

ESAT

Chemistry

Alcohols and Carboxylic Acids

Free lesson notes

Covers	C13.5, C13.6 (with C13.1)
Format	Lesson, worked examples, self-check
Price	Free

About this lesson

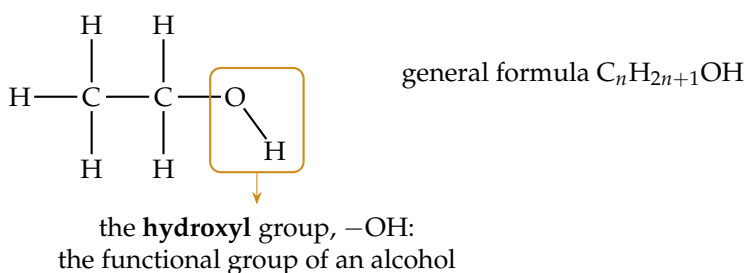
A glass of wine, the vinegar on chips, the smell of pear drops and the alcohol in a hand gel all come from three closely linked families of carbon compounds. **Alcohols** contain the -OH group, **carboxylic acids** contain the -COOH group, and **esters**, made by joining an acid to an alcohol, supply many natural and artificial smells and flavours. They also connect to the polyesters of the previous lesson.

This lesson teaches each family from scratch: the functional group, how to draw and name the members from one to six carbons, how they behave (combustion, reaction with sodium, oxidation, reaction as weak acids, ester formation), and how ethanol is manufactured by two different routes. Specification codes: C13.5 (alcohols), C13.6 (carboxylic acids, weak acids, salts, esters), with C13.1 (homologous series, formulae, combustion, isomers). Relative atomic masses are given in questions where needed: $\text{H} = 1$, $\text{C} = 12$, $\text{O} = 16$, $\text{Na} = 23$.

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1 The alcohols: a homologous series with the -OH group

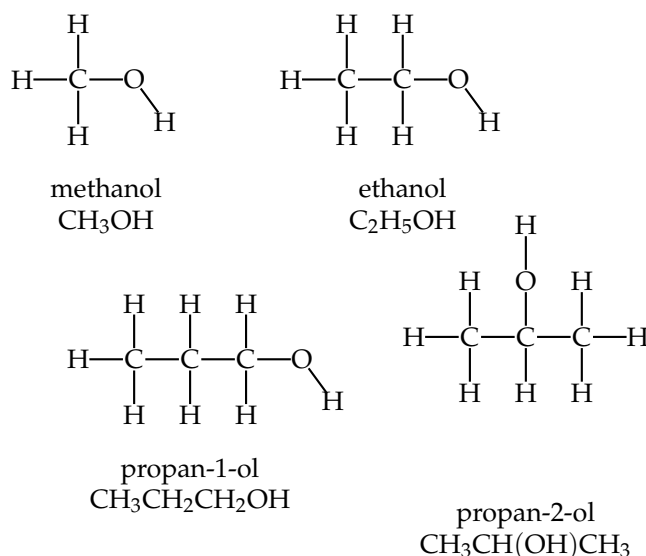
A **functional group** is the atom or group of atoms that gives a family of organic compounds its characteristic reactions. The functional group of an **alcohol** is the **hydroxyl** group, -OH , bonded to a carbon atom of an alkane-like chain. (The -OH is attached by a covalent bond to carbon; it is not a hydroxide ion and the compounds are not alkalis.)



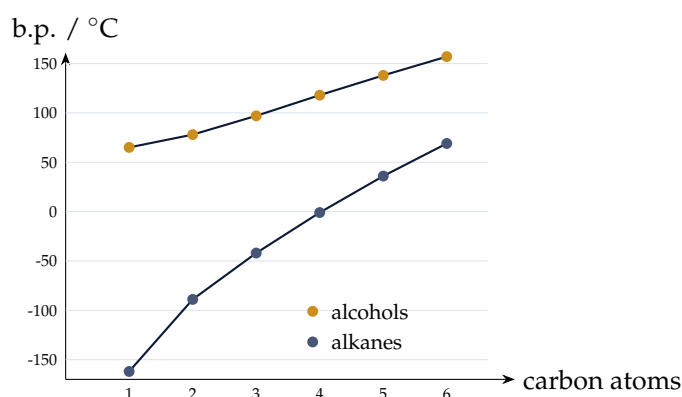
Think of an alcohol as an alkane in which one hydrogen has been swapped for -OH . An alkane is $\text{C}_n\text{H}_{2n+2}$, so the alcohol is $\text{C}_n\text{H}_{2n+1}\text{OH}$ (or $\text{C}_n\text{H}_{2n+2}\text{O}$ in total). Members of a family that differ by one CH_2 form a **homologous series**, with the same general formula and similar chemistry. The names use the alkane stem with the ending **-ol**:

carbons	name	molecular formula	structural formula
1	methanol	CH_4O	CH_3OH
2	ethanol	$\text{C}_2\text{H}_6\text{O}$	$\text{CH}_3\text{CH}_2\text{OH}$
3	propan-1-ol	$\text{C}_3\text{H}_8\text{O}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
4	butan-1-ol	$\text{C}_4\text{H}_{10}\text{O}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
5	pentan-1-ol	$\text{C}_5\text{H}_{12}\text{O}$	$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$
6	hexan-1-ol	$\text{C}_6\text{H}_{14}\text{O}$	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OH}$

The number in the name. From three carbons upwards the -OH can sit on different carbons, which gives *isomers*. The number tells you which carbon of the longest chain carries the -OH , counted from the end that gives the lower number. In propan-1-ol it is on the end carbon; in propan-2-ol it is on the middle carbon. Both are $\text{C}_3\text{H}_8\text{O}$ but they are different compounds with slightly different properties.



Physical properties. Small alcohols are colourless liquids (not gases, unlike the alkanes with the same number of carbons) because the O–H bond is polar and the molecules attract each other strongly by hydrogen bonding, so more energy is needed to separate them. Boiling points rise along the series as the molecules get bigger. Methanol, ethanol and propanol mix completely with water; the larger the hydrocarbon part, the less soluble the alcohol is.



At every chain length the alcohol boils at a much higher temperature than the alkane with the same number of carbons.

Worked example: formula and isomers

Give the molecular formula of the alcohol with six carbons, and say how many alcohol isomers have the formula $\text{C}_6\text{H}_{14}\text{O}$.

$n = 6$ in $\text{C}_n\text{H}_{2n+1}\text{OH}$ gives $\text{C}_6\text{H}_{13}\text{OH}$, that is $\text{C}_6\text{H}_{14}\text{O}$ (hexanol). With three carbons the –OH can be on an end carbon (propan-1-ol) or on the middle carbon (propan-2-ol). Any other position gives the same molecule drawn backwards, so there are 2 alcohol isomers.

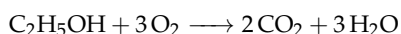
Common mistakes

- Writing the alcohol group as –HO or confusing it with hydroxide. It is –OH, covalently bonded to carbon, and the compound is neutral.
- Counting the number in the name from the wrong end. Number from the end that gives the –OH the lowest number (so $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ is propan-1-ol, never propan-3-ol).
- Saying alcohols and alkanes of similar size have similar boiling points. The –OH raises the boiling point greatly.

2 Reactions of alcohols

Combustion. Like all organic fuels, alcohols burn in plenty of oxygen to give carbon dioxide and water, releasing heat. Ethanol and methanol are used as fuels, and ethanol is blended into petrol. Method for balancing: carbons first, then

hydrogens, then oxygen last, remembering the oxygen already in the alcohol.

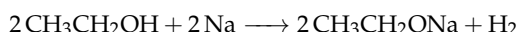


Oxygen check: the right has $2 \times 2 + 3 = 7$ oxygen atoms; the left has 1 (in the alcohol) + 6 = 7. Alcohols give a cleaner, less sooty (blue) flame than hydrocarbons of the same size because they already contain some oxygen, but with too little air they give carbon monoxide just as alkanes do.

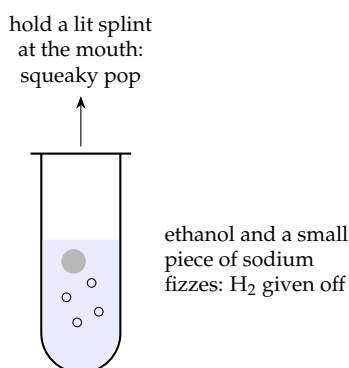
Worked example: mass of carbon dioxide

What mass of carbon dioxide forms when 9.2 g of ethanol burns completely? (M_r of ethanol = 46, of CO_2 = 44.)
 Moles of ethanol = $9.2/46 = 0.20$. From the equation 1 mole of ethanol gives 2 moles of CO_2 , so 0.40 mol of CO_2 .
 Mass = $0.40 \times 44 = 17.6$ g.

