

Topic 7 – Arenes

Revision Notes

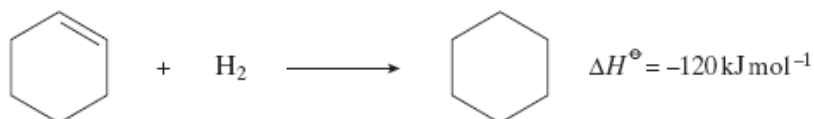
1. Structure of Benzene

a) History

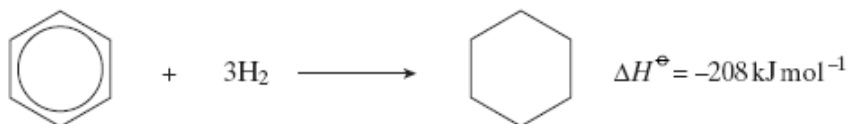
- Molecular formula is C_6H_6
- Structure proposed by Kekulé had ring of carbons with alternating single and double bonds (double bonds are shorter than single bonds)
- There are problems with this structure. Firstly, all of the C-C bond lengths in benzene are the same and are in between the length of a C-C and a C=C. Secondly, if benzene contained double bonds it would undergo addition reactions (like alkenes). However, benzene actually undergoes substitution rather than addition

b) Enthalpies of hydrogenation

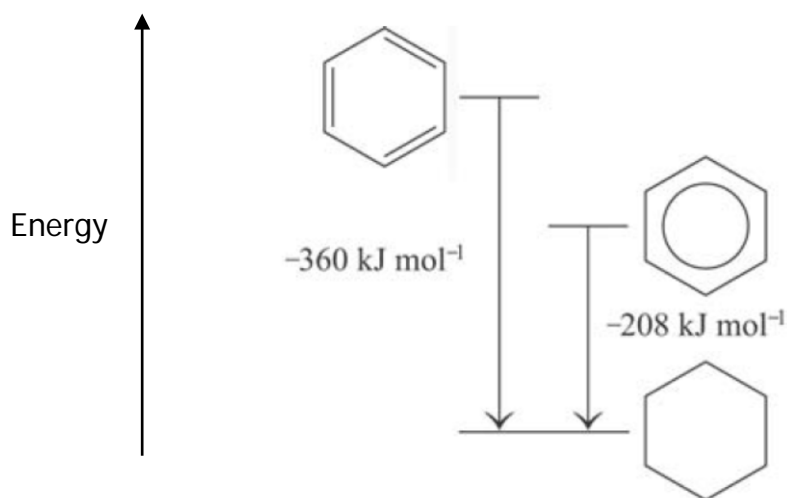
- The enthalpy of hydrogenation of cyclohexene is -120 kJ mol^{-1}



- If benzene had alternating double and single bonds, we would expect its enthalpy of hydrogenation to be $3 \times -120 = -360 \text{ kJ mol}^{-1}$
- However, its actual enthalpy of hydrogenation is only -208 kJ mol^{-1}

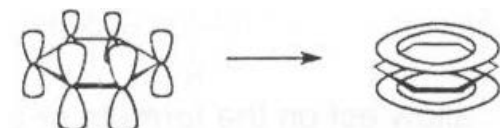


- Benzene is 152 kJ mol^{-1} lower in energy (more stable) than the hypothetical structure containing alternating double and single bonds



c) Delocalisation of electrons

- The accepted structure for benzene is a planar (flat) ring of 6 carbon atoms, each of which is also bonded to an H
- Each carbon has a spare p-orbital. These overlap sideways to form π -bonds (which are rings of delocalised electrons, one above the plane and one below the plane).



- Delocalisation of electrons gives benzene thermodynamic stability. (Stability means lower in energy.)
- Benzene undergoes substitution reactions rather than addition to maintain delocalisation of electrons

2. Reactions of Arenes

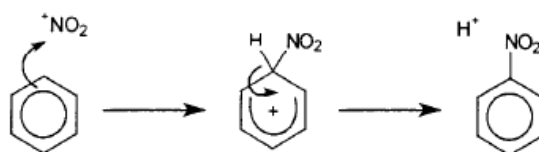
- The high electron density in the π -bonds make benzene attractive to electrophiles (electron pair acceptors).
- The mechanism for the following reactions of benzene is **electrophilic substitution**

a) Nitration

- Equation $\text{C}_6\text{H}_6 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$
- Reagents concentrated HNO_3 and concentrated H_2SO_4 (the nitrating mixture)
- Conditions 60 °C

