A-LEVEL CHEMISTRY • EXERCISE SHEET

33.1 Carboxylic acids

Name: _____ Class: _____ Date: _____ **Total: 32 marks**

KEY WORDS acidity 酸性 • acyl chloride 酰氯 • phenol 苯酚 • carboxylic acid 羧酸 • alcohol 醇

Objective

Build the skills to answer exam questions on **carboxylic acids** 羧酸 — making them, the special acids that oxidise further, and the trends in **acidity** 酸性.

You must be able to:

- make benzoic acid by side-chain oxidation; make an acyl chloride from an acid
- recall which carboxylic acids can be oxidised further
- explain the acidity order alcohol < phenol < carboxylic acid
- explain how chlorine substituents affect acid strength

1 Worked examples

Acidity trends

acidity increases

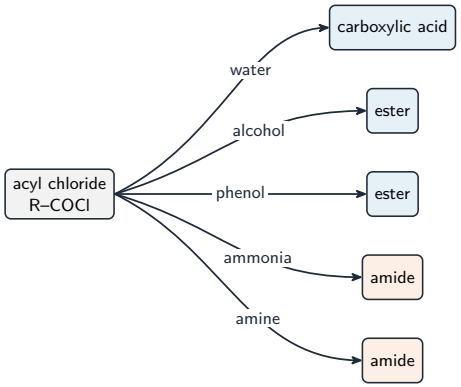
carboxylic acid → $RCOO^-$:
charge spread over *two O* (strongest)

phenol → phenoxide:
charge spread *into the ring*

more spreading
⇒ more stable anion
⇒ stronger acid

alcohol → RO^-:
charge on one O, *not spread* (weakest)

The more the negative charge on the conjugate base is spread out, the more stable the ion and the stronger the acid



Carboxylic acids and their acyl chloride reactions

- **acidity:** alcohol < phenol < **carboxylic acid** — the carboxylate spreads its charge over **two** oxygens.
- **electron-withdrawing** Cl atoms (inductive effect) pull electron density away, spread the charge more → **stronger** acid; more Cl (and closer to –COOH) = stronger.
- **make benzoic acid:** methylbenzene + hot alkaline $KMnO_4$, then acid (whole side-chain → –COOH).

Making them, testing them, and the acidity comparison

Four routes to a carboxylic acid:

From	Reagents
a primary alcohol	$K_2Cr_2O_7$ / dilute H_2SO_4, heated **under reflux** (distilling instead stops at the aldehyde)
an aldehyde	the same oxidising mixture
a nitrile	hydrolysis with dilute acid, heated
an ester or amide	hydrolysis, acid or alkaline (alkaline gives the salt, then acidify)

Two acids oxidise further, and that is examinable. Methanoic acid, HCOOH, still has an H on the carbonyl carbon, so it behaves as an aldehyde too: it reduces Fehling's and Tollens'. **Ethanedioic acid**, $(COOH)_2$, is oxidised by warm acidified $KMnO_4$ to carbon dioxide, decolourising the purple solution.

The reactions to know: with a reactive metal → salt + hydrogen; with a carbonate → salt + water + **carbon dioxide** (effervescence, the test that distinguishes an acid from a phenol); with an alcohol and an acid catalyst → an ester; with $LiAlH_4$ → a primary alcohol; with PCl_5 or $SOCl_2$ → an acyl chloride.

Why a carboxylic acid is more acidic than an alcohol or phenol — the standard 3-mark comparison:

- In the **carboxylate** ion the negative charge is delocalised over **two oxygen atoms** and both C–O bonds are equal, so the anion is very stable and the equilibrium lies well to the right.
- In the **phenoxide** ion the charge is delocalised into the **ring**, which stabilises it but less effectively, so phenol is a weaker acid.
- In an **alkoxide** the charge is localised on **one oxygen**, with an electron-releasing alkyl group making it worse; ethanol is barely acidic at all.

Order: carboxylic acid > phenol > water > alcohol. **Electron-withdrawing groups increase acidity** by pulling charge away from the carboxylate: chloroethanoic acid is stronger than ethanoic acid, and trichloroethanoic acid stronger still.

