

Making and reacting esters and acyl chlorides

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Lesson

Quick answer: Carboxylic acids react with alcohols, in the presence of concentrated sulfuric acid, to form esters and water in a reversible equilibrium. Esters hydrolyse back to acids and alcohols, completely with alkali. Acyl chlorides, RCOCl , react far faster with water, alcohols, ammonia and amines by nucleophilic addition-elimination.

Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** A Level 3.3.9

What are carboxylic acids and how do they react?

Carboxylic acids contain the -COOH group and are named with the ending **-oic acid**, for example ethanoic acid, CH_3COOH . They are weak acids: they dissociate only partly in water, $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$. They still show typical acid reactions, producing salts called carboxylates.

Reagent	Equation	Observation
Magnesium	$2\text{CH}_3\text{COOH} + \text{Mg} \rightarrow (\text{CH}_3\text{COO})_2\text{Mg} + \text{H}_2$	fizzing, hydrogen gas
Sodium carbonate	$2\text{CH}_3\text{COOH} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{CH}_3\text{COONa} + \text{H}_2\text{O} + \text{CO}_2$	effervescence, CO_2 turns limewater milky
Sodium hydroxide	$\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$	no visible change, warms slightly

Acid molecules hydrogen-bond strongly, often in pairs, so they have high boiling points and the small ones dissolve in water.

How are esters made?

An **ester** forms when a carboxylic acid is heated with an alcohol and a few drops of concentrated sulfuric acid, which acts as a catalyst. The OH of the acid and the H of the alcohol leave as water. The reaction is reversible, so the mixture contains all four substances at equilibrium.

Definition

An **ester** contains the group -COO- joined to an alkyl group on each side, written RCOOR' . The name is the alkyl group from the alcohol followed by the stem of the acid with the ending -oate: ethanol and ethanoic acid give ethyl ethanoate.



The ester name = alkyl group from the alcohol + stem from the acid

The reversible arrows show that an equilibrium mixture forms

Esterification is a reversible reaction: reactants and products coexist at equilibrium.

Worked example

1.00 mol of ethanoic acid and 1.00 mol of ethanol reach equilibrium with 0.667 mol of ester. Find K_c .

Acid = alcohol = $1.00 - 0.667 = 0.333$ mol; water = 0.667 mol. Volume cancels, so $K_c = (0.667 \times 0.667) / (0.333 \times 0.333) = \mathbf{4.0}$.

Worked example

Predict the amount of ester when 1.00 mol of acid is mixed with 2.00 mol of ethanol ($K_c = 4.0$).

Let x = amount of ester. Then $x^2 / [(1 - x)(2 - x)] = 4$, so $3x^2 - 12x + 8 = 0$ and $x = 0.845$ mol (the other root exceeds 1). Using more alcohol raises the yield to **0.845 mol**, compared with 0.667 mol.

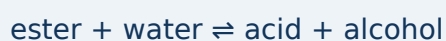
To push the equilibrium to the right, use an excess of one reagent or remove water or the ester as it forms. A catalyst speeds up the approach to equilibrium but does not change K_c .

How are esters broken down?

Water splits an ester back into acid and alcohol. With dilute acid under reflux the reaction is the reverse of esterification and is incomplete. With aqueous sodium hydroxide the carboxylic acid is converted to its salt as soon as it forms, so the reaction goes to completion:

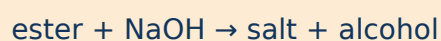


Acid hydrolysis



dilute H_2SO_4 , reflux
reversible, incomplete

Alkaline hydrolysis



aqueous NaOH , reflux
irreversible, goes to completion

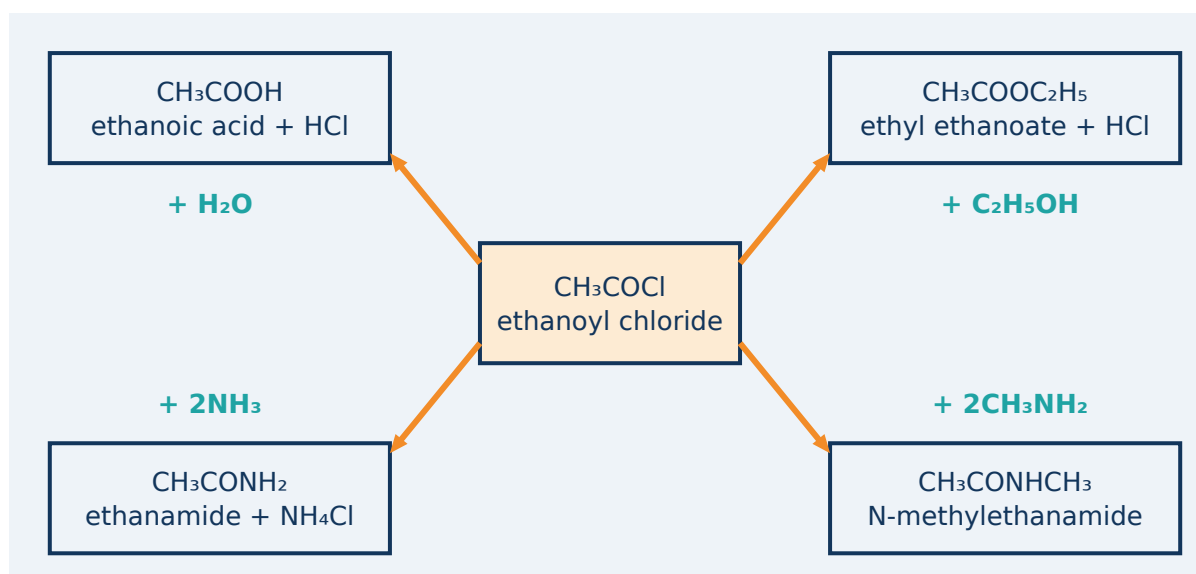
The salt RCOO^-Na^+ cannot react back with the alcohol

Alkaline hydrolysis is preferred in the lab because it is irreversible.

