

Chapter 18a (AS-Level)

Hydroxy compounds – Alcohols

The different types of alcohols

There are three types of alcohols:

1. **Primary alcohols:**

In primary alcohols, the -OH group is attached to a carbon atom which is attached to only one alkyl group (or no alkyl group as in methanol):

Examples include:



Ethanol

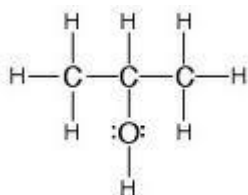


Propan-2-ol

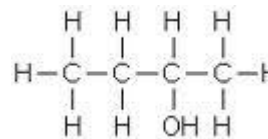
2. **Secondary alcohols:**

In secondary alcohols, the -OH group is attached to a carbon atom which is attached to 2 alkyl groups:

Examples include:



Propan-2-ol

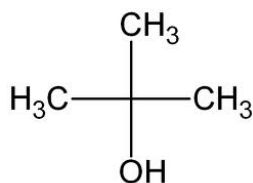


Butan-2-ol

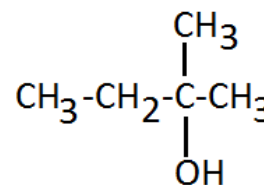
3. **Tertiary alcohols:**

In tertiary alcohols, the -OH group is attached to a carbon atom which is attached to 3 alkyl groups:

Examples include:



2-methylpropan-2-ol



2-methylbutan-2-ol

Physical properties

Some points to remember:

- The boiling points of the alcohols increase as the carbon chain increases in size
- The boiling points of the alcohols are higher than corresponding alkanes, which is due to:
 - Hydrogen bonding that occurs between -OH groups of alcohols
 - Alkanes have no lone pairs so only Van der Waal's forces present

Solubility of alcohols in water (miscibility in water)

Small chain alcohols are completely soluble in water. However, solubility falls as the length of the hydrocarbon tails of the alcohols increases. Once you get to 4 carbon atoms and beyond, the fall in solubility is noticeable.

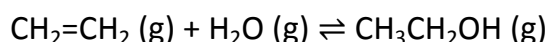
Smaller alcohols can form hydrogen bonds with the water molecules as well as the larger chain molecules, but the bigger chain alcohols would be forcing their way between the water molecules, breaking the hydrogen bonds as the tail cannot have hydrogen bonds.

The hydrocarbon tails only exert weak Van der Waal's forces which are not enough to keep the liquids mixed.

Manufacture of alcohols

Ethanol is manufactured from the hydrolysis of ethene, which is the reaction of steam with ethene, in the presence of solid silicon dioxide coated with phosphoric acid.

The reaction is reversible:



Conditions:

- 300°C
- 60-70 ATM
- H_3PO_4 acid catalyst

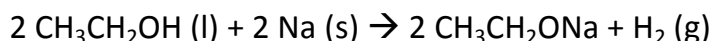
Reactions of alcohols

Reactions in which the O-H bond is broken

Reaction with sodium

Metallic sodium reacts with ethanol in a less vigorous reaction than with water. It reacts readily to produce hydrogen gas and a colourless solution of sodium ethoxide ($\text{CH}_3\text{CH}_2\text{O}^-\text{Na}^+$).

Sodium ethoxide is an alkoxide.



If the solution is tested with phenolphthalein indicator, the solution turns pink, indicating a high pH.

The reaction is used to:

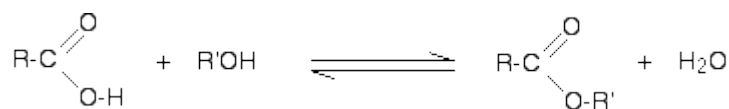
- Indicate the presence of an $-\text{OH}$ group in alcohols
- Remove small traces of sodium safely



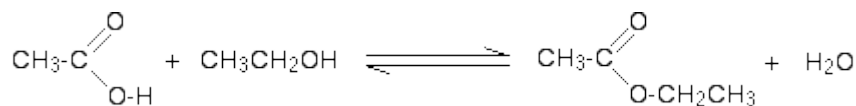
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Esterification

Esters are produced when carboxylic acids are heated with alcohols in the presence of a strong acid like sulphuric acid. The process is slow and reversible. The general equation for esterification is:



For example, the reaction of ethanol with ethanoic acid produces ethyl ethanoate:

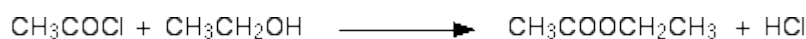


Esters like ethyl ethanoate have fruity smells and are naturally found in fruits.

