

OCR A Chemistry A-level

Module 4.2: Alcohols, Haloalkanes and Analysis Detailed Notes

This work by [PMT Education](https://www.pmt.education) is licensed under [CC BY-NC-ND 4.0](https://creativecommons.org/licenses/by-nc-nd/4.0/)

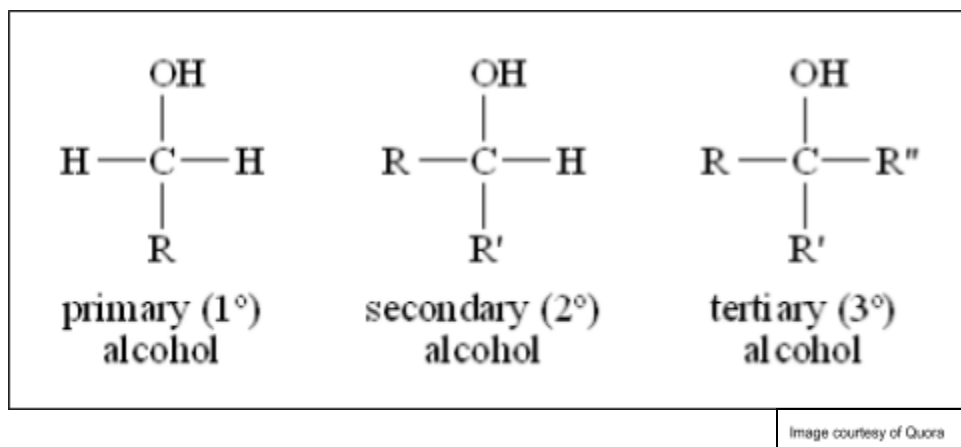




4.2.1 Alcohols

Properties of Alcohols

Alcohols contain an **-OH group** and follow the general formula $C_nH_{2n+1}OH$. They can be produced via two main methods of fermentation or hydration. Alcohols are named according to **IUPAC** rules and have the suffix **-ol**. Alcohols can be **primary (1°)**, **secondary (2°)** or **tertiary (3°)**, depending on the position of the hydroxyl group.



Alcohols are **polar molecules** since there is a large difference in **electronegativity** between carbon and oxygen. The oxygen is very electronegative, so can **hydrogen bond** to water molecules. This ability means that alcohols are **water soluble**.

Hydrogen bonds are a much stronger intermolecular force than van der Waals forces so more energy is required to overcome them. Alcohols have both types of intermolecular force present between molecules, so are much **less volatile** than alkanes which only have van der Waals forces present.

Reactions of Alcohols

Combustion

When burned in air, alcohols react with **oxygen** to form **carbon dioxide** and **water**. Alcohols make good **fuels** by reacting in this way as lots of **energy** is also released.

Example:



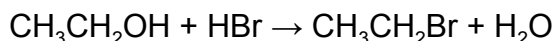


Reactions with Halogenating Agents

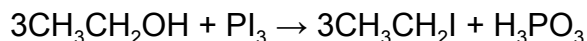
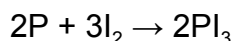
Alcohols can react with **halogenating agents** via **nucleophilic substitution**. The **-OH** group is replaced by a **halogen**, producing a **haloalkane**.

PCl₅ is used to produce **chloroalkanes**. This can be used as a **test for alcohols** because their reaction with PCl₅ produces **white steamy fumes** that turn damp blue litmus paper red.

A reaction mixture of concentrated **sulfuric acid** and **potassium bromide** can be used to produce **bromoalkanes**. The potassium bromide reacts with the sulfuric acid to form HBr. This then reacts with the alcohol to produce the bromoalkane.



A reaction mixture of **red phosphorus** with iodine can be used to produce **iodoalkanes**. First, the phosphorus reacts with the iodine to produce **phosphorus(III) iodide**. This then reacts with the alcohol to form the iodoalkane.



Elimination Reactions

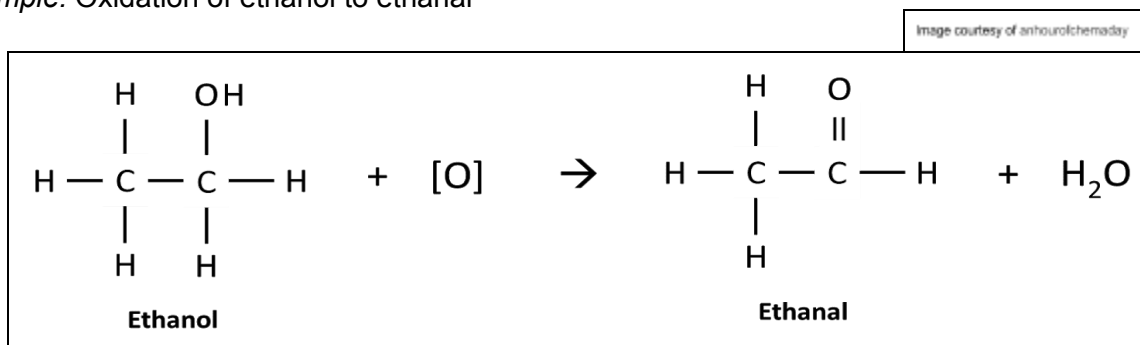
Alkenes can be formed from the **dehydration of alcohols**, where a molecule of **water is removed** from the molecule. In order to do this, the alcohol is heated with **concentrated phosphoric acid**.

