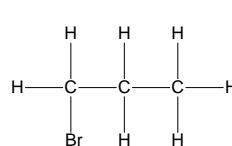


10 Halogenoalkanes

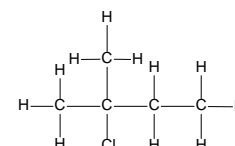
Naming Halogenoalkanes

Based on original alkane, with a *prefix* indicating halogen atom:
Fluoro for F; **Chloro** for Cl; **Bromo** for Br; **Iodo** for I.

Substituents are listed **alphabetically**



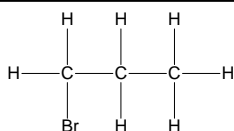
1-bromopropane



2-chloro-2-methylbutane

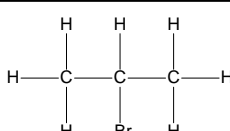
Classifying Halogenoalkanes

Halogenoalkanes can be classified as primary, secondary or tertiary depending on the number of carbon atoms attached to the C-X functional group.



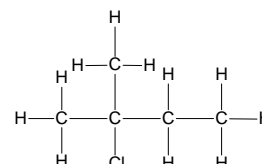
Primary halogenoalkane

One carbon attached to the carbon atom adjoining the halogen



Secondary halogenoalkane

Two carbons attached to the carbon atom adjoining the halogen



Tertiary halogenoalkane

Three carbons attached to the carbon atom adjoining the halogen

Reactions of Halogenoalkanes

Halogenoalkanes undergo either **substitution** or **elimination** reactions

Nucleophilic substitution reactions

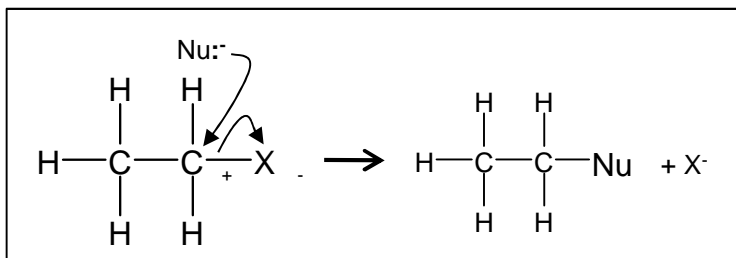
Substitution: swapping a halogen atom for another atom or groups of atoms

Nucleophile: electron pair donator e.g. :OH^- , :NH_3 , CN^-

The Mechanism: We draw (or **outline**) mechanisms to show in detail how a reaction proceeds

:Nu represents any nucleophile – they always have a **lone pair** and act as **electron pair donors**

The nucleophiles attack the positive carbon atom



The carbon has a small positive charge because of the electronegativity difference between the carbon and the halogen



We use curly arrows in mechanisms (with two line heads) to show the movement of two electrons

A curly arrow will always **start** from a **lone pair** of electrons or the **centre of a bond**

The rate of these substitution reactions depends on the strength of the C-X bond

The weaker the bond, the easier it is to break and the faster the reaction.

The iodoalkanes are the fastest to substitute and the fluoroalkanes are the slowest. The strength of the C-F bond is such that fluoroalkanes are very unreactive

	Bond enthalpy / kJmol^{-1}
C-I	238
C-Br	276
C-Cl	338
C-F	484

Comparing the rate of hydrolysis reactions

Hydrolysis is defined as the splitting of a molecule (in this case a halogenoalkane) by a reaction with water



Aqueous silver nitrate is added to a halogenoalkane and the halide leaving group combines with a silver ion to form a **SILVER HALIDE PRECIPITATE**.

The precipitate only forms when the halide ion has left the halogenoalkane and so the rate of formation of the precipitate can be used to compare the reactivity of the different halogenoalkanes.

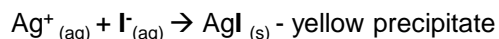
The **quicker** the **precipitate** is formed, the **faster** the **substitution** reaction and the **more reactive** the haloalkane

The rate of these substitution reactions depends on the strength of the C-X bond . The weaker the bond, the easier it is to break and the faster the reaction.

If the experiment is repeated using primary, secondary and tertiary halogenoalkanes, the order of reactivity will be:

Tertiary > secondary > primary
Reacts first

Water is a **poor nucleophile** but it can react **slowly** with halogenoalkanes in a substitution reaction



The iodoalkane forms a precipitate with the silver nitrate first as the C-I bond is weakest and so it hydrolyses the quickest

$\text{AgI}_{(\text{s})}$ - yellow precipitate
 $\text{AgBr}_{(\text{s})}$ - cream precipitate
 $\text{AgCl}_{(\text{s})}$ - white precipitate

