AQA Chemistry A-level

3.3.10: Aromatic Chemistry

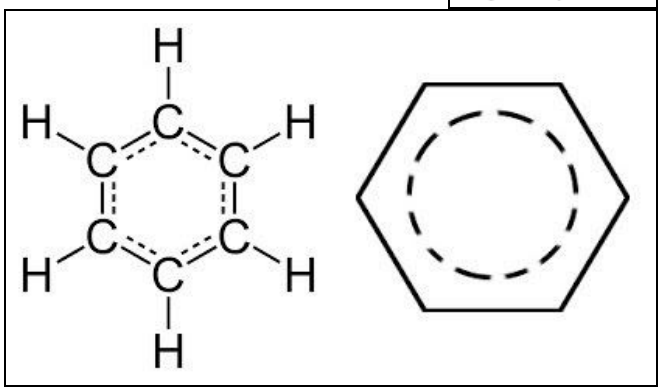
Detailed Notes

3.3.10.1 - Bonding

Benzene is an **aromatic compound** consisting of a ring of **six carbon atoms** with **six hydrogen atoms** and a ring of **delocalised electrons**:

Example:

Image courtesy of Quora



Each bond in the benzene ring has an **intermediate length** in between that of a double and single bond.

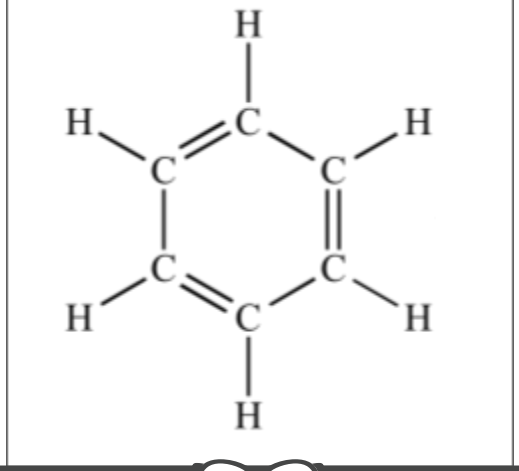
The outer electron from the **p-orbital** of each carbon atom is **delocalised** to form the central ring. This ring structure makes benzene **very stable** compared to other molecules of a similar size.

Cyclohexatriene vs. Benzene

When benzene was first discovered its structure was not known. It was predicted from empirical measurements that it had a structure similar to that of **cyclohexatriene**, with three double bonds and three single bonds.

Example:

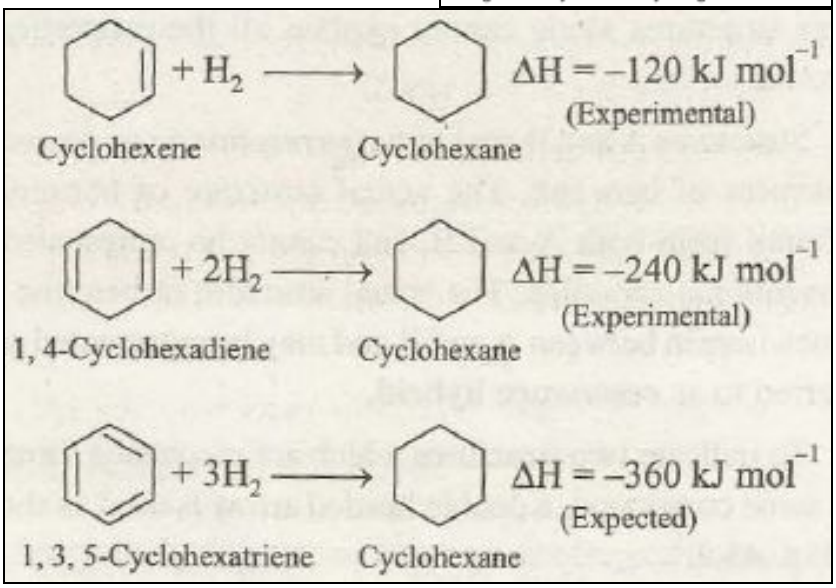
Image courtesy of www.chem.ucla.edu



Therefore the enthalpy change of hydrogenation for benzene was **predicted to be -360kJmol^{-1}**, three times the enthalpy change of cyclohexene.

