Exercise walk-through

Carboxylic acids ▪ 33.1

eXercise

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

Method — Acidity trends

- **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 $\rightarrow$ **stronger** acid; more Cl (and closer to –COOH) $=$ stronger.
- **make benzoic acid:** methylbenzene $+$ hot alkaline $KMnO_4$, then acid (whole side-chain $\rightarrow$ –COOH).

Method — Acidity trends

acidity increases ↑

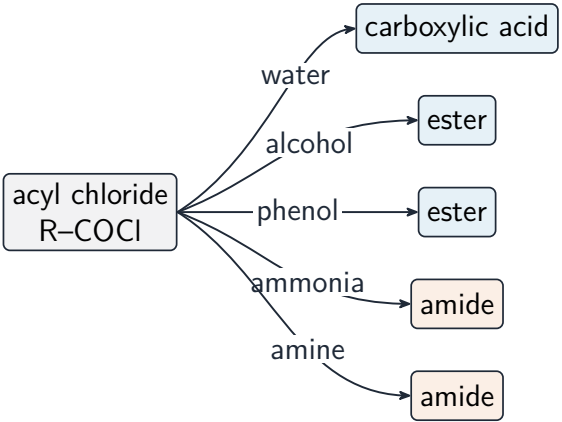
carboxylic acid → $RCOO^-$:
charge spread over *two O* (strongest)

phenol → phenoxide:
charge spread *into the ring*

more spreading
⇒ more stable anion
⇒ stronger acid

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

Method — Acidity trends



(each also gives HCl)

Carboxylic acids and their acyl chloride reactions

Practice 2.1 ▪ 2 marks

Give the reagents to oxidise methylbenzene to benzoic acid.

Solution 2.1

Method: Acidity trends

Worked steps

hot alkaline $KMnO_4$ (potassium manganate(VII)) M1; then dilute acid (acidify) A1.

Practice 2.2 ▪ 1 mark

State which is the stronger acid: ethanoic acid or chloroethanoic acid.

Solution 2.2

Method: Acidity trends

Worked steps

chloroethanoic acid B1.

Exam-style 3.1 ▪ 1 mark

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

A one oxygen atom

B two oxygen atoms

C the benzene ring only

D no atoms

Solution 3.1

Method: Acidity trends

A one oxygen atom

B two oxygen atoms ✓

C the benzene ring only

D no atoms

Worked steps

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

Exam-style 3.2 ▪ 1 mark

Which is the **strongest** acid?

A ethanoic acid, CH_3COOH

B chloroethanoic acid, $CH_2ClCOOH$

C dichloroethanoic acid, $CHCl_2COOH$

D trichloroethanoic acid, CCl_3COOH

Solution 3.2

A ethanoic acid, CH_3COOH

B chloroethanoic acid, $CH_2ClCOOH$

C dichloroethanoic acid, $CHCl_2COOH$

D trichloroethanoic acid, CCl_3COOH ✓

Worked steps

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

Exam-style 3.3 ▪ 2 marks

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

Solution 3.3

Method: Acidity trends

Worked steps

when a carboxylic acid loses H^+, the charge is delocalised over two oxygen atoms, making a very stable carboxylate ion **M1**; an alkoxide (RO^-) cannot spread its charge, so it is less stable and the alcohol is far less acidic **A1**.

Exam-style 3.4 ▪ 3 marks

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

Solution 3.4

Method: Acidity trends

Worked steps

chlorine is electron-withdrawing and pulls electron density away through the inductive effect **M1**; this helps spread out the negative charge on the conjugate base, stabilising the ion **M1**; three Cl atoms in CCl_3COOH do this much more than the CH_3 in ethanoic acid, so it is a far stronger acid **A1**.