↑ forms faster

Nucleophilic substitution with aqueous hydroxide ions

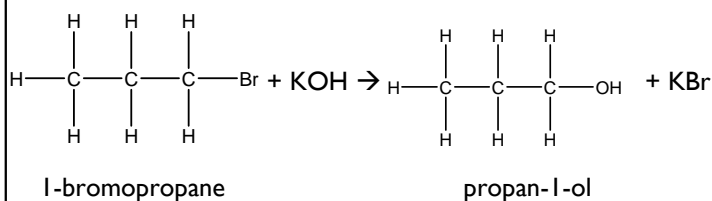
Change in functional group: halogenoalkane → alcohol

Reagent: potassium (or sodium) hydroxide

Conditions: In aqueous solution; Heat under reflux

Mechanism: Nucleophilic Substitution

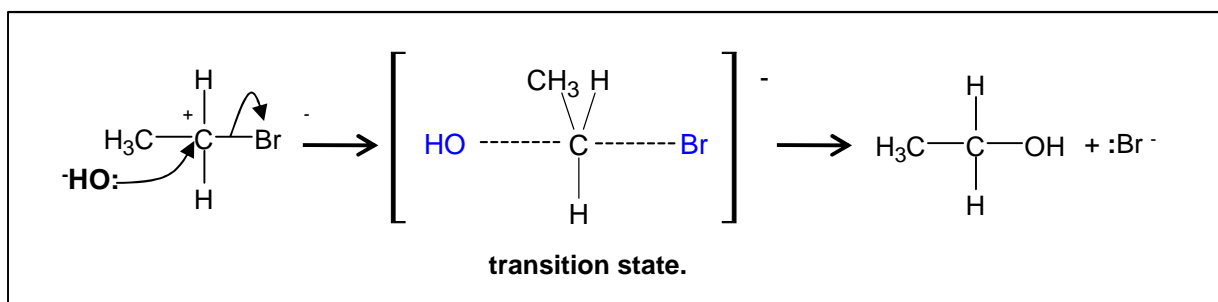
Role of reagent: Nucleophile, OH^-



The OH^- is a stronger nucleophile than water as it has a full negative charge and so is more strongly attracted to the C^+

The **aqueous** conditions needed is an important point. If the solvent is changed to **ethanol** an elimination reaction occurs

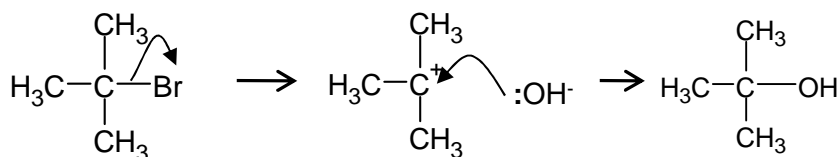
$\text{S}_{\text{N}}2$ nucleophilic substitution mechanism for halogenoalkanes



This mechanism occurs with primary halogenoalkanes

SN₁ nucleophilic substitution mechanism for tertiary halogenoalkanes

Tertiary haloalkanes undergo nucleophilic substitution in a different way



The Br first breaks away from the haloalkane to form a carbocation intermediate

The hydroxide nucleophile then attacks the positive carbon

Tertiary halogenoalkanes undergo this mechanism as the tertiary carbocation is made stabilised by the electron releasing methyl groups around it. (see alkenes topic for another example of this). Also the bulky methyl groups prevent the hydroxide ion from attacking the halogenoalkane in the same way as the mechanism above

Primary halogenoalkanes don't do the SN₁ mechanism because they would only form an unstable primary carbocation.

Nucleophilic substitution with ammonia

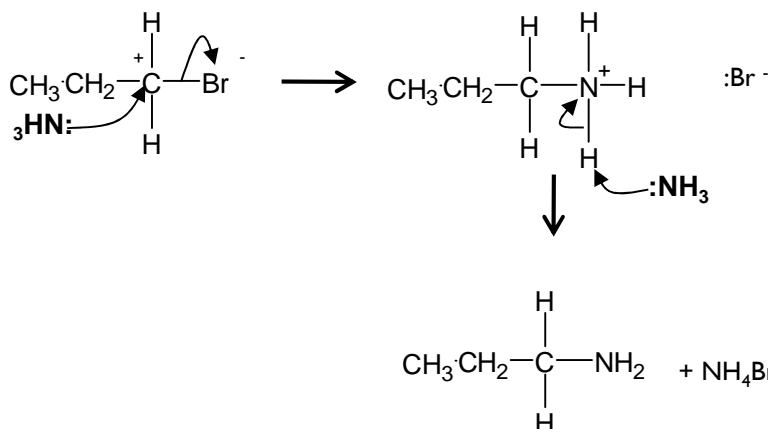
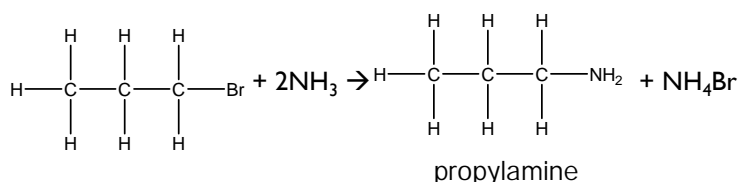
Change in functional group: halogenoalkane → amine

