This page gives details of some reactions of benzene and methylbenzene (toluene) not covered elsewhere in this section. It deals with the combustion, hydrogenation and sulfonation of benzene and methylbenzene (toluene), and with the oxidation of side chains attached to benzene rings.

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## Combustion

Like any other hydrocarbons, benzene and methylbenzene burn in a plentiful supply of oxygen to give carbon dioxide and water. For example:

For benzene:

\[ \text{2C}_6\text{H}_6 + 15\text{O}_2 \rightarrow 12\text{CO}_2 + 6\text{H}_2\text{O} \]

... and methylbenzene:

\[ \text{C}_6\text{H}_5\text{CH}_3 + 9\text{O}_2 \rightarrow 7\text{CO}_2 + 4\text{H}_2\text{O} \]

However, for these hydrocarbons, combustion is hardly ever complete, especially if they are burnt in air. The high proportion of carbon in the molecules means that you need a very high proportion of oxygen to hydrocarbon to get complete combustion. Look at the equations.

As a general rule, the hydrogen in a hydrocarbon tends to get what oxygen is available first, leaving the carbon to form carbon itself, or carbon monoxide, if there isn't enough oxygen to go round.

The arenes tend to burn in air with extremely smoky flames - full of carbon particles. You almost invariably get incomplete combustion, and the arenes can be recognised by the smokiness of their flames.

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## Hydrogenation

Hydrogenation is an addition reaction in which hydrogen atoms are added all the way around the benzene ring. A cycloalkane is formed. For example:

With benzene:

\[ \text{C}_6\text{H}_6 + 3\text{H}_2 \rightarrow \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \]

... and methylbenzene:
These reactions destroy the electron delocalisation in the original benzene ring, because those electrons are being used to form bonds with the new hydrogen atoms.

Although the reactions are exothermic overall because of the strengths of all the new carbon-hydrogen bonds being made, there is a high activation barrier to the reaction.

The reactions are done using the same finely divided nickel catalyst that is used in hydrogenating alkenes and at similar temperatures (around 150°C), but the pressures used tend to be higher.

**sulfonation**

sulfonation involves replacing one of the hydrogens on a benzene ring by the sulfonic acid group, \(-\text{SO}_3\text{H}\).

**The sulfonation of benzene**

There are two equivalent ways of sulfonating benzene:

- Heat benzene under reflux with concentrated sulfuric acid for several hours.

- Warm benzene under reflux at 40°C with fuming sulfuric acid for 20 to 30 minutes. Fuming sulfuric acid, \(\text{H}_2\text{S}_2\text{O}_7\), can usefully be thought of as a solution of sulfur trioxide in concentrated sulfuric acid.

\[
\begin{align*}
\text{CH}_3
\end{align*}
\text{C}_6\text{H}_5 + \text{H}_2\text{SO}_4 \rightarrow \text{C}_5\text{H}_5\text{SO}_3\text{H} + \text{H}_2\text{O}
\]

Or:

\[
\text{[C}_6\text{H}_6 + \text{H}_2\text{SO}_4 \rightarrow \text{C}_5\text{H}_5\text{SO}_3\text{H} + \text{H}_2\text{O]}
\]

The product is benzenesulfonic acid.

**The sulfonation of methylbenzene**

Methylbenzene is more reactive than benzene because of the tendency of the methyl group to "push" electrons towards the ring.
The effect of this greater reactivity is that methylbenzene will react with fuming sulfuric acid at 0°C, and with concentrated sulfuric acid if they are heated under reflux for about 5 minutes.

As well as the effect on the rate of reaction, with methylbenzene you also have to think about where the sulfonic acid group ends up on the ring relative to the methyl group. Methyl groups have a tendency to "direct" new groups into the 2- and 4- positions on the ring (assuming the methyl group is in the 1- position). Methyl groups are said to be 2,4-directing.

So you get a mixture which mainly consists of two isomers. Only about 5 - 10% of the 3- isomer is formed. The main reactions are:

\[
\text{C}_\text{H}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{C}_\text{H}_3\text{SO}_3\text{H} + \text{H}_2\text{O}
\]

and:

\[
\text{C}_\text{H}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{C}_\text{H}_3\text{SO}_3\text{H} + \text{H}_2\text{O}
\]

In the case of sulfonation, the exact proportion of the isomers formed depends on the temperature of the reaction. As the temperature increases, you get increasing proportions of the 4- isomer and less of the 2- isomer. This is because sulfonation is reversible. The sulfonic acid group can fall off the ring again, and reattach somewhere else. This tends to favour the formation of the most thermodynamically stable isomer. This interchange happens more at higher temperatures.

The 4- isomer is more stable because there is no cluttering in the molecule as there would be if the methyl group and sulfonic acid group were next door to each other.

Side chain oxidation in alkylbenzenes

An alkylbenzene is simply a benzene ring with an alkyl group attached to it. Methylbenzene is the simplest alkylbenzene. Alkyl groups are usually fairly resistant to oxidation. However, when they are attached to a benzene ring, they are easily oxidised by an alkaline solution of potassium manganate(VII) (potassium permanganate).

Methylbenzene is heated under reflux with a solution of potassium manganate(VII) made alkaline with sodium carbonate. The purple colour of the potassium manganate(VII) is eventually replaced by a dark brown precipitate of manganese(IV) oxide. The mixture is finally acidified with dilute sulfuric acid.

Overall, the methylbenzene is oxidised to benzoic acid.
Interestingly, any alkyl group is oxidised back to a -COOH group on the ring under these conditions. So, for example, propylbenzene is also oxidised to benzoic acid.

Contributors

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