Carboxylic Acids and Derivatives

Mark Scheme

Level	International A Level
Subject	Chemistry
Exam Board	Edexcel
Topic	Rates, Equilibria & Further Organic Chemistry
Sub Topic	Carboxylic Acids and Derivatives
Booklet	Mark Scheme

Time Allowed: **47 minutes**

Score: **/39**

Percentage: **/100**

Grade Boundaries:

A*	A	B	C	D	E	U
>85%	'77.5%	70%	62.5%	57.5%	45%	<45%

Question Number	Correct Answer	Reject	Mark
1	**C**		**(1)**

Question Number	Correct Answer	Reject	Mark
2 (a)	B		**1**

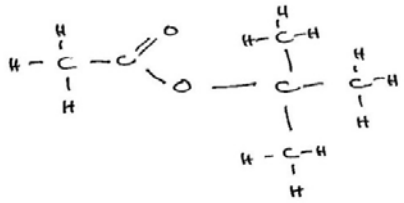
Question Number	Correct Answer	Reject	Mark
2(b)	D		**1**

Question Number	Correct Answer	Reject	Mark
2(c)	B		**1**

Question Number	Acceptable Answers	Reject	Mark
3a	Q: C=O (1750-1735 ester saturated) **and** R: C—O (1250-1230 ethanoate) **(1)** Functional group: ester/ ethanoate **(1)**	C=O aldehyde Just O ‖ C=O	2

Question Number	Acceptable Answers	Reject	Mark
3b(i)	(**Y** reacts with sodium carbonate to give CO_2) so is a (carboxylic) acid **(1)** M_r = 60 from mass spectrum **(1)** IGNORE Fragmentation CH_3COOH /ethanoic acid **(1)**	 CH_3COOH^+	3

Question Number	Acceptable Answers	Reject	Mark
3b(ii)	(Reacts with sodium to give H_2) so is an alcohol **and** cannot be oxidized so a tertiary alcohol ALLOW No colour change with (acidified) dichromate to justify tertiary alcohol **(1)** $(CH_3)_3COH$ ALLOW Displayed or skeletal formula 2-methylpropan-2-ol Structural, displayed or skeletal formula shown in equation **(1)** $(CH_3)_3COH + Na \rightarrow (CH_3)_3CO^{(-)}Na^{(+)} + ½ H_2$ ALLOW $C_4H_9OH + Na \rightarrow C_4H_9O^{(-)}Na^{(+)} + ½ H_2$ Multiples TE if primary or secondary alcohol given for structure **(1)**		3

Question Number	Acceptable Answers	Reject	Mark
3b(iii)	Displayed formula of $(CH_3COOC(CH_3)_3)$  ALLOW Alkyl groups not fully displayed TE on primary or secondary alcohol in b(ii)		1

Question Number	Acceptable Answers	Reject	Mark
3b(iv)	No marks for this part can be awarded unless a structure is shown in either (iii) or (iv) Two peaks because there are 2 different hydrogen environments **(1)** Relative area 3:1/ 9:3/ 1:3 /3:9 (because there are 9H in one, 3H in the other) **(1)** Both singlets **because** there are no H atoms on adjacent C / by application of n + 1 rule **(1)** ALLOW TE for ester formed from ethanoic aid and butan-1-ol / butan-2-ol ONLY For butan-1-ol 5 peaks **(1)** 3:2:2:2:3 **(1)** Singlet, triplet, pentet/quintet, sextet, triplet by application of n + 1 rule **(1)** For butan-2-ol 5 peaks **(1)** 3:3:1:2:3 **(1)** Singlet, doublet, sextet, pentet/quintet, triplet by application of n + 1 rule **(1)**		3

(Total for Question 3 = 12 marks)

