

WJEC Chemistry A-level

4.2: Aromaticity

Detailed Notes

Welsh Specification

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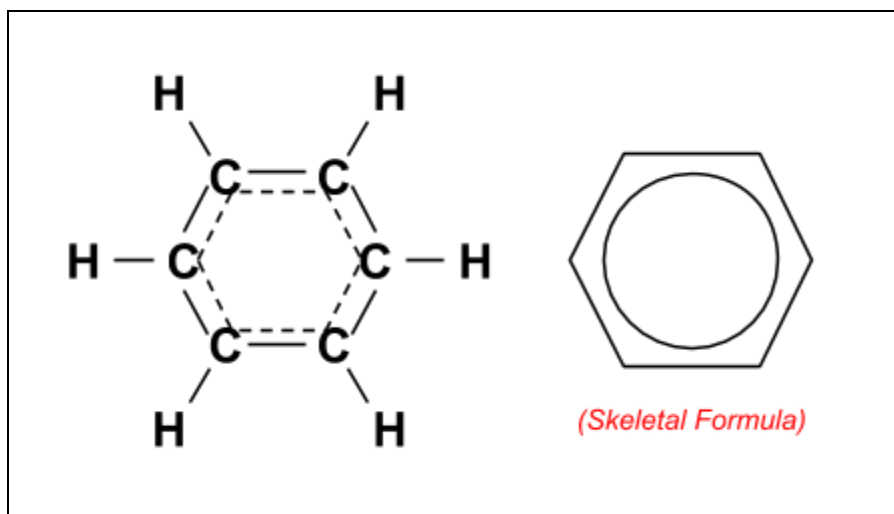
Aromatic Bonding

The structure and bonding of aromatic compounds is pretty unique due to the behaviour of **delocalised electrons** within the compound.

Benzene

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

Example:



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

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

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 solubility** as they are **nonpolar** molecules, meaning they generally cannot be dissolved in water.

This low polarity and high stability also means aromatic compounds **resist addition reactions**, as it would require the stable delocalised ring to be broken. Arenes tend to react via **substitution mechanisms** instead.





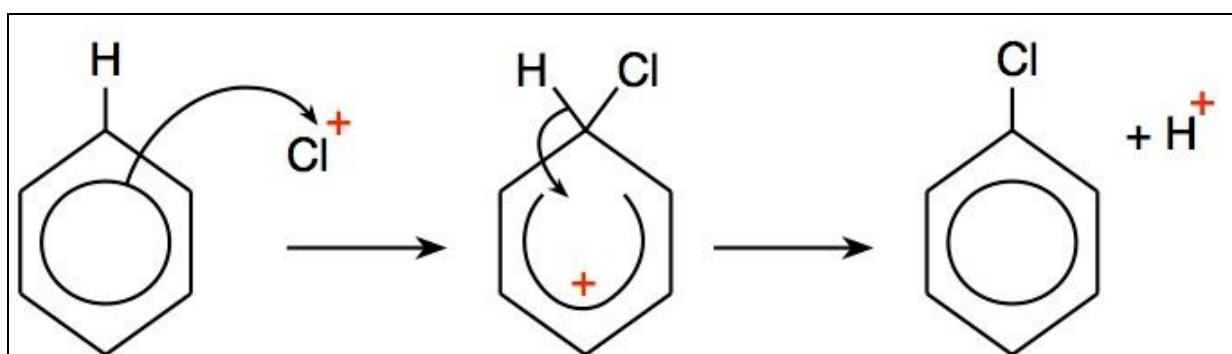
Electrophilic Substitution

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**. It is then restored in the process of **electrophilic substitution**.

Halogenation of Benzene

In this mechanism, an unusual and highly unstable form of halide ion with a **+1 charge** acts as an electrophile, attacking the electron ring. A **halogen carrier catalyst** is used to generate the positively charged halide ion. As a result, a **halobenzene** compound is formed.

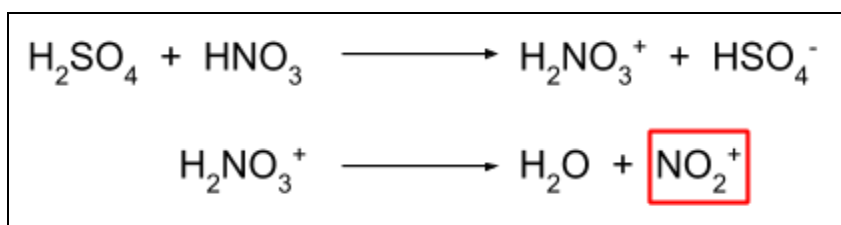
Mechanism



Nitration of Benzene

In this form of electrophilic substitution, the electrophile is the **NO₂⁺ ion**. This is a **reactive intermediate**, produced in the reaction of concentrated **sulfuric acid** (H₂SO₄) with concentrated **nitric acid** (HNO₃).

