

Carboxylic Acids and Derivatives

01 · PROPERTIES

–COOH hydrogen bonds strongly, and in a non-polar solvent two molecules pair into a **dimer**. Boiling points are therefore higher than those of alcohols of similar M_r .

Short chains are soluble in water; solubility falls as the hydrocarbon chain grows.

02 · WHY THEY ARE ACIDIC

$\text{RCOOH} \rightleftharpoons \text{RCOO}^- + \text{H}^+$. The **carboxylate ion is stabilised by delocalisation** over both oxygens, so the equilibrium lies further right than for an alcohol.

They are still **weak** acids, only partially dissociated. Electron-withdrawing groups strengthen them: $\text{CCl}_3\text{COOH} \gg \text{CH}_2\text{ClCOOH} > \text{CH}_3\text{COOH}$, because chlorine pulls charge away and stabilises the anion further.

03 · ACID REACTIONS

Reagent	Products
NaOH	salt + water
Na_2CO_3	salt + H_2O + CO_2 (fizzes)
Na	salt + H_2
alcohol / conc. H_2SO_4	ester + water
LiAlH_4 in dry ether	primary alcohol
PCl_5	acyl chloride + HCl + POCl_3

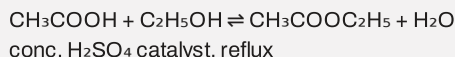
The carbonate test is the standard way to confirm –COOH: only a carboxylic acid among the common organics fizzes.

04 · MAKING CARBOXYLIC ACIDS

Oxidise a primary alcohol or an aldehyde: reflux with acidified $\text{K}_2\text{Cr}_2\text{O}_7$.

Hydrolyse a nitrile with dilute HCl under reflux, or an ester or amide with acid or alkali. Oxidising a methyl side chain on a benzene ring with hot alkaline KMnO_4 gives benzoic acid.

05 · ESTERIFICATION



Reversible, so the yield is limited; remove the ester by distillation to drive it right.

Name the acid part second: ethyl ethanoate = ethanol + ethanoic acid.

06 · ESTERS — PROPERTIES AND USES

No O–H, so no hydrogen bonding between molecules: esters are volatile with sweet fruity smells, used as flavourings, perfumes, solvents and plasticisers.

Natural fats and oils are esters of glycerol with long-chain fatty acids; unsaturated ones are liquid because the cis double bonds stop the chains packing.

07 · HYDROLYSIS OF ESTERS

Acid hydrolysis — dilute H_2SO_4 , reflux
ester + $\text{H}_2\text{O} \rightleftharpoons$ acid + alcohol · reversible, incomplete

Alkaline hydrolysis — $\text{NaOH}(\text{aq})$, reflux
ester + $\text{NaOH} \rightarrow$ salt + alcohol · irreversible, better yield

With a fat this is **saponification**, and the sodium salt of the fatty acid is soap.

08 · ACYL CHLORIDES A2

RCOCl is far the most reactive derivative: chlorine is electronegative and a good leaving group, so the carbonyl carbon is strongly δ^+ .

Every reaction is vigorous at room temperature and gives off **steamy HCl fumes**.

09 · REACTIONS OF ACYL CHLORIDES A2

- + $\text{H}_2\text{O} \rightarrow$ carboxylic acid + HCl
- + $\text{ROH} \rightarrow$ ester + HCl
- + $\text{NH}_3 \rightarrow$ amide + HCl
- + $\text{RNH}_2 \rightarrow$ N-substituted amide + HCl
- + $\text{C}_6\text{H}_5\text{OH} \rightarrow$ phenyl ester + HCl

All are **nucleophilic acyl substitution**: the nucleophile attacks the δ^+ carbon, then Cl^- leaves.

10 · ORDER OF REACTIVITY A2

acyl chloride > ester > amide

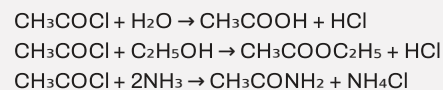
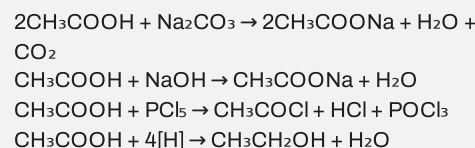
The better the leaving group and the more δ^+ the carbon, the faster the attack. This is why acyl chlorides make esters and amides in one step where the acid itself needs a catalyst and an equilibrium.

11 · WORKED EXAMPLE — IDENTIFY THE ESTER

An ester $\text{C}_4\text{H}_8\text{O}_2$ is refluxed with $\text{NaOH}(\text{aq})$. Acidifying the mixture gives a compound that fizzes with Na_2CO_3 ; the other product gives a positive tri-iodomethane test.

Fizzes $\rightarrow$ carboxylic acid formed
 CHI_3 positive $\rightarrow$ the alcohol is ethanol
 $\text{C}_4\text{H}_8\text{O}_2 - \text{C}_2\text{H}_5\text{O} = \text{C}_2\text{H}_3\text{O} \rightarrow$ ethanoate
 $\rightarrow$ **ethyl ethanoate**, $\text{CH}_3\text{COOC}_2\text{H}_5$

12 · EQUATIONS TO KNOW



13 · RELATIVE ACID STRENGTHS

Acid	pK_a
CCl_3COOH	0.7
CH_2ClCOOH	2.9
CH_3COOH	4.8
phenol	10.0

More electronegative atoms near the –COOH pull electron density away from the anion, spreading the charge and stabilising it — so the acid is stronger and pK_a smaller.

14 · PRACTICAL POINTS

Esterification and hydrolysis are both done **under reflux**: the condenser returns volatile material so nothing is lost and the mixture can be heated for long enough.

Acyl chlorides are handled in dry apparatus and a fume cupboard — they hydrolyse violently in moist air, releasing HCl .

MARKS LOST HERE

- Naming the ester the wrong way round; the alkyl group from the alcohol comes first.
- Writing esterification with a single arrow; it is an equilibrium.
- Giving the free acid as the product of alkaline hydrolysis; it is the sodium salt until you acidify.
- Saying phenol fizzes with carbonate — only carboxylic acids do.