

Carboxylic acids and esters: AS Chemistry notes

These notes cover the carboxylic acids and esters content of Cambridge International AS Chemistry (9701): how carboxylic acids are made, their reactions, esterification, the hydrolysis of esters, and how esters are named and used. A reaction map and ten exam-style questions with full answers come at the end.

1. Carboxylic acids: structure and properties

1.1 The functional group

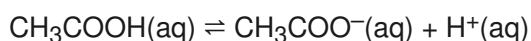
Carboxylic acids contain the **carboxyl group**, -COOH , in which a carbon atom is double bonded to one oxygen atom and single bonded to an -OH group. The general formula of the saturated, unbranched series is $\text{C}_n\text{H}_{2n+1}\text{COOH}$ (or $\text{C}_n\text{H}_{2n}\text{O}_2$ counting all carbons).

Naming: take the longest carbon chain including the carboxyl carbon, use the alkane stem and replace the final "-e" with "-oic acid". The carboxyl carbon is always carbon 1.

HCOOH methanoic acid; CH_3COOH ethanoic acid; $\text{CH}_3\text{CH}_2\text{COOH}$ propanoic acid; $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ butanoic acid; $\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$ 2-methylpropanoic acid.

1.2 Weak acids

Carboxylic acids are **weak acids**: they only partially dissociate in water.



The anion formed, the **carboxylate ion**, is stabilised because the negative charge is delocalised over both oxygen atoms. This is why carboxylic acids are more acidic than alcohols, whose alkoxide ion has the charge on one oxygen only. Salts are named as carboxylates: $\text{CH}_3\text{COO}^-\text{Na}^+$ is sodium ethanoate.

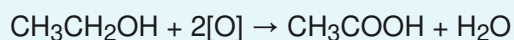
2. Making carboxylic acids

2.1 Oxidation of primary alcohols

Primary alcohols are oxidised first to aldehydes and then to carboxylic acids. To obtain the acid, the alcohol is **heated under reflux** with an **excess** of oxidising agent, so that any aldehyde formed cannot escape and is oxidised further.

Reagent and conditions to learn: acidified potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7$ with dilute H_2SO_4 , heated under reflux (acidified potassium manganate(VII) also works).

Observation: with dichromate the colour changes from **orange to green** as $\text{Cr}_2\text{O}_7^{2-}$ is reduced to Cr^{3+} .



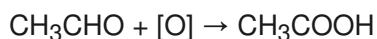
The symbol $[\text{O}]$ stands for oxygen supplied by the oxidising agent and is accepted in balanced organic



oxidation equations. Compare: if the aim is the aldehyde, the alcohol is heated with a limited amount of oxidising agent and the aldehyde is **distilled off** as soon as it forms.

2.2 Oxidation of aldehydes

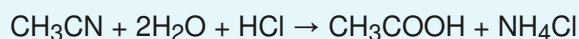
Aldehydes are readily oxidised to carboxylic acids by the same reagent, acidified $K_2Cr_2O_7$ on heating.



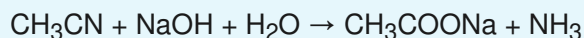
2.3 Hydrolysis of nitriles

A nitrile, $R-C\equiv N$, is hydrolysed to a carboxylic acid by heating under reflux with dilute acid or dilute alkali. This route is useful because nitriles can be made from halogenoalkanes with KCN, which **adds one carbon atom** to the chain.

Acid hydrolysis: heat under reflux with dilute HCl (or dilute H_2SO_4). The acid is formed directly.



Alkaline hydrolysis: heat under reflux with aqueous NaOH. The carboxylate salt forms and ammonia is given off; the free acid is obtained by then adding excess dilute strong acid.



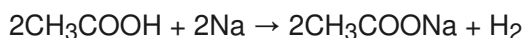
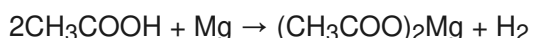
Worked example: a two-step synthesis. Suggest how propanoic acid can be made from bromoethane.

Bromoethane has two carbon atoms; propanoic acid has three, so a carbon must be added. Step 1: heat bromoethane under reflux with KCN in ethanol to form propanenitrile, $CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$ (nucleophilic substitution). Step 2: heat propanenitrile under reflux with dilute HCl, $CH_3CH_2CN + 2H_2O + HCl \rightarrow CH_3CH_2COOH + NH_4Cl$.

