CHAPTER 26: Benzene and Its Compounds

26.1 Introduction to Aromatic Compounds
26.2 Reactions of Benzene and Alkylbenzene
26.3 Introduction to Phenols
26.4 Reactions of Phenols

Learning outcomes:

(a) describe the chemistry of arenes as exemplified by the following reactions of benzene and methylbenzene:
   (i) substitution reactions with chlorine and with bromine.
   (ii) nitration.
   (iii) complete oxidation of the side-chain to give a benzoic acid.
   (iv) hydrogenation of the benzene ring to form a cyclohexane ring
(b) (i) describe the mechanism of electrophilic substitution in arenes, as exemplified by the formation of nitrobenzene and bromobenzene.
   (ii) suggest the mechanism of other electrophilic substitution reactions, given data.
   (iii) describe the effect of the delocalisation of electrons in arenes in such reactions.
(c) predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions.
(d) apply the knowledge of positions of substitution in the electrophilic substitution of arenes.
(e) recall the chemistry of phenol, as exemplified by the following reactions:
   (i) with bases.
   (ii) with sodium.
   (iii) with diazonium salts.
   (iv) nitration of, and bromination of, the aromatic ring
(f) describe and explain the relative acidities of water, phenol and ethanol.
(g) deduce the presence of a CH₂CH(OH)⁻ group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane.
(h) describe the reaction of CH₃CO⁻ compounds with alkaline aqueous iodine to give tri-iodomethane.
26.1 Introduction to Aromatic Compounds

Aliphatic and aromatic compounds

1) i. *Aliphatic compounds* are organic compounds that have carbon atoms joined together in straight chains, branched chains or non-aromatic rings.
ii. *Aromatic compounds* are organic compounds that contain one or more benzene ring (in A-level). Examples of aromatic compounds:

![Nitrobenzene](image)

The structure of benzene

1) Benzene is a **hexagonal and planar molecule** with the formula C₆H₆.

2) In benzene, each carbon atom undergoes *sp² hybridisation* to give three hybrid orbitals and an unchanged p orbital which is perpendicular to the plane containing the three hybrid orbitals.

3) Two of the hybrid orbitals overlap with two other hybrid orbitals of carbon atoms and the other overlaps with the orbital of hydrogen. The unchanged p orbitals overlap with one another *via a system of π bond* to give a **giant molecular orbital**. This orbital is above and below the plane containing the carbon atoms.

4) The six electrons from each p orbital are then **delocalised** around the ring. A delocalised electron does not belong to any carbon atom. This delocalisation of electrons gives benzene a **relatively stable structure**.
5) In a benzene molecule, **all the C-C bonds are identical**, with a bond length of 140 pm. This bond length is longer than a double bond but shorter than a single bond. The bond angle between carbon atoms is **120°**.

6) The stability of benzene is shown in its reluctance to undergo addition reactions. This is because when electrons are added, **the delocalisation will be broken and so does the stability**.

7) There are two common symbols for benzene, the right one is generally preferred over the left one because it indicates that the electrons are delocalised.

8) Before this modern structure was discovered, the Kekulé structure (right) was used. However, the Kekulé structure could not account for the unexplained properties of benzene.
   i. The structure has three double bonds, so **it should undergo addition reactions** like other alkenes do. However for real benzene, it does not undergo addition reactions easily.
   ii. Single and double bonds have different bond length, therefore Kekulé's benzene **should have a distorted hexagonal shape**. However in real benzene, all the C-C bonds are identical and it is a perfect hexagon.

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**Introduction to arenes**

1) Arenes are aromatic hydrocarbons, that is, hydrocarbon that contains at least one benzene ring.

2) Arenes have **higher melting and boiling points than aliphatic hydrocarbons**.
   i. This is because in aromatic hydrocarbons, **temporary dipoles can be easily set up** between the delocalised electrons. Hence the van der Waals'
forces are stronger.
ii. Benzenes with side chains also have permanent dipole forces between them. This is because the presence of side chains makes them a polar molecule.

26.2 Reactions of Benzene and Alkylbenzene

Reactivity of benzene

1) Unlike alkenes, benzene is resistant to addition reactions. This is because it involves breaking the delocalised electron system and thus losing its stability.

2) Instead, benzene undergoes substitution reactions. This involves replacing one or more hydrogen atoms with another group of atoms.

3) Benzene is particularly attractive to electrophiles due to its high electron density. Therefore benzene mainly undergoes electrophilic substitution.

