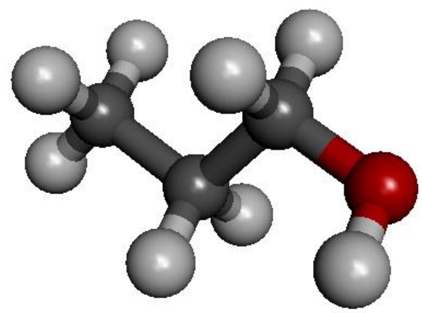
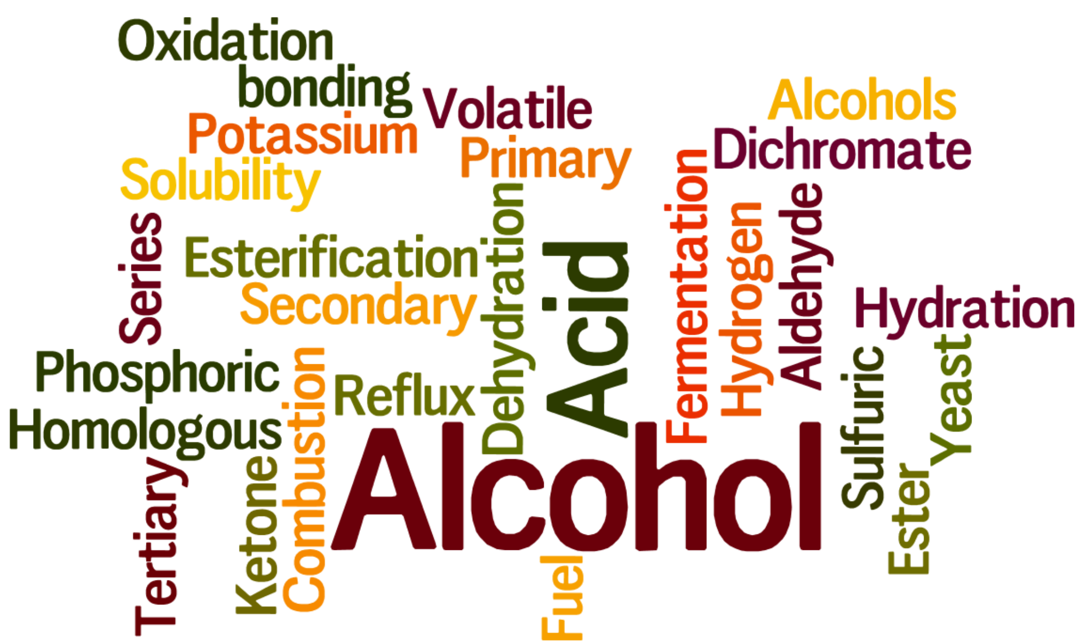
AS Chemistry
F322: Chains, Energy & Resources
2.2.1 Alcohols

Plymstock School

Alcohols.

P.J.McCormack



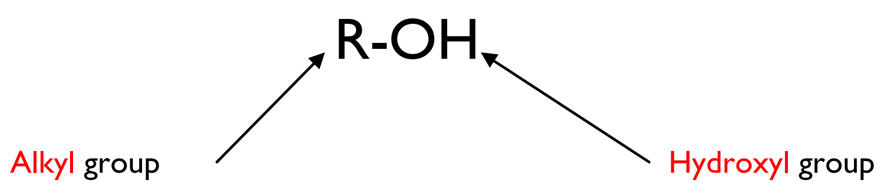


1. Introduction

The alcohols are a group of organic compounds that contain one or more **hydroxy** groups, (-OH) attached to an alkyl group in a covalent structure.

Monohydric alcohols contain **only one –OH group per molecule**. **Polyhydric** alcohols contain **more than one –OH group per molecule**. Polyhydric alcohols are more viscous and have higher boiling points than monohydric alcohols because the degree of hydrogen bonding is much greater.

The general formula of a simple alcohol is $C_nH_{2n+1}OH$:

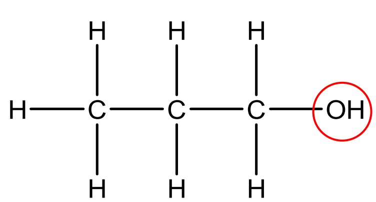


The alcohols represent an important group of compounds. Their uses vary from alcoholic drinks to solvents, antifreeze, fuels and cosmetics.

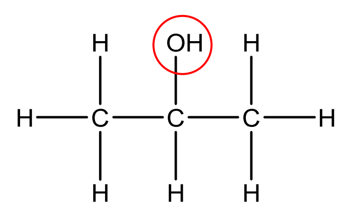
Naming Alcohols

The name of an alcohol consists of a first part, which indicates the chain length (methan, ethan, propan etc.). This stem is followed by the suffix –**ol**. Thus CH_3-OH is methanol and CH_3CH_2-OH is ethanol.

