Carboxylic acids and derivatives

A-Level Chemistry

Carboxylic acids

A **carboxylic acid** 羧酸 has the –COOH (carboxyl) functional group. It is a weak acid.

Vinegar is a dilute solution of ethanoic acid, a carboxylic acid

Making carboxylic acids

- **oxidation** 氧化 of a primary **alcohol** 醇 or an **aldehyde** 醛 with acidified $K_2Cr_2O_7$ or $KMnO_4$, with **reflux** 回流 (so it is fully oxidised).
- **hydrolysis** 水解 of a **nitrile** 腈 with dilute acid or alkali, then acidifying.
- hydrolysis of an **ester** 酯 with dilute acid or alkali and heat, then acidifying.

Reactions of carboxylic acids

These reactions all show that carboxylic acids are acids:

- **with a reactive metal** (a **redox** 氧化还原 reaction): gives a **salt** 盐 and hydrogen.

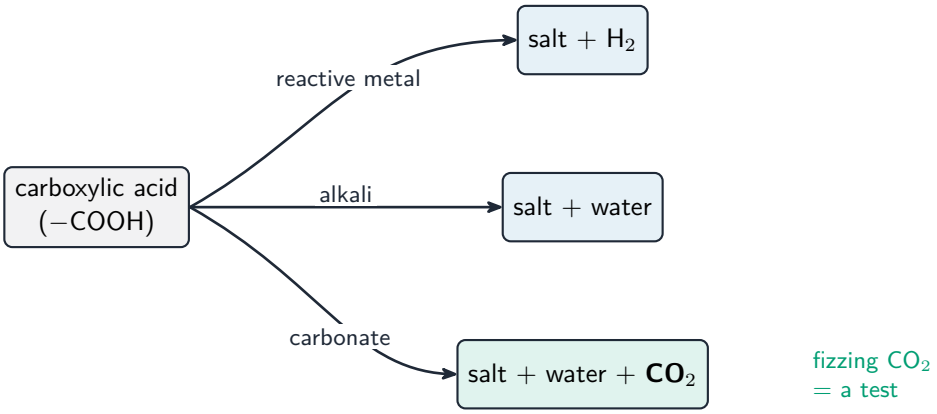
$$2CH_3COOH + Mg \rightarrow (CH_3COO)_2Mg + H_2$$

- **with an alkali** (a **neutralisation** 中和): gives a salt and water.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

- **with a carbonate** 碳酸盐: gives a salt, water and carbon dioxide. The fizzing of CO_2 is a test for a carboxylic acid.

$$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + H_2O + CO_2$$



Carboxylic acids behave as acids: a salt with a metal (+ H_2), with an alkali (+ water), or with a carbonate (+ water + CO_2 —the fizz is a test)

Two reactions change the functional group:

- **esterification** 酯化 with an alcohol (concentrated H_2SO_4 catalyst) gives an ester.
- **reduction** 还原 by $LiAlH_4$ gives a primary alcohol.

Esters

An ester has the –COO– group. It often smells sweet or fruity.

Esters give many fruits and perfumes their sweet smell

Making esters

An ester forms in a **condensation** 缩合 reaction between an alcohol and a carboxylic acid, with concentrated H_2SO_4 as catalyst. A water molecule is lost, and the reaction is reversible:

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

$$CH_3COOH \quad + \quad HOC_2H_5 \quad \rightleftharpoons \quad CH_3CO\ O\ C_2H_5 \quad + \quad H_2O$$

the –OH (acid) and –H (alcohol) leave as water; the C–O–C ester link forms

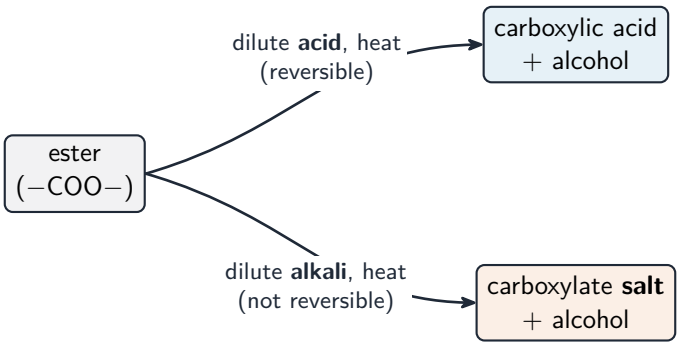
(concentrated H_2SO_4 catalyst; reversible)

Esterification is a condensation: the –OH from the acid and the –H from the alcohol leave as water, forming the C–O–C ester link

Hydrolysis of esters

Hydrolysis splits the ester back apart. The conditions change the products:

- **dilute acid** and heat: reversible. Gives back the carboxylic acid and the alcohol.
- **dilute alkali** and heat: not reversible. Gives the alcohol and the **salt** of the carboxylic acid (the carboxylate ion).



Hydrolysing an ester: dilute acid (reversible) gives the carboxylic acid and alcohol; dilute alkali (not reversible) gives the carboxylate salt and alcohol

Worked example. Name the ester made from ethanol and propanoic acid, and say which part comes from which. In an ester name the **alcohol** gives the first word (the alkyl part) and the **acid** gives the second (the -oate part). Ethanol supplies C_2H_5- and propanoic acid supplies CH_3CH_2COO-, so the ester is **ethyl propanoate**, $CH_3CH_2COOC_2H_5$. It is made by refluxing the two with a concentrated H_2SO_4 catalyst, and the reaction is **reversible**, so the yield is never complete. The trap is naming it backwards: **propyl ethanoate** is a completely different ester (made from propan-1-ol and ethanoic acid). Alcohol first, acid second.

Exam tips

- Carboxylic acids react with carbonates to give $\mathbf{CO_2}$ (fizzing) —this distinguishes them from phenols.
- Explain acid strength via the **delocalised carboxylate ion**; electron-withdrawing groups (e.g. Cl) increase strength.
- **Esterification** (with concentrated H_2SO_4) is reversible; name esters as *alkyl alkanoate*.
- Know the products of **acid vs alkaline** hydrolysis of an ester (they differ).