Reaction with sodium. Sodium reacts with alcohols by replacing the hydrogen of the $-\text{OH}$ group. Hydrogen gas is given off and a sodium alkoxide (a salt-like compound) forms. For ethanol:

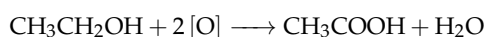


The product is sodium ethoxide. It fizzes steadily but much more gently than sodium in water; the metal does not melt or catch fire. The gas is tested with a lit splint (squeaky pop).

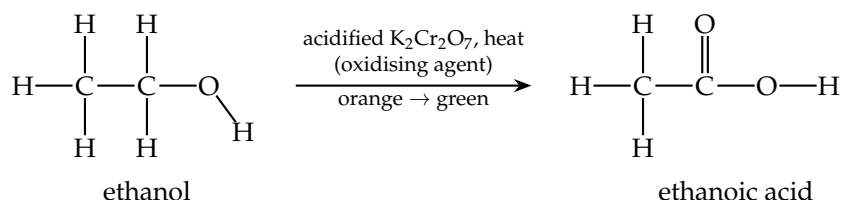


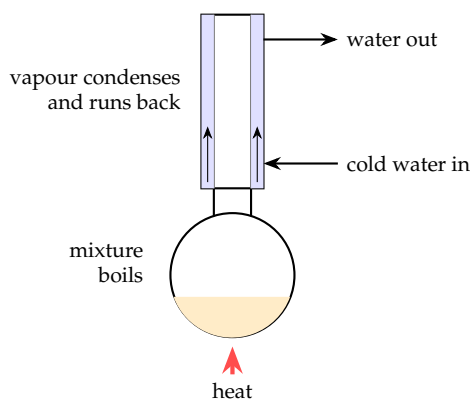
Because the reaction uses the $\text{O}-\text{H}$ hydrogen, it is a test for the $-\text{OH}$ group, but remember that water and carboxylic acids also give hydrogen with sodium. The ratio is always 2 alcohol : 1 H_2 .

Oxidation. An alcohol can be oxidised to a carboxylic acid. Heating ethanol with an oxidising agent such as **acidified potassium dichromate(VI)** gives ethanoic acid, and the dichromate changes from **orange to green** as it is reduced. Ethanol left open to the air also slowly oxidises, because bacteria in the air turn it into ethanoic acid; this is why wine goes sour and becomes vinegar. A reaction that must be heated while the liquid is boiling uses **reflux**: the flask is fitted with a vertical condenser so the vapours condense and run back, and nothing is lost.



where $[\text{O}]$ stands for oxygen supplied by the oxidising agent.





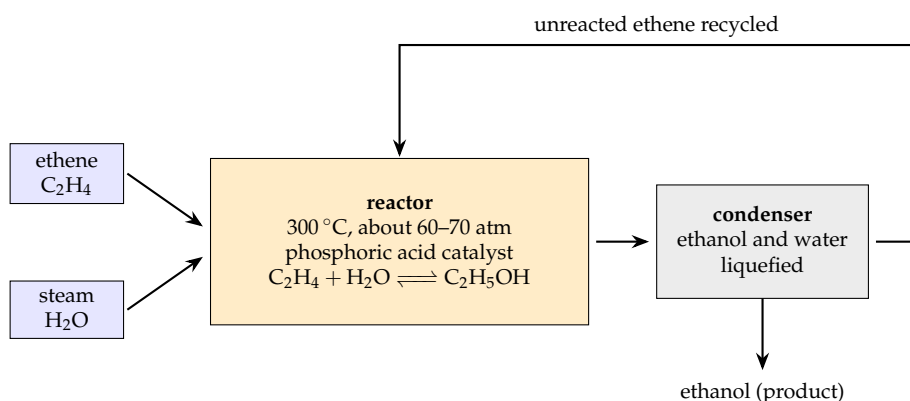
Common mistakes

- Balancing oxygen in the combustion equation without counting the oxygen already in the alcohol.
- Claiming that the gas from sodium and ethanol is oxygen or carbon dioxide. It is hydrogen.
- Giving the dichromate colour change the wrong way round. It goes orange to green when it oxidises the alcohol.
- Heating a volatile mixture in an open flask. Without reflux the ethanol (and the acid it forms) escape as vapour.

