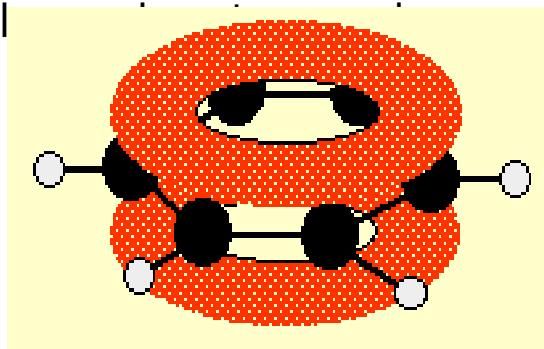# Arenes

Arenes are aromatic hydrocarbons. The term "aromatic" originally referred to their pleasant smells, but now implies a particular sort of delocalised bonding. The arenes are based on benzene rings. The simplest of them is benzene itself, C_6H_6.

●Benzene, C_6H_6, is a planar molecule containing a ring of six carbon atoms each with a hydrogen atom attached.

●The six carbon atoms form a perfectly regular hexagon. All the carbon-carbon bonds have exactly the same lengths - somewhere between single and double bonds.

●There are delocalised electrons above and below the plane of the ring.

●This diagram shows one of the molecular orbitals containing two of the delocalised electrons, which may be found anywhere within the two "doughnuts". The other molecular orbital

Arenes

● The presence of the delocalised electrons makes benzene particularly stable.

● Benzene resists addition reactions because that would involve breaking the delocalisation and losing that stability.

● Benzene is represented by the symbol below, where the circle represents the delocalised electrons, and each corner of the hexagon has a carbon atom with a hydrogen attached.
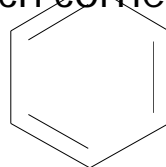
The carbon atoms are bonded by sigma bonds, and the overlap of the p orbitals cause molecular orbitals shaped like doughnuts above and below the ring, one from each carbon. The electrons are delocalised and form pi bonds. This is often known as aromatic stability.
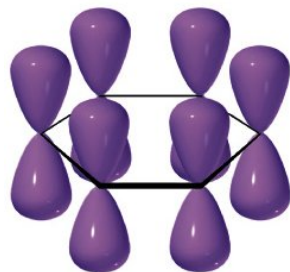
Kekulé structure

Kekulé was the first to suggest a sensible structure for benzene. The carbons are arranged in a hexagon, and he suggested alternating double and single bonds between them. Each carbon atom has a hydrogen attached to it.

Although the Kekulé structure was a good attempt in its time, there are serious problems with it.

Problems with the chemistry

Because of the three double bonds, you might expect benzene to have reactions like ethene such as addition reactions due to the carbon – carbon double bonds being very electron dense and hence susceptible to electrophiles.