3. Reactions of carboxylic acids

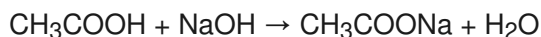
3.1 As acids: with reactive metals

Carboxylic acids react with reactive metals such as Mg, Zn and Na to give a salt and hydrogen. This is a **redox** reaction: the metal is oxidised and H^+ is reduced. The reaction is slower than with a strong acid of the same concentration because $[H^+]$ is lower.



3.2 As acids: with alkalis

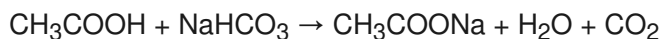
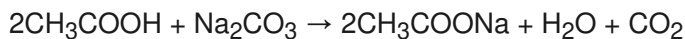
Neutralisation with an alkali gives a salt and water.



The ionic equation is $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$. The weak acid is written as the undissociated molecule.

3.3 As acids: with carbonates and hydrogencarbonates

Carboxylic acids react with carbonates to give a salt, water and carbon dioxide, seen as **effervescence**. The gas turns limewater milky.



Exam tip: a test for the –COOH group. Add aqueous sodium carbonate or sodium hydrogencarbonate. Effervescence of CO_2 shows a carboxylic acid. Alcohols do not react. Alcohols and carboxylic acids both react with sodium metal to give hydrogen, so sodium cannot tell them apart; carbonate can.

Worked example: gas volume. Calculate the volume of carbon dioxide, measured at room temperature and pressure, formed when 3.00 g of ethanoic acid reacts with excess sodium carbonate. Use the molar gas volume at r.t.p. from the Data Booklet ($24.0 \text{ dm}^3 \text{ mol}^{-1}$).

$$M_r(\text{CH}_3\text{COOH}) = 2(12.0) + 4(1.0) + 2(16.0) = 60.0$$

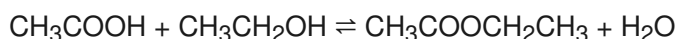
$$n(\text{CH}_3\text{COOH}) = 3.00 / 60.0 = 0.0500 \text{ mol}$$

From the equation, 2 mol acid give 1 mol CO_2 , so $n(\text{CO}_2) = 0.0250 \text{ mol}$

$$V = 0.0250 \times 24.0 = 0.600 \text{ dm}^3 \text{ (600 cm}^3\text{)}$$

3.4 With alcohols: esterification

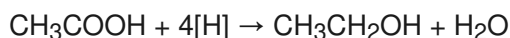
A carboxylic acid reacts with an alcohol to form an **ester** and water. The reaction is a **condensation** reaction (a small molecule, water, is eliminated as two molecules join) and is reversible.



ethanoic acid + ethanol $\rightleftharpoons$ ethyl ethanoate + water. Full conditions are in section 4.

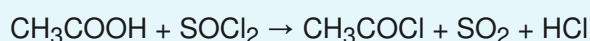
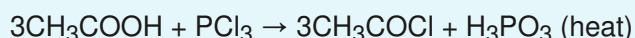
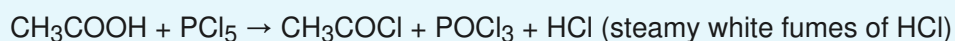
3.5 Reduction to primary alcohols

Carboxylic acids are reduced to primary alcohols by lithium tetrahydridoaluminate, LiAlH_4 , in dry ether. NaBH_4 is not a strong enough reducing agent for this. $[\text{H}]$ represents hydrogen from the reducing agent.



3.6 Conversion to acyl chlorides

The $-\text{OH}$ of the carboxyl group can be replaced by $-\text{Cl}$ to form an **acyl chloride**, RCOCl , which is far more reactive than the acid. All three reagents below work at room temperature or with gentle warming (PCl_3 needs heat), and all must be used in the absence of water. (In 9701 this is listed in the A Level acyl chlorides section.)



The product is ethanoyl chloride. SOCl_2 (thionyl chloride) is often preferred because both by-

products are gases and leave the mixture, making the acyl chloride easy to purify.

Acyl chlorides react rapidly with alcohols at room temperature to give esters **irreversibly**, which gives a better yield than direct esterification: $\text{CH}_3\text{COCl} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{HCl}$.

4. Esterification conditions

Conditions to learn: carboxylic acid + alcohol, a few drops of **concentrated sulfuric acid** as catalyst, **heat under reflux**.

