



## Cambridge International AS & A Level

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**CHEMISTRY**

**9701/42**

Paper 4 A Level Structured Questions

**February/March 2022**

**2 hours**

You must answer on the question paper.

No additional materials are needed.

### INSTRUCTIONS

- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working and use appropriate units.

### INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].
- The Periodic Table is printed in the question paper.
- Important values, constants and standards are printed in the question paper.

This document has **28** pages. Any blank pages are indicated.

## 2

1 Iodine is found naturally in compounds in many different oxidation states.

(a) Iodide ions,  $I^-$ , react with acidified  $H_2O_2(aq)$  to form iodine,  $I_2$ , and water. This reaction mixture is shaken with cyclohexane,  $C_6H_{12}$ , to extract the  $I_2$ . Cyclohexane is immiscible with water.

(i) Identify the role of  $H_2O_2(aq)$  in its reaction with  $I^-$  ions in acidic conditions.

Write an ionic equation for the reaction.

role .....

ionic equation .....

..... [2]

(ii)  $15.0\text{cm}^3$  of  $C_6H_{12}$  is shaken with  $20.0\text{cm}^3$  of an aqueous solution containing  $I_2$  until no further change is seen.

It is found that  $0.390\text{g}$  of  $I_2$  is extracted into the  $C_6H_{12}$ .

The partition coefficient of  $I_2$  between  $C_6H_{12}$  and water,  $K_{pc}$ , is 93.8.

Calculate the mass of  $I_2$  that remains in the aqueous layer.

Show your working.

mass of  $I_2$  in aqueous layer = ..... g [2]

(iii) Suggest how the value of  $K_{pc}$  of  $I_2$  between hexan-2-one,  $CH_3(CH_2)_3COCH_3$ , and water compares to the value given in (a)(ii).

Explain your answer.

.....

.....

.....

..... [2]

(b) The Group 1 iodides all form stable ionic lattices and are soluble in water.

(i) Define enthalpy change of solution.

.....

.....

..... [1]

(ii) Use the data in Table 1.1 to calculate the enthalpy change of solution of potassium iodide, KI.

**Table 1.1**

process	enthalpy change, $\Delta H/\text{kJ mol}^{-1}$
$\text{K}^+(\text{g}) + \text{I}^-(\text{g}) \rightarrow \text{KI}(\text{s})$	-629
$\text{K}^+(\text{g}) \rightarrow \text{K}^+(\text{aq})$	-322
$\text{I}^-(\text{g}) \rightarrow \text{I}^-(\text{aq})$	-293

enthalpy change of solution = .....  $\text{kJ mol}^{-1}$  [1]

(iii) Suggest the trend in the magnitude of the lattice energies of the Group 1 iodides, LiI, NaI, KI.

Explain your answer.

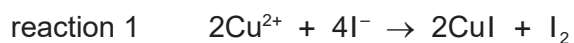
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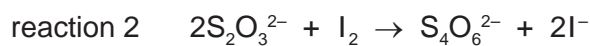
.....

..... [2]

- (c) The concentration of  $\text{Cu}^{2+}(\text{aq})$  in a solution can be determined by the reaction of  $\text{Cu}^{2+}$  ions with  $\text{I}^-$  ions.



The  $\text{I}_2$  produced in reaction 1 is titrated against a solution containing thiosulfate ions,  $\text{S}_2\text{O}_3^{2-}$ , using a suitable indicator.



- (i) A  $25.0 \text{ cm}^3$  portion of a  $\text{Cu}^{2+}(\text{aq})$  solution reacts with an excess of  $\text{I}^-(\text{aq})$ . The end-point of the titration occurs when  $22.30 \text{ cm}^3$  of  $0.150 \text{ mol dm}^{-3} \text{ S}_2\text{O}_3^{2-}(\text{aq})$  is added.

Calculate the concentration of  $\text{Cu}^{2+}(\text{aq})$  in the original solution.

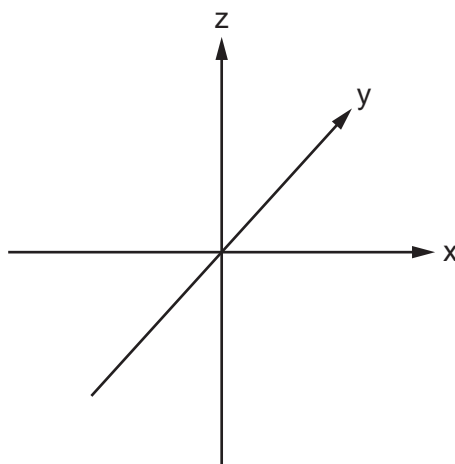
concentration of  $\text{Cu}^{2+}(\text{aq}) = \dots\dots\dots \text{ mol dm}^{-3}$  [2]

- (ii) Identify a suitable indicator for the titration.

..... [1]

- (iii) Copper(I) and copper(II) both contain electrons in all five 3d orbitals.

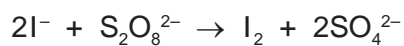
Sketch the shape of a  $3d_{xy}$  orbital on the axes provided.



[1]

## 5

- (d) The reaction of  $I^-$  ions with persulfate ions,  $S_2O_8^{2-}$ , can be catalysed by  $Fe^{3+}$  ions.



