Unit 14 · Carboxylic Acids and Their Derivatives

STUDY NOTES

WHAT NEB'S GRADE 12 EXAM ASKS

- **CDC's grid (2078):** Organic Chemistry (Units 8–17 together): 33 of 75 marks; 2 MCQs, 3 short and 2 long questions
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** long: CH_3CH_2COOH, C_6H_5COOH, $ClCH_2CH_2COOH$ in ascending acid strength, with reasons; long: ethanol + ethanoic acid (conc. H_2SO_4) → ethyl ethanoate
- **MCQ (1 mark)**
  - test: $NaHCO_3$; functional isomer $HCOOCH_3$; sodium benzoate + soda lime → benzene; strongest acid
  - P_2O_5 → anhydride; Hofmann → amine one C fewer; alcoholysis → ester; Kolbe → salicylic acid; fruit smells: esters
  - Claisen, transesterification, HVZ (Cl_2, red P); aspirin's structure; solubility falls as the chain grows
- **Short (5 marks, in parts)**
  - b.p. of ethanoic acid vs propan-1-ol; methanoic vs ethanoic acid (pH, Tollens'); order acids by strength with reasons
  - ethanoic acid → methanamine; equations with $NaHCO_3$, $SOCl_2$, soda lime; ester made and saponified
  - reactivity acid chloride > amide; why –COOH gives no 2,4-DNP ppt; nitration of benzoic acid (slow, meta)
  - an example each: Claisen, HVZ, ethanolysis of ethanoyl chloride, electrophilic substitution of benzoic acid
- **Long (8 marks)**: anomalous methanoic acid; identify A–E from CH_3COOH; V → W → X → Y → Z ($SOCl_2$, NH_3, Br_2/KOH, HNO_2); ester P, $C_8H_{16}O_2$, from its hydrolysis products; three preparations of ethanoic acid

Key terms

Carboxyl group: –COOH (carbonyl + hydroxyl); **R–COOH**; monocarboxylic $C_nH_{2n+1}COOH$; dicarboxylic: oxalic acid HOOC–COOH.

Decarboxylation: loss of CO_2 (–COOH or $–COO^-$ removed).

Acid derivatives: –OH replaced: acid chloride RCOCl, amide $RCONH_2$, ester RCOOR′, anhydride $(RCO)_2O$; all keep the **acyl group** R–CO–.

Nucleophilic acyl substitution: Nu attacks C=O → tetrahedral intermediate → C=O re-forms, leaving group pushed out.

Saponification: alkaline hydrolysis of an ester (fat → soap + glycerol), complete.

HVZ reaction: acid with α-H + Cl_2 or Br_2, red P → α-halo acid.

Claisen condensation: ester with α-H + $NaOC_2H_5$ → **β-keto ester** + ethanol.

Hofmann bromamide: $RCONH_2 + Br_2 + NaOH \rightarrow RNH_2$ (one C fewer).

Naming and isomers

Formula	IUPAC	Common
HCOOH	methanoic acid	formic acid (ants, sisnu)
CH_3COOH	ethanoic acid	acetic acid (vinegar, 4–5%)
CH_3CH_2COOH	propanoic acid	propionic acid
$CH_3CH_2CH_2COOH$	butanoic acid	butyric acid (rancid ghee)
$(CH_3)_2CHCOOH$	2-methylpropanoic acid	isobutyric acid
C_6H_5COOH	benzoic acid	benzoic acid

- longest chain **with** the carboxyl carbon, which is **C-1** (not written); α **= C-2**, β = C-3: α-chloropropionic = **2-chloropropanoic acid**
- ring: numbered from the C bearing –COOH: m-nitrobenzoic = 3-nitrobenzoic acid
- **chain**: butanoic / 2-methylpropanoic acid; **functional**: acids and esters: $C_2H_4O_2$ ethanoic acid / methyl methanoate; $C_3H_6O_2$ propanoic acid, methyl ethanoate, ethyl methanoate
- carboxyl C **sp^2**, flat, 120°; in the acid C=O 123 pm, C–O 136 pm; in the ion both equal

