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.

Preliminary step: Formation of the strongly electrophilic bromine cation

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 6-electron system of benzene.

Ferric bromide and other Lewis acids enhance the electrophilic strength of bromine by forming a complex anion, in this case $\text{FeBr}_3^2$. At the same time, this complexation creates the strongly electrophilic bromine cation, which reacts with nucleophiles.
Step 1: The electrophile forms a sigma-bond to the benzene ring, generating a positively charged Wheland intermediate.

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 \(\pi\)-electron system of benzene.
Step 2: A proton is removed from this intermediate via an electrophile elimination reaction, yielding a substituted benzene ring.

The π-electrons of the benzene ring are polarized by the electrophile, and two electrons are diverted to form σ-bond to the bromine atom. The positive charge is thereby relocated on the six-carbon ring, where it is conjugated with the remaining double bonds. The resulting intermediate is a benzenonium cation. Since the aromatic character of benzene is lost, the activation energy (ΔG°) for this reaction is large. Note that the charge alternates so it is greatest ortho and para to the location of the bromine attack.
This mechanism for electrophilic aromatic substitution should be considered in context with other mechanisms involving carbocation intermediates. These include $S_N^1$ and $E_1$ 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 (coordination).
2. The cation may transfer a proton to a base, giving a double bond product (electrophile elimination).
3. The cation may rearrange to a more stable carbocation, and then react by mode #1 or #2.

$S_N^1$ and $E_1$ 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 Wheland intermediate) 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 (i.e., proton loss).

**Synthesis of benzene derivatives via electrophilic aromatic substitution**

This section is on the general mechanism of how an electrophilic atom becomes a part of a benzene ring through the substitution of a hydrogen. Common reactions that proceed by electrophilic aromatic substitution include the nitration...
and sulfonation of benzene, hydration of benzene, Friedel-Crafts acylation and Friedel-Crafts alkylation. The catalysts and co-reagents serve to generate the strong electrophilic species needed to effect the initial step of the substitution. The specific electrophile \((E^+\) or \(E\)) believed to function in each type of reaction is listed in the right hand column.

### Specific Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reagent</th>
<th>Catalyst</th>
<th>Product</th>
<th>(E^+ ) or (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Halogenation</strong></td>
<td>(X_2 ) ((X=\text{Cl, Br}))</td>
<td>(\text{FeX}_3)</td>
<td>(\text{ArCl, ArBr})</td>
<td>(X^+)</td>
</tr>
<tr>
<td></td>
<td>(X_2 ) ((X = \text{I}))</td>
<td>(\text{HNO}_3)</td>
<td>(\text{ArI})</td>
<td>(\text{H}_2\text{O-I}^+)</td>
</tr>
<tr>
<td><strong>Nitration</strong></td>
<td>(\text{HNO}_3)</td>
<td>(\text{H}_2\text{SO}_4)</td>
<td>(\text{ArNO}_2)</td>
<td>+(\text{NO}_2)</td>
</tr>
<tr>
<td><strong>Sulfonation</strong></td>
<td>(\text{H}_2\text{SO}_4\text{ or H}_2\text{S}_2\text{O}_7)</td>
<td>None</td>
<td>(\text{ArSO}_3\text{H})</td>
<td>(\text{SO}_3)</td>
</tr>
<tr>
<td><strong>Friedel-Crafts alkylation</strong></td>
<td>(\text{RX, ArCH}_2\text{X})</td>
<td>(\text{AlCl}_3)</td>
<td>(\text{Ar-R, Ar-CH}_2\text{Ar})</td>
<td>(R^+)</td>
</tr>
<tr>
<td><strong>Friedel-Crafts acylation</strong></td>
<td>(\text{ROH})</td>
<td>(\text{HF, H}_2\text{SO}_4\text{, or BF}_3)</td>
<td>(\text{Ar-R})</td>
<td>(R^+)</td>
</tr>
<tr>
<td></td>
<td>(\text{RCH=CH}_2)</td>
<td>(\text{H}_3\text{PO}_4\text{ or HF})</td>
<td>(\text{Ar-CHRCH}_3)</td>
<td>(R^+)</td>
</tr>
<tr>
<td></td>
<td>(\text{RCOCl})</td>
<td>(\text{AlCl}_3)</td>
<td>(\text{Ar-COR})</td>
<td>(\text{RC}^+=\text{O})</td>
</tr>
</tbody>
</table>

**Electrophilic aromatic substitution reactions – Halogenation**

**Study Note**

The general mechanism is the key to understanding electrophilic aromatic substitution. You will see similar equations written for nitration, sulphonation, acylation, etc., but the general mechanism is always the same – the major difference being the identity of the electrophile in each case. All involve an electrophilic addition step which is quickly followed by an electrophile elimination step.

Halogenation is an example of electrophilic aromatic substitution. In electrophilic aromatic substitutions, a benzene is attacked by an electrophile which results in substitution of hydrogens. However, halogens are not electrophilic enough to break the aromaticity of benzenes, which require a catalyst (such as \(\text{FeCl}_3\)) to activate. See above for a detailed examination of the mechanism for bromination of benzene.
Exercises

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

\[ \text{Product} \]

2. What product would result from the given reagents?

\[ \text{Product} \]

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

\[ \text{Product} \]

4. Draw the formation of Cl\(^+\) from AlCl\(_3\) and Cl\(_2\).

5. Draw the mechanism of the reaction between Cl\(^+\) and a benzene.

Solutions

[reveal-answer q="789315"]Show Answer[/reveal-answer]
[hidden-answer a="789315"]
1. Cl\textsubscript{2} and AlCl\textsubscript{3} or Cl\textsubscript{2} and FeCl\textsubscript{3}

2. No Reaction

3.