Write equations to show how  $Fe^{3+}$  catalyses this reaction.

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

- (e) An orange precipitate of  $HgI_2$  forms when  $Hg^{2+}$  ions are added to  $KI(aq)$ .  
 The solubility of  $HgI_2$  at  $25^\circ C$  is  $1.00 \times 10^{-7} g dm^{-3}$ .

Calculate the solubility product,  $K_{sp}$ , of  $HgI_2$ .  
 Include units in your answer.

[ $M_r$ :  $HgI_2$ , 454.4]

value of  $K_{sp}$  = .....

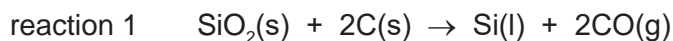
units = .....

[3]

[Total: 19]

2 Silicon is the second most abundant element by mass in the Earth's crust.

(a) In industry, silicon is extracted from  $\text{SiO}_2$  by reaction with carbon at over  $2000^\circ\text{C}$ .



(i) Explain why the entropy change,  $\Delta S$ , of reaction 1 is positive.

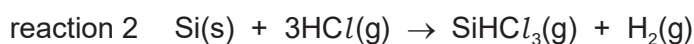
.....  
 ..... [1]

(ii) Reaction 1 is highly endothermic.

Suggest the effect of an increase in temperature on the feasibility of this reaction.  
 Explain your answer.

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

(b) Silicon is purified by first heating it in a stream of  $\text{HCl}(\text{g})$  to form  $\text{SiHCl}_3$ . The  $\text{SiHCl}_3$  formed is then distilled to remove other impurities.



(i) Table 2.1 shows some standard entropy data.

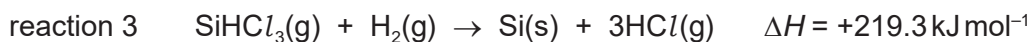
**Table 2.1**

compound	standard entropy, $S^\ominus/\text{JK}^{-1}\text{mol}^{-1}$
Si(s)	19
HCl(g)	187
SiHCl <sub>3</sub> (g)	314
H <sub>2</sub> (g)	131

Use the data in Table 2.1 to calculate  $\Delta S^\ominus$  for reaction 2.

$\Delta S^\ominus = \dots\dots\dots \text{JK}^{-1}\text{mol}^{-1}$  [2]

- (ii) Reaction 3 is the reverse of reaction 2 and is used to obtain pure silicon.



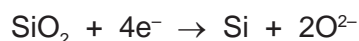
Use this information and your answer to **(b)(i)** to calculate the temperature, in K, at which reaction 3 becomes feasible.

Show your working.

[If you were unable to answer **(b)(i)**, you should use  $\Delta S^\ominus = -150 \text{ J K}^{-1} \text{ mol}^{-1}$  for reaction 2. This is not the correct answer to **(b)(i)**.]

temperature = ..... K [2]

- (c) Silicon can also be produced by electrolysis of  $\text{SiO}_2$  dissolved in molten  $\text{CaCl}_2$ . The relevant half-equation for the cathode is shown.



Calculate the time, in seconds, required to produce 1.00g of Si by this electrolysis, using a current of 6.00A.

Assume no other substances are produced at the cathode.

time = ..... s [2]

[Total: 9]

3 Titanium is a transition element in Period 4. It is commonly found as  $\text{TiO}_2$  in minerals.

(a) (i) Define transition element.

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

(ii) Identify **two** typical properties of transition elements.

1 .....  
 2 ..... [1]

(b) The  $\text{TiO}^{2+}$  ion forms when  $\text{TiO}_2$  reacts with an excess of sulfuric acid.

$\text{TiO}^{2+}$  can be reduced by zinc metal in acidic conditions to form a purple solution containing  $\text{Ti}^{3+}(\text{aq})$ .

(i)  $\text{TiO}^{2+}(\text{aq})$  is a colourless ion.

Suggest why.

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

(ii) Give the electronic configuration of an isolated  $\text{Ti}^{3+}$  ion.

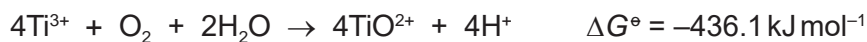
$1s^2$  ..... [1]

(iii) Write an ionic equation for the reduction of  $\text{TiO}^{2+}$  by zinc metal in acidic conditions.

..... [1]



(c) Acidified  $\text{Ti}^{3+}(\text{aq})$  reacts with oxygen dissolved in water as shown.



The standard reduction potential,  $E^\ominus$ , of  $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$  is +1.23 V.

(i) Calculate the standard reduction potential,  $E^\ominus$ , in V, of the  $\text{TiO}^{2+}(\text{aq})/\text{Ti}^{3+}(\text{aq})$  half-cell. Show your working.

$$E^\ominus = \dots\dots\dots \text{ V [3]}$$

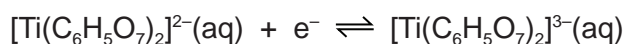
(ii) When aqueous citrate ions,  $\text{C}_6\text{H}_5\text{O}_7^{3-}$ , are added to  $\text{Ti}^{3+}(\text{aq})$ , the  $[\text{Ti}(\text{C}_6\text{H}_5\text{O}_7)_2]^{3-}(\text{aq})$  complex forms.