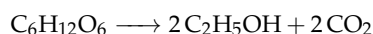
3 Making ethanol: hydration and fermentation

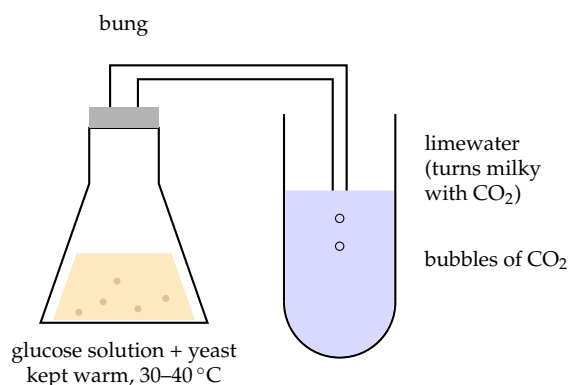
Ethanol is the most important alcohol and is made in two quite different ways.

Hydration of ethene (industrial). Ethene, obtained by cracking crude oil, reacts with steam. The reaction is reversible, so it is carried out at about 300 °C and 60–70 atmospheres with a **phosphoric acid catalyst**. The mixture leaving the reactor is cooled so that ethanol (and unreacted steam) condense; the unreacted ethene is recycled so that none is wasted.



Fermentation (from plants). Yeast contains enzymes that convert sugars, for example glucose from sugar cane or corn, into ethanol and carbon dioxide. The conditions are **warm, about 30–40 °C** (too cold and the enzymes are slow; too hot and they are denatured), **aqueous**, and **without oxygen** (anaerobic). With oxygen, bacteria would oxidise the ethanol to ethanoic acid and spoil the product.





Fermentation stops at about 15–20% ethanol because the yeast is killed by the alcohol it makes. To get stronger spirits the liquid must be concentrated by fractional distillation, which separates the ethanol (b.p. 78 °C) from water (100 °C) because of their different boiling points.

Comparing the two routes.

	hydration of ethene	fermentation
raw material	ethene (from finite crude oil)	sugars (renewable crops)
rate and type	fast, continuous	slow, batch
product	pure ethanol	dilute solution; distillation needed
conditions	high temperature and pressure	low temperature, atmospheric pressure
best used for	industrial use, solvent	drinks, biofuel

Worked example: balancing fermentation

Show that the fermentation equation is balanced and find the mass of ethanol from 180 g of glucose if the reaction is complete. (M_r : glucose = 180, ethanol = 46.)

Atoms: left C = 6, H = 12, O = 6; right $2 \times 2 + 2 = 6$ C, $2 \times 6 = 12$ H, $2 \times 1 + 2 \times 2 = 6$ O. Balanced. Moles of glucose = $180/180 = 1$, giving 2 mol ethanol, mass = $2 \times 46 = 92$ g.

Exam tip

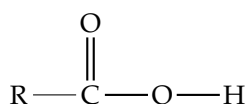
“Renewable” does not automatically mean “better”: fertile land is used to grow the crop and energy is needed to distil. Examiners reward a specific advantage (renewable raw material, lower temperature) and a specific disadvantage (slow, impure, needs distillation).

Common mistakes

- Forgetting that fermentation needs *no oxygen*.
- Using a high temperature for fermentation. Above about 40 °C the enzymes denature.
- Writing steam as “water at room temperature”. The industrial reactant is steam at high temperature and pressure.

4 Carboxylic acids

The functional group of a **carboxylic acid** is the **carboxyl** group, —COOH . It is a carbon atom joined to an oxygen by a double bond (C=O) and to a hydroxyl group (—OH) at the same time; this combination gives behaviour quite different from either on its own.

