



UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
Cambridge International Level 3 Pre-U Certificate
Principal Subject

CANDIDATE
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CHEMISTRY

9791/03

Paper 3 Part B Written

May/June 2012

2 hours 15 minutes

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen in the spaces provided.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
DO NOT WRITE IN ANY BARCODES.

Answer **all** questions.
You may lose marks if you do not show your working or if you do not include appropriate units.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use	
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6	
Total	

This document consists of **18** printed pages and **2** blank pages.



1 Fig. 1.1 shows the structures of two allotropes of carbon.

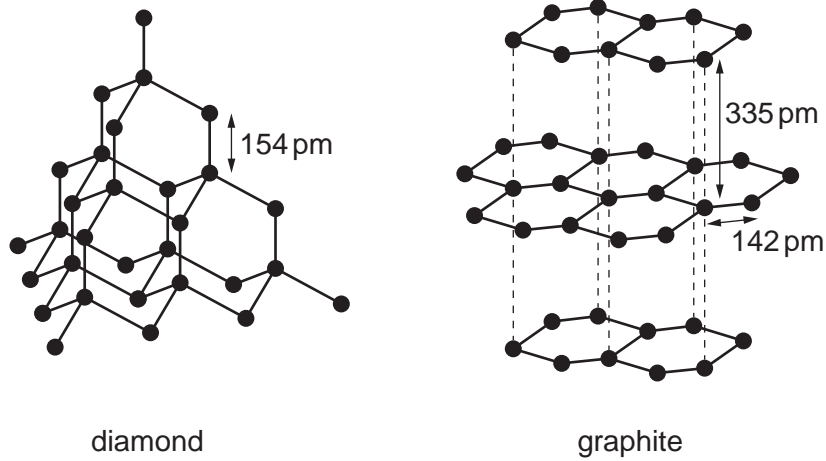


Fig. 1.1

(a) With reference to Fig. 1.1

(i) explain the meaning of the term *allotropes*.

.....

 [1]

(ii) describe the bonding in graphite and explain the difference between the two bond lengths shown in its structure.

.....

 [3]

(iii) State how and explain why the hardness and electrical conductivity of each allotrope differ.

.....

 [4]

(b) Group 14 is considered to represent a spectrum of behaviour ranging from non-metal at the top of the Group, through metalloid, to true metal at the bottom.

With reference to

- electrical conductivity of the element
- structure and bonding in the oxides

justify this statement.

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[3]

(c) Tin(IV) oxide, SnO₂, is easily prepared by oxidation of tin but lead(IV) oxide, PbO₂, can only be prepared by the action of very powerful oxidising agents on lead(II) compounds.

PbO₂ decomposes on heating to lead(II) oxide, PbO.

PbO can also be prepared by heating lead in air but SnO is sensitive to oxidation.

Explain this information.

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[2]

[Total: 13]

- 2 (a) When aqueous barium chloride is added to a solution containing sulfate ions a white precipitate of barium sulfate is formed. This white precipitate is very sparingly soluble in water.

- (i) Write the **ionic** equation, including state symbols, for the formation of the white precipitate.

.....[1]

- (ii) Write the expression for the solubility product, K_{sp} , of barium sulfate.

[1]

- (iii) Given that K_{sp} for barium sulfate is $1.08 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ at 298 K, calculate the concentration of sulfate ions in a saturated solution of barium sulfate. Give your answer to **three** significant figures.

..... mol dm^{-3} [2]

- (iv) Regulations state that the maximum permitted level of sulfate ions in drinking water is 250 mg dm^{-3} ($1 \text{ mg} = 1 \times 10^{-3} \text{ g}$).

200 cm^3 of aqueous barium chloride was added to 300 cm^3 of drinking water and a white precipitate formed. Assume that the sample of water contained the maximum permitted level of sulfate ions. Calculate the minimum concentration, in mol dm^{-3} , of barium chloride in the solution that was added to the sample of drinking water.

..... mol dm^{-3} [3]

- (b) The electrode potential of silver in contact with a solution of silver ions, $\text{Ag}^+(\text{aq})$, is impossible to measure directly but can be measured using a standard hydrogen electrode. Using this method the standard electrode potential of silver, E^\ominus , is found to be +0.80V.

