Hydroxy compounds

Making alcohols, their classification, combustion, substitution, reaction with sodium, oxidation, dehydration, the tri-iodomethane test, and the acidity of alcohols compared with water.

16.1 Alcohols

Classification

A **primary** alcohol has the –OH carbon attached to one other carbon (R–CH_2OH); a **secondary** to two (R_2CHOH); a **tertiary** to three (R_3COH). Some alcohols have more than one –OH group (ethane-1,2-diol).

Preparation

Method	Reagents and conditions
Hydration of an alkene	steam, H_3PO_4 catalyst
Alkene to a diol	cold dilute acidified $KMnO_4$
Substitution of a halogenoalkane	NaOH(aq), heat
Reduction of an aldehyde or ketone	$NaBH_4$ or $LiAlH_4$
Reduction of a carboxylic acid	$LiAlH_4$ (gives a primary alcohol)
Hydrolysis of an ester	dilute acid or dilute alkali, heat

Reactions

- **Combustion:** $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$.
- **Substitution of –OH** to form a halogenoalkane: $HX(g)$; KCl with concentrated H_2SO_4 or H_3PO_4; PCl_3 with heat; PCl_5; $SOCl_2$. For bromide/HBr generation, prefer a suitable non-oxidising acid such as H_3PO_4 rather than assuming concentrated sulfuric acid cannot oxidise bromide.
- **With sodium:** $2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$ (effervescence, less vigorous than with water).
- **Dehydration to an alkene:** heated Al_2O_3 catalyst, or concentrated H_2SO_4 and heat.
- **Oxidation** with acidified $K_2Cr_2O_7$ or acidified $KMnO_4$:

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- a **primary** alcohol gives an **aldehyde** if distilled off as it forms, or a **carboxylic acid** if **refluxed** with excess oxidant;
- a **secondary** alcohol gives a **ketone**;
- a **tertiary** alcohol is **not oxidised** (no H on the carbon bearing –OH).

The colour change of the dichromate is **orange to green** ($Cr_2O_7^{2-} \rightarrow Cr^{3+}$); permanganate goes from purple to colourless ($MnO_4^- \rightarrow Mn^{2+}$). Use $[O]$ in the equation: $CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$.

> **Distil to collect the aldehyde (it has a lower boiling point than the alcohol and acid, because it has no hydrogen bonding), but reflux to oxidise all the way to the acid.**

Tri-iodomethane (iodoform) test

Warm with alkaline aqueous iodine. A **yellow precipitate of** CHI_3 shows a $CH_3CH(OH)-$ group in the alcohol, $CH_3CH(OH)R$ (including ethanol, but not methanol). The alcohol is oxidised to a CH_3CO- compound, which is cleaved to give CHI_3 and the carboxylate ion RCO_2^-.

Acidity of alcohols

Alcohols are **very weak acids**. Alkyl electron donation can destabilise an alkoxide ion relative to hydroxide, but solvent effects also matter, so a blanket claim that every alcohol is weaker than water is too broad. Ordinary alcohols are not usefully converted into alkoxides by aqueous NaOH, but do react with sodium metal, releasing hydrogen.

> **TRY IT**
>
> A compound $C_4H_{10}O$ is oxidised by acidified dichromate to a product that gives a yellow precipitate with alkaline iodine. Deduce the compound.

It is a secondary alcohol with a $CH_3CH(OH)$ group: **butan-2-ol**, oxidised to butanone, $CH_3COC_2H_5$.

Classify the OH-bearing carbon, not the whole skeleton

Count carbon neighbours of the carbon carrying OH. Butan-1-ol is primary, butan-2-ol secondary and 2-methylpropan-2-ol tertiary. Methanol has no carbon neighbour and is a special simplest alcohol; do not force its structure into an R group without checking what R represents. A molecule can have several OH groups whose local classifications differ.

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Hydrogen bonding between alcohol molecules helps explain relatively high boiling points compared with similar-sized hydrocarbons. Short-chain alcohols interact well with water, but as the non-polar carbon portion grows the balance becomes less favourable and water solubility generally falls. The OH group does not make an arbitrarily long carbon chain completely water-soluble.