Reagent: NH₃ dissolved in ethanol

Conditions: Heating under pressure in a sealed tube

Mechanism: Nucleophilic Substitution

Type of reagent: Nucleophile, :NH₃



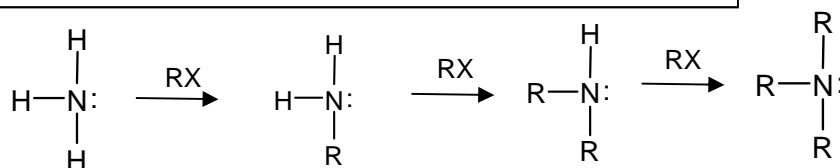
Naming amines:

In the above example propylamine, the propyl shows the 3 C's of the carbon chain.

Sometimes it is easier to use the IUPAC naming for amines e.g. Propan-1-amine

Further substitution reactions can occur between the haloalkane and the amines formed leading to a lower yield of the amine. Using excess ammonia helps minimise this.

Further reactions



Elimination reaction of halogenoalkanes

Elimination: removal of small molecule (often water) from the organic molecule

Elimination with alcoholic hydroxide ions

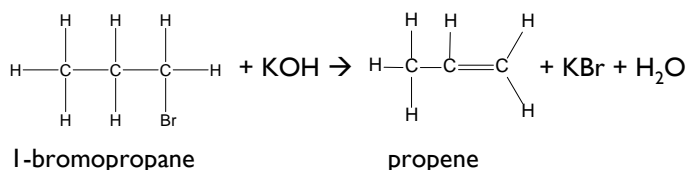
Change in functional group: halogenoalkane → alkene

Reagents: Potassium (or sodium) hydroxide

Conditions: In *ethanol*; Heat

Mechanism: Elimination

Role of reagent: Base, OH⁻



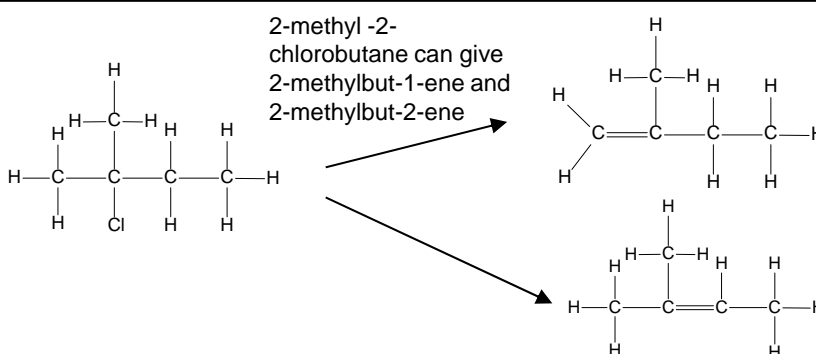
Note the importance of the solvent to the type of reaction here.

Aqueous: substitution

Alcoholic: elimination

Often a mixture of products from both elimination and substitution occurs

With unsymmetrical secondary and tertiary halogenoalkanes two (or sometimes three) different structural isomers can be formed



The structure of the halogenoalkane also has an effect on the degree to which substitution or elimination occurs in this reaction.

Primary tends towards substitution

Tertiary tends towards elimination

Uses of halogenoalkanes

Haloalkanes have been used as **refrigerants**, **fire retardants**, pesticides and **aerosol propellants**

chloroalkanes and chlorofluoroalkanes can be used as solvents

CH₂Cl₂ was used as the solvent in dry cleaning

Some halogenoalkanes have low flammability

Many of these uses have now been stopped due to the toxicity of halogenoalkanes and also their detrimental effect on the ozone layer

6E Alcohols

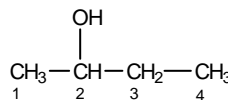
General formula alcohols $C_nH_{2n+1}OH$

Naming Alcohols

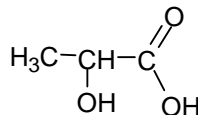
These have the ending **-ol** and if necessary the position number for the OH group is added between the name stem and the **-ol**

If the compound has an **-OH** group in addition to other functional groups that need a suffix ending then the OH can be named with the prefix **hydroxy-**:

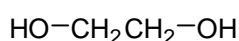
If there are two or more **-OH** groups then di, tri are used. Add the 'e' on to the stem name though



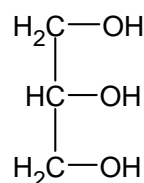
Butan-2-ol



2-hydroxypropanoic acid



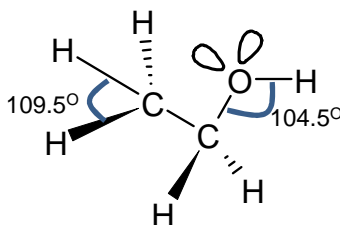
Ethane-1,2-diol



propane-1,2,3-triol

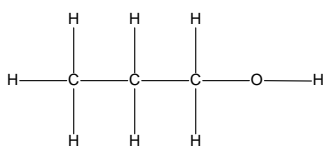
Bond angles in Alcohols

All the H-C-H bonds and C-C-O are 109.5° (tetrahedral shape), because there are 4 bond pairs of electrons repelling to a position of minimum repulsion.