- (i) Complete the cell diagram in Fig. 2.1 for the cell used to measure the standard electrode potential of silver. State the concentration of $\text{H}^+(\text{aq})$ used.

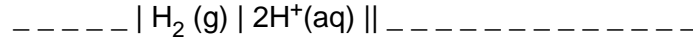


Fig. 2.1

concentration of $\text{H}^+(\text{aq}) = \text{-----}$ [3]

- (ii) When an excess of aqueous sodium chloride is added to the right-hand half-cell the silver ions will be precipitated as solid silver chloride, AgCl . Use Le Chatelier's principle to explain qualitatively how the cell emf will change as a result.

.....

 [2]

- (iii) At 298K the expression below can be used to calculate the concentration of silver ions in solution under non-standard conditions, from a measurement of the electrode potential.

$$E = E^\ominus - 0.030 \log \frac{1}{[\text{Ag}^+(\text{aq})]^2}$$

E = electrode potential of silver under non-standard conditions

E^\ominus = standard electrode potential of silver = +0.80V

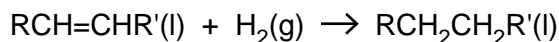
The addition of excess aqueous sodium chloride, $\text{NaCl}(\text{aq})$, to the right-hand half-cell results in a chloride ion concentration of 2.1 mol dm^{-3} .

Given that K_{sp} for silver chloride, AgCl , is $1.8 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ at 298K, calculate the value of E , in the cell shown in Fig. 2.1, after the addition of the excess aqueous sodium chloride to the right-hand half-cell.

$E = \text{-----} \text{ V}$ [3]

[Total: 15]

- 3 (a) The reaction shown represents the hydrogenation of a vegetable oil.



This reaction can be catalysed by several different transition metals and gives an example of heterogeneous catalysis.

State the three stages involved in a typical reaction involving a heterogeneous catalyst.

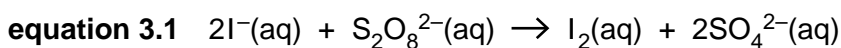
1.

2.

3.

[1]

- (b) An example of homogeneous catalysis is the use of iron(II) ions or iron(III) ions to catalyse the reaction between iodide ions and peroxydisulfate ions, $\text{S}_2\text{O}_8^{2-}$. This reaction is given in equation 3.1.



The relevant half-equations are given in Table 3.1.

Table 3.1

half-equation	E^\ominus / V
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{SO}_4^{2-}(\text{aq})$	+2.01
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{I}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$	+0.54

- (i) What is meant by the term *homogeneous catalysis*?

.....
 [1]

- (ii) Use the data in Table 3.1 to calculate the standard cell potential, E_{cell}^\ominus , of the reaction shown in equation 3.1.

..... V [1]

- (iii) Use your answer from (b)(ii) to calculate the standard Gibbs energy change, $\Delta_r G^\ominus$, of the reaction shown in equation 3.1. Give the sign and units in your answer.

..... [2]

- (iv) Explain how your answer to (b)(iii) confirms that the reaction shown in equation 3.1 represents the feasible direction of reaction.

.....
..... [1]

- (v) State and explain why, despite being feasible, the reaction shown in equation 3.1 is not seen to occur in the absence of a catalyst.

.....
.....
..... [2]

- (vi) By constructing suitable equations from the data in Table 3.1, explain why the reaction between iodide and peroxodisulfate can be catalysed by either iron(II) or iron(III) ions.

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.....
..... [3]

- (c) Fig. 3.1 represents part of the structure of chymotrypsin, an enzyme produced by the pancreas that is responsible for catalysing the hydrolysis of certain proteins in the small intestine during the digestive process.

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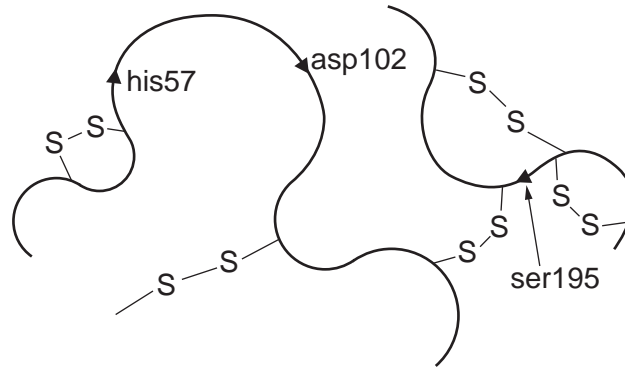


Fig. 3.1

The three main amino acids involved in the catalytic activity of the enzyme are labelled in Fig. 3.1 as his57, asp102 and ser195.

