1 **Z** is a molecule which contains the elements carbon, hydrogen and oxygen only.

Z contains only alkene and carboxyl functional groups.

(a) Complete Table 6.1 by describing the observations that occur when two different reagents are added to separate samples of **Z**(aq).

Table 6.1

reagent added to **Z**(aq)	observation
$Br_2(aq)$	
$Na_2CO_3(s)$	

[2]

(b) Table 6.2 shows the percentage by mass of each element present in **Z**.

Table 6.2

element	percentage by mass / %
carbon	41.38
hydrogen	3.45
oxygen	55.17

Using the data in Table 6.2, demonstrate that the empirical formula of **Z** is CHO.
Show your working.

[1]

(c) Fig. 6.1 shows the mass spectrum of **Z**.

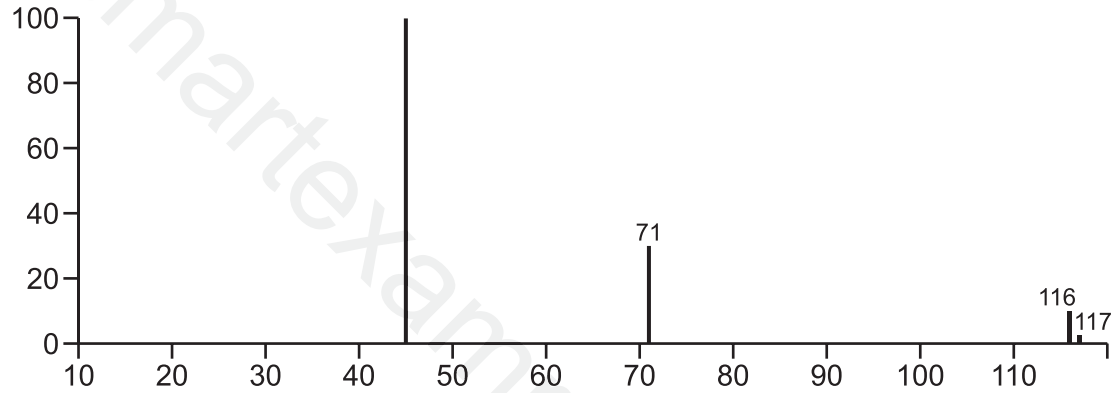


Fig. 6.1

(i) Deduce the molecular formula of **Z**. Explain your answer by referring to the molecular ion peak in Fig. 6.1 and the empirical formula of **Z**.

[1]

(ii) Use Fig. 6.1 to suggest the formulae of the fragments with *m* / *e* peaks at 45 and at 71.

m / *e* 45 .....

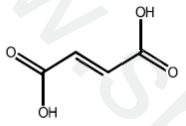
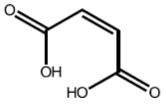
m / *e* 71 .....

[2]

(iii) Suggest the structure of **Z** using relevant information from Table 6.1, **(b)** and **(c)**.

[1]

MARK SCHEME:

5(a)	<table><tr><td>$Br_2(aq)$</td><td>orange to colourless **OR** orange disappears</td></tr><tr><td>$Na_2CO_3(s)$</td><td>fizzing OR bubbles **OR** effervescence</td></tr></table>	**2**
5(b)	C : H : O 41.38 / 12 3.45 / 1 55.17 / 16 3.45 3.45 3.45 (so $C_{(1)}H_{(1)}O_{(1)}$)	**1**
(c)(i)	Look for some reference to 116 as the mass of the molecular ion **AND** mass of $C_{(1)}H_{(1)}O_{(1)}$ = 29 to conclude molecular formula is $C_4H_4O_4$ 116 / 29 = 4 so $C_4H_4O_4$	**1**
(c)(ii)	**M1** *m / e* 45: ^+COOH OR $^+CHO_2$ **M2** *m / e* 71: $C_3H_3O_2^+$	**2**
(c)(iii)	 **OR** 	**1**

