

Oxidising alcohols and testing carbonyl compounds

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Lesson

Quick answer: Primary alcohols are oxidised to aldehydes and then carboxylic acids, secondary alcohols to ketones, and tertiary alcohols resist oxidation; acidified dichromate turns from orange to green. Aldehydes give silver mirrors with Tollens' reagent, ketones do not. Carbonyl compounds undergo nucleophilic addition, for example with cyanide ions.

Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** A Level 3.3.5

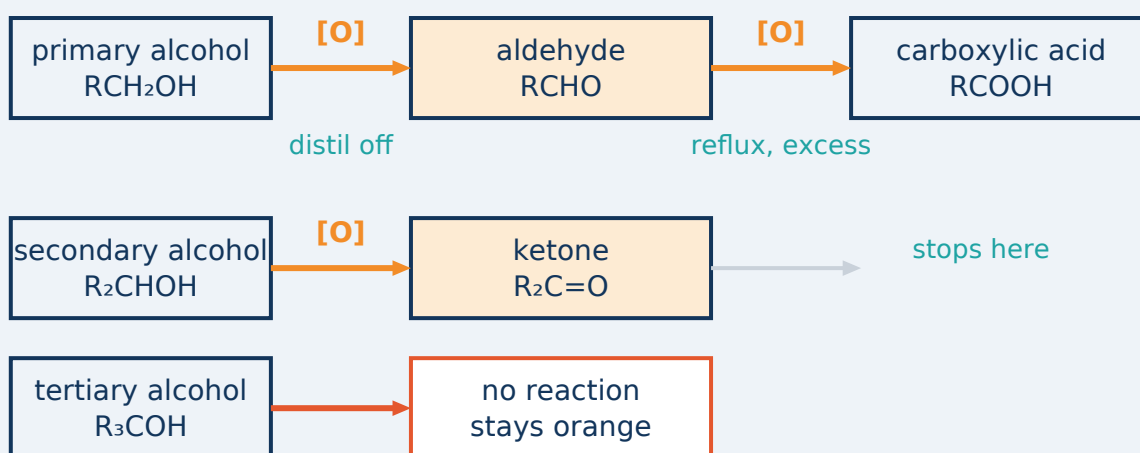
How are alcohols classified, and how are they oxidised?

An alcohol is **primary**, **secondary** or **tertiary** according to how many carbon atoms are bonded to the carbon carrying the OH group: one (or none), two or three. This matters because oxidation removes a hydrogen from that carbon, and tertiary alcohols have none to lose.

The usual oxidising agent is acidified potassium dichromate(VI). The orange dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, is reduced to the green chromium(III) ion, Cr^{3+} , so a colour change tells you that oxidation has happened. In equations the oxidant is written as $[\text{O}]$.

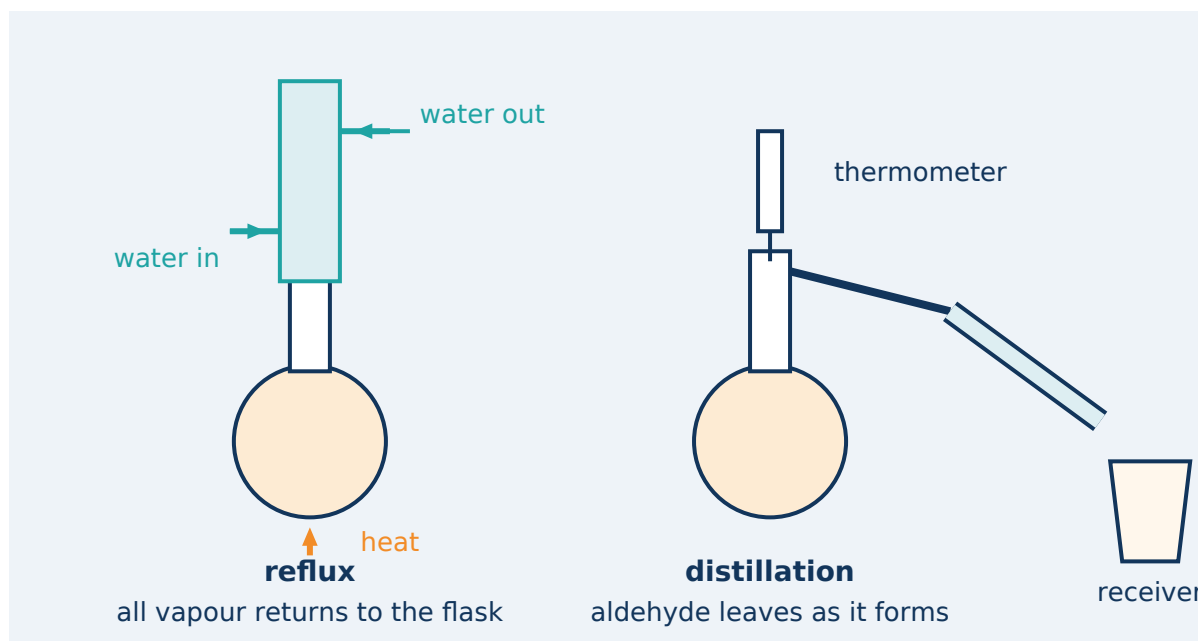
Alcohol	Conditions	Product	Colour change
Primary	warm gently, distil the product out at once	aldehyde	orange to green
Primary	heat under reflux with excess oxidant	carboxylic acid	orange to green
Secondary	heat under reflux	ketone	orange to green
Tertiary	warm	no reaction	stays orange

