

Exercise walk-through

# 33.3

## Acyl chlorides

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A-Level Chemistry

# Relative acidities

acidity increases ↑

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

**phenol** → phenoxide:  
charge spread *into the ring*  
more spreading  
⇒ more stable anion  
⇒ stronger acid

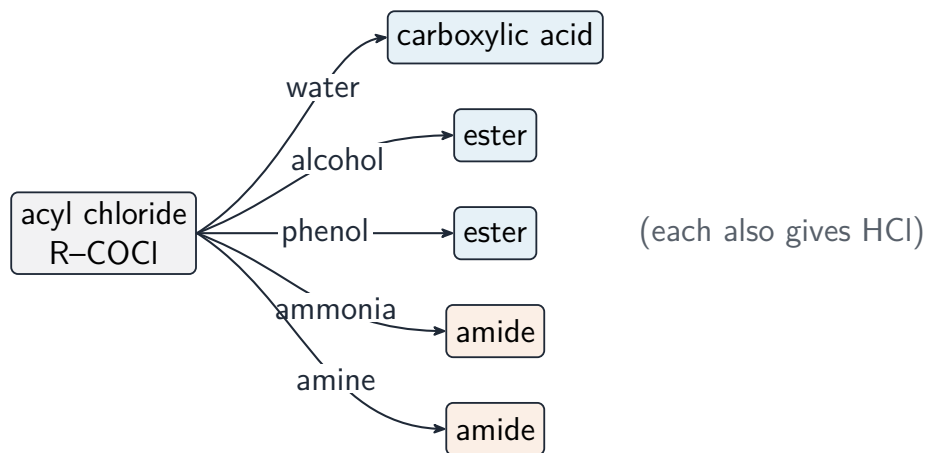
**alcohol** →  $\text{RO}^-$ :  
charge on one O, *not spread* (weakest)

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



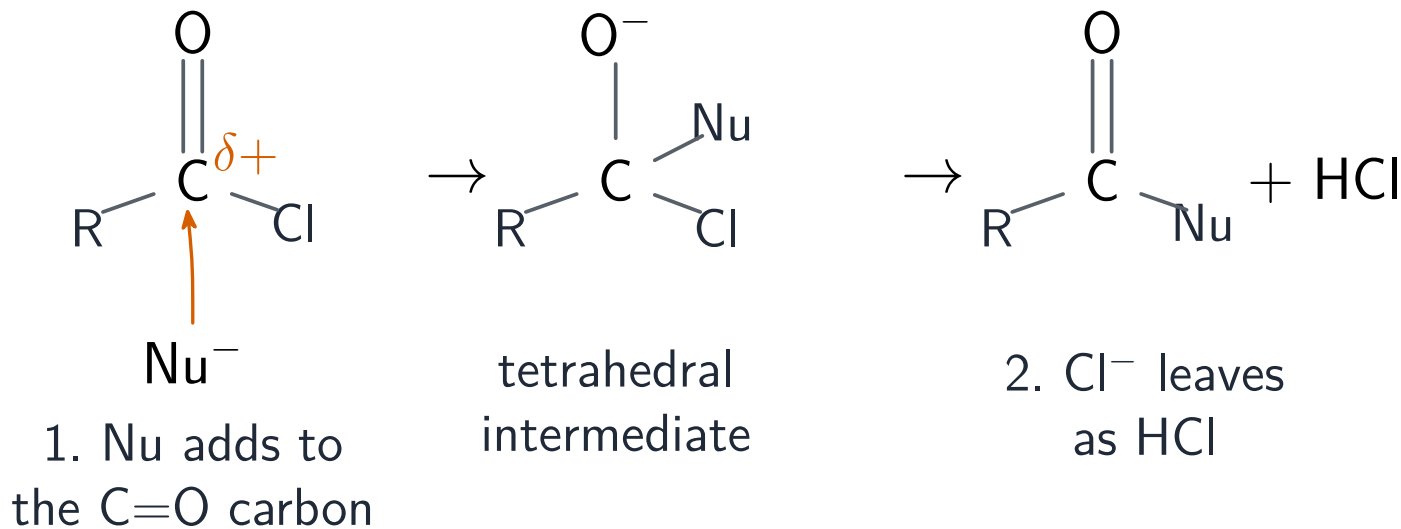
**Acyl chlorides** are very reactive. At room temperature (all give  $\text{HCl}$ ):