Explain, in terms of d-orbitals, why  $\text{Ti}^{3+}$  is able to form complex ions.

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

(iii) Acidified  $[\text{Ti}(\text{C}_6\text{H}_5\text{O}_7)_2]^{3-}(\text{aq})$  does not react with oxygen dissolved in water, unlike acidified  $\text{Ti}^{3+}(\text{aq})$ .

Suggest what this means for the value of the standard reduction potential,  $E^\ominus$ , of the following half-cell.

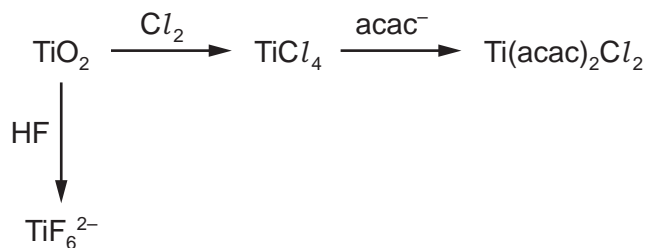


Explain your answer.

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

(d) Some reactions of  $\text{TiO}_2$  are shown in Fig. 3.1.

The anion,  $\text{acac}^-$ , is a bidentate ligand.



**Fig. 3.1**

(i) The titanium ions in  $\text{TiF}_6^{2-}$  and  $\text{Ti}(\text{acac})_2\text{Cl}_2$  have a coordination number of 6.

State what is meant by coordination number.

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

(ii) Write an equation for the formation of  $\text{TiF}_6^{2-}$  from  $\text{TiO}_2$ .

..... [1]

(iii) State what is meant by bidentate ligand.

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

(iv)  $\text{Ti}(\text{acac})_2\text{Cl}_2$  shows both optical and geometrical (cis/trans) isomerism.

$\text{Ti}(\text{acac})_2\text{Cl}_2$  exists as three stereoisomers.

The structure of one stereoisomer of  $\text{Ti}(\text{acac})_2\text{Cl}_2$  is shown in Fig. 3.2.

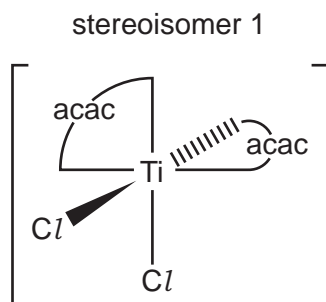
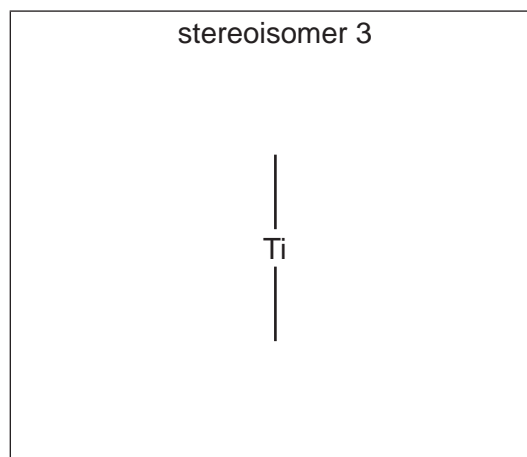
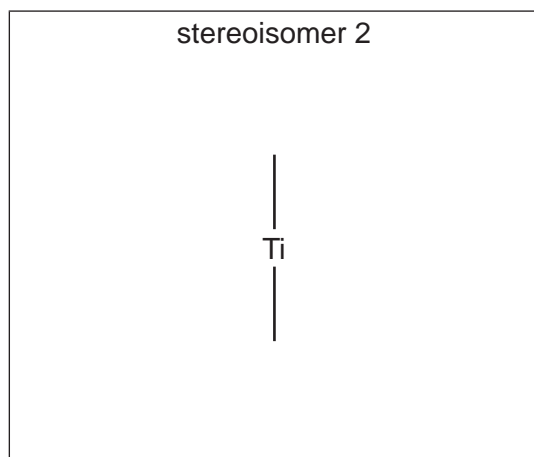


Fig. 3.2

Complete the structures of the other two stereoisomers of  $\text{Ti}(\text{acac})_2\text{Cl}_2$ .



[2]

(v) The  $\text{acac}^-$  anion is symmetrical.

Deduce which, if any, of stereoisomers 1, 2 and 3 in (d)(iv) are polar.  
Explain your answer.

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

[Total: 19]

4 Compounds **F** and **J** are shown in Fig. 4.1.

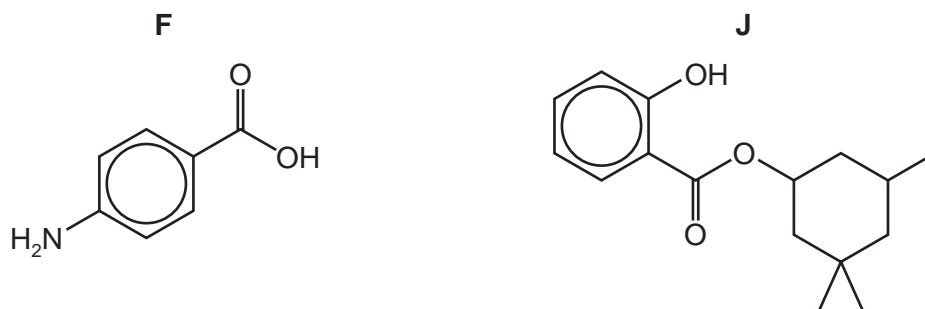


Fig. 4.1

(a) **F** and **J** both contain the arene functional group.