2 Fig. 5.1 shows the mass spectrum of ketone **Z**, $C_5H_{10}O$.

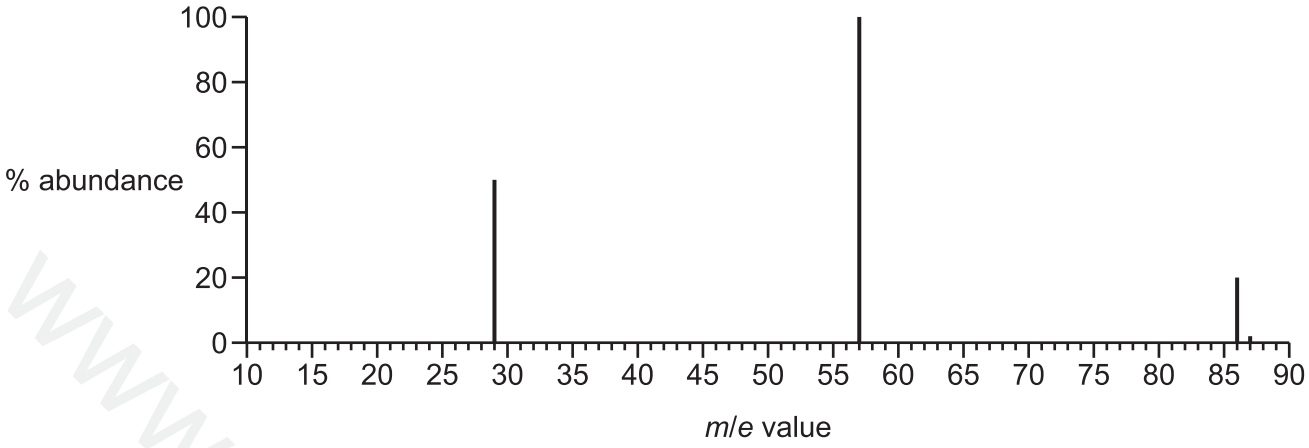


Fig. 5.1

Use the information in Fig. 5.1 to suggest the formulae of the fragments with *m/e* peaks at 29 and 57. Deduce the identity of **Z**.

m/e = 29 .....

m/e = 57 .....

identity of **Z** .....

[3]

[Total: 14]

MARK SCHEME:

29	$C_2H_5^+$	**3**
57	$COCH_2CH_3^+$ **OR** $C_3H_5O^+$ **OR** $CH_2COCH_3^+$	
identity of **Z**	pentan-3-one / $CH_3CH_2COCH_2CH_3$ pentan-2-one / $CH_3COCH_2CH_2CH_3$	

3 **X** is a product of the substitution reaction that occurs when $CHCl F_2$ reacts with Br_2.

There is only one naturally occurring isotope of fluorine, ^{19}F.

The mass spectrum of **X** shows molecular ion peaks at m/e = 164, 166 and 168.

Complete Table 3.3 to show **all** the molecular ions responsible for each peak.

Table 3.3

m/e	formulae of molecular ions
164	
166	
168	$(CF_2{}^{37}Cl^{81}Br)^+$

[2]

MARK SCHEME:

M1 *m/e 164* $(CF_2{}^{35}Cl^{79}Br)^+$ **M2** *m/e 166* $(CF_2{}^{37}Cl^{79}Br)^+$ **AND** $(CF_2{}^{35}Cl^{81}Br)^+$	**2**

4 **(a)** But-2-ene reacts with $KMnO_4$ to form organic product, **Y**.

Y does not react with Na_2CO_3.
A gas is produced when an excess of Na is added to **Y**.

(i) Describe the conditions for the $KMnO_4$ used in the reaction to form **Y** from but-2-ene.

..... [1]

(ii) 24.0 cm^3 of gas is produced when an excess of Na is added to 0.001 mol of **Y**, when measured under room conditions.
Assume that 1 mol of gas occupies 24.0 dm^3 under room conditions.

Deduce a possible structure of **Y**. Explain your answer.

.....

.....

.....
[3]

(b) **Z** contains three types of atom: carbon, hydrogen and a halogen. The mass spectrum of **Z** is recorded. Fig. 5.1 shows a section of the mass spectrum at *m*/*e* greater than 63.
The fragment at *m*/*e* = 64 is the molecular ion peak.

