

Edexcel IAL Chemistry A-level

Topic 10: Organic Chemistry: Halogenoalkanes, Alcohols and Spectra Detailed notes

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Topic 10A: General Principles

Classification of Reactions

Reactions can be classified according to what happens to the reactants during the reaction and the identity of the end products. The **polarity** of a bond will influence the types of reactions it may undergo. The main types of reactions are:

- **Addition** - In an addition reaction the reactants combine to form a **single product**.
- **Elimination** - In an elimination reaction a pair of atoms or two groups of atoms are **removed** from a molecule.
- **Substitution** - In a substitution reaction one functional group is **replaced** with a **different functional group**.
- **Oxidation** - A species **loses** at least one electron and is oxidised.
- **Reduction** - A species **gains** at least one electron and is reduced.
- **Hydrolysis** - A reaction in which a molecule is **broken down** by its reaction with **water**.
- **Polymerisation** - A reaction in which many small molecules known as **monomers** join together to form a long, repeating molecule called a **polymer**.

Mechanisms

Reaction mechanisms show the **movement of electrons** within a reaction. The movement of electrons is indicated by **curly arrows**. The mechanisms show how this movement of electrons results in the formation of products from reactants.

Bond breaking

Reactions involve the **rearrangement of atoms and bonds** and therefore require breaking and making bonds. There are two types of covalent bond breaking: **homolytic** and **heterolytic**.

In **heterolytic fission** one atom receives both electrons from the breaking of the covalent bond, while the other atom receives none. This bond-breaking forms **ions**: the atom that gains both of the electrons will form a negative ion and the other atom will form a positive ion.

This, therefore, forms one **electrophile** (the positive ion) and one **nucleophile** (the negative ion).

Electrophile: A species that can **accept electrons** in a reaction, to form a chemical bond.

Nucleophile: A species that can **donate electrons** in a reaction, to form a chemical bond.

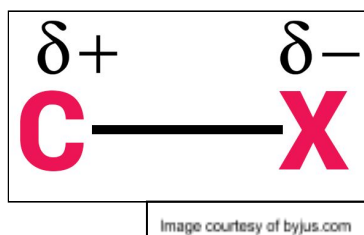


Topic 10B: Halogenoalkanes

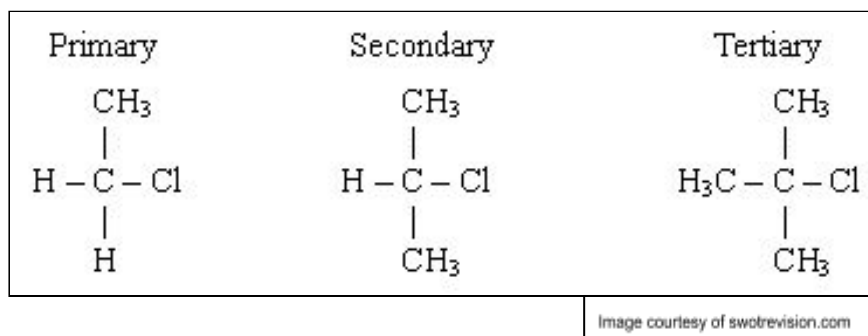
Introduction to Halogenoalkanes

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

Example:



Halogenoalkanes can be classed as **primary, secondary or tertiary** halogenoalkanes 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. Along with the fact that the carbon-fluorine bond is **shorter**, this 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 halogenoalkanes as you move **down** the group.

Nomenclature

Halogenoalkanes are named using **halogen prefixes** and **alkane stems**.

Prefixes:

Halogen functional group	Prefix
Fluorine	Fluoro-
Chlorine	Chloro-
Bromine	Bromo-
Iodine	Iodo-



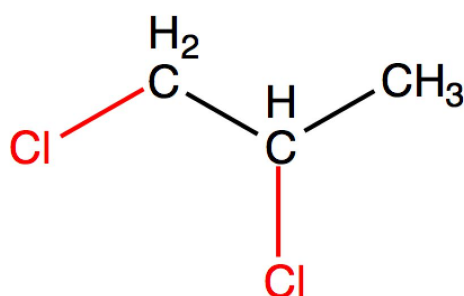
Stem:

Number of C atoms	Prefix	Alkane example
1	Meth-	Methane
2	Eth-	Ethane
3	Prop-	Propane
4	But-	Butane
5	Pent-	Pentane
6	Hex-	Hexane
7	Hept-	Heptane
8	Oct-	Octane
9	Non-	Nonane
10	Dec-	Decane

If more than one particular side chain or functional group is present then one of the following prefixes is added: **di-** (2), **tri-** (3), **tetra-** (4), etc.