Oxidation of Alcohols

Primary and **secondary** alcohols can be **oxidised** to produce various products but **tertiary** alcohols are **not easily oxidised**.

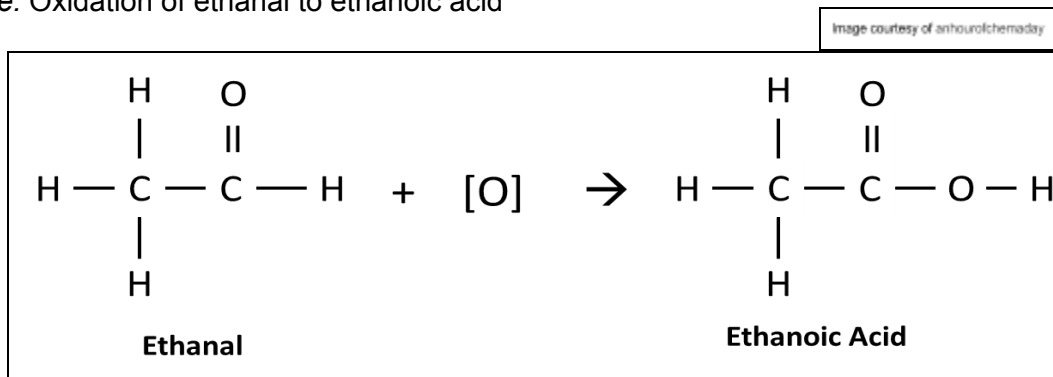
When primary alcohols are heated in the presence of **acidified potassium dichromate(VI)**, they are **oxidised** to aldehydes. **Distillation** is required to separate the **aldehyde** product.

Example: Oxidation of ethanol to ethanal



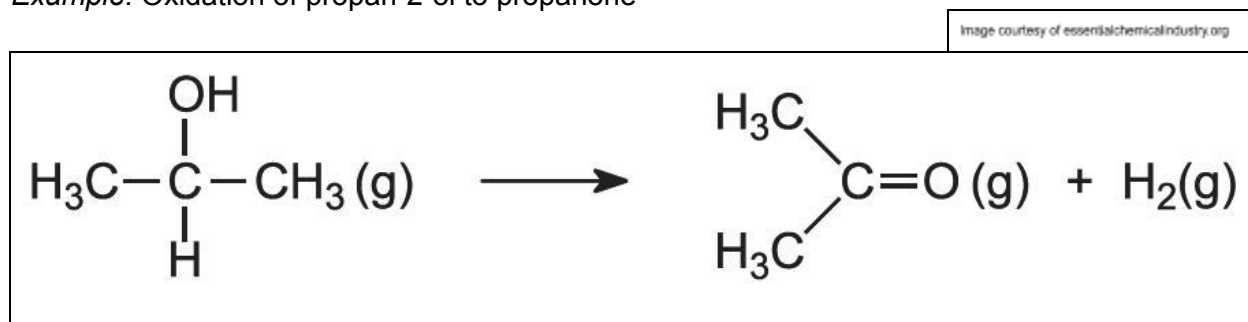
When an aldehyde is heated further with acidified potassium dichromate(VI) under **reflux** conditions, the aldehyde is **oxidised** to produce **carboxylic acids**. This shows primary alcohols are oxidised to aldehydes and then to carboxylic acids.

Example: Oxidation of ethanal to ethanoic acid



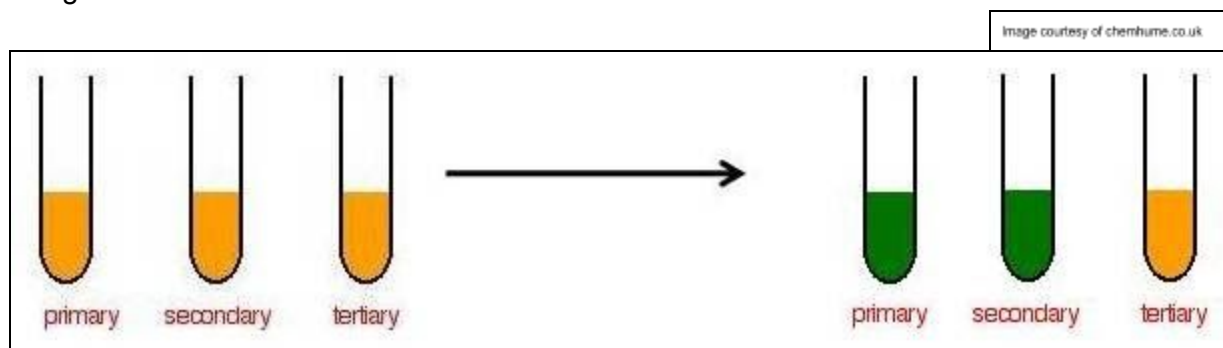
Secondary alcohols can be oxidised to **ketones** when heated in the presence of **acidified potassium dichromate(VI)**.

Example: Oxidation of propan-2-ol to propanone



Potassium Dichromate(VI) ($\text{K}_2\text{Cr}_2\text{O}_7$)

Potassium dichromate(VI) is used in the oxidation of alcohols as the **oxidising agent**. It is reduced as the alcohol is oxidised. A colour change from **orange to green** is observed when the alcohol is oxidised with potassium dichromate(VI). This **colour change** occurs due to a change in **oxidation state** of the **chromium ion**.