(i) Identify the other functional groups in **F** and **J**.

**F**: .....

**J**: .....

[2]

(ii) State the number of chiral centres in a molecule of **F** and in a molecule of **J**.

number of chiral centres in: **F** = ..... **J** = .....

[1]

(b) A student proposes a multi-step synthesis of **F** from benzene, as shown in Table 4.1.

(i) Complete Table 4.1 by providing relevant details of the reagents and conditions for steps 1 and 4, and the structure of product **D**.

Table 4.1

step	organic reactant	reagent(s) and conditions	organic product
1		.....	
2		concentrated HNO <sub>3</sub> and concentrated H <sub>2</sub> SO <sub>4</sub>	<b>D</b>
3	<b>D</b>	hot alkaline KMnO <sub>4</sub> then dilute H <sub>2</sub> SO <sub>4</sub>	<b>E</b> 
4		.....	<b>F</b> 

[3]

- (ii) In a second multi-step synthesis, the student changes the order in which the reagents and conditions are used. The reaction scheme is shown in Fig. 4.2. **G** is the major product of this synthesis.

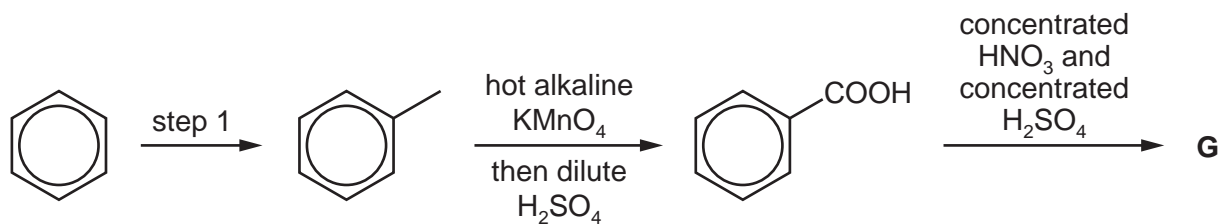


Fig. 4.2

Draw the structure of **G**.

Explain why **G** is the major product of the synthesis rather than **E**.



.....

.....

.....

[2]

- (c) **J** reacts under suitable conditions with NaOH(aq).  
After acidification of the reaction mixture, compounds **K** and **L** form.

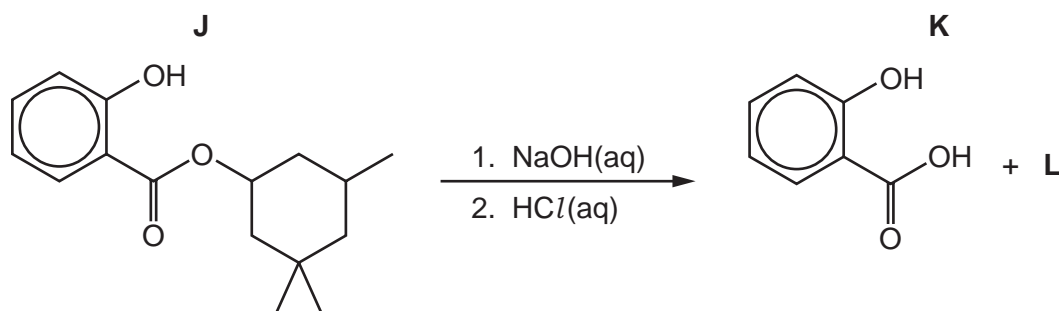


Fig. 4.3

- (i) Give the molecular formula of **L**.

..... [1]

- (ii) State the **two** types of reaction that occur when **J** reacts with NaOH(aq).

1 .....

2 .....

[2]

- (d) **K** can also be synthesised from phenol, C<sub>6</sub>H<sub>5</sub>OH.

Fig. 4.4 shows several reactions of phenol.

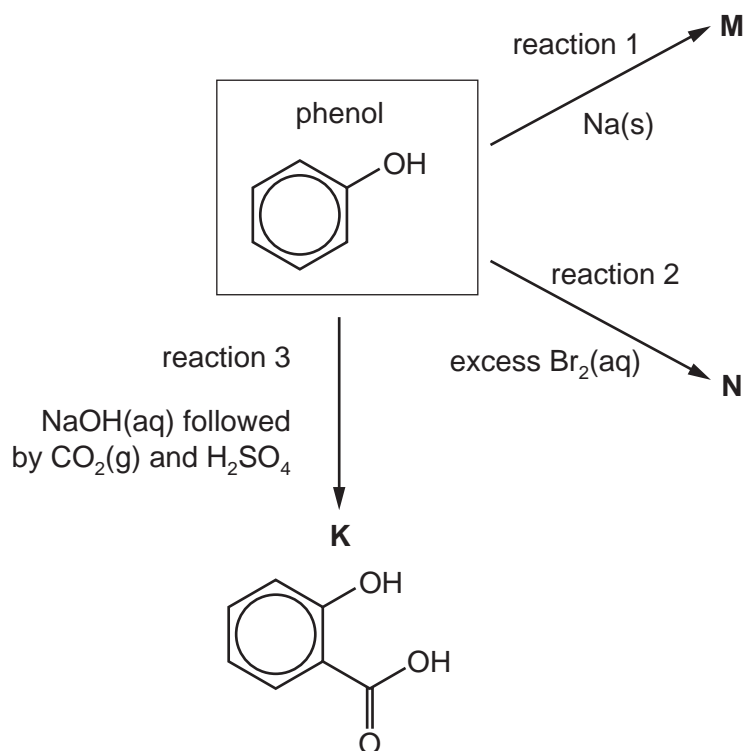


Fig. 4.4

(i) Write an equation for the formation of **M** in reaction 1.