For chain lengths of three or more carbon atoms, the alcohols have numbers to indicate the position of the –OH group along the carbon chain. The numbering of the carbon chain starts at the end of the chain closest to the first substituted group, -OH. So $CH_3CH_2CH_2OH$ is propan-1-ol and $CH_3CH(OH)CH_3$ is propan-2-ol:



Propan-1-ol



Propan-2-ol

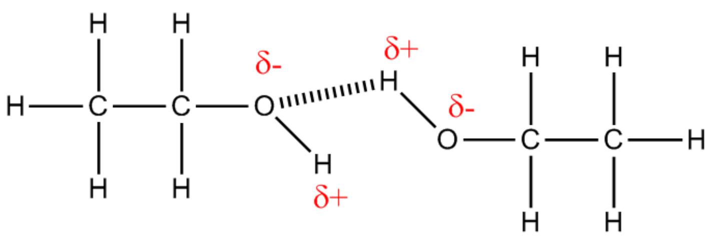
When the numbering could begin at either end, due to **two substituted groups**, it starts at the end nearest the substituted group that comes first alphabetically – $CH_3CH(C_2H_5)CH(OH)CH_3$ is 2-ethylbutan-3-ol i.e.

2.2.1 (a) – Physical Properties of Alcohols

The physical properties of alcohols are explained in terms of intermolecular forces; hydrogen bonding .and van der Waals interactions.

Hydrogen bonding.

Hydrogen bonding occurs between molecules where a hydrogen atom attached to a very electronegative element such as fluorine, oxygen or nitrogen. In the case of alcohols, there are hydrogen bonds set up between the slightly positive hydrogen (δ+) atoms and lone pair of electrons on oxygen (δ-) in other molecules. The hydrogen atoms are slightly positive because the bonding electrons are pulled away from them towards the very electronegative oxygen atoms.

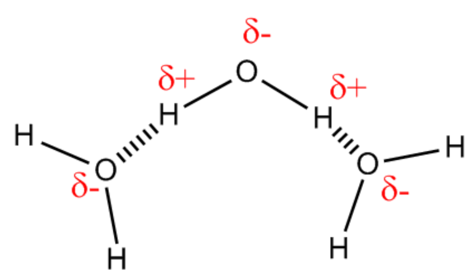


Hydrogen bonding between two alcohol molecules

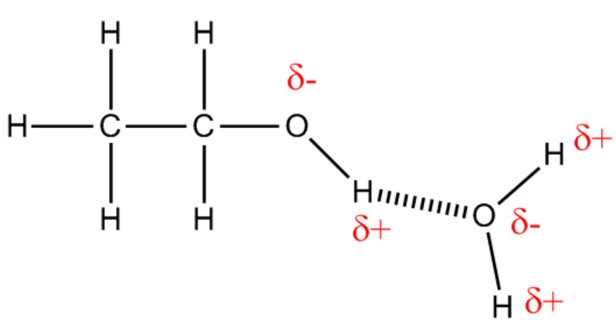
The hydroxy, -OH, functional group in alcohols enables them to form **hydrogen bonds** i.e. the hydrogen is attached to an electronegative atom (O) that has two lone pairs of electrons. Alcohols, consequently, can form hydrogen bonds with themselves and with water.

Exam Tip: Explain all physical properties in terms of hydrogen bonding

In water the two hydrogen atoms in a water molecule can form two hydrogen bonds to two oxygen atoms in **two** other water molecules.



Hydrogen bonding in water



Hydrogen bonding between ethanol and water

However, in alcohols there is only **one** hydrogen atom able to form hydrogen bonds and so there is **less hydrogen bonding** in alcohols. As a consequence of this the boiling points of methanol (M_r= 32) and ethanol (M_r=46) are much lower than water.

Nevertheless, the hydrogen bonding between alcohol molecules is still very significant and **alcohols have higher boiling points than the equivalent alkanes.**

Volatility.

Volatile – the ease at which a liquid evaporates.

Trend: The volatility decreases with increasing carbon chain length.

