Topic 2.10

ALCOHOLS

Preparation of ethanol
Ethanol as a biofuel
Elimination reactions of alcohols
Oxidation reactions of alcohols
Tests for aldehydes

ALCOHOLS

Alcohols are saturated molecules containing an –OH group. The H atom in the O-H bond can hydrogen bond with other alcohol molecules and with water, which is why alcohols have relatively high boiling points and many are soluble in water.

Ethanol, C_2H_5OH, is the most commercially important of the alcohols. In pure form it is used as a fuel and as a solvent, and in impure form is present in alcoholic drinks.

1. The manufacture of ethanol

Ethanol can be manufactured industrially in two ways – **fermentation of sugars** and **hydration of ethene**. The method used depends on the desired purity of the ethanol and the availability of the different raw materials in the country where it is manufactured.

i) fermentation of sugars

At 35 – 55 ^{o}C, sugars such as glucose can be fermented by yeast and turned into ethanol and carbon dioxide. This process must be carried out in the absence of air:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

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

Ethanol for human consumption is manufactured during this process. Some ethanol made in this way is also used as fuels in countries such as Brazil, which have an abundant supply of sugar cane.

ii) hydration of ethene

At 300 ^{o}C and 60 atmospheres with a concentrated H_3PO_4 catalyst, H_2O can be added to ethene to make ethanol:

$$C_2H_4 + H_2O \rightarrow C_2H_5OH$$

This process has a number of advantages:

- it is a relatively fast process
- it is a continuous flow process, which means that ethene can be entered into the vessel continuously and the reaction never has to be stopped
- it produces pure ethanol

There are also a number of disadvantages associated with this process:

- it requires fairly high technology
- it uses a lot of energy
- the ethene comes from crude oil, which is a non-renewable resource

Ethanol for use in industry is manufactured during this process.

2. Ethanol as a fuel

Ethanol is a useful fuel; it burns with a clean flame and is increasingly used in cars:

$C_2H_6O(l) + 3O_2(g) \rightarrow 3CO_2(g) + 3H_2O(g)$

If the ethanol used has been produced by fermentation, then it can be classified as a renewable fuel. A fuel derived or produced from renewable biological sources is known as a **biofuel**.

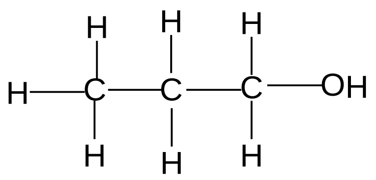
Biofuels are **carbon-neutral**. Although they release carbon dioxide when they are burned, they come from plant sources which absorb carbon dioxide from the atmosphere during photosynthesis while they are growing. Thus there are no net emissions of carbon dioxide during the process from growing to combustion.

3. Primary, secondary and tertiary alcohols

Alcohols can be divided into three classes: primary, secondary and tertiary.

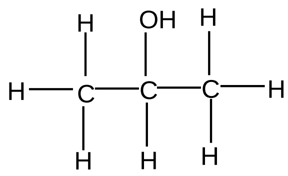
Primary alcohols are those in which the carbon attached to the OH is attached to 0 or 1 other carbon atom. In other words, they are molecules in which the functional group is at the end of the chain.

Eg propan-1-ol



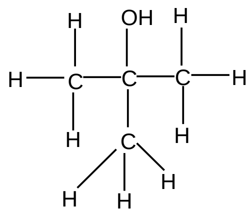
Secondary alcohols are those in which the carbon attached to the OH is attached to 2 other carbon atoms. In other words, they are molecules in which the functional group is not at the end of the chain.

Eg propan-2-ol



Tertiary alcohols are those in which the carbon atom attached to the OH is attached to 3 other carbon atoms. In other words, they are molecules in which the functional group is attached to a carbon which also has a branch attached to it.

Eg 2-methypropan-2-ol



3. Reactions of alcohols

Alcohol molecules are saturated and polar, containing a δ+ve carbon. Thus alcohols tend to undergo nucleophilic substitution reactions.

The OH can combine with an adjacent H atom to form a stable H_2O molecule. Thus alcohols can also undergo **elimination** reactions.

Alcohols can lose hydrogen and undergo a variety of **oxidation** reactions.

a) elimination reactions

Like halogenoalkanes, alcohols can undergo elimination to give alkenes. Since alcohols lose water when they undergo elimination, the reaction is also called dehydration.

The ethanol should be heated and passed over a catalyst (pumice can be used).It can also be refluxed at 180°C with concentrated sulphuric acid.