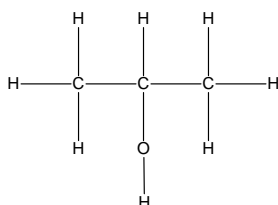
The H-O-C bond is 104.5° (bent line shape), because there are 2 bond pairs of electrons and 2 lone pairs repelling to a position of minimum repulsion. Lone pairs repel more than bond pairs so the bond angle is reduced.

Different types of alcohols



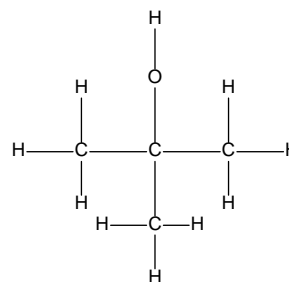
Propan-1-ol
Primary

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

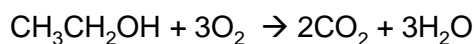


methylpropan-2-ol
Tertiary

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

1. Combustion of Alcohols

Alcohols combust with a clean flame

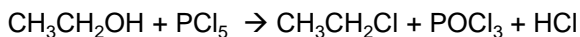


2. Substitution reactions of Alcohols to form Halogenoalkanes

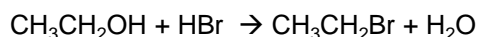
Various halogenating compounds can be used to substitute the $-\text{OH}$ group for a halogen

$\text{PCl}_5 / \text{PCl}_3 / \text{conc HCl} / \text{SOCl}_2 / \text{mixture of NaCl} + \text{H}_2\text{SO}_4$ can all be used for substituting a Cl

Reaction with phosphorous (V) halide

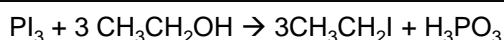


This reaction with PCl_5 (phosphorous(v)chloride) can be used as a test for alcohols. You would observe misty fumes of HCl produced.



For Br use KBr , 50% concentrated H_2SO_4 to produce HBr

Reaction with phosphorous (III) iodide



The **phosphorous (III) iodide** is produced in situ by reacting red phosphorus and iodine.

The reaction of KI and $\text{conc H}_2\text{SO}_4$ can't be used to produce HI because the sulphuric acid will oxidise the hydrogen halides to other products

3. Oxidation reactions of the alcohols

Potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ is an oxidising agent that causes alcohols to oxidise.

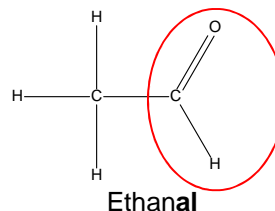
The exact reaction, however, depends on the type of alcohol, i.e. whether it is primary, secondary, or tertiary, and on the conditions.

Partial Oxidation of Primary Alcohols

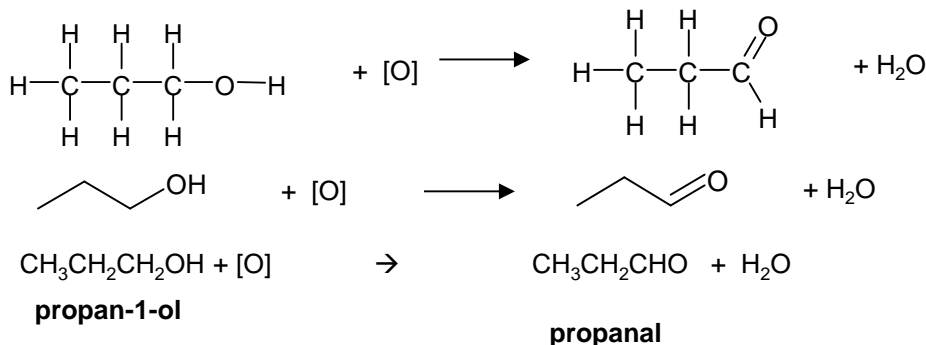
Reaction: primary alcohol \rightarrow aldehyde

Reagent: potassium dichromate (VI) solution and dilute sulphuric acid.

