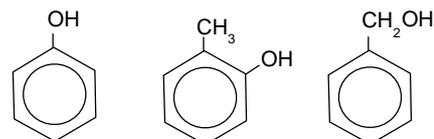


ALCOHOLS

Classification

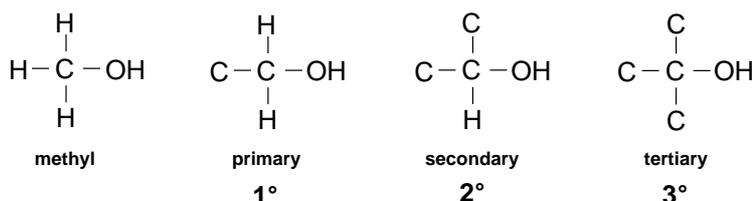
- Aliphatic**
- general formula $C_nH_{2n+1}OH$ - provided there are no rings
 - named as substituted alkanes by removing the final -e and adding -ol
 - for isomers the position of the OH is given by a number - *propan-1-ol and propan-2-ol*
- Aromatic**
- in aromatic alcohols (or phenols) the OH must be **attached directly to a benzene ring**
 - an OH on a side chain of a benzene ring behaves as a typical aliphatic alcohol.

Q.1 Which of the structures is/are classified as phenols?



Structural differences

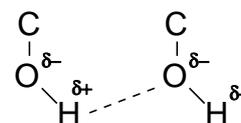
- alcohols are classified according to the environment of the OH functional group
- chemical behaviour, especially with oxidation, often depends on the structural type



Physical properties

Boiling point Increases with molecular size due to increased van der Waals' forces. Alcohols have **higher boiling points** than similar molecular mass alkanes due to the added presence of **inter-molecular hydrogen bonding**. More energy is required to separate the molecules.

		M_r	bp / °C
ethanol	C_2H_5OH	46	+78
propane	C_3H_8	44	-42



intermolecular hydrogen bonding in alcohols

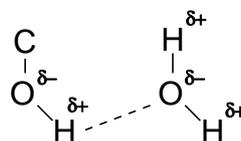
Boiling point also increases for "straight" chain isomers. Greater branching = lower inter-molecular forces.

		bp / °C
butan-1-ol	$CH_3CH_2CH_2CH_2OH$	118
butan-2-ol	$CH_3CH_2CH(OH)CH_3$	100
2-methylpropan-2-ol	$(CH_3)_3COH$	83

Solubility

Low molecular mass alcohols are **miscible with water** due to **hydrogen bonding** between the two molecules.

Alcohols are themselves very good solvents, being able to dissolve a large number of organic molecules.



intermolecular hydrogen bonding with water

CHEMICAL PROPERTIES

General Lone pairs on the oxygen atom of alcohols make them **Lewis Bases** (lone pair donors).

They can use a lone pair to

- pick up protons
- behave as nucleophiles.

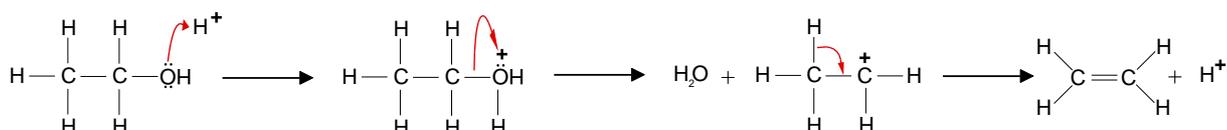
Elimination *Reagent* conc. sulphuric acid (H₂SO₄) or conc. phosphoric acid (H₃PO₄)

Conditions reflux 180°C

Product alkene

Equation e.g. $\text{C}_2\text{H}_5\text{OH}_{(l)} \longrightarrow \text{CH}_2 = \text{CH}_{2(g)} + \text{H}_2\text{O}_{(l)}$

Mechanism

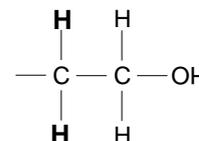


Step 1 protonation of the alcohol using a lone pair on oxygen

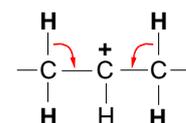
Step 2 loss of a water molecule to generate a carbocation

