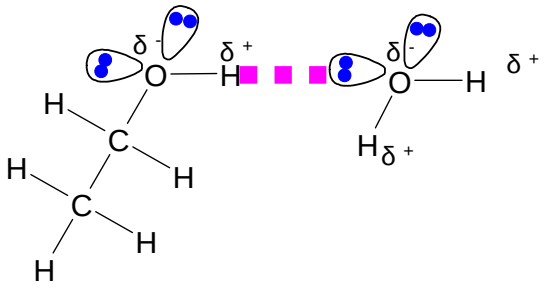
4.2.1 Alcohols

General formula alcohols $C_nH_{2n+1}OH$

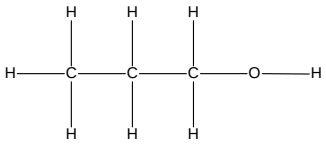
The alcohols have relatively low volatility due to their ability to form hydrogen bond between alcohol molecules.



The smaller alcohols (up to 3 carbons) are soluble in water because they can form hydrogen bonds with water. The longer the hydrocarbon chain the less soluble the alcohol.

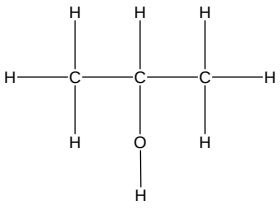
Uses of alcohols
Ethanol is 'alcohol' in alcoholic drinks. Ethanol is commonly used as a solvent in the form of methylated spirits. Methanol is used as a petrol additive to improve combustion and is increasing important as a feedstock in the production of organic chemicals;

Classifying Alcohols



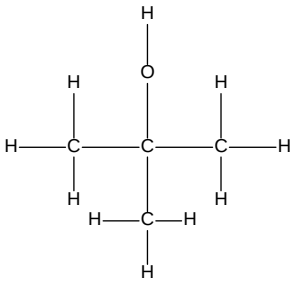
Propan-1-ol
Primary

Primary alcohols are alcohols where 1 carbon is attached to the carbon adjoining the oxygen



Propan-2-ol
Secondary

Secondary alcohols are alcohols where 2 carbon are attached to the carbon adjoining the oxygen



methylpropan-2-ol
Tertiary

Tertiary alcohols are alcohols where 3 carbon are attached to the carbon adjoining the oxygen

Reactions of alcohols

Complete Combustion
In excess oxygen alcohols will burn with complete combustion.

The products of *complete* combustion are CO_2 and H_2O.

$CH_3CH_2OH\ (l) + 3\ O_2(g) \rightarrow 2CO_2(g) + 3\ H_2O(l)$

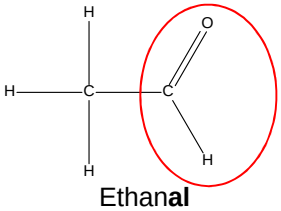
Oxidation reactions of the alcohols

Potassium dichromate $K_2Cr_2O_7$ is an oxidising agent that causes alcohols to oxidise.

The exact reaction, however, depends on the type of alcohol, i.e. whether it is primary, secondary, or tertiary, and on the conditions.

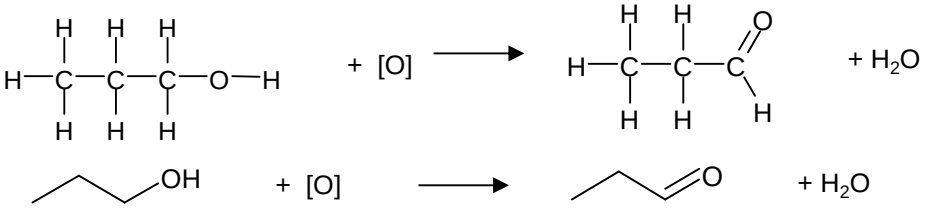
Partial Oxidation of Primary Alcohols

Reaction: primary alcohol → aldehyde
Reagent: potassium dichromate (VI) solution and dilute sulfuric acid.
Conditions: (use a limited amount of dichromate) warm gently and **distil** out the aldehyde as it forms:



Ethan**al**

An aldehyde's name ends in **–al**
It always has the C=O bond on the first carbon of the chain so it does not need an extra number



$CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2CHO + H_2O$

propan-1-ol **propanal**

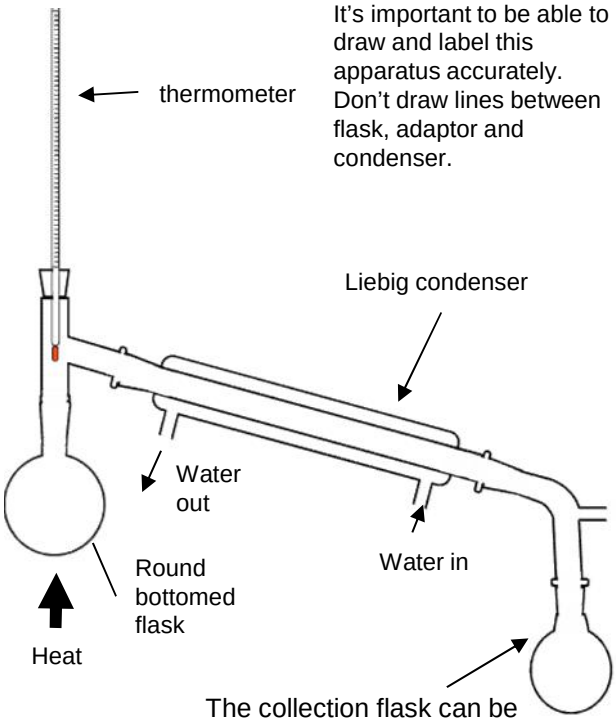
Observation: the orange dichromate ion ($Cr_2O_7^{2-}$) reduces to the green Cr^{3+} ion

Write the oxidation equations in a simplified form using [O] which represents O from the oxidising agent

When writing the formulae of aldehydes in a condensed way write **CHO** and not COH e.g.CH_3CH_2**CHO**

Distillation

In general used as separation technique to separate an organic product from its reacting mixture. In order to maximise yield collected, only collect the distillate at the approximate boiling point of the desired aldehyde and not higher.



It's important to be able to draw and label this apparatus accurately. Don't draw lines between flask, adaptor and condenser.

Note the bulb of the thermometer should be at the T junction connecting to the condenser to measure the correct boiling point

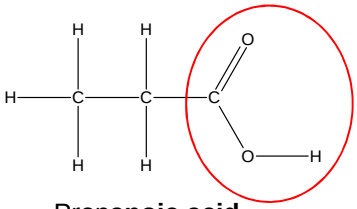
Note the water goes in the bottom of the condenser to go against gravity. This allows more efficient cooling and prevents back flow of water.

Electric heaters are often used to heat organic chemicals. This is because organic chemicals are normally highly flammable and could set on fire with a naked flame.

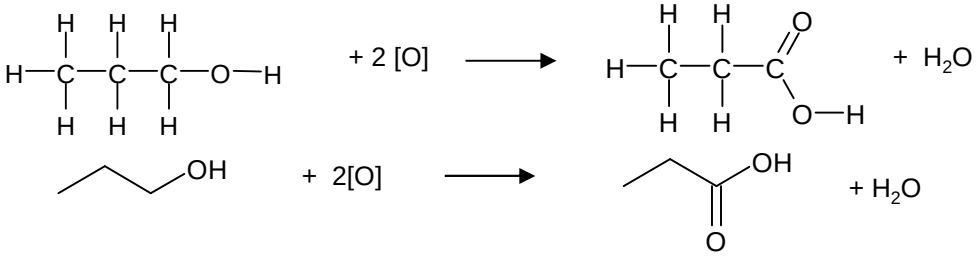
The collection flask can be cooled in ice to help improve the yield of distillate

Full Oxidation of Primary Alcohols

Reaction: primary alcohol → carboxylic acid
Reagent: potassium dichromate(VI) solution and dilute sulfuric acid
Conditions: use an excess of dichromate, and **heat under reflux**: (distil off product after the reaction has finished)



Prop**anoic acid**



$CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2COOH + H_2O$

propan-1-ol **Propanoic acid**

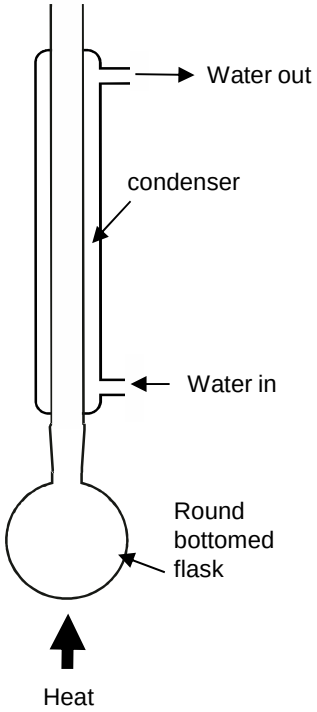
Observation: the orange dichromate ion ($Cr_2O_7^{2-}$) reduces to the green Cr^{3+} ion

Reflux

Reflux is used when heating organic reaction mixtures for long periods. The condenser prevents organic vapours from escaping by condensing them back to liquids.