If multiple prefixes are present, they are included in **alphabetical order**.

Example: The skeletal structure of 1,2-dichloropropane



Reactions of Halogenoalkanes

To produce Alcohols

Halogenoalkanes can react with **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

Halogenoalkanes 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



Halogenoalkanes 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 the breaking down of the halogenoalkane, releasing 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 forms allows you to identify the **relative stability** of the halogenoalkanes, because the faster the precipitate forms, the **less stable** the halogenoalkane, 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 would react faster than bromoalkanes and chloroalkanes, and bromoalkanes would react faster than chloroalkanes.

To produce Amines

Halogenoalkanes can react with **alcoholic ammonia** (for example, with ethanolic NH_3) to form **amines** in a **nucleophilic substitution** reaction. **Ammonia** acts as a **nucleophile**.

To produce Nitriles

Halogenoalkanes can react with **alcoholic potassium cyanide** (KCN) to form **nitriles** in a **nucleophilic substitution** reaction. The **cyanide ion, CN^-** , acts as a **nucleophile**. This reaction adds on a carbon atom, so it can be used in synthesis routes to increase the length of carbon chains.

Nucleophilic Substitution

Nucleophiles

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^-
- :NH_3
- :OH^-

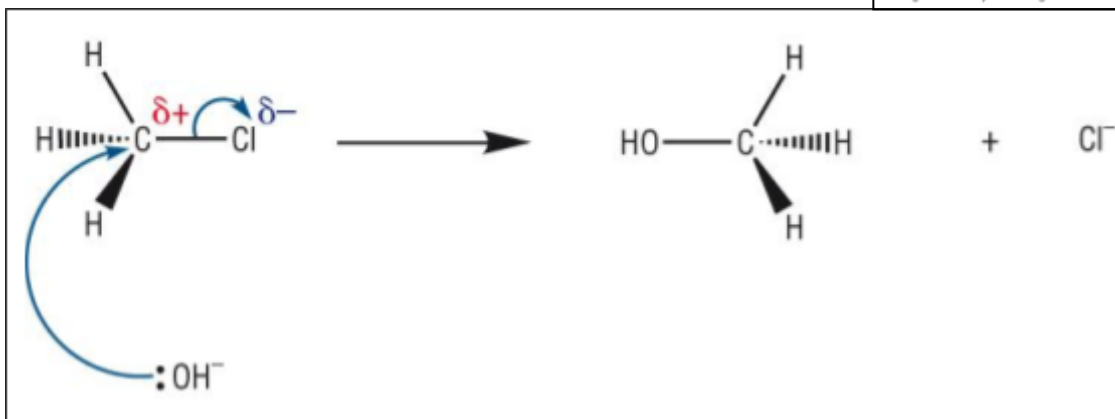
They must be shown with the **lone electron pair** to make it clear that they are nucleophiles.



Nucleophilic Substitution

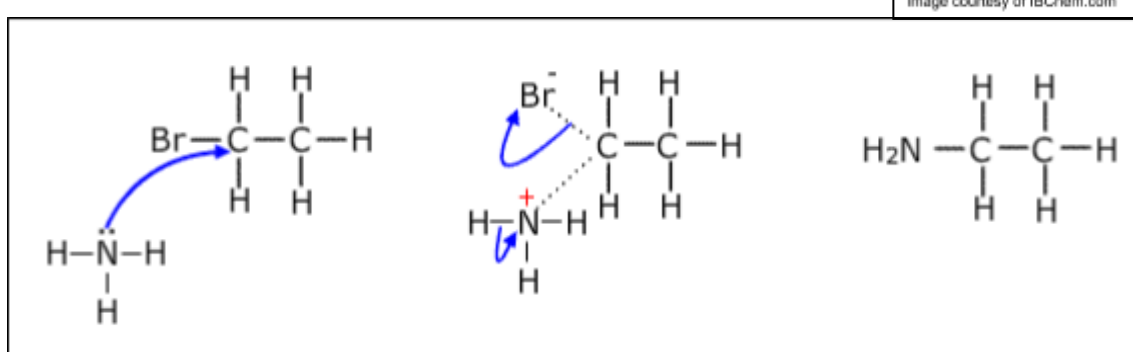
Nucleophilic substitution is the reaction mechanism that shows how nucleophiles attack halogenoalkanes. From halogenoalkanes, aqueous potassium hydroxide is used to produce **alcohols**, potassium cyanide is used to produce **nitriles** and ammonia is used to produce **amines**.

