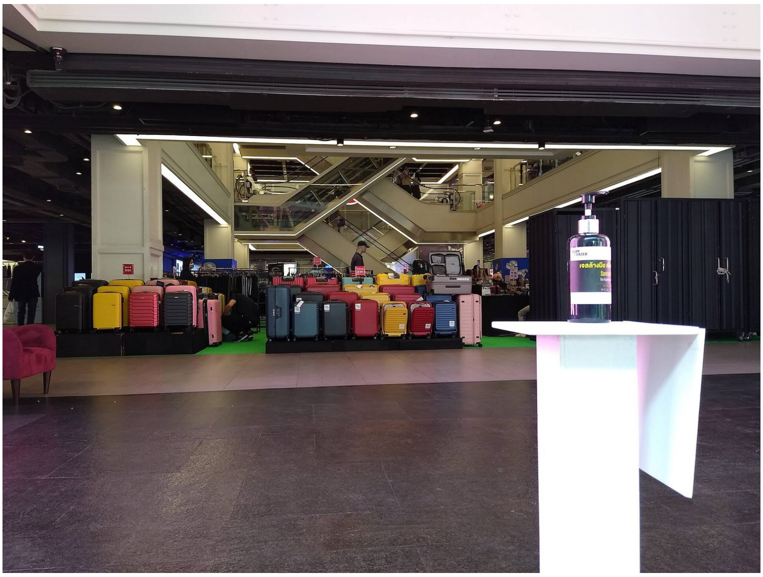
Hydroxy compounds

A-Level Chemistry

Alcohols

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



Ethanol, the alcohol in hand sanitiser, kills microbes

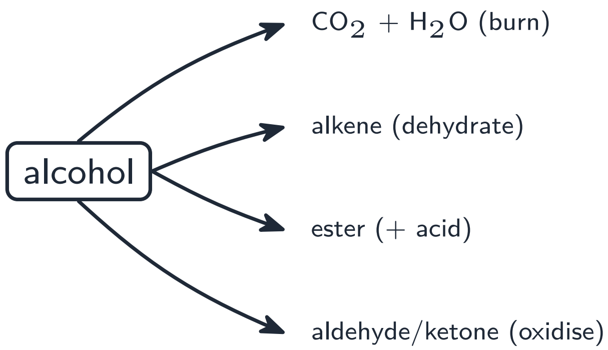
Making alcohols

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.

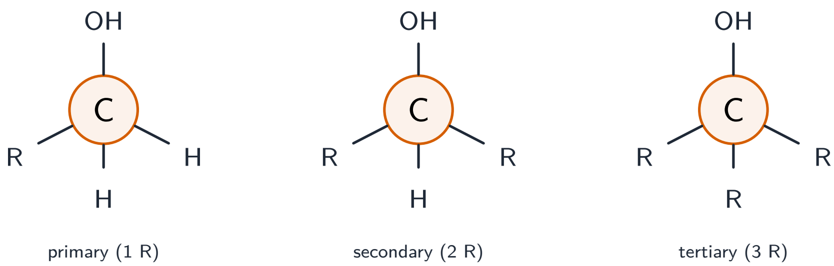
- **oxidation** 氧化 with acidified $K_2Cr_2O_7$ (or $KMnO_4$). The product depends on the class of alcohol (see below).
- **dehydration** 脱水 to an alkene, using a hot Al_2O_3 catalyst or concentrated acid.
- **ester formation**: an alcohol reacts with a carboxylic acid (with concentrated H_2SO_4 catalyst) to make an ester.



An alcohol can burn, dehydrate, esterify or be oxidised

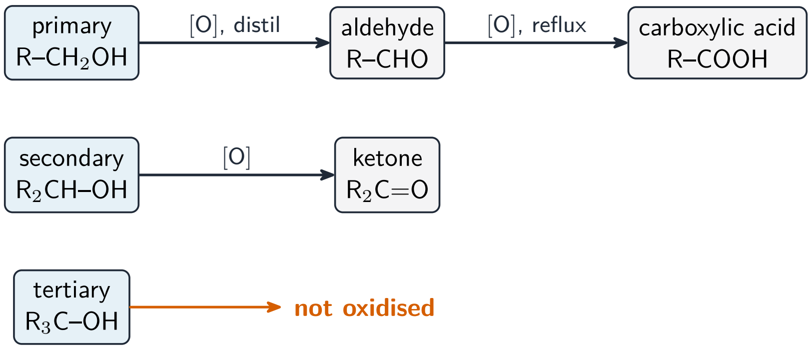
Three classes and how oxidation tells them apart

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.