Preparation

- **1° alcohol or aldehyde**, $K_2Cr_2O_7/H^+$ (reflux; orange → green): $CH_3CH_2OH \longrightarrow CH_3CHO \longrightarrow CH_3COOH$;

vinegar:
$CH_3CH_2OH + O_2 \xrightarrow{\text{Acetobacter}} CH_3COOH + H_2O$

- **nitriles**, boiled with acid (one C more from R–X + KCN):
  $CH_3CN + 2\,H_2O + HCl \longrightarrow CH_3COOH + NH_4Cl$ (via CH_3CONH_2); C_6H_5CN, $C_6H_5CONH_2 \rightarrow$ benzoic acid
- **dicarboxylic acids**, heat:
  $HOOC{-}COOH \xrightarrow{\Delta} HCOOH + CO_2$ (glycerol);
  $HOOC{-}CH_2{-}COOH \xrightarrow{\Delta} CH_3COOH + CO_2$
  - succinic acid loses **water**:
    $HOOC{-}CH_2CH_2{-}COOH \xrightarrow{\Delta} (CH_2CO)_2O + H_2O$ (succinic anhydride)
- **alkoxide + CO** (heat, pressure; one C more):
  $CH_3ONa + CO \longrightarrow CH_3COONa$;
  $CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$
- **trihaloalkane** + aq. alkali:
  $CHCl_3 + 3\,KOH \longrightarrow HC(OH)_3 + 3\,KCl$;
  $HC(OH)_3 \longrightarrow HCOOH + H_2O$
- **benzoic acid** from toluene (any alkyl with an H next to the ring → –COOH):
  - $C_6H_5CH_3 + 2\,KMnO_4 \xrightarrow{\Delta} C_6H_5COOK + 2\,MnO_2 + KOH + H_2O$;
    $C_6H_5COOK + HCl \longrightarrow C_6H_5COOH + KCl$
  - industry: $2\,C_6H_5CH_3 + 3\,O_2 \xrightarrow[150\,^\circ C]{\text{Co salt}} 2\,C_6H_5COOH + 2\,H_2O$

Physical properties

- C_1–C_3 pungent liquids; C_4–C_6 oily, rancid; from about C_{10} waxy solids; ethanoic acid freezes at 17 °C (glacial); m.p. even-carbon acids above odd neighbors
- **b.p. highest**: two molecules held by **two** H bonds (O–H to C=O), a ring-shaped **dimer**; ethanoic acid 118 °C vs propan-1-ol 97 °C (both 60 g/mol); HCOOH 101, C_2H_5COOH 141 °C
- C_1–C_4 mix with water (H bonds); solubility falls as the hydrophobic chain grows; benzoic acid slightly soluble

Acidity

$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$; ethanoic acid pKa 4.76 (ethanol 15.9); 0.1 M: about 1 in 75 ionized

- **carboxylate** ion: charge shared **equally by two O** (resonance), both C–O equal → stable
- acid order: **RCOOH > C_6H_5OH > ROH**
- with NaOH, NH_4OH (salt + water); Na_2O, CaO; Na_2CO_3 and **$NaHCO_3$ → CO_2** (the test; phenols, alcohols don't); Na → H_2 (alcohols too)
  - $CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + H_2O + CO_2$
  - $2\,CH_3COOH + CaO \longrightarrow (CH_3COO)_2Ca + H_2O$

Substituents (pKa)

- **−I** groups (–NO_2, –CN, halogens, –CF_3; on a chain –OH, –OCH_3) **stronger**; **+I** alkyl **weaker**: HCOOH (3.75) > CH_3COOH (4.76) > C_2H_5COOH (4.87)
- more groups: Cl_3CCOOH (0.66) > $Cl_2CHCOOH$ (1.35) > $ClCH_2COOH$ (2.87) > CH_3COOH
- on XCH_2COOH: F (2.59) > Cl (2.87) > Br (2.90) > I (3.18)
- closer: $CH_3CHClCOOH$ (2.83) > $ClCH_2CH_2COOH$ (4.0) > CH_3CH_2COOH (4.87)
- ring: 4-nitrobenzoic (3.44) > benzoic (4.20) > 4-methoxybenzoic (4.47) (+M at o, p weakens)
- **model paper**: $CH_3CH_2COOH < C_6H_5COOH < ClCH_2CH_2COOH$ (4.87, 4.20, about 4.0)

