

Carboxylic Acids & Derivatives

A-Level Chemistry ■ Topic 33

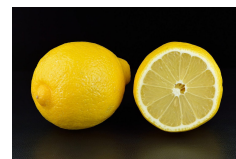
A-Level Chemistry



Carboxylic Acids & Derivatives

What we will cover

- 1 Relative acidities
- 2 Acyl chlorides
- 3 Addition–elimination
- 4 Ease of hydrolysis



citric acid is a carboxylic acid

1 Acids and acyl chlorides

Carboxylic Acids & Derivatives

↳ Acids and acyl chlorides

Relative acidities

↑ 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)

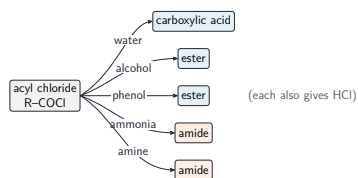
Acidity rises: alcohol < phenol
< **carboxylic acid** 羧酸.

The acid is strongest because its anion spreads the charge over **two** oxygens.
Chlorine 氯 (electron-withdrawing, **inductive effect** 诱导效应) makes it even more acidic.

Carboxylic Acids & Derivatives

↳ Acids and acyl chlorides

Acyl chlorides



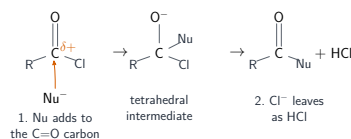
Acyl chlorides 酰氯 are very reactive. At room temperature (all give HCl):

- water → the acid
- alcohol/phenol → an ester
- ammonia or an amine → an **amide** 酰胺

Carboxylic Acids & Derivatives

↳ Acids and acyl chlorides

The addition–elimination mechanism



All these follow **addition–elimination** 加成消去:

- a nucleophile **adds** to the δ^+ carbonyl carbon
- then HCl is **eliminated** as the $\text{C}=\text{O}$ reforms

Ease of hydrolysis



How easily a chloride reacts with water:

acyl chloride $\gg$ alkyl chloride $\gg$ aryl chloride

An **acyl chloride** 酰氯 reacts violently with cold water; an aryl chloride does not (its C–Cl is strengthened by the ring). Aspirin is an **ester** 酯.

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Recap

Worked example – acyl chlorides

Give the product and the observation when ethanoyl chloride is added to (a) water and (b) ethanol.

- Both Cl and O pull electrons, so the carbonyl C carries a **large δ^+** – nucleophiles attack easily.
- (a) $\text{CH}_3\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HCl}$. Violent; **steamy white fumes**.
- (b) $\text{CH}_3\text{COCl} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{HCl}$: ethyl ethanoate.
- No catalyst, no reflux, not reversible** – unlike the acid + alcohol route.

Acyl chlorides are the **re-active** way to make esters and amides: fast, one-way, high yield. The steamy HCl is the giveaway.

Topic 33 – key takeaways

1 Acidity

alcohol < phenol < carboxylic acid

2 Acyl chlorides

react with water, alcohols, amines

3 Mechanism

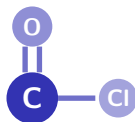
addition–elimination; nucleophile adds, HCl leaves

4 Hydrolysis

acyl $\gg$ alkyl $\gg$ aryl chloride

Check yourself

- Which is most acidic: alcohol, phenol or acid?
- What does an acyl chloride give with ammonia?
- Name the acyl chloride mechanism.
- Which chloride hydrolyses fastest?



Answers 1. the carboxylic acid 2. an amide 3. addition–elimination 4. the acyl chloride