Module 2A – Alcohols and halogenoalkanes

Making ethanol

- Ethanol is made in 1 of 2 ways:

1) Hydration of ethene:

$$H_2C{=}CH_2(g) + H_2O(g) \xrightarrow[300^\circ C\ 60\ atm]{H_3PO_4} CH_3CH_2OH(l)$$

- This is a reversible reaction and only about 5% of ethene is converted to ethanol.
- Unreacted gases are recycled - this gives a 95% conversion.

2) Fermentation:

- Fermentation is the natural production of alcohol.
- The sugar in fruit ferments using yeast on the skin.
- It is a slow process done at around 25^oC.
- Glucose is converted to ethanol and carbon dioxide by the enzyme, zymase in the yeast:

$$C_6H_{12}O_6(aq) \xrightarrow[37^\circ C]{yeast} 2CH_3CH_2OH(aq) + 2CO_2(g)$$

- The reaction is anaerobic which means it does not require oxygen.
- This prevents oxidation of ethanol into aldehydes or carboxylic acids. These affect the flavour.
- Above 37^oC the enzyme becomes denatured and fermentation stops.
- When the ethanol concentration reaches 14%, fermentation stops. This is when the alcohol kills the yeast.

Uses of alcohols:

Ethanol in alcoholic drinks:

- Not only used in alcoholic drinks but also in perfumes.
- Mixed with different hops, barley and water gives different types of drinks.
- Spirits have to be distilled in order to get a higher alcohol %

Ethanol as a fuel:

- Ethanol can make up 10% of petrol, it gives it a higher octane rating so burns more efficiently.
- As the ethanol is made from a renewable source it makes this petrol more environmentally friendly.

Ethanol in methylated spirits:

- Methylated spirits is a mixture of ethanol and methanol with some dye added.
- This makes it toxic and therefore exempt form tax making it much cheaper.
- Even a small amount can cause severe organ damage and death.
- It is used mainly as a good hydrocarbon solvent.

Uses of methanol:

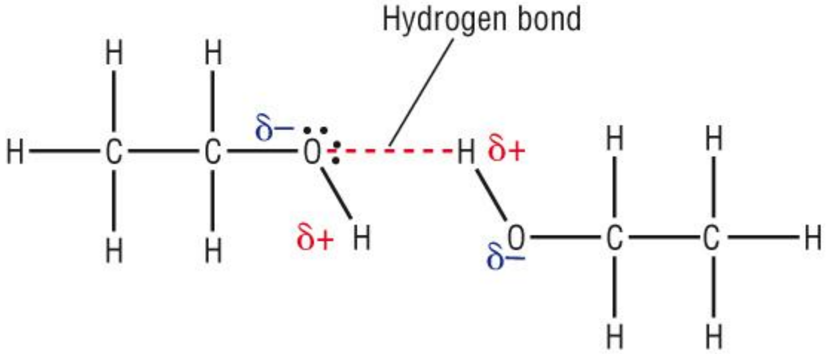
- Methanol can be used as a high performance clean burning fuel.
- Methanol is also used as a feedstock for the chemical industry.

Properties of alcohols

Physical properties:

- The physical properties of alcohols are influenced by their ability to form **hydrogen bonds:**

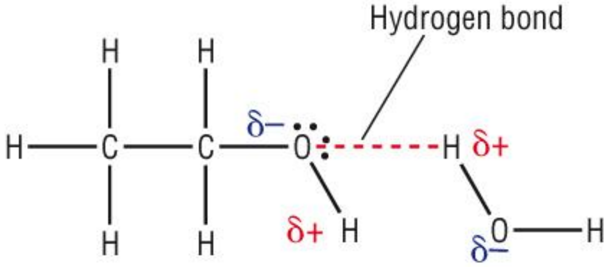
Volatility and boiling points:



- Alcohols have hydrogen bonds whereas their corresponding alkane (by Mr) has Van der Waal's forces of attraction.
- As hydrogen bonds are stronger than Van der Waal's they have **higher boiling points**.
- This means that their **volatility** is much **lower**.

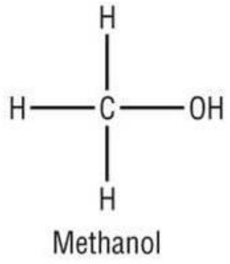
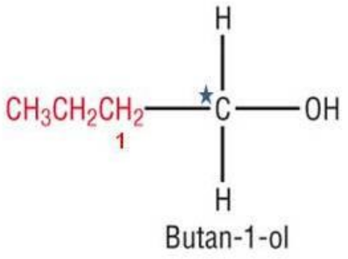
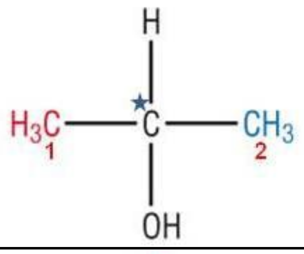
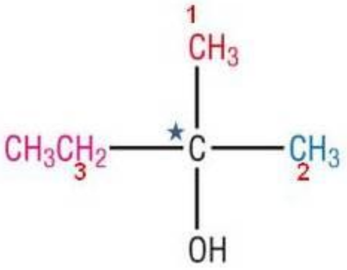
Solubility:

- Alcohols are also soluble in water as they will form hydrogen bonds with water (whereas alkanes will not):



- Their **solubility** however **decreases as the carbon chain increases**.
- Only the first 3 alcohols are soluble in water.
- The hydrocarbon chain does not form hydrogen bonds and as it gets longer it interferes with the ability for the OH group to hydrogen bond with water.