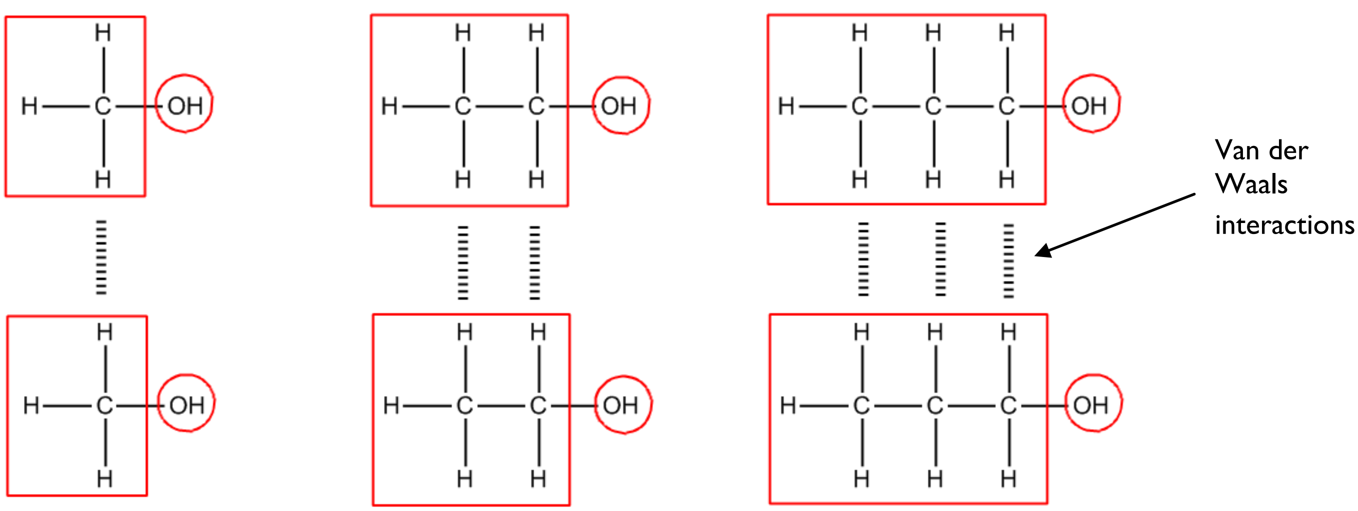
Explanation: Alcohols are relatively low volatile compounds as they possess hydrogen bonds between the molecules, resulting in more energy required to separate the molecules when compared to alkanes.

Alcohols are less volatile than alkanes due to alcohols having hydrogen bonds between the molecules whereas alkanes have weaker van der Waals interactions. Hydrogen bonds are stronger intermolecular bonds than van der Waals resulting in more energy required to separate the alcohol molecules from each other.

Boiling Points.

Trend: The boiling point of alcohols increases with increasing an increase in carbon chain length.

Explanation:. As the carbon chain length increases there is the same amount of hydrogen bonding but an increase in the amount van der Waals interaction due to an increased surface area of the molecules.



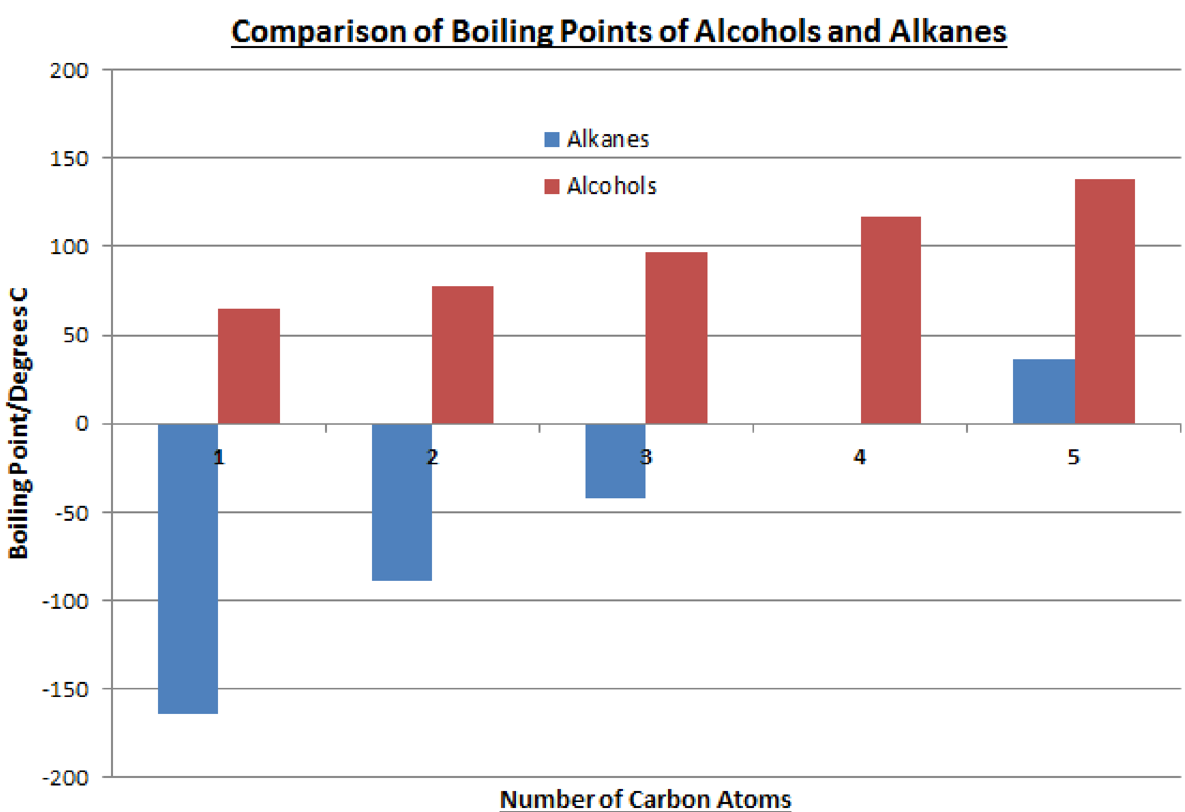
The table below shows the comparison of the boiling points of alcohols and equivalent alkanes in terms of carbon chain length.

