Organic Chemistry – Arenes and Phenols

Arenes - Structure of benzene
The term arene includes all compounds with a delocalised π-system: these are also called aromatic compounds. e.g. benzene, C₆H₆.

Kekulé suggested the following structure for this compound.

\[
\begin{align*}
\text{H} & \quad \text{C} \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{H} & \quad \text{C} \quad \text{C} \quad \text{H}
\end{align*}
\]

X-ray diffraction studies provide information about bond lengths.
Bond lengths  
C-C in cyclohexane 0.154 nm  
C=C in cyclohexene 0.133 nm

This would give benzene a distorted hexagon. However, X-ray diffraction studies show that the C-C bond lengths in benzene are all 0.139 nm. This means that the Kekule structure is incorrect.

The benzene ring is a flat, regular hexagon, with six electrons in the delocalised π-“sandwich” above and below the ring.
The σ-bonds are built up in a similar way to ethene, leaving an unused 2p orbital on each of the six carbons. These can overlap sideways in both directions, resulting in a delocalised π-electron cloud, containing six π-electrons and stretching over all six atoms, in a "sandwich" which lies above and below the plane of the ring:

Thus the C–C bonds in benzene are all equal, each of length between a single and a double bond.

The delocalised structure is much more stable (lower in enthalpy content) than one with three double bonds - probably by more than 150 kJ/mol⁻¹ and so benzene is much less reactive than ethene, since reaction involves loss of at least part of this extra stabilisation. Ethene also has two π-electrons between the C atoms, while benzene has only one.

Thermochemical evidence
Evidence for this extra stable structure for benzene is provided by thermochemical evidence.

In the presence of a nickel catalyst hydrogen can be added to a double bond. When this is carried out with cyclohexene the following reaction takes place.

\[
\text{C}_6\text{H}_{10} + \text{H}_2 \rightarrow \text{C}_6\text{H}_{12} \quad \Delta H = -120 \text{ kJmol}^{-1}
\]

This would suggest that a similar reaction using benzene would give us the following reaction

\[
\text{C}_6\text{H}_6 + 3\text{H}_2 \rightarrow \text{C}_6\text{H}_{12} \quad \Delta H = -360 \text{ kJmol}^{-1}
\]

The measured value for the hydrogenation of benzene is actually -208 kJmol⁻¹.
This indicates that benzene is more stable than would be expected from a structure with three C=C.

Spectroscopic evidence
The infra-red spectrum of a compound containing a double bond shows an absorption between 1610 and 1680 cm⁻¹. This absorption however is absent in benzene compounds.

Reactions of Benzene
Benzene requires much more forcing conditions to make it react than does ethene:
- benzene does not decolorise bromine water.
- benzene will not react with hydrogen at an appreciable rate under conditions at which ethene reacts (e.g. 150°C and normal pressures, over a nickel catalyst).
- benzene will not react with oxidising agents like alkaline KMnO₄.

Reactions of Arenes
The main reactions which benzene does undergo are with electrophiles, but since it has a lower electron density between carbon atoms than ethene, benzene requires stronger electrophiles and more forcing conditions.
Once an electrophile has added on to the ring, the subsequent step is likely to be loss of a proton, leading to electrophilic substitution rather than addition, since the stable delocalised π-system is regained.

Combustion
Arenes have the equivalent of three double bonds per molecule and so tends to produce incomplete combustion, so when it burns it produces a smoky flame.

Nitration of Arenes
Arenes can be nitrated if they are mixed with conc nitric and sulphuric acids at temps below 50°C.

\[
\text{C}_6\text{H}_6 (l) + \text{HNO}_3 (l) \rightarrow \text{C}_6\text{H}_5\text{NO}_2 (l) + \text{H}_2\text{O} (l)
\]

Nitrobenzene

The sulphuric acid protonates the nitric acid, which ionises, forming the nitronium ion, NO₂⁺.

\[
\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-
\]

If the temperature is raised above 50°C there is a chance of multiple nitrations occurring.
**Bromination of Arenes**

Arenes will react with halogens in the presence of a halogen carrier catalyst, Fe, FeBr₃, Al or AlCl₃.

\[
C₆H₆(l) + Br₂(l) \rightarrow C₆H₅Br(l) + HBr
\]

\[\text{Br} + \text{HBr}\]

**Sulphonation of Arenes**

Arenes will react with concentrated (fuming) sulphuric acid to form sulphonic acids. The reaction is carried out at room temperature.

\[
C₆H₆ + H₂SO₄ \rightarrow C₆H₅SO₃H + H₂O
\]

Sulphonic acid groups are often used in organic synthesis to increase the water solubility of large organic drug molecules.

**Feidel-Craft Alkylation**

**Alkylation:** Reaction with a halogenoalkane in the presence of the catalyst AlCl₃.

\[
C₆H₆(l) + CH₃Cl → C₆H₅CH₃(l) + HCl
\]

This is an important reaction in organic synthesis as it is a C-C bond forming reaction.