Classification of alcohols:

 Methanol  Butan-1-ol	**Primary (1°)**	**Butan – 1 – ol**. This is a **Primary (1°)** alcohol. When the OH carbon (*) is attached to only **1 other carbon atom**.
	**Secondary (2°)**	**Propan – 2 – ol**. This is a**Secondary (2°)** alcohol. When the OH carbon (*) is attached to **2 other carbon atoms**.
	**Tertiary (3°)**	**2 Methylbutan – 2 – ol**. This is a**Tertiary (3°)** alcohol. When the OH carbon (*) is attached to **3 other carbon atoms**.

- When alcohols contain more than 1 hydroxyl group they are known as **diols** (2), **triols** (3) etc.

Combustion and oxidation of alcohols

The combustion of alcohols

- In a plentiful supply of oxygen, alcohols will burn to form carbon dioxide and water.
- Balancing is more tricky due to the oxygen in the alcohol.

	$C_2H_5OH_{(l)}$	+	$O_{2(g)}$	→	$2CO_{2(g)}$	+	$3H_2O_{(g)}$
C	**2**				**1 x2 = 2**		
H	**6**						**2 x3 =6**
O	**1**		**2**		**4**	**+**	**3**
O	**(7-1 = 6)**		**2 x3 = 6**		**=**	**7**	

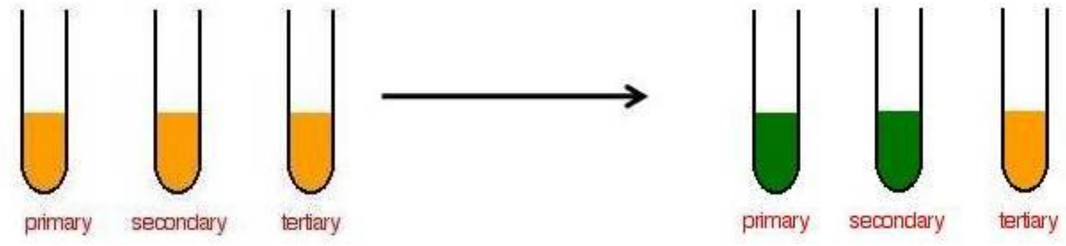
- You have to **take one oxygen away** before you multiply the **O_2**'s up

Oxidation of alcohols:

- To oxidise alcohols we use acidified potassium dichromate solution.
- This is orange in colour and is a mixture of Sulphuric acid, H_2SO_4 and $K_2Cr_2O_7$.
- The orange colour is due to the Cr^{6+} ions in $K_2Cr_2O_7$.
- If it oxidises (ie the Cr^{6+} ions become reduced) then the solution turns green.
- The green solution is due to Cr^{3+} ions.

$$Cr^{6+}_{(aq)} + 3e^- \rightarrow Cr^{3+}_{(aq)}$$

Orange **Green**



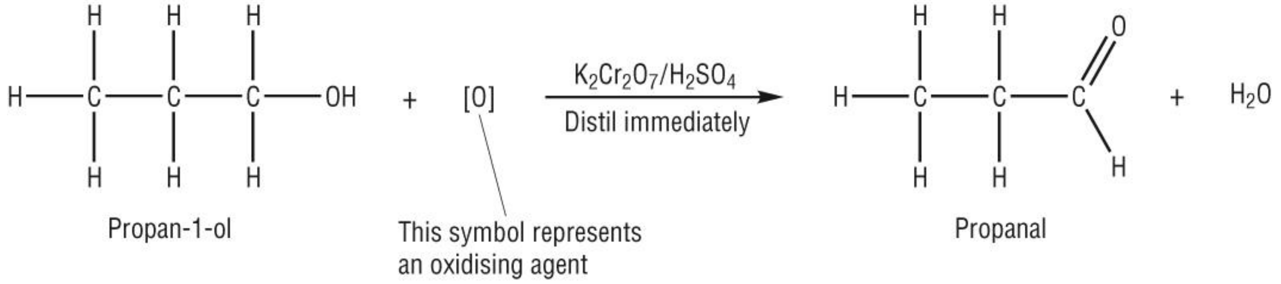
- **The results show that only primary and secondary alcohols can be oxidised / tertiary alcohols cannot be oxidised**

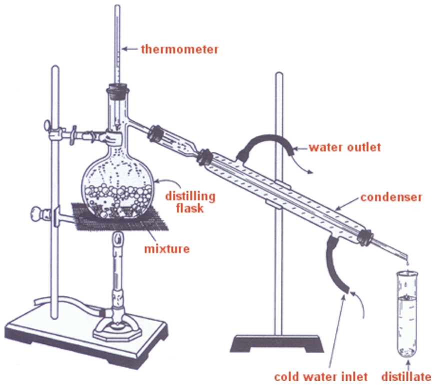
Primary alcohols:

- Primary alcohols when oxidised can form 2 products:

1a) Primary alcohol → Aldehyde:

- Gentle heating of primary alcohols with acidified potassium dichromate make an aldehyde:
- Notice that the OH is removed with a hydrogen on that carbon leaving a C=O.
- As the C=O is formed at the end of the molecule, an aldehyde is formed:

