CIE Chemistry A Level

17 : Hydroxy Compounds

Notes
Alcohols

Alcohols are organic compounds which contain a hydroxyl group, -OH. Alcohols can be separated into three different categories:

- **Primary alcohol**: \( \text{H} - \text{C} - \text{OH} \)
- **Secondary alcohol**: \( \text{R}_2 - \text{C} - \text{OH} \)
- **Tertiary alcohol**: \( \text{R}_2 - \text{C} - \text{OH} \)

**Combustion**

Water and carbon dioxide are produced when alcohols undergo complete combustion. A relatively large amount of energy is produced meaning they can be used as fuels.

\[
\text{CH}_3\text{OH} + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \\
\text{CH}_3\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} 
\]

Incomplete combustion of alcohols occurs when there is a limited supply of oxygen. This produces water as well as carbon monoxide, carbon and/or carbon dioxide:

\[
2\text{CH}_3\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO} + 2\text{C} + 6\text{H}_2\text{O} 
\]

**Substitution to halogenoalkanes**

Alcohols can react with halides to form halogenoalkanes. During this substitution reaction, the hydroxyl group is replaced by a halogen atom.

**Reactions with hydrogen halides**

- **Primary** and **secondary** alcohols react very, very slowly with hydrogen chloride, HCl. **Tertiary** alcohols react rapidly with concentrated hydrochloric acid at room temperature:
  \[
  (\text{CH}_3)_2\text{COH} + \text{HCl} \rightarrow (\text{CH}_3)_2\text{CCl} + \text{H}_2\text{O} 
  \]
- **Hydrogen bromide** reacts with alcohols. Typically the alcohol is treated with potassium bromide and concentrated sulfuric acid as these two reactants will produce hydrogen bromide:
  \[
  \text{CH}_3\text{CH}_2\text{OH} + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O} 
  \]
- **Hydrogen iodide** reacts with alcohols. Typically the alcohol is treated with potassium iodide and phosphoric(V) acid. Phosphoric(V) acid is used in this reaction instead of sulfuric acid as sulfuric acid will readily oxidise the iodide ions to iodine:
  \[
  \text{CH}_3\text{CH}_2\text{OH} + \text{HI} \rightarrow \text{CH}_3\text{CH}_2\text{I} + \text{H}_2\text{O} 
  \]

**Reactions with phosphorus halides**

Alcohols react with phosphorus(III) halides to produce halogenoalkanes:

\[
3\text{CH}_3\text{CH}_2\text{OH} + \text{PCl}_3 \rightarrow 3\text{CH}_3\text{CH}_2\text{Cl} + \text{H}_3\text{PO}_3 \\
3\text{CH}_2\text{OH} + \text{PBr}_3 \rightarrow 3\text{CH}_3\text{Br} + \text{H}_3\text{PO}_3 \\
3\text{CH}_3\text{CH}_2\text{OH} + \text{PI}_3 \rightarrow 3\text{CH}_3\text{CH}_2\text{I} + \text{H}_3\text{PO}_3 
\]
Phosphorus(V) chloride will react violently with alcohols to produce steamy fumes of hydrogen chloride.

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{HCl} + \text{POCl}_3 \]

Reaction with sulfur dichloride oxide
Sulfur dichloride oxide reacts with alcohols at room temperature to produce chloroalkanes.

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{SOCl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{SO}_2 + \text{HCl} \]

Reaction with sodium
When sodium reacts with an alcohol, a salt and bubbles of hydrogen gas are produced.

Ethanol and sodium
When ethanol reacts with sodium, sodium ethoxide and hydrogen gas are produced. This equation can be applied to other alcohols by substituting R for CH$_3$CH$_2$ (where R is any group):

\[ 2\text{CH}_3\text{CH}_2\text{OH} + 2\text{Na} \rightarrow 2\text{CH}_3\text{CH}_2\text{ONa} + \text{H}_2 \]

Sodium ethoxide (CH$_3$CH$_2$ONa) is an ionic compound because the positive sodium ion (Na$^+$) is attracted to the negative ethoxide ion (CH$_3$CH$_2$O$^-$).