- (i) What is the name of the region of the enzyme molecule that contains the three labelled amino acids and interacts with the protein being hydrolysed?

.....[1]

The first stage of the mechanism of action of chymotrypsin is illustrated in Fig. 3.2.

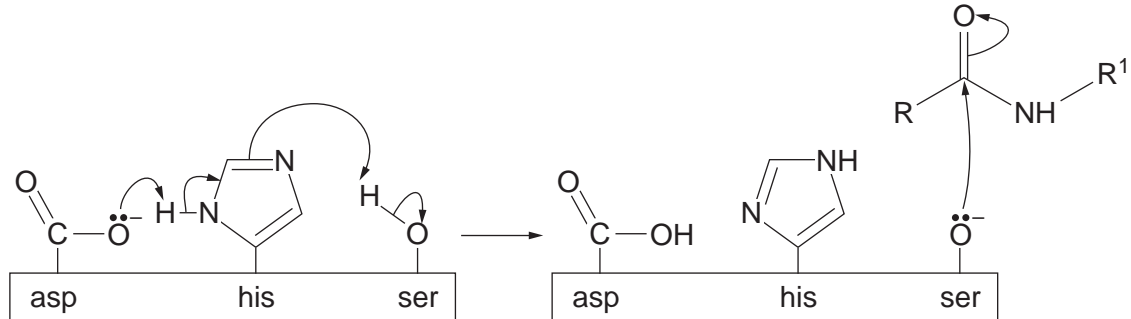


Fig. 3.2

- (ii) Explain what is represented by a curly arrow as used in the mechanism shown in Fig. 3.2.

.....[1]

- (iii) With reference to Fig. 3.2, explain why the action of this enzyme would be inhibited if the pH was too low.

.....

.....

.....[2]

(iv) Chymotrypsin is denatured by sodium hydroxide, with the mechanism dependent on the pH.

- At pH12 the reaction is first order with respect to both the chymotrypsin and the hydroxide.
- In the presence of excess alkali the denaturation of the enzyme was monitored.
- The plot of the time course of the reaction is shown in Fig. 3.3.

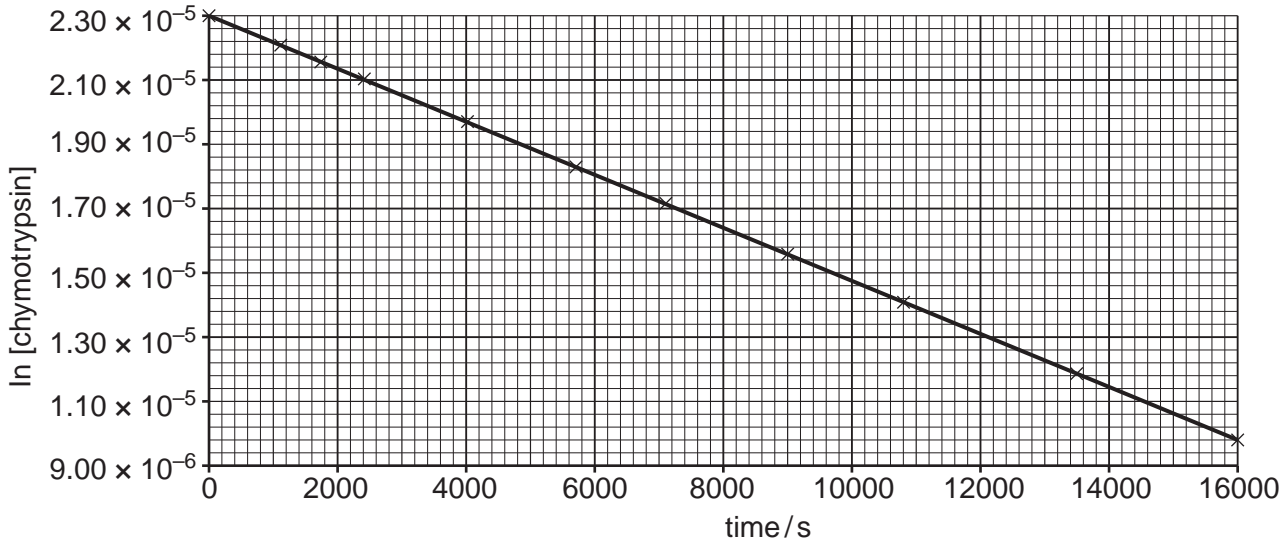


Fig. 3.3

The first order rate equation, equation 8 in the Data Booklet, can be rewritten as in equation 3.2.