Benzene rarely does this. Instead, it usually undergoes substitution reactions in which one of the hydrogen atoms is replaced by something new.
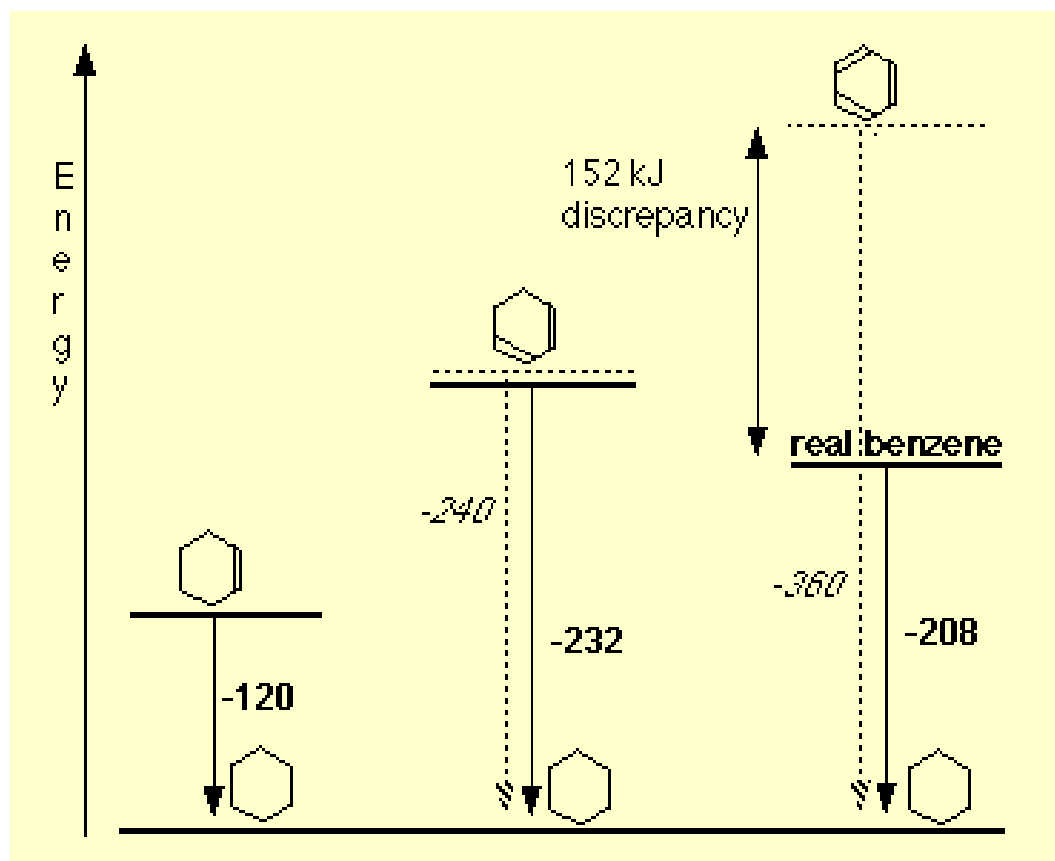
Kekulé structure

Problems with the shape

Benzene is a planar molecule and Kekulé structure also predicts this. But the Kekulé structure would not be a perfect hexagon, instead due to the different sizes of carbon-carbon single and double bonds, the structure would not be a perfect hexagon.

Problems with the stability of benzene

Real benzene is a lot more stable than the Kekulé structure would give it credit for. Every time you do a thermochemistry calculation based on the Kekulé structure, you get an answer which is wrong by about 150 kJ mol-1. This is most easily shown using enthalpy changes of hydrogenation.

Kekulé structure

This means that real benzene is about 150 kJ mol-1 more stable than the Kekulé structure gives it credit for. This increase in stability of benzene is known as the delocalisation energy or resonance energy of benzene. The first term (delocalisation energy) is the more commonly used.

Properties of Arenes

Boiling points

Benzene boils at 80°C - slightly higher than other hydrocarbons of similar molecular size (pentane and hexane, for example). This is presumably due to the ease with which temporary dipoles can be set up involving the delocalised electrons.

Methylbenzene boils at 111°C. It is a bigger molecule and so the van der Waals dispersion forces will be bigger.

Methylbenzene also has a small permanent dipole, so there will be dipole-dipole attractions as well as dispersion forces. The dipole is due to the CH3 group's tendency to "push" electrons away from itself.

Properties of Arenes

Melting Points

You might have expected that methylbenzene's melting point would be higher than benzene's as well, but it isn't - it is much lower! Benzene melts at 5.5°C methylbenzene at -95°C.

Molecules must pack efficiently in the solid if they are to make best use of their intermolecular forces. Benzene is a tidy, symmetrical molecule and packs very efficiently. The methyl group sticking out in methylbenzene tends to disrupt the closeness of the packing. If the molecules aren't as closely packed, the intermolecular forces don't work as well and so the melting point falls.

Properties of Arenes

Solubility in water

The arenes are insoluble in water. Benzene is quite large compared with a water molecule. In order for benzene to dissolve it would have to break lots of existing hydrogen bonds between water molecules. You also have to break the quite strong van der Waals dispersion forces between benzene molecules. Both of these cost energy.