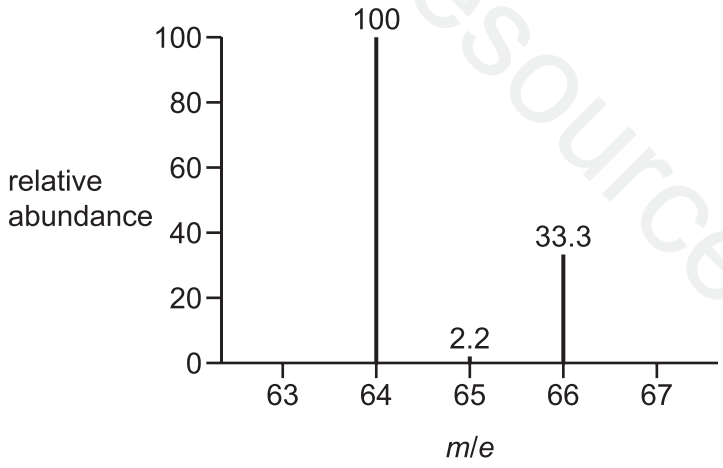


Fig. 5.1

(i) Deduce the number of carbon atoms present in a molecule of **Z** using Fig. 5.1.
Show your working.

..... [1]

(ii) Deduce which halogen is present in **Z** using Fig. 5.1. Explain your answer.

.....

..... [1]

(iii) There are also peaks at *m*/*e* = 29 and *m*/*e* = 49.

Suggest the formulae of these fragments.
Deduce the name of **Z**.

m/*e* = 29 .....

m/*e* = 49 .....

name of **Z** .....
[3]

MARK SCHEME:

(a)(i)	cold + dilute	**1**
(a)(ii)	**M1** unbranched 4C structure **AND** any number of –OH in any position **M2** 0.001 mol H_2 made from 0.001 mol **Y** **AND** R–OH + Na → RONa + ½H_2 **OR** use of 1 OH (group) → ½H_2 **M3** $CH_3CH(OH)CH(OH)CH_3$	**3**
(b)(i)	100 × 2.2 / 1.1 × 100 = 2	**1**
(b)(ii)	chlorine / C*l* **AND** peak at M+2 represents the molecular ion with 37–C*l* (rather than 35–C*l* as relative abundance of (peaks) M: M+2 is 100:33 / 3:1) **OR** relative abundance of (peaks) M: M+2 is 100:33.3 / 3:1 (so peak at M+2 contains 37–C*l*)	**1**
(b)(iii)	m / e = 29: $C_2H_5^+$ m / e = 49: CH_2Cl^+ name of Z: chloroethane	**3**

5 Both functional groups in one molecule of **Y** react with an inorganic reagent to form one molecule of **Q** and one molecule of methanol, CH_3OH, as shown in Fig. 6.3.

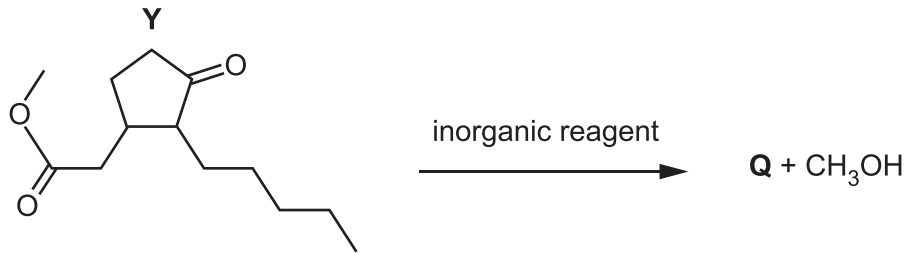


Fig. 6.3

(i) Part of the mass spectrum for **Q** is shown in Fig. 6.4. Only peaks with *m*/*e* greater than 198 are shown.