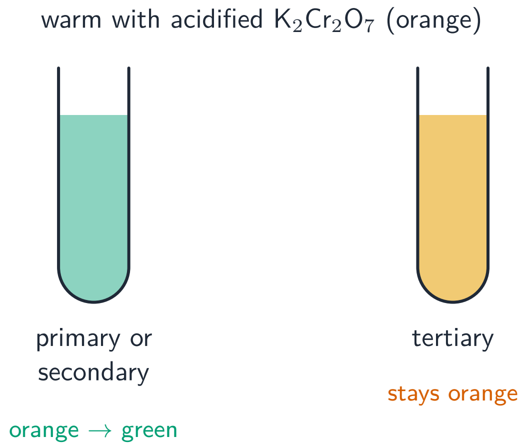
The class is set by the carbon holding the –OH: one R group makes it primary, two secondary, three tertiary — which decides how it oxidises

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



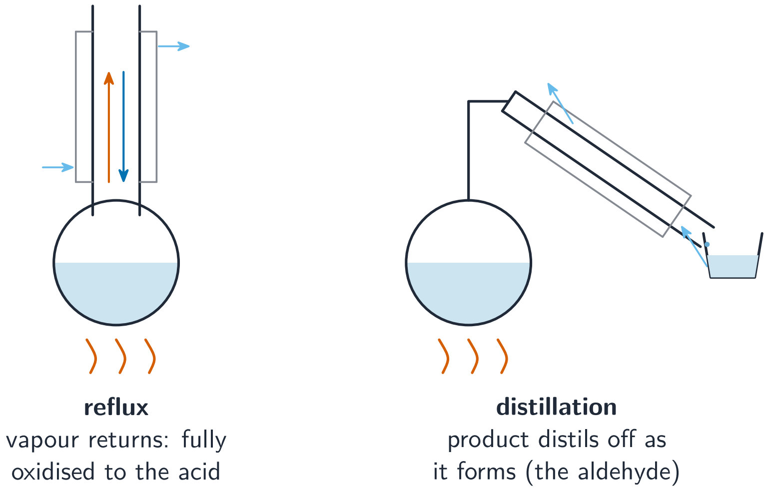
Oxidation by class: a primary alcohol gives an aldehyde then a carboxylic acid, a secondary gives a ketone, a tertiary is not oxidised

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.

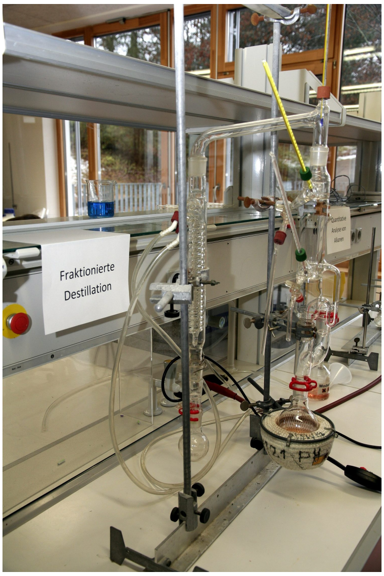


Acidified dichromate turns orange to green with a primary or secondary alcohol, but stays orange with a tertiary alcohol

- **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.



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.

Worked example. Three unlabelled bottles hold butan-1-ol, butan-2-ol and 2-methylpropan-2-ol. How does warming each with acidified $K_2Cr_2O_7$ tell them apart? What matters is how many hydrogens sit on the **carbon carrying the OH**. Butan-1-ol is **primary** (two such hydrogens): the orange dichromate turns **green**, and by distilling you collect an **aldehyde** (butanal), or by refluxing you get the **carboxylic acid** (butanoic acid). Butan-2-ol is **secondary** (one such hydrogen): also **green**, but the product is a **ketone** (butanone), which will not oxidise further. 2-methylpropan-2-ol is **tertiary** (**no** such hydrogen): there is nothing to remove, so the dichromate stays **orange**. The colour only separates the tertiary from the other two - to split primary from secondary you must identify the **product** (an aldehyde gives a silver mirror with Tollens', a ketone does not).

Exam tips

- Classify the alcohol as **primary, secondary or tertiary** first — it decides the oxidation product.
- **Oxidation** with acidified $K_2Cr_2O_7$ (orange $\rightarrow$ green): primary $\rightarrow$ aldehyde (distil) $\rightarrow$ acid (reflux); secondary $\rightarrow$ ketone; tertiary $\rightarrow$ no reaction.
- Distinguish the conditions for **aldehyde vs acid** from a primary alcohol (distillation vs reflux).
- Name esters correctly (the acid part comes second, ending "-oate").