Mechanism: Alcohol



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

Mechanism: Amines



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

Nucleophilic substitution reactions can only occur for **primary** and **secondary** alkanes.

10C: Alcohols

Introduction to 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.



Example:

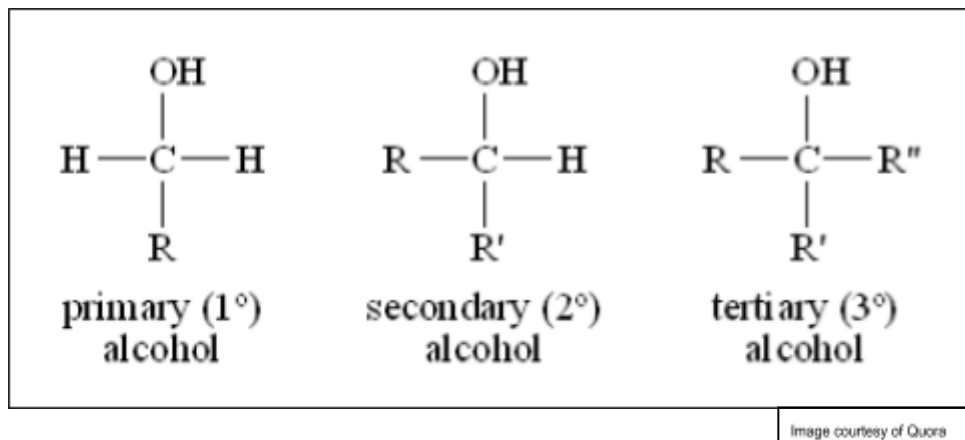
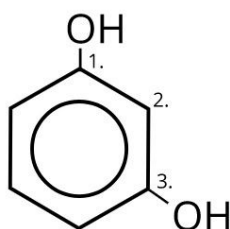


Image courtesy of Quora

Example: Benzene-1,3-diol



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.

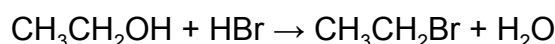


Reactions with Halogenating Agents

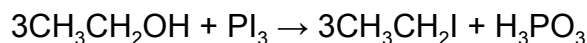
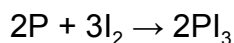
Alcohols can react with **halogenating agents** via **nucleophilic substitution**. The **-OH** group is replaced by a **halogen**, producing a **halogenoalkane**.

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 50% 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, **concentrated phosphoric acid** is added as a reagent.

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:

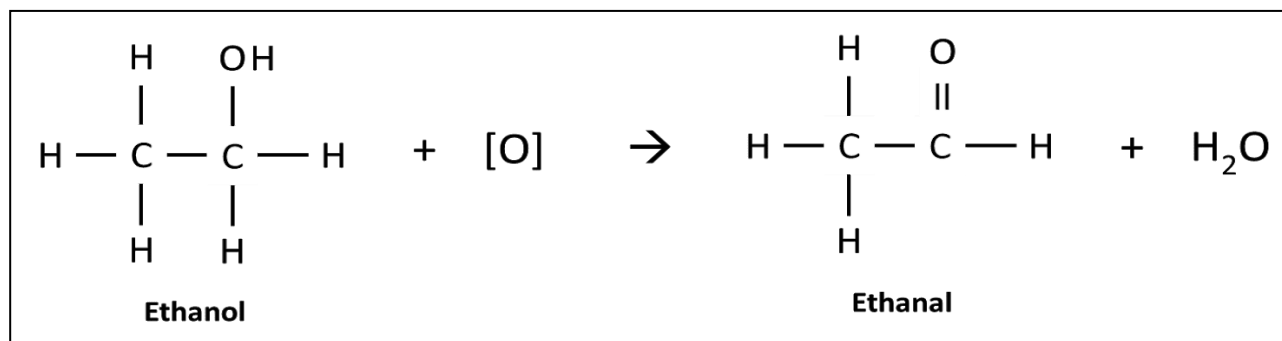


Image courtesy of anhourofchemaday

When heated further under **reflux** conditions, primary alcohols are **oxidised further** to **carboxylic acids**.

