ALCOHOLS

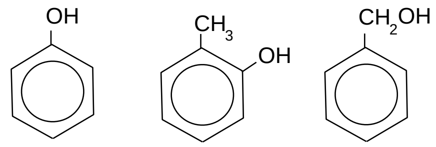
Aliphatic

- **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 a number - *propan-1-ol / propan-2-ol*

Aromatic

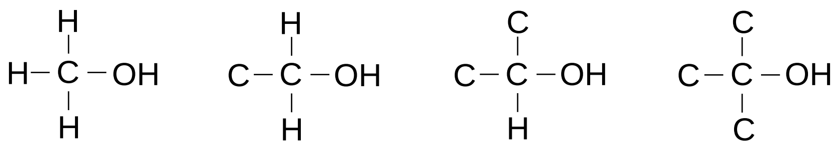
- in aromatic alcohols, the OH must be **attached directly to a benzene ring**
- an OH on a side chain of a benzene ring behaves as a typical aliphatic alcohol.

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



Structures

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

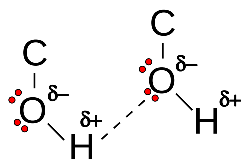


methyl **primary 1°** **secondary 2°** **tertiary 3°**

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



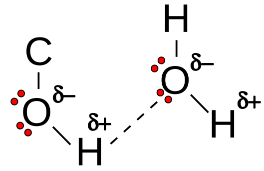
intermolecular hydrogen bonding in alcohols

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

PREPARATION OF ALCOHOLS

Laboratory
- **from haloalkanes** - reflux with aqueous sodium or potassium hydroxide.
- **from aldehydes** - reduction with sodium tetrahydridoborate(III) - $NaBH_4$.
- **from alkenes** - acid catalysed hydration using conc. sulphuric acid.

Industrial **Fermentation**

Reagent(s) GLUCOSE - from hydrolysis of starch

Conditions yeast
warm but no higher than 37°C

Equation $\mathbf{C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2\ CO_2}$

Direct hydration

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

Conditions
- catalyst - phosphoric acid
- high temperature and pressure

Equation $\mathbf{C_2H_4 + H_2O \rightleftharpoons C_2H_5OH}$

Q.2 *List some advantages and disadvantages of the two major industrial methods.*

Fermentation *advantage(s)*

disadvantage(s)

Hydration *advantage(s)*

disadvantage(s)

Uses *ethanol*
-
-
-

methanol
- fuel, **added to petrol** to improve combustion properties
- **solvent**
- a **feedstock** for important industrial processes

CHEMICAL PROPERTIES

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

They can use a lone pair to
- pick up protons
- behave as nucleophiles.

Elimination

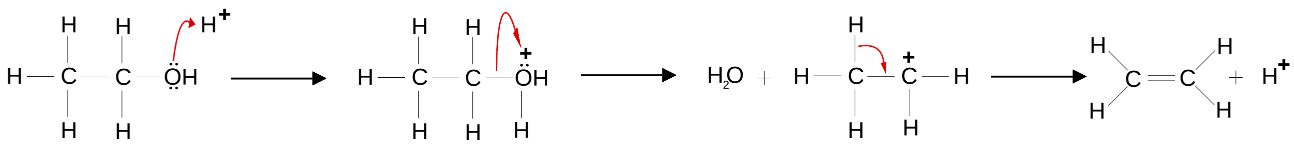
Reagent conc. sulphuric acid (H_2SO_4) or conc. phosphoric acid (H_3PO_4)

Conditions reflux 180°C

Product alkene

Equation *e.g.* $\mathbf{C_2H_5OH}$(l) ———> $\mathbf{CH_2 = CH_2}$(g) + $\mathbf{H_2O}$(l)

Mechanism

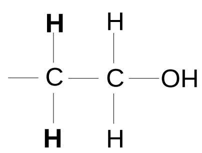


Step 1 protonation of the alcohol using a lone pair on oxygen

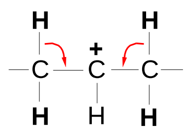
Step 2 loss of a water molecule to generate a carbocation

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 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

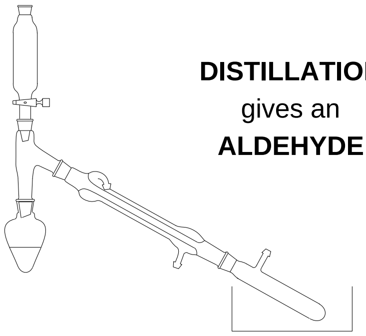
Provides a way of differentiating between primary, secondary and tertiary alcohols. Reagents include acidified potassium dichromate(VI) or potassium manganate(VII)

