

#### 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.

\[
\begin{align*}
\text{C}_6\text{H}_6 + \text{Br}_2 & \rightarrow \text{C}_6\text{H}_5\text{Br} + \text{HBr}
\end{align*}
\]

or:

![Chemical structure of bromobenzene]
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.

![Chemical structure showing chlorine molecule becoming polarized and bonding electrons repelled by nearby delocalized electrons in benzene.]

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**

![Chemical structure showing the removal of hydrogen by the \(\text{AlCl}_4^-\) ion, regenerating the aluminum chloride catalyst.]

**Stage two**

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

Jim Clark (Chemguide.co.uk)