Number of hydrogens on the carbon carrying OH decides the product



Oxidation of alcohols with acidified dichromate: the number of hydrogens on the C-OH carbon controls the outcome.

For example, propan-1-ol gives propanal, then propanoic acid: $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O}$, and $\text{CH}_3\text{CH}_2\text{CHO} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{COOH}$. An aldehyde boils at a lower temperature than its alcohol (no hydrogen bonding between its molecules), so distilling it away as it forms stops it being oxidised further.



Reflux keeps the mixture in the flask until oxidation is complete; distillation removes the lower-boiling aldehyde at once.

Worked example

Ethanol (4.60 g) is oxidised by distillation to ethanal. The yield is 65 %. Find the mass of ethanal.

$n(\text{ethanol}) = 4.60 / 46.0 = 0.100 \text{ mol}$. Ratio 1 : 1, so theoretical mass = $0.100 \times 44.0 = 4.40 \text{ g}$. Actual mass = $0.65 \times 4.40 = \mathbf{2.86 \text{ g}}$.

How can you tell an aldehyde from a ketone?

Both contain the carbonyl group $\text{C}=\text{O}$, which is polar because oxygen is more electronegative than carbon. An aldehyde has the group $-\text{CHO}$ at the end of the chain; a ketone has $\text{C}=\text{O}$ inside the chain. Only aldehydes are easily oxidised, because the $\text{C}=\text{O}$ carbon of an aldehyde carries a hydrogen.

Definition

A **carbonyl group** is a carbon atom double-bonded to oxygen, $\text{C}=\text{O}$. In an aldehyde it ends the chain ($-\text{CHO}$); in a ketone it sits inside the chain.

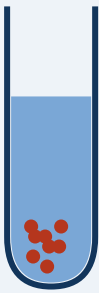
Positive results for an aldehyde such as ethanal



2,4-DNPH
orange precipitate



Tollens'
silver mirror



Fehling's
brick-red precipitate

A ketone gives the DNPH precipitate only

Carbonyl tests: DNPH detects any C=O; Tollens' and Fehling's detect aldehydes only.

Test	Aldehyde	Ketone
2,4-dinitrophenylhydrazine (2,4-DNPH)	orange precipitate	orange precipitate
Tollens' reagent, warm	silver mirror	no change
Fehling's solution, warm	blue to brick-red precipitate	stays blue

2,4-DNPH detects the carbonyl group but cannot separate aldehydes from ketones. However, the precipitate can be purified and its melting point compared with a data table, which identifies the carbonyl compound.