Conditions: (use a limited amount of dichromate) warm gently and **distil** out the aldehyde as it forms:



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



Observation: the orange dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) reduces to the green Cr^{3+} ion

Write the oxidation equations in a simplified form using $[\text{O}]$ which represents O from the oxidising agent

When writing the formulae of aldehydes in a condensed way write **CHO** and not COH e.g. $\text{CH}_3\text{CH}_2\text{CHO}$

Reaction of Alcohols with Dehydrating Agents

Reaction: Alcohol \rightarrow Alkene

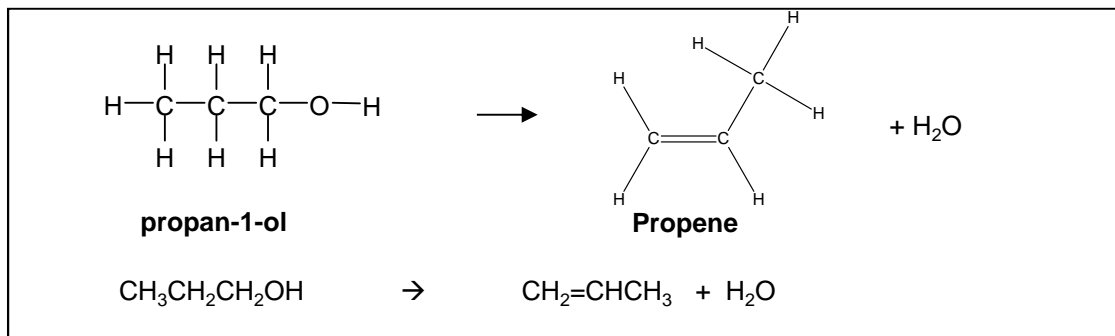
Reagents: Concentrated Phosphoric acid

Conditions: warm (under reflux)

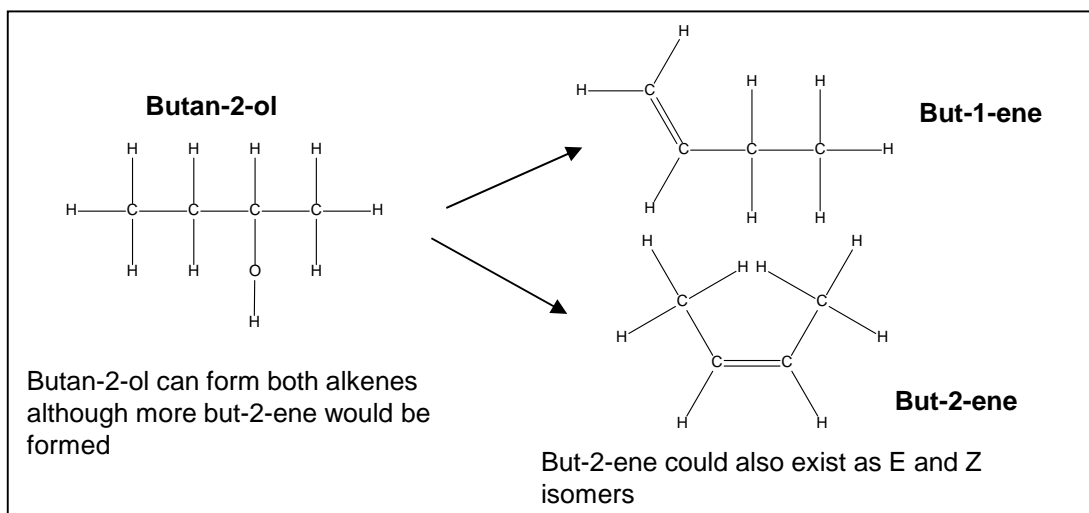
Role of reagent: dehydrating agent/catalyst

Type of reaction: acid catalysed elimination

Dehydration Reaction: removal of a water molecule from a molecule



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



Producing alkenes from alcohols provides a possible route to polymers without using monomers derived from oil

Organic techniques

Distillation

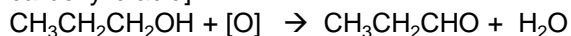
In general used as separation technique to separate an organic product from its reacting mixture. Need to collect the distillate of the approximate boiling point range of the desired liquid.