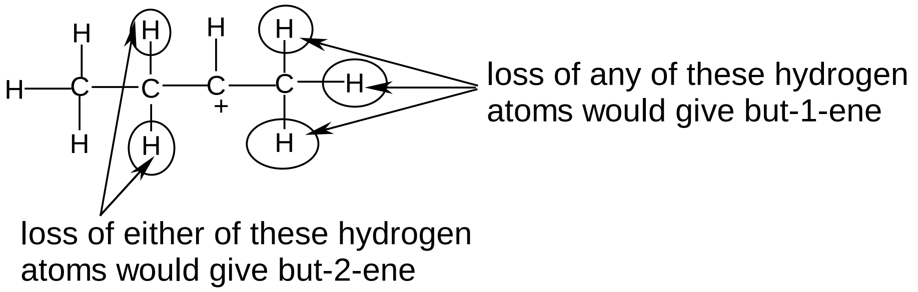
Alkenes produced in this way can be polymerised. This method therefore allows polymers to be produced without using crude oil (assuming that the original ethanol was produced by fermentation).

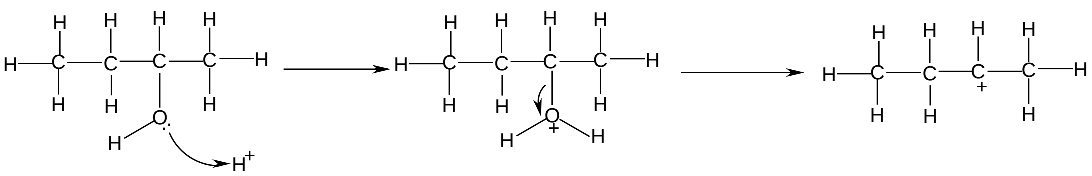
The dehydration of alcohols is favoured by acidic conditions, as the -OH group becomes protonated by H^+ ions which produces a water molecule which then leaves. The acid acts as a catalyst. The detailed mechanism is not required.

The H which is lost comes from a carbon atom which is adjacent to the carbon atom attached to the OH group. In some cases, this can lead to more than one product.

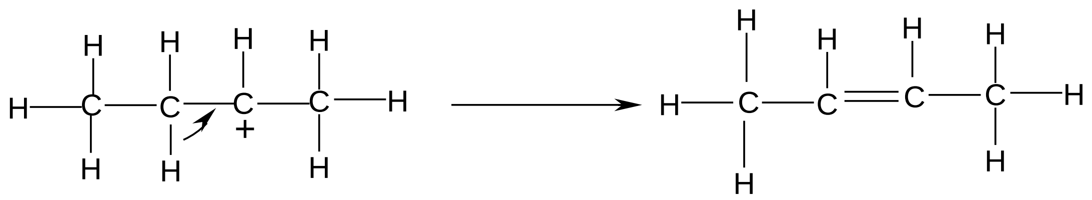
Eg butan-2-ol:

When butan-2-ol undergoes elimination, two different products can be formed depending on which H atom is lost:

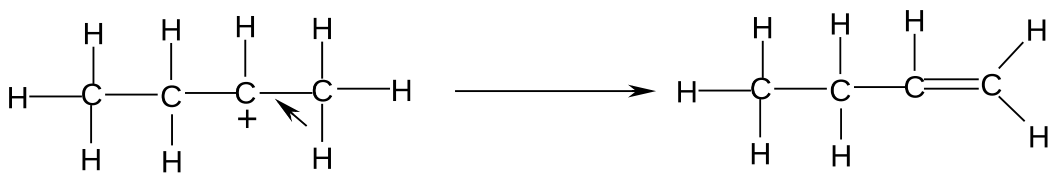




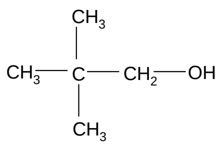
Butan-2-ol → but-2-ene:



Butan-2-ol → but-1-ene



NB Alcohols which have no H atoms on the C atom adjacent to the OH group cannot undergo elimination:

Eg dimethylpropanol: 

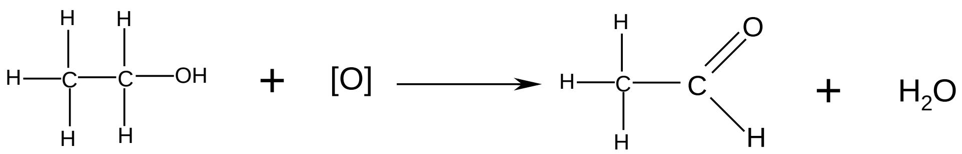
b) oxidation reactions

Oxidation in organic chemistry can be regarded as the addition of oxygen or the removal of hydrogen. As the full equations are quite complex, the oxidising agent is represented by the symbol [O].