Common mistake

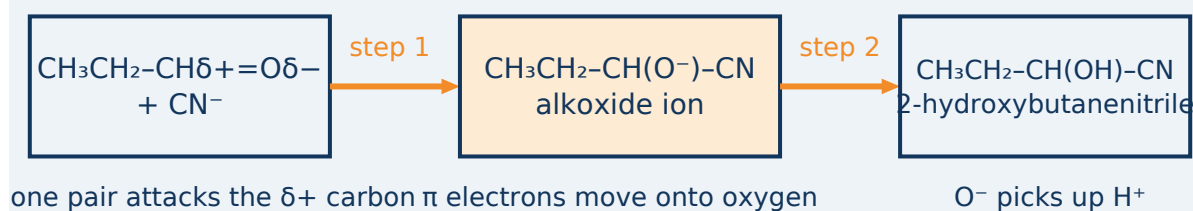
Do not claim that a ketone gives a silver mirror or that 2,4-DNPH distinguishes aldehydes from ketones. Also remember that a tertiary alcohol does not turn dichromate green.

What happens when carbonyl compounds react with nucleophiles?

The carbon of C=O has a partial positive charge, so it is attacked by nucleophiles. Sodium borohydride, NaBH₄, acts as a source of H⁻ ions and reduces aldehydes to primary alcohols and ketones to secondary alcohols, for example $\text{CH}_3\text{COCH}_3 + 2[\text{H}] \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$.

Hydrogen cyanide (made from KCN and acid) adds across C=O by nucleophilic addition. The cyanide ion attacks the carbon, the π electrons move to oxygen, and the oxygen then takes a proton to make a hydroxynitrile. The extra carbon from CN lengthens the chain, and the nitrile can later be hydrolysed to a hydroxy acid.

Nucleophilic addition of HCN to propanal



The planar $C=O$ is attacked from either face, so a racemic mixture forms

Nucleophilic addition: CN^- adds to the carbonyl carbon, then the oxygen is protonated.

Key law

Nucleophilic addition to $C=O$: a nucleophile attacks the δ^+ carbon, the π bond breaks, and the oxygen becomes O^- and is protonated. For an unsymmetrical carbonyl the product has a chiral carbon but forms as a racemic mixture with no optical activity.

Worked example

Give the product of propanal and HCN and explain why it is optically inactive.

$CH_3CH_2CHO + HCN \rightarrow CH_3CH_2CH(OH)CN$, **2-hydroxybutanenitrile**. The central carbon has four different groups (H, OH, CN, C_2H_5), so it is chiral. The planar $C=O$ is attacked equally from both faces, giving equal amounts of two enantiomers: a racemic mixture that does not rotate plane-polarised light.

Lina's tip

Count the hydrogens on the carbon bearing OH: two means primary (aldehyde, then acid), one means secondary (ketone), zero means tertiary (nothing happens).

Key points to remember

- Primary alcohol: aldehyde (distil) then acid (reflux); secondary: ketone; tertiary: no reaction
- $Cr_2O_7^{2-}$ (orange) is reduced to Cr^{3+} (green)
- Tollens' reagent: silver mirror with aldehydes only; Fehling's: brick-red precipitate with aldehydes only
- 2,4-DNPH: orange precipitate with any aldehyde or ketone; melting point identifies the compound
- $C=O$ carbon is δ^+ : nucleophilic addition of CN^- gives a hydroxynitrile as a racemic mixture

Oxidising alcohols and testing carbonyl compounds: frequently

asked questions

Why do tertiary alcohols not oxidise?

The carbon bearing the OH has no hydrogen to remove, and oxidation would need a C-C bond to break. Under mild conditions the tertiary alcohol therefore stays unchanged and dichromate remains orange.

How do you stop a primary alcohol oxidising all the way to the acid?

Use a slight excess of alcohol and distil the aldehyde out as soon as it forms. The aldehyde has a lower boiling point because it cannot hydrogen-bond to itself.

What does Tollens' reagent contain?

It is a solution of the diamminesilver(I) ion, $[\text{Ag}(\text{NH}_3)_2]^+$, in alkali. An aldehyde reduces Ag^+ to silver metal, which coats the tube as a mirror, while the aldehyde is oxidised to a carboxylate.

Why does a ketone resist oxidation by Tollens' reagent?

A ketone has no hydrogen on the carbonyl carbon, so oxidation would have to break a C-C bond. Mild oxidants cannot do this.

Why is the product of HCN addition usually optically inactive?

The planar carbonyl group is attacked equally from above and below, giving equal amounts of two mirror-image products. Their rotations cancel in the racemic mixture.