..... [1]

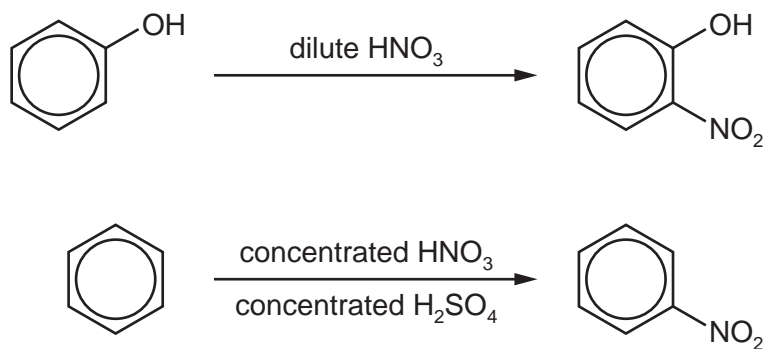
(ii) Draw **N**, the product of reaction 2.

[1]

(iii) Explain why phenol is a weaker acid than **K**.

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

(e) Phenol and benzene both react with nitric acid, as shown in Fig. 4.5.



**Fig. 4.5**

Explain why the reagents and conditions for these two reactions are different.

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

[Total: 18]

5 2-Chloropropanoic acid,  $\text{CH}_3\text{CHClCOOH}$ , is used in many chemical syntheses.

(a) (i) An equilibrium is set up when  $\text{CH}_3\text{CHClCOOH}$  is added to water.

Write the equation for this equilibrium.

..... [1]

(ii) 0.150 mol of  $\text{CH}_3\text{CHClCOOH}$  dissolves in  $250\text{ cm}^3$  of distilled water to produce a solution of pH 1.51.

Calculate the  $\text{p}K_{\text{a}}$  of  $\text{CH}_3\text{CHClCOOH}$ .

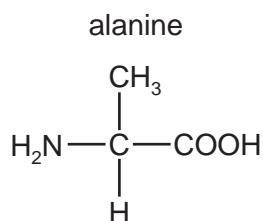
$\text{p}K_{\text{a}} = \dots\dots\dots$  [2]

(iii) An equal concentration of aqueous propanoic acid has pH 2.55.

Explain the difference in the pH of solutions of equal concentration of  $\text{CH}_3\text{CHClCOOH}$  and propanoic acid.

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

(b) When  $\text{CH}_3\text{CHClCOOH}$  reacts with aqueous  $\text{NH}_3$ , alanine forms.



**Fig. 5.1**

Alanine is an amino acid. Its isoelectric point is 6.1.

(i) State what is meant by isoelectric point.

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

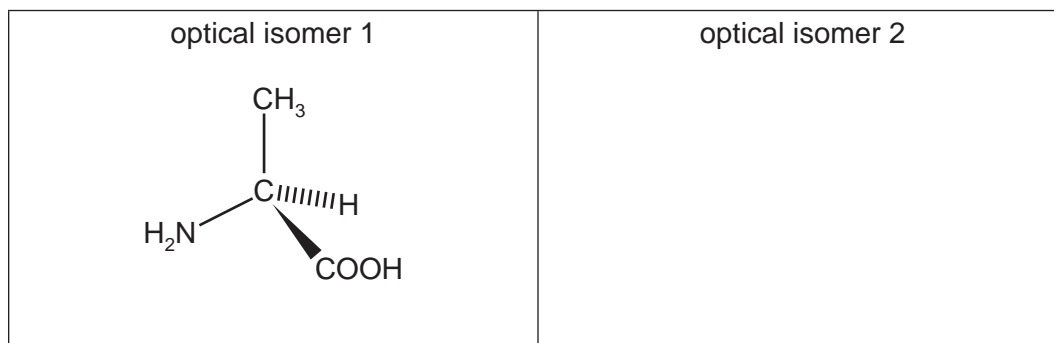


(ii) Give the structural formula of alanine at pH 2.

..... [1]

(iii) Alanine exists as a pair of optical isomers. The structure of one optical isomer is shown in Fig. 5.2.

Draw the three-dimensional structure of the other optical isomer of alanine.



**Fig. 5.2**

[1]

(iv) Polymer **C** forms from the reaction between alanine and 4-aminobutanoic acid,  $\text{H}_2\text{N}(\text{CH}_2)_3\text{COOH}$ .

Draw a repeat unit of **C**. The functional group formed should be displayed.

[2]

(v) State the type of polymerisation shown in (b)(iv).