The same reaction makes soap. A fat is a triglyceride, an ester of propane-1,2,3-triol (glycerol) with three fatty acids, and heating it with NaOH gives glycerol and three sodium carboxylate molecules, which are the soap. Biodiesel is made by reacting plant oils with methanol, which swaps glycerol for methanol to form methyl esters.

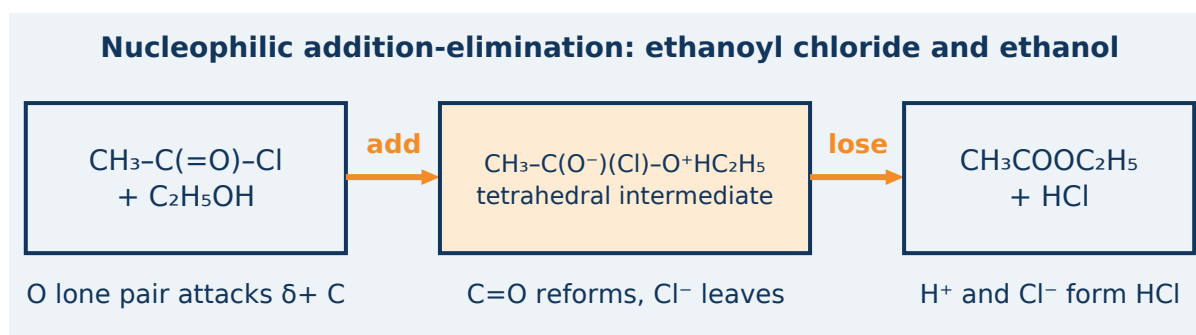
Why are acyl chlorides so reactive?

An acyl chloride, RCOCl , is made by warming a carboxylic acid with thionyl chloride: $\text{CH}_3\text{COOH} + \text{SOCl}_2 \rightarrow \text{CH}_3\text{COCl} + \text{SO}_2 + \text{HCl}$. Both by-products are gases, so the product is easy to separate. The carbonyl carbon has a large δ^+ charge because both oxygen and chlorine pull electrons away, and Cl^- is a good leaving group. Acyl chlorides therefore react with water, alcohols, ammonia and amines at room temperature, giving off misty HCl.



Ethanoyl chloride reacts quickly at room temperature with every common nucleophile.

The mechanism is **nucleophilic addition-elimination**: the nucleophile adds to the $\text{C}=\text{O}$ carbon to give a tetrahedral intermediate, then the $\text{C}=\text{O}$ re-forms and chloride leaves.



In addition-elimination the nucleophile adds first, then chloride is eliminated.

Common mistake

Do not write esterification with a one-way arrow: it is an equilibrium ($\rightleftharpoons$). Also do not put the acid part first in the name: $\text{CH}_3\text{COOC}_2\text{H}_5$ is ethyl ethanoate, not "ethanoate ethyl". Acyl chloride reactions are not reversible and need no catalyst.

Worked example

7.85 g of ethanoyl chloride ($M = 78.5 \text{ g/mol}$) reacts with excess ethanol. The yield is 85 %. Find the mass of ethyl ethanoate ($M = 88.0 \text{ g/mol}$).

$n = 7.85 / 78.5 = 0.100 \text{ mol}$. Theoretical mass = $0.100 \times 88.0 = 8.80 \text{ g}$. Actual = $0.85 \times 8.80 = \mathbf{7.48 \text{ g}}$.

Lina's tip

To name an ester, treat it like a surname and first name: the alkyl "surname" comes from the alcohol and is on the oxygen side; the "first name" is the acid stem and is on the $\text{C}=\text{O}$ side. For hydrolysis, break the $\text{C}-\text{O}$ single bond next to the $\text{C}=\text{O}$.

Key points to remember

- Esterification: $\text{RCOOH} + \text{R}'\text{OH} \rightleftharpoons \text{RCOOR}' + \text{H}_2\text{O}$, conc. H_2SO_4 catalyst, reflux; K_c about 4 for ethyl ethanoate
- Ester name = alkyl from alcohol + acid stem + -oate (ethyl ethanoate)
- Alkaline hydrolysis is irreversible and gives a carboxylate salt plus an alcohol
- $\text{RCOOH} + \text{SOCl}_2 \rightarrow \text{RCOCl} + \text{SO}_2 + \text{HCl}$
- Acyl chlorides react with H_2O , ROH , NH_3 and amines at room temperature by addition-elimination

Making and reacting esters and acyl chlorides: frequently asked questions

Why is esterification done under reflux?

Heating speeds up the slow reaction, and reflux condenses vapours so that volatile reactants and the ester do not escape. The mixture can then reach equilibrium.

Why does alkaline hydrolysis go to completion?

The hydroxide converts the carboxylic acid into its carboxylate ion as it forms. That ion is negative and does not react with the alcohol, so the reverse reaction cannot occur.

Why use an acyl chloride instead of a carboxylic acid to make an ester?

The reaction is fast at room temperature and irreversible, so the yield is high. The drawback is that acyl chlorides are corrosive and give off HCl .

What is the role of concentrated sulfuric acid in esterification?

It acts as a catalyst, and it also absorbs some of the water formed, which moves the equilibrium slightly towards the ester.

How is soap made from fat?

A fat is a triglyceride. Heating it with sodium hydroxide hydrolyses the three ester links, giving glycerol and three sodium carboxylate molecules, which are the soap.