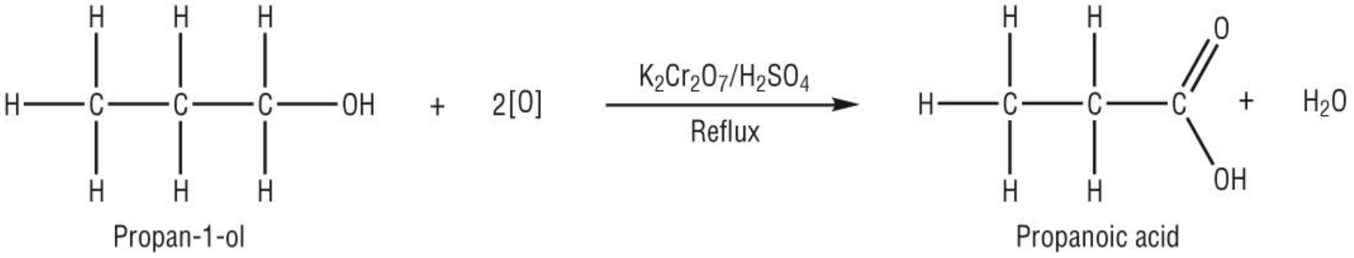


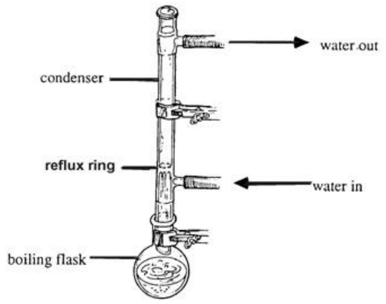


- The aldehyde has to be distilled off as it forms as it can be oxidised further.

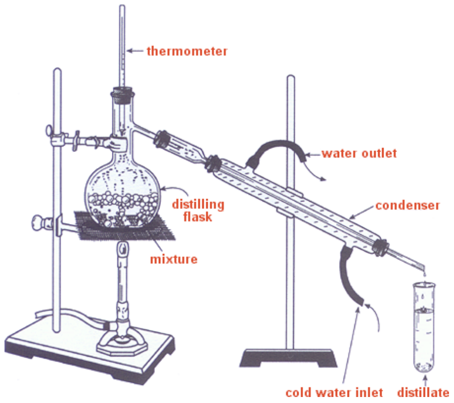
1b) Primary alcohol → Carboxylic acid:

- On stronger heating with excess (see the equation) acidified potassium dichromate the alcohol will be completely oxidised passing through the aldehyde stage to form a carboxylic acid:





Refluxing allows you to heat / boil volatile liquids for a long time. The condenser stops the volatile liquids evaporating off.

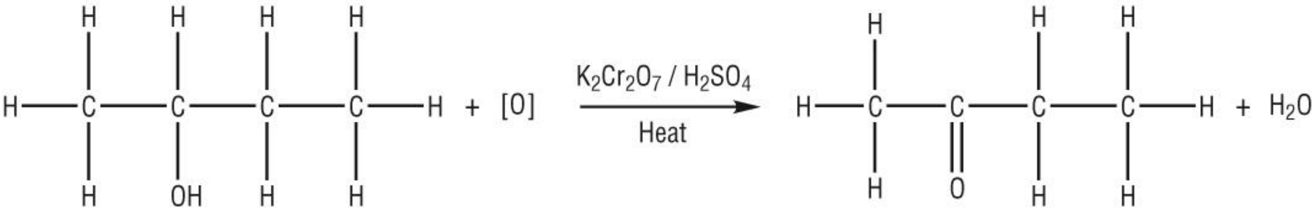


Distillation evaporates and condenses liquids at different temperatures. Collect the liquid you want around its boiling point and discard any others

- When making the carboxylic acid the mixture is refluxed.
- We do not need to worry about oxidising the aldehyde as we need to do this to reach the carboxylic acid.

2) Secondary alcohols:

- Secondary alcohols can be oxidised by acidified potassium dichromiate.
- Notice that the OH is removed with a hydrogen on that carbon leaving a C=O.
- As the C=O is formed not at the end of the molecule, a ketone is formed:



Butan-2-ol

Butanone

3) Tertiary alcohols:

- Although tertiary alcohols have an OH group, it does not have a hydrogen on that carbon to be removed:

As you saw in the demo: Tertiary alcohols cannot be oxidised

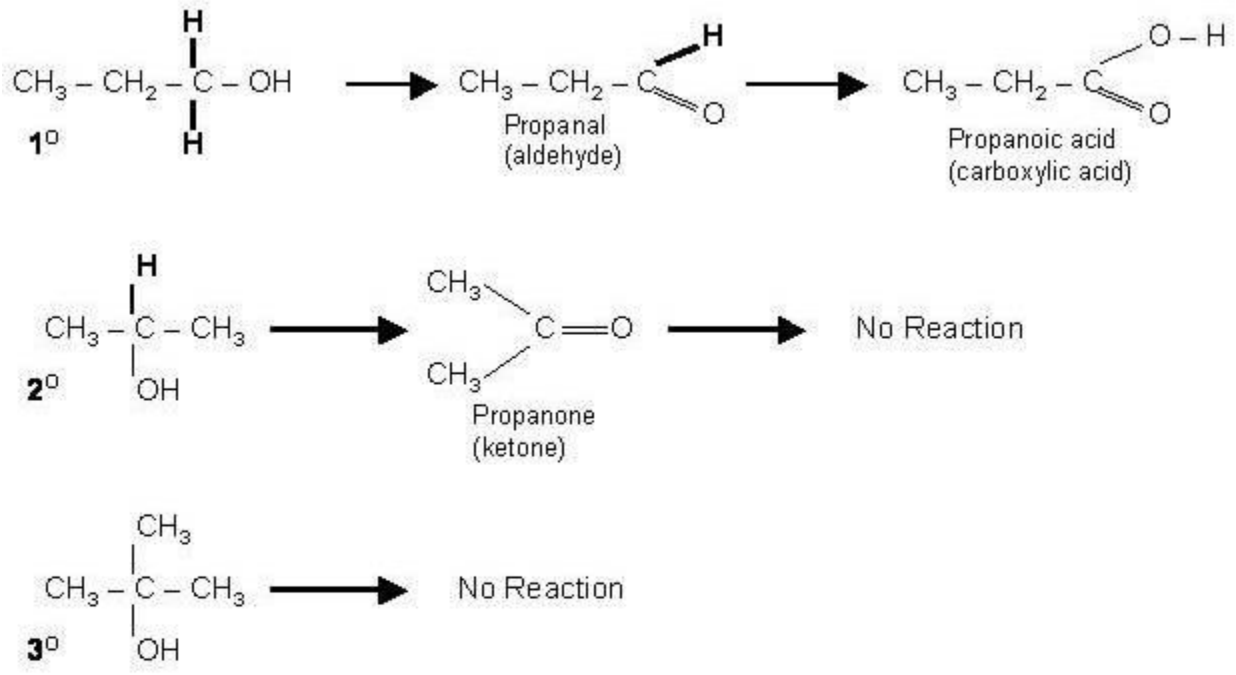
Summary of alcohol oxidation

- [O] can be used to show these oxidation reactions as the mechanism is complicated:

Primary alcohol → Aldehyde → Carboxylic acid

Secondary alcohol → Ketone → No reaction

Tertiary alcohol → No reaction



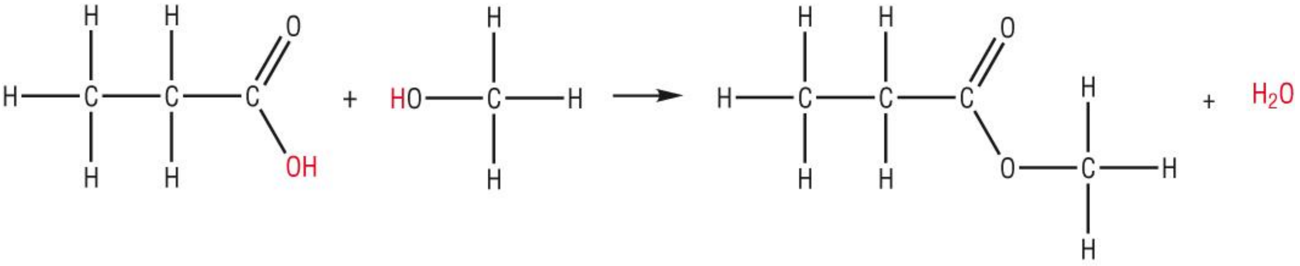
Esterification and dehydration of alcohols

Esterification:

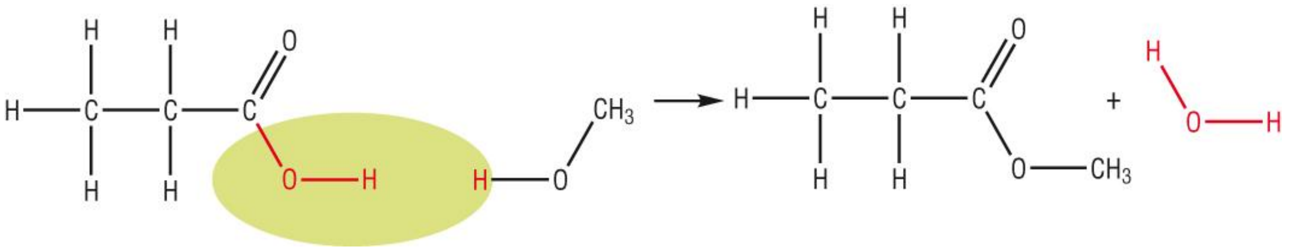
- An ester is formed when an alcohol is warmed with a carboxylic acid:

$$CH_3CH_2COOH + CH_3OH \longrightarrow CH_3CH_2COOCH_3 + H_2O$$

Propanoic acid Methanol Methyl propanoate

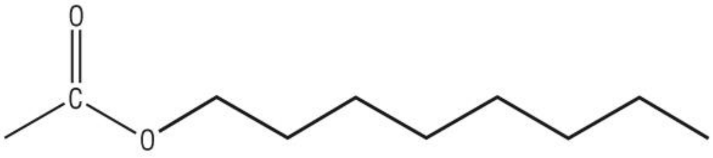


- The reaction is known as **esterification**.
- Concentrated sulphuric acid is used as an acid catalyst.
- In the reaction the C **-** OH bond in the carboxylic acid breaks along with the O **-** H bond in the alcohol.
- The **OH** and **H** join together forming water, **H_2O**:

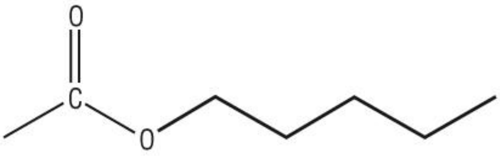


Esters:

- Are used as good solvents and in adhesives.
- They have a sweet smell so are more known for their uses in perfumes and food flavour additives:

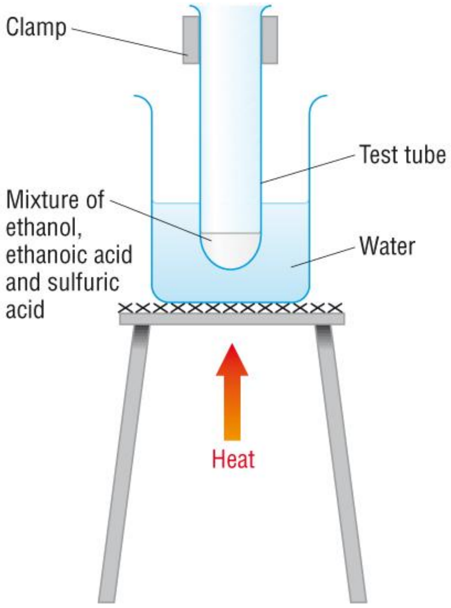


Octyl ethanoate, $CH_3COO(CH_2)_7CH_3$



Pentyl ethanoate, $CH_3COO(CH_2)_4CH_3$

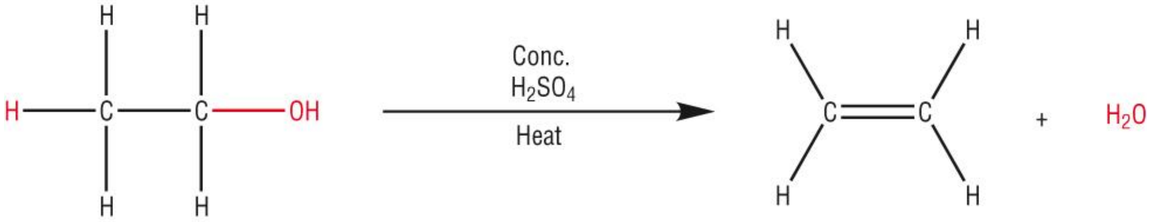
Preparing an ester:



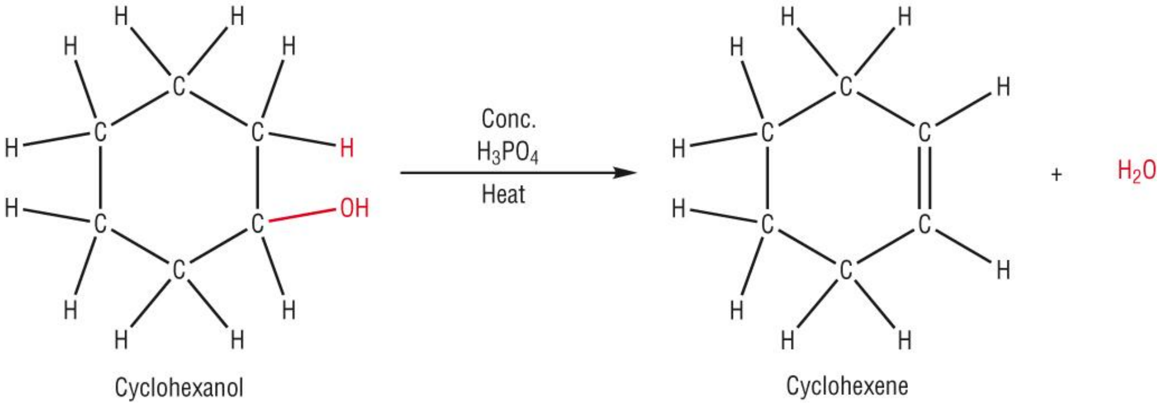
- These can easily be prepared by adding $1cm^3$ of each of the carboxylic acid and alcohol in a boiling tube as shown in the diagram.
- A few drops of concentrated sulphuric acid catalyst is added to the mixture and heated at 80^oC for ~5 mins.
- pouring the contents into a beaker of cold water will show the ester floating as an oil on the surface.

Dehydration of an alcohol:

- **Water** can be removed from an alcohol in the presence of an acid catalyst to form an **alkene**.



- The catalyst is usually concentrated phosphoric acid, H_3PO_4 or concentrated sulphuric acid, H_2SO_4.
- It is heated under reflux, then distilled.



Introduction to halogenoalkanes

- Halogenoalkanes have the general formula $C_nH_{2n+1}X$. X is a halogen.
- In the past they have been used as refrigerants and as propellants in aerosols.
- They are no longer used in these due to their environmental impact on the ozone layer (later).
- they are however used extensively in synthesis.

Naming the halogenoalkanes

- When a hydrogen is replaced by a halogen, the prefix **fluoro-**, **chloro-**, **bromo-** and **iodo-** are used:-

$CH_3 - Cl$	**Chloro**methane
$CH_3 - CH_2Br$	**Bromo**ethane

- 2 isomers can be derived from a monosubstituted propane:-

$CH_3 - CH_2 - CH_2Cl$	**1 – Chloro**propane
$CH_3 - CHCl - CH_3$	**2 – Chloro**propane

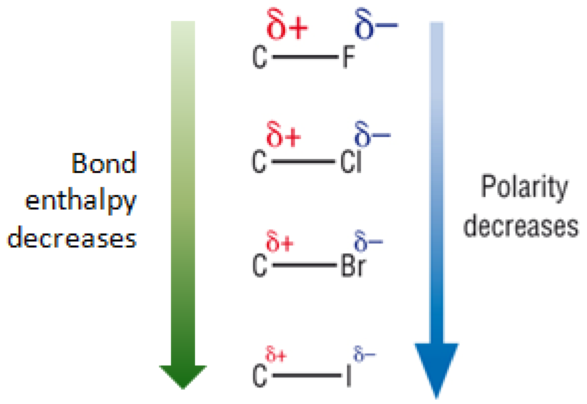
- Multi halogen substituted compounds use **di**, **tri** to indicate how many of that halogen is present in the compound:-

$CH_2Br - CH_2Br$	**1,2 - dibromo**ethane

Reactivity of the halogenoalkanes:

Bond enthalpy

- Weaker bonds break more easily.
- Meaning more of them will break at the same temperature.



