



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.

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

It is found that 0.390g 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 = 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.

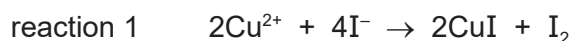
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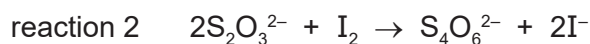
.....

..... [2]

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



The 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 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 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.

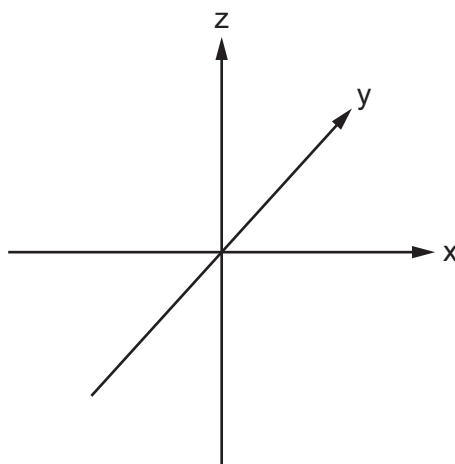
concentration of $\text{Cu}^{2+}(\text{aq}) = \dots\dots\dots \text{ mol dm}^{-3}$ [2]

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

..... [1]

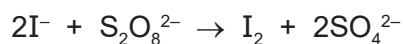
- (iii) Copper(I) and copper(II) both contain electrons in all five 3d orbitals.

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



[1]

- (d) The reaction of I^- ions with persulfate ions, $\text{S}_2\text{O}_8^{2-}$, 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 $\text{KI}(\text{aq})$.
 The solubility of HgI_2 at 25°C is $1.00 \times 10^{-7} \text{g dm}^{-3}$.

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

[M_r : HgI_2 , 454.4]

value of K_{sp} =

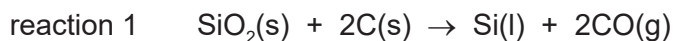
units =

[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 SiO_2 by reaction with carbon at over 2000°C .



(i) Explain why the entropy change, ΔS , of reaction 1 is positive.

.....
 [1]

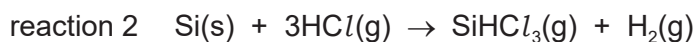
(ii) Reaction 1 is highly endothermic.

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 SiHCl_3 . The SiHCl_3 formed is then distilled to remove other impurities.



(i) Table 2.1 shows some standard entropy data.

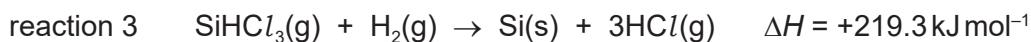
Table 2.1

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

Use the data in Table 2.1 to calculate ΔS^\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.



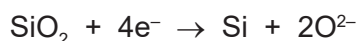
Use this information and your answer to **(b)(i)** to calculate the temperature, in K, at which reaction 3 becomes feasible.

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 SiO_2 dissolved in molten 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 TiO_2 in minerals.

(a) (i) Define transition element.

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

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

1

2 [1]

(b) The TiO^{2+} ion forms when TiO_2 reacts with an excess of sulfuric acid.

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]

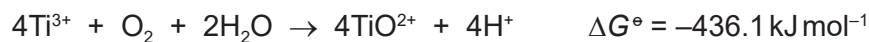
(ii) Give the electronic configuration of an isolated Ti^{3+} ion.

$1s^2$ [1]

(iii) Write an ionic equation for the reduction of 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.

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

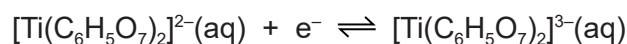
(ii) When aqueous citrate ions, $\text{C}_6\text{H}_5\text{O}_7^{3-}$, are added to $\text{Ti}^{3+}(\text{aq})$, the $[\text{Ti}(\text{C}_6\text{H}_5\text{O}_7)_2]^{3-}(\text{aq})$ complex forms.

Explain, in terms of d-orbitals, why 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 TiO_2 are shown in Fig. 3.1.

The anion, acac^- , is a bidentate ligand.

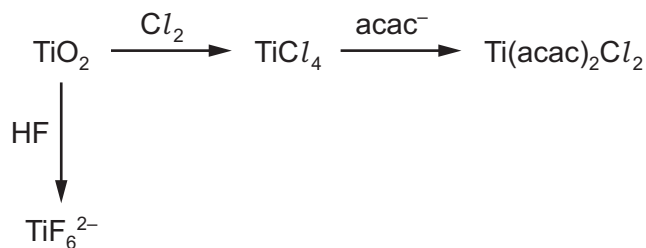


Fig. 3.1

(i) The titanium ions in 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 TiF_6^{2-} from 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.