Example:

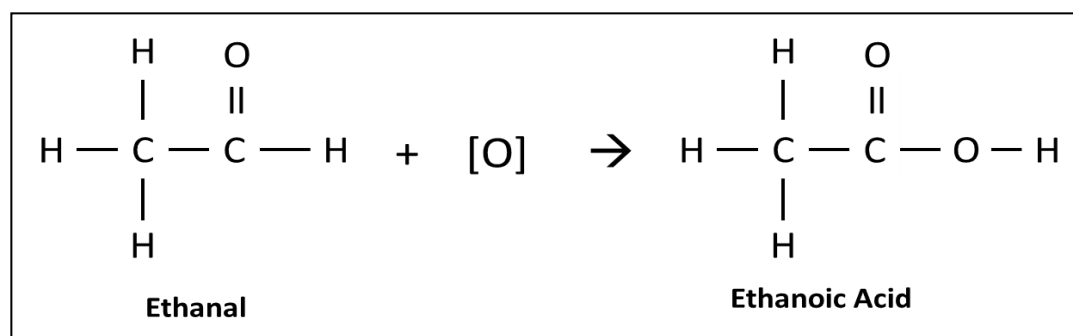


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Secondary alcohols can be oxidised when heated in the presence of **acidified potassium dichromate(VI)** to produce **ketones**.

Example:

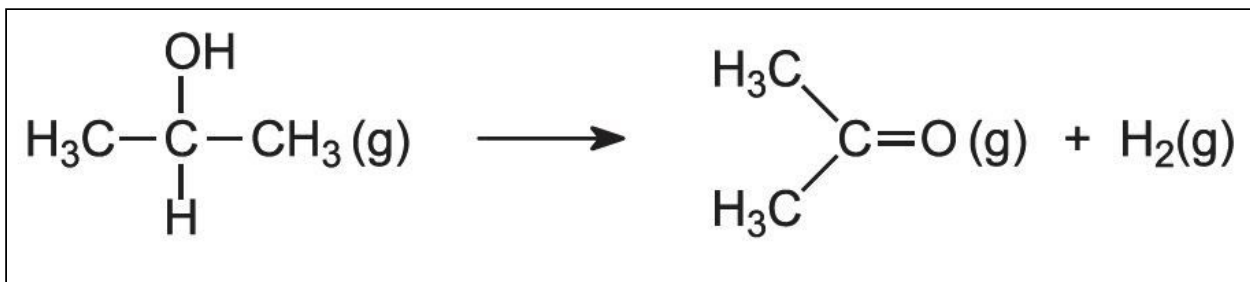


Image courtesy of essentialchemicalindustry.org

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).

