

F324: Rings, Polymers & Analysis

4.3.2 – Spectroscopy MARK SCHEME

1. (a) **infrared – 1 mark only**

shows (very broad) peak between 2500–3300 (cm^{-1})
(due to O–H bond) ✓

ALLOW (very broad) peak around 3000 (cm^{-1}) OR any stated value between 2500 and 3300 (cm^{-1}) for O–H

DO NOT ALLOW peak in range 3200–3550 (cm^{-1})

IGNORE any reference to C=O or C–O as both are also present in an ester OR to fingerprint region

^{13}C NMR – 2 marks

(CH_3)₂CHCH₂COOH has 4 peaks (due to 4 different C environments) ✓

(CH_3)₃CCOOH has 3 peaks (due to 3 different C environments) ✓

ALLOW ' ^{13}C NMR detects the number of/different C environments' for 1 ✓, suitable example for the 2nd mark 3

3

(b) **splitting pattern**

explains any two in terms of 'n + 1 rule' for two marks ✓✓

Explains any one peak for 1 mark ✓

1 mark for correct ester

if two splitting patterns are correctly analysed ignore the third

- *singlet* therefore adjacent C (if any) has no Hs

ALLOW singlet because next or bonded to an O

- *multiplet* OR split into 7 therefore adjacent Cs have lots of/6 Hs

ALLOW multiplet/heptet because next to 2 CH₃s

- *doublet* therefore adjacent C is bonded to 1H

ALLOW doublet because next to a CH

must spell one of multiplet / heptet, singlet, doublet correctly

max = 2 marks

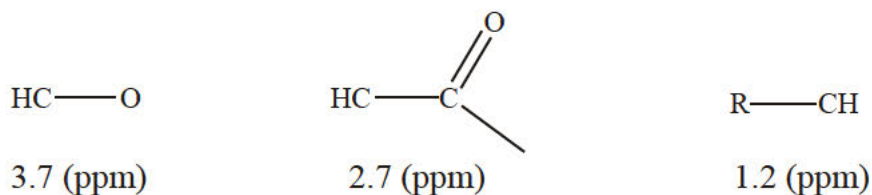
chemical shifts

two marks if any two absorptions are identified correctly ✓✓

one mark if any one absorption is identified correctly ✓

ALLOW tolerance on δ values; 3.6–3.8, 2.6–2.8 and 1.1–1.3 (ppm)

- peak ~3.7 (ppm) – bonded to an O
- peak ~2.7 (ppm) – indicates it is next to a C=O
- peak ~1.2 (ppm) – bonded to other Cs **OR** part of a chain

max = 2 marks*ALLOW any two gets 2 marks, any one scores 1 mark**ALLOW peaks labelled on the spectrum**ALLOW singlet must be bonded to O, multiplet to C=O and doublet to CH or R for both chemical shift marks**if two chemical shifts are correctly identified **IGNORE** the third*compound identified as $(\text{CH}_3)_2\text{CHCOOCH}_3$ ✓✓compound identified as $\text{CH}_3\text{COOCH}(\text{CH}_3)_2$ ✓

6

[9]

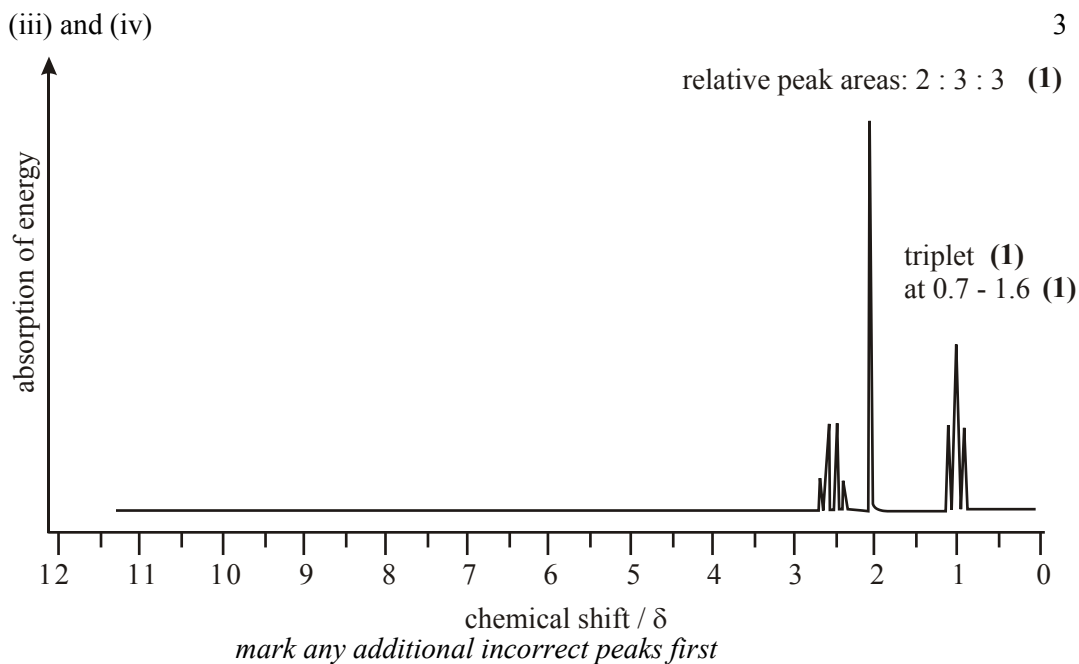
2. (i) the peak is due to the $\text{CH}_3\text{CO}-$ group (1)