Step 3 loss of a proton (H⁺) to give the alkene

Note 1 There must be a hydrogen atom on a carbon atom adjacent the carbon with the OH on it



Note 2 Alcohols with the OH in the middle of a chain can have two ways of losing water. In **Step 3** of the mechanism, a proton can be lost from either side of the carbocation. This can give a **mixture of alkenes from unsymmetrical alcohols**



Elimination

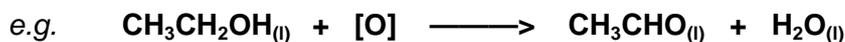
Method 2 *Conditions* Pass vapour over a heated catalyst of pumice or aluminium oxide

Q.3 *Butan-2-ol reacts with concentrated sulphuric acid to give THREE isomeric alkenes. What are they and how are they formed?*

Oxidation of Alcohols

Provides a way of differentiating between primary, secondary and tertiary alcohols
The usual reagents are acidified potassium dichromate(VI) or potassium manganate(VII)

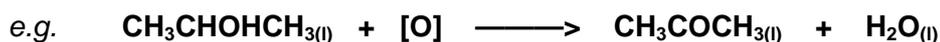
Primary **Easily oxidised to aldehydes and then to carboxylic acids.**



- it is essential to **distil off the aldehyde** before it gets oxidised to the acid
- the alcohol is dripped into a warm solution of the oxidising agent - acidified $\text{K}_2\text{Cr}_2\text{O}_7$
- because the **aldehyde has a low boiling point** - no hydrogen bonding - it distils off
- if it didn't distil off it would be oxidised to the equivalent carboxylic acid
- to oxidise an alcohol straight to the acid you would reflux the mixture

<i>compound</i>	<i>formula</i>	<i>intermolecular bonding</i>	<i>boiling point</i>
ETHANOL	$\text{C}_2\text{H}_5\text{OH}$	HYDROGEN BONDING	78°C
ETHANAL	CH_3CHO	DIPOLE-DIPOLE	23°C
ETHANOIC ACID	CH_3COOH	HYDROGEN BONDING	118°C

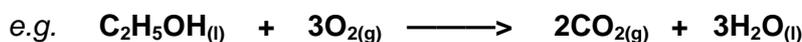
Secondary **Easily oxidised to ketones**



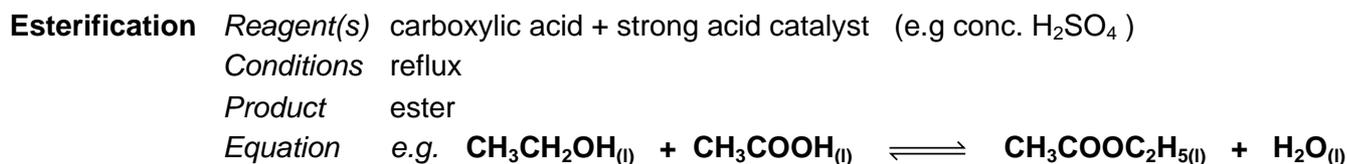
N.B. On prolonged treatment with a powerful oxidising agent they can be further oxidised to a mixture of acids with fewer carbon atoms than the original alcohol.

Tertiary **Not oxidised under these conditions.** They do break down with very vigorous oxidation

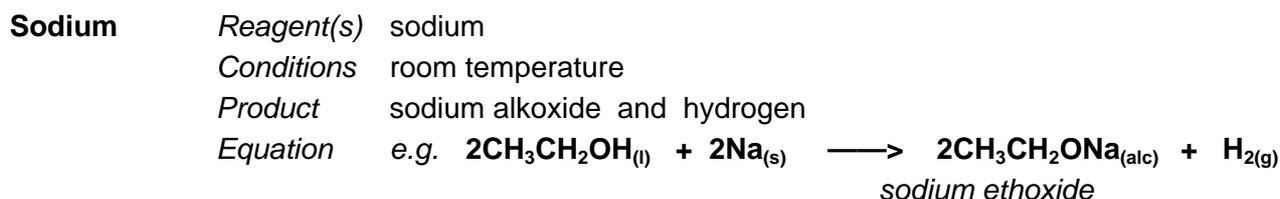
Combustion Alcohols make useful fuels



- have high enthalpies of combustion
- do not contain sulphur so there is less pollution
- can be obtained from renewable resources