This reaction can be used to remove alcohol groups from a compound or to safely dispose of small amounts of sodium (as sodium reacts explosively with water).

Oxidation to carbonyl compounds and carboxylic acids
Alcohols undergo oxidation when reacted with potassium or sodium dichromate(VI). During this reaction, the orange potassium dichromate(VI) turns green. The products of this reaction vary depending on the classification of the alcohol (primary, secondary or tertiary). When writing an equation, [O] is used to denote the oxidising agent.

Primary alcohols
Primary alcohols can be partially oxidised to aldehydes.

\[ \text{CH}_3\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} \]

With further oxidation, aldehydes become carboxylic acids.

\[ \text{CH}_3\text{CHO} + [\text{O}] \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O} \]

The full oxidation reaction can be written as:

\[ \text{CH}_3\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \]

Secondary alcohols
Secondary alcohols are oxidised to ketones. No further oxidation can take place.

\[ \text{CH}_3\text{C(OH)HCH}_3 + [\text{O}] \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2\text{O} \]

Tertiary alcohols
Tertiary alcohols do not undergo oxidation.
Dehydration to alkenes
Alcohols can be dehydrated to form alkenes. This can be carried out using aluminium oxide or an acid as a catalyst.

Dehydration of ethanol using aluminium oxide
If ethanol vapour is passed over an aluminium oxide catalyst, the ethanol is cracked, producing ethene and water.

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{CH}_2 + \text{H}_2\text{O}
\]

Dehydration of ethanol using acid catalyst
Concentrated sulfuric or phosphoric acid can be used as acid catalysts to produce ethene from ethanol. When ethanol is heated with excess sulfuric acid (a strong oxidising agent), the alcohol is further oxidised to carbon dioxide and the acid is reduced to sulfur dioxide. These gases must be removed from the reaction. Phosphoric acid is often used in place of concentrated sulfuric acid because it is a weaker oxidising agent meaning the reaction is safer.

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{CH}_2 + \text{H}_2\text{O}
\]

If an alcohol is unsymmetrical, a variety of products will be produced from dehydration. For example, dehydration of butan-2-ol will produce but-2-ene, cis-but-1-ene and trans-but-1-ene.

Formation of esters by esterification with carboxylic acids
Esters can be formed when an alcohol and a carboxylic acid are heated together in the presence of an acid catalyst (commonly sulfuric acid). The process is known as esterification.

The diagram on the left shows an ester. The left side of this compound is derived from the carboxylic acid and the right side from the alcohol. This ester was formed from ethanoic acid and ethanol and it is called ethyl ethanoate. ‘Ethyl’ comes from the alcohol and ‘ethanoate’ from the carboxylic acid.
Formation of esters by acylation with acyl chlorides (A Level only)

Esters can also be produced from **alcohols** and **acyl chlorides**. Alcohol react vigorously with acyl chlorides, releasing steamy fumes of hydrochloric acid.

**Phenyl benzoate:**

**Benzoyl chloride** is very **unreactive** because the -COCl group is directly attached to a stable **benzene ring**. To produce the ester phenyl benzoate, phenol is first converted into an ionic compound by **dissolving it in sodium hydroxide**. This produces the **phenoxide** ion:
The phenoxide ion is more reactive than the phenol so this ion can react with benzoyl chloride to produce phenyl benzoate (see the following page).

\[
\begin{align*}
\text{benzoyl chloride} & \quad + \quad \text{sodium phenoxide} \\
\xrightarrow{\text{reaction}} \\
\text{phenyl benzoate} & \quad + \quad \text{NaCl}
\end{align*}
\]

**Deducing the presence of CH₃CH(OH)- group in an alcohol**

The presence of a CH₃CH(OH)- group can be detected in an alcohol using alkali aqueous iodine, I₂. Iodine is added to the alcohol, followed by sodium hydroxide. If the CH₃CH(OH)- group is present, a yellow precipitate of tri-iodomethane, CHI₃, will be produced.

\[
\text{RCH(OH)CH}_3 + 4\text{I}_2 + 6\text{NaOH} \rightarrow \text{RCOONa} + \text{CHI}_3 + 5\text{NaI} + 5\text{H}_2\text{O}
\]