..... [1]

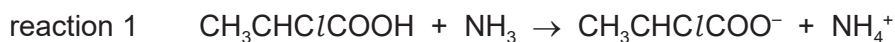
(vi) Scientists are investigating **C** as a replacement for poly(propene) in packaging.

Suggest an advantage of using **C** instead of poly(propene).

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

- (c) A student studies the reaction of  $\text{CH}_3\text{CHClCOOH}$  with aqueous  $\text{NH}_3$  to determine the reaction mechanism.

The student finds that when  $\text{CH}_3\text{CHClCOOH}$  and  $\text{NH}_3$  are added in a 1 : 1 stoichiometric ratio, the conjugate acid and base of the reactants are quickly formed.



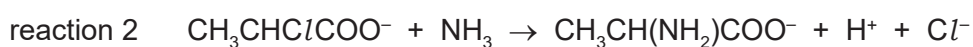
- (i) Identify the conjugate acid–base pairs in reaction 1.

conjugate acid–base pair I ..... and .....

conjugate acid–base pair II ..... and .....

[1]

In an excess of  $\text{NH}_3$ ,  $\text{CH}_3\text{CHClCOO}^-$  undergoes a nucleophilic substitution reaction.



A student investigates the rate of reaction 2. The student mixes  $\text{CH}_3\text{CHClCOO}^-$  with a large excess of  $\text{NH}_3$ . The graph in Fig. 5.3 shows the results obtained.

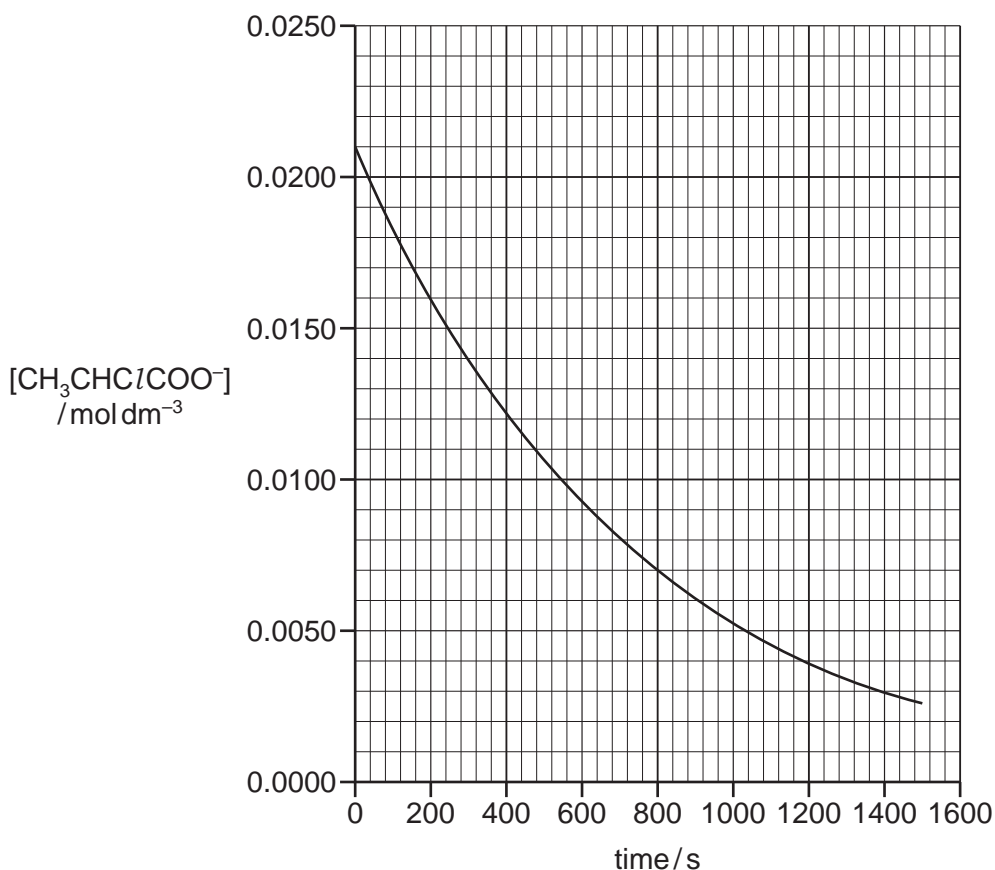


Fig. 5.3

- (ii) Use the graph in Fig. 5.3 to show that reaction 2 is first order with respect to  $[\text{CH}_3\text{CHClCOO}^-]$ .

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

- (iii) Explain why a **large** excess of  $\text{NH}_3$  needs to be used in order to obtain the results in Fig. 5.3.

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

- (iv) The student measures the effect of changing the concentration of  $\text{NH}_3$  on the rate of reaction 2. Table 5.1 shows the results obtained.

**Table 5.1**

experiment	$[\text{CH}_3\text{CHClCOO}^-]$ / $\text{mol dm}^{-3}$	$[\text{NH}_3]$ / $\text{mol dm}^{-3}$	initial rate of reaction / $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.00120	0.00300	$1.47 \times 10^{-5}$
2	0.00120	0.00450	$2.21 \times 10^{-5}$

Use the information in Table 5.1 and in (c)(ii) to determine whether the nucleophilic substitution reaction proceeds via an  $\text{S}_{\text{N}}1$  or an  $\text{S}_{\text{N}}2$  mechanism.