The boiling points depend on intermolecular forces (between molecules). Alkanes only have van der Waal's forces between their molecules, whereas alcohols have both van der Waal's forces and hydrogen bonding.

Number of Carbon Atoms	Alkane	Molecular Mass	Boiling Point ^{0} C
1	Methane	16	-164
2	Ethane	30	-89
3	Propane	44	-42
4	Butane	58	-0.5
5	Pentane	72	36

Alcohol	Molecular Mass	Boiling Point ^{0} C
Methanol	32	65
Ethanol	46	78
Propanol	60	97
Butanol	74	117
Pentanol	88	138

Although ethane and methanol are of similar size (in terms of molecular mass) the contribution of the hydrogen bonding in methanol means that its boiling point is much higher.



The boiling points of alcohols are also affected by isomerism. If the –OH group is moved to the centre of the carbon chain the molecule becomes more spherical, with a smaller surface area. This reduces the van der Waal's forces. It also makes the –OH less accessible and reduces hydrogen bonding. Butan-1-ol has a boiling point of 117^{0}C but 2-methylpropan-1-ol boils at 108^{0}C.

Water Solubility.

Hydrogen bonding in the smaller molecules of alcohols enables them to dissolve easily in water (miscible). However, as the hydrocarbon chain length increases the solubility rapidly decreases. This is because the longer hydrocarbon chains form stronger van der Waal's forces between themselves rather than with the water.

Name	Formula	Solubility g/100g H_2O
Methanol	CH_3OH	∞
Ethanol	CH_3CH_2OH	∞
Propan-1-ol	$CH_3CH_2CH_2OH$	∞
Butan-1-ol	$CH_3CH_2CH_2CH_2OH$	7.9
Pentan-1-ol	$CH_3CH_2CH_2CH_2CH_2OH$	2.4
Hexan-1-ol	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	0.6

2.2.1 (b) – Preparation of Ethanol

(i) Fermentation.

About 5% of the world's production of ethanol is produced by fermentation. This process is carried out by yeast in the presence of glucose but in the absence of air (anaerobic respiration). The weak ethanol solution produced (5 – 15%) can be converted into ethanol by distillation (boiling point 78°C)

If oxygen is present then the yeast converts the glucose (carbohydrate) into carboxylic acid (ethanoic acid) rather than ethanol. Oxidation occurs rather than fermentation.

The enzyme **zymase** in yeast converts the glucose into ethanol and carbon dioxide:

$$C_6H_{12}O_6(aq) \xrightarrow[37^\circ C]{\text{yeast}} 2\,C_2H_5OH(aq) + 2CO_2(g)$$

The main use of fermentation is the production of alcoholic drinks but it is also becoming an important way of producing car fuel (Brazil – sugar cane).

This process has a number of advantages:

- it is a low-technology process, which means it can be used anywhere
- it does not use much energy
- it uses sugar cane as a raw material, which is a renewable resource

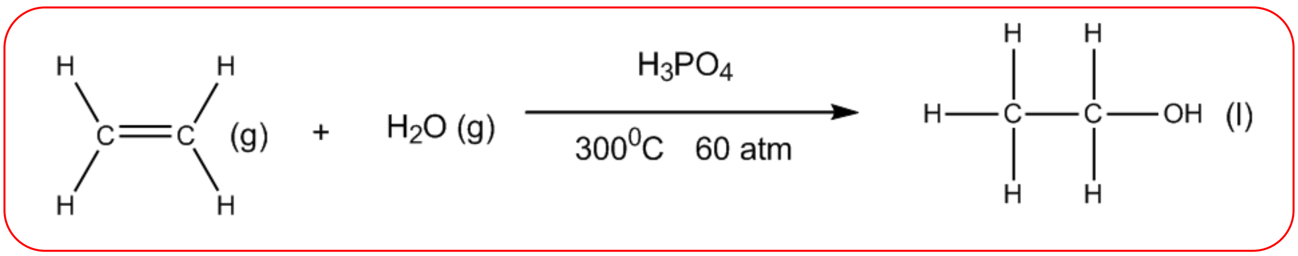
There are, however, a few disadvantages associated with this process:
- it is a batch process, which means that once the reaction has finished the vessel needs to emptied before the reaction can be started again
- it is a relatively slow process
- it produces fairly impure ethanol

(ii) Reaction of Ethene with Steam

In those countries, which have good supplies of crude oil or natural gas, ethanol, for industrial use, is made from ethene.

The ethene is produced by **cracking**. This is a process in which large molecules are broken down into smaller (and more useful) molecules by heating the oil in the presence of a catalyst (Al_2O_3).

The ethene and steam are passed over a **phosphoric acid (H_3PO_4) catalyst, at about 300^{0}C and 60 atmospheres pressure**. *The reaction is called hydration.*



2.2.1 (c) Uses of Ethanol

Ethanol has a variety of uses including
- Alcoholic drinks
- As a fuel
- As a solvent
- In cosmetics manufacture
- As an intermediate in the manufacture of many other chemicals

Wines and beers produced by fermentation are coloured and flavoured by substances from the starting material or by other products of the fermentation (or added, like hops for 'bitter' beer). Fermented brews can contain up to 5 – 15% by volume of ethanol. At this concentration, yeast is killed and fermentation stops.