Reactions of the –COOH

- **PCl_3, PCl_5, $SOCl_2$** → acid chloride:
  - $3\,CH_3COOH + PCl_3 \longrightarrow 3\,CH_3COCl + H_3PO_3$
  - $CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$
  - $CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$ (gases leave: product pure)
- **$LiAlH_4$** (dry ether, then H_3O^+) → 1° alcohol:
  $CH_3COOH + 4\,[H] \longrightarrow CH_3CH_2OH + H_2O$; $NaBH_4$, H_2/Ni leave –COOH alone
- **P_2O_5**, heat: $2\,CH_3COOH \longrightarrow (CH_3CO)_2O + H_2O$
- **soda lime** (one C fewer):
  $CH_3COONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$; sodium benzoate → **benzene**
- **HVZ**:
  $CH_3CH_2COOH + Cl_2 \xrightarrow{\text{red P}} CH_3CHClCOOH + HCl$;
  $CH_3COOH \rightarrow ClCH_2COOH \rightarrow Cl_2CHCOOH \rightarrow Cl_3CCOOH$; not without α-H (benzoic, $(CH_3)_3CCOOH$); P makes PCl_3 → acid chloride → enol
- C=O of –COOH gives **no** carbonyl additions (2,4-DNP): shared with the –OH by resonance

Benzoic acid's ring: –COOH −I, −M → **deactivated, meta** (resonance puts + on o, p carbons); no Friedel–Crafts (ties up $AlCl_3$)

- $C_6H_5COOH + HNO_3 \xrightarrow{\text{conc. } H_2SO_4} C_6H_4(NO_2)COOH + H_2O$ (3-nitrobenzoic acid)
- SO_3 (fuming H_2SO_4) → 3-sulphobenzoic acid; Br_2/$FeBr_3$ → 3-bromobenzoic acid + HBr

Methanoic acid, anomalous (H–COOH is also HO–CHO: reducing)

- Tollens': $HCOOH + 2\,[Ag(NH_3)_2]OH \longrightarrow 2\,Ag + CO_2 + 4\,NH_3 + 2\,H_2O$ (silver mirror)
- Fehling's:
  $HCOOH + 2\,Cu^{2+} + 4\,OH^- \longrightarrow Cu_2O + CO_2 + 3\,H_2O$ (red)
- acidified $KMnO_4$ decolorized:
  $2\,KMnO_4 + 3\,H_2SO_4 + 5\,HCOOH \longrightarrow K_2SO_4 + 2\,MnSO_4 + 5\,CO_2 + 8\,H_2O$
- $HgCl_2$: $HCOOH + 2\,HgCl_2 \longrightarrow Hg_2Cl_2 + CO_2 + 2\,HCl$ (white), then $HCOOH + Hg_2Cl_2 \longrightarrow 2\,Hg + CO_2 + 2\,HCl$ (black)

- conc. H_2SO_4: HCOOH $\longrightarrow$ CO + H_2O; strongest of its series (3.75)

Derivatives

- CH_3COCl **ethanoyl chloride** (fuming, b.p. 51 °C, reacts with water); CH_3CONH_2 **ethanamide** (solid, m.p. 81 °C, b.p. 221 °C: N–H H bonds); $(CH_3CO)_2O$ **ethanoic anhydride** (b.p. 140 °C); $CH_3COOC_2H_5$ **ethyl ethanoate** (fruity, b.p. 77 °C)
- b.p. below the acid's: acid chloride, ester (no O–H); above: amide, anhydride

Preparation

- acid chloride: PCl_3, PCl_5, $SOCl_2$ (above); stored dry
- amide: $CH_3COOH + NH_3 \longrightarrow CH_3COONH_4$; $CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O$; amine $\rightarrow$ N-substituted: $CH_3COOH + CH_3NH_2 \xrightarrow{\Delta} CH_3CONHCH_3 + H_2O$
- anhydride: P_2O_5; or $CH_3COCl + CH_3COONa \longrightarrow (CH_3CO)_2O + NaCl$
- **ester** (Fischer; conc. H_2SO_4 catalyst and takes water; reversible, K $\approx$ 4, two-thirds): $CH_3COOH + C_2H_5OH \underset{}{\overset{\text{conc. } H_2SO_4}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$
  - the water's O from the **acid** (^{18}O in methanol ends in the ester; Roberts and Urey, 1938)