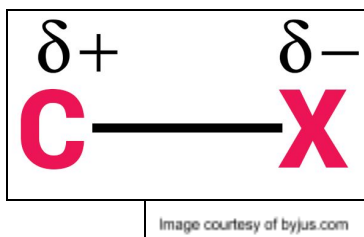


4.2.2 Haloalkanes

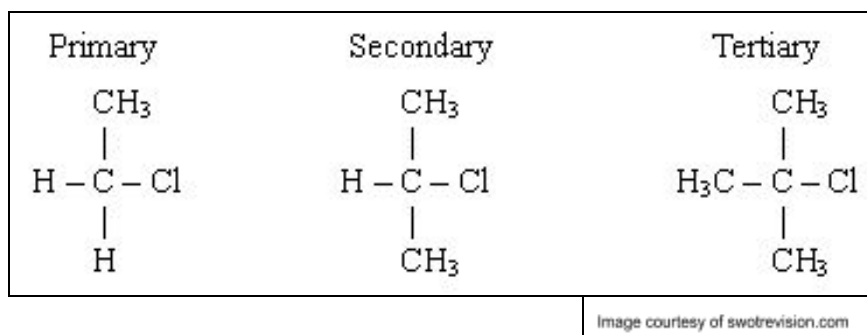
Introduction to Haloalkanes

Haloalkanes contain **polar bonds** since the halogens are more **electronegative** than the carbon atom. This means electron density is drawn towards the halogen, forming **$\delta+$ and $\delta-$ regions**.

Example: The electronegative carbon-halogen bond here X indicates the halogen atom.



Haloalkanes can be classed as **primary, secondary or tertiary** haloalkanes depending on the position of the halogen within the carbon chain.



Relative Reactivity

Reactivity varies depending on the halogen present in the molecule. **Electronegativity** of the halogens **decreases down the group**, meaning that a carbon-fluorine bond is much more **polar** than a carbon-iodine bond. The increased polarity, along with the fact that the carbon-fluorine bond is **shorter**, means that the carbon-fluorine bond is much stronger than the carbon-iodine bond.

The **greater the Mr** of the halogen in the polar bond, the **lower the bond enthalpy**. A lower bond enthalpy means the bond can be **broken** more easily. Therefore, the **rate of reaction increases** for haloalkanes as you move **down** the group.





Substitution Reactions of Haloalkanes

To Produce Alcohols

Haloalkanes can react with an **aqueous alkali**, such as aqueous sodium or potassium hydroxide, to produce **alcohols** in a **nucleophilic substitution** reaction. The **hydroxide ion** acts as a **nucleophile**.

To Produce Alkenes

Haloalkanes can react with **ethanolic potassium hydroxide** (KOH) to produce **alkenes** in an **elimination** reaction. The **hydroxide ion** acts as a **base**.

Hydrolysis with Silver Nitrate

Haloalkanes can be **broken down** in their reaction with **aqueous silver nitrate and ethanol**. The **water** in the solution acts as a **nucleophile** which leads to formation of the alcohol and releases the halide ions into the solution. The **halide ions** then react with the **silver ions** from silver nitrate to form **silver precipitates**.

The **colour** of the precipitate allows you to identify the halide ion present. The rate at which the precipitates form allows you to identify the **relative stability** of the haloalkanes, because the faster the precipitate forms, the **less stable** the haloalkane, and therefore the more quickly it is **hydrolysed**.

| Cl ⁻ | Br ⁻ | I ⁻ |
|--------------------------|--------------------------|--------------------------|
| White precipitate (AgCl) | Cream precipitate (AgBr) | Yellow Precipitate (AgI) |

Reactivity depends on the **strength** of the **C-X bond** (where X is a halogen atom) and not the bond polarity. Bond strength **decreases** with **increasing Mr**. Therefore, iodoalkanes react faster than bromoalkanes and chloroalkanes, and bromoalkanes react faster than chloroalkanes.

Nucleophilic Substitution

Nucleophiles

A nucleophile is an **electron pair donor**. These species are '**positive liking**'. They contain a lone electron pair that is attracted to **δ⁺ regions** of molecules. Some of the most common nucleophiles are:

- CN⁻
- :NH₃
- :OH

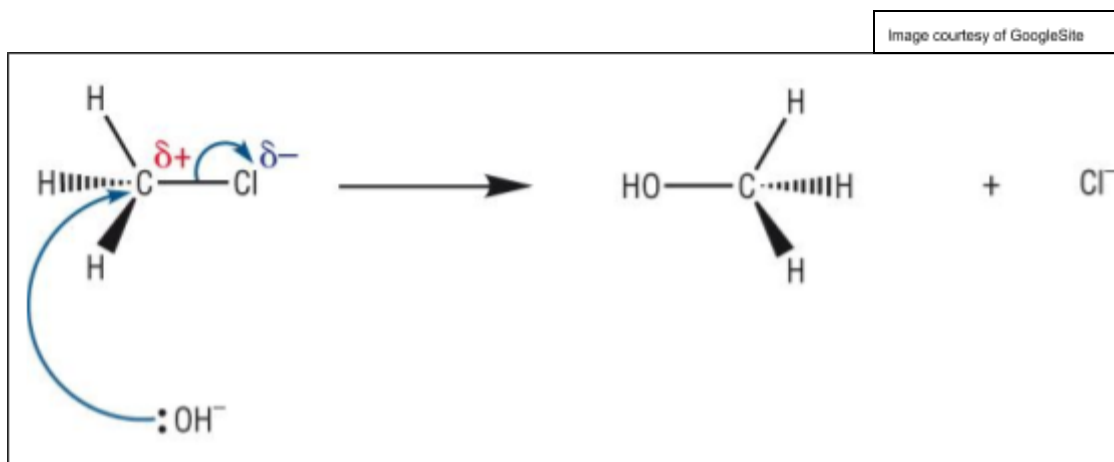




Nucleophilic Substitution Mechanism

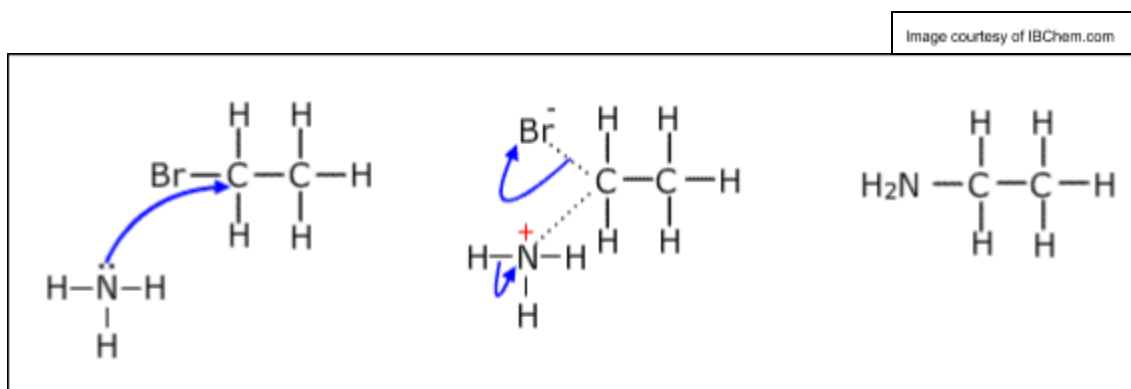
Nucleophilic substitution is the reaction mechanism that shows how **nucleophiles** attack haloalkanes. Aqueous potassium hydroxide is used to produce **alcohols**, potassium cyanide is used to produce **nitriles** and ammonia is used to produce **amines**.

Mechanism - Producing Alcohols



The nucleophile attacks the δ^+ carbon and the electrons are transferred to the chlorine.

Mechanism - Producing Amines



*The intermediate has a positively charged nitrogen (N^+).
Electrons are transferred to the nitrogen by the loss of a hydrogen atom.*

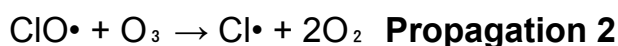
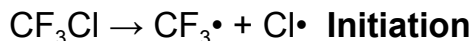
The **greater the Mr** of the halogen in the polar bond, the **lower the bond enthalpy**. This means the bond can be broken more easily. Therefore the rate of reaction for these haloalkanes is faster. Nucleophilic substitution reactions can only occur for **1° (primary) and 2° (secondary)** haloalkanes.





Environmental Concerns from Use of Organohalogen Compounds

Ultraviolet (UV) radiation in the upper atmosphere can cause **CFCs** to produce halogen **radicals**. These radicals catalyse the breakdown of the Earth's protective **ozone** layer. CFCs are **chlorofluorocarbons** - haloalkanes containing carbon, chlorine and fluorine atoms only. The radical mechanism for the breakdown of ozone, **O₃**, is shown below.



The chlorine radical is **regenerated** in the second propagation step, so is **catalytic** in the breakdown of ozone. This means a small amount of CFC released can cause a lot of damage.

4.2.3 Organic Synthesis

Practical Skills

There are many different techniques that can be used to **prepare** and then **purify** an organic compound.

Heating under Reflux

Reflux apparatus is used to **continually heat** the contents of the flask to allow reactions like the **oxidation** of primary alcohols to proceed all the way to the formation of carboxylic acids. The **condenser** helps ensure the vapours condense and **return** to the flask for further heating. This ensures the product vapours can not escape.