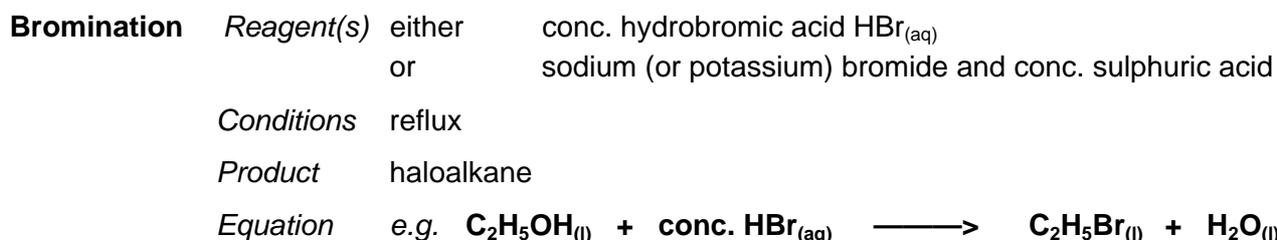


One **advantage of concentrated H_2SO_4** is that it is also a **dehydrating agent** and removes water as it is formed causing the equilibrium to move to the right and thus **increasing the yield** of ester.

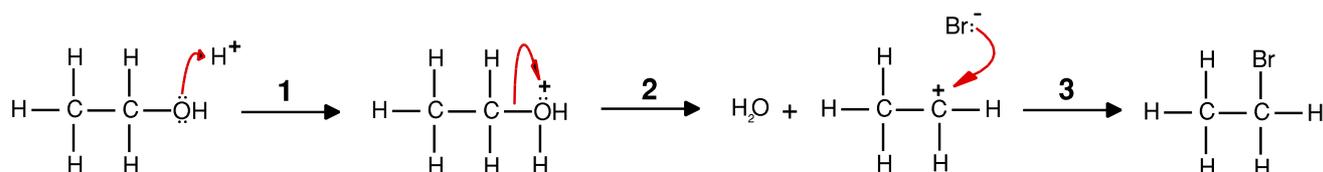


Alcohols are organic chemistry's equivalent of water; water reacts with sodium to produce hydrogen and so do alcohols. The reaction is **slower with alcohols than with water**.

Alkoxides are white, ionic crystalline solids e.g. $\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+$



Mechanism The mechanism starts off in a similar way to the dehydration (protonation of the alcohol and loss of water) but the carbocation (carbonium ion) is attacked by a nucleophilic bromide ion in step 3.



- Step 1** protonation of the alcohol using a lone pair on oxygen
Step 2 loss of a water molecule to generate a carbocation (carbonium ion)
Step 3 a bromide ion behaves as a nucleophile and attacks the carbocation

IDENTIFYING ALCOHOLS USING INFRA RED SPECTROSCOPY

INFRA RED SPECTROSCOPY

Chemical bonds vibrate at different frequencies. When an infra red (IR) radiation is passed through a liquid sample of an organic molecule, some frequencies are absorbed. These correspond to the frequencies of the vibrating bonds.

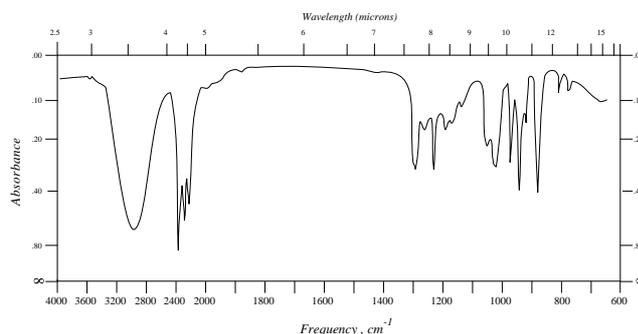
Most spectra are very complex due to the large number of bonds present and each molecule produces a unique spectrum. However the presence of certain absorptions can be used to identify functional groups.