2 Practice

2.1 Give the reagents to oxidise methylbenzene to benzoic acid. [2]

2.2 State which is the stronger acid: ethanoic acid or chloroethanoic acid. [1]

2.3 Give the reagents and conditions for making propanoic acid from propan-1-ol. [3]

2.4 State the observation when ethanoic acid is added to sodium carbonate, and name the gas. [2]

2.5 Explain why chloroethanoic acid is a stronger acid than ethanoic acid. [2]

3 Exam-style questions

3.1 A carboxylic acid is more acidic than phenol because its conjugate base spreads the negative charge over: [1]

- **A** one oxygen atom
- **B** two oxygen atoms
- **C** the benzene ring only
- **D** no atoms

3.2 Which is the **strongest** acid? [1]

- **A** ethanoic acid, CH_3COOH
- **B** chloroethanoic acid, $CH_2ClCOOH$
- **C** dichloroethanoic acid, $CHCl_2COOH$
- **D** trichloroethanoic acid, CCl_3COOH

3.3 Explain, in terms of the conjugate base, why a carboxylic acid is more acidic than an alcohol. [2]

3.4 Trichloroethanoic acid is a much stronger acid than ethanoic acid. Explain why, in terms of the inductive effect. [3]

3.5 (a) Give the reagents and conditions for oxidising butan-1-ol to butanoic acid, and explain why reflux rather than distillation is used. [3]

(b) Explain, in terms of the anion formed, why ethanoic acid is a stronger acid than ethanol. [3]

(c) Explain why phenol is a weaker acid than ethanoic acid. [2]

(d) Describe a chemical test that would distinguish ethanoic acid from phenol, giving the reagent and the observation with each. [3]

(e) Methanoic acid gives a positive result with Tollens' reagent, but ethanoic acid does not. Explain why. [2]

(f) Name the product and give the reagent when butanoic acid is treated with $LiAlH_4$. [2]

Solutions

2.1 hot alkaline $KMnO_4$ (potassium manganate(VII)); then dilute acid (acidify).

2.2 chloroethanoic acid.

2.3 Acidified potassium dichromate(VI); heat; under reflux.

2.4 Effervescence, or bubbles of gas; carbon dioxide.

2.5 The chlorine atom is electron-withdrawing, so it pulls electron density away from the carboxylate ion and spreads the negative charge further, making the anion more stable and the acid stronger.

3.1 B. The carboxylate ion spreads its negative charge over two oxygen atoms.

3.2 D. Three electron-withdrawing chlorine atoms spread the charge most, giving the strongest acid.

3.3 when a carboxylic acid loses H^+, the charge is delocalised over two oxygen atoms, making a very stable carboxylate ion; an alkoxide (RO^-) cannot spread its charge, so it is less stable and the alcohol is far less acidic.

3.4 chlorine is electron-withdrawing and pulls electron density away through the inductive effect; this helps spread out the negative charge on the conjugate base, stabilising the ion; three Cl atoms in CCl_3COOH do this much more than the CH_3 in ethanoic acid, so it is a far stronger acid.

3.5 (a) Acidified potassium dichromate(VI), heated; reflux returns the vapour to the flask so the oxidation continues to the acid, while distillation would remove the aldehyde as soon as it formed.
(b) In the ethanoate ion the negative charge is delocalised over two oxygen atoms, so the anion is much more stable; in the ethoxide ion the charge is localised on one oxygen and the alkyl group releases electron density towards it, making it less stable, so the equilibrium lies much further left.
(c) In the phenoxide ion the charge is delocalised into the benzene ring rather than over two oxygens, which stabilises it less effectively than in a carboxylate.
(d) Add aqueous sodium carbonate to each; ethanoic acid gives effervescence of carbon dioxide; phenol gives no reaction, because it is too weak an acid to release carbon dioxide from a carbonate.
(e) Methanoic acid has a hydrogen atom attached to the carbonyl carbon, so it has an aldehyde group and can be oxidised further, reducing the Tollens' reagent.
(f) Butan-1-ol; lithium tetrahydridoaluminate in dry ether.