Aldehydes and Ketones

Mark Scheme 2

Level	International A Level
Subject	Chemistry
Exam Board	Edexcel
Topic	Rates, Equilibria & Further Organic Chemistry
Sub Topic	Aldehydes and Ketones
Booklet	Mark Scheme 2

Time Allowed: **74 minutes**

Score: **/61**

Percentage: **/100**

Grade Boundaries:

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

Question Number	Acceptable Answers	Mark
1(a)(i)		**3**

	$CH_3CH_2CH_2CH_3$	O_2	CH_3CO_2H	H_2O
$\Delta H^{\ominus}_f$ / kJ mol^{-1}	**−126.5**	0	**−484.5**	**−285.8**
$S^{\ominus}$ / J mol^{-1} K^{-1}	**310.1**	205	**159.8**	**69.9**

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)

Question Number	Acceptable Answers	Mark
1(a) (ii)	**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	**2**

Question Number	Acceptable Answers	Mark
1(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
1(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
1(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
1(b)	**No e:** 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
1(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
1(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
1(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>1(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></td></tr>
</table>

Allow heptet / septet /sevenlet and similar words that indicate 7</td><td>4</td></tr>
</table>

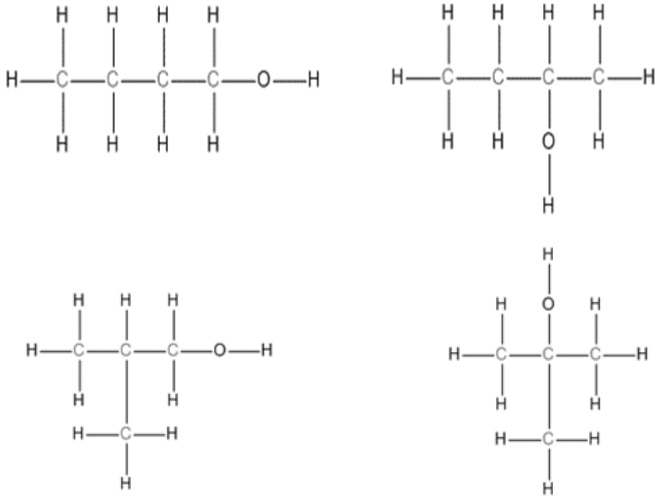
Total for Question 1 = 23 marks

Question Number	Acceptable Answers	Mark
2(a)(i)	(K_c =) $\frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$ **ALLOW** C_2H_5OH for ethanol **ALLOW** CH_3CO_2H for ethanoic acid **ALLOW** $CH_3CO_2CH_2CH_3$ / $CH_3CO_2C_2H_5$ /$CH_3COOC_2H_5$ for ethyl ethanoate **IGNORE** state symbols, even if incorrect	**(1)**

Question Number	Acceptable Answers	Mark
2(a)(ii)	**Stand alone marks** the enthalpy change is (very) small/close to zero **OR** reaction is slightly exothermic **(1)** therefore, (the magnitude of) $\Delta S_{surroundings}$ (= $-\Delta H/T$) **changes very little** **(1)** **IGNORE** $\Delta S_{surroundings}$ is positive/small/less/decreases ΔS_{total} / K_c changes very little (provided there is no change of state) **(1)** Ignore references to ΔS_{system}	**(3)**

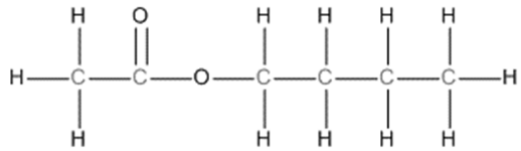
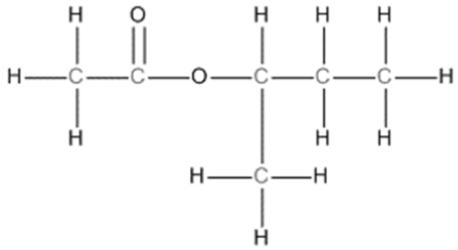
Question Number	Acceptable Answers	Reject	Mark
2(a)*(iii)	**If final answer is 5.1143/5.1, award 6 marks** If not, award marks as follows **Marks 1 and 2** If mol CH_3COOH left = 0.040 **(2)** Otherwise: mol NaOH/total mol of acid = 45.0 x 1.00/1000 = 0.045 **(1)** mol CH_3COOH left = mol NaOH/total mol of acid – 0.005 **(1)** **Marks 3 to 6** mol CH_3CH_2OH at eqm = 0.140 **(1)** mol $CH_3COOCH_2CH_3$ at eqm = 0.080 **(1)** mol H_2O at eqm = 0.358 **(1)** $K_c = \frac{0.080}{V} \times \frac{0.358}{V} \div \frac{0.040}{V} \times \frac{0.140}{V}$ $= 5.1143$ **(1)** **consequential** on their expression for K_c shown/used here and their numbers of moles **ALLOW** K_c expression without the Vs but **do not allow** this sixth mark if the moles are divided by a specific volume e.g. 45 to calculate the concentration **IGNORE** SF except 1 SF in final answer	any units	**(6)**