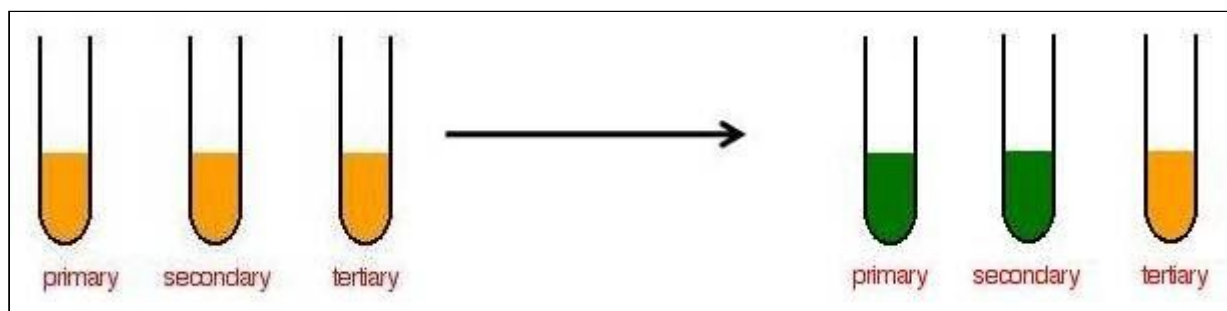


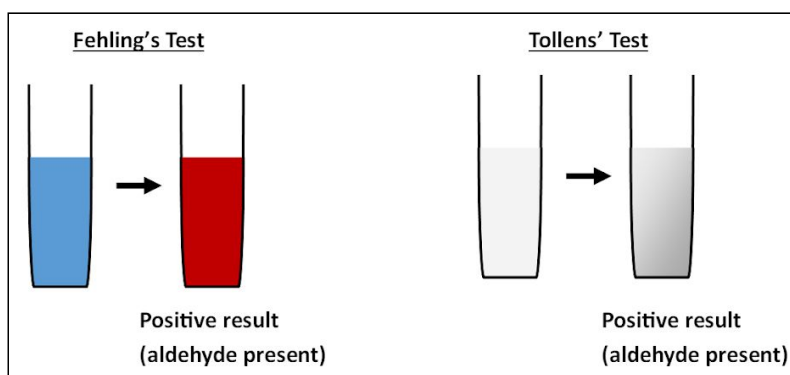
Image courtesy of chemhume.co.uk

Test for Aldehydes

Aldehydes are tested for using **Tollen's reagent** or **Fehling's solution**.

A few drops of **Fehling's solution** are added and the test tube is gently warmed. If an aldehyde is present a **red precipitate** will form. If no aldehyde is present the solution will remain **blue**.

Aldehydes can be identified in the same way using **Tollen's reagent**. If an aldehyde is present a layer of silver will form on the walls of the test tube. If no aldehyde is present the solution will remain colourless.



Ketones will not give a positive result with either of these tests.

Test for Carboxylic Acids

Carboxylic acids react with metal carbonates to form a **salt** and **carbon dioxide** gas.

Sodium carbonate or **sodium hydrogencarbonate** can be used to identify the presence of a carboxylic acid from the complete oxidation of primary alcohols. A salt will form and the solution will **effervesce** as a gas is released. If this carbon dioxide gas is bubbled through **limewater** it will cause the limewater to turn **cloudy** due to the formation of a white precipitate.

Experimental Techniques

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.

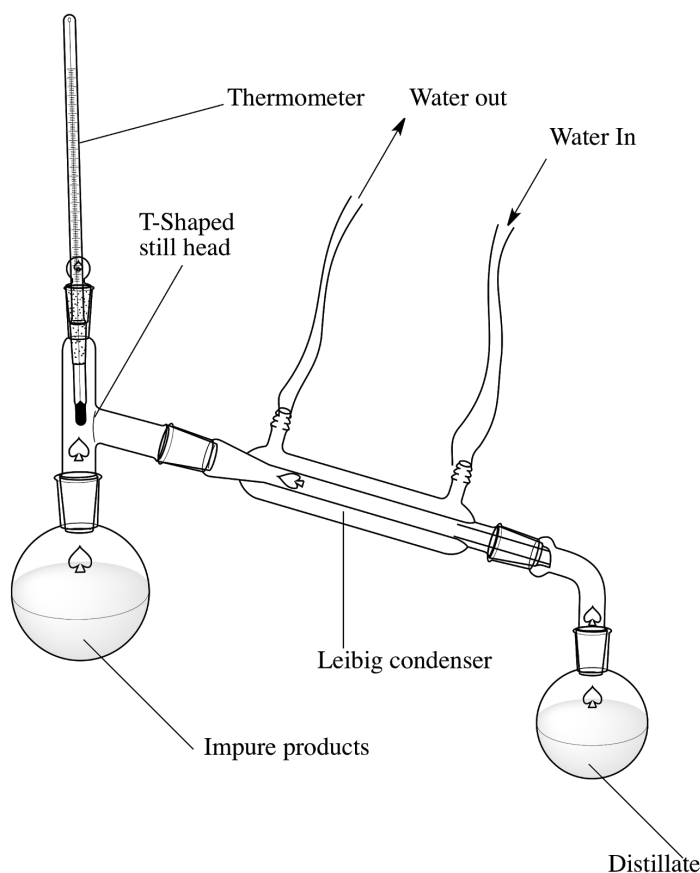


Separating Funnel

A separating funnel is used to separate two liquids with **different densities**. The mixture is added to the flask and 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.

