Hydroxy compounds

A-Level Chemistry

Alcohols

An **alcohol** 醇 has the –OH (hydroxyl) functional group.

Ethanol, the alcohol in hand sanitiser, kills microbes

Making alcohols

Method	Reagents and conditions
addition of steam to an alkene	$H_2O(g)$, H_3PO_4 catalyst (**electrophilic addition** 亲电加成)
an **alkene** 烯烃 with cold dilute $KMnO_4$	gives a **diol** 二醇 (two –OH groups)
substitution of a **halogenoalkane** 卤代烷	NaOH(aq), heat
reduction 还原 of an **aldehyde** 醛 or **ketone** 酮	$NaBH_4$ or $LiAlH_4$
reduction of a **carboxylic acid** 羧酸	$LiAlH_4$
hydrolysis 水解 of an **ester** 酯	dilute acid or alkali, heat

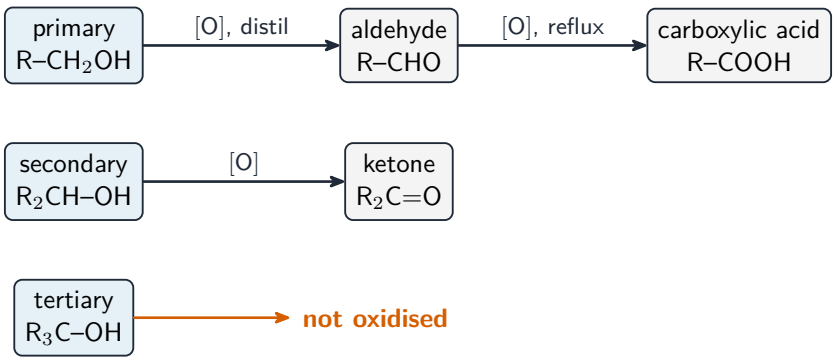
Reactions of alcohols

- **combustion**: alcohols burn in oxygen to give carbon dioxide and water.
- **substitution** to a halogenoalkane, for example with HX, PCl_5, PCl_3 and heat, or $SOCl_2$.
- **with sodium**: alcohols react with sodium metal to give hydrogen and a sodium alkoxide —like water, but more slowly.
- **oxidation** 氧化 with acidified $K_2Cr_2O_7$ (or $KMnO_4$). The product depends on the class of alcohol (see below).
- **dehydration** 脱水 to an alkene, using a hot Al_2O_3 catalyst or concentrated acid.
- **ester formation**: an alcohol reacts with a carboxylic acid (with concentrated H_2SO_4 catalyst) to make an ester.

Three classes and how oxidation tells them apart

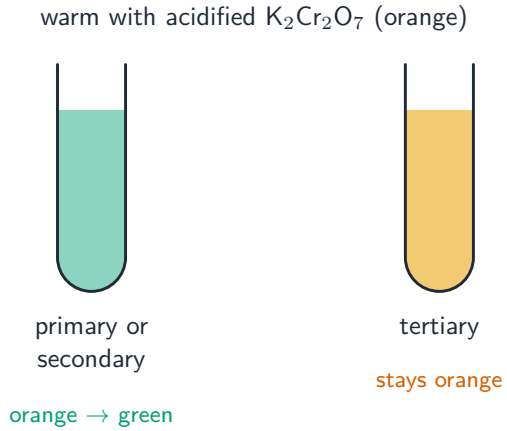
An alcohol is **primary** 伯, **secondary** 仲 or **tertiary** 叔, depending on how many carbons are joined to the carbon holding the –OH. Some molecules have more than one –OH group.

Class	Oxidation product
primary	**aldehyde** (by **distillation** 蒸馏), then **carboxylic acid** (by **reflux** 回流)
secondary	a **ketone**
tertiary	not oxidised



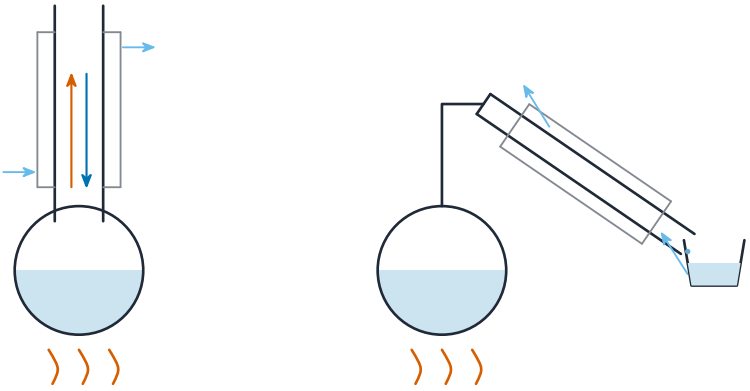
Oxidation by class: a primary alcohol gives an aldehyde then a carboxylic acid, a secondary gives a ketone, a tertiary is not oxidised

In a quick test, acidified $K_2Cr_2O_7$ turns from **orange to green** with a primary or secondary alcohol, but stays orange with a tertiary alcohol.



Acidified dichromate turns orange to green with a primary or secondary alcohol, but stays orange with a tertiary alcohol

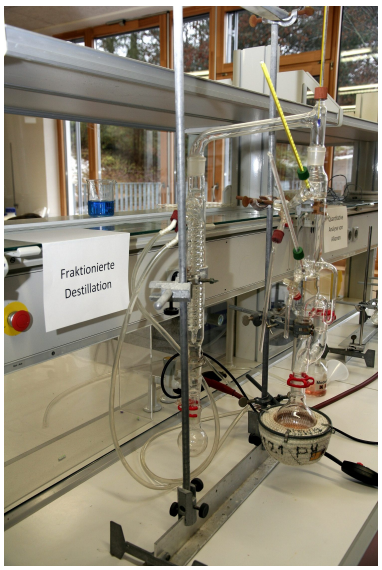
- **distillation** removes the aldehyde as it forms, before it can be oxidised further.
- **reflux** keeps boiling the mixture and returning the vapour, so the alcohol is fully oxidised to the carboxylic acid.



reflux
vapour returns: fully oxidised to the acid

distillation
product distils off as it forms (the aldehyde)

Distillation removes the aldehyde as it forms; reflux keeps boiling and returning the vapour, fully oxidising to the acid



A real distillation set-up: the vapour boils off, cools in the condenser and is collected — the same idea separates ethanol from a fermented mixture

The iodoform test

If you warm an alcohol that contains the $CH_3CH(OH)-$ group with alkaline aqueous iodine, you get a pale yellow precipitate of **tri-iodomethane** 三碘甲烷 (CHI_3) and the ion RCO_2^-. This is a useful test for that group.

Acidity of alcohols

The –OH group makes alcohols very weakly acidic: they can lose the H^+ to form an RO^- ion. But their **acidity** 酸性 is **lower** than that of water. This is because the alkyl group pushes electron density onto the oxygen, which makes the RO^- ion less stable, so the alcohol holds onto its H^+ more tightly.