equation 3.2 $\ln C_t = -kt + \ln C_0$

Given that equation 3.2 is in the form $y = mx + c$, explain how the graph in Fig. 3.3 confirms that the denaturation is first order with respect to chymotrypsin and how the conditions chosen give rise to first order kinetics overall.

.....

 [2]

(v) Use the graph in Fig. 3.3 to calculate the value of the first order rate constant for this denaturation.

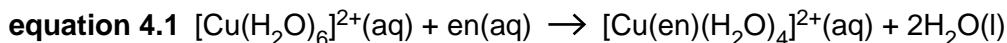
$k =$ [2]

[Total: 19]

- 4 The light blue colour of aqueous copper(II) sulfate is due to the presence of the hexaaquacopper(II) ion, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$.

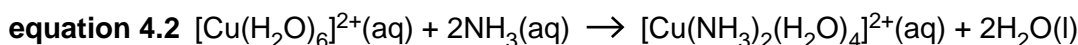
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Equations 4.1 and 4.2 show two different partial ligand substitution reactions of the hexaaquacopper(II) ion. In equation 4.1 'en' represents 1,2-diaminoethane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.



$$\Delta_r H^\ominus = -54 \text{ kJ mol}^{-1};$$

$$\Delta_r S^\ominus = +23 \text{ J K}^{-1} \text{ mol}^{-1}$$



$$\Delta_r H^\ominus = -46 \text{ kJ mol}^{-1};$$

$$\Delta_r S^\ominus = -8.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

- (a) Explain why the enthalpy changes, $\Delta_r H^\ominus$, of the reactions shown in equations 4.1 and 4.2 are so similar.

.....

 [2]

- (b) Comment on the values of the entropy changes, $\Delta_r S^\ominus$, of the reactions shown in equations 4.1 and 4.2 and explain why they are different.

.....

 [2]

- (c) The cation produced in the reaction shown in equation 4.2 can exist as two different isomers.

- (i) State the type of isomerism exhibited by this cation.

..... [1]

- (ii) Draw and label the two different isomers of this cation.

[2]

(d) Further ligand substitution leads to the production of the complex ion $[\text{Cu}(\text{en})_3]^{2+}$, which also exhibits isomerism.

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(i) State the type of isomerism exhibited by $[\text{Cu}(\text{en})_3]^{2+}$.

..... [1]

(ii) Draw 3-D representations of the two isomers of $[\text{Cu}(\text{en})_3]^{2+}$.

[2]

[Total: 10]

- 5 Pantothenic acid, vitamin B₅, is a water-soluble vitamin needed to form coenzyme-A (CoA), and it is critical in the metabolism and synthesis of carbohydrates, proteins and fats.

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The skeletal formula of pantothenic acid is shown in Fig. 5.1.

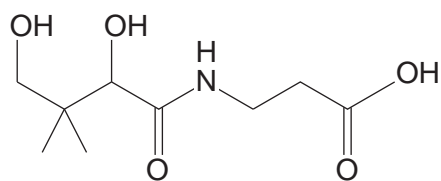


Fig. 5.1

- (a) Name fully all the functional groups present in a molecule of pantothenic acid.

.....

.....

.....

..... [4]

- (b) Give the structures of the organic products that would be formed if pantothenic acid was

- (i) hydrolysed by reaction with aqueous acid,

[2]

- (ii) reacted with sodium metal.

[2]

(c) Pantothenic acid is a chiral molecule and the full name of the biologically active form includes the prefixes R and (+).

(i) On Fig. 5.1 draw a circle around the chiral carbon in the molecule. [1]

(ii) Explain the meaning of each of the prefixes in the name R-(+)-pantothenic acid.

(+)

.....

R

.....

.....