<table>
<tr><th>Question Number</th><th>Acceptable Answers</th><th>Mark</th></tr>
<tr><td>4(a)(i)</td><td>
<table>
<tr><td></td><td>$CH_3CH_2CH_2CH_3$</td><td>O_2</td><td>CH_3CO_2H</td><td>H_2O</td></tr>
<tr><td>$\Delta H^{\ominus}_f$ / kJ mol^{-1}</td><td>−126.5</td><td>0</td><td>−484.5</td><td>−285.8</td></tr>
<tr><td>$S^{\ominus}$ / J mol^{-1} K^{-1}</td><td>310.1</td><td>205</td><td>159.8</td><td>69.9</td></tr>
</table>
6 values correct 3 marks

4 / 5 values correct 2 marks

2/3 values correct 1 mark

0/1 values correct 0 marks

Ignore values multiplied by balancing numbers in addition to correct values eg for water 2 x −285.8 (=571.6)
</td><td>3</td></tr>
</table>

<table>
<tr><th>Question Number</th><th>Acceptable Answers</th><th>Mark</th></tr>
<tr><td>4(a)(ii)</td><td>If answer is − 2256.6 / − 2257 (kJ mol^{-1}), award 2 marks
[(2 x −285.8) + (4 x −484.5)]
− (2 x −126.5) (1)

= − 2256.6 / − 2257 (kJ mol^{-1}) (1)
Allow answer converted to J mol^{-1}
Allow TE from incorrect data in table in (a)(i)
Allow (1) for cycle wrong way round
eg (+) 2256.6 / (+)2257 (kJ mol^{-1})
Allow (1) for using correct values but not multiplied by balancing numbers eg -643.8 (kJ mol^{-1})

Ignore SF except 1SF</td><td>2</td></tr>
</table>

Question Number	Acceptable Answers	Mark
4(a) (iii)	**If answer is −866.2 (J mol^{-1}K^{-1}), award 2 marks** [(2 x 69.9) + (4 x 159.8)] − [(2 x 310.1) + (5 x 205)] **(1)** −866.2 (J mol^{-1}K^{-1}) **(1)** **Allow** answer converted to kJ mol^{-1}K^{-1} **Allow** TE from incorrect data in table in (a)(i) **Allow** (1) for cycle wrong way round eg (+) 866.2(J mol^{-1}K^{-1}) **Allow** (1) for using correct values but error(s) in balancing numbers eg -285.4 (J mol^{-1}K^{-1}) **Ignore** SF except 1SF	**2**

Question Number	Acceptable Answers	Mark
4(a) (iv)	**If answer is (+)6706.3 J mol^{-1} K^{-1} or (+)6.7063 kJ mol^{-1} K^{-1}, award 3 marks** ΔS_{surr} at 298 K = $-\Delta H$/T = − (−2256.6 x 1000) / 298 **(1)** = 7572.483… (J mol^{-1}K^{-1}) **Allow** rounding to 3SF or more **(1)** **Allow** correct answers given in kJ mol^{-1} K^{-1} eg 7.5725 kJ mol^{-1} K^{-1} $\Delta S_{tot} = \Delta S_{surr} + \Delta S_{sys}$ / ΔS_{tot} = −866.2 + 7572.5 / ΔS_{tot} = (+)6706.3 J mol^{-1} K^{-1} **OR** -0.8662 + 7.5725 / ΔS_{tot} = (+)6.7063 kJ mol^{-1} K^{-1} **(1)** **Allow** TE from (a)(ii) and (a)(iii) **Ignore** SF except 1SF in final answer	**3**

Question Number	Acceptable Answers	Mark
4(a)(v)	**1st mark: consideration of ΔS_{system}** ΔS_{sys} is not (significantly) changed /is unchanged /remains (approximately) constant **(1)** **2nd mark: consideration of ΔS_{surr}** (Higher temperature makes) ΔS_{surr} /-ΔH/T is smaller / decreases / less positive Comment **Allow** more negative **(1)** **No TE** if ΔS_{surr} is –ve in (a)(iv) **3rd mark: consideration of ΔS_{total}** **EITHER** reduces ΔS_{tot} / makes ΔS_{tot} less positive / makes ΔS_{tot} closer to zero (so would not produce a greater yield) **OR** ΔS_{tot} is very large (so K is very large) so the effect of change in temperature is negligible **(1)** **NOTE** if ΔS_{surr} is –ve in (iv), then allow increases ΔS_{tot} / makes ΔS_{tot} more positive / makes ΔS_{tot} closer to zero (so would produce a greater yield). **NOTE** IF no reference / an incorrect reference made to ΔS_{system}, then only the 2nd and 3rd marks can be awarded	**3**