not split, so next to a C with no protons / has no neighbouring proton /
 δ value is in the range 2.0 – 2.9 (1)

2

- (ii) adjacent to a C with three protons / to a CH_3 (1)

1



[6]

3. IR

Similarities

Any 2 of the following three peaks (must give the quoted range)

peak corresponding to OH in all three ($3230 - 3550 \text{ cm}^{-1}$) (1)

peak corresponding to NH in all three ($3100 - 3500 \text{ cm}^{-1}$) (1)

peak corresponding to CO in all three ($1000 - 1300 \text{ cm}^{-1}$) (1)

2 max

Differences

only shown in the fingerprint region (1)

1

Mass Spec

similarities

M_r (75)/ base peak will be the same (1)

1

$M + 1$ peak same (1)

1

Differences

Fragmentation pattern may show differences between isomers
/ specific example, eg CH_3^+ at m/e 15 (1)

1

(MAX 5)

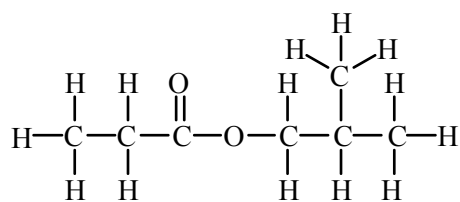
QWC

Use of any two terms from: functional group / amino group /
hydroxy group / fingerprint / fragmentation / fragment ion(s) /
base peak or molecular ion / $M + 1$ peak / m/e

1

[6]

4. (a)



propanoate and ester group (1) 2-methyl propyl (1)

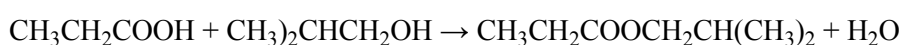
2

(b) propanoic acid (1)
(2-)methylpropan-1-ol (1)

heat (1)

conc. H_2SO_4 (1)

(allow *ecf* from part (a) for the equation)



reactants (1)

products (1)

6

(c) mass spectrum / spectrometry (1)

molecular ion peak /

m/e or mass of the peak furthest right (1) AW

2

[10]

5. δ value / chemical shift gives the 'type' of proton /
chemical environment (1) AW
example quoted from data sheet (1)

number of peaks gives the number of different types of proton /
chemical environments (1)

relative / ratio of (1)

peak areas gives the number of protons (of each type) (1)

splitting gives number of neighbouring / adjacent protons (1)

description of $n + 1$ rule / example of doublet, triplet or quadruplet
showing 1, 2 and 3 protons neighbouring (carbon) atom (1) AW

D_2O can be used to identify OH groups (1)

ANY 7 marks out of 8

7

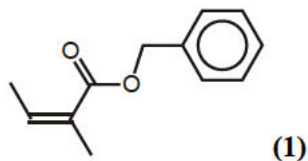
Quality of written communication mark for correct use and
organisation of at least two of the following technical terms:
proton, environment, singlet (doublet *etc.*), ppm, equivalent,
chemical shift, splitting, labile, integration

1

[8]

6. (a) (i) alkene (1)
ester (1)
allow "C=C double bond" 2

i.