The only new forces between the benzene and the water would be van der Waals dispersion forces. These aren't as strong as hydrogen bonds (or the original dispersion forces in the benzene), and so you wouldn't get much energy released when they form.

It simply isn't energetically profitable for benzene to dissolve in water. It would, of course, be even worse for larger arene molecules.
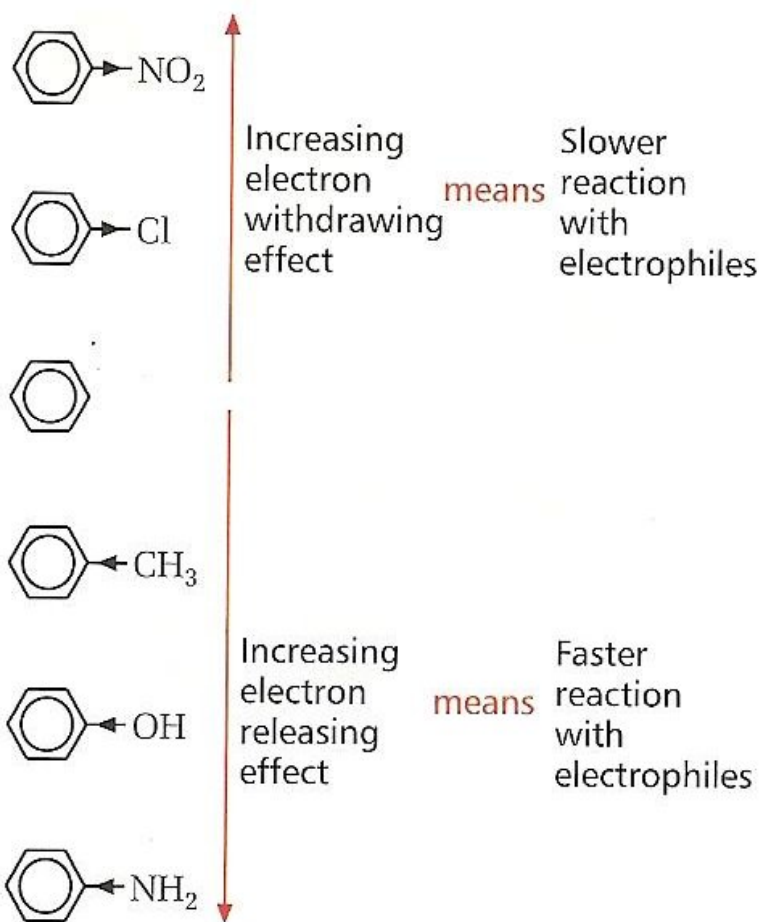
Reactivity of Arenes

Benzene

As was discussed last lesson, benzene does not undergo addition reactions. Adding something new to the ring would need you to use some of the delocalised electrons to form bonds with whatever you are adding. That results in a major loss of stability as the delocalisation is broken.

Instead, benzene mainly undergoes substitution reactions - replacing one or more of the hydrogen atoms by something new. That leaves the delocalised electrons as they were.

Methylbenzene

The tendency of the CH3 group to "push" electrons away from itself also has an effect on the ring, making methylbenzene react more quickly than benzene itself.

Electron Withdrawing Effects

NO$_2$

Increasing electron withdrawing effect **means** Slower reaction with electrophiles

Cl

CH$_3$

Increasing electron releasing effect **means** Faster reaction with electrophiles

OH

NH$_2$

Fig 1.5 *Electron-withdrawing and electron-releasing substituents*

Inductive effects

A substituent attached to an arene can effect its reactivity depending on the properties of the group. An electronegative element or molecule will withdraw electrons from the ring, which will cause electrophilic substitution to be less likely.

On the flip side a substituent with an electronegativty of less than hydrogen will cause electrophilic substitution to

Reaction of Arenes

Combustion

Arenes burn in air with flames that are noticeably smoky. This is due to their high carbon-hydrogen ratio. There is usually unburned carbon remaining when they burn in air and this produces soot. A smoky flame suggests an aromatic compound.

Mechanism of electrophilic substitution reactions

Suppose the electrophile is a positive ion El+.