Classic AS reaction using distillation

Reaction: primary alcohol \rightarrow aldehyde

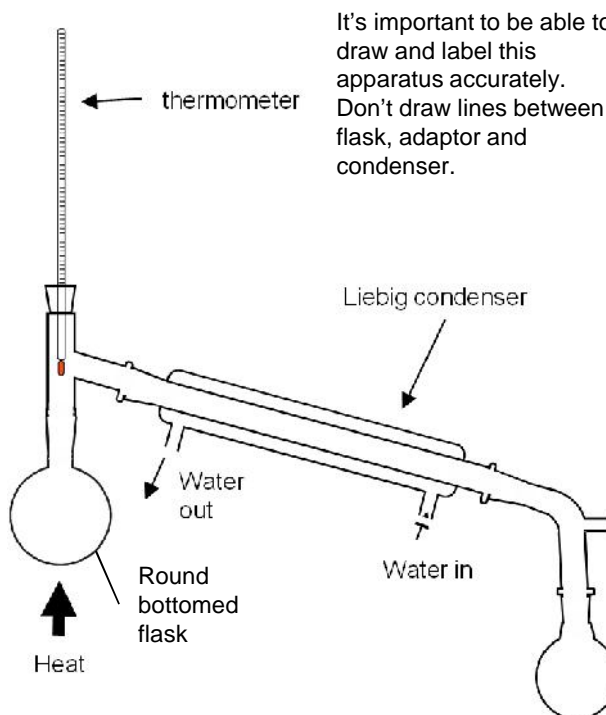
Reagent: potassium dichromate (VI) solution and dilute sulphuric acid.

Conditions: use a limited amount of dichromate and **warm gently and distil** out the aldehyde as it forms [This prevents further oxidation to the carboxylic acid]



Observation

Orange dichromate solution changes to green colour of Cr^{3+} ions



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

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.

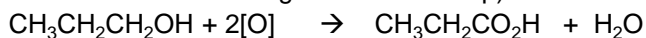
Never seal the end of the condenser as the build up of gas pressure could cause the apparatus to explode. This is true of any apparatus where volatile liquids are heated

Classic AS reaction using reflux

Reaction: primary alcohol \rightarrow carboxylic acid

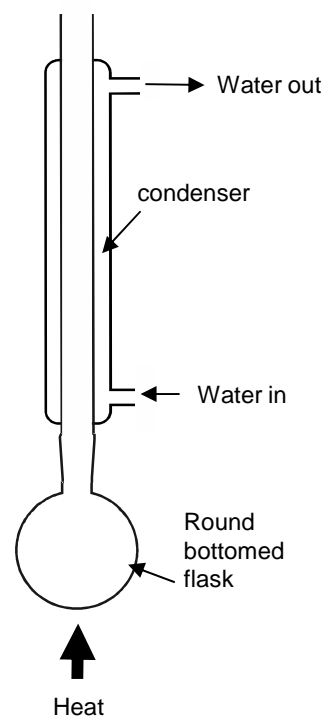
Reagent: potassium dichromate(VI) solution and dilute sulphuric acid

Conditions: use an excess of dichromate, and **heat under reflux:** (distill off product after the reaction has finished using distillation set up)



Observation

Orange dichromate solution changes to green colour of Cr^{3+} ions



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

It's important to be able to draw and label this apparatus accurately.

- Don't draw lines between flask and condenser.
- Don't have top of condenser sealed
- Condenser must have outer tube for water that is sealed at top and bottom
- Condenser must have two openings for water in and out that are open

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.

Purifying an organic liquid

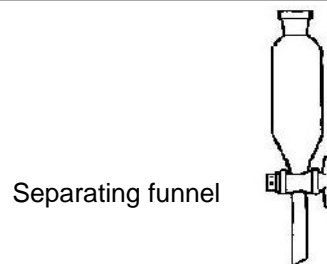
- Put the distillate of impure product into a separating funnel
- wash product by adding either
 - sodium hydrogencarbonate solution, shaking and releasing the pressure from CO_2 produced.
 - Saturated sodium chloride solution
- Allow the layers to separate in the funnel, and then run and discard the aqueous layer.
- Run the organic layer into a clean, dry conical flask and add three spatula loads of drying agent (anhydrous sodium sulphate) to dry the organic liquid.
- Carefully decant the liquid into the distillation flask
- Distill to collect pure product

Sodium hydrogencarbonate will neutralise any remaining reactant acid.

Sodium chloride will help separate the organic layer from the aqueous layer

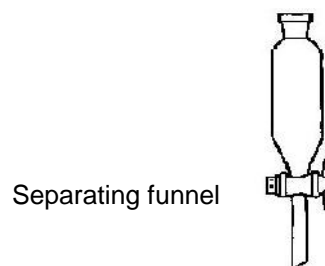
The drying agent should

- be insoluble in the organic liquid
- not react with the organic liquid



Solvent extraction

Mix organic solvent and oil-water mixture in a separating funnel then separate the oil layer.
Distil to separate oil from organic solvent
Add anhydrous CaCl_2 to clove oil to dry oil
Decant to remove CaCl_2



Measuring boiling point

Purity of liquid can be determined by measuring a boiling point. This can be done in a distillation set up or by simply boiling a tube of the sample in an heating oil bath.

Pressure should be noted as changing pressure can change the boiling point of a liquid

Measuring boiling point is not the most accurate method of identifying a substance as several substances may have the same boiling point.

To get a correct measure of boiling point the thermometer should be above the level of the surface of the boiling liquid and be measuring the temperature of the saturated vapour.