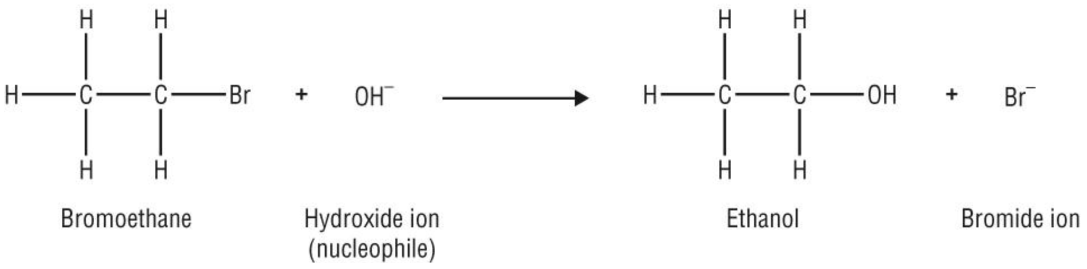
Bond polarity

- Greater electronegativity makes a larger δ-, meaning the carbon will have a larger δ+.
- Attracts nucleophiles more

Hydrolysis of halogenoalkanes:

- Halogenoalkanes will react with hot aqueous hydroxide ions to produce an alcohol, usually sodium hydroxide.
- The reaction is called **hydrolysis** and is usually carried out under **reflux**:

Hydrolysis: is a reaction with water or aq hydroxide ions that break a chemical compound into two compounds



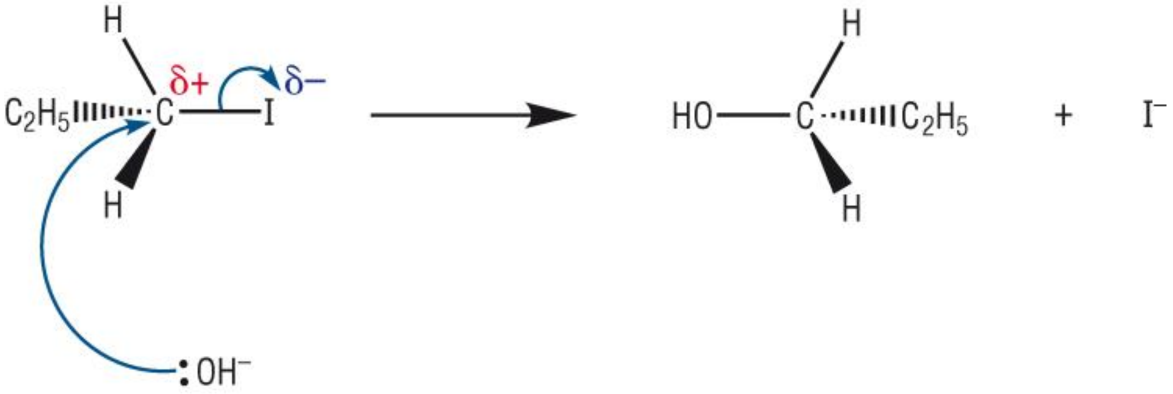
Reactions of the halogenoalkanes

Nucleophilic substitution reactions: Hydrolysis

- During hydrolysis, the halogen is replaced by the hydroxide ion.
- The negative hydroxide ion is attracted to the **δ+** carbon in the molecule, this is known as nucleophilic attack.
- The lone pair electrons from the hydroxide form a dative covalent bond with the carbon.
- This carbon would have too many bonds so the carbon iodine bond breaks.
- As the electrons are already nearest the **δ-** iodine.
- When the carbon - iodine bond breaks heterolytically, the electrons go with the iodine forming iodide, I^- ions.

The mechanism:

- The mechanism shows the movement of electrons with arrows.
- In Module 1A: An arrow with a double head shows the movement of a pair of electrons.



Rate of hydrolysis of primary halogenoalkanes:

- The rates of hydrolysis can be determined by heating the halogenoalkane with aq silver nitrate and ethanol.
- The aq in silver nitrate acts as the nucleophile
- The silver nitrate is the test for the halides which are substituted during hydrolysis.
- The ethanol is a common solvent for the halogenoalkane and silver nitrate to mix.
- As hydrolysis occurs the halogen is substituted with OH.

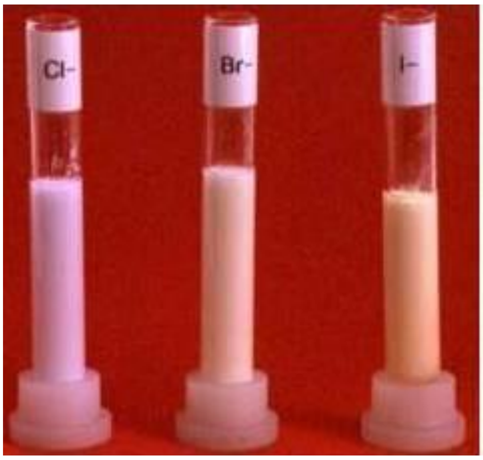
$$CH_3CH_2CH_2CH_2Cl_{(aq)} + H_2O_{(aq)} \rightarrow CH_3CH_2CH_2CH_2OH_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)}$$

- The halide formed react with silver nitrate forming the precipitates.

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$$

White ppt

- The precipitate that forms first indicates which halogenoalkane hydrolyses first:
- Rate can be calculated by 1/time taken for the precipitate to appear.
- In order for the test to be controlled, the test must be done with the same amounts, similar halogenoalkanes, and at a constant temperature



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The procedure:

- **Measure an equal amount of each of the halogenalkane and place in a water bath at 50°C.**
- **Put another tube of ethanol, water and silver nitrate into another tube and place in the water bath.**
- **Once all the tubes have reached the same temperature add an equal amounts of the silver nitrate mixture to each of the 3 halogenoalkanes.**
- **Start timing and record the times at which each of the precipitates form.**
- **The order of which the precipitates appear is indicated in the diagram to the left.**

Polarity vs bond enthalpy (energy):

- 2 factors can affect the rate of hydrolysis:

1) Polarity:

- Electronegativity of the halogens decreases as you go down group 7.
- This means that the C – Cl bond will be more polar than the C – Br bond which will be more polar than the C – I bond:

δ+ δ– □ δ+ □δ– □ δ+□δ–
C – Cl > C – Br > C – I

- The **C - Cl** bond is the most polar of the 3 halogenoalkanes.
- This means that the δ+ carbon in the **C - Cl** bond would attract nucleophiles more readily.
- This means that it would give the fastest reaction.