Two of the electrons in the delocalised system are attracted towards the X+ and form a bond with it. This has the effect of breaking the delocalisation, although not completely. The ion formed in this step isn't the final product. It immediately goes on to react with something else. It is just an intermediate.

There is still delocalisation in the intermediate formed, but it only covers part of the ion. When you write one of these mechanisms, draw the partial delocalisation to take in all the carbon atoms apart from the one that the X has become attached to.
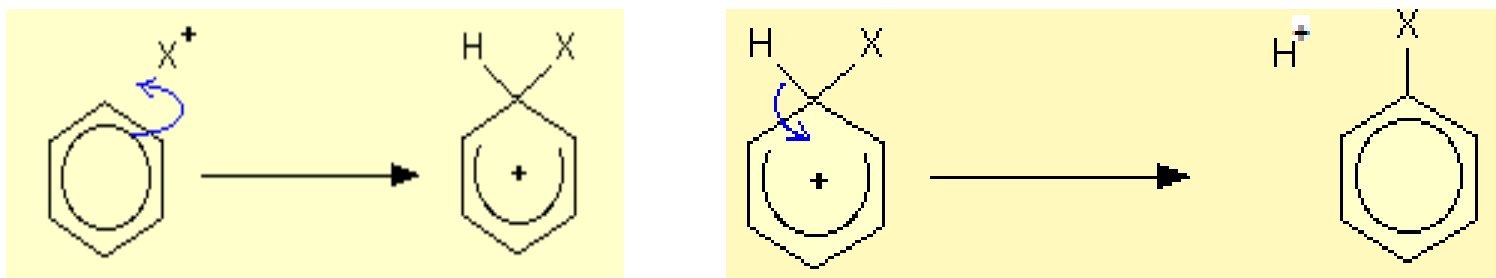
Reaction of Arenes - Halogenation

Halogenation is the substitution of a halogen atom for one of the hydrogen atoms on the aromatic ring. Halogens can act as electrophiles. However they are not strong enough to react on their own, and they therefore need a catalyst.

Suitable catalysts are Iron filings or aluminium halides. The catalysts work by acting as halogen carriers.
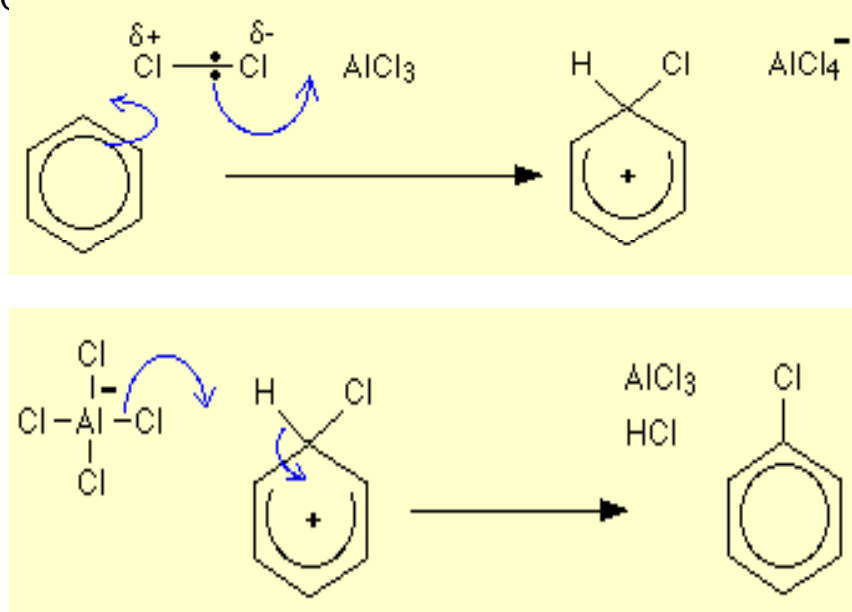
The hydrogen is removed by the AlCl4- ion which was formed in the first stage. The aluminium chloride catalyst is re-generated in this second stage

