

4.2 – Aromaticity

Original structure of benzene

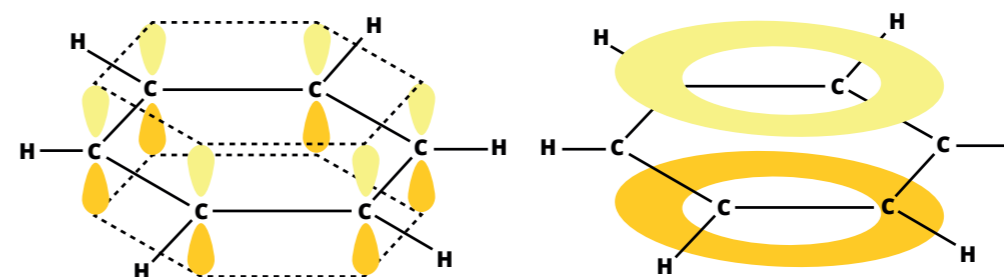
Benzene is a colourless liquid with the molecular formula C_6H_6 .

In 1865, Kekule suggested that it was a six-membered ring, containing alternating single and double bonds. This structure was proved to be incorrect because:

- benzene does not undergo addition reactions (unlike compounds with double bonds)
- each C—C bond length is equal (shorter than a C—C single bond and longer than a C=C double bond)
- the enthalpy of hydrogenation is less than expected. (If it contained three double bonds, it would be $3 \times -120 \text{ kJ mol}^{-1}$, but it is in fact -208 kJ mol^{-1} . This difference of 152 kJ mol^{-1} is called the resonance energy; it is a more stable structure than thought.)

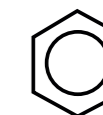
Structure and bonding in benzene

Benzene is a planar molecule, the bond angles between three adjacent carbon atoms being 120° . Each carbon atom is bonded to two other carbon atoms and a hydrogen atom by σ bonds. The fourth outer shell electron is in a 2p orbital, above and below the plane of the carbon ring. These p orbitals overlap, forming π bonds to give a delocalised electron structure above and below the plane of the ring.



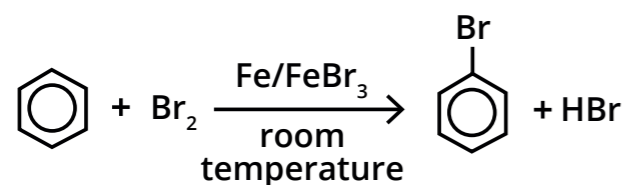
The more the electrons are delocalised, the more stable the compound. The extra stability in benzene is called 'delocalisation' or 'resonance' energy. Unlike alkenes, benzene does not undergo addition reactions. The process would disrupt the stable delocalised π electron system and the resulting product would be less stable.

The hexagon represents all 6 carbon atoms and 6 hydrogen atoms in a benzene molecule. The circle represents the delocalised electrons.

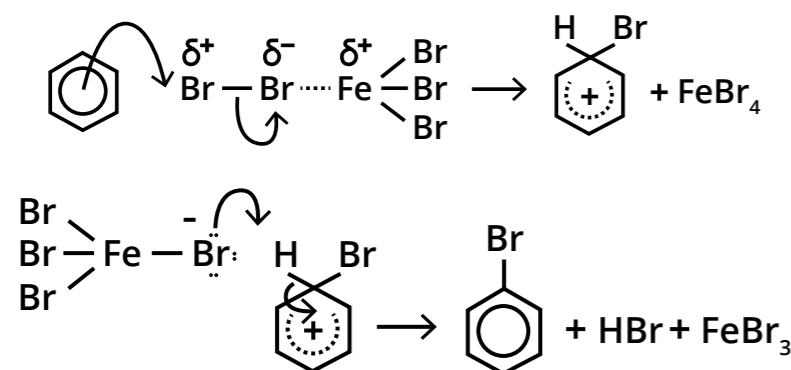


Halogenation

Benzene reacts with bromine in the presence of an iron(III) bromide catalyst. The overall reaction is:



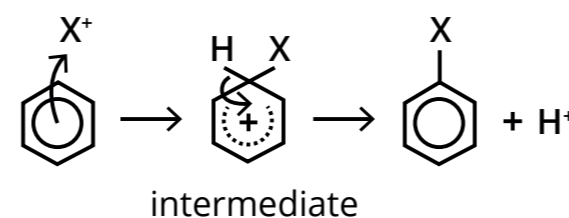
The catalyst is needed to polarise the bromine molecule to give $\text{Br}\delta^+ - \text{Br}\delta^-$. One mechanism for the bromination is:



Chlorination of benzene can be carried out in the same way, using anhydrous aluminium chloride as a catalyst.

Electrophilic substitution

Benzene has a delocalised ring of electrons above and below the plane of the carbon atoms. This area of high electron density makes it susceptible to attack by an electrophile. If a hydrogen atom is replaced by an electrophile, the delocalisation can be maintained. These reactions follow a general pattern.

