Unit 14 · Carboxylic Acids and Their Derivatives

ANSWER KEY · FOR TEACHERS

Full marks 37

Give the marks for the points in the marking scheme; an answer in other words that says the same is right.

1 Key words

1. α-carbon
2. dimer
3. carboxylate
4. HVZ
5. soda lime
6. Rosenmund
7. Claisen
8. Hofmann

K · 4

Each carries 0.5 mark.

2 Label the diagram

1. RCOOR′ ester
2. $RCONH_2$ amide
3. RCHO aldehyde
4. RCOR′ ketone

U · 2

Each carries 0.5 mark.

3 Multiple choice

i. **d.** trichloroethanoic acid — U · 1

Each chlorine pulls electrons (−I) and spreads the carboxylate's charge: pK_a trichloroethanoic 0.66, chloroethanoic 2.87, ethanoic 4.76, propanoic 4.87.

ii. **b.** $NaHCO_3$ solution — K · 1

Carboxylic acids are strong enough to set CO_2 free from hydrogencarbonate; phenol is not.

iii. **b.** ethanoic acid and CO_2 — K · 1

$HOOC–CH_2–COOH$ loses CO_2 from one end, leaving CH_3COOH.

iv. **b.** its molecule also has an aldehyde group, H–C=O — U · 1

H–C(=O)–OH can be read as HO–CHO: it is both an acid and an aldehyde, so it is oxidized to CO_2 and water.

v. **a.** acid chloride > anhydride > ester > amide — K · 1

The weaker the leaving group is as a base, the faster the reaction: Cl^- leaves best, NH_2^- worst.

4 Short answers

a. MARKING SCHEME — U · 2

- ✓ Both hydrogen-bond, but two acid molecules join by two hydrogen bonds into a dimer.
- ✓ The dimer is twice as heavy and held together, so more energy is needed to separate the molecules.

b. MARKING SCHEME — U · 2

- ✓ In the ethanoate ion the negative charge is shared equally by two electronegative oxygen atoms (resonance), so the ion is stable.
- ✓ In ethoxide the charge stays on one oxygen, so ethanol keeps its proton.

c. MARKING SCHEME — A · 2

- ✓ $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$; $CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$
- ✓ With $SOCl_2$ the other products, SO_2 and HCl, are gases and escape, so the acid chloride is easily got pure.

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d. MARKING SCHEME A · 2

✓ $CH_3CH_2COOH + Cl_2 \xrightarrow{\text{red P}} CH_3CHClCOOH + HCl$

✓ 2-Chloropropanoic acid: the chlorine goes on the α-carbon.

e. MARKING SCHEME U · 3

✓ Conditions: dilute NaOH, cold against sodium ethoxide, then acid.

✓ Reactants: aldehydes or ketones against esters (with α-hydrogens).

✓ Products: a β-hydroxy carbonyl, nothing lost, against a β-keto ester with an alcohol lost.

5 Long answer

ANSWER A · 4

i. With PCl_5 (or $SOCl_2$): $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

ii. With ethanol and a little concentrated sulphuric acid (esterification):
$CH_3COOH + C_2H_5OH \overset{\text{conc. } H_2SO_4}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$

iii. Through the acid chloride with ammonia: $CH_3COCl + 2\,NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$

iv. Neutralize with NaOH, then heat the sodium salt with soda lime:
$CH_3COONa + NaOH \xrightarrow[\Delta]{\text{CaO}} CH_4 + Na_2CO_3$

MARKING SCHEME

✓ Ethanoyl chloride, with the equation.

✓ Ethyl ethanoate, with the equation.

✓ Ethanamide, with the equation.

✓ Methane by decarboxylation, with the equation.

6 Numerical problems

a. ANSWER A · 4

i. 20 mL holds 1.0 g; $1.0 \div 60 =$ **0.0167 mol**.

ii. $CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + H_2O + CO_2$, one mole each: $NaHCO_3 = 0.0167 \times 84 =$ **1.40 g**; $CO_2 = 0.0167 \times 22.4\ L =$ **0.373 L** (373 mL).

iii. $K_a = 10^{-4.76} = 1.74 \times 10^{-5}$; $[H^+] = \sqrt{(1.74 \times 10^{-5} \times 0.10)} = 1.32 \times 10^{-3}$ M, **pH = 2.88**; ionized = $1.32 \times 10^{-3} \div 0.10 \times 100 =$ **1.3%**.

MARKING SCHEME

✓ 0.0167 mol.

✓ 1.40 g of $NaHCO_3$.

✓ 373 mL of CO_2.

✓ pH 2.88, about 1.3% ionized.

b. ANSWER A · 4

i. $NaOH = 0.0250\ L \times 0.20\ M = 5.0 \times 10^{-3}$ mol, so 5.0×10^{-3} mol of acid: $M = 0.37 \div 0.0050 =$ **74 g/mol**.

ii. $14n + 46 = 74$, so n = 2: C_2H_5COOH, **propanoic acid**.

iii. $C_2H_5COONa + NaOH \xrightarrow[\Delta]{\text{CaO}} C_2H_6 + Na_2CO_3$: **ethane**, $5.0 \times 10^{-3} \times 22.4\ L =$ **112 mL**.

iv. 10^(4.76 − 0.66) = $10^{4.1} \approx$ **1.3×10^4 times**.

MARKING SCHEME

✓ 74 g/mol.

✓ Propanoic acid.

✓ Ethane, 112 mL.

✓ About 1.3×10^4 times.

7 Think

ANSWER

All three are stronger than butanoic acid (4.82), because chlorine pulls electrons (−I) and spreads the carboxylate's charge. The pull fades along the chain, so the nearer the chlorine is to the –COOH, the

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stronger the acid. Fluorine is more electronegative than chlorine, so it pulls harder: 2-fluorobutanoic acid should be the stronger acid.

MARKING SCHEME

- ✓ An electron-withdrawing chlorine stabilizes the carboxylate and strengthens the acid.
- ✓ The effect weakens with distance: $\alpha > \beta > \gamma$.
- ✓ Fluorine, more electronegative, gives a stronger acid.

8 Activity: Vinegar and baking soda

(not marked)

WHAT STUDENTS SHOULD FIND

All three fizz, since each holds a carboxylic acid (ethanoic, citric, acetylsalicylic acid) strong enough to set free carbon dioxide from sodium hydrogencarbonate: $CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + H_2O + CO_2$. Bubbled through limewater the gas turns it milky, the test for CO_2; a burning splint held over the cup goes out.

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	7	11	16	3	**37**

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