More Reactions of Arenes

Nitration is the substitution of a NO2 group for one of the hydrogen atoms on an arene ring. The electrophile is generated in the reaction mixture of concentrated nitric and sulphuric acids. The electrophile is the "nitronium ion" or the "nitryl cation", NO2$^+$.

$$HNO_3 + H_2SO_4 \quad \text{-->} \quad NO_2^+ + H_2O + HSO_4^-$$
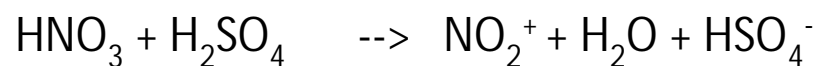
Benzene is treated with a mixture of concentrated nitric acid and concentrated sulphuric acid at a temperature not exceeding 50°C. As temperature increases there is a greater chance of getting more than one nitro group, -NO2, substituted onto the ring.
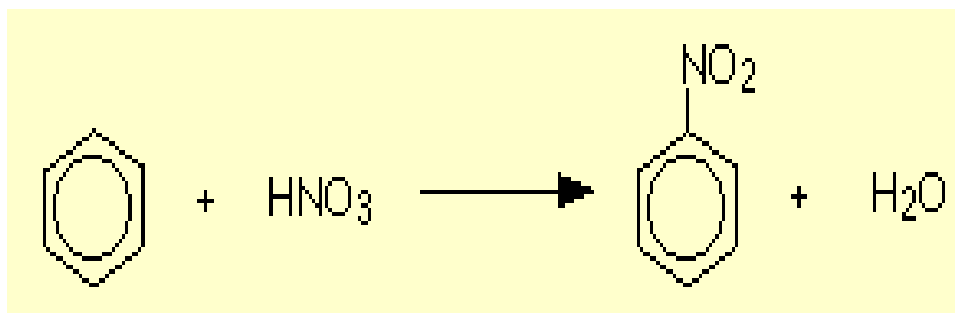
Note that the Sulphuric acid does not appear. It is acting as a catalyst.

More Reactions of Arenes

The mechanism is as follows:
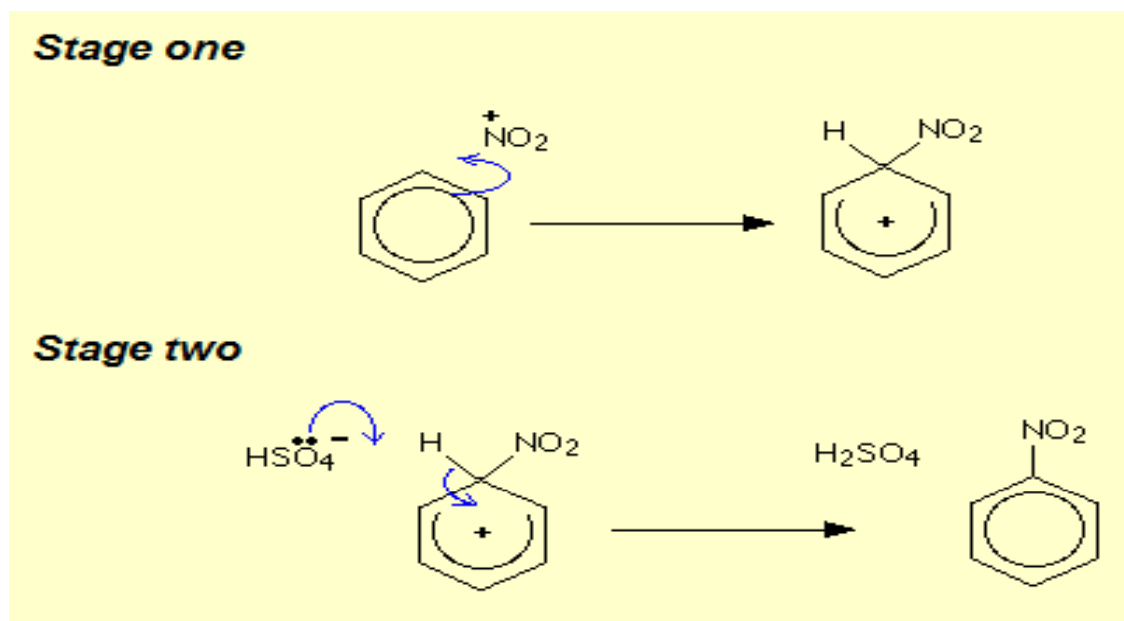
A little dinitrobenzene may also be formed by the further attack of NO2+ on nitrobenzene (which is now more suspectible to attack due to the electron inductive effect of the NO2+ group). This extra group will go the the 3 position to give the disubstituted product 1,3-dinitrobenzene. To actually produce this warm the reaction mixture during the experiment. The disubstituted product can be separated easily as it is a solid at room temperature.
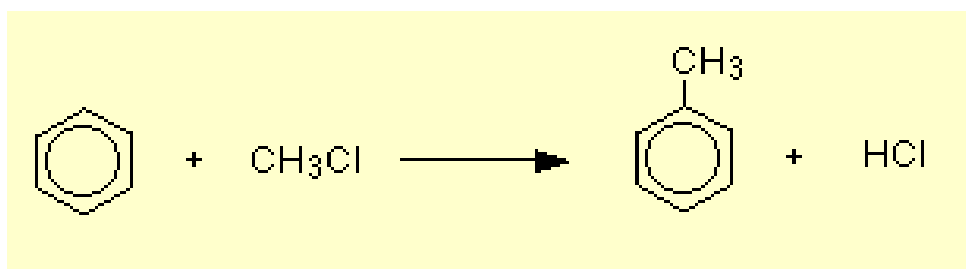
Friedel-Crafts Alkylation