BOND	COMPOUND	ABSORBANCE	RANGE
O-H	alcohols	broad	3200 cm^{-1} to 3600 cm^{-1}
O-H	carboxylic acids	medium to broad	2500 cm^{-1} to 3500 cm^{-1}
C=O	ketones, aldehydes esters and acids	strong and sharp	1600 cm^{-1} to 1750 cm^{-1}

Differentiation	Compound	O-H	C=O
	ALCOHOL	YES	NO
	ALDEHYDE / KETONE	NO	YES
	CARBOXYLIC ACID	YES	YES
	ESTER	NO	YES

BUTAN-1-OL

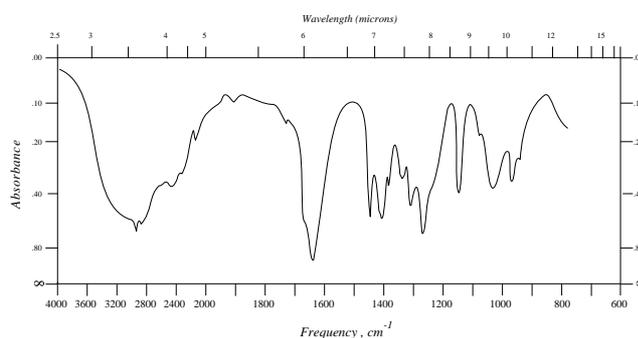
O-H absorption



PROPANOIC ACID

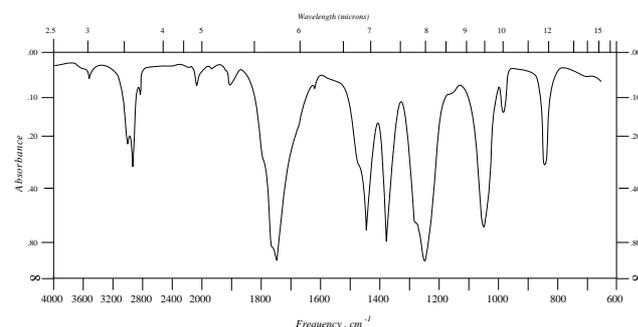
O-H absorption

C=O absorption



ETHYL ETHANOATE

C=O absorption



INDUSTRIAL PREPARATION OF ETHANOL - SUMMARY

FERMENTATION

Reagent(s) GLUCOSE - from hydrolysis of starch

Conditions yeast
warm but no higher than 37°C

Equation $\text{C}_6\text{H}_{12}\text{O}_6 \longrightarrow 2 \text{C}_2\text{H}_5\text{OH} + 2 \text{CO}_2$



- **LOW ENERGY PROCESS**
- **USES RENEWABLE RESOURCES - PLANTS**
- **SIMPLE EQUIPMENT**



- **SLOW**
- **PRODUCES IMPURE ETHANOL**
- **BATCH PROCESS**

HYDRATION OF ETHENE

Reagent(s) ETHENE - from cracking of fractions from distilled crude oil

Conditions catalyst - phosphoric acid
high temperature and pressure

Equation $\text{C}_2\text{H}_4 + \text{H}_2\text{O} \longrightarrow \text{C}_2\text{H}_5\text{OH}$



- **FAST**
- **PURE ETHANOL PRODUCED**
- **CONTINUOUS PROCESS**



- **HIGH ENERGY PROCESS**
- **EXPENSIVE PLANT REQUIRED**
- **USES NON-RENEWABLE FOSSIL FUELS TO MAKE ETHENE**

USES

- **ALCOHOLIC DRINKS**
- **SOLVENT** - industrial alcohol / methylated spirits (methanol is added)
- **FUEL** - used as a petrol substitute in countries with limited oil reserves