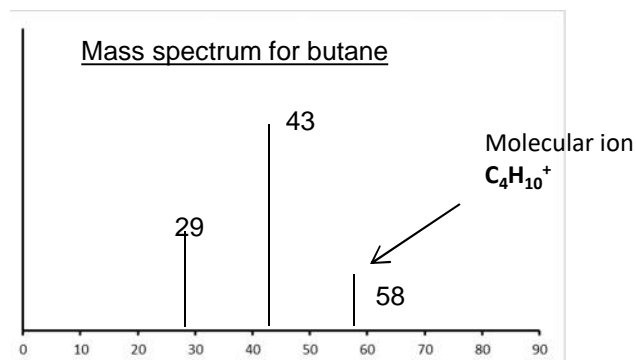
10D. Mass spectra and IR

Mass spectrometry

Measuring the M_r of an organic molecule

If a molecule is put through a mass spectrometer it will often break up and give a series of peaks caused by the fragments. The peak with the largest m/z , however, will be due to the complete molecule and will be equal to the M_r of the molecule. This peak is called the parent ion or **molecular ion**

Spectra for C_4H_{10}



Fragmentation

When organic molecules are passed through a mass spectrometer, it detects both the whole molecule and fragments of the molecule.



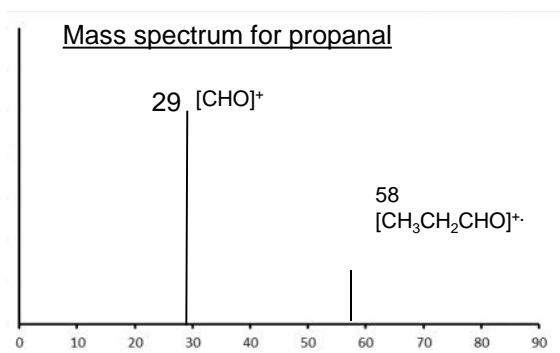
The molecule loses an electron and becomes both an ion and a free radical

Several peaks in the mass spectrum occur due to fragmentation. The Molecular ion fragments due to covalent bonds breaking: $[M]^+ \rightarrow X^+ + Y\cdot$

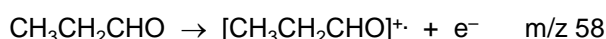
This process produces an ion and a free radical. The ion is responsible for the peak

Relatively stable ions such as carbocations R^+ such as $CH_3CH_2^+$ and acylium ions $[R-C=O]^+$ are common. The more stable the ion, the greater the peak intensity.

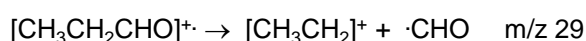
The peak with the highest mass/charge ratio will be normally due to the original molecule that hasn't fragmented (called the molecular ion). As the charge of the ion is +1 the mass/charge ratio is equal to M_r .



Equation for formation molecular ion



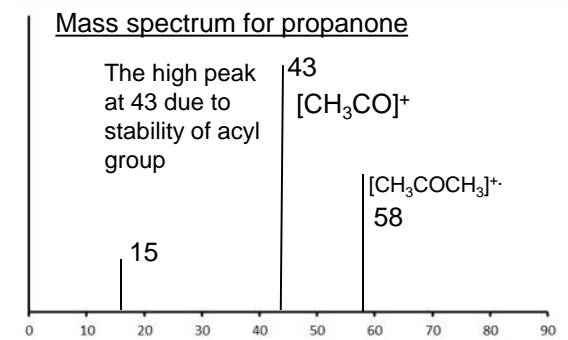
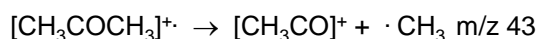
Equations for formation of fragment ions from molecular ions



Equation for formation molecular ion



Equations for formation of fragment ions from molecular ions



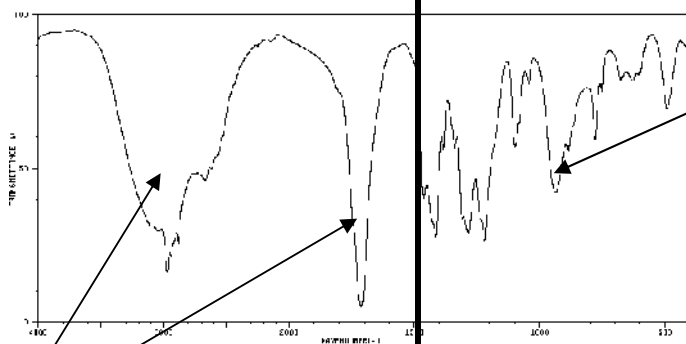
It is not possible for propanone to fragment to give a peak at 29 so the fragmentation patterns can distinguish between the structural isomers of propanone and propanal

Infrared spectroscopy

Certain bonds in a molecule absorb infra-red radiation at characteristic frequencies causing the covalent bonds to vibrate

Complicated spectra can be obtained than provide information about the types of bonds present in a molecule

ABOVE 1500 cm^{-1} – “Functional group identification”



BELOW 1500 cm^{-1} – “Fingerprinting”

Complicated and contains many signals – picking out functional group signals difficult.

