9701 CHEMISTRY · TOPICS 18 & 32 · AS + A LEVEL

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

$RCOOH \rightleftharpoons RCOO^- + H^+$. 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: $CCl_3COOH \gg CH_2ClCOOH > CH_3COOH$, 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 $K_2Cr_2O_7$.

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

$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$
conc. H_2SO_4 catalyst, reflux

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 + $H_2O \rightleftharpoons$ acid + alcohol · reversible, incomplete

Alkaline hydrolysis — NaOH(aq), reflux
ester + NaOH → 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

+ H_2O → carboxylic acid + HCl
+ ROH → ester + HCl
+ NH_3 → amide + HCl
+ RNH_2 → N-substituted amide + HCl
+ C_6H_5OH → 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 $C_4H_8O_2$ is refluxed with NaOH(aq). Acidifying the mixture gives a compound that fizzes with Na_2CO_3; the other product gives a positive tri-iodomethane test.

Fizzes → carboxylic acid formed
CHI_3 positive → the alcohol is ethanol
$C_4H_8O_2 - C_2H_5O = C_2H_3O$ → ethanoate
→ **ethyl ethanoate**, $CH_3COOC_2H_5$

12 · EQUATIONS TO KNOW

$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + H_2O + CO_2$
$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
$CH_3COOH + PCl_5 \rightarrow CH_3COCl + HCl + POCl_3$
$CH_3COOH + 4[H] \rightarrow CH_3CH_2OH + H_2O$

$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$
$CH_3COCl + C_2H_5OH \rightarrow CH_3COOC_2H_5 + HCl$
$CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$

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.