4.

5.
Nitration and Sulfonation

Nitration and sulfonation of benzene are two examples of electrophilic aromatic substitution. The nitronium ion (NO$_2^+$) and sulfur trioxide (SO$_3$) are the electrophiles and individually react with benzene to give nitrobenzene and benzenesulfonic acid respectively.

Nitration of Benzene

The source of the nitronium ion is through the protonation of nitric acid by sulfuric acid, which causes the loss of a water molecule and formation of a nitronium ion.

\[
\begin{align*}
\text{Benzene} & \quad \overset{\text{HNO}_3}{\rightarrow} \quad \text{Nitrobenzene} \\
\end{align*}
\]

Sulfuric acid activation of nitric acid

The first step in the nitration of benzene is to activate HNO$_3$ with sulfuric acid to produce a stronger electrophile, the nitronium ion.

\[
\begin{align*}
\text{HNO}_3 + \text{H}_2\text{SO}_4 & \rightarrow \text{HNO}_2^+ - \text{N}^+ - \text{O}^- + \text{HSO}_4^- \\
\end{align*}
\]

Because the nitronium ion is a good electrophile, it is attacked by benzene to produce nitrobenzene.
**Mechanism**

Mechanism forms of the intermediate can be seen in the generalized electrophilic aromatic substitution.

**Sulphonation of benzene**

Sulphonation is a reversible reaction that produces benzenesulphonic acid by adding sulfate trioxide and fuming sulfuric acid. The reaction is reversed by adding hot aqueous acid to benzenesulphonic acid to produce benzene.

**Mechanism**

To produce benzenesulphonic acid from benzene, fuming sulfuric acid and sulfate trioxide are added. Fuming sulfuric acid, also referred to as oleum, is a concentrated solution of dissolved sulfate trioxide in sulfuric acid. The sulfur in sulfate trioxide is electrophilic because the oxygens pull electrons away from it because oxygen is very electronegative. The benzene attacks the sulfur (and subsequent proton transfers occur) to produce benzenesulphonic acid.

**Reverse sulphonation**

Sulphonation of benzene is a reversible reaction. Sulfur trioxide readily reacts with water to produce sulfuric acid and heat. Therefore, by adding heat to benzenesulphonic acid in diluted aqueous sulfuric acid the reaction is reversed.
Further applications of nitration and sulfonation

Nitration is used to add nitrogen to a benzene ring, which can be used further in substitution reactions. The nitro group acts as a ring deactivator. Having nitrogen present in a ring is very useful because it can be used as a directing group as well as a masked amino group. The products of aromatic nitrations are very important intermediates in industrial chemistry.

Because sulfonation is a reversible reaction, it can also be used in further substitution reactions in the form of a directing blocking group because it can be easily removed. The sulfonic group blocks the carbon from being attacked by other substituents and after the reaction is completed it can be removed by reverse sulfonation. Benzenesulfonic acids are also used in the synthesis of detergents, dyes, and sulfa drugs. Benzenesulfonyl chloride is a precursor to sulfonamides, which are used in chemotherapy.

Outside Links

Aromatic Sulfonation

A YouTube element has been excluded from this version of the text. You can view it online here: http://pb.libretexts.org/ochem2walker/?p=68

Interactive 3D Reaction: http://www.chemtube3d.com/Electrophil...20benzene.html
Aromatic Nitration

A YouTube element has been excluded from this version of the text. You can view it online here: http://pb.libretexts.org/ochem2walker/?p=68

- Interactive 3D Reaction: http://www.chemtube3d.com/Electrophi...20benzene.html
Exercises

1. What is/are the required reagent(s) for the following reaction:

   ![Chemical structure](image)

2. What is the product of the following reaction:

   ![Chemical reaction](image)

3. Why is it important that the nitration of benzene by nitric acid occurs in sulfuric acid?
4. Write a detailed mechanism for the sulfonation of benzene, including all resonance forms.

5. Draw an energy diagram for the nitration of benzene. Draw the intermediates, starting materials, and products. Label the transition states.

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**Solutions**

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1. SO$_3$ and H$_2$SO$_4$ (fuming)

2. 

![Benzene molecule]

3. Sulfuric acid is needed in order for a good electrophile to form. Sulfuric acid protonates nitric acid to form the nitronium ion (water molecule is lost). The nitronium ion is a very good electrophile and is open to attack by benzene. Without sulfuric acid the reaction would not occur.

4. 

![Sulfonation mechanism]

5. 

Reduction of Nitro groups

Electrophilic nitration introduces a deactivating, meta-directing substituents on an aromatic ring. The attached nitrogen is in a high oxidation state, and reduction converts the nitro into an electron donating amino group. Reduction is easily achieved either by catalytic hydrogenation (H₂ + catalyst), or with reducing metals in acid. Examples of this reduction are shown here.

**Nitro Group Reduction**

1. \[
\text{CH}_3\text{NO}_2 \xrightarrow{3\text{H}_2 \ & \ Pt} \text{CH}_3\text{NH}_2\]

2. \[
\text{CH}_3\text{NO}_2 \xrightarrow{\text{Fe} \ & \ \text{HCl}} \text{CH}_3\text{NH}_2 \cdot 2\text{HCl}\]

3. \[
\text{CHO} \xrightarrow{\text{SnCl}_2 \ & \ \text{HCl}} \text{CHO} \cdot \text{NH}_2\]

Several alternative methods for reducing nitro groups to amines are known. These include zinc or tin in dilute mineral acid, and sodium sulfide in aqueous ammonia solution. The procedures described above are sufficient for most cases.
Khan Academy videos

Friedel-Crafts alkylation

Friedel-Crafts acylation

References


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