This part of the spectrum is unique for every compound, and so can be used as a “fingerprint”.

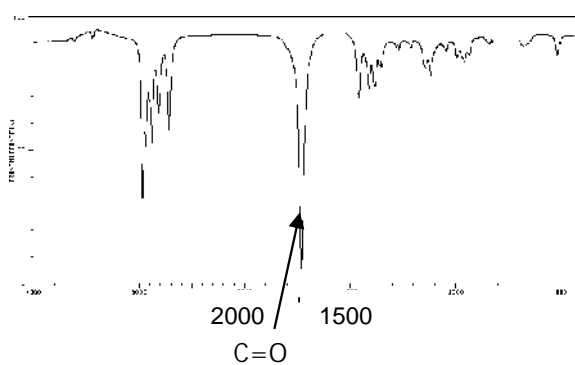
e.g. C=O 1640 – 1750 cm^{-1}
O-H (acid) 2500- 3300 cm^{-1}

A computer will compare the IR spectra against a database of known pure compounds to identify the compound

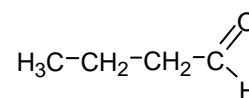
Use an IR absorption table provided in exam to deduce presence or absence of particular bonds or functional groups

Bond	Wavenumber
C-O	1000-1300
C=O	1640-1750
C-H	2850 -3100
O-H Carboxylic acids	2500-3300 Very broad
N-H	3200-3500
O-H Acohols, phenols	3200- 3550 broad

Use spectra to identify particular functional groups e.g. an alcohol from an absorption peak of the O–H bond, or C=O stretching absorption in aldehydes and ketones

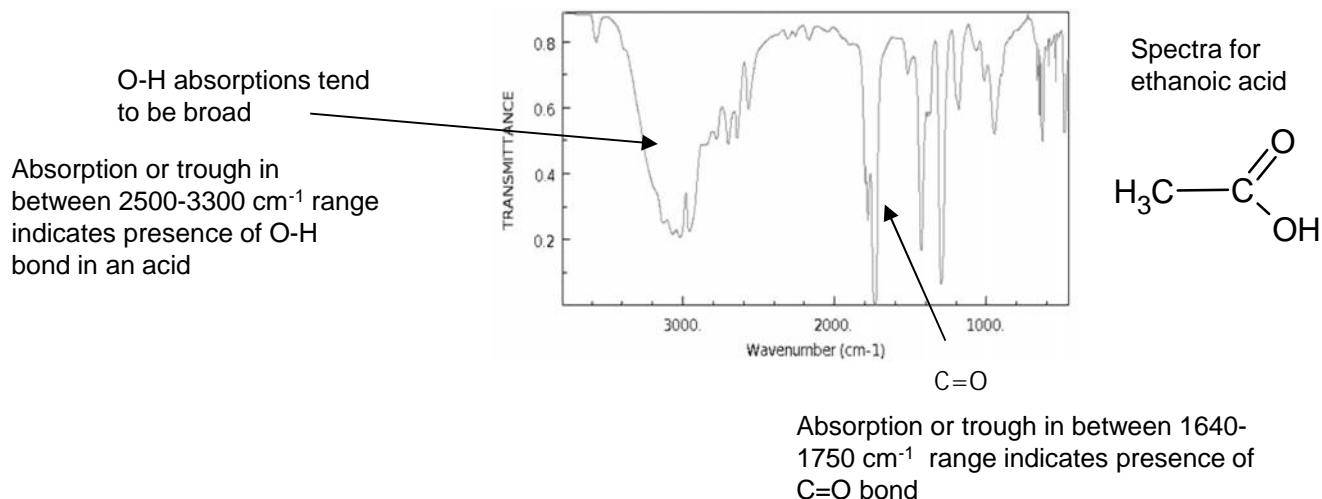


Spectra for
butanal



Absorption or trough in between 1640-1750 cm^{-1} range indicates presence of C=O bond

Always quote the wave number range from the data sheet



Molecules which change their polarity as they vibrate can absorb infrared radiation. E.g. C-H, C=O, O-H

Molecules such as H_2 , O_2 and N_2 cannot change their polarity as they vibrate so can absorb infrared radiation and don't register on an infra red spectrum

The absorption of infra-red radiation by bonds in this type of spectroscopy is the same absorption that bonds in CO_2 , methane and water vapour in the atmosphere do that cause them to be greenhouse gases.

H_2O , CO_2 , CH_4 and NO molecules absorb IR radiation and are greenhouse gases, whilst O_2 and N_2 are not.