Carboxylic acids and derivatives

Making carboxylic acids, their reactions as acids and with alcohols, reduction, and the formation and hydrolysis of esters.

18.1 Carboxylic acids

The functional group is **–COOH**. Carboxylic acids are named with the suffix **-oic acid** (ethanoic acid, CH_3COOH).

Preparation of carboxylic acids

- **Oxidation** of a primary alcohol or an aldehyde with acidified $K_2Cr_2O_7$ or $KMnO_4$ under **reflux**.
- **Hydrolysis of a nitrile** with dilute acid or dilute alkali (heat), then acidify if alkali was used: $CH_3CN + 2H_2O + H^+ \rightarrow CH_3COOH + NH_4^+$.
- **Hydrolysis of an ester** with dilute acid or dilute alkali and heat, then acidify.

Reactions

- **With a reactive metal** (redox): $2CH_3COOH + Mg \rightarrow (CH_3COO)_2Mg + H_2$.
- **With an alkali** (neutralisation): $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$.
- **With a carbonate** (acid–base): $2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + H_2O + CO_2$. Effervescence with sodium carbonate or hydrogencarbonate is a test for a carboxylic acid (alcohols and phenols do not react with $NaHCO_3$).
- **Esterification** with an alcohol: $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$, with concentrated H_2SO_4 as catalyst and heat. It is reversible, so the yield is limited unless the ester is distilled off or water removed.
- **Reduction** with $LiAlH_4$ in dry ether gives a **primary alcohol**: $CH_3COOH + 4[H] \rightarrow CH_3CH_2OH + H_2O$. ($NaBH_4$ is not strong enough.)

Carboxylic acids are weak acids (partially dissociated), with hydrogen bonding giving them higher boiling points than alcohols of similar M_r, and good solubility in water for the short-chain ones.

Note Academy

Structure, acidity and physical properties

The O–H hydrogen can be donated as a proton. The resulting carboxylate ion spreads its negative charge over two oxygens, stabilising the conjugate base compared with a simple alkoxide. This helps explain reaction with aqueous hydroxide and carbonate under conditions where ordinary alcohols do not react. Weak acidity means partial ionisation in water, not inability to neutralise a strong base.

Hydrogen bonding contributes to high boiling points and interaction with water. Short-chain acids dissolve well; longer non-polar chains reduce the relative influence of the acid group. Acid molecules can form hydrogen-bonded pairs in suitable environments. Boiling mainly overcomes intermolecular attractions, rather than breaking the covalent C=O bond.

Worked comparison: ethanoic acid with sodium metal gives hydrogen, with NaOH gives water, and with sodium hydrogencarbonate gives water and carbon dioxide. All form ethanoate salts. For the hydrogencarbonate reaction, the released gas comes from carbonate chemistry, not destruction of the acid's carbonyl group. Distinguish salt formation, gas identity and reaction type.

> **TRY IT**
>
> Balance the reaction of ethanoic acid with calcium carbonate.

Answer: $2CH_3COOH + CaCO_3 \rightarrow Ca(CH_3COO)_2 + H_2O + CO_2$. The 2+ cation needs two ethanoate ions, and two acid protons convert carbonate to water and carbon dioxide.

Choose a route by counting carbons

Oxidation of a primary alcohol to its acid retains carbon count. Going from a halogenoalkane through a nitrile adds one carbon before hydrolysis. Ester hydrolysis separates two organic fragments, so identify the acid-derived fragment before naming products. These distinctions prevent a superficially correct functional-group sequence from making the wrong molecule.

Worked route: bromoethane becomes propanenitrile with ethanolic cyanide and heat, then propanoic acid by heated acidic hydrolysis. Bromoethane to ethanol with aqueous hydroxide, followed by oxidation under reflux, instead gives ethanoic acid. Cyanide is the extra carbon source in the first route.

Carboxylic-acid reduction with $LiAlH_4$ gives a primary alcohol after suitable work-up. The simplified equation uses four $[H]$ per acid group. Sodium borohydride normally reduces aldehydes and ketones without reducing carboxylic acids under the usual syllabus conditions, making reagent selection essential for a multifunctional compound.

