

Hydroxy compounds

A-Level Chemistry

Alcohols

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



Ethanol, the alcohol in hand sanitiser, kills microbes

Image: Maryamarce, CC BY-SA 4.0 (commons.wikimedia.org)

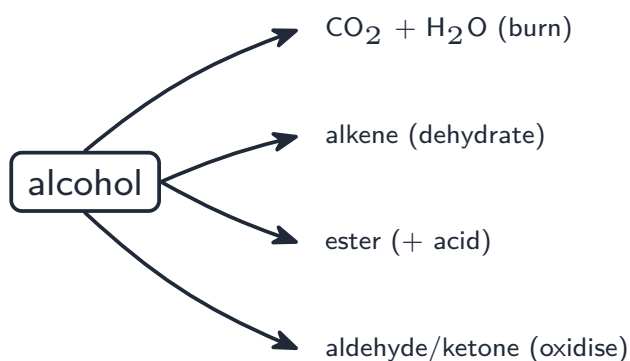
Making alcohols

Method	Reagents and conditions
addition of steam to an alkene	$\text{H}_2\text{O(g)}$, 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 $\text{K}_2\text{Cr}_2\text{O}_7$ (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.

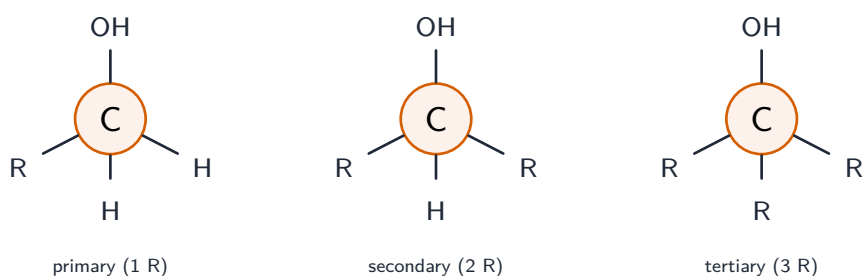
- **ester formation:** an alcohol reacts with a carboxylic acid (with concentrated H_2SO_4 catalyst) to make an ester.



An alcohol can burn, dehydrate, esterify or be oxidised

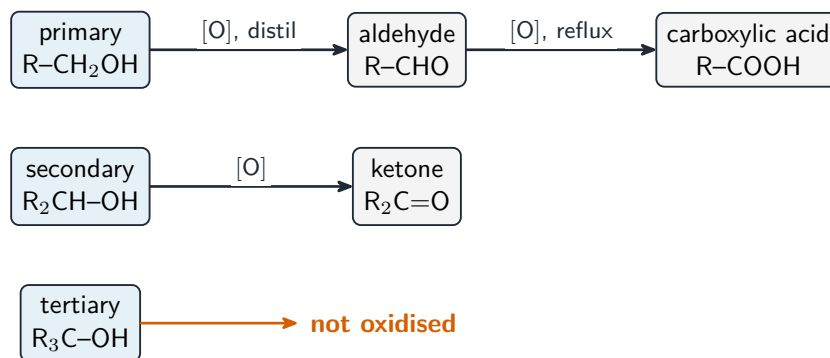
Three classes and how oxidation tells them apart

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



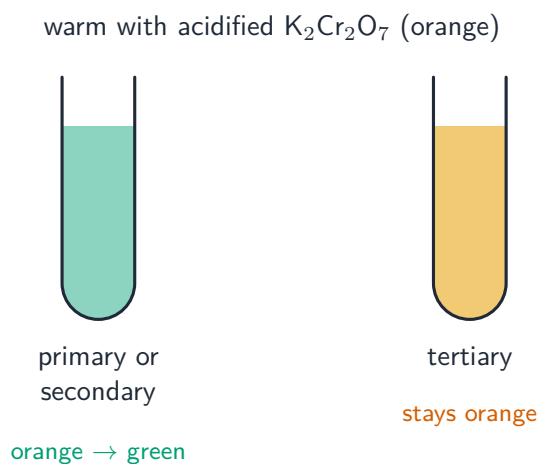
The class is set by the carbon holding the $-\text{OH}$: one R group makes it primary, two secondary, three tertiary—which decides how it oxidises

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



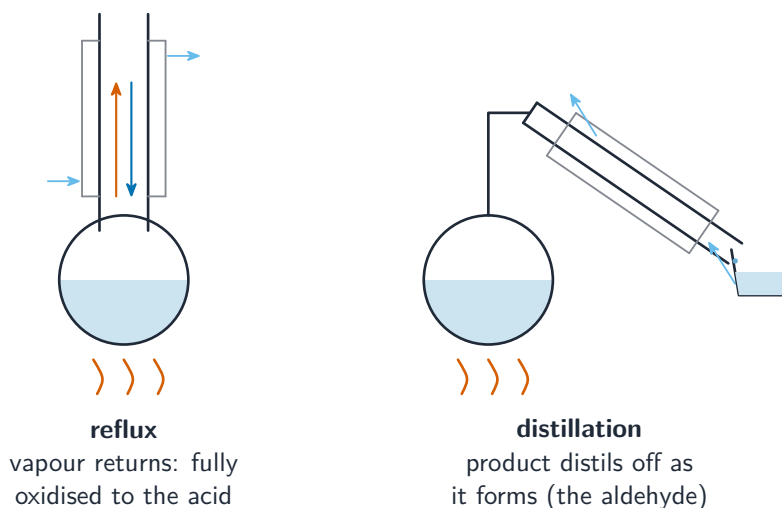
Oxidation by class: a primary alcohol gives an aldehyde then a carboxylic acid, a secondary gives a ketone, a tertiary is not oxidised

In a quick test, acidified $\text{K}_2\text{Cr}_2\text{O}_7$ turns from **orange to green** with a primary or secondary alcohol, but stays orange with a tertiary alcohol.

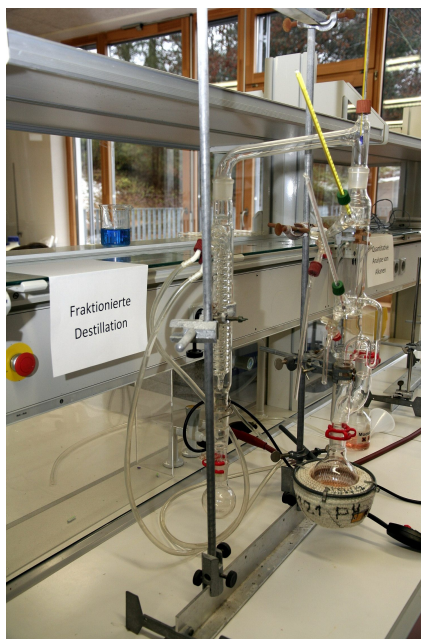


Acidified dichromate turns orange to green with a primary or secondary alcohol, but stays orange with a tertiary alcohol

- **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

Image: Chemie-Verbände Baden-Württemberg, CC BY 2.0 (commons.wikimedia.org)

The iodoform test

If you warm an alcohol that contains the $\text{CH}_3\text{CH}(\text{OH})-$ 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 $\text{K}_2\text{Cr}_2\text{O}_7$ 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 $\text{K}_2\text{Cr}_2\text{O}_7$ (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").