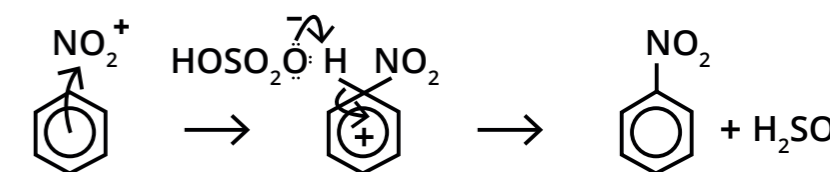


Nitration

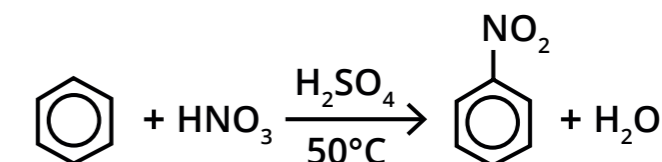
The electrophile is the nitronium ion, NO_2^+ , produced by the reaction between conc. nitric acid and conc. sulfuric acid.



One mechanism for the nitration is:



The overall reaction is:



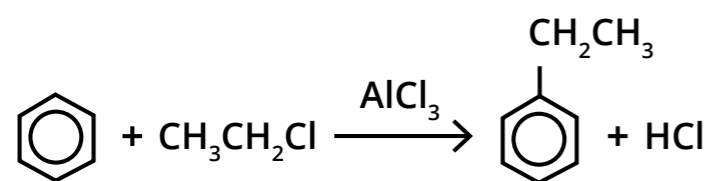
If the temperature exceeds 50°C , then some 1,3-dinitrobenzene is also produced.

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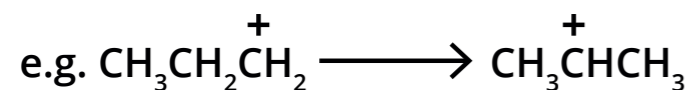
Friedel-Crafts alkylation

The reaction is similar to halogenation but uses a halogenoalkane instead of a halogen, e.g.:

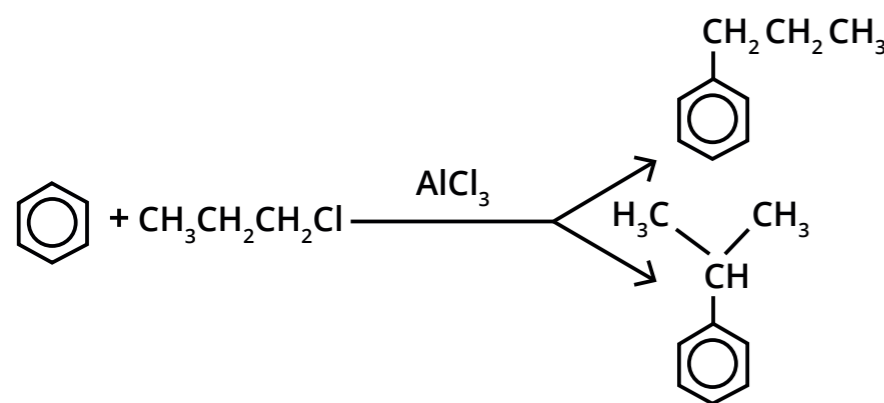
One problem is the further alkylation of the ring, e.g. 1,2- and 1,4-diethylbenzene can also form.



Another problem is that a primary carbocation formed during the reaction may rearrange to a secondary carbocation.



The reaction of benzene with 1-chloropropane gives mainly (1-methylethyl)benzene rather than 1-propylbenzene as the organic product.



Strength of C—Cl bond in chlorobenzene

Chloroalkanes react with aqueous sodium hydroxide in a nucleophilic substitution reaction to give alcohols.

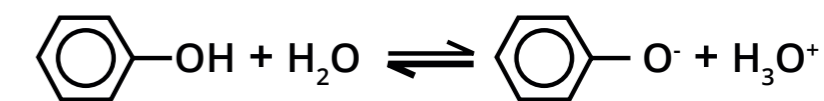


Chlorobenzene does not react with aqueous sodium hydroxide. (Adding HNO_3 followed by AgNO_3 , 1-chlorobutane gives a white precipitate, chlorobenzene gives no reaction.)

It is resistant to nucleophilic substitution because nucleophiles would be repelled by the stable π system of electrons. In chlorobenzene, a non-bonding p electron pair on chlorine overlaps with the ring π -system of electrons. This makes the C—Cl bond stronger than in chloroalkanes and much more energy is needed to break it.

Acidity of phenol

Phenols are more acidic than alcohols as they can lose a hydrogen ion because the phenoxide formed is stabilised.



One of the lone pairs on the oxygen atom overlaps with the delocalised π system on the benzene ring. This overlap leads to a delocalisation which extends from the ring out over the oxygen atom. The negative charge is no longer localised on the oxygen but spread out around the whole ion.

Basicity of phenylamine

Phenylamine is less basic than alkyl amines because the lone pair of electrons on the nitrogen atom interacts with the delocalised electrons in the benzene ring. This reduces the availability of the lone pair on the nitrogen to accept a proton.