A-LEVEL CHEMISTRY • EXERCISE SHEET

33.3 Acyl chlorides

Name: _____ Class: _____ Date: _____ **Total: 28 marks**

KEY WORDS acyl chloride 酰氯 • addition–elimination 加成消去 • amide 酰胺 • amine 胺 • hydrolysis 水解

Objective

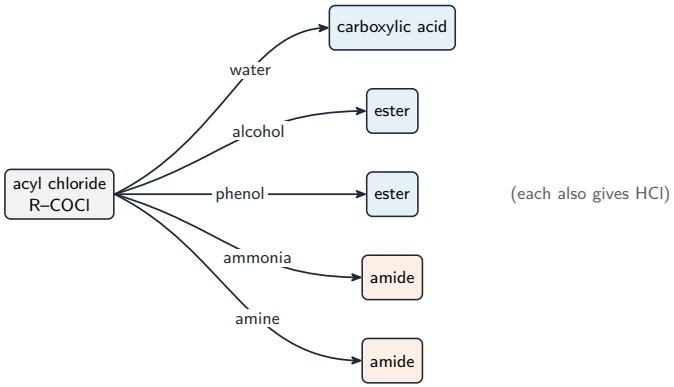
Build the skills to answer exam questions on **acyl chlorides** 酰氯 — their reactions, the **addition–elimination** 加成消去 mechanism, and the order of ease of **hydrolysis** 水解.

You must be able to:

- give the products of an acyl chloride with water, alcohols, phenol, ammonia and amines
- describe the addition–elimination mechanism
- explain the order acyl chloride ≫ alkyl chloride ≫ aryl chloride

1 Worked examples

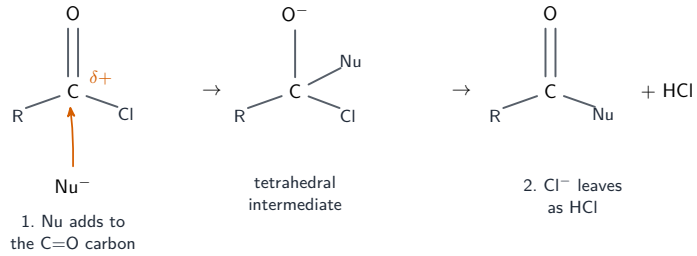
■ Reactions and mechanism



(each also gives HCl)

Acyl chlorides are very reactive: with water, an alcohol, phenol, ammonia or an amine they give the labelled product + HCl

Reactant	Product (+ HCl)
water	carboxylic acid
alcohol / phenol	ester
ammonia	amide
amine	(N-substituted) amide



Addition–elimination: the nucleophile adds to the δ+ carbonyl carbon, then C=O reforms and Cl⁻ leaves as HCl

■ Acyl chlorides: one mechanism, five nucleophiles

An **acyl chloride** 酰氯 RCOCl is the most reactive carboxylic acid derivative, because chloride is a good leaving group and the carbonyl carbon carries a large δ+ (both the oxygen and the chlorine withdraw electrons).

Every reaction is the same mechanism: addition–elimination 加成消去.

1. The nucleophile's lone pair attacks the δ+ carbonyl carbon.
2. The C = O π bond breaks, and the electrons go onto the oxygen — a tetrahedral intermediate with a negative oxygen.
3. The oxygen re-forms the double bond and **expels the chloride ion**.
4. A proton is lost from the attacking group, and HCl leaves (visible as **steamy white fumes**).

Nucleophile	Product	Note
water	carboxylic acid	vigorous, steamy fumes of HCl
an alcohol	**ester**	better than esterification: fast, and it goes to completion
ammonia	primary **amide**	
a primary amine	N-substituted amide	
phenol	aryl ester	phenol is too weak a nucleophile for a carboxylic acid, so this route is needed

Worked example. Give the product and the mechanism type when ethanoyl chloride

reacts with methylamine, and explain why the reaction is faster than the corresponding reaction of ethanoic acid.

1. Product: $CH_3CONHCH_3$, N-methylethanamide, plus HCl.
2. Mechanism: nucleophilic addition–elimination.
3. Faster because the chloride is a much better leaving group than the $-OH$ of the acid, and the carbonyl carbon in the acyl chloride is more $\delta+$, so it is attacked more readily.

△ **Draw the arrows from the lone pair, and show the intermediate.** The intermediate with the negatively charged oxygen is a mark on its own, and so is the arrow that expels the chloride.

2 Practice

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

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

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

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

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

3 Exam-style questions

3.1 Ethanoyl chloride reacts with ammonia to give: [1]

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

3.2 Which order of ease of hydrolysis is correct? [1]

- **A** aryl chloride ≫ alkyl chloride ≫ acyl chloride
- **B** acyl chloride ≫ alkyl chloride ≫ aryl chloride
- **C** alkyl chloride ≫ acyl chloride ≫ aryl chloride
- **D** they hydrolyse equally easily

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

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

3.5 Ethanoyl chloride, CH_3COCl, 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	

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

(c) Name the type of mechanism. [1]

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

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

Solutions

2.1 ethanoic acid.

2.2 addition–elimination (nucleophilic).

2.3 Ethyl propanoate.

2.4 A vigorous reaction; steamy white fumes of hydrogen chloride are produced.

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.

3.1 B. Acyl chloride + ammonia → amide (ethanamide) + HCl.

3.2 B. Acyl chloride ≫ alkyl chloride ≫ aryl chloride.

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.

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.

3.5 (a) Ethanoic acid; methyl ethanoate; ethanamide; phenyl ethanoate.
(b) Curly arrow from the nitrogen's lone pair to the $\delta+$ carbonyl carbon; arrow from the C = O π 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 HCl.
(c) Nucleophilic addition–elimination.
(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.
(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.