2) Bond enthalpy (energy):

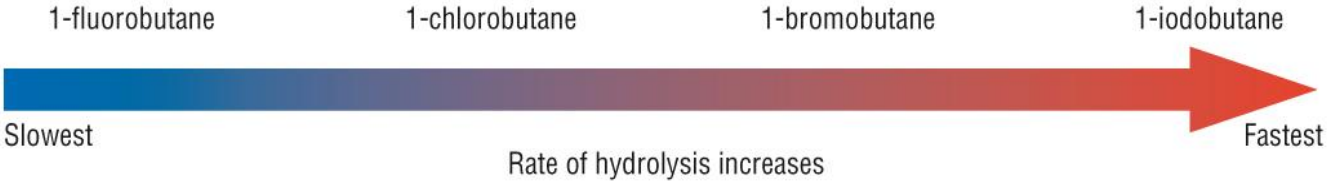
- The bond energies give us a good indication of the reactivity of the halogenoalkanes:

E(C – Cl) = 340 KJ mol^{-1}
E(C – Br) = 280 KJ mol^{-1}
E(C – I) = 240 KJ mol^{-1}

- The weakest would be expected to break first.
- The one that breaks first will form a precipitate with Ag^+ first:
- The **C - I** bond is the weakest of the 3 halogenoalkanes.
- This means that the bond would break more readily.
- This means that it would give the fastest reaction.

Bond enthalpies:

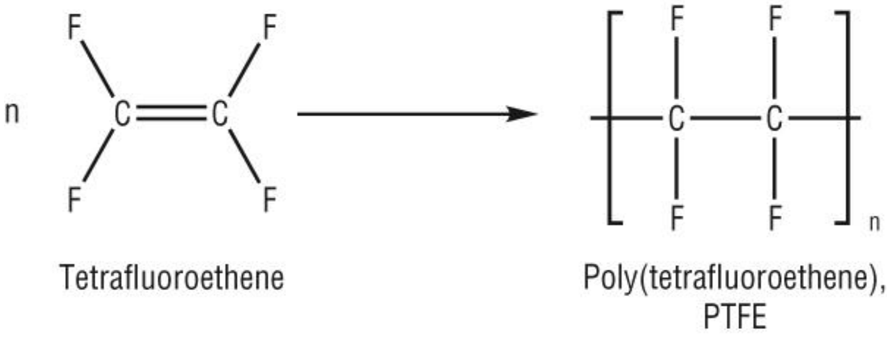
- In hydrolysis, bond enthalpy is more important than polarity:



Halogenoalkanes and the environment:

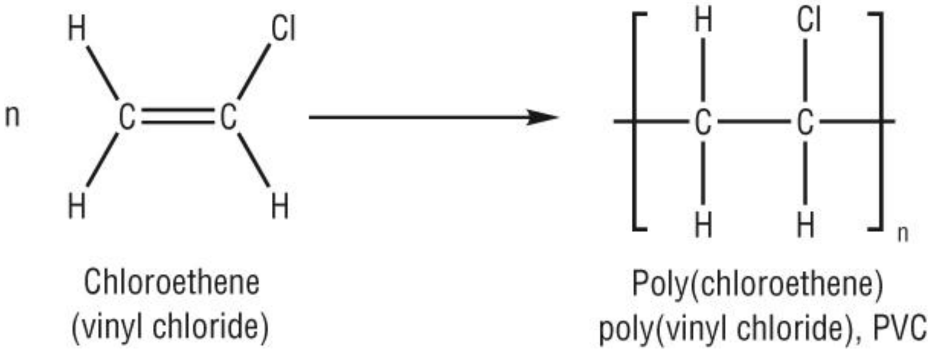
Halogen - containing polymers:

1) PTFE - poly(tetrafluoroethane)



- Used in the non – stick coating on saucepans and in electrical insulation.
- C - F bonds are very strong and make it impervious to heat and chemical attack hence it is used as a coating on pans.

2) PVC – poly(chloroethene):



- Used inn drainpipes, window frames etc.

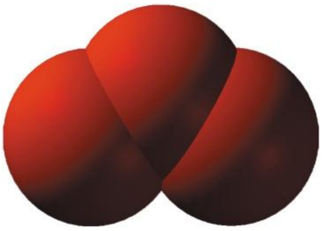
Chlorofluorocarbons, CFC's - enter Thomas Midgley