What is alkylation?

Alkylation means substituting an alkyl group into something - in this case into a benzene ring. A hydrogen on the ring is replaced by a group like methyl or ethyl and so on.

Benzene reacts at room temperature with a chloroalkane (for example, chloromethane or chloroethane) in the presence of aluminium chloride as a catalyst. On this page, we will look at substituting a methyl group, but any other alkyl group could be used in the same way.

Substituting a methyl group gives methylbenzene.

With this kind of reaction the alkyl group can be any group so it is often shown as R. R+ is a good electrophile that attacks the benzene ring to form substitution products in the same way as other electrophiles. So the mechanism above is a simple electrophilic substitution

Friedel-Crafts Acylation

What is acylation?

An acyl group is an alkyl group attached to a carbon-oxygen double bond. If "R" represents any alkyl group, then an acyl group has the formula RCO-. Acylation means substituting an acyl group into something - in this case, into a benzene ring. In the example which follows we are substituting a CH3CO- group into the ring, but you could equally well use any other acyl group.

The most reactive substance containing an acyl group is an acyl chloride (also known as an acid chloride). These have the general formula RCOCl.

Benzene is treated with a mixture of ethanoyl chloride, CH3COCl, and aluminium chloride as the catalyst. The mixture is heated to about 60°C for about 30 minutes.
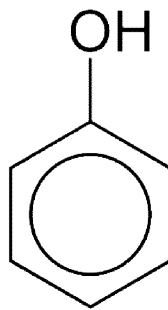

A Ketone
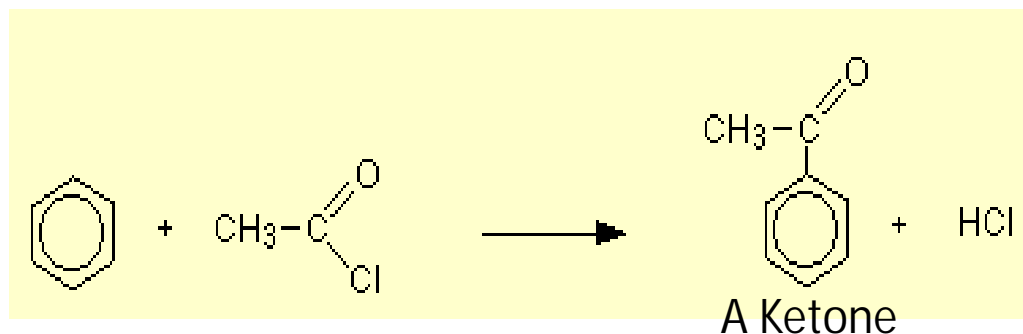
Phenols

Phenols are aromatic compounds in which one or more of the hydrogen atoms of the ring are replaced by an OH group. Phenols still have the aromatic pi-system. Phenol itself is a pale pink crystalline solid.

