Topic 4 – Aromatic Chemistry
Revision Notes

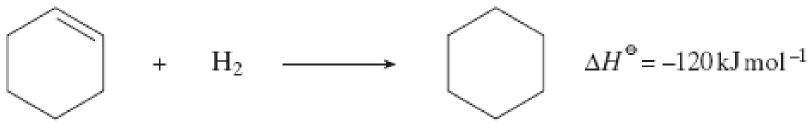
1. Structure of Benzene

a) History

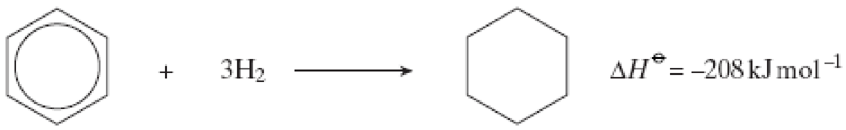
- Molecular formula is C_6H_6
- Structure proposed by Kekulé had ring of carbons with alternating single and double bonds (double bonds are shorter than single bonds)
- There are problems with this structure. Firstly, all of the C-C bond lengths in benzene are the same and are in between the length of 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}



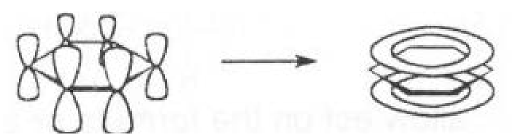
- If benzene had alternating double and single bonds, we would expect its enthalpy of hydrogenation to be 3 x -120 = -360 kJ mol^{-1}
- However, its actual enthalpy of hydrogenation is only -208 kJ mol^{-1}



- Benzene is 152 kJ mol^{-1} lower in energy 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

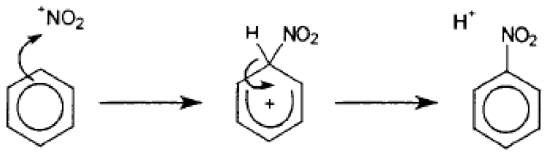
2. Reactions of benzene

- 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 $\quad$ **$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$**
- Reagents $\quad$ concentrated HNO_3 and concentrated H_2SO_4 (the nitrating mixture)
- Conditions $\quad$ 60 C

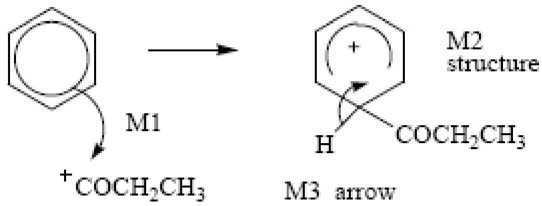
- Generation of electrophile: $\quad HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$
- The electrophile is NO_2^+ which is called the nitronium ion
- Product is nitrobenzene
- Mechanism:



- Aromatic nitro compounds can be used as explosives e.g. TNT, trinitrotoluene
- The nitro group (NO_2) is reduced to NH_2 in the synthesis of dyes

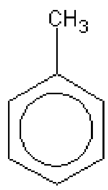
b) Friedel-Crafts Acylation

- Equation $\quad$ **$C_6H_6 + CH_3CH_2COCl \rightarrow C_6H_5COCH_2CH_3 + HCl$**
- Reagents $\quad CH_3CH_2COCl$ (propanoyl chloride) and $AlCl_3$
- Generation of electrophile $\quad CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2CO^+ + AlCl_4^-$
- Product is phenylpropanone
- Regeneration of catalyst $\quad H^+ + AlCl_4^- \rightarrow HCl + AlCl_3$

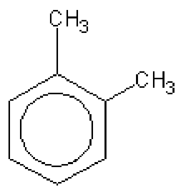


3. Naming Arenes

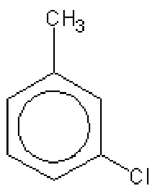
On a ring, the first substituent determines which carbon is numbered 1.



Methylbenzene



1,2-dimethylbenzene



3-chloromethylbenzene