> **TRY IT**
>
> Why is 2-methylpropan-1-ol primary despite its branched carbon skeleton?

Answer: Its OH-bearing CH_2 carbon has only one carbon neighbour. Classification is local; the nearby branch does not make that carbon tertiary.

Choosing oxidation conditions to control the product

Primary alcohol oxidation removes two hydrogens overall to form an aldehyde, then adds oxygen to give a carboxylic acid. Secondary alcohol oxidation gives a ketone. Under normal acidified dichromate conditions, tertiary alcohols do not undergo the analogous oxidation because the OH-bearing carbon lacks the required hydrogen; harsh conditions can cause other chemistry, so "cannot ever be oxidised" is too absolute.

Worked route: propan-1-ol plus $[O]$ gives propanal and water. Distilling the more volatile aldehyde away as it forms reduces its further contact with oxidant. With excess oxidant under reflux, propanoic acid is obtained: $CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2COOH + H_2O$. Propan-2-ol instead gives propanone with one $[O]$ equivalent in the simplified equation.

Reflux permits prolonged heating while returning condensed volatile material to the reaction flask. Distillation removes a volatile product for collection. These techniques have different purposes; using the same reagent without the appropriate apparatus does not guarantee the desired oxidation stage.

> **TRY IT**
>
> Describe the reagent, observation and product when butan-2-ol is warmed with acidified dichromate.

Answer: Acidified potassium dichromate(VI), warming, gives an orange-to-green change and butanone. A ketone is formed because the original OH-bearing carbon is secondary.

Sodium, substitution and dehydration

Sodium replaces the acidic OH hydrogen to form an alkoxide and hydrogen. It does not replace the whole OH group with sodium. The stoichiometry is two moles alcohol per mole hydrogen. In a sample containing water, sodium also reacts with water, so bubbling cannot be used uncritically to measure alcohol alone.

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Worked calculation: 0.0200 mol dry ethanol reacts with excess sodium to release 0.0100 mol hydrogen, equivalent to 0.240 dm³ at a stipulated molar volume of 24.0 dm³ mol⁻¹. Ethanoate is **not** the salt formed: C_2H_5ONa is sodium ethoxide, whereas CH_3COONa is sodium ethanoate.

Dehydration removes OH and a hydrogen from an adjacent carbon, forming C=C. Butan-2-ol can give more than one alkene; draw possible adjacent positions and consider cis/trans forms. Substitution by chlorine using PCl_5 instead gives a chlorinated carbon skeleton with the same carbon count, together with $POCl_3$ and HCl.

> TRY IT
>
> Explain why oxidation of ethanol to ethanal and dehydration of ethanol to ethene are different reaction types.

Answer: Oxidation changes the carbon's bonding to hydrogen/oxygen and forms a carbonyl. Dehydration eliminates water and forms C=C. Both change the molecular formula, but that alone does not identify the reaction type.

Interpreting the iodoform test structurally

A positive test requires the alcohol to be oxidisable to ethanal or a methyl ketone. Look for $CH_3CH(OH)R$, with ethanol as the case where R is H. Methanol fails because it cannot produce the required methyl-carbonyl structure. Tertiary alcohols fail the ordinary preliminary oxidation even if they contain methyl groups.

Worked comparison: propan-2-ol gives propanone, which contains CH_3CO-, so the test is positive. Propan-1-ol gives propanal, lacking that methyl-carbonyl arrangement, so it is negative. The positive observation is a **yellow precipitate** of CHI_3, not merely disappearance of iodine colour.

> TRY IT
>
> Which gives a positive iodoform test: ethanol, methanol or 2-methylpropan-2-ol?

Answer: Ethanol. It oxidises to ethanal, which gives the test. Methanol lacks the carbon arrangement, while the tertiary alcohol is not oxidised to the required carbonyl under these conditions.

Chapter check: link classification to oxidation product, specify distillation or reflux, and track which part of the OH group is changed. Compare further reactions with **carbonyls** and **carboxylic acids**.

References and further reading

Scope follows section 16 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original

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teaching examples; numerical examples are illustrative unless a specific source is identified.

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