..... [3]

(d) The acid dissociation constant, K_a , for pantothenic acid is $3.98 \times 10^{-5} \text{ mol dm}^{-3}$, whilst that of propanoic acid is $1.32 \times 10^{-5} \text{ mol dm}^{-3}$.

(i) Calculate the pH of a 0.20 mol dm^{-3} solution of pantothenic acid.

pH = [3]

(ii) The inductive effect can be used to account for the difference in the acid dissociation constants of pantothenic acid and propanoic acid. Explain why.

.....

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.....

..... [3]

- (e) A derivative of pantothenic acid, pantothenol, is a more stable form of the vitamin. It is often used in multivitamin supplements as it is converted to pantothenic acid in the body. Its structure is shown in Fig. 5.2.

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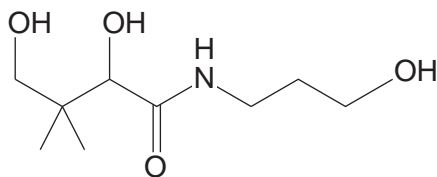


Fig. 5.2

The structural formula of pantothenol is $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{CHOHCONH}(\text{CH}_2)_3\text{OH}$ and its molecular formula is $\text{C}_9\text{H}_{19}\text{NO}_4$.

- (i) With reference to the concept of functional group level, explain what type of reaction is involved in the conversion of pantothenol into pantothenic acid.

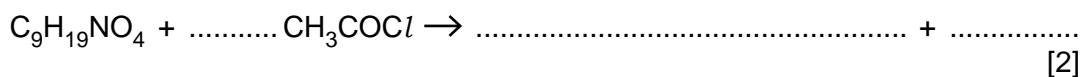
.....

 [2]

- (ii) Give the structural formula of the organic product of the reaction of pantothenol with ethanoyl chloride.

[1]

- (iii) Complete and balance the equation below for the reaction of pantothenol with ethanoyl chloride, using **molecular formulae** for the products.



[2]

[Total: 23]

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QUESTION 6 BEGINS ON PAGE 16

6 Fig. 6.1 shows the structures of a pair of isomers.

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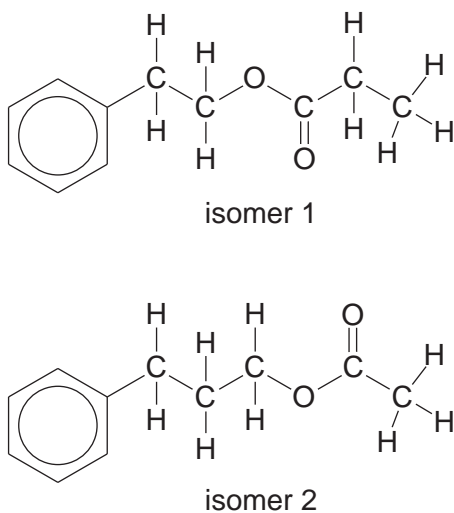


Fig. 6.1

(a) Give the molecular formula of these isomers.

..... [1]

(b) What type of isomerism is shown by these two isomers?

..... [1]

(c) Isomer 1 is named 2-phenylethyl propanoate. Give the name of isomer 2.

..... [1]

(d) The ^1H NMR spectrum of one of the isomers is shown in Fig. 6.2.