Example:

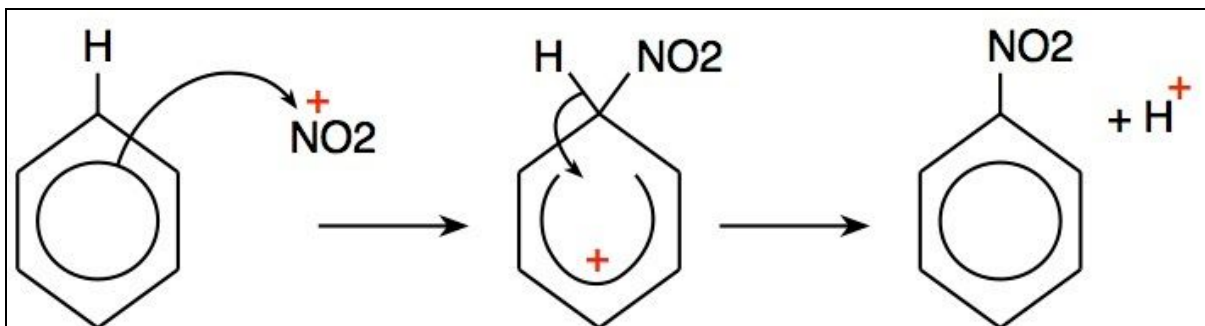


When heated with benzene the combination of these reagents lead to the **substitution of the NO₂⁺ electrophile** onto the benzene ring, releasing a hydrogen ion. This hydrogen ion reacts with the **HSO₄⁻** ion from the first reaction, producing **sulfuric acid**. This shows how sulfuric acid is a **catalyst** for this reaction since it does not get used up.





Mechanism - electrophilic substitution



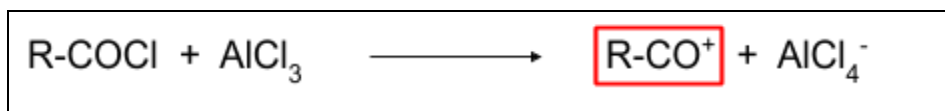
This reaction shows a **mono-substitution**, where a single NO_2^+ **electrophile** is substituted under conditions of 55°C . At temperatures greater than this, **multiple substitutions** can occur. It is vital that only one substitution occurs for the production of aromatic amines.

Friedel-Crafts Alkylation

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

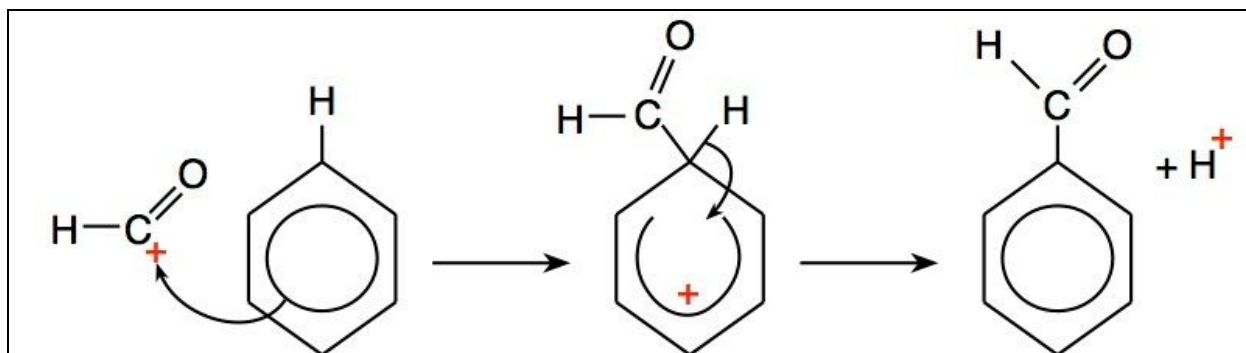
In order for this to occur, a reactive intermediate must be produced from the **acyl chloride** and an **aluminium chloride catalyst**.

Example:



This reactive intermediate is then attacked by the electron dense benzene ring.

Mechanism





At the end of the reaction, the H^+ ion removed from the ring reacts with the AlCl_4^- ion from the formation of the reactive intermediate to **reform aluminium chloride**. This shows how AlCl_3 is a catalyst for the reaction because it reforms at the end of the reaction.

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 explosives.

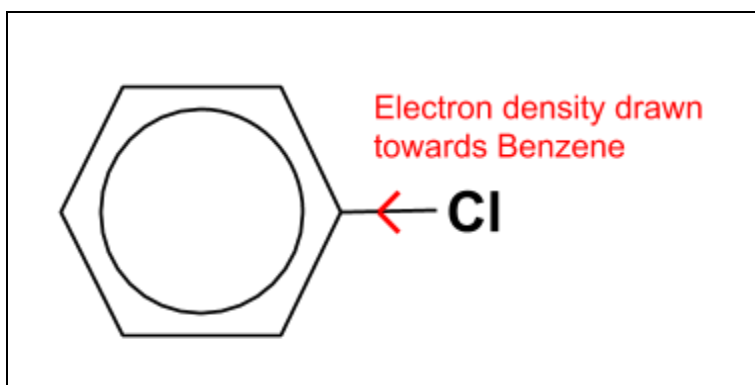
The Negative Inductive Effect

In organic molecules, different functional groups can **affect bond strengths** within the molecule by **changing electron density** around the bond.

Benzene rings draw electron density **towards** themselves, away from any substituent group such as a halogen atom. This is called the **negative inductive effect**.

In particular, in the following example, there is some **overlap** between **p-electrons** on the chlorine and the delocalised **π -system** in the benzene ring. This gives some **π -character** to the bond, which strengthens it.

Example:



As a result, the bond strength between Benzene and the halogen atom is **increased**, making it less likely for a reaction to occur as the molecule is **more stable**.