Distillation

Distillation apparatus is used to separate liquids with **different boiling points**. The pear-shaped 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.



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. A common anhydrous salt used for drying is **sodium sulphate**.

Boiling point determination

Determining the boiling point of a compound and comparing it to a databook value is a way of testing its **purity**. 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.

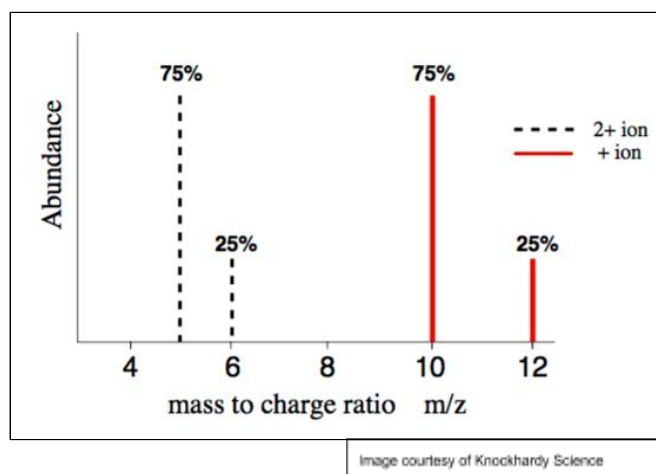
10D: Mass spectra and IR

Mass Spectrometry

Mass spectrometry is an **analytical technique** used to identify different isotopes and to find the overall **relative atomic mass** of an element. Further details of the process can be found in **Topic 2**.

During the ionisation process, a **2+ charged ion** may be produced. Its mass to charge ratio (m/z) is halved - this can be seen on spectra as a trace at **half the expected m/z value**.

Example:



Using this spectrum, the **A_r can be calculated**:

Example:

$$A_r = \frac{m/z \times \text{abundance}}{\text{Total abundance}} = \frac{(10 \times 75) + (12 \times 25)}{(75 + 25)} = 10.5$$

Infrared (IR) Spectrometry

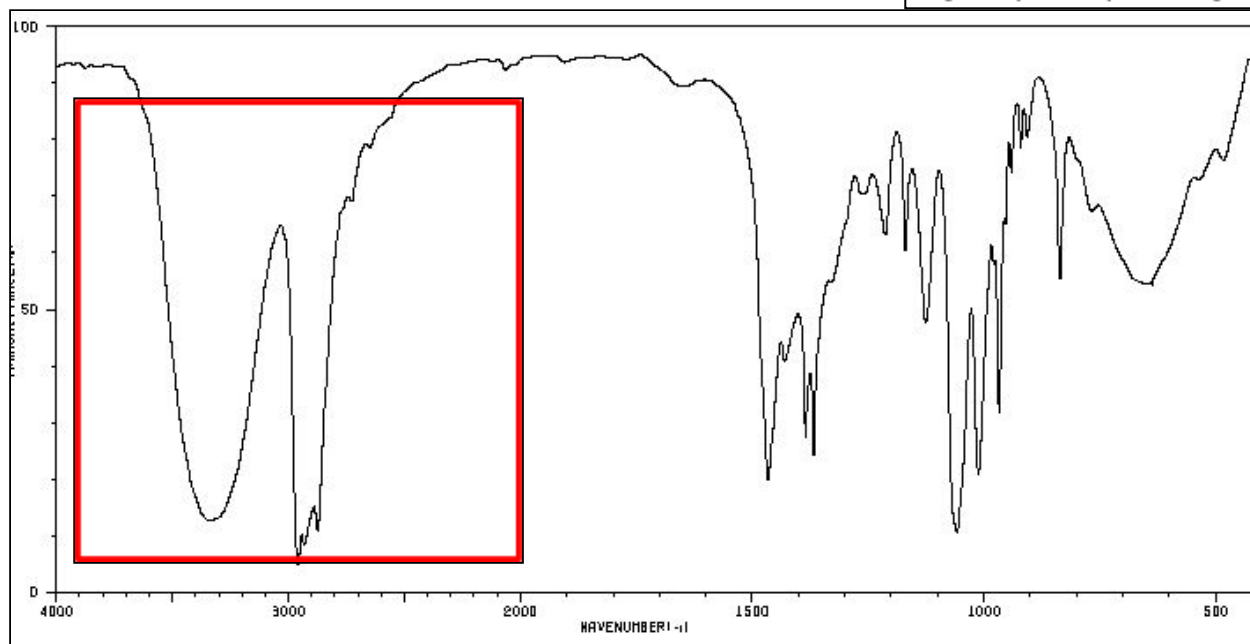
Infrared spectroscopy is an analytical technique which uses **infrared (IR) radiation** to determine the **functional groups** present in organic compounds. The IR radiation is passed through a sample where the different types of bonds **absorb** the radiation in different amounts. These varying amounts 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