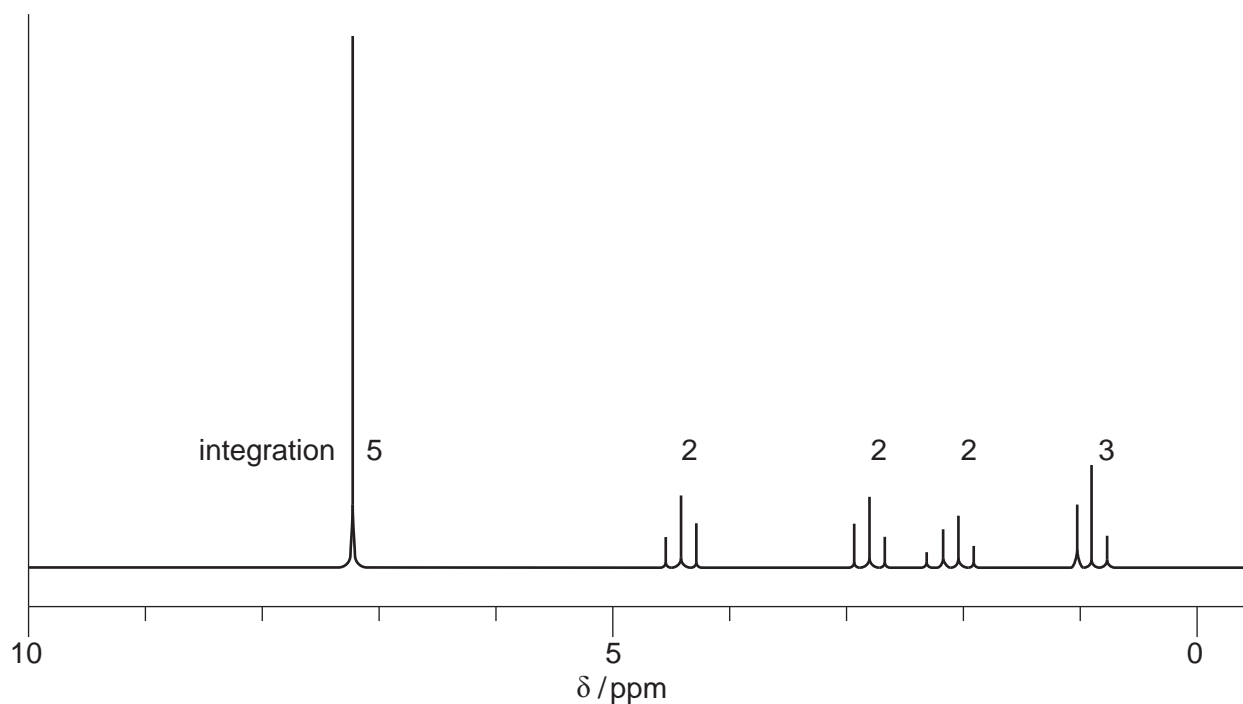


Fig. 6.2

Explain which of the two isomers corresponds to the ¹H NMR spectrum in Fig. 6.2. You should refer to the splitting patterns and integration values of **all** the peaks in your answer. Note that the phenyl group protons appear as a single peak.

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[6]

(e) **X** and **Y** are two compounds that can be made by hydrolysis of isomer 1 in Fig. 6.1.

X has the composition by mass C, 48.6%; H, 8.11%; O, 43.2%. The mass spectrum of **X** is shown in Fig. 6.3.

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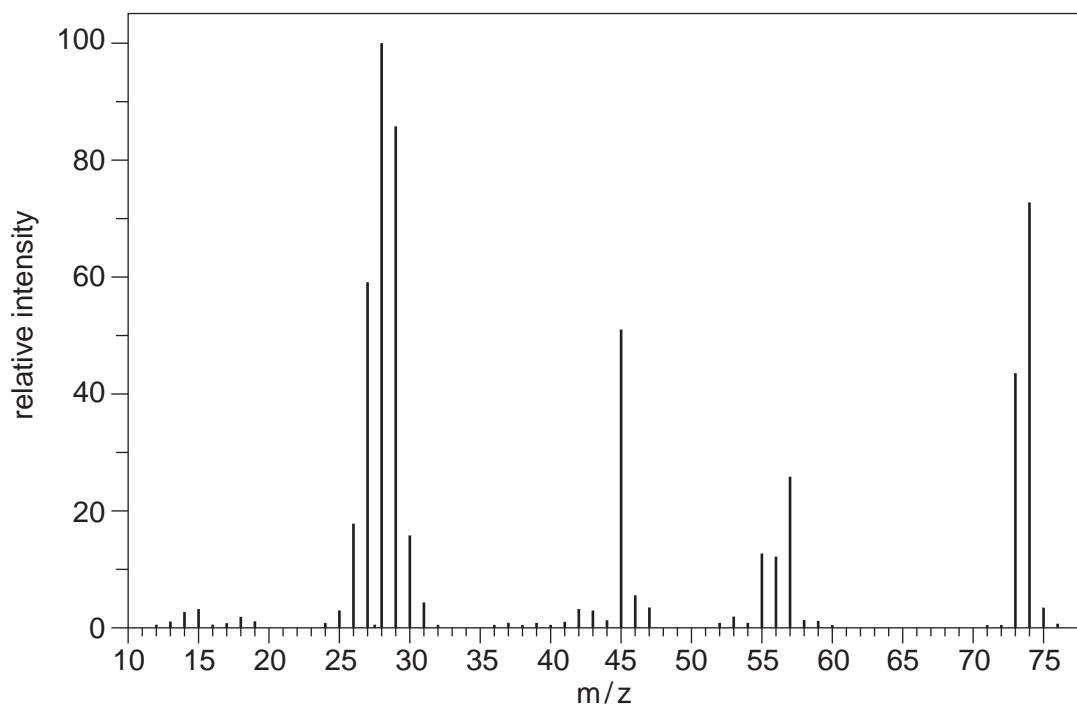