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

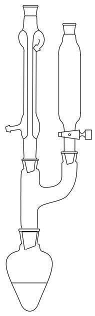
e.g. $\mathbf{CH_3CH_2OH}(l) + [O] \longrightarrow \mathbf{CH_3CHO}(l) + \mathbf{H_2O}(l)$

then $\mathbf{CH_3CHO}(l) + [O] \longrightarrow \mathbf{CH_3COOH}(l)$

- it is essential to **distil off the aldehyde** before it gets oxidised to the acid
- the alcohol is dripped into a warm solution of acidified $K_2Cr_2O_7$
- 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



DISTILLATION gives an **ALDEHYDE**



REFLUXING gives a **CARBOXYLIC ACID**

compound	*formula*	*intermolecular bonding*	*boiling point*
ETHANOL	C_2H_5OH	HYDROGEN BONDING	78°C
ETHANAL	CH_3CHO	DIPOLE-DIPOLE	23°C
ETHANOIC ACID	CH_3COOH	HYDROGEN BONDING	118°C

Secondary **Easily oxidised to ketones**

e.g. $\mathbf{CH_3CHOHCH_3}(l) + [O] \longrightarrow \mathbf{CH_3COCH_3}(l) + \mathbf{H_2O}(l)$

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 vigorous oxidation*

Combustion Alcohols make useful fuels

e.g. $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

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

Esterification

Reagent(s) carboxylic acid + strong acid catalyst (e.g conc. H_2SO_4)

Conditions reflux

Product ester

Equation *e.g.* $CH_3CH_2OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

ethanol *ethanoic acid* *ethyl ethanoate*

An **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.

Q.4 *Name these esters;* $HCOOC_2H_5$

CH_3COOCH_3

$CH_3CH_2COOCH_3$

Complete the equations;

$+ \rightleftharpoons HCOOC_2H_5 + H_2O$

$+ \rightleftharpoons CH_3COOCH_3 + H_2O$

$+ \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$

$CH_3CH_2CH_2OH + CH_3CH_2COOH \rightleftharpoons \quad +$

IDENTIFYING ALCOHOLS USING INFRA RED SPECTROSCOPY

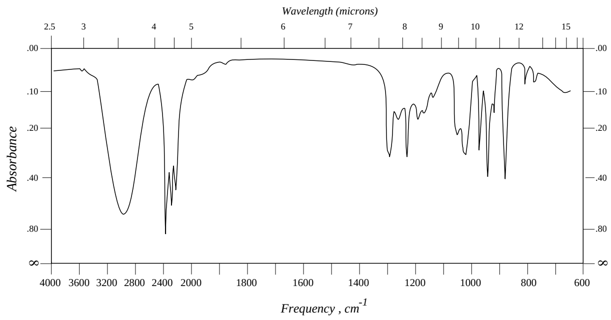
BOND	COMPOUND	ABSORBANCE	RANGE
O-H	alcohols	broad	3200 cm^{-1} to 3600 cm^{-1}
O-H	carboxylic acids	medium to broad	2500 cm^{-1} to 3500 cm^{-1}
C=O	ketones, aldehydes esters and acids	strong and sharp	1600 cm^{-1} to 1750 cm^{-1}

Differentiation

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

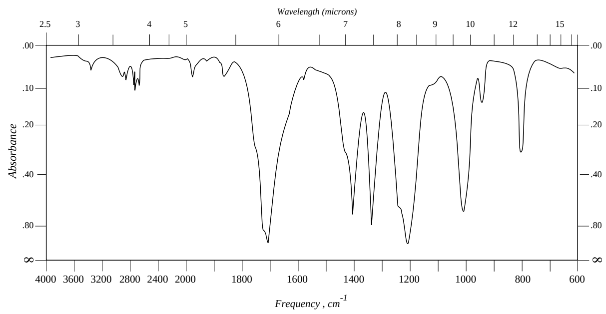
ALCOHOL

O-H absorption



ALDEHYDE

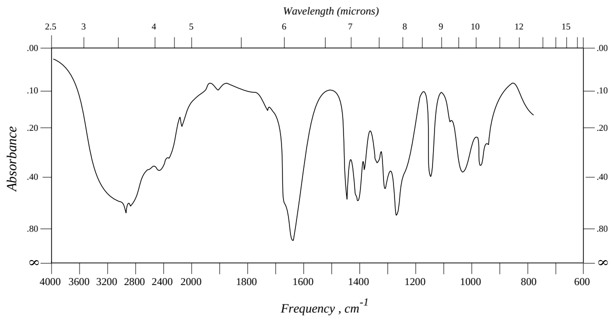
C=O absorption



CARBOXYLIC ACID

O-H absorption

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 $$C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2\ CO_2$$

✔
- **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 $$C_2H_4 + H_2O \longrightarrow C_2H_5OH$$

✔
- **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