> **TRY IT**
>
> Which nitrile produces butanoic acid on hydrolysis?

Note Academy

Answer: Butanenitrile, $CH_3CH_2CH_2CN$, with four carbons including the nitrile carbon. Hydrolysis changes the group but does not add another carbon.

18.2 Esters

The ester group is **–COO–**. The name comes from the alcohol part (alkyl) first and the acid part (-oate) second, so $CH_3COOCH_2CH_3$ is **ethyl ethanoate**.

Preparation of esters

By **condensation** of a carboxylic acid and an alcohol with concentrated H_2SO_4 as catalyst, heating under reflux (see above). Esters have fruity smells.

Hydrolysis

- **With dilute acid** and heat (reflux): reversible, giving the carboxylic acid and the alcohol.

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

- **With dilute alkali** (e.g. NaOH) and heat: **not reversible**, giving the alcohol and the **carboxylate salt**; acidifying then gives the acid.

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

Alkaline hydrolysis goes to completion because the carboxylate ion is not attacked by the alcohol.

> **TRY IT**
>
> An ester is hydrolysed by NaOH(aq) to give sodium propanoate and methanol. Name the ester.

The acid part is propanoate and the alcohol part methyl: **methyl propanoate**, $CH_3CH_2COOCH_3$.

Keep the acid and alcohol fragments distinct

Write $RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$. The carbonyl remains on the acid-derived fragment; the group directly bonded to the ester oxygen comes from the alcohol. Naming that group first does not mean it includes the carbonyl carbon.

Worked example: propanoic acid and ethanol form ethyl propanoate, $CH_3CH_2COOCH_2CH_3$, containing five carbons. Methanol and butanoic acid form methyl butanoate, another five-carbon ester with different connectivity. Both have the same molecular formula but give different hydrolysis products.

Note Academy

TRY IT

Give the acid and alcohol needed for propyl ethanoate.

Answer: Ethanoic acid and propan-1-ol. The ester is $CH_3COOCH_2CH_2CH_3$. Propanoic acid plus ethanol would instead make ethyl propanoate.

Rate, equilibrium and practical preparation

Concentrated sulfuric acid catalyses esterification and heating increases rate. Reflux retains volatile components during heating. The closed-mixture equilibrium limits conversion; excess alcohol or removal of water/ester can favour product formation. A catalyst alone changes neither equilibrium constant nor final equilibrium yield at fixed temperature.

Worked calculation: 0.100 mol acid reacts with 0.0800 mol alcohol. The maximum ester amount is 0.0800 mol from the 1 : 1 equation. Isolating 0.0500 mol gives 62.5% of that stoichiometric maximum. This yield includes effects of equilibrium, side reactions and recovery losses; it is not a direct measurement of equilibrium constant.

Many small esters have characteristic fruity odours, but not every ester has the same smell and odour is not a conclusive identity test. Separation and suitable analytical evidence establish identity and purity. Avoid identifying a product solely because it “smells sweet”.

Hydrolysis and the work-up step

Acid-catalysed hydrolysis gives acid plus alcohol reversibly. Excess water favours hydrolysis. Alkali gives carboxylate plus alcohol; removal of free acid through salt formation makes this effectively irreversible under the reaction conditions. Acidifying afterwards protonates the carboxylate, allowing isolation of the free acid.

Worked example: ethyl propanoate with aqueous NaOH gives sodium propanoate and ethanol. Subsequent HCl converts the propanoate into propanoic acid. Writing the acid as the major product while leaving the mixture strongly alkaline ignores its acid–base reaction.

TRY IT

State the organic products of methyl butanoate hydrolysis with dilute acid and with NaOH separately.

Answer: Acid gives butanoic acid and methanol. NaOH gives sodium butanoate and methanol; further acidification gives butanoic acid.

Note Academy

Chapter check: distinguish free acid from carboxylate, track both ester fragments and justify conditions through reaction rate and equilibrium. More reactive derivatives follow in **A Level carboxylic chemistry**.

References and further reading

Scope follows section 18 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 teaching examples; numerical examples are illustrative unless a specific source is identified.

Note Academy