Fig. 6.3

(i) Calculate the empirical formula of **X**.

empirical formula of **X** [2]

(ii) Deduce the molecular formula of **X**.

molecular formula of **X** [1]

(iii) Identify the particle responsible for the peak at m/z 45.

..... [2]

(iv) Explain the origin and relative intensity of the peak at m/z 75.

.....

 [2]

(f) The IR spectrum of **Y** is shown in Fig. 6.4.

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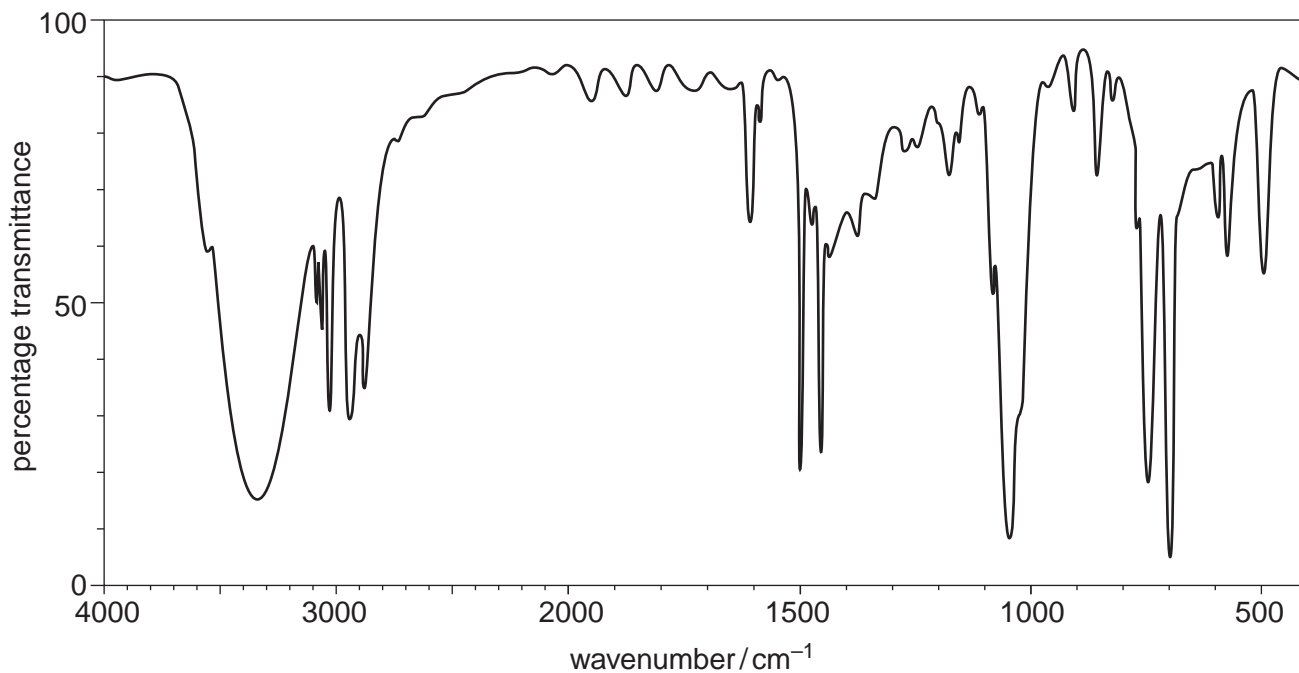


Fig. 6.4

- (i) Show the structure of **Y** and explain how the spectrum in Fig. 6.4 confirms the identity of the functional group present.

.....

 [2]

- (ii) Show the structure of **X** and explain how its IR spectrum will compare to that of **Y**.

.....

 [2]

[Total: 20]

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