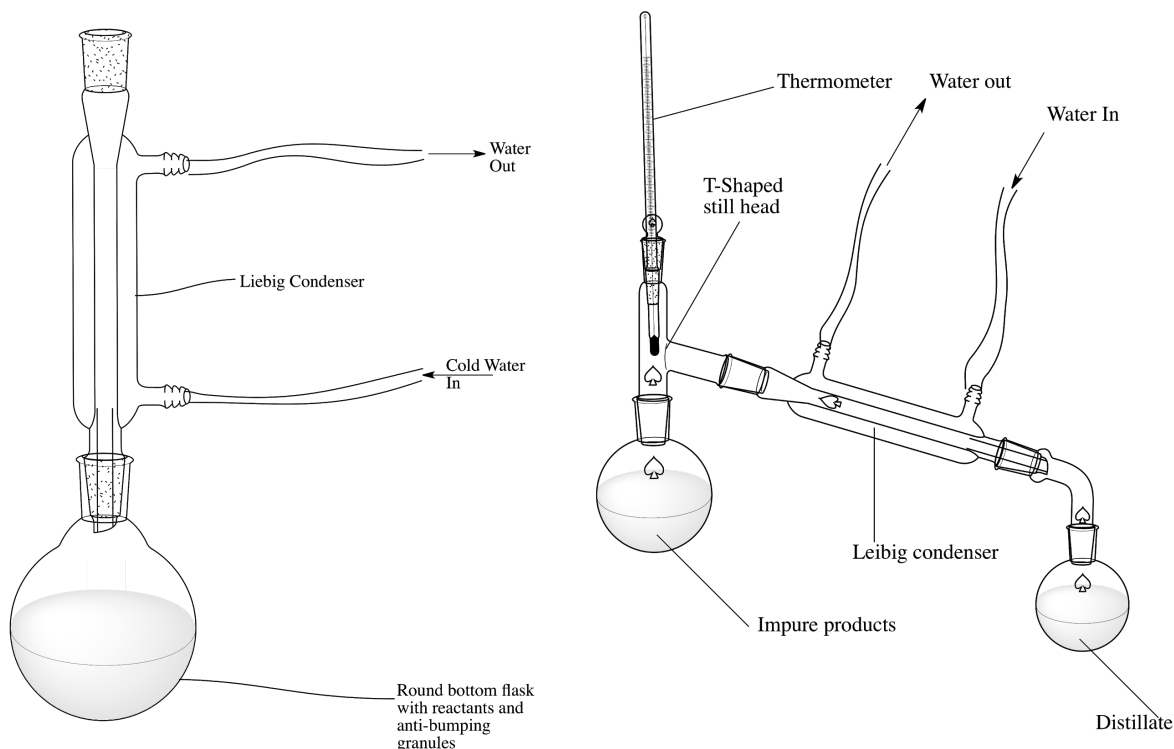
Distillation

Distillation apparatus is used to separate liquids with **different boiling points**. The round-bottomed flask is heated and the liquid with the lower boiling point will **evaporate** first. It rises out of the flask and into the attached tubing which is surrounded by a condenser. The condenser causes the vapour to **cool and condense** back into a liquid, which is then collected in a separate flask.





Diagrams: Reflux apparatus (left) and distillation apparatus (right)



Separating Funnel

A separating funnel is used to separate two liquids with **different densities**. The mixture is added to the flask, and then the flask is stoppered and inverted to mix the contents. The liquids are allowed to **separate** into **two layers**. The tap can then be opened to collect the bottom, denser liquid in one flask and the second, less dense liquid in a second flask. Usually these layers will be distinguished to be an aqueous and an organic layer.

Redistillation

Subsequent distillations can be carried out to obtain a purer product.

Boiling point determination

Determining the boiling point of a compound and comparing it to a databook value is a way of testing the **purity** of a substance. The purer a substance, the **closer** to the databook boiling point value it will be. If a sample has a low purity, the melting or boiling point will take place over a **range** of temperatures.

To determine the boiling point, the substance is packed into a **Thiele tube** which has an **inverted capillary tube** in it. The substance is heated to above its boiling point and allowed to cool. When it **condenses** into a liquid it will be drawn into the capillary tube and the temperature at which this change occurs is taken to be the boiling point.





Drying

A compound can be dried by the addition of an **anhydrous** (contains no water) **salt**. The anhydrous salt will **absorb moisture and water** present, thus drying and purifying the compound. Common anhydrous salts used for drying are **magnesium sulphate** and **calcium chloride**.

Synthetic Routes

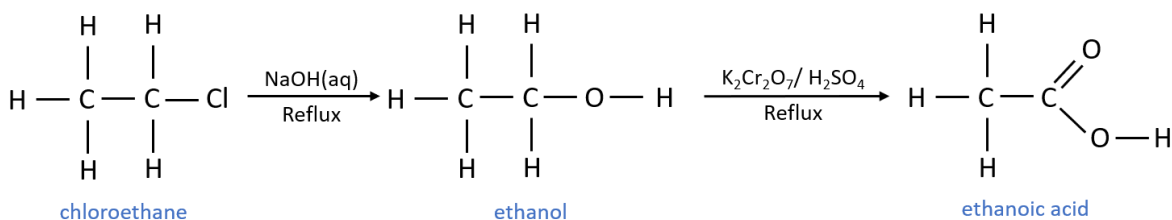
Synthetic routes are the routes which can be used to produce a **certain product from a starting organic compound**. It is important that you understand the different methods and **conditions** required to convert compounds to other products.

Multi-Stage Synthesis

Some organic molecules can be prepared using a **multi-stage synthesis**. Typically, this involves two stages: reactant → intermediate → product. It can cover more stages.

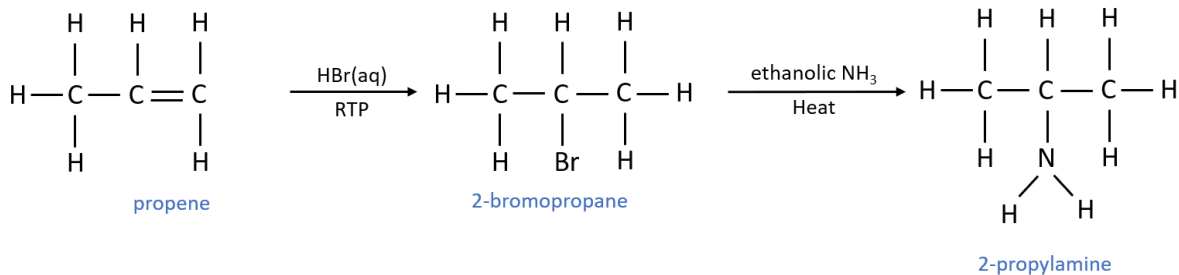
Example 1

Below is a diagram showing how ethanoic acid can be formed from chloroethane:



Example 2

2-propylamine can be formed from propene as follows:



Analysing Synthetic Routes

When **synthesising** an organic compound, several factors are considered before deciding which synthetic route to use:

- **Type of reaction** - addition reactions are more sustainable than substitution or elimination reactions as there are no waste products.
- **Reagents** - renewable reagents with few safety concerns are preferred.
- **By-products** - less harmful by-products are favoured as there would be fewer safety and environmental concerns. If the by-products can be used in another industry, the process is more sustainable.
- **Conditions** - choose the reaction with the most energy efficient and safe conditions.

Identification of Functional Groups

Individual **functional groups** covered in this module can be identified through various tests as described in their sections above. These include:

- Test for unsaturation - bromine water
- Test for 1°/2° alcohols - acidified potassium dichromate(vi)
- Test for aldehydes - Tollens' reagent
- Test for haloalkanes - aqueous silver nitrate with ethanol

4.2.4 Analytical Techniques

Infrared Spectroscopy

Infrared (IR) radiation causes **covalent bonds** to **vibrate** and absorb energy.

Infrared spectroscopy is an analytical technique that uses **infrared (IR) radiation** to determine the **functional groups** present in organic compounds.

The IR radiation is passed through a sample where the different types of bonds **absorb** the radiation in different amounts. These varying amounts of absorbance are **measured and recorded**, allowing certain bonds, and thus functional groups, to be identified.

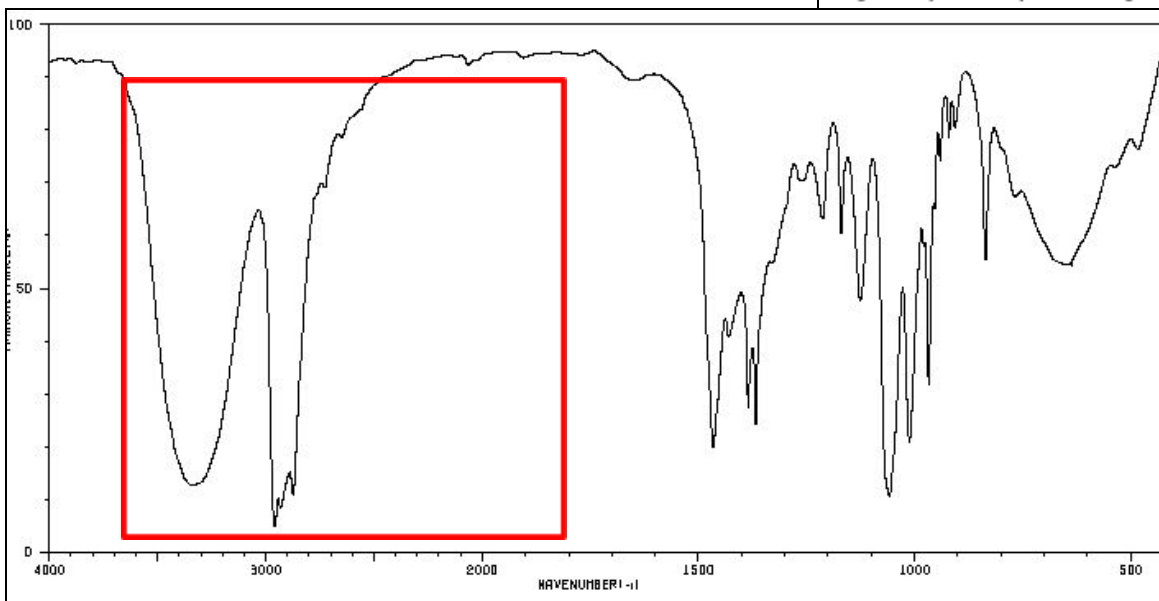
A **spectrum** is produced from the measurements, which has **characteristic curves** for the different functional groups:





-OH Alcohol Group

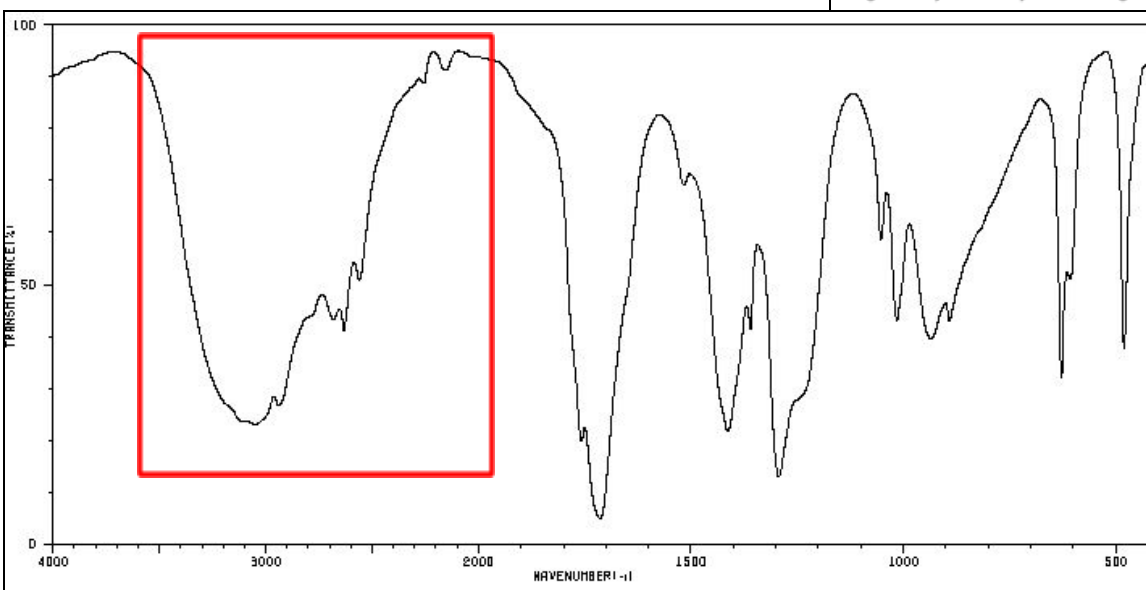
Image courtesy of Chemistry Stack Exchange