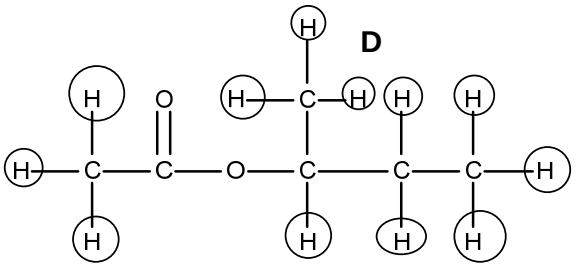
Question Number	Acceptable Answers	Mark
2(b)(i)	**EITHER** C : H : O mol 64.9 : 13.5 : 21.6 12 1 16 = 5.408: 13.5 : 1.35 **(1)** **=** 4.006 : 10 : 1 = 4 : 10 : 1 use of 74 to show molecular formula is $C_4H_{10}O$ eg M_r is (4x12)+(10x1)+16 =74 **(1)** **OR** C atoms = 64.9 x 74 / 100 x 12 = 4 H atoms = 13.5 x 74 / 100 x 1 = 10 O atoms = 21.6 x 74 / 100 x 16 = 1 This may be done in 2 steps eg C 64.9 x 74 / 100 = 48 48 / 12 = 4 All 3 correct scores **2** Any 2 correct scores **1** **OR** % C = 48 x 100 / 74 = 64.9 % H = 10 x 100 / 74 = 13.5 % O = 16 x 100 / 74 = 21.6 All 3 correct scores **(2)** Any 2 correct scores **(1)**	**(2)**

Question Number	Acceptable Answers	Reject	Mark
2(b)(ii)	 Alcohols can be in any order **ALLOW** OH All **FOUR** correct scores **(2)** Two or three correct scores **(1)** **ALLOW all four** skeletal/structural/mixture of displayed and structural **(1)** **IGNORE** optical isomers of butan-2-ol	molecular formula OH-C.. on left of structure once only more than 1 H missing from a bond	**(2)**

Question Number	Acceptable Answers	Mark
2(b)(iii)	$CH_3C^+HOH/[CH_3CHOH]^+$ **ALLOW** $CH_3CHOH^+/^+CH_3CHOH$ **(1)** $^+CH_2CH_2OH/[CH_2CH_2OH]^+$ **ALLOW** $CH_2CH_2OH^+/C_2H_4OH^+$ **(1)** Only penalise missing + once. **Note:** If no structures given, allow 1 mark for $C_2H_5O^+$ but do not award the mark if $C_3H_9^+$ is given as well	**(2)**

Question Number	Acceptable Answers	Mark
2(b)(iv)	butan-1-ol and butan-2-ol **OR** structures **OR** identified by number from (b)(ii)	**(1)**

Question Number	Acceptable Answers	Reject	Mark
2(b)(v)	  **ALLOW** any unambiguous structures e.g. displayed, structural, skeletal or a combination of these, TE from (b)(iv)	C_4H_9 structures with more than 1 H missing from a bond	**(1)**

Question Number	Acceptable Answers	Mark
2(b)(vi)	No structure is given or an ester formed from a different alcohol eg propanol scores **(0)** **First mark - structure** **Correct structure** **(1)**  Protons can be labelled or circled and labelled **ALLOW** any unambiguous structure eg displayed, structural, skeletal or a combination of these. **Five peaks correct scores (2)** **Three or four peaks correct scores (1)** **Splitting** **Any two correct scores (2)** **No** splitting for peak B as there is no H attached to the adjacent carbon **OR** application of the (n+1) rule to peak **A** (which is a multiplet/sextet) **OR** application of the (n+1) rule to peak **C** (which is a multiplet/quintet) **OR** application of the (n+1) rule to peak **D** (which is a doublet) **OR** application of the (n+1) rule to peak **E** (which is a triplet) If ester has been formed from butan-1-ol, maximum 2 marks for identification of peaks **B**, **C** and **E** **and** 2 marks for correct splitting in any two of peaks **B**, **C** and **E** If ester has been formed from either of the other 2 alcohols, 1 ark for identification of peak **B**, 1 mark for explaining why there is no splitting in peak **B**	**(5)**

(Total for Question 2 = 23 marks)

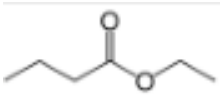
Question Number	Acceptable Answers	Reject	Mark
3(a)	$CH_3CH_2CH_2C\equiv N$ **ALLOW** displayed formula	$CH_3CH_2CH_2CN$ molecular formula	 **1**