**Phenol (A Level only)**

Phenol is an aromatic hydrocarbon consisting of one alcohol group bonded to the benzene ring:

**Reactions with bases**

Phenol is a weak acid. A hydrogen ion can be removed from the hydroxyl group and transferred to a base. The position of equilibrium for the reaction below lies far to the left which means that phenol is a weak acid.

\[
\begin{align*}
\text{OH} & \quad + \quad \text{H}_2\text{O} \quad \xrightleftharpoons{} \quad \text{O}^- \quad + \quad \text{H}_3\text{O}^+
\end{align*}
\]

Phenol is able to donate a hydrogen ion because the phenoxide ion is relatively stable. The lone pair on the oxygen atom is delocalised into the pi system which is above and below the benzene ring. This means that the negative charge is dispersed among the carbon atoms so the compound is more stable.
Reaction with sodium hydroxide
When phenol reacts with sodium hydroxide, colourless sodium phenoxide is formed.

![Reaction with sodium hydroxide](image)

Reaction with sodium carbonate
Phenol isn’t acidic enough to react with sodium carbonate.

Reactions with sodium
Phenol reacts with metals in the same way that most acids. Hydrogen gas and a salt are produced. The reaction occurs slower than comparable acid-metal reactions because phenol is a weak acid.

![Reactions with sodium](image)

Reactions with diazonium salts
Diazonium salts contain the diazonium ion, $R-N_2^+$ (where R is any organic group). In the case of the following example, we will be looking at the diazonium ion when it is attached to a benzene ring.

Before a diazonium salt is reacted with phenol, phenol is dissolved in sodium hydroxide to give the phenoxide ion:

![Reactions with diazonium salts](image)

Cold benzenediazonium chloride is then added to the sodium phenoxide solution. The diazonium and phenoxide ions react together to form an azo compound. An azo compound contains two benzene rings that are joined together with a nitrogen bridge. The product can be identified as a yellow solution or precipitate.
Nitration and bromination of the aromatic ring

Phenol is more reactive than benzene because it contains an -OH functional group. The lone pair on the oxygen atom is delocalised into the pi system. This increases the electron density, making phenol more likely to be attacked by electrophiles. The effect of the OH group is sometimes referred to as the 2,4-directing effect. This is because the incoming groups tend to bond to the second and fourth carbons from the hydroxyl group.

Nitration
Phenol reacts with dilute and concentrated nitric acid:

- **Dilute** nitric acid
  The 2,4-directing effect of the hydroxyl group causes a mixture of 2-nitrophenol and 4-nitrophenol to be produced. The reaction for 2-nitrophenol is shown below.

  \[
  \text{OH} + \text{HNO}_3 \rightarrow \text{OHNO}_2 + \text{H}_2\text{O}
  \]

- **Concentrated** nitric acid
  The compound 2,4,6-trinitrophenol is formed.

  \[
  \text{OH} + 3\text{HNO}_3 \rightarrow \text{ONO}_2 + 3\text{H}_2\text{O}
  \]

Bromination
When bromine water is added to a solution of phenol, the orange bromine water is decolourised. 2,4,6-tribromophenol (white precipitate) and hydrogen bromide are formed.

\[
\text{OH} + 3\text{Br}_2 \rightarrow \text{Br}_2\text{OH} + 3\text{HBr}
\]

Relative acidities of water, phenol and ethanol

The relative acidities are as follows: phenol > water > ethanol

- Phenol is the **most acidic** because the phenoxide ion (formed when phenol donates a proton) is **relatively stable**. The **lone pair** on the oxygen atom is **delocalised** into the pi system meaning the negative charge is dispersed among the carbon atoms. This means that phenol is **more likely to donate a hydrogen ion** than water or ethanol.

- Ethanol and water have similar acidities but **ethanol is the least acidic**. This is because of the **positive inductive effect**. The alkyl group in the ethoxide ion “pushes” electrons away from itself, towards the oxygen. This **increases the electron density of the oxygen**, making it more likely to bond to a hydrogen ion and reform ethanol.