- Generation of electrophile $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$
- Product is nitrobenzene

- Mechanism:

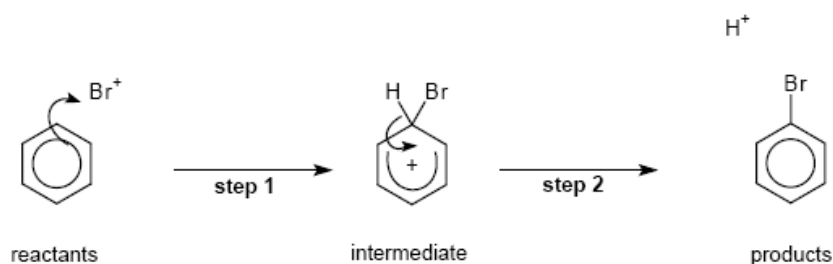


b) Halogenation

- Equation $\text{C}_6\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{HCl}$
- Reagents Cl_2 and halogen carrier (Fe, FeCl_3 or AlCl_3)

- Generation of electrophile $\text{Cl}_2 + \text{AlCl}_3 \rightarrow \text{Cl}^+ + \text{AlCl}_4^-$
- Product is chlorobenzene, halogen carrier acts as a catalyst
- NOTE – It works in exactly the same way for Br_2 with FeBr_3 or AlBr_3

- Mechanism:

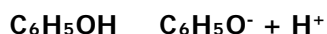


c) Comparison with alkenes

- An alkene has a double bond, which means it reacts readily with electrophiles.
- Benzene is less reactive with electrophiles because its delocalised electrons make it more stable. The delocalised electrons are not easily disrupted so the activation energy for benzene is higher than for an alkene.
- Benzene is, therefore, more resistant to bromination than an alkene such as cyclohexene and benzene needs a catalyst to polarise the halogen.

3. Properties of Phenol

- Phenol is more reactive than benzene
- Phenol is weak acid (proton donor). However, it is a stronger acid than ethanol

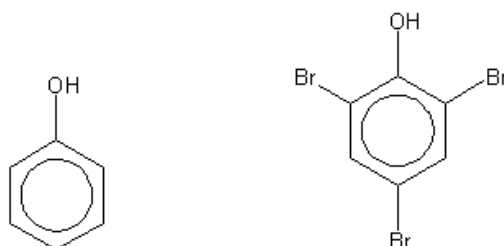
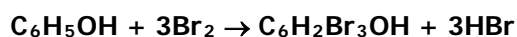


- The phenol functional group has antiseptic properties

4. Reactions of Phenol

a) Bromination

Phenol reacts with bromine to form 2,4,6-tribromophenol and HBr.



Goes from orange to colourless and white precipitate formed

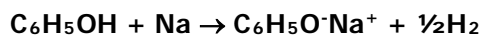
Bromination of phenol is easier than bromination of benzene:

- The OH activates the benzene ring
- The electron-pair from an oxygen p-orbital is donated to the benzene ring
- There is more electron density on the ring
- This attracts electrophiles more

Compared with benzene, phenol does not need a catalyst to react with bromine
Phenol also tri-substitutes whereas benzene mono-substitutes

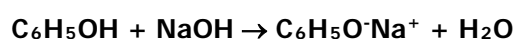
b) With sodium

Phenol reacts with sodium to form sodium phenoxide and hydrogen (effervescence seen)



c) With aqueous alkalis

Phenol reacts with sodium hydroxide to form sodium phenoxide and water .this is a neutralisation reaction

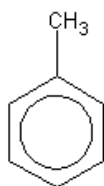


d) Uses of phenols

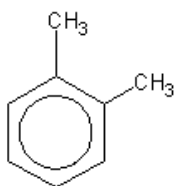
Phenols are used in the production of antiseptics (like TCP, trichlorophenol), disinfectants, plastics and resins for paints

5. Naming Arenes

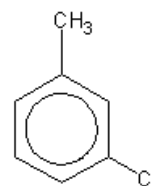
On a ring, the first substituent determines which carbon is numbered 1.



Methylbenzene



1,2-dimethylbenzene



3-chloromethylbenzene