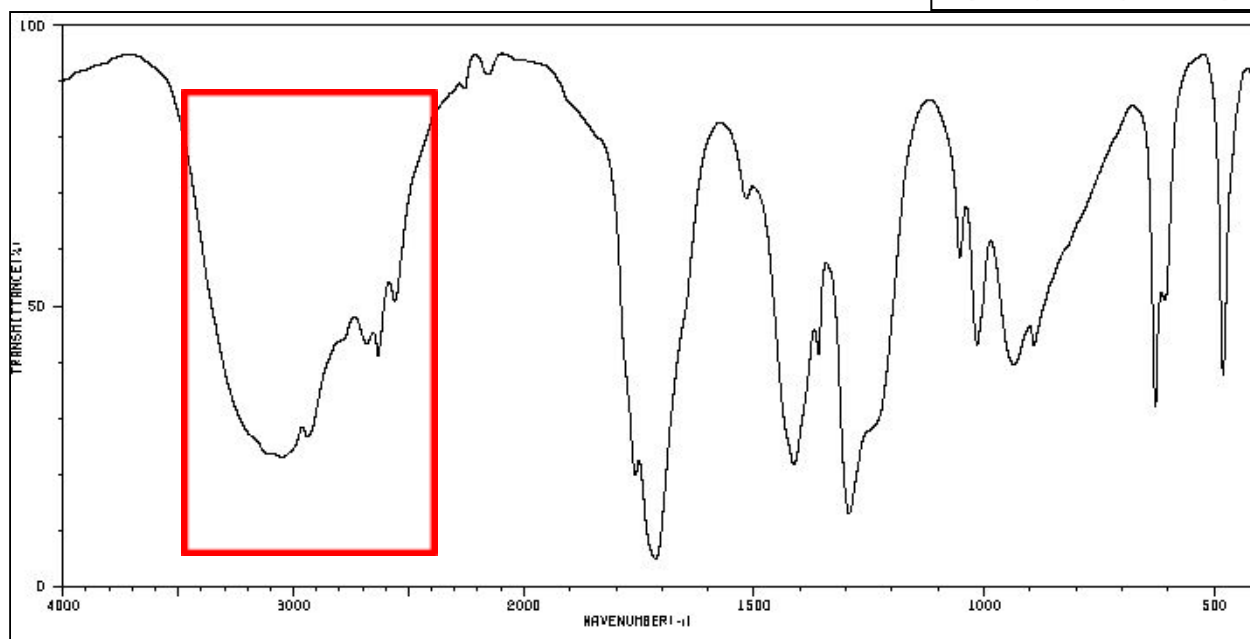
Image courtesy of Chemistry Stack Exchange



*The characteristic -OH alcohol group peak is in the range **3230 - 3550 cm⁻¹**.*