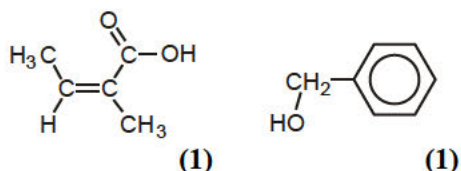


1

- ii. $C_{12}H_{14}O_2$ (1) 1

- (b) same structural formula/order of bonds,
different spacial arrangement **AW** (1)
description or diagram showing **B** and how it is different from **A** (1) ☐ 2

(c)



2

- (d) (i) peak at 1680-1750 (cm^{-1}) due to C=O (1)
peak at 1000-1300 (cm^{-1}) due to C-O / (1) 2

- (ii) 2500-3300 / 3230-3550 (cm^{-1}) **(1)**
O-H / carboxylic acid/alcohol is **not** present in **A** (1)
allow 1 mark for ~500-1500 (cm^{-1}) which is a unique
fingerprint region etc 2

[12]

7. (a) low boiling point / easily turns to a gas **AW** (1) 1

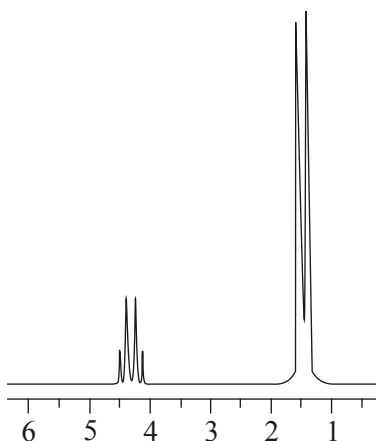
- (b) 2,4-dinitrophenylhydrazine / 2,4-DNP(H) / Brady's reagent (1)
purify/recrystallise the product/solid (derivative) (1)
measure the melting point /mp (1)
compare the result with data book/known values (1) 4

[5]

8. (a) (i) Molecular ion peak: the peak caused by the unfragmented molecule / the peak with the highest m/e value / the peak that tells you the Mr. 1
- Base peak : peak with the greatest (relative) intensity / peak representing most stable/abundant fragment
NOT the tallest / biggest / most common peak 1
- (ii) The molecular ion is too unstable / will have been completely fragmented / may not carry a positive charge 1
NOT peak too small to be seen / too little ion present
- (b) IR spectrum:
 C=O peak at approx 1650 cm^{-1} ($1680\text{--}1750\text{ cm}^{-1}$) 1
 broad O-H peak at value(s) between $2500\text{--}3300\text{ cm}^{-1}$ 1
ignore any references to C-O peak at $1000\text{--}1300\text{ cm}^{-1}$
 mass spectrum:
 Fragment with m/e = 31 is CH_2OH^+ 1
 Fragment at m/e = 45 is COOH^+ 1
 penalise missing + sign once only
- (c) 2 proton peak at $\delta = 3.3\text{--}4.3$ – singlet ($-\text{CH}_2-$) 1
 1 proton peak at $\delta = 3.5\text{--}5.5$ – singlet ($-\text{OH}$) 1
 1 proton peak at $\delta = 11.0\text{--}11.7$ – singlet ($-\text{COOH}$) 1
 (ranges of chemical shift (δ) values taken from data sheet)
 • penalise each error once only
 • ignore peak areas/heights unless incorrectly labelled
 Labelled diagram of the structure of G proposed by the student may be used to provide evidence for the positioning of peaks on the sketched spectrum.
Both OH and COOH protons disappear on shaking with D_2O 1

[11]

9. (i)



splitting:

doublet (1)

quartet (1)

ignore any other peaks

position:

doublet peak is at ~1.4 and

quartet peak is at ~4.3 (1)

*allow ecf from **one** incorrect splitting pattern*

areas:

1 and 3 on the correct peaks

(or either way round as ecf if any errors above) (1)

4

(ii) 4 (1)

OH/labile protons now visible AW (1)

2

[6]

10. (a) (i) Find the m/e of (1)

... the peak furthest to the right / with highest m/e or mass (1)

2

allow attempts to cater for the ^{13}C peak

$\text{C}_2\text{H}_3\text{O}_2$ /empirical formula has $M_r = 59$ (1)

so M_r of molecular formula is $^{118}/_{59} = 2$ /twice the empirical formula (1)

2

(b) (i) OH peak disappears (with D_2O / on the second spectrum)

1

- (ii) no of peaks: one **(1)**
 splitting: none **(1)**
 all four protons equivalent / in the same environment **(1)** 3
if the wrong structure is chosen allow ecf for:
two peaks (1),
splitting (1)(1) (as last 2 marks for part (ii))

[8]

- 11.** (i) **A** C_3H_6 **(1)** **B** C_4H_8 **(1)** 2
 (ii) **A** $\text{CH}_3\text{CH}=\text{CH}_2$ (or displayed) ('sticks' penalised once) 1
 (iii) C_3H_5^+ **(1)** for formula and **(1)** for charge 2

[5]