Explain your answer.

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

- (v) Describe the effect of an increase in temperature on the rate of reaction of  $\text{CH}_3\text{CHClCOO}^-$  and  $\text{NH}_3$ .  
Explain your answer.

.....

.....

.....

..... [2]

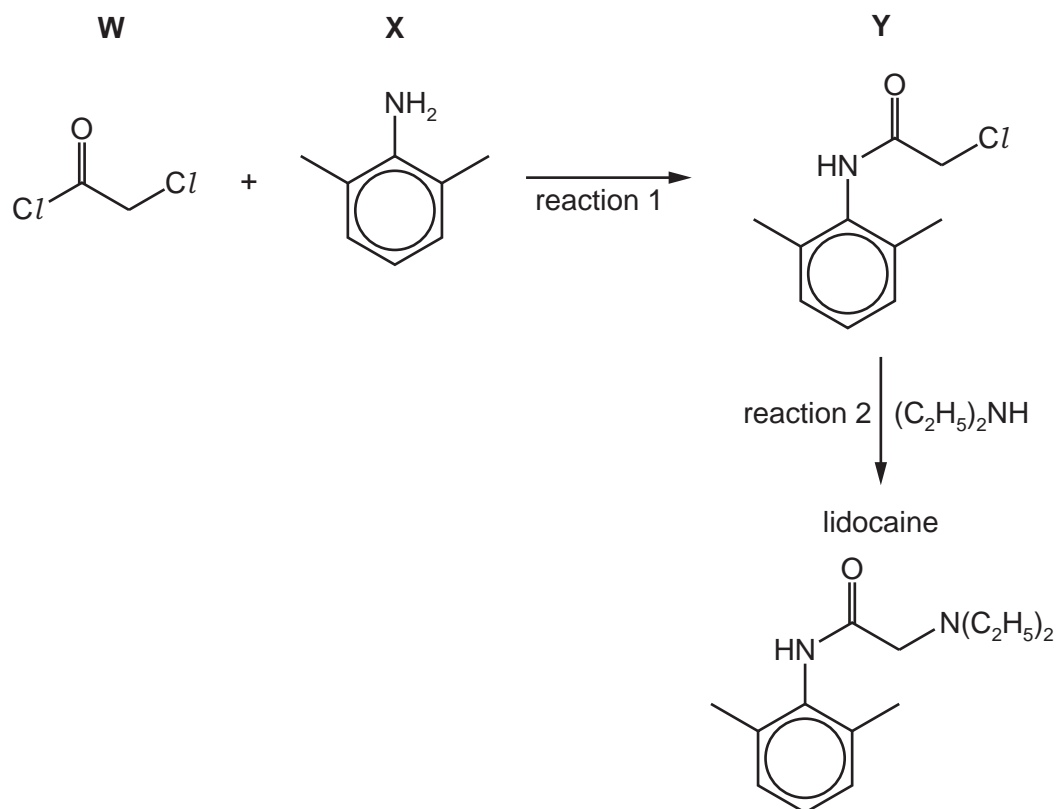
- (vi) When an excess of  $\text{CH}_3\text{CHClCOO}^-$  is used, further substitution reactions occur. One product has the formula  $\text{C}_6\text{H}_9\text{NO}_4^{2-}$ .

Suggest the structure of  $\text{C}_6\text{H}_9\text{NO}_4^{2-}$ .

[1]

[Total: 21]

- 6 Lidocaine is used as an anaesthetic. A synthesis of lidocaine is shown in Fig. 6.1.



**Fig. 6.1**

- (a) **W** can be formed by reacting  $\text{HOCH}_2\text{COOH}$  with an excess of  $\text{SOCl}_2$ .

Write an equation for this reaction.

..... [1]

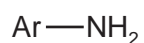
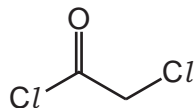
- (b) After **W** and **X** have reacted together, an excess of  $\text{CH}_3\text{COONa}(\text{aq})$  is added to the reaction mixture.

Suggest why.

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

(c) The reaction of **W** with **X**, reaction 1, follows an addition–elimination mechanism.

Complete the mechanism for the reaction of **W** with **X**.  
Include all relevant curly arrows, lone pairs of electrons, charges and partial charges.  
Use Ar–NH<sub>2</sub> to represent **X**.



[4]

(d) (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH reacts with **Y** in reaction 2.

Explain why (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH can act as a nucleophile.

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

- (e) The purity of lidocaine can be checked using thin-layer chromatography. Ethyl ethanoate is used as the solvent.

The  $R_f$  values of **X** and lidocaine are given in Table 6.1.

**Table 6.1**

compound	$R_f$
<b>X</b>	0.49
lidocaine	0.71

- (i) Identify the substances used as the mobile and stationary phases in this thin-layer chromatography experiment.

mobile phase .....

stationary phase .....

[1]

- (ii) Describe how an  $R_f$  value can be calculated.

.....

..... [1]

- (iii) Suggest why the  $R_f$  value for **X** is less than that for lidocaine.

.....

..... [1]

(f) The proton ( $^1\text{H}$ ) NMR spectrum of lidocaine is shown in Fig. 6.2.