*The characteristic -OH alcohol group peak is in the range $3230 - 3550 \text{ cm}^{-1}$.
It is a broad, curved peak.*

-OH Acid Group

Image courtesy of Chemistry Stack Exchange

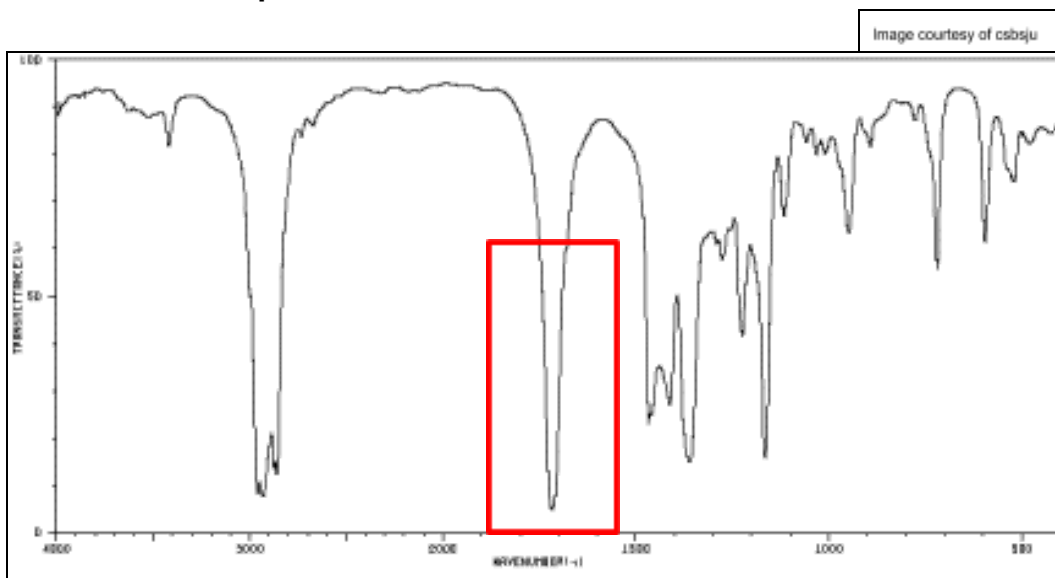


*The characteristic -OH acid group peak is in the range $2500 - 3300 \text{ cm}^{-1}$.
It overlaps with the C-H region, hence the peak is not a smooth curve.*



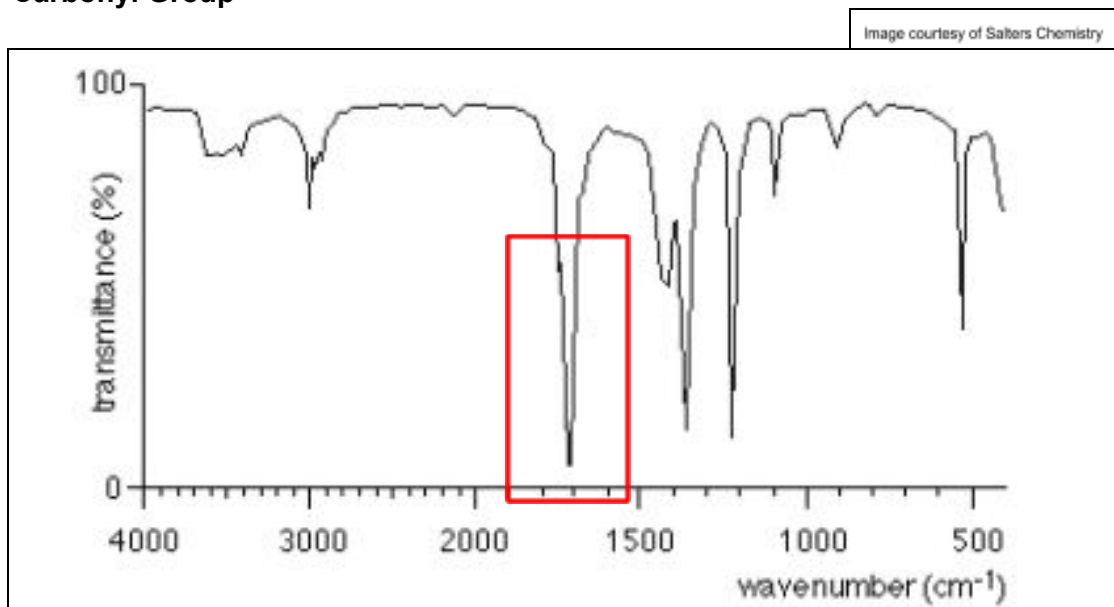


C=C Unsaturated Group



The characteristic C=C peak is in the range **1620-1680 cm⁻¹**.
It is a sharp peak.