- 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

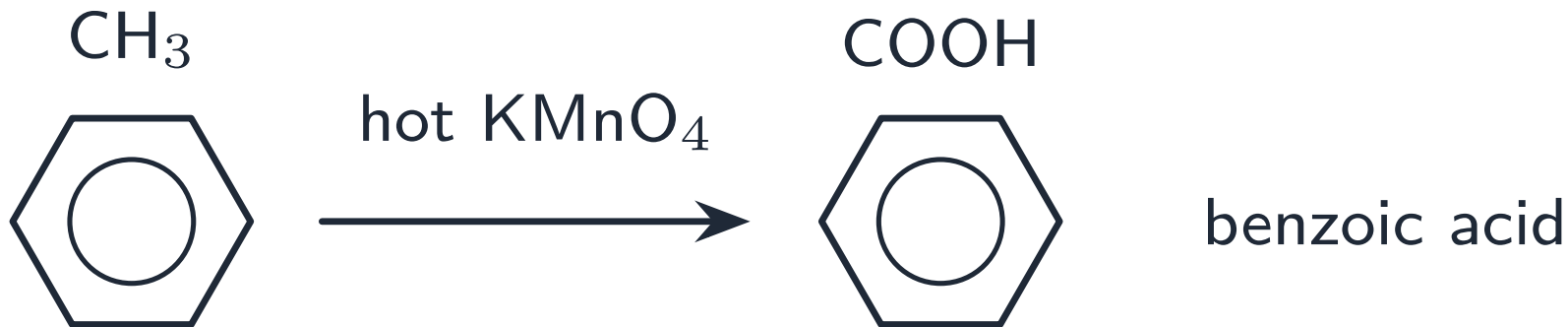


How easily a chloride reacts with water:

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  $\text{KMnO}_4$  oxidises a methyl side-chain to a  $\text{COOH}$  group

## Exercises 2.1-2.3

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**2.1** Name the product when ethanoyl chloride reacts with water. [1]

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**2.2** Name the type of mechanism by which acyl chlorides react. [1]

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**2.3** Give the organic product when propanoyl chloride reacts with ethanol. [1]

## Exercises 2.1-2.3

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**2.1** Name the product when ethanoyl chloride reacts with water. [1]

**2.1**

- ethanoic acid
- 

**2.2** Name the type of mechanism by which acyl chlorides react. [1]

**2.2**

- addition-elimination (nucleophilic)
- 

**2.3** Give the organic product when propanoyl chloride reacts with ethanol. [1]

**2.3**

- Ethyl propanoate

## Exercises 2.4-2.5

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**2.4** State the observation when an acyl chloride is added to water. [2]

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**2.5** Explain why acyl chlorides are more reactive than carboxylic acids towards nucleophiles. [2]

## Exercises 2.4·2.5

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**2.4** State the observation when an acyl chloride is added to water. [2]

**2.4**

- A vigorous reaction; steamy white fumes of hydrogen chloride are produced
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**2.5** Explain why acyl chlorides are more reactive than carboxylic acids towards nucleophiles. [2]

**2.5**

- Chloride is a much better leaving group than the hydroxyl of an acid; and the carbonyl carbon is more  $\delta+$  because both the oxygen and the chlorine withdraw electrons, so it is attacked more readily

## Exercises 3.1-3.2

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**3.1** Ethanoyl chloride reacts with ammonia to give:

[1]

☐

- A an ester
- B ethanamide
- C ethanoic acid
- D an amine

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**3.2** Which order of ease of hydrolysis is correct?

[1]

☐

- A aryl chloride  $\gg$  alkyl chloride  $\gg$  acyl chloride
- B acyl chloride  $\gg$  alkyl chloride  $\gg$  aryl chloride
- C alkyl chloride  $\gg$  acyl chloride  $\gg$  aryl chloride
- D they hydrolyse equally easily

## Exercises 3.1·3.2

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3.1 Ethanoyl chloride reacts with ammonia to give:

[1]

☐

- A an ester
- B ethanamide
- C ethanoic acid
- D an amine

3.1 B

- Acyl chloride + ammonia
- amide (ethanamide) + HCl

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3.2 Which order of ease of hydrolysis is correct?

[1]

☐

- A aryl chloride  $\gg$  alkyl chloride  $\gg$  acyl chloride
- B acyl chloride  $\gg$  alkyl chloride  $\gg$  aryl chloride
- C alkyl chloride  $\gg$  acyl chloride  $\gg$  aryl chloride
- D they hydrolyse equally easily

3.2 B

- Acyl chloride  $\gg$  alkyl chloride  $\gg$  aryl chloride

## Exercises 3.3-3.4

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**3.3** Describe the **addition–elimination** mechanism for the reaction of ethanoyl chloride with an alcohol. [3]

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**3.4** Explain why an acyl chloride is hydrolysed far more easily than an aryl chloride (e.g. chlorobenzene). [2]