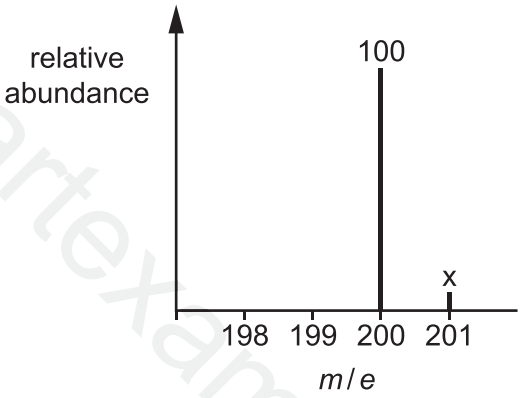


Fig. 6.4

Calculate the relative abundance, x, of the peak at *m*/*e* = 201.

Show your working.

x = ... [2]

(ii) **Q** contains **only** hydroxyl functional groups.

Complete Table 6.1 to show the observations that occur when 2,4-dinitrophenylhydrazine (2,4-DNPH reagent) is added to separate samples of **Y** and **Q**.

Table 6.1

	observation on addition of 2,4-DNPH reagent
Y	
Q	

[1]

(iii) Under certain conditions, 0.0020 mol of **Q** reacts with an excess of sodium to produce a total of 44.8 cm^3 of gas at s.t.p.

Calculate the number of hydroxyl groups present in a molecule of **Q**.

Show your working.

number of hydroxyl groups = ... [2]

(iv) Use Table 6.2 to describe and explain **two** differences between the infrared spectrum of **Y** and **Q** in the region above 1500 cm^{-1}.

.....

.....

..... [2]

Table 6.2

bond	functional groups containing the bond	characteristic infrared absorption range (in wavenumbers) / cm^{-1}
C–O	hydroxy, ester	1040–1300
C=C	aromatic compound, alkene	1500–1680
C=O	amide carbonyl, carboxyl ester	1640–1690 1670–1740 1710–1750
C≡N	nitrile	2200–2250
C–H	alkane	2850–2950
N–H	amine, amide	3300–3500
O–H	carboxyl hydroxy	2500–3000 3200–3650

Mark Scheme:

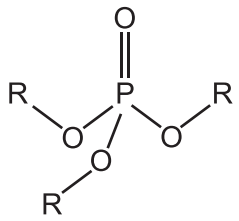
)(i)	**M1** deduce n = 12 (from **Y** – 1C (in methanol)) **M2** (100 × x) ÷ (1.1 × 100) = 12 (so) x = 13.2	**2**

(ii)	<table><tr><td></td><td>observation on addition of 2,4–DNPH</td></tr><tr><td>**Y**</td><td>orange precipitate</td></tr><tr><td>**Q**</td><td>no precipitate</td></tr></table> Both correct for one mark	**1**
(iii)	ROH + Na → RONa + 1 / 2H_2 (0.002 mol **Q** produced 0.002 mol H_2 gas so) 2 OH groups **M1** *answer indicates that OH group(s) in* **Q** *react with Na to produce the H_2 in the ratio 1 mol OH : ½ mol H_2* **M2** *uses data to show 2OH groups*	**2**
(iv)	**M1 Y** will have absorption / peak / trough between 1670–1740 due to C=O (**Q** will not) **M2 Q** will have absorption / peak / trough between 3200–3600 due to O-H (**Y** will not)	**2**

6 Phosphoric(V) acid, H_3PO_4, is used in both inorganic and organic reactions.

(d) H_3PO_4 also reacts with alcohols to form organophosphates.

Organophosphates are compounds similar to esters. They have the general structure shown in Fig. 3.2.



R = alkyl group

Fig. 3.2

(ii) Compound **T** is a simple organophosphate.

The mass spectrum of **T** shows a molecular ion peak at m/e = 182. This peak has a relative intensity of 12.7.

The relative intensity of the M+1 peak is 0.84.

Deduce the number of carbon atoms in **T**.
Hence suggest the molecular formula of **T**.

Assume that phosphorus and oxygen exist as single isotopes.

Show your working.

number of carbon atoms in **T** = ...

molecular formula of **T** = ...
[3]

Mark Scheme:

	$\frac{0.84}{12.7} \times \frac{100}{1.1}$ $(= 6.013)$	1
	no. of carbon atoms = 6	1
	molecular formula = $C_6H_{15}O_4P$	1