Unusually phenol is a pink crystalline solid. The hydrogen bonds between phenol molecules cause phenol to be a solid.

Although phenols and alcohols both contain the OH functional group they behave differently. Alcohols tend to react by substitution of the OH group with another nucleophile – the C-OH bond breaks. In phenol the -OH group is more firmly attached to the ring. The bond most likely to break is therefore the O-H bond.

Bonding In Phenols

The bonding in the benzene ring interacts with that in the OH group. The lone pair of electrons on the oxygen overlaps with the delocalised pi-system on the benzene ring to form an extended delocalised pi orbital.

As a result of this delocalised the C-O bond has some double bond character. It is stronger than a normal C-O single bond in an alcohol but not as strong as a C=O bond. We can see this by comparing their bond lengths.

This extra strength of the bond means the C-O bond in phenol is harder to break than the C-O bond in alcohols.

Another reason that it is not as readily attacked as a normal C-O bond is that the positive charge on the carbon is spread throughout the whole delocalised system, which therefore makes it less susceptible to attack by nucleophiles.

Reactivity Of Phenols

Phenols will react fairly readily by breaking the O-H bond, and losing a H+ ion. This makes phenols somewhat acidic. When it loses the H+ ion we get a phenoxide ion.
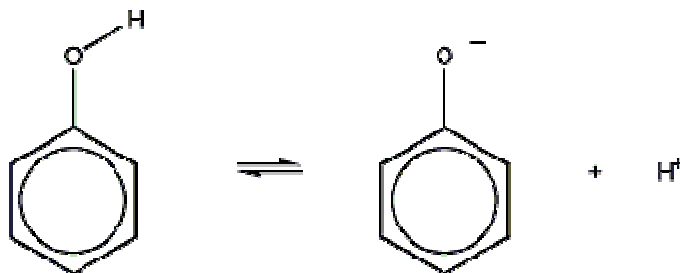
This phenoxide ion is relatively stable because of the overlaps of the pi orbitals on oxygen with the delocalised ring system. Alkoxide ion such as ethoxide ($C_2H_5O^-$) on the overhand are very unstable because there is no such delocalisation.

As well as reactions of the OH group the benzene ring can also react. Due to the oxygen's lone pair of electrons it activates the ring (remember the inductive effect from last lesson?) This causes phenol to be more susceptible to electrophilic substitution than benzene itself.

Reactions of Phenol

Combustion

Phenol burns in air with a smoky flame, just like other aromatic compounds.

Reactions of the OH group in phenol

Phenol is a weak acid. When it loses the H+ ion it from a phenoxide ion. This is relatively stable owing to the delocalisation of the negative charge. It therefore has some of the typical acid reactions.

Reactions with alkalis

Phenol is only slightly soluble in water but dissolves in aqueous sodium hydroxide to form the salt sodium phenoxide and water.

Reaction with alkali metals

Alkali metal phenoxides can also be made by direct reaction of molten phenol with alkali metal. Hydrogen is give off. For example, with sodium, we get sodium phenoxide and hydrogen.

Phenol is not strong enough acid to react with sodium carbonate solution to produce carbon

Phenols in Industry

Antiseptics and disinfectants both kill germs. Antiseptics may be aplied to the skin while disinfectants are normally only applied to surfaces. Phenol causes blistering to the skin. It was however the first antiseptic used in operations and saved lots of lives. Some of its derivatives are not only better germicides, but are also safer to use.

Many household disinfectants are aqueous solutions of phenol derivative. TCP (2,4,6 trichlorophenol) and Dettol (4-chloro-3,5-dimethylphenol) are just two of them. Disinfec eyes fluid are also derivatives of phenol.