Points examiners ask about:

- **Role of concentrated H_2SO_4 :** it is a catalyst (provides H^+). Because it is also a dehydrating agent, it absorbs some of the water formed, helping to shift the equilibrium to the right.
- **Heating under reflux:** the reaction is slow at room temperature; reflux allows prolonged heating without loss of volatile reactants or products.
- **Reversibility:** the equilibrium constant is modest, so the yield is limited. It can be raised by using an excess of the cheaper reactant (usually the alcohol) or by removing the ester or water as it forms.
- **Separating the product:** esters of small molecules are volatile and can be distilled out of the mixture. The crude ester is washed with aqueous sodium carbonate to remove acid (effervescence stops when all acid is removed), then with water, dried with an anhydrous salt such as anhydrous CaCl_2 or MgSO_4 , and redistilled.

Worked example: percentage yield. 9.00 g of ethanoic acid was heated under reflux with excess ethanol and a little concentrated sulfuric acid. After purification, 8.80 g of ethyl ethanoate was obtained. Calculate the percentage yield.

$$M_r(\text{CH}_3\text{COOCH}_2\text{CH}_3) = 4(12.0) + 8(1.0) + 2(16.0) = 88.0$$

$$n(\text{acid}) = 9.00 / 60.0 = 0.150 \text{ mol}; \text{ mole ratio acid : ester} = 1 : 1, \text{ so theoretical } n(\text{ester}) = 0.150 \text{ mol}$$

$$\text{Theoretical mass} = 0.150 \times 88.0 = 13.2 \text{ g}$$

$$\text{Percentage yield} = 8.80 / 13.2 \times 100 = 66.7\%$$

5. Naming esters

An ester has the general structure $\text{R}-\text{COO}-\text{R}'$, where $\text{R}-\text{CO}-$ comes from the carboxylic acid and $-\text{R}'$ comes from the alcohol.

Rule: the name is two words, **alkyl alkanoate**. The first word is the alkyl group from the **alcohol**; the second word comes from the **acid**, with "-oic acid" changed to "-oate".

Acid	Alcohol	Ester formula	Ester name
methanoic acid	ethanol	$\text{HCOOCH}_2\text{CH}_3$	ethyl methanoate
ethanoic acid	methanol	$\text{CH}_3\text{COOCH}_3$	methyl ethanoate

ethanoic acid	ethanol	$\text{CH}_3\text{COOCH}_2\text{CH}_3$	ethyl ethanoate
propanoic acid	methanol	$\text{CH}_3\text{CH}_2\text{COOCH}_3$	methyl propanoate
butanoic acid	propan-1-ol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_3$	propyl butanoate

Worked example: reading a formula. Name $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and identify the acid and alcohol it is made from.

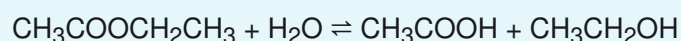
Split at the single-bonded oxygen: $\text{CH}_3\text{CH}_2\text{CO}-$ contains three carbons including the $\text{C}=\text{O}$ carbon, so it comes from propanoic acid. $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ is a butyl group from butan-1-ol. Name: **butyl propanoate**.

6. Hydrolysis of esters

Hydrolysis is the breaking of a bond by reaction with water. Esters are hydrolysed back to a carboxylic acid (or its salt) and an alcohol. Both routes need heating under reflux.

6.1 Acid hydrolysis

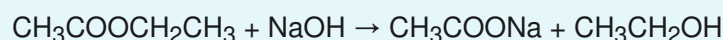
Conditions: heat under reflux with dilute acid, such as dilute H_2SO_4 or dilute HCl (the acid is a catalyst).



This is the reverse of esterification and is **reversible**, so hydrolysis is incomplete. A large excess of water (from the dilute acid) pushes the equilibrium towards the acid and alcohol.

6.2 Alkaline hydrolysis

Conditions: heat under reflux with dilute aqueous alkali, such as NaOH(aq) .



This reaction **goes to completion** because the carboxylic acid formed is immediately converted to the carboxylate ion, which does not react with the alcohol. The products are the **salt** of the acid and the alcohol. To obtain the free carboxylic acid, the mixture is acidified with a dilute strong acid such as HCl : $\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH}$.

6.3 Comparing the two methods

Feature	Acid hydrolysis	Alkaline hydrolysis
Reagent	dilute H_2SO_4 or HCl , catalyst	NaOH(aq) , a reactant used up
Extent	reversible, incomplete	goes to completion
Products	carboxylic acid + alcohol	carboxylate salt + alcohol
Usual choice	when the free acid is wanted directly	when a full yield is wanted; acidify afterwards

Alkaline hydrolysis of fats and oils (esters of propane-1,2,3-triol, also called glycerol, with long-chain carboxylic acids) gives propane-1,2,3-triol and sodium salts of the long-chain acids, which are soaps. This is called **saponification**.