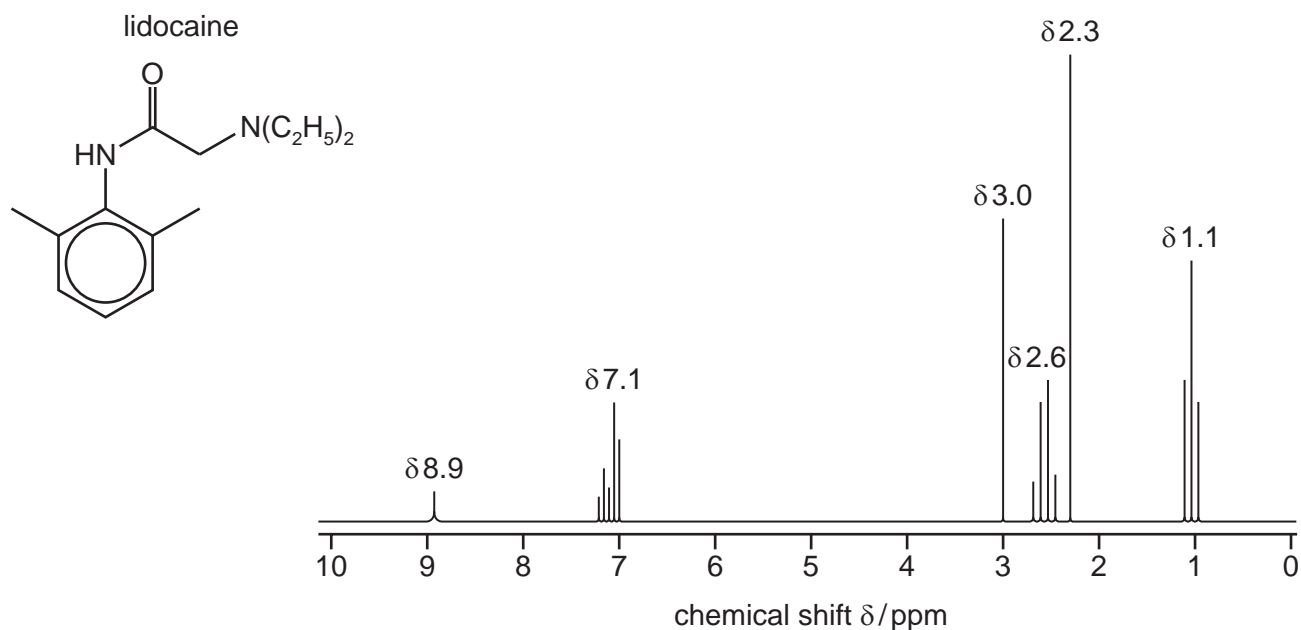


Fig. 6.2

Table 6.2

environment of proton	example	chemical shift range $\delta$ /ppm
alkane	$-\text{CH}_3$ , $-\text{CH}_2-$ , $>\text{CH}-$	0.9–1.7
alkyl next to $\text{C}=\text{O}$	$\text{CH}_3-\text{C}=\text{O}$ , $-\text{CH}_2-\text{C}=\text{O}$ , $>\text{CH}-\text{C}=\text{O}$	2.2–3.0
alkyl next to aromatic ring	$\text{CH}_3-\text{Ar}$ , $-\text{CH}_2-\text{Ar}$ , $>\text{CH}-\text{Ar}$	2.3–3.0
alkyl next to electronegative atom	$\text{CH}_3-\text{O}$ , $-\text{CH}_2-\text{O}$ , $-\text{CH}_2-\text{Cl}$	3.2–4.0
attached to alkene	$=\text{CHR}$	4.5–6.0
attached to aromatic ring	$\text{H}-\text{Ar}$	6.0–9.0
aldehyde	$\text{HCOR}$	9.3–10.5
alcohol	$\text{ROH}$	0.5–6.0
phenol	$\text{Ar}-\text{OH}$	4.5–7.0
carboxylic acid	$\text{RCOOH}$	9.0–13.0
alkyl amine	$\text{R}-\text{NH}-$	1.0–5.0
aryl amine	$\text{Ar}-\text{NH}_2$	3.0–6.0
amide	$\text{RCONHR}$	5.0–12.0



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(i) Name the splitting patterns at  $\delta$  2.6 and  $\delta$  1.1.

$\delta$  2.6 .....  $\delta$  1.1 ..... [1]

(ii) The relative peak area of the peaks at  $\delta$  3.0 and  $\delta$  2.3 is 1 : 3 respectively.

Identify the protons in the  $^1\text{H}$  NMR spectrum of lidocaine that are responsible for the peaks at the following chemical shift values.

$\delta$  7.1 .....

$\delta$  3.0 .....

$\delta$  2.3 ..... [2]

(iii) Predict the number of peaks in the **carbon-13** ( $^{13}\text{C}$ ) NMR spectrum of lidocaine.

..... [1]

[Total: 14]



**Important values, constants and standards**

molar gas constant	$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^4 \text{ C mol}^{-1}$
Avogadro constant	$L = 6.022 \times 10^{23} \text{ mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19} \text{ C}$
molar volume of gas	$V_m = 22.4 \text{ dm}^3 \text{ mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (4.18 $\text{J g}^{-1} \text{ K}^{-1}$ )