-OH Acid Group

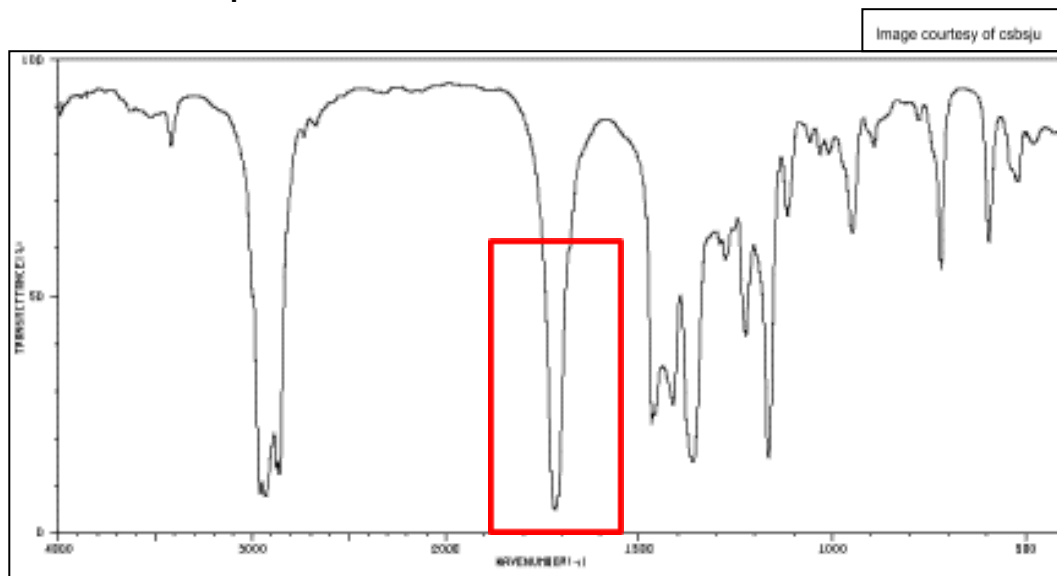
Image courtesy of Chemistry Stack Exchange



*The characteristic -OH acid group peak is in the range **2500 - 3300 cm⁻¹**.*

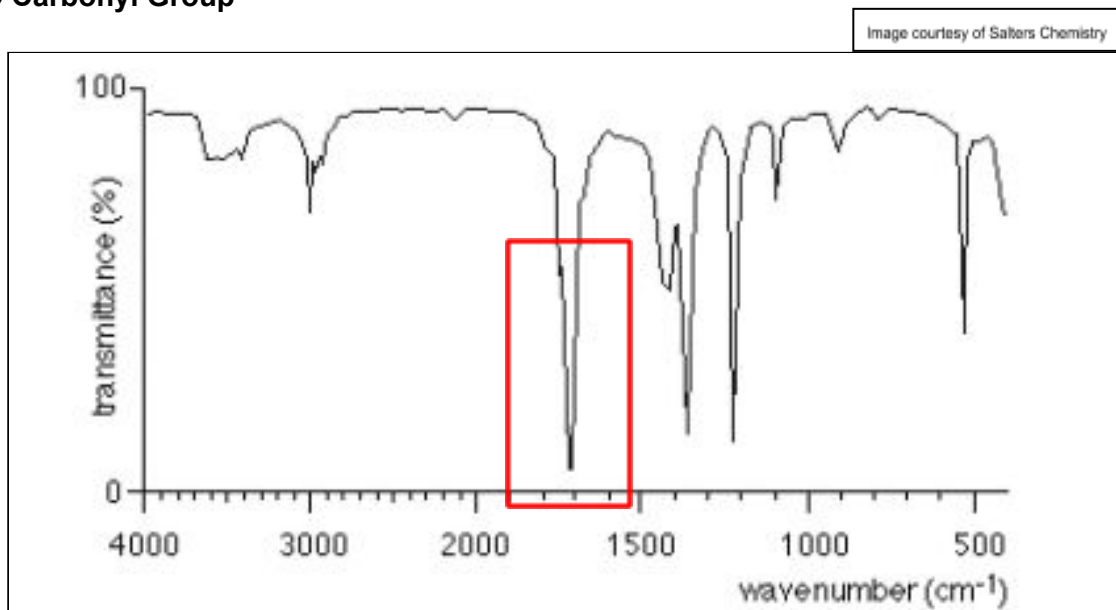


C=C Unsaturated Group



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

C=O Carbonyl Group



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

Fingerprint Region

Each IR spectrum has a **fingerprint region** to the right-hand side, from 500-1500 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**.