Example:

Image courtesy of chemistry-assignment.com



It was later discovered that the enthalpy change of hydrogenation of benzene was **actually -208kJmol^{-1}** leading to the conclusion of its **different, unusual structure**.

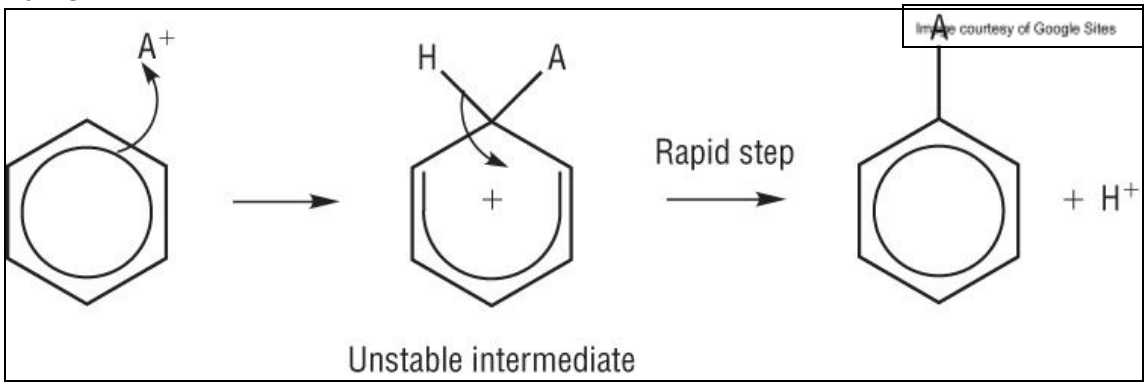
Arenes

Compounds that **contain benzene as part of their structure** are called arenes or aromatic compounds. They have **high melting points** due to the high stability of the delocalised ring, but **low boiling points** as they are **non-polar** molecules and **often cannot be dissolved** in water.

3.3.10.2 - Electrophilic Substitution

The delocalised ring in benzene is an **area of high electron density** making it susceptible to attack from **electrophiles**. When these species attack the electron ring, it is **partially destroyed** then **restored** in the process of **electrophilic substitution**. This mechanism means aromatic amines and nitrobenzene can be produced from benzene.

Mechanism



The electrophile is shown as A^+.

Nitrobenzene

In this form of electrophilic addition, the electrophile is the **NO_2^+ ion**. This is a **reactive intermediate**, produced in the reaction of concentrated sulfuric acid (H_2SO_4) with concentrated nitric acid (HNO_3).

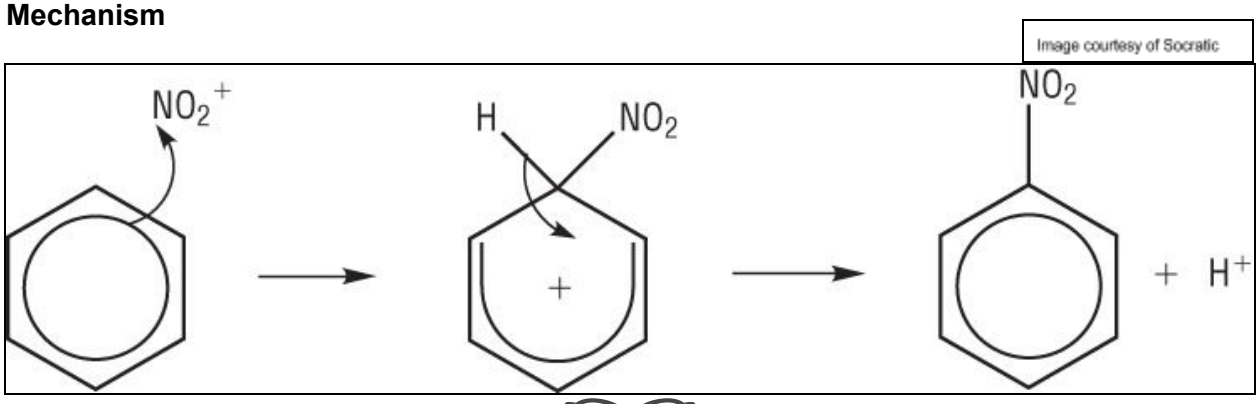
Example:

$$H_2SO_4 + HNO_3 \longrightarrow H_2NO_3^+ + HSO_4^-$$

$$H_2NO_3^+ \longrightarrow H_2O + NO_2^+$$

When heated with benzene these reagents lead to the **substitution of the NO_2^+ electrophile** onto the benzene ring, **removing a hydrogen** ion.

Mechanism



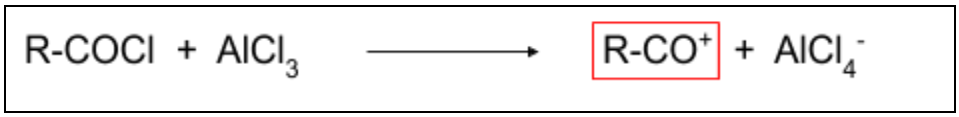
This reaction shows a **mono-substitution** of a single NO_2^+ electrophile which takes place when the reaction temperature is **55°C**. At temperatures greater than this, multiple substitutions can occur. It is vital that only one substitution occurs for the production of **aromatic amines**.

Friedel-Crafts Acylation

The delocalised electron ring in benzene can also act as a **nucleophile**, leading to the **attack on acyl chlorides**. This reaction is known as **Friedel-Crafts acylation**.

In order for it to take place, a **reactive intermediate** must be produced from the acyl chloride and an **aluminium chloride catalyst**.

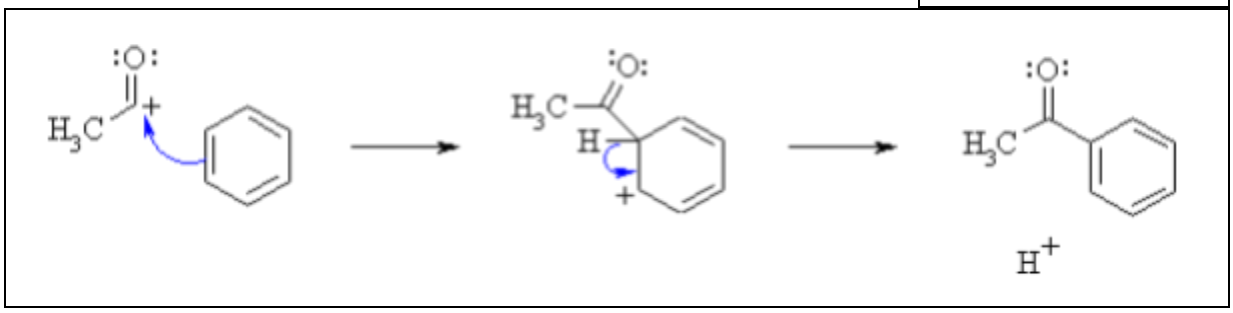
Example:



This reactive intermediate is then attacked by the benzene ring.

Mechanism

Image courtesy of the University of Calgary



At the end of the reaction, the **H^+ ion** removed from the ring reacts with the **$AlCl_4^-$ ion** to reform the aluminium chloride, showing it to be a **catalyst**.

The product of this reaction is a **phenylketone**. In this case, the benzene group is called a **phenyl group**. These molecules are commonly used in the industrial production of dyes, pharmaceuticals and even explosives.