7. Uses of esters

- **Flavourings and perfumes:** many esters of small molecules have sweet, fruity smells and are used in food flavourings, sweets and perfumes.
- **Solvents:** ethyl ethanoate is used as a solvent in glues, paints, varnishes and some nail varnish removers.
- **Plasticisers:** some larger esters are added to polymers such as PVC to make them more flexible.
- **Fats and oils:** natural triesters used as food and as the raw material for soaps and biodiesel.

8. Reaction map

Read each row as "starting compound → product". R stands for an alkyl group.

From	To	Reagent	Conditions	Type
primary alcohol RCH_2OH	carboxylic acid RCOOH	$\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4(\text{aq})$, excess	heat under reflux	oxidation
aldehyde RCHO	carboxylic acid RCOOH	$\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4(\text{aq})$	heat	oxidation
nitrile RCN	carboxylic acid RCOOH	dilute HCl or H_2SO_4	heat under reflux	hydrolysis
nitrile RCN	carboxylate salt RCOONa	$\text{NaOH}(\text{aq})$	heat under reflux; acidify to get RCOOH	hydrolysis
RCOOH	salt + H_2	reactive metal (Mg , Zn , Na)	room temperature	redox
RCOOH	salt + H_2O	$\text{NaOH}(\text{aq})$	room temperature	neutralisation
RCOOH	salt + H_2O + CO_2	Na_2CO_3 or NaHCO_3	room temperature	acid-base
RCOOH	ester RCOOR'	alcohol $\text{R}'\text{OH}$, conc. H_2SO_4	heat under reflux	condensation (esterification)
RCOOH	primary alcohol RCH_2OH	LiAlH_4	dry ether	reduction
RCOOH	acyl chloride RCOCl	PCl_5 , PCl_3 or SOCl_2	anhydrous; heat with PCl_3	substitution of $-\text{OH}$
RCOCl	ester RCOOR'	alcohol $\text{R}'\text{OH}$	room temperature	condensation (addition-elimination)

ester RCOOR'	RCOOH + R'OH	dilute H ₂ SO ₄ or HCl	heat under reflux	acid hydrolysis
ester RCOOR'	RCOONa + R'OH	NaOH(aq)	heat under reflux	alkaline hydrolysis

Quick check

Use A_r: H = 1.0, C = 12.0, O = 16.0, Mg = 24.3. Molar gas volume at r.t.p. = 24.0 dm³ mol⁻¹ (Data Booklet).

1. State the reagent and conditions needed to convert propan-1-ol into propanoic acid, and describe the colour change seen.
2. Explain why the conditions for making a carboxylic acid from a primary alcohol differ from those for making an aldehyde.
3. Outline a two-step synthesis of butanoic acid from 1-bromopropane. Give reagents, conditions and equations.
4. Write a balanced equation for the reaction of propanoic acid with magnesium, and calculate the volume of hydrogen at r.t.p. formed from 1.48 g of propanoic acid with excess magnesium.
5. Describe a simple chemical test to distinguish ethanoic acid from ethanol. State what is observed in each case.
6. Name the esters CH₃COOCH₂CH₂CH₃ and HCOOCH₃, and name the acid and alcohol used to make each.
7. Write the equation for the formation of methyl propanoate from its acid and alcohol. State the conditions and explain two roles of concentrated sulfuric acid.
8. 6.00 g of propanoic acid was esterified with excess methanol and 4.40 g of methyl propanoate was obtained. Calculate the percentage yield.
9. Ethyl methanoate is hydrolysed separately by dilute HCl and by NaOH(aq). Write an equation for each, and explain why alkaline hydrolysis goes to completion.
10. Give the equation for the reaction of ethanoic acid with thionyl chloride, and explain why converting the acid to an acyl chloride first can give a better yield of an ester than direct esterification.

1. Reagent: acidified potassium dichromate(VI) (K₂Cr₂O₇ with dilute H₂SO₄), used in excess. Conditions: heat under reflux. Colour change: orange to green, as Cr₂O₇²⁻ is reduced to Cr³⁺. Equation: CH₃CH₂CH₂OH + 2[O] → CH₃CH₂COOH + H₂O.

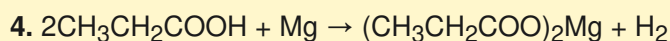
2. Oxidation of a primary alcohol happens in two stages: alcohol → aldehyde → carboxylic acid. To stop at the aldehyde, a limited amount of oxidising agent is used and the aldehyde, which has a lower boiling point than the alcohol (no hydrogen bonding between its molecules), is distilled off as it forms so it cannot be oxidised further. To make the acid, excess oxidising agent is used and the mixture is heated under reflux, so the aldehyde condenses back into the flask and is oxidised to the acid.

