Carboxylic acids and their derivatives

Naming and properties of carboxylic acids, how they are made and what they react with, acyl chlorides, esters and their hydrolysis, and condensation polymers such as polyesters.

Carboxylic acids

Carboxylic acids contain the $-COOH$ group, named with the suffix **-oic acid**: ethanoic acid, propanoic acid, 2-methylbutanoic acid. The carbon of the COOH is carbon 1.

Physical properties

Carboxylic acids form **hydrogen bonds** with each other, often as **dimers** in the pure liquid, so they have **higher boiling temperatures** than alcohols or aldehydes of similar M_r. Small acids are **soluble in water** because they form hydrogen bonds with water. Solubility decreases as the carbon chain grows.

Making carboxylic acids

- **Oxidation** of primary alcohols (heated under reflux with acidified potassium dichromate(VI)) or of aldehydes.
- **Hydrolysis of nitriles**: heat under reflux with dilute acid, $RCN + 2H_2O + H^+ \rightarrow RCOOH + NH_4^+$.

Reactions of carboxylic acids

Reagent	Conditions	Product	Observations
$LiAlH_4$	Dry ether	**Primary alcohol** (reduction)	
Bases, carbonates or metals	Room temperature	**Salt** (and CO_2 or H_2)	With carbonates, effervescence
PCl_5	Room temperature	**Acyl chloride**	Steamy fumes of HCl
An alcohol with concentrated H_2SO_4 catalyst	Warm, reflux	**Ester** and water	Sweet, fruity smell

$$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + H_2O + CO_2$$

Note Academy

Esterification

$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

The reaction is **reversible** and slow, so the mixture is heated under reflux with a few drops of concentrated sulfuric acid as a catalyst. **Names:** the ester is named from the alcohol (alkyl part first) and the acid: **ethyl ethanoate**. The ester is used as a solvent, and in flavourings and perfumes.

NOTE

To identify the parts of an ester, the part before the O in $-COO-$ comes from the acid, and the alkyl group after it comes from the alcohol. Methyl propanoate is $CH_3CH_2COOCH_3$.

Acyl chlorides

Acyl chlorides have the group $-COCl$ and are named with the suffix **-oyl chloride**: ethanoyl chloride, CH_3COCl. They are very **reactive**, because the carbon is attached to two electronegative atoms (O and Cl) and is strongly $\delta+$, and they react vigorously at room temperature.

Reagent	Product	Observations
Water	Carboxylic acid and HCl	Steamy fumes
Alcohol	**Ester** and HCl	Fumes of HCl
Concentrated ammonia	**Primary amide** and ammonium chloride	White smoke/solid
Amine	**N-substituted amide** and HCl (a salt with excess amine)	

$CH_3COCl + NH_3 \rightarrow CH_3CONH_2 + HCl$

Reactions with water, alcohols, ammonia and amines are examples of **nucleophilic addition–elimination**.

Acyl chlorides are better than carboxylic acids for making esters and amides. The reaction is fast, goes to completion and is not reversible, though it needs dry conditions and gives off corrosive HCl.

Esters: hydrolysis

Acidic hydrolysis: heat the ester under reflux with dilute acid (HCl or H_2SO_4). It is the **reverse of esterification**, so it is reversible and gives an equilibrium mixture of the carboxylic acid and alcohol.

$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$

Note Academy

Alkaline hydrolysis: heat with aqueous **sodium hydroxide**. It goes to **completion** because the **carboxylate salt** forms, and the alcohol is formed too.

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

The acid is released by adding a strong acid to the salt. Alkaline hydrolysis of **fats and oils** (esters of propane-1,2,3-triol, glycerol) is the process of **saponification**, which makes soap.

Condensation polymerisation: polyesters

A **condensation polymer** forms when monomers join with the **loss of a small molecule**, such as water or HCl, at each link.

Polyesters form from a **dicarboxylic acid** (or its diacyl chloride) and a **diol**. The link is an **ester linkage**, $-COO-$.

$$n\,HOOC-C_6H_4-COOH + n\,HOCH_2CH_2OH \rightarrow [-OC-C_6H_4-COO-CH_2CH_2-O-]_n + 2n\,H_2O$$

This is **poly(ethylene terephthalate)** (PET, Terylene). The repeat unit contains one acid unit and one diol unit. The monomers are found by breaking the chain at each ester link and adding OH to the carbonyl end and H to the oxygen end.

Polyesters are **biodegradable** in some cases, because the ester link can be hydrolysed, unlike the C–C chains of addition polymers. They are used in fibres, bottles and plastics.

> **TRY IT**
>
> Draw the repeat unit of the polyester formed from butanedioic acid and ethane-1,2-diol.

$[-OC-CH_2CH_2-CO-O-CH_2CH_2-O-]$. The CO at one end is bonded to O at the other, and the chain continues in both directions.

Note Academy