'Spirits' are made by the inefficient distillation of the fermented liquid, to raise the alcohol proportion to 30 – 45%. Whisky is obtained by distilling a mixture similar to beer, brandy is made from wine and vodkas from fermented mashed potato.

Most spirits have a strength of around 40%. Occasionally the old term 'degrees proof' is used. A 100% proof spirit contains about 52% of alcohol.

The production of ethanol is becoming important as a way of producing alternative car fuel, especially in those countries with limited oil reserves. 'Gasohol' contains up to 20% ethanol in lead-free petrol; car performance is hardly affected. In Brazil production from some sugar cane plantations is used exclusively for this purpose.

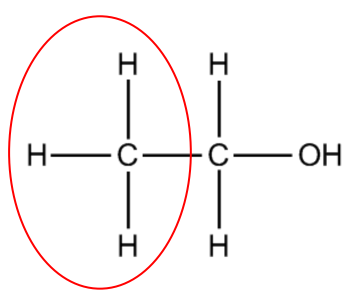
Methanol is also used as a petrol additive to improve combustion and its increasing importance as a feedstock in the production of organic chemicals. It is cheap and burns with a cleaner flame than the hydrocarbons used in petrol. However, volume for volume it produces less energy, so bigger fuel tanks would be needed. It also absorbs water, it is hygroscopic, so it corrodes parts of the engine.

Alcohols are used as a solvent in a variety of compounds. Ethanol is made into methylated spirit by the addition of the more toxic methanol plus a purple dye.

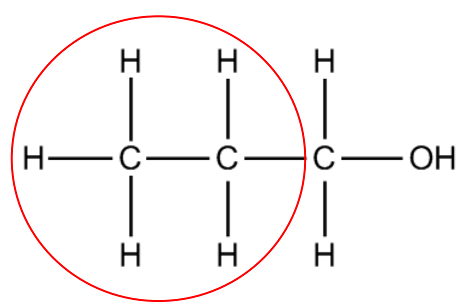
2.2.1 (d) Classification of Alcohols.

Alcohols can be divided into **three classes** depending on the **number of alkyl groups** linked to the carbon that is attached to the O-H group. The three classes are called **primary, secondary** and **tertiary alcohols**.

Primary alcohols contain the –CH_2OH group. They have a maximum of ***one other alkyl* group** (R) linked to the carbon attached to the –OH group e.g.

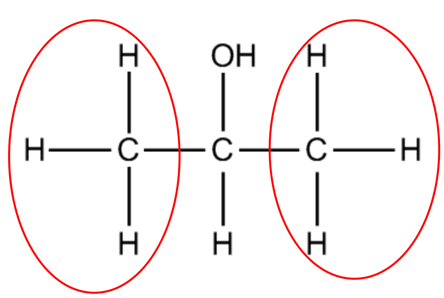


Ethanol

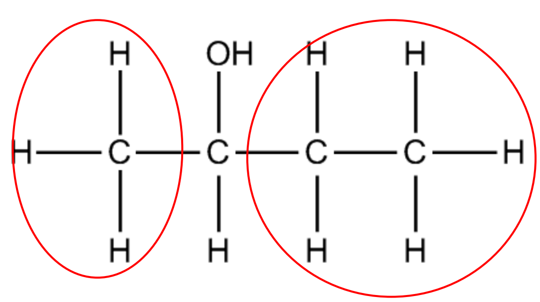


Propan-1-ol

Secondary alcohols contain the CHOH group. They have ***two alkyl groups*** linked to the carbon atom that is attached to the –OH group e.g.

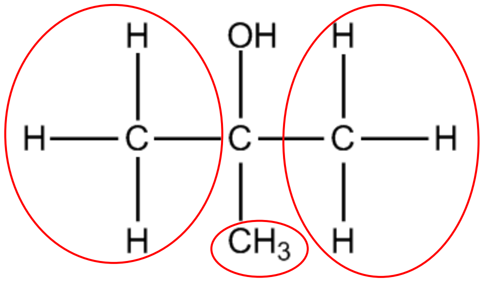


Propan-2-ol

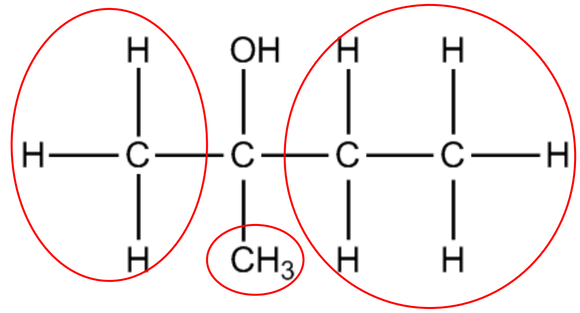


Butan-2-ol

Tertiary alcohols contain the -COH group. They have ***three alkyl groups*** linked to the carbon atom that is attached to the –OH group e.g.