a) mild oxidation of primary and secondary alcohols

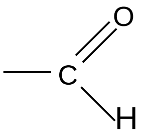
If a **primary alcohol** is mixed with an oxidising agent, two hydrogen atoms can be removed and an **aldehyde** will be formed:

Eg $CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$



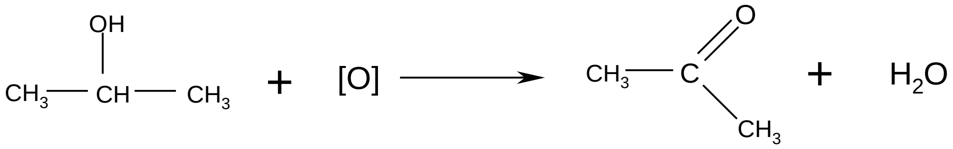
Ethanol Ethanal

An aldehyde is a molecule containing the following group:



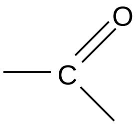
If a **secondary alcohol** is mixed with an oxidising agent, two hydrogen atoms can be removed and a **ketone** will be formed:

Eg $CH_3CH(OH)CH_3$ + [O] → CH_3COCH_3 + H_2O



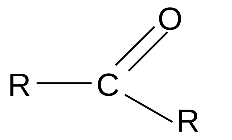
Propan-2-ol propanone

A ketone is a molecule containing the following group:



Tertiary alcohols are not readily oxidised since they do not have available H atoms to give up.

Aldehydes and ketones are collectively known as **carbonyls** and can be represented by the general formula $C_nH_{2n}O$

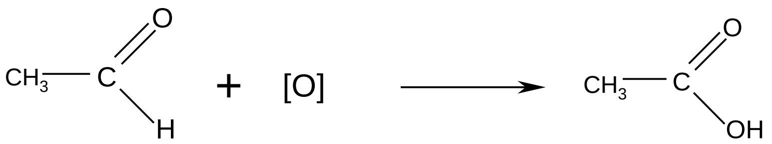


In aldehydes, one of the R groups is a H atom. In ketones, neither of the R groups is a H atom.

b) further oxidation of aldehydes

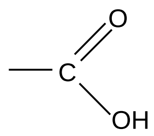
If an **aldehyde** is mixed with an oxidising agent, an oxygen atom can be added to the group and a **carboxylic acid** will be formed:

Eg $CH_3CHO + [O] \rightarrow CH_3COOH$



Ethanal Ethanoic acid

A carboxylic acid is a molecule containing the following group:



Ketones cannot be oxidised into carboxylic acids since there is no C-H bond into which an oxygen atom can be inserted.

c) **reagents and conditions for oxidation**

The oxidising agent most widely used in organic chemistry is potassium dichromate ($K_2Cr_2O_7$) in dilute sulphuric acid (H_2SO_4).
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
The $Cr_2O_7^{2-}(aq)$ ion is orange and the Cr^{3+} ion is green. Thus this reduction process is accompanied by a colour change from orange to green.

If primary alcohols are oxidised, it is possible to form both aldehydes and carboxylic acids. The major product will depend on the conditions used.

Carbonyls are more volatile than alcohols and carboxylic acids, since there is no hydrogen bonding between aldehyde molecules. Thus if a distillation apparatus is used, the volatile aldehyde can be distilled off as it is formed. If reflux apparatus is

used, the aldehyde remains in the reaction vessel and is converted into the carboxylic acid.
Thus distillation apparatus should be used to make carbonyls and reflux apparatus should be used to make carboxylic acids. Heat and an excess of the oxidising agent also improve the yield of carboxylic acid.

Secondary alcohols are oxidised to make ketones only. The distillation apparatus is still favoured since the ketone is volatile so can be distilled off as it is formed.