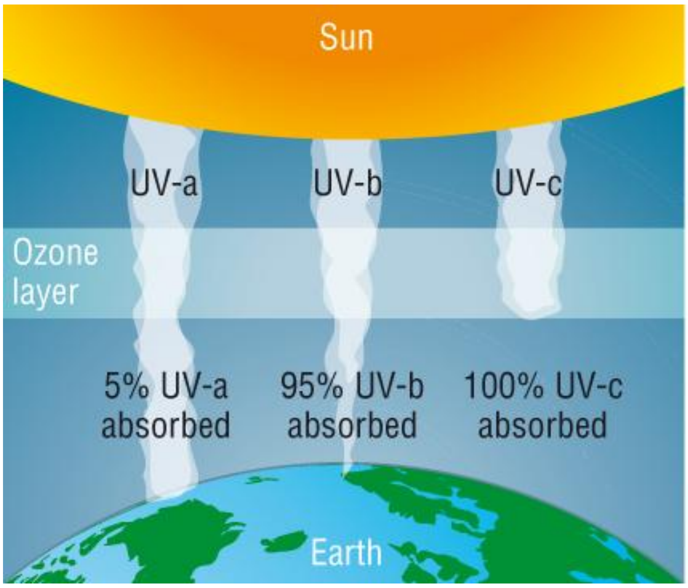
- From the late 1800's to the 1930's gases like ammonia, chloromethane and sulphur dioxide was used as refrigerants.
- 2 of these gases are toxic and when the refrigerators (and air conditioning) leaked, people would die!!
- Thomas Midgley developed a non toxic refrigerant, freon (CCl_2F_2) or CFC's.
- He famously demonstrated the non toxic nature by inhaling the gas and extinguishing a flame by slowly exhaling over it.
- These were used as coolants in refrigerators, aerosol propellants and blowing agents.
- They were also used as blowing agents - the gas in expanded polystyrene foam (now replaced with CO_2.

Trouble with CFCs

- CFC's have a devastating effect on the ozone layer.
- The ozone layer filters out harmful UV light which can cause **skin cancer.**
- CFC's were used in refrigeration and aerosol propellants.
- The stability of CFC's has been the problem and the concentration has slowly built up in the atmosphere.
- In the stratosphere CFC's absorb UV light forming chlorine radicals.
- It is these chlorine radicals that break down ozone to oxygen:

The ozone layer





- Ozone is 3 oxygen atoms joined together.

- We are producing ozone where we don't want it and destroying it where we do want it.
- Low level ozone in the troposphere causes respiratory problems.
- The destruction of high level ozone allows harmful UV radiation to reach earth.

- Ozone acts like a big pair of sunglasses filtering out most of the harmful UV radiation.
- Prior to the formation of ozone our planet was scorched and no life could survive.
- UV radiation is divided into a, b, and c.
- C is the most harmful and is blocked out completely by ozone.
- A is the weakest and only a small amount is absorbed by ozone. This is the one that gives you a tan and ages your skin prematurely.

Ozone formation:

- The first step is the homolytic fission of an oxygen molecule by UV light:

$$O_{2(g)} \quad + \quad UV \quad \rightarrow \quad 2O_{(g)}$$

- This is an oxygen atom which contains 2 unpaired electrons, sometimes called a **di -radical**.
- The oxygen atoms reacts with oxygen molecules forming ozone. This gives out heat - exothermic:

$$O_{(g)} \quad + \quad O_{2(g)} \quad \rightarrow \quad O_{3(g)} \quad + \quad \text{Heat}$$

How the ozone layer works:

- Ozone absorbs UV radiation breaking the molecule into oxygen molecules and atoms:

$$O_{3(g)} \quad + \quad UV \quad \rightarrow \quad O_{2(g)} \quad + \quad O_{(g)}$$

- The oxygen atom then react with an oxygen molecule:

$$O_{(g)} \quad + \quad O_{2(g)} \quad \rightarrow \quad O_{3(g)} \quad + \quad \text{Heat}$$

- Overall, UV is converted to heat energy and this process continues until the 2 reactions reach an equilibrium:

$$O_{(g)} \quad + \quad O_{2(g)} \quad \rightleftharpoons \quad O_{3(g)}$$

Removal of ozone:

$$O_{(g)} \quad + \quad O_{3(g)} \quad \rightarrow \quad 2O_{2(g)}$$

- Oxygen atoms remove ozone. This is a slow reaction but the balance can be affected easily (later).

Ozone depletion

1) CFC's:

- UV light breaks the C – Cl bond releasing chlorine radical

$$CF_2Cl_2 \rightarrow CF_2Cl^{\cdot} + Cl^{\cdot}$$

- This chlorine radical catalyses the decomposition of ozone with the chlorine radical coming out unchanged (and available for more ozone decomposition).

$$Cl^{\cdot} + O_3 \rightarrow ClO^{\cdot} + O_2 \text{ Step 1}$$

$$ClO^{\cdot} + O \rightarrow Cl^{\cdot} + O_2 \text{ Step 2}$$

Overall

$$O_{(g)} \quad + \quad O_{3(g)} \quad \rightarrow \quad 2O_{2(g)}$$

- Free radicals react fast and the chlorine radical could decompose as many as 100000 ozone molecules.
- The oxygen radical in step 2 is produced from UV dissociation of oxygen and ozone in the stratosphere.

2) Nitrogen oxide:

- Nitrogen oxides are formed by lightening strikes and aircraft engines:

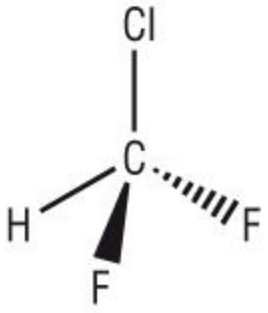
$$^{\cdot}NO + O_3 \rightarrow {}^{\cdot}NO_2 + O_2 \text{ Step 1}$$

$$^{\cdot}NO_2 + O \rightarrow {}^{\cdot}NO + O_2 \text{ Step 2}$$

Overall

$$O_{(g)} \quad + \quad O_{3(g)} \quad \rightarrow \quad 2O_{2(g)}$$

The way forward - alternatives to CFCs



- HCFCs are being used as a temporary replacement until something more suitable is found
- Again they are non toxic and non - flammable.
- They do still deplete ozone but are only about a tenth of the amount.

Ozone friendly products:

- Although these contain no CFCs, they usually contain hydrocarbons like butane.
- This means they are flammable - not ideal!!