ALCOHOLS

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Alcohols form a homologous series with the general formula C_nH_{2n+1} OH.

Alcohols are compounds that have hydroxyl groups bonded to saturated, sp^3 - hybridized carbon atoms; (phenols have hydroxyl groups bonded to an aromatic ring).

The polar — OH group readily forms hydrogen bonds to similar groups in other molecules.

Alcohols can be thought of as organic derivatives of water in which one of the water hydrogens is replaced by an organic substituent: R-O-H, versus H-O-H. The geometry around the oxygen atom in alcohols is similar to that of the water molecule, with two lone pairs of electrons:

Alcohols occur naturally and have a wide range of valuable industrial and pharmaceutical applications. For example, ethanol is used as a fuel additive, an industrial solvent, and a beverage; menthol, an alcohol isolated from peppermint oil, is used as a flavouring agent; BHT (FYI: butylated hydroxytoluene) is widely used as a food additive to prolong shelf life and protect against oxidation.

Nomenclature

Alcohols are named by adding the suffix ' --ol' to the alkane stem of the compound. The longest carbon chain that contains the -OH group is chosen as the stem. A digit can precede the '-ol' to describe the position of the –OH group along the chain.

Alcohols can be subdivided into 3 categories: according to the number of carbon atoms attached to the same C-atom as the -OH group, (i.e. the hydroxyl bearing carbon):

	primary (1^0)	secondary (2^0)	tertiary (3^0)
E.g.	propanol	propan-2-ol	2-methyl propan-2-ol

Assignment: Draw all possible isomers with the formula: C_4H_9OH
(There are five isomers in all: two are primary alcohols, two are secondary alcohols, and one is tertiary alcohol)

The hydrogen atoms attached to the same C-atom as the -OH group are readily oxidized and so these three alcohols behave differently to oxidizing agents such as acidified $KMnO_4$ / $K_2Cr_2O_7$.

Certain commonly occurring alcohols have trivial names that are accepted by IUPAC. The IUPAC name for an alcohol is – ol, where the – e of the alkane is dropped and replaced by – ol.

C_6H_5 - CH_2OH	OH - CH_2CH_2 - OH	CH_3-CH(OH)-CH_3
benzyl alcohol	Ethylene glycol (antifreeze)	isopropyl alcohol
phenylmethanol	ethan-1,2-diol	(Rubbing alcohol)
		(propan-2-ol)
$(CH_3)_3$-C-OH	HO-CH_2-CH(OH)CH_2(OH)	
Tert-butyl alcohol	glycerol, glycerin (strong attraction for water .:	
2-methyl-propan-2-ol	propan-1,2,3-triol (used in lotions, creams)	

Assignment: Write structural formulae for the following:
a) 2-methyl propan-1-ol (b) prop-2-ene-1-ol (c) 2-methylbutan-1-ol

Shape of the Hydroxy Compounds

The geometry around the oxygen atom in alcohols is similar to that of the water molecule, with two lone pairs of electrons.

	:O:	:O:	:O:
	/ \	/ \	/ \
	H H	H_3C H	R H
Bond Angle	104^0	109^0	105^0

Why the increased bond angle in methanol? The CH_3- group is large compared to the H-atom in H_2O, .: more repulsion, hence the atoms are pushed out ⟶ increasing the bond angle.

Physical Properties

Alcohols change state gradually from liquids ⟶ solids : why?
Lower member alcohols are soluble : why?
Solubility decreases as chain length increases : why?
Alcohols have much higher boiling points than the corresponding alkanes : why?

Because of the polarity of the O - H group, this confers a measure of polar character to the molecule as a whole. Alcohols are substantially less volatile, have higher melting points and greater water solubility than the corresponding hydrocarbons. The lower alcohols (C_1, C_2, C_3, and some isomers of C_4) are totally miscible with water, due to hydrogen bonding between the alcohol molecules and water molecules:

As the length of the alkyl chain increases, van-der-Waals attraction predominates between the molecules of the alcohol, and so the miscibility with water decreases.
All alcohols, (recall H-bonding), have ethers, (recall only dipole-dipole interaction) as
(As chain length increases, the polar part becomes less significant, i.e the hydrophilic O - H part is less significant than the "water-insoluble" hydrophobic hydrocarbon backbone.)

Alcohols have much higher boiling points than the corresponding alkanes : why?

