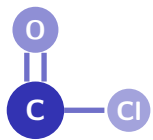
Carboxylic Acids & Derivatives

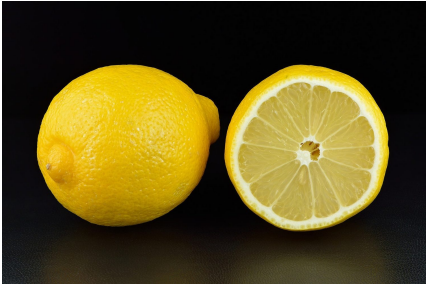
A-Level Chemistry ▪ Topic 33

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

1 Acids and acyl chlorides

Relative acidities

acidity increases ↑

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

phenol → phenoxide:
charge spread *into the ring*

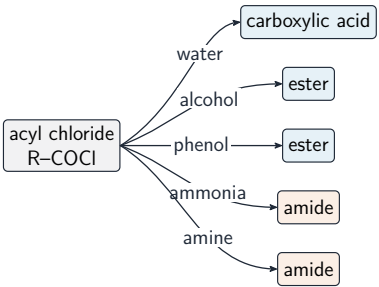
more spreading
⇒ more stable anion
⇒ stronger acid

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.

Acyl chlorides



(each also gives HCl)

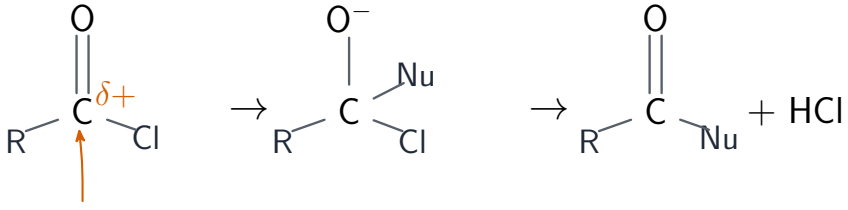
Acyl chlorides 酰氯 are very reactive. At room temperature (all give HCl):

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

The addition–elimination mechanism

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

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



1. Nu adds to the C=O carbon

tetrahedral intermediate

2. Cl^- leaves as HCl

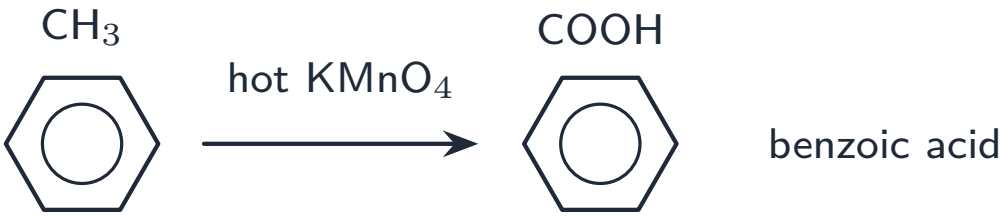
Ease of hydrolysis

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.

Making and reacting



Hot KMnO4 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 $K_2Cr_2O_7$ take it on to CO_2
ethanedioic acid, HOOCCOOH	warm acidified $KMnO_4$ oxidises it to CO_2 – which is why it is used to standardise permanganate

And an **alkylbenzene** 烷基苯 such as methylbenzene: hot alkaline $KMnO_4$ then dilute acid oxidises the whole side chain back to one $-COOH$, giving **benzoic acid** 苯甲酸 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.

2 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 $\delta+$ – nucleophiles attack easily.
- (a) $CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$. Violent; steamy white fumes.
- (b) $CH_3COCl + C_2H_5OH \rightarrow CH_3COOC_2H_5 + HCl$: ethyl ethanoate.
- No catalyst, no reflux, not reversible – unlike the acid + alcohol route.

Acyl chlorides are the reactive way to make esters and amides: fast, one-way, high yield. The steamy HCl is the give-away.

Topic 33 – key takeaways

1 Acidity

alcohol $<$ phenol $<$ carboxylic acid

2 Acyl chlorides

react with water, alcohols, amines

3 Mechanism

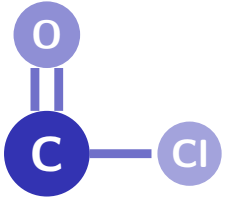
addition–elimination; nucleophile adds, HCl leaves

4 Hydrolysis

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

Check yourself

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