Question Number	Acceptable Answers	Reject	Mark
3(b)	**IGNORE** conditions and solvents, even if incorrect **Step 1** $LiAlH_4$ **IGNORE** dry ether/ followed by H_2O **ALLOW** lithium tetrahydridoaluminate((III)) lithium aluminium hydride **(1)** **Step 2** PCl_5 **ALLOW** phosphorus(V) chloride/ phosphorus pentachloride HCl /(concentrated) hydrochloric acid PCl_3 / phosphorus(III) chloride/ phosphorus trichloride $SOCl_2$ / thionyl chloride **(1)** **Step 4** HCl/ HCl(aq)/ HCl in water or H_2O **ALLOW** any strong acid/ H^+/ NaOH/ sodium hydroxide **followed by** HCl / hydrochloric acid **(1)** **Step 5** CH_3CH_2OH/ C_2H_5OH (and any strong acid) **ALLOW** ethanol **(1)**	incorrect formulae, including subscripts written as large numbers or superscripts eg $LiAlH4/LiAlH^4$ any charges $NaBH_4$ H_2/ hydrogen dilute hydrochloric acid just 'dilute acid' just 'concentrated acid' just 'H_2O/ water' $OHCH_2CH_3$	**4**

Question Number	Acceptable Answers	Reject	Mark
3(c)	$2CH_3CH_2CH_2COOH + Na_2CO_3 \rightarrow$ $2CH_3CH_2CH_2COO^{(-)}Na^{(+)} + CO_2 + H_2O$ **ALLOW** butanoic acid as $CH_3CH_2CH_2CO_2H$/ $CH_3(CH_2)_2\ COOH$/$CH_3(CH_2)_2CO_2H$/ C_3H_7COOH/$C_3H_7CO_2H$ and the salt as $CH_3CH_2CH_2CO_2H$ / $CH_3(CH_2)_2\ COO^{(-)}Na^{(+)}$ / $CH_3(CH_2)_2CO_2^{(-)}Na^{(+)}$ / $C_3H_7COO^{(-)}Na^{(+)}$/ $C_3H_7CO_2^{(-)}Na^{(+)}$ all product formulae correct **(1)** correct balanced equation **(1)** **ALLOW** correct ionic equation for **(1)** $2CH_3CH_2CH_2COOH + CO_3^{2-} \rightarrow$ $2CH_3CH_2CH_2COO^{-} + CO_2 + H_2O$ **IGNORE** state symbols even if incorrect		**2**

Question Number	Acceptable Answers	Reject	Mark
3(d)	**Any two correct points from:** **First point** butanoic acid has 4 peaks, butan-1-ol has 5 peaks **OR** butanoic acid has one peak fewer **OR** butan-1-ol has one peak more **ALLOW** butanoic acid has fewer peaks/ butan-1-ol has more peaks **(1)** **IGNORE** butanoic acid has 4 proton environments and butan-1-ol has 5 **Second point** ratio of peak heights/ area under each peak is 3:2:2:1 for butanoic acid **and** 3:2:2:2:1 for butan-1-ol **(1)** **Third point** the OH (hydrogens) have different chemical shifts **OR** butanoic acid has a (COOH) peak at 10-12 (ppm) (and butan-1-ol does not) **OR** butan-1-ol has (an OH) peak at 2-4 (ppm) (and butanoic acid does not) **(1)** **Fourth point** peak at 3.0-1.8 (ppm) for H-C-C=O in acid and not in the alcohol **OR** peak at 3.0-4.4 (ppm) for H-C-O- in alcohol and not in acid **OR** the hydrogens on the alpha carbon have different chemical shifts **(1)** **IGNORE** reference to splitting patterns	incorrect numbers of peaks quoted different number of peaks area under peaks in the ratio 8:10 incorrect data quoted incorrect data quoted	**2**

Question Number	Acceptable Answers	Reject	Mark
3(e)	**First mark – bond and range** C=O(stretching) in butanoic acid (has an absorption at) 1725 – 1700 (cm^{-1}) **(1)** **Second mark – bond and both ranges** O-H/ OH (stretching) in butan-1-ol 3750 – 3200 (cm^{-1}) **and** O-H/ OH (stretching) in butanoic acid 3300 – 2500 (cm^{-1}) **ALLOW** COOH in butanoic acid **(1)** **ALLOW** any wavenumber or range of wavenumbers within the ranges above and ranges written in reverse order If no other marks are awarded, then **ALLOW** 1 mark if all 3 ranges are identified but bonds are missing/incorrect **IGNORE** reference to fingerprint region	COOH/ incorrect name of bond/ 1740 – 1720 (cm^{-1})/ other incorrect range incorrect name of bonds	**2**

Question Number	Acceptable Answers	Reject	Mark
3(f)	 **IGNORE** bond lengths and bond angles **ALLOW** any orientation		**1**

Question Number	Acceptable Answers	Reject	Mark
3(g)	**First step** – PCl_5/ phosphorus(V) chloride/ phosphorus pentachloride **ALLOW** PCl_3 / phosphorus(III) chloride/ phosphorus trichloride $SOCl_2$ / thionyl chloride **(1)** **Second step – conditional on first mark** CH_3CH_2OH/ C_2H_5OH/ ethanol **(1)** **Advantage - stand alone mark** higher yield (of ester) **OR** reaction goes to completion/ not an equilibrium reaction/ not reversible **OR** no heat energy needed/ reacts at room temperature/ no (concentrated acid) catalyst needed **(1)** **IGNORE** atom economy/ faster/ requires less energy	HCl	**3**

Total for Question 3 = 15 marks