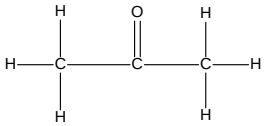
Never seal the end of the condenser as the build up of gas pressure could cause the apparatus to explode. This is true of any apparatus where volatile liquids are heated including the distillation set up.

Anti-bumping granules are added to the flask in both distillation and reflux to prevent vigorous, uneven boiling by **making small bubbles** form instead of large bubbles.



Oxidation of Secondary Alcohols

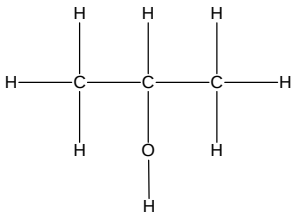
Reaction: secondary alcohol → ketone
Reagent: potassium dichromate(VI) solution and dilute sulfuric acid.
Conditions: heat under reflux



Propan**one**

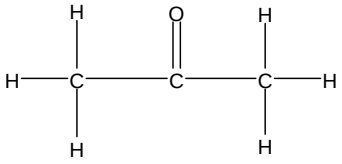
Ketones end in **-one**

When ketones have 5C's or more in a chain then it needs a number to show the position of the double bond. E.g. pentan-2-one



propan-2-ol

+ [O]



Propanone

+ H_2O

Observation: the orange dichromate ion ($Cr_2O_7^{2-}$) reduces to the green Cr^{3+} ion

There is no further oxidation of the ketone under these conditions.

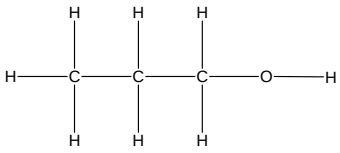
Tertiary alcohols cannot be oxidised at all by potassium dichromate: This is because there is no hydrogen atom bonded to the carbon with the OH group

Reaction of alcohols with dehydrating agents

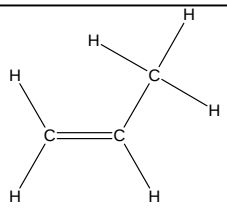
Reaction: Alcohol → Alkene

Reagents: Concentrated sulfuric or phosphoric acid
Conditions: warm (under reflux)
Role of reagent: dehydrating agent/catalyst
Type of reaction: **acid catalysed** elimination

Dehydration reaction: removal of a water molecule from a molecule



propan-1-ol

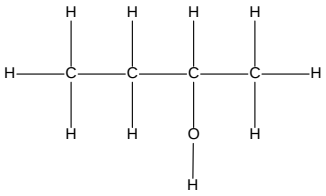


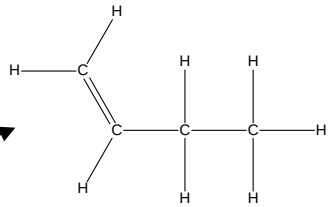
Propene

+ H_2O

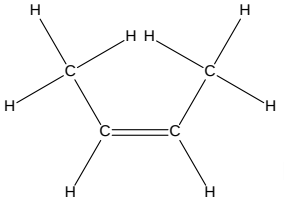
Some 2º and 3º alcohols can give more than one product, when the double bond forms between different carbon atoms

Butan-2-ol





But-1-ene



But-2-ene

Butan-2-ol can form both alkenes although more but-2-ene would be formed

But-2-ene could also exist as E and Z isomers

Substitution reactions of Alcohols to form Haloalkanes

A mixture of a halide ions with concentrated acid NaCl + H_2SO_4 can used for substituting a halogen on to an alcohol

Various other halogenating compounds can be used to substitute the –OH group for a halogen

Reaction: Alcohol → Haloalkane

Reagents: Concentrated sulfuric and sodium halide

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

$CH_3CH_2OH + HCl \rightarrow CH_3CH_2Cl + H_2O$