## Exercises 3.3·3.4

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**3.3** Describe the **addition–elimination** mechanism for the reaction of ethanoyl chloride with an alcohol. [3]

### 3.3

- the nucleophile (the alcohol's O lone pair) adds to the slightly positive carbonyl carbon, forming a tetrahedral intermediate; the C=O double bond reforms; the C–Cl bond breaks and HCl is eliminated, giving the ester

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**3.4** Explain why an acyl chloride is hydrolysed far more easily than an aryl chloride (e.g. chlorobenzene). [2]

### 3.4

- the carbonyl carbon of an acyl chloride is strongly  $\delta+$  and easily attacked by a nucleophile; in an aryl chloride the C–Cl bond is strengthened by overlap with the ring and the ring repels nucleophiles, so it resists hydrolysis

## Exercise 3.5 (a)

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**3.5** Ethanoyl chloride,  $\text{CH}_3\text{COCl}$ , reacts with a range of nucleophiles.

(a) Complete the table by naming the organic product of each reaction.

[4]

| Nucleophile | Organic product |
|-------------|-----------------|
| water       |                 |
| methanol    |                 |
| ammonia     |                 |
| phenol      |                 |

## Exercise 3.5 (a)

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**3.5** Ethanoyl chloride,  $\text{CH}_3\text{COCl}$ , reacts with a range of nucleophiles.

(a) Complete the table by naming the organic product of each reaction.

[4]

| Nucleophile | Organic product |
|-------------|-----------------|
| water       |                 |
| methanol    |                 |
| ammonia     |                 |
| phenol      |                 |

(a)

- Ethanoic acid; methyl ethanoate; ethanamide; phenyl ethanoate

## Exercise 3.5 (b)

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**3.5** Ethanoyl chloride,  $\text{CH}_3\text{COCl}$ , reacts with a range of nucleophiles.

(b) Draw the mechanism for the reaction with ammonia, showing curly arrows and the intermediate. [4]

## Exercise 3.5 (b)

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**3.5** Ethanoyl chloride,  $\text{CH}_3\text{COCl}$ , reacts with a range of nucleophiles.

(b) Draw the mechanism for the reaction with ammonia, showing curly arrows and the intermediate. [4]

(b)

- Curly arrow from the nitrogen's lone pair to the  $\delta+$  carbonyl carbon; arrow from the  $\text{C}=\text{O}$   $\pi$  bond onto the oxygen, giving the tetrahedral intermediate with a negative oxygen; arrow from the oxygen re-forming the double bond, with a second arrow expelling the chloride ion; loss of a proton to give ethanamide, and  $\text{HCl}$

## Exercise 3.5 (c)

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**3.5** Ethanoyl chloride,  $\text{CH}_3\text{COCl}$ , reacts with a range of nucleophiles.

(c) Name the type of mechanism.

[1]

## Exercise 3.5 (c)

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**3.5** Ethanoyl chloride,  $\text{CH}_3\text{COCl}$ , reacts with a range of nucleophiles.

(c) Name the type of mechanism.

[1]

(c)

- Nucleophilic addition–elimination

## Exercise 3.5 (d)

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**3.5** Ethanoyl chloride,  $\text{CH}_3\text{COCl}$ , reacts with a range of nucleophiles.

(d) Explain why an ester is better prepared from an acyl chloride than from the corresponding carboxylic acid. [3]

## Exercise 3.5 (d)

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**3.5** Ethanoyl chloride,  $\text{CH}_3\text{COCl}$ , reacts with a range of nucleophiles.

(d) Explain why an ester is better prepared from an acyl chloride than from the corresponding carboxylic acid. [3]

(d)

- The reaction with an acyl chloride is fast and goes essentially to completion; esterification of a carboxylic acid is slow, needs an acid catalyst and reaches an equilibrium, so the yield is limited; the acyl chloride route therefore gives a higher yield in less time

## Exercise 3.5 (e)

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**3.5** Ethanoyl chloride,  $\text{CH}_3\text{COCl}$ , reacts with a range of nucleophiles.

(e) Suggest why phenol reacts with ethanoyl chloride but not appreciably with ethanoic acid. [2]

## Exercise 3.5 (e)

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**3.5** Ethanoyl chloride,  $\text{CH}_3\text{COCl}$ , reacts with a range of nucleophiles.

(e) Suggest why phenol reacts with ethanoyl chloride but not appreciably with ethanoic acid. [2]

(e)

- Phenol is a weak nucleophile because its oxygen lone pair is delocalised into the ring; the acyl chloride is reactive enough to be attacked even by a weak nucleophile, whereas the far less reactive carboxylic acid is not