2-methyl propan-2-ol



2-methyl butan-2-ol

2.2.1 (e) Combustion of Alcohols.

In a plentiful supply of oxygen alcohols burn very readily to form carbon dioxide and water.

$$C_2H_5OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

In a limited amount of oxygen alcohols combust to form carbon monoxide and water.

$$C_2H_5OH(g) + 2O_2(g) \rightarrow 2CO(g) + 3H_2O(g)$$

2.2.1(f) Oxidation of Alcohols.

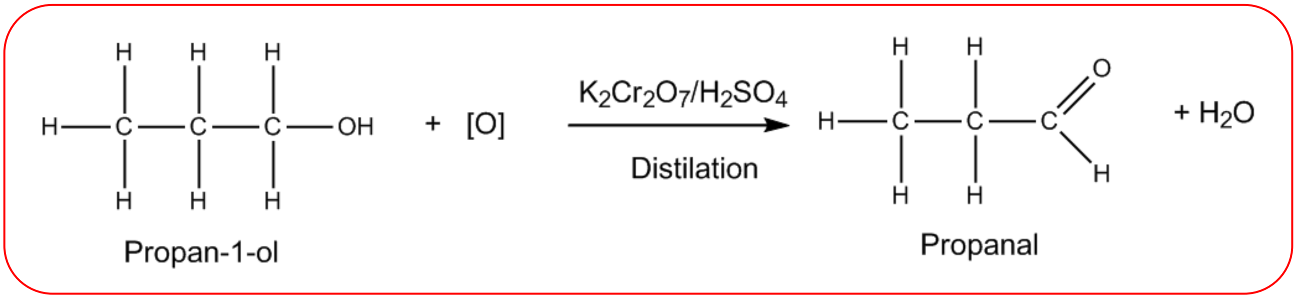
Primary and secondary alcohols can be oxidised using an oxidising agent. The oxidising agent used to oxidise primary and secondary alcohols is **potassium dichromate** ($K_2Cr_2O_7$) in acidic conditions (H^+). The acid used to acidify potassium dichromate is **sulfuric acid** (H_2SO_4). During oxidation of alcohols water is always produced.

Potassium dichromate is an orange colour and changes to a green colour during the reaction.

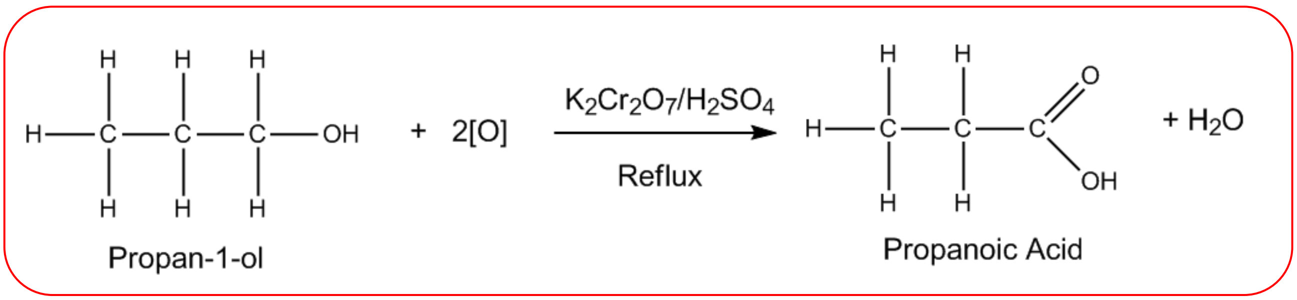
(i) Oxidation of Primary Alcohols

On gentle heating **primary alcohols** are oxidised to an **aldehyde**. The symbol [O] is used to represent an oxidising agent in the equation. Gentle heating involves distillation where the product of the reaction, the aldehyde is removed as it is formed, which prevents further oxidation to the carboxylic acid.

Oxidation of primary alcohols produces an aldehyde, then further oxidation will produce a carboxylic acid.



On strong heating of a **primary alcohol** a **carboxylic acid** is formed.



Reflux: The continual boiling and condensing of a reaction mixture to ensure the reaction goes to completion without the mixture billing dry.

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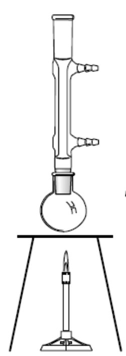

Distillation: The process of separating a mixture of liquids due to the difference in boiling points.