C=O Carbonyl Group



The characteristic C=O peak is in the range **1680-1750 cm⁻¹**.
It is a sharp peak.



Interpreting IR Spectra

An infrared spectrum of an organic compound can be used to **identify** any **functional groups** present:

- An **alcohol** from an absorption peak of the O–H bond.
- An **aldehyde** or **ketone** from an absorption peak of the C=O bond.
- A **carboxylic acid** from an absorption peak of the C=O bond and a broad absorption peak of the O–H acid bond.
- Most organic compounds will produce a peak at approximately 3000 cm^{-1} due to absorption by C–H bonds.

Fingerprint Region

Each IR spectrum has a **fingerprint region** on the right-hand side, from $500\text{-}1500\text{ cm}^{-1}$. This is unique for each species, containing **tiny differences** between each species. This means it acts as a molecules' 'fingerprint', allowing it to be **identified**.

Environmental

There is a link between the absorption of infrared radiation by **atmospheric gases** containing C=O, O–H and C–H bonds (e.g. CO_2 , H_2O and CH_4), and **global warming**. As a result, there is a need for changes to be made to **renewable** energy resources.

Uses of Infrared Spectroscopy

IR spectroscopy can be used to monitor gases causing **air pollution** (e.g. CO and NO from car emissions) and in modern breathalysers to measure ethanol in people's breath.

Mass Spectrometry

Mass spectrometry is an **analytical technique** used to identify different molecules and find the overall relative molecular mass.

Time of Flight (TOF) Mass Spectrometry

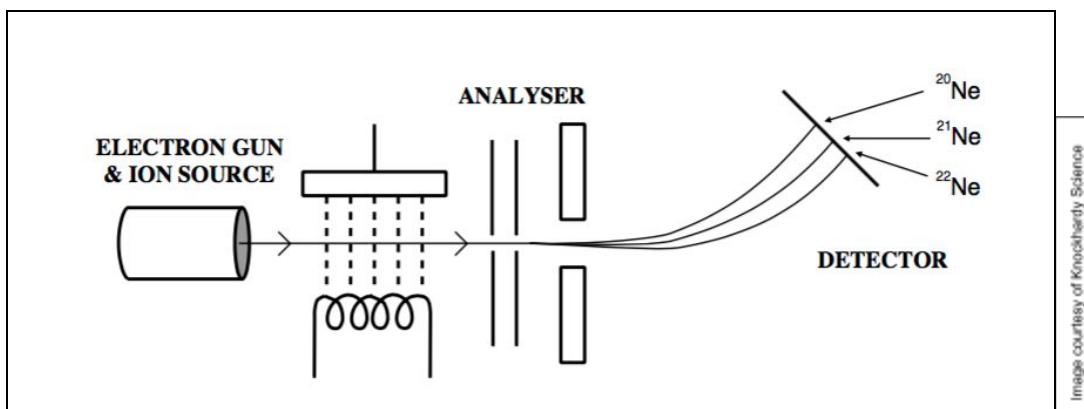
TOF mass spectrometry records the time it takes for ions to reach a detector. Using this, **spectra** can be produced showing **each isotope present along with their relative abundances**.

1. **Ionisation** - A sample is **vaporised** and injected into the mass spectrometer where a **high voltage** is passed over the chamber. This causes electrons to be removed from the atoms (they are ionised) leaving **+1 charged ions** in the chamber.





- Acceleration** - These positively charged ions are then **accelerated** towards a negatively charged **detection plate**.
- Ion Drift** - The ions are then deflected by a **magnetic field** into a **curved path**. The radius of the path is dependent on the charge and mass of the ion.



- Detection** - When the positive ions hit the negatively charged detection plate, they **gain an electron**, producing a **flow of charge**. The greater the current produced, the greater the abundance of that particular ion.
- Analysis** - The current values are then used in combination with the **flight times** to produce a **spectra print-out** with the relative abundance of each isotope displayed.

Using this print-out spectra, the **M_r** (relative molecular mass) **can be calculated** by looking at the **m/z** value of the **molecular ion peak**. This is the peak that is furthest to the right on the spectrum.

The mass spectra of organic compounds may contain a very small **$M+1$ peak** (one greater than the molecular ion peak) from the small proportion of **carbon-13** isotopes present.

Fragmentation

Sometimes organic compounds **fragment** in the mass spectrometer. This means that peaks at **smaller m/z** values than the molecular ion peak appear on the **spectrum**. The molecular ions break down into a **fragment ion** and a **radical**. The radical is uncharged so is not detected. The **m/z** value of a fragment peak can be used to suggest the **M_r** and **structure** of a fragment ion.

Combined Techniques

The **analytical techniques** covered in this chapter can be used together to **predict** the structure of unknown compounds. A combination of **functional group tests**, **infrared spectroscopy** and **mass spectrometry** can be used to identify organic structures.