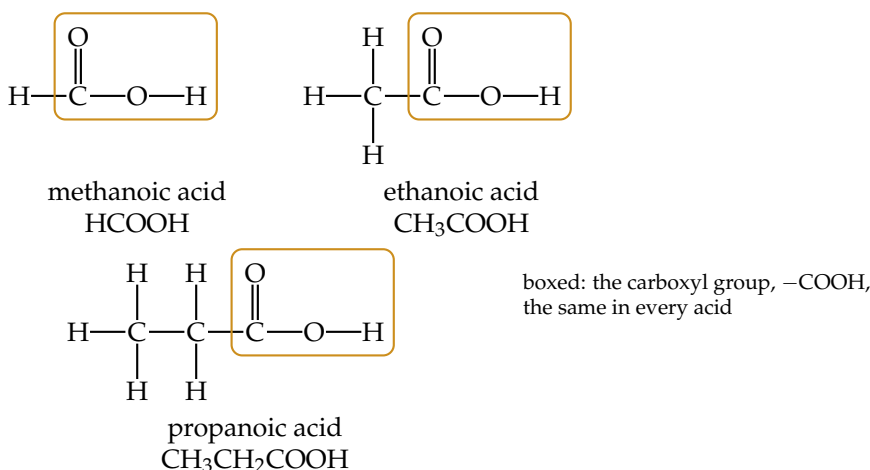


carbonyl C=O and hydroxyl —OH
on the *same* carbon
= carboxyl group, —COOH

R is H or an alkyl group, e.g. CH_3

The names use the alkane stem with the ending **-oic acid**. Crucially, the carbon of the -COOH group *is counted in the carbon chain*: ethanoic acid has two carbons in total, one in CH_3 and one in COOH . The general formula is $\text{C}_n\text{H}_{2n+1}\text{COOH}$ (or $\text{C}_n\text{H}_{2n}\text{O}_2$ in total for n carbons):

carbons	name	molecular formula	structural formula
1	methanoic acid	CH_2O_2	HCOOH
2	ethanoic acid	$\text{C}_2\text{H}_4\text{O}_2$	CH_3COOH
3	propanoic acid	$\text{C}_3\text{H}_6\text{O}_2$	$\text{CH}_3\text{CH}_2\text{COOH}$
4	butanoic acid	$\text{C}_4\text{H}_8\text{O}_2$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
5	pentanoic acid	$\text{C}_5\text{H}_{10}\text{O}_2$	$\text{CH}_3(\text{CH}_2)_3\text{COOH}$
6	hexanoic acid	$\text{C}_6\text{H}_{12}\text{O}_2$	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$



Methanoic acid is found in ant and nettle stings; ethanoic acid is the acid in vinegar (about 5% solution). The first members are colourless liquids with sharp smells and, like the alcohols, have higher boiling points than alkanes of similar size because of hydrogen bonding. Small acids dissolve readily in water.

Worked example: formula and relative formula mass

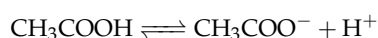
Work out the molecular formula and M_r of butanoic acid. (A_r : $\text{H} = 1$, $\text{C} = 12$, $\text{O} = 16$.)
 Four carbons including the COOH carbon: $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$. Count: $\text{C} = 4$, $\text{H} = 3 + 2 + 2 + 1 = 8$, $\text{O} = 2$, so $\text{C}_4\text{H}_8\text{O}_2$. $M_r = 4 \times 12 + 8 \times 1 + 2 \times 16 = 88$.

Common mistakes

- Not counting the COOH carbon. $\text{CH}_3\text{CH}_2\text{COOH}$ has three carbons and is propanoic acid, not butanoic acid.
- Misusing $\text{C}_n\text{H}_{2n+1}\text{COOH}$: here n counts the carbons *excluding* the acid carbon, so the total is $n + 1$ carbons (ethanoic acid is $n = 1$).
- Mixing up -ol (alcohol), -oic acid (acid) and -oate (ester) endings.

5 Weak acids and their reactions

An acid is a substance that releases hydrogen ions, H^+ , in water. A **strong** acid, such as hydrochloric acid, ionises *completely*: essentially every molecule splits into H^+ and Cl^- . Carboxylic acids are **weak** acids: only a small fraction of molecules ionise, and the process is reversible, so most molecules stay intact:

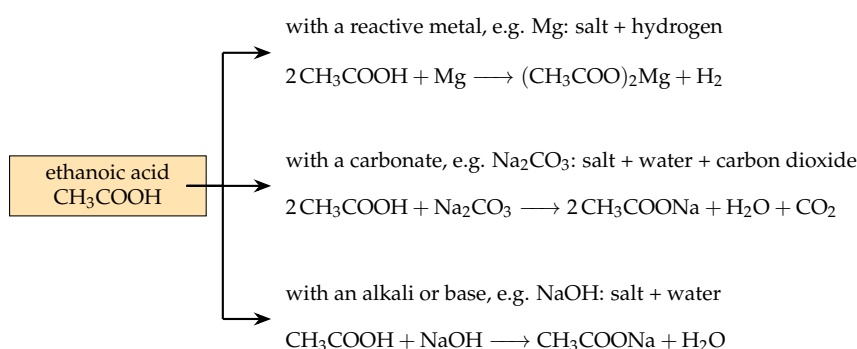


(Only the hydrogen of the -OH in the -COOH group ionises, not the hydrogens on the carbon.)

strong acid, e.g. HCl	weak acid, e.g. CH ₃ COOH
$\text{H}^+ \text{A}^-$ $\text{H}^+ \text{A}^-$ $\text{H}^+ \text{A}^-$ $\text{H}^+ \text{A}^-$ $\text{H}^+ \text{A}^-$ $\text{H}^+ \text{A}^-$ $\text{H}^+ \text{A}^-$ $\text{H}^+ \text{A}^-$ $\text{H}^+ \text{A}^-$	HA HA HA HA $\text{H}^+ \text{A}^-$ HA HA HA HA
fully ionised: many H^+	mostly molecules: few H^+

Strong and weak are not the same as concentrated and dilute. Strong/weak describes how much the acid ionises; concentrated/dilute describes how much acid is dissolved. A weak acid at the same concentration as a strong acid has fewer H^+ ions, so a higher pH (about 3 for 0.1 mol dm^{-3} ethanoic acid compared with 1 for hydrochloric acid) and a slower reaction with a metal or carbonate. The total amount of base needed to neutralise them is the same, however, because as H^+ is used up the equilibrium shifts and more acid ionises until all of it has reacted.

Typical acid reactions. Carboxylic acids react like any other acid, and the salts they make are named after the acid with the ending **-oate** (ethanoic acid gives ethanoates, methanoic gives methanoates, propanoic gives propanoates).



Observations: with magnesium, steady fizzing of hydrogen (squeaky pop); with a carbonate, vigorous effervescence of carbon dioxide (it turns limewater milky), which is the standard test to distinguish a carboxylic acid from an alcohol, since an alcohol does *not* react with carbonates; with an alkali, no visible change but the pH rises towards 7 and the temperature rises slightly.

Worked example: titration

25.0 cm³ of ethanoic acid is neutralised by 20.0 cm³ of 0.100 mol dm⁻³ sodium hydroxide. Find the concentration of the acid in g dm⁻³. (*M_r* of CH₃COOH = 60.)

CH₃COOH + NaOH → CH₃COONa + H₂O is 1 : 1. Moles of NaOH = $0.100 \times 0.0200 = 0.00200 \text{ mol}$ = moles of acid. Concentration = $0.00200 / 0.0250 = 0.0800 \text{ mol dm}^{-3}$. Mass concentration = $0.0800 \times 60 = 4.8 \text{ g dm}^{-3}$.

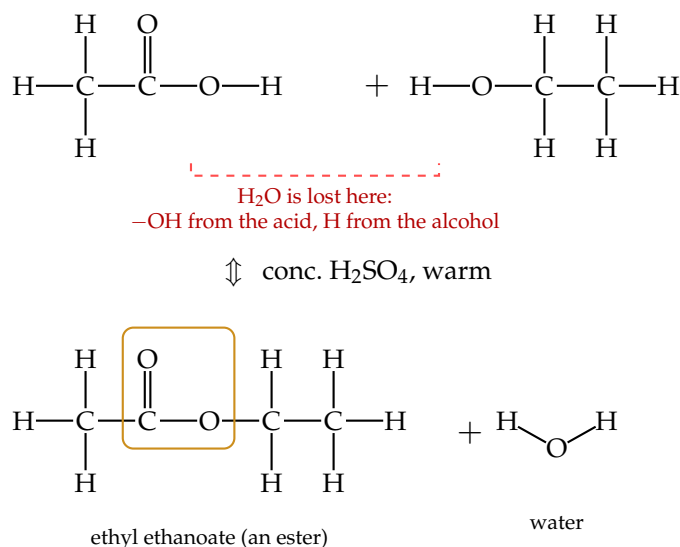
Common mistakes

- Saying a weak acid is a dilute acid (or a strong acid is concentrated). They are different ideas.
- Thinking a weak acid needs less alkali to neutralise it. Equal moles of a monobasic acid need equal moles of NaOH, strong or weak.
- Writing the salt of ethanoic acid as "sodium ethanoic" or "sodium ethanoic acid". It is sodium ethanoate.
- Forgetting that two ethanoic acid molecules react with one Mg or one CO₃²⁻ in the equations (balance the charges).