The reason for the unusually high boiling points and solubility of alcohols and phenols is due to the fact that like water, they are highly associated in solution due to the formation of strong intermolecular hydrogen bonds. The positively polarised hydroxyl hydrogen atom from one molecule forms a weak hydrogen bond to the negatively polarised oxygen atom of another molecule. The presence of a great many such hydrogen bonds in solution means that extra energy is required to break them during the boiling process. See Table below:

Molecule	**propan-1-ol,**	**chloroethane**	**butane**
Formula	C_3H_7OH	Cl– C_2H_5	C_4H_{10}
Molar mass (g mol$^{-1)}$	60	65	58
b.p (^{0}C)	97	12.5	-5

Branched chains have lower bp than the straight chain molecules, indicating greater compactness sterically).
The strength of the IMFA's increases with the size of the molecule, .: increasing boiling point. (octanol: bp = 195 ^{O}C).

Isomerism

Alcohols show chain, positional and optical isomerism.
Ethers are isomers of alcohols, but they do not contain the –OH group. See later notes on ethers.

C_2H_6O has two isomers: ethanol methoxymethane (dimethyl ether)

Also structural isomerism exhibited:
C_3H_7OH: propan -1-ol propan-2-ol methoxyethane

Preparation of Alcohols

1. Hydration of an alkene:
Conditions:
Markovnikov's Rule:

$$-C=C- \xrightarrow{H^{+1}/H_2SO_4} -\underset{H}{\underset{|}{C}}-\underset{OSO_3H}{\underset{|}{C}} \xrightarrow{H^{+1}/OH^{-1}} -\underset{H}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}-$$

2. Hydrolysis of a halogenoalkane:
Conditions: cold, dilute aqueous alkali:

$$R-X + OH^{-1} \longrightarrow R-OH + X^{-1}$$

Chemical Properties

All alcohols burn well in air, but only the combustion of ethanol is of everyday importance. Ethanol is used as a fuel.

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

Ethanol is marketed as 'methylated spirit' for the use of fuel in stoves, and as a common solvent. This contains about 90 % ethanol, together with 5 % water, 5 % methanol, and pyridine. The poisonous methanol is added to make it undrinkable, and hence exempt from the large excise duty charged on spirits. The pyridine gives it a bitter taste, which makes it unpalatable.

The other reactions of alcohols can be divided into three groups:

- reactions involving the breaking of the O – H bond
- reactions involving the breaking of the C – H bond
- oxidation of the – CHOH group (not in tertiary alcohols, these do not contain an H atom attached to the C– atom)

1. **Reaction with alkali metals (reaction involving the fission of -O-H bond)**

Note: in the past we have encountered… $H\text{-}OH + Na \longrightarrow NaOH + \frac{1}{2} H_{2\,(g)}$

We now encounter: $R\text{-}OH + Na \longrightarrow NaOR + \frac{1}{2} H_{2\,(g)}$

Example: $C_2H_5OH + Na \longrightarrow C_2H_5ONa + \frac{1}{2} H_{2\,(g)}$

C_2H_5ONa, sodium ethoxide is a white solid, soluble in water, to give a strongly alkaline solution, and is soluble in ethanol.

This is used as a **test for an – OH group.**
The alcohol can be regenerated from the alkoxide salt by addition of water:

$$CH_3ONa + H_2O \longrightarrow CH_3OH + NaOH$$

2. **Reaction with Carboxylic Acids: Esterification**

Alcohols react with carboxylic acids to form esters, esterification is used in food flavorings and analegesics (methyl salicylate). The reaction is catalysed by strong acids, this is an example of homogeneous catalysis: the catalyst makes the reactive site more reactive or the leaving group more stable.
The conc. H_2SO_4 plays a dual role:
(1) acts as a catalyst, to increase the rate of the reaction
(2) to shift the position of the equilibrium to the right, acting as a dehydrating agent, absorbs H_2O

Note: mechanism is whereby the -OH is removed from the carboxylic acid, H^{+1} ionizes from the alcohol:
Proof of Mechanism:

$$C_2H_5O^{18}\text{-}H + HO\text{-}OCCH_3 \rightleftharpoons CH_3\overset{\overset{\large O}{\|}}{C}\text{–}O^{18}\text{-}C_2H_5 + H_2O$$

labelled oxygen isotope in alcohol — oxygen isotope found in ester, not in water, ethyl ethanoate

Def: **Condensation reaction**

Naming esters:

3. Conversion to Alkyl Halides

If the acid used is concentrated HCl, HBr or HI, the halide ion, X^{-1} will displace the H_2O from the protonated alcohol forming an alkyl halide. Therefore the overall product will be the replacement of the hydroxyl group by the halogen.

This is a very useful method for the preparation of alkyl halides, and is used as a **test to distinguish between primary, secondary and tertiary alcohols**. It relies on the fact that alcohols are soluble in the reagent (conc. HCl), whereas the halogenoalkane formed are not, therefore a cloudiness is produced in the solution.

$$R\text{–}OH + H\text{-}X \longrightarrow R\text{–}X + H_2O \qquad X = Cl, Br, I$$

Again, as explained above, the reaction works best for 3^0 alcohols, the reaction is so rapid with tertiary alcohols that it is often carried out simply by bubbling the pure HX gas into a cold solution of the alcohol, or by adding the 3^0 alcohol to a concentrated solution of $HX_{(aq)}$.