Reactivity: acid chloride > anhydride > ester > amide

- leaving group: Cl^- (weakest base, best) > $RCOO^-$ > $R'O^-$ > NH_2^-
- lone pair shared with C=O: Cl poorly, O well, N best (carbonyl least positive)
- a more reactive derivative gives a less reactive one, not back

Reagent	Acid chloride	Anhydride	Ester	Amide
H_2O	RCOOH + HCl (fast)	2RCOOH	RCOOH + R′OH (H^+, reversible)	RCOOH + NH_4Cl (boil, acid)
R′OH	ester + HCl	ester + RCOOH	new ester (transesterification)	ester + NH_3 (H^+, slow)
NH_3	amide + NH_4Cl	amide + RCOOH	amide + R′OH	
$LiAlH_4$	1° alcohol	2 RCH_2OH	RCH_2OH + R′OH	**RCH_2NH_2** (amine)

- $CH_3COCl + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + HCl$; $CH_3COCl + 2\,NH_3 \longrightarrow CH_3CONH_2 + NH_4Cl$
- **Rosenmund**: $CH_3COCl + H_2 \xrightarrow[\Delta]{Pd/BaSO_4} CH_3CHO + HCl$ ($BaSO_4$ poisons Pd; HCHO not by this)
- $(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + CH_3COOH$; aspirin: salicylic acid + $(CH_3CO)_2O$
- $CH_3CONH_2 + NaOH \xrightarrow{\Delta} CH_3COONa + NH_3$ (smell of NH_3: amide test)
- **saponification**: $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$; fat: $(C_{17}H_{35}COO)_3C_3H_5 + 3\,NaOH \longrightarrow C_3H_5(OH)_3 + 3\,C_{17}H_{35}COONa$
- transesterification: $CH_3COOC_2H_5 + CH_3OH \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOCH_3 + C_2H_5OH$
- **Claisen**: $2\,CH_3COOC_2H_5 \xrightarrow[H_3O^+]{NaOC_2H_5} CH_3COCH_2COOC_2H_5 + C_2H_5OH$ (ethyl 3-oxobutanoate); crossed with ethyl benzoate (no α-H)
- **Hofmann**: $CH_3CONH_2 + Br_2 + 4\,NaOH \longrightarrow CH_3NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O$; benzamide $\rightarrow$ aniline; propanamide $\rightarrow$ ethanamine
- **amides amphoteric**: N lone pair delocalized onto O $\rightarrow$ very weak base (H^+ on **O**); weakly acidic N–H: $2\,CH_3CONH_2 + 2\,Na \longrightarrow 2\,CH_3CONHNa + H_2$; $2\,CH_3CONH_2 + HgO \longrightarrow (CH_3CONH)_2Hg + H_2O$

Chains

- $CH_3COOH \xrightarrow{SOCl_2} CH_3COCl \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2$ (methanamine)
- $CH_3COOH \xrightarrow{SOCl_2} CH_3COCl \xrightarrow[}{H_2,\ Pd/BaSO_4} CH_3CHO \xrightarrow{HCN} CH_3CH(OH)CN \xrightarrow{H_3O^+} CH_3CH(OH)COOH$

COMMON MISTAKES

✗ succinic acid gives CO_2 on heating
✓ loses **water**: succinic anhydride.

✗ toluene + O_2 gives HCl
✓ benzoic acid + **H_2O**.

✗ $RCOOH + PCl_3 \rightarrow RCOCl + H_3PO_3$
✓ **3**$RCOOH + PCl_3 \rightarrow$ **3**$RCOCl + H_3PO_3$.

✗ bromination of benzoic acid with $FeBr_2$, no HBr
✓ **$FeBr_3$**, + **HBr**.

✗ –OH, $-OCH_3$ always weaken an acid
✓ only on a ring at **o, p** (+M); on a chain they **strengthen** (−I).

✗ CH_3COCl ethyl chloride
✓ **ethanoyl** (acetyl) chloride.

✗ amides protonate on N
✓ on the **O**; resonance arrow $\leftrightarrow$, not $\rightleftharpoons$.

✗ Hoffmann bromamide
✓ **Hofmann**.

✗ acid chloride + R′OH gives only ester
✓ ester + **HCl**.

✗ ester as reactive as the acid; OH^- leaving group
✓ order acid chloride > anhydride > ester > amide.