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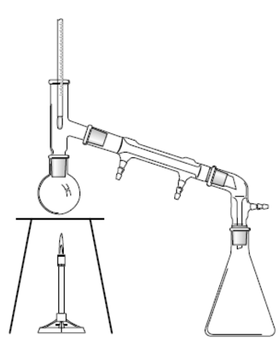
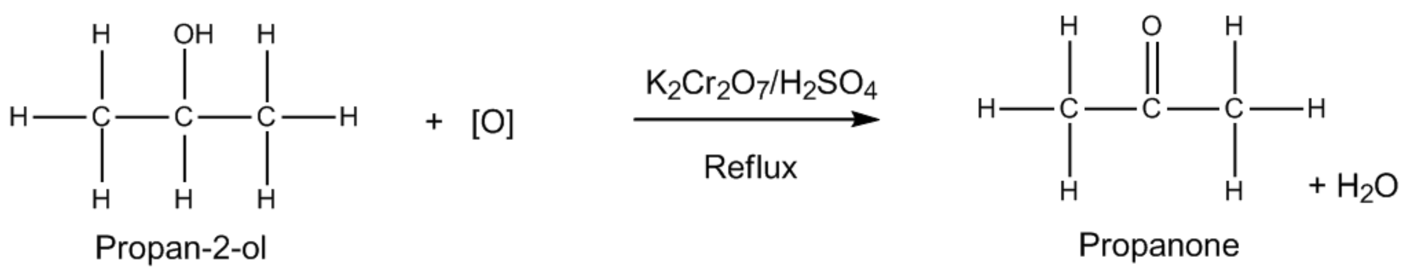


(ii) Oxidation of Secondary Alcohols.

Oxidation of a **secondary** alcohol produces a **ketone**. The same oxidising agent is used as for primary alcohols, **acidified potassium dichromate** ($H^+/K_2Cr_2O_7$), where $H^+ = H_2SO_4$.



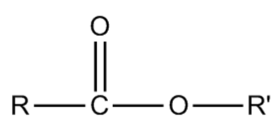
Oxidation of a secondary alcohol

(iii) Oxidation of Tertiary Alcohols.

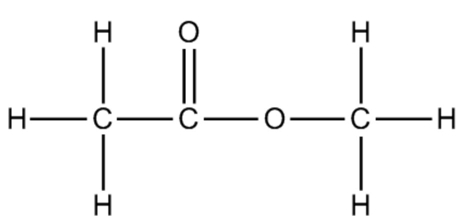
Tertiary alcohols cannot be oxidised. No reaction occurs with acidified potassium dichromate; the oxidising agent remains the same colour, orange.

<u>2.2.1 (g) – Esterification</u>.

When an alcohol reacts with a carboxylic acid in the presence of a concentrated acid catalyst an ester is formed. The reaction is called <u>**esterification**</u>. Esters have the functional group –COO-



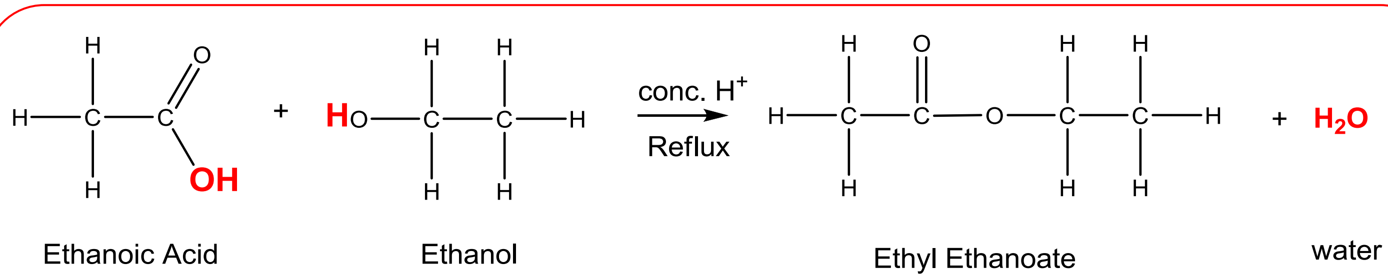
e.g. methyl ethanoate



The acid catalyst used during esterification is **concentrated sulfuric acid** (H_2SO_4) which can be abbreviated to H^+.

The general equation for esterification is:

Carboxylic Acid + Alcohol → Ester + Water



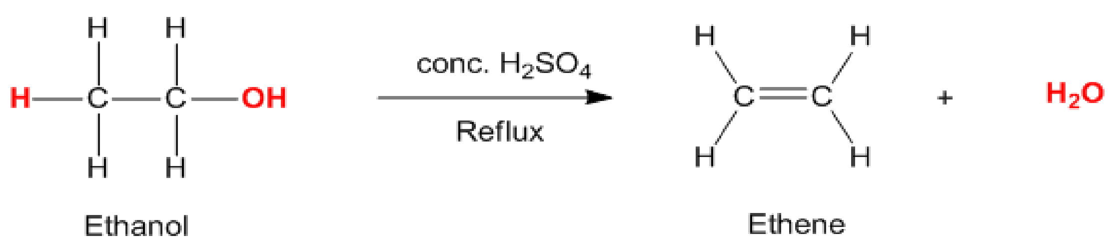
Esterification reaction between ethanoic acid and ethanol

During esterification water is produced from the -OH of the carboxylic acid and the -H from the alcohol. Esters have a fruity aroma and are used for flavourings and fragrances in food and perfumes. They are also are used as adhesives and solvents in the chemical industry.

2.2.1 (h) – Elimination of Water from Alcohols.