Type of alcohol	**Observation on adding conc. HCl**
R_3COH (tertiary)	Immediate cloudiness appears in the solution
R_2CHOH (secondary)	Cloudiness apparent within 5 minutes
RCH_2OH (primary)	No cloudiness apparent unless warmed

4. Dehydration of Alcohols (alkanols)

(a) Alcohols can be dehydrated (-elimination of water), to give alkenes. Good dehydrating agents include: Al_2O_3, conc. $H_3PO_{4(aq)}$, conc. $H_2SO_{4(aq)}$.

The reaction using **concentrated H_3PO_4 is preferred** because, unlike sulphuric acid, it is not also an oxidising agent, and so the formation of by-products is minimised.

Tertiary alcohols lose water when treated with mineral acid under fairly mild conditions, but primary and secondary alcohols require higher temperature.

$$R\text{-}CH_2\text{-}OH < R_2\text{-}CH\text{-}OH < R_3\text{-}C\text{-}OH$$

Increasing ease of dehydration →

The different classes of alcohols dehydrate under different conditions:

Ethanol ⟶ ethene
propan-2-ol ⟶ prop-1-ene
2-methyl propan-2-ol ⟶ 2-methyl pro-1-ene

(b) Under milder conditions, in the presence of an excess of an alcohol, an **ether is produced**:

$$R—OH + H—O—R' \longrightarrow R—O—R' + H_2O$$

This is an example of a **condensation reaction**, see following notes on ethers.

5. Oxidation of Alcohols

Primary and secondary alcohols are easily oxidised by heating with an acidified solution of potassium dichromate(VI). The orange dichromate (VI) ions are reduced to green chromium (III) ions.

Tertiary alcohols are not easily oxidised.

Secondary alcohols are oxidised to ketones.

$$CH_3\,CH(OH)\,CH_3 \xrightarrow[\text{Heat}]{K_2Cr_2O_7\ +H_2SO_4} CH_3\,COCH_3$$

propan-2-ol ⟶ propanone

Primary alcohols are oxidised to aldehydes, which i turn are even more easily oxidised to carboxylic acids:

$$CH_3CH_2CH_2OH \xrightarrow{K_2Cr_2O_7\ +H_2SO_4} CH_3CH_2CH{=}O \xrightarrow{\text{more oxidant}} CH_3CH_2COOH$$

propan-1-ol ⟶ propanal ⟶ propanoic acid

This oxidation reaction can be used to distinguish between primary, secondary and tertiary alcohols:

Type of alcohol	**observation on warming with $K_2Cr_2O_7 + H_2SO_{4(aq)}$**	**effect of distillate on universal indicator**
R_3COH (tertiary)	stays orange	neutral (stays green), –water produced,
R_2CHOH (secondary)	turns green	neutral stays green, –ketone produced
RCH_2OH (primary)	turns green	acidic (goes red), –carboxylic acid produced

ETHERS

Ethers are isomers of alcohols, but they do not contain the —OH group. Ethers have the functional group —C— O — C —.

Ethers are named by adding '—oxy' to the prefix of the smaller hydrocarbon and joining it to the alkane name of the larger hydrocarbon group.
Example: $CH_3 — O — C_2H_5$ is methoxyethane

Preparation
Ethers are formed when two molecules of alcohol react, in the presence of an excess of an alcohol, under milder conditions of dehydration.

$$R—OH + H—O—R' \longrightarrow R—O—R' + H_2O$$

This is an example of a **condensation reaction**.

Example: propan-1-ol ⟶ propoxypropane + water

Ethers are polar molecules, due to the electronegativity of the oxygen atom, hence they experience dipole-dipole interactions; and are non-linear, with bond angles of 109^0. Ethers cannot form intermolecular hydrogen bonds with each other, because they do not contain a strongly polar $H^{\delta+}$ atom.

Their boiling points, although higher than the corresponding alkanes, are therefore much lower than those of the isomeric alcohols. See Table below:

Compound	**Formula**	**Boiling Point (^oC)**
propane	$CH_3 — CH_2 — CH_3$	– 42
methoxymethane	$CH_3 — O — CH_3$	–24
ethanol	$CH_3 — CH_2 — OH$	78

The lower ethers are quite soluble in water due to hydrogen bonding with water molecules. Ethers are good solvents for polar and non-polar substances.

Ethers are quite inert, showing almost none of the reactions of alcohols. This inertness is a factor that makes them useful as solvents.