Thus the oxidation reactions of alcohols and aldehydes can be summarised as follows:

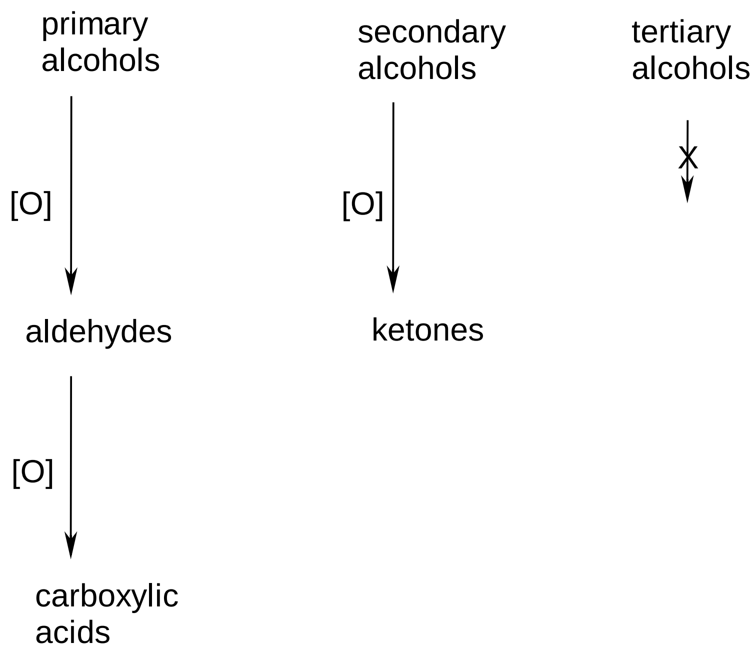
$R\text{-}CH_2OH + [O] \rightarrow R\text{-}CHO + H_2O$ (primary alcohol → aldehyde)
$K_2Cr_2O_7$, H_2SO_4, mild conditions, distillation.

$R\text{-}CH_2OH + 2[O] \rightarrow R\text{-}COOH + H_2O$ (primary alcohol → carboxylic acid)
Excess $K_2Cr_2O_7$, H_2SO_4, heat, reflux

$R\text{-}CHO + [O] \rightarrow R\text{-}COOH$ (aldehyde → carboxylic acid)
Excess $K_2Cr_2O_7$, H_2SO_4, heat, reflux

$R_1\text{-}CH(OH)\text{-}R_2 + [O] \rightarrow R_1\text{-}CO\text{-}R_2 + H_2O$ (secondary alcohol → ketone)
$K_2Cr_2O_7$, H_2SO_4, heat, distillation

Summary of oxidation reactions of alcohols and carbonyls



4. Tests to distinguish between aldehydes and ketones

a) Tollen's reagent

Aldehydes and ketones can be distinguished by their reaction with ammoniacal silver nitrate (known as Tollen's reagent). Aledehydes are reducing agents since they can be oxidised to carboxylic acids, but ketones are not reducing agents. **Ammoniacal silver nitrate, or Tollen's reagent, is an oxidising agent and will react with aldehydes on boiling**:

In the presence of aldehydes, the colourless Ag^{+} ions are reduced to metallic silver, which forms on the surface of the test tube.

The presence of a "silver mirror" indicates that an aldehyde is present.

b) Fehling's solution

Aldehydes and ketones can also be distinguished by their reaction with Fehling's solution. Fehling's solution is a complex solution containing Cu^{2+} ions. Aldehydes are reducing agents but ketones are not. Cu^{2+} is an oxidising agent and will react with aldehydes on heating.

In the presence of aldehydes, the blue Cu^{2+} is reduced to the red copper (I) oxide, Cu_2O.

The presence of a brick red precipitate of Cu_2O indicates that an aldehyde is present.

5. Summary of reactions of alcohols and carbonyls

Primary alcohol → aldehyde Reagent: potassium dichromate and dilute sulphuric acid Conditions: warm, distillation Equation: $RCH_2OH + [O] \rightarrow RCHO + H_2O$ Type of reaction: oxidation
Secondary alcohol → ketone Reagent: potassium dichromate and dilute sulphuric acid Conditions: heat, distillation Equation: $R_1CH(OH)R_2 + [O] \rightarrow R_1COR_2 + H_2O$ Type of reaction: oxidation
aldehyde → carboxylic acid Reagent: potassium dichromate and dilute sulphuric acid Conditions: heat, reflux Equation: $R\text{-}CHO + [O] \rightarrow R\text{-}COOH$ Type of reaction: oxidation
Alcohols → alkenes Reagent: concentrated sulphuric acid Conditions: heat Equation: $R_1R_2CHC(OH)R_3R_4 \rightarrow R_1R_2C{=}CR_3R_4 + H_2O$ Type of reaction: elimination