**Feidel-Craft Acylation**

**Acylation:** Reaction with an acyl chloride in the presence of the catalyst AlCl₃. Conditions: Anhydrous AlCl₃ as a catalyst.

\[
C₆H₆(l) + CH₃COCI(l) \rightarrow C₆H₅COCH₃(l) + HCl(g)
\]

This is an important reaction in organic synthesis as it is a C-C bond forming reaction.
**Addition reaction with hydrogen**

This reaction is unlike all those above in that whereas most reactions of benzene are substitution this is an **addition process**. In the presence of a nickel catalyst hydrogen can add on to a benzene ring across the double bonds.

This reaction requires Raney nickel, which is a particularly finely divided form of the metal, and the temperature of 200°C is higher than that used for addition to an alkene.

The more extreme conditions for this reaction compared with those needed for addition of hydrogen to an alkene because of the extra stability of the delocalized electron ring structure.

\[
\text{+} \quad \text{3H}_2 \quad \overset{\text{Nickel}}{\text{200°C}} \quad \text{+}
\]

**Mechanisms - Electrophilic substitution.**

Arenes commonly undergo **electrophilic substitution** reactions.

In this type of substitution two of the delocalised \(\pi\) electrons on the benzene ring are donated to the electrophile.

An unstable \(\pi\)-complex containing both an electrophile and a leaving group is formed as an intermediate.

**Nitration**

Nitration is carried out under reflux at 55-60°C using a nitrating mixture.

This contains equal amounts of concentrated nitric acid and sulphuric acid.

The sulphuric acid protonates the nitric acid, which ionises, forming the **nitronium ion**, \(\text{NO}_2^+\) (sometimes called the nitryl cation):

\[
\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \iff \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^- 
\]

The nitronium ion is a powerful electrophile, and this pulls out an electron pair from the \(\pi\)--system, adding on to the ring:

\[\text{Note a carbocationic intermediate is formed. This first step, addition of an electrophile, is similar to the attack of bromine on ethene.} \]

However, the positive benzene intermediate can lose much more energy by giving up a proton to a base than it could by adding on a nucleophile.

The loss of a proton (to an \(\text{HSO}_4^-\)) ion restores the full delocalisation energy, and sulphuric acid is reformed, as a catalyst.
**Bromination**
The reaction with bromine also follows the same mechanism.

Aluminium chloride is used as a **halogen carrier catalyst** which helps form the electrophile.

\[
\text{Br-Br} + \text{AlCl}_3 \rightarrow \text{Br}^{d+}---\text{Br}---\text{AlCl}_3^{d-}
\]

The mechanism is then the same as for nitration.

\[
\text{CH}_3-\text{Br} + \text{AlCl}_3 \rightarrow \text{d+CH}_3---\text{Br}---\text{AlCl}_3^{d-}
\]

The delocalised π-system requires a large activation energy to disrupt (hence the need for a catalyst). The positive benzene intermediate once again restores the full delocalisation energy by losing H⁺ (hence substitution rather than addition).

Chlorine reacts in a similar way, giving C₆H₅Cl and HCl, and also needing Al or Fe to be present (forming AlCl₃ or FeCl₃).

**Alkylation**
Alkylation follows the same mechanism.

Halogenoalkanes are weak electrophiles because their polar bond. e.g. CH₃⁺-Br⁻. The catalyst AlCl₃ makes the halogenoalkane a better electrophile.

\[
\text{CH}_3-\text{Br} + \text{AlCl}_3 \rightarrow \text{d+CH}_3---\text{Br}---\text{AlCl}_3^{d-}
\]

**Acylation**
Acylation also follows the same mechanism.

The electrophile is again improved by AlCl₃.

\[
\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{C}^+\text{O} + \text{Cl}^-\text{AlCl}_3^-
\]
Phenols

Phenols are compounds in which the -OH group is directly attached to the benzene ring. Phenol itself is a white crystalline solid which is sparingly soluble in water at room temperature. The benzene ring helps to stabilise a negative charge on the phenoxy ion, C₆H₅O⁻, and this makes phenol appreciably acidic (unlike ethanol, which is neutral, a solution of phenol in water has a pH of about 5).

Reactions of phenol

Phenol with sodium hydroxide
Phenol dissolves in aqueous sodium hydroxide because phenol behaves as an acid and gives up its proton to the hydroxide ion which is a base. A soluble ionic product is formed.

\[
\text{Phenol} + \text{NaOH} \rightarrow \text{Phenoxide ion} + \text{NaOH}
\]

Phenol with bromine - electrophilic substitution.
The hydroxyl group in phenol can donate electrons back to the delocalised π-system, helping to stabilise the intermediates of electrophilic substitution and so making phenol much more reactive than benzene. It will react immediately with bromine water, decolorising it and forming a white precipitate of 2,4,6-tribromophenol.

\[
\text{Phenol} + 3\text{Br}_2 \rightarrow \text{Phenol} \rightarrow \text{Bromophenol}
\]

Nitration of Phenol.
Phenol can be nitrated with dilute nitric acid. This once again shows that the delocalised π-system, makes phenol much more reactive than benzene.

\[
2\text{Phenol} + \text{HNO}_3 \rightarrow \text{2Phenol nitrate}
\]

Uses of phenols
Phenol, in dilute solution, was the first successful antiseptic used by Lister (called carbolic acid). Now substituted phenols are used both as antiseptics (to keep surfaces free of pathogens) and as disinfectants (to kill pathogens already present).