3. Butanoic acid has four carbons; 1-bromopropane has three, so a carbon is added via a nitrile. Step 1: heat under reflux with KCN in ethanol: CH₃CH₂CH₂Br + KCN → CH₃CH₂CH₂CN + KBr

(nucleophilic substitution, product butanenitrile).

Step 2: heat under reflux with dilute HCl: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN} + 2\text{H}_2\text{O} + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{NH}_4\text{Cl}$.

(Alternatively, heat with NaOH(aq) and then acidify with dilute HCl.)



$$M_r(\text{CH}_3\text{CH}_2\text{COOH}) = 3(12.0) + 6(1.0) + 2(16.0) = 74.0$$

$$n(\text{acid}) = 1.48 / 74.0 = 0.0200 \text{ mol}$$

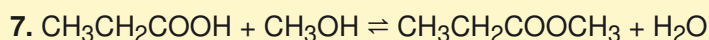
$$n(\text{H}_2) = 0.0200 / 2 = 0.0100 \text{ mol}$$

$$V = 0.0100 \times 24.0 = 0.240 \text{ dm}^3 \text{ (240 cm}^3\text{)}$$

5. Add aqueous sodium carbonate (or sodium hydrogencarbonate) to each. Ethanoic acid: effervescence; the gas (CO_2) turns limewater milky. $2\text{CH}_3\text{COOH} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{CH}_3\text{COONa} + \text{H}_2\text{O} + \text{CO}_2$. Ethanol: no visible change, because ethanol is not acidic enough to react with carbonate. (Sodium metal is not a suitable test, as both give hydrogen.)

6. $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$: the acid part $\text{CH}_3\text{CO}-$ has two carbons (ethanoic acid); the alkyl part $-\text{CH}_2\text{CH}_2\text{CH}_3$ is propyl (propan-1-ol). Name: propyl ethanoate.

HCOOCH_3 : the acid part $\text{HCO}-$ has one carbon (methanoic acid); the alkyl part is methyl (methanol). Name: methyl methanoate.



Conditions: a few drops of concentrated H_2SO_4 , heat under reflux.

Roles of concentrated H_2SO_4 : (1) catalyst, providing H^+ ions that speed up the reaction; (2) dehydrating agent, removing some of the water produced so that the position of equilibrium shifts to the right, increasing the yield of ester.

8. $M_r(\text{propanoic acid}) = 74.0$; $M_r(\text{methyl propanoate}, \text{CH}_3\text{CH}_2\text{COOCH}_3, \text{C}_4\text{H}_8\text{O}_2) = 4(12.0) + 8(1.0) + 2(16.0) = 88.0$

$$n(\text{acid}) = 6.00 / 74.0 = 0.0811 \text{ mol}$$

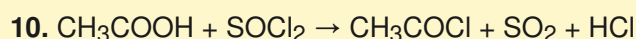
Mole ratio 1 : 1, so theoretical mass of ester = $0.0811 \times 88.0 = 7.14 \text{ g}$ (using the unrounded moles, 7.135 g)

$$\text{Percentage yield} = 4.40 / 7.135 \times 100 = 61.7\% \text{ (62\%)}$$

9. Acid hydrolysis (heat under reflux with dilute HCl, catalyst): $\text{HCOOCH}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{HCOOH} + \text{CH}_3\text{CH}_2\text{OH}$ (products methanoic acid and ethanol).

Alkaline hydrolysis (heat under reflux with NaOH(aq)): $\text{HCOOCH}_2\text{CH}_3 + \text{NaOH} \rightarrow \text{HCOONa} + \text{CH}_3\text{CH}_2\text{OH}$ (products sodium methanoate and ethanol).

Alkaline hydrolysis goes to completion because the carboxylic acid formed reacts at once with the alkali to give the carboxylate ion. The carboxylate ion cannot react with the alcohol to re-form the ester, so the reverse reaction cannot occur and all the ester is used up.



Direct esterification is a reversible reaction that reaches equilibrium, so not all the acid is converted to ester. The acyl chloride reacts with an alcohol rapidly at room temperature and the reaction is not reversible (the by-product is HCl gas, which escapes), for example $\text{CH}_3\text{COCl} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{HCl}$. So the conversion to ester is almost complete and no catalyst or prolonged heating is needed. With SOCl_2 the by-products SO_2 and HCl are gases, making the acyl chloride easy to separate.