Question Number	Acceptable Answers	Mark
4(b)	**Note:** All we are looking for are the correct ranges, exactly as given below (i.e. the bonds do not have to be stated, as they follow from the correct ranges) Peak between **1725 – 1700** (cm^{-1}) (would appear due to C=O group (in alkyl carboxylic acid)) **Allow** peak between **3300 – 2500** (cm^{-1}) (due to OH group (in carboxylic acid))	**1**

Question Number	Acceptable Answers	Mark
4(c)	increase sourness / sharpness of flavour **OR** preservative / prevents growth of microbes / prevents food decay / prevents food decomposition /kills microbes **OR** acidity regulator / buffer **Allow** improves flavouring **Ignore** reduce pH/ make (slightly) acidic/just 'flavouring'	**1**

Question Number	Acceptable Answers	Mark
4(d)(i)	**Working must be shown** **EITHER** % of oxygen = 40% **(1)** Amount of C = 52.5/12 = 4.375 (mol) Amount of H = 7.5/1 = 7.5 (mol) Amount of O = 40/16 = 2.5 (mol) **(1)** Ratio 1.75 C : 3 H : 1 O ≡ 7 C : 12 H : 4 O **Ignore** SF in mol and ratios **(1)** **OR** % of C in $C_7H_{12}O_4$ = $\frac{84}{160}$ x 100 = 52.5% **(1)** % of H in $C_7H_{12}O_4$ = $\frac{12}{160}$ x 100 = 7.5% **(1)** % of O in $C_7H_{12}O_4$ = $\frac{64}{160}$ x 100 = 40 % **(1)** **OR** No C atoms = $\frac{52.5 \times 160}{100 \times 12}$ = 7 **(1)** No H atoms = $\frac{7.5 \times 160}{100 \times 1}$ = 12 **(1)** No O atoms = $\frac{40 \times 160}{100 \times 16}$ = 4 **(1)**	**3**

Question Number	Acceptable Answers	Reject	Mark
4(d)(ii)	Largest/highest m/e or m/z value (is 160) **OR** Mass (/charge ratio) or m/e or m/z of molecular/parent ion/ $C_7H_{12}O_4^+$ (=160(=M_r)) **Allow** last peak / peak on rhs (is at 160) **Allow** peak before last (is at 160 due to M+1 peak at 161)	Highest peak Just 'there is a peak at 160'	**1**

<table>
<tr><th>Question Number</th><th>Acceptable Answers</th><th>Mark</th></tr>
<tr><td>4(d)
(iii)</td><td>For ‘chemical shift’ column, allow any range or any single value within range and allow range in the opposite order eg 3.0-1.8
<table>
<tr><td>Feature of compound X</td><td>Chemical shift / ppm for TMS</td><td>Splitting patterns</td><td>Relative area below peak</td></tr>
<tr><td>CH$_3$</td><td>0.1 – 1.9</td><td>doublet</td><td>3 (1)</td></tr>
<tr><td>CH</td><td>1.8 – 3.0 (1)</td><td>septuplet / heptuplet / splits into 7 / 7 splits (1)</td><td>1</td></tr>
<tr><td>COOH</td><td>10 – 12.0 (1)</td><td>singlet</td><td>1</td></tr>
</table>
Allow heptet / septet /sevenlet and similar words that indicate 7</td><td>4</td></tr>
</table>

Total for Question 4 = 23 marks