4) The reactivity of benzene is also affected by the presence of other group(s) in the benzene ring. This is known as substituent group effect, and it will be explained later.

Electrophilic substitution

1) Electrophilic substitution is the replacement of an atom or a group of atom by an electrophile. In benzene, the electrophile replaces the hydrogen atom(s).

2) The general mechanism of electrophilic substitution:
   i. Suppose, an electrophile X⁺ is generated from a compound XY. The electrophile is attracted to the electron-rich region of the benzene ring.
   ii. Two electrons from the delocalised electron system are used to form a co-ordinate bond with the electrophile.
   iii. An intermediate with the delocalised electron system partially broken is formed.
iv. Y⁻ ion, from XY has a lone pair of electrons on it and it forms a bond with the hydrogen ion. The hydrogen loses its electrons to the delocalised electron system to bond with Y. The delocalised electron system is now restored.

3) Summary of reactions that benzene and alkylbenzene undergoes:
   i. Halogenation (addition of halogen) into the ring and side chain.
   ii. Nitration (addition of nitro group, NO₂).
   iii. Oxidation of side chain.
   iv. Hydrogenation.

Reaction of benzene - halogenation

1) Reagent : Chlorine/bromine gas, Cl₂/Br₂
   Condition : Aluminium chloride, AlCl₃ or iron(III) chloride, FeCl₃
   Product : Halobenzene

2) Benzene reacts with chlorine/bromine in the presence of halogen carriers such as aluminium chloride, AlCl₃ to form chloro- or bromobenzene, respectively. One hydrogen atom in the benzene ring is substituted by the halogen.

3) Use chlorine as an example of halogen:
   \[ C₆H₆ + Cl₂ \rightarrow C₆H₅Cl + HCl \]

4) The mechanism of this reaction - electrophilic substitution.
   i. Aluminium chloride polarises the Cl-Cl bond to create the electrophile Cl⁺.
      \[ Cl₂ + AlCl₃ \rightarrow Cl⁺ + AlCl₄⁻ \]
   ii. The electrophile is attracted to the benzene, it then bonds with the benzene using two electrons from the delocalised electron system. Note that the delocalised electron system is partially broken in the intermediate.
iii. A hydrogen ion is expelled from the ring by AlCl₃⁻ and leaving its electrons in the ring. The delocalised electron system is now restored. Steamy fumes of hydrogen chloride is also observed.

![Diagram](image)

**Reaction of benzene - nitration**

1) **Reagent**: Concentrated nitric acid, HNO₃  
   **Condition**: Reflux at a temperature lower than 50 °C and the presence of concentrated sulfuric acid, H₂SO₄ as catalyst  
   **Product**: Nitrobenzene

2) Nitration happens when one or more hydrogen atoms in benzene is replaced by a nitro group, NO₂.

3) Benzene reacts with nitric acid in the presence of concentrated sulfuric acid to give nitrobenzene.

   \[ C₆H₆ + HNO₃ \rightarrow C₆H₅NO₂ + H₂O \]

4) The mechanism of this reaction - electrophilic substitution.  
   i. The electrophile, nitronium ion, NO₂⁺ is formed by the reaction of nitric acid and sulfuric acid.

   \[ HNO₃ + 2H₂SO₄ \rightarrow NO₂⁺ + 2HSO₄⁻ + H₃O⁺ \]

   ii. As before, the electrophile is attracted to the benzene ring and forms a bond with it. The delocalised electron system is partially broken.

   ![Diagram](image)

   iii. Hydrogen ion is expelled and it bonds with HSO₄⁻ to regenerate the catalyst. The delocalised electron system is restored.
5) If the temperature exceeds 50 °C, 1,3-dinitrobenzene will be formed as well. Notice that the second nitro group is added to the 3 position of the ring.

\[
\text{Ph} + \text{HNO}_3 \rightarrow \text{Ph} - \text{NO}_2 + \text{H}_2\text{O}
\]

Substituent group effect

1) If a benzene already has a first substituent in it, second incoming substituent is affected by the nature of the first substituent.

2) The first substituent has an effect on:  
   i. **the position of the incoming second substituent.**  
      - If X is an **electron-withdrawing group**, it deactivates the ring and it is **3-directing**.
      - Examples are -NO₂, -CN, -COOH, -CHO and -COR.
      - If X is an **electron-donating group**, it activates the ring and it is **2,4-directing**.
      - Examples are -OH, -NH₂, -C₆H₅ and alkyl groups.
      - **The only exception are halogens**, they are electron-withdrawing but they are 2,4-directing.
   
   ii. **the rate at which the second substituent is introduced.**  
      - If X is an **electron-withdrawing group**, it deactivates the ring and the **rate of reaction decreases**
      - If X is an **electron-donating group**, it activates the ring and the **rate of reaction increases**.