Esters can also be formed from alcohols and acyl chlorides.

Adding an acyl chloride to an alcohol is a vigorous exothermic reaction, which produces clouds of hydrogen chloride gas at room temperature.

For example, if ethanoyl chloride is mixed with ethanol, ethyl ethanoate is formed along with HCl gas:



The reaction is reversible; equilibrium is well to the right as the HCl gas escapes and so more ester and HCl has to be produced, so it is written as irreversible.

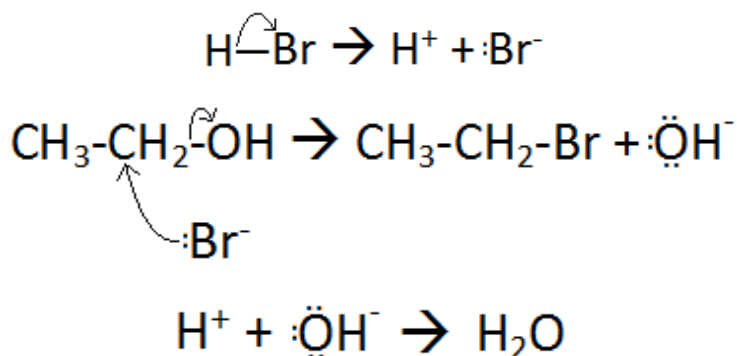
Reactions in which the C-O bond is broken

Substitution to form halogenoalkanes

When ethanol is heated with concentrated sulphuric acid and sodium bromide, bromoethane is formed. Concentrated sulphuric acid and sodium bromide react to form hydrogen bromide and sodium hydrogen sulphate:



With ethanol, HBr acts as a nucleophile, substituting the Br atom for the -OH group of ethanol:



This reaction is a reverse of hydrolysis of an alkyl halide.

For alkyl halides containing Cl or I, there are different ways of making them: one stop shop for all your problems

- Chloroalkanes can be made by reacting alcohols with phosphorous (III) chloride PCl_3 , phosphorous (V) chloride, PCl_5 or SOCl_2 , sulphur dichloride oxide:



- Iodoalkanes can be made by warming an alcohol with a mixture of red phosphorous and iodine. PI_3 is formed which then reacts with alcohol:



Reactions that involve the breaking of the C-C or C-H bonds

Mild oxidation

Oxidation is the addition of oxygen. The oxidizing agent used here is potassium dichromate(VI) acidified with dilute sulphuric acid.

If oxidation occurs, the orange colour of potassium dichromate solution changes into a green solution containing chromate ions.

With primary alcohols

Primary alcohols can be oxidized into aldehydes or carboxylic acids, depending on the reaction conditions. Carboxylic acids are formed when aldehydes formed are oxidized further.

- Partial oxidation

Aldehydes are produced if you use an excess of alcohol and if the aldehyde is distilled as it is formed (there is not enough oxidizing agent to oxidise the aldehyde).

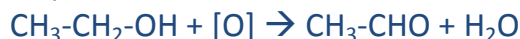
The reaction is:



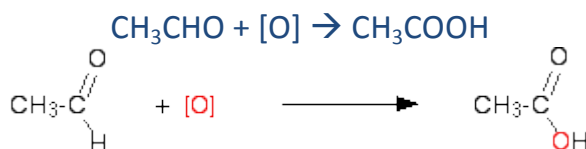
Here the colour of the solution changes from orange to green.

- Full oxidation

Here an excess of an oxidizing agent is used and the mixture is heated under reflux, making sure that no aldehyde can escape.