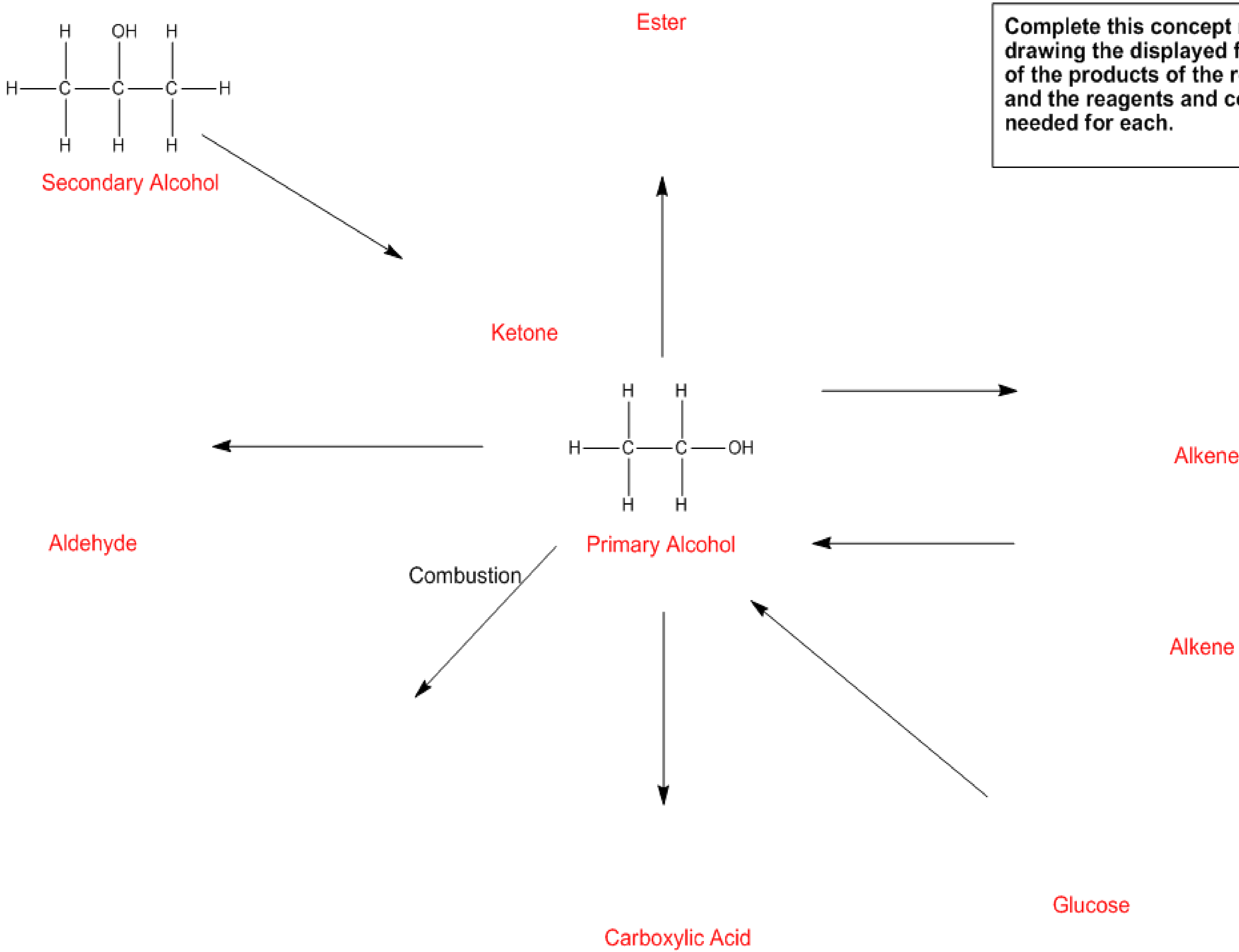
Alcohols can be dehydrated (lose water) to form an alkene by heating them with a catalyst. The reaction mechanism for this reaction is called ***elimination***.

The catalyst used in ***concentrated*** **phosphoric acid (H_3PO_4)** or ***concentrated*** **sulfuric acid (H_2SO_4).** The alcohol is heated under reflux to produce an alkene.



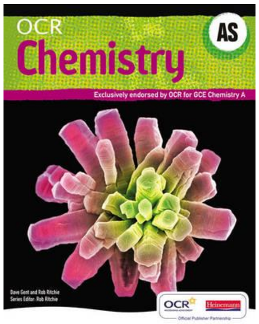
Elimination of water from ethanol

Complete this concept map by drawing the displayed formula of the products of the reactions and the reagents and condituon needed for each.



Additional Reading.

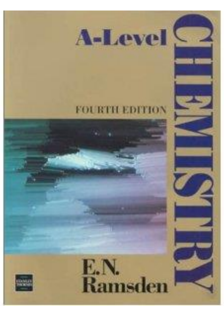
1. OCR Chemistry AS textbook (Heinemann) pages 148-155



2. www.chemguide.co.uk

http://goo.gl/MJQ8X

3. A-level Chemistry (Google Books)



http://goo.gl/z659l

4. www.knockhardy.org.uk

http://goo.gl/1SyD8 - notes
http://goo.gl/z9NsM - PowerPoint