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:

![Diagram of benzene reacting with chlorine](image)

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:

![Diagram of benzene reacting with bromine](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 Cl by Br, or each Al by Fe. As a chlorine molecule approaches the benzene ring, the delocalized electrons in the ring repel electrons in the chlorine-chlorine bond.

\[
\text{chlorine molecule becomes polarised}
\]

\[
\text{bonding electrons repelled by the nearby delocalised electrons in benzene}
\]

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

\[
\begin{align*}
\delta^+ & \quad \text{Cl} & \quad \delta^- & \quad \text{AlCl}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{AlCl}_3 & \quad \text{Cl} \\
\end{align*}
\]

Stage two

\[
\begin{align*}
\text{Cl} & \quad \text{AlCl}_3 & \quad \text{Cl} \\
\end{align*}
\]

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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