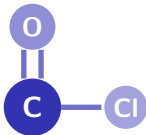


Carboxylic Acids & Derivatives

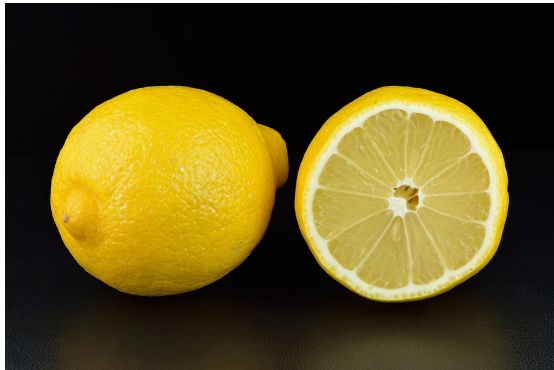
A-Level Chemistry ■ Topic 33

A-Level Chemistry



What we will cover

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



citric acid is a carboxylic acid



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

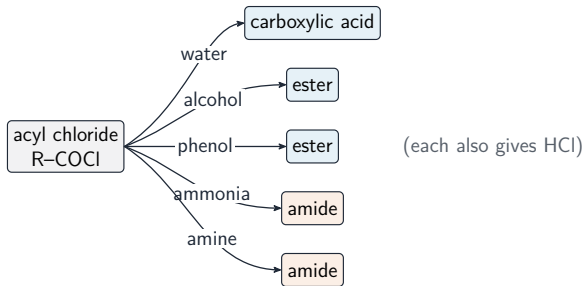
alcohol → RO^- :

charge on one O, *not spread* (weakest)

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

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

Acyl chlorides



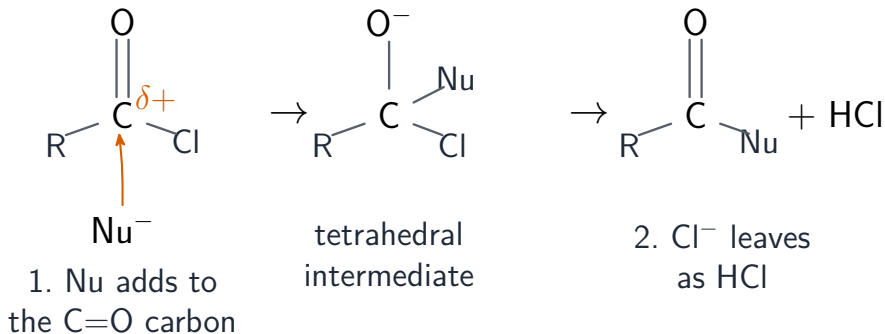
Acyl chlorides are very reactive. At room temperature (all give HCl):

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

The addition–elimination mechanism

All these follow **addition–elimination** :

- a nucleophile **adds** to the $\delta+$ carbonyl carbon
- then HCl is **eliminated** as the C=O reforms



Ease of hydrolysis

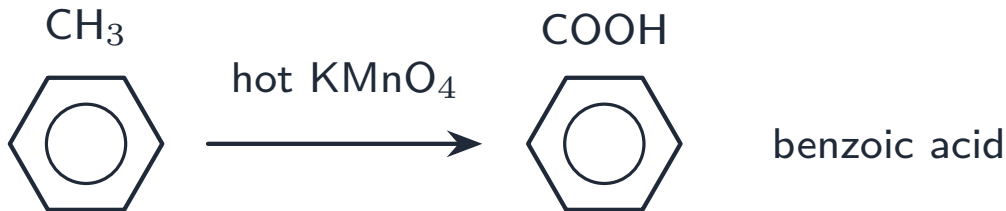


How easily a chloride reacts with water:

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

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

Making and reacting



Hot KMnO_4 oxidises a methyl side-chain to a COOH group

Two acids that oxidise further

Most carboxylic acids resist oxidation. Two do not, and the exam asks why:

methanoic acid,
HCOOH

it still carries an aldehyde-like H on the carbonyl, so Fehling's, Tollens', acidified KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ take it on to CO_2

ethanedioic acid,
HOCCOOH

warm acidified KMnO_4 oxidises it to CO_2 – which is why it is used to standardise permanganate

And an **alkylbenzene** such as methylbenzene: hot alkaline KMnO_4 then dilute acid oxidises the **whole side chain** back to one $-\text{COOH}$, giving **benzoic acid** however long the chain was.

Exam tips

- **Acyl chlorides** are very reactive – learn their products with water (HCl), alcohols (esters), ammonia (amides) and amines.
- Reactivity order of derivatives: **acyl chloride** > **ester** > **amide**.
- Acid strength: electron-withdrawing groups (e.g. Cl) **increase** it – explain via the carboxylate ion.



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 $\delta+$** – 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

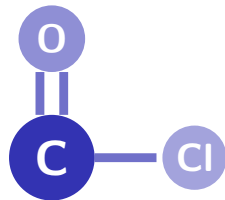
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Hydrolysis

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

Check yourself

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



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