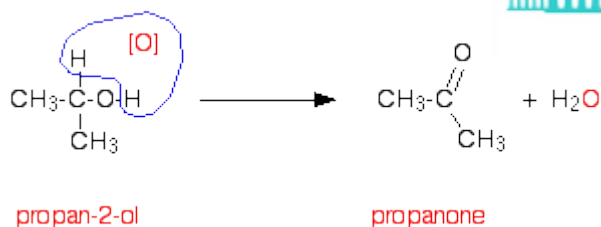


Then:



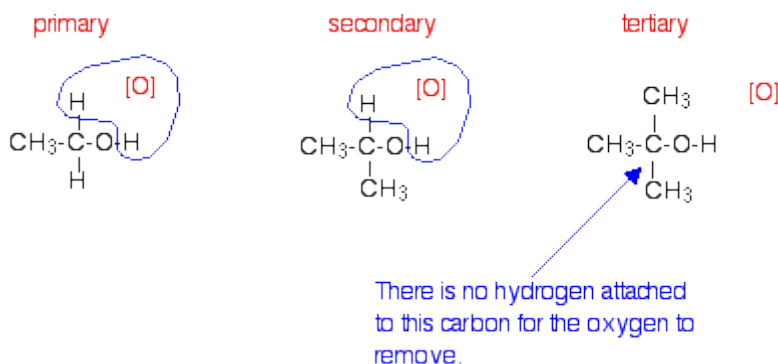
With secondary alcohols

Secondary alcohols are oxidised into ketones only. For example, heating propan-2-ol with acidified potassium dichromate(VI), Propanone formed.



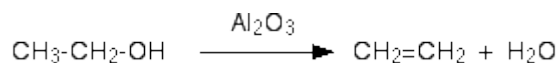
With tertiary alcohols

No reaction occurs, because the oxidizing agent has to remove one hydrogen from the –OH group and another from the same carbon atom.

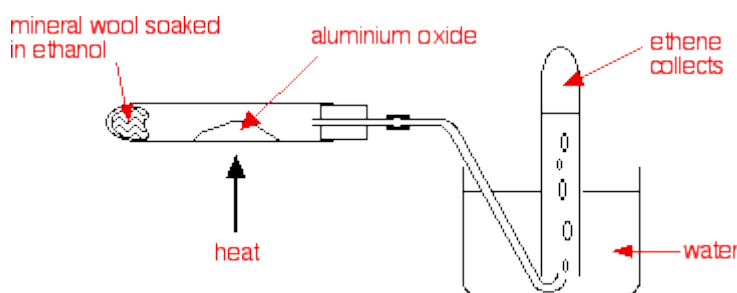


The dehydration of ethanol to give ethene

This is a simple way of making gaseous alkenes like ethene. If ethanol vapour is passed over heated aluminium oxide powder, the ethanol is essentially cracked to give ethene and water vapour.



To make a few test tubes of ethene, you can use this apparatus:



It wouldn't be too difficult to imagine scaling this up by boiling some ethanol in a flask and passing the vapour over aluminium oxide heated in a long tube.

Uses of alcohols

Uses of ethanol

Drinks

The "alcohol" in alcoholic drinks is simply ethanol.

Industrial methylated spirits (meths)

Ethanol is usually sold as industrial methylated spirits which is ethanol with a small quantity of methanol added and possibly some colour. Methanol is poisonous, and so the industrial methylated spirits is unfit to drink. This avoids the high taxes which are levied on alcoholic drinks (certainly in the UK!).

As a fuel

Ethanol burns to give carbon dioxide and water and can be used as a fuel in its own right, or in mixtures with petrol (gasoline). "Gasohol" is a petrol / ethanol mixture containing about 10 - 20% ethanol.

Because ethanol can be produced by fermentation, this is a useful way for countries without an oil industry to reduce imports of petrol.



As a solvent

Ethanol is widely used as a solvent. It is relatively safe, and can be used to dissolve many organic compounds which are insoluble in water. It is used, for example, in many perfumes and cosmetics.

Uses of methanol

As a fuel

Methanol again burns to form carbon dioxide and water.



It can be used as a petrol additive to improve combustion, or work is currently being done on its use as a fuel in its own right.

As an industrial feedstock

Most methanol is used to make other things - for example, methanal (formaldehyde), ethanoic acid, and methyl esters of various acids. In most cases, these are in turn converted into further products.

END OF LESSON