6 Esters

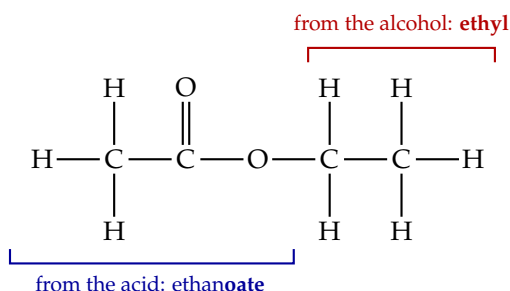
When a carboxylic acid is warmed with an alcohol and a little concentrated sulfuric acid (the **catalyst**), they join to form an **ester** and water. This is **esterification**, and the reaction is reversible:





Look at where the water comes from: the —OH of the acid and the H of the alcohol's —OH . The ester link, —COO— , is what remains. This is the same linkage that forms in polyesters (a diol with a dicarboxylic acid), which is why polyesters are condensation polymers.

Naming an ester has two parts, in this order. The first word comes from the *alcohol* (an alkyl group: methyl, ethyl, propyl...), the second from the *acid* with the ending **-oate**. So ethanoic acid + ethanol gives **ethyl ethanoate**. The same pair swapped (propanoic acid + methanol) gives methyl propanoate, a different compound, even though both are $\text{C}_4\text{H}_8\text{O}_2$.

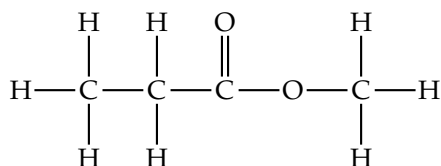


Reading a displayed ester. Find the $\text{C}(=\text{O})\text{—O}$ link. The carbons *on the carbonyl side*, including the carbonyl carbon, are the acid part; the carbons *beyond the single-bonded oxygen* are the alcohol (alkyl) part. Esters are volatile liquids with sweet, fruity smells, used in perfumes, food flavourings and as solvents. Unlike alcohols and acids, they have no O—H group, so they cannot hydrogen-bond to each other and have lower boiling points than the acid of the same size; they are poorly soluble in water.

Practical. Warm the acid, alcohol and a few drops of concentrated sulfuric acid in a flask (a water bath or reflux, because the alcohol is flammable). Pour the mixture into aqueous sodium carbonate to remove unreacted acid (fizzing) and smell the fruity layer. Heating the ester with water and acid or alkali reverses the reaction (**hydrolysis**). Because the reaction is reversible the yield is well below 100%.

Worked example: naming and an ester yield

(a) Name the ester drawn. (b) Calculate the mass of ethyl ethanoate formed from 6.0 g of ethanoic acid with excess ethanol at 60% yield. (M_r : acid = 60, ester = 88.)



(a) The carbonyl side has three carbons (acid: propanoic); the oxygen is bonded to CH_3 (alcohol: methanol). So this is methyl propanoate ($\text{C}_4\text{H}_8\text{O}_2$). (b) $6.0/60 = 0.10$ mol of acid gives 0.10 mol of ester at 100% yield: $0.10 \times 88 = 8.8$ g. At 60% the mass is 5.28 g.

Common mistakes

- Naming the ester the wrong way round. The *alkyl* part (from the alcohol) comes first: ethyl ethanoate comes from ethanol and ethanoic acid.
- Giving the sulfuric acid as a reactant. It is the catalyst and is not used up.
- Forgetting that water forms and that the reaction is reversible, so the yield is not 100%.