Reaction of alkylbenzene - halogenation

1) **Reagent** : Chlorine/bromine gas, Cl₂/Br₂  
   **Condition** : Into the ring - Aluminium chloride, AlCl₃ or iron(III) chloride, FeCl₃ as catalyst, **absence of UV light**
   
   Into the alkyl group - Absence of catalyst but **presence of UV light**

   **Product** : Halo-alkylbenzene

2) In the **presence of halogen carriers and the absence of UV light** at room temperature, the halogen is substituted **into the ring** via electrophilic substitution.
3) Take methylbenzene as an example, since methyl group is electron-donating and 2,4-directing, the incoming halogen is substituted at the 2 or 4 position. 2-chloro and 4-chloromethylbenzene are produced.

\[
C_6H_5CH_3 + Cl_2 \rightarrow C_6H_5ClCH_3 + HCl
\]

4) In the presence of UV light and the absence of halogen carriers, the halogen is substituted into the alkyl group via free-radical substitution. Take methylbenzene as an example, (chloromethyl)benzene is produced.

\[
C_6H_5CH_3 + Cl_2 \rightarrow C_6H_5(CH_2Cl) + HCl
\]

5) Further substitutions are possible, producing (dichloromethyl)benzene and (trichloromethyl)benzene.

Reaction of alkylbenzene - nitration

1) Reagent : Concentrated nitric acid, HNO₃  
Condition : Reflux at a temperature lower than 30 °C and the presence of concentrated sulfuric acid, H₂SO₄ as catalyst  
Product : Nitro-alkylbenzene

2) Since methyl group activates the ring, making the ring more reactive, the temperature has to be lowered to 30 °C to prevent multiple substitutions.
3) Methyl group is an electron-donating group, it activates the ring and is 2,4-directing, therefore the nitro group is substituted at the 2 or 4 positions.

4) Take methylbenzene as an example, 2-nitro and 4-nitromethylbenzene is produced.

\[
\begin{align*}
\text{CH}_3 \text{C} &+ \text{HNO}_3 \rightarrow \text{CH}_3\text{NO}_2 \ + \text{H}_2\text{O} \\
\text{CH}_3 \text{C} &+ \text{HNO}_3 \rightarrow \text{NO}_2 \ + \text{H}_2\text{O}
\end{align*}
\]

5) If the temperature exceeds 30 °C, multiple substitutions by nitro groups is possible. However, each time a nitro group substitutes, the rate of reaction of the next substitution decreases because nitro group is electron-withdrawing. Therefore, 2,4,6-trinitromethylbenzene is rare.

Reaction of alkylbenzene - oxidation

1) **Reagent** : Acidified potassium manganate(VII), KMnO₄  
   **Condition** : Heat or reflux  
   **Product** : Benzoic acid

2) When methylbenzene is heated under reflux with acidified potassium manganate(VII), **side-chain oxidation occurs**. Benzoic acid is produced.

\[
\begin{align*}
\text{CH}_3 \text{C} &+ 3\text{[O]} \underset{\text{reflux}}{\xrightarrow{\text{MnO}_7/\text{H}^+}} \text{CO}_2\text{H} \ + \text{H}_2\text{O} \\
\text{benzoic acid}
\end{align*}
\]

3) **Any carbon side-chain group is oxidised to -COOH group** under these conditions.
Reaction of alkylbenzene - hydrogenation

1) **Reagent** : Hydrogen gas, H₂  
   **Condition** : Heat in the presence of nickel, Ni catalyst at 150 °C  
   **Product** : Cyclohexanes

2) In hydrogenation, hydrogen atoms are added to the benzene ring. **The delocalised electron system is permanently broken.**

3) With benzene:

   ![Benzene reaction diagram]

4) With methylbenzene:

   ![Methylbenzene reaction diagram]

26.3 **Introduction to Phenols**

**What are phenols?**

1) Phenols are benzene compounds which have an -OH group attached directly to it.

2) In a phenol molecule, **one of the lone pairs on the oxygen overlaps with the delocalised electron system** to give a structure like this:  

   ![Phenol structure diagram]