7 Putting it together: working out the unknown

Exam questions often give you a few clues and ask for the compound. Use the clues like a detective, in this order:

1. **Carbonate test or pH:** fizzing with sodium carbonate gives CO_2 , so the compound is a carboxylic acid ($-\text{COOH}$). An alcohol or ester does not fizz.
2. **Sodium:** hydrogen given off by a neutral organic liquid suggests an alcohol (an acid also does it, but the carbonate test separates them).
3. **Formula and M_r :** divide the percentages by the A_r values to get the empirical formula, then compare the empirical mass with the M_r to get the molecular formula.
4. **Hydrolysing an ester:** add the masses back. The ester's $M_r = M_r(\text{acid}) + M_r(\text{alcohol}) - 18$.

Worked example: an unknown compound

A liquid has the composition 48.7% C, 8.1% H and 43.2% O by mass, $M_r = 74$, and it fizzes with sodium carbonate. Identify it. (A_r : H = 1, C = 12, O = 16.)
Moles in 100 g: C = $48.7/12 = 4.06$; H = $8.1/1 = 8.1$; O = $43.2/16 = 2.70$. Divide by 2.70: C 1.50, H 3.0, O 1.00; double to whole numbers: $\text{C}_3\text{H}_6\text{O}_2$. Its mass is $3 \times 12 + 6 + 32 = 74$, matching M_r , so the molecular formula is $\text{C}_3\text{H}_6\text{O}_2$. Fizzing with carbonate means an acid: $\text{CH}_3\text{CH}_2\text{COOH}$, propanoic acid. (The isomers methyl ethanoate and ethyl methanoate are esters and would not fizz.)

Worked example: hydrolysis of an ester

An ester of $M_r = 102$ is hydrolysed to give ethanoic acid ($M_r = 60$) and an alcohol. Find the M_r of the alcohol and name the ester.
 $M_r(\text{alcohol}) = 102 + 18 - 60 = 60$. The alcohol $\text{C}_3\text{H}_7\text{OH}$ has $M_r = 36 + 8 + 16 = 60$, so it is propanol, and the ester is propyl ethanoate.

Key ideas

- Alcohols $\text{C}_n\text{H}_{2n+1}\text{OH}$: $-\text{OH}$; burn; give H_2 with sodium; oxidise to acids (orange $\rightarrow$ green).
- Ethanol: hydration of ethene (steam, H_3PO_4 , 300°C , 60–70 atm) or fermentation (yeast, $30\text{--}40^\circ\text{C}$, no oxygen).
- Carboxylic acids $-\text{COOH}$: weak acids; salts end -oate; react with metals, carbonates, bases.
- Esters $-\text{COO}-$: acid + alcohol (acid catalyst), alkyl name first, -oate second; sweet smell.

Check yourself

Try these without looking back, then compare with the answers on the next page.

1. Give the molecular formula and name of the alcohol with four carbons (straight chain, -OH on the end carbon).
2. What is observed, and what gas forms, when sodium is added to ethanol?
3. State three conditions for the fermentation of glucose to ethanol, and why oxygen must be excluded.
4. Write the equation for the hydration of ethene and give two conditions.
5. What is the colour change when ethanol is oxidised by acidified potassium dichromate(VI), and what is the organic product?
6. Why is ethanoic acid called a weak acid? Name its salt with sodium hydroxide.
7. Name the products when ethanoic acid reacts with magnesium carbonate.
8. Name the ester made from propanoic acid and methanol, and say which reagent is the catalyst.

Answers to the self-check

1. $\text{C}_4\text{H}_9\text{OH}$, i.e. $\text{C}_4\text{H}_{10}\text{O}$: butan-1-ol.
2. Steady fizzing; hydrogen gas forms (squeaky pop with a lit splint), and sodium ethoxide is left.
3. Yeast (enzymes), warm ($30\text{--}40^\circ\text{C}$), aqueous solution, no air. With oxygen the ethanol is oxidised to ethanoic acid (vinegar).
4. $\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{OH}$; steam at about 300°C and 60–70 atm with a phosphoric acid catalyst.
5. Orange to green; ethanoic acid.
6. It ionises only partially in water (reversible). The salt is sodium ethanoate.
7. Magnesium ethanoate, water and carbon dioxide.
8. Methyl propanoate; concentrated sulfuric acid is the catalyst.

Next step

Heurisco's *ESAT Chemistry: Alcohols and Carboxylic Acids Practice Set* has twenty original exam-style questions on this lesson, with structures, apparatus and boiling-point data, in order of difficulty, with a full worked solution for each.