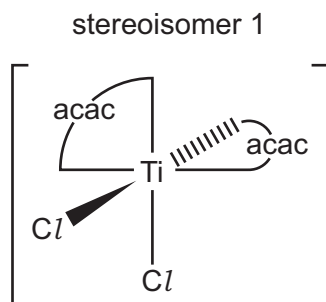
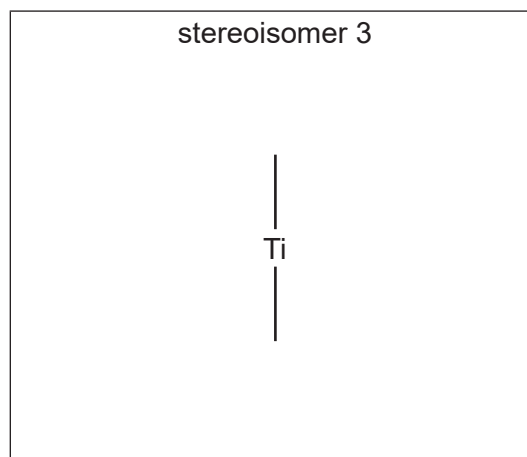
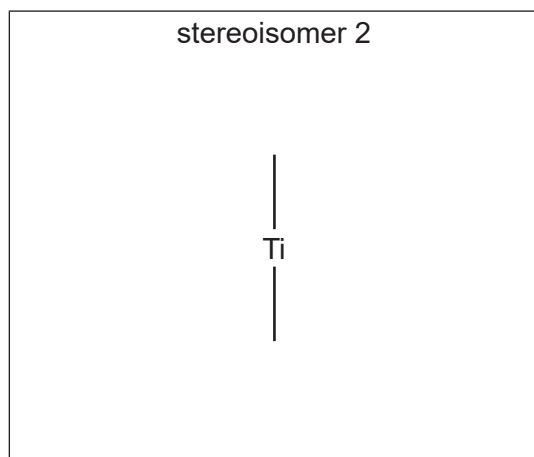


Fig. 3.2

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



[2]

(v) The 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.

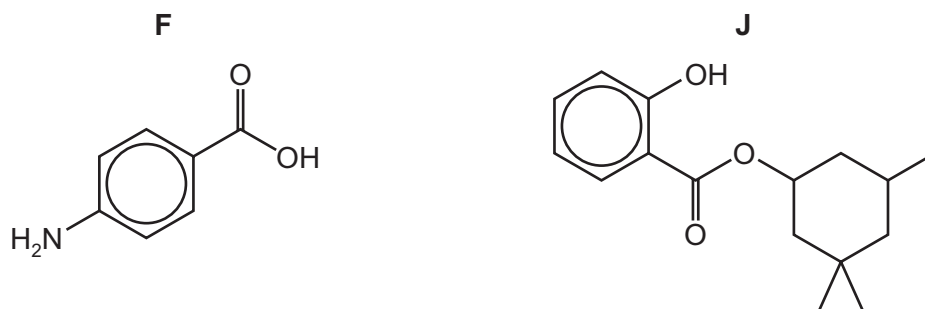


Fig. 4.1

(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 ₃ and concentrated H ₂ SO ₄	D
3	D	hot alkaline KMnO ₄ then dilute H ₂ SO ₄	E
4		F

[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.

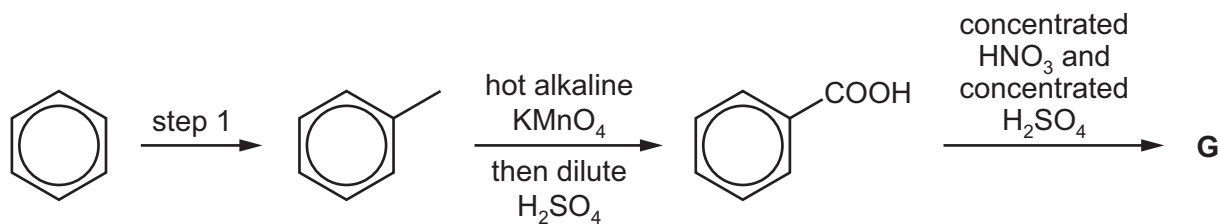


Fig. 4.2

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.

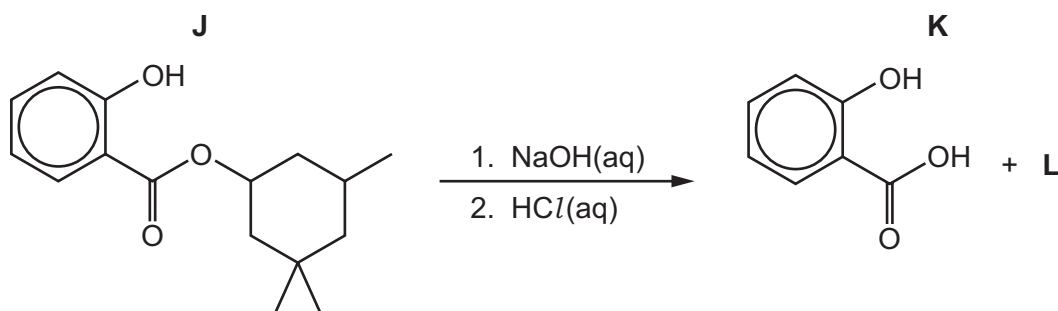


Fig. 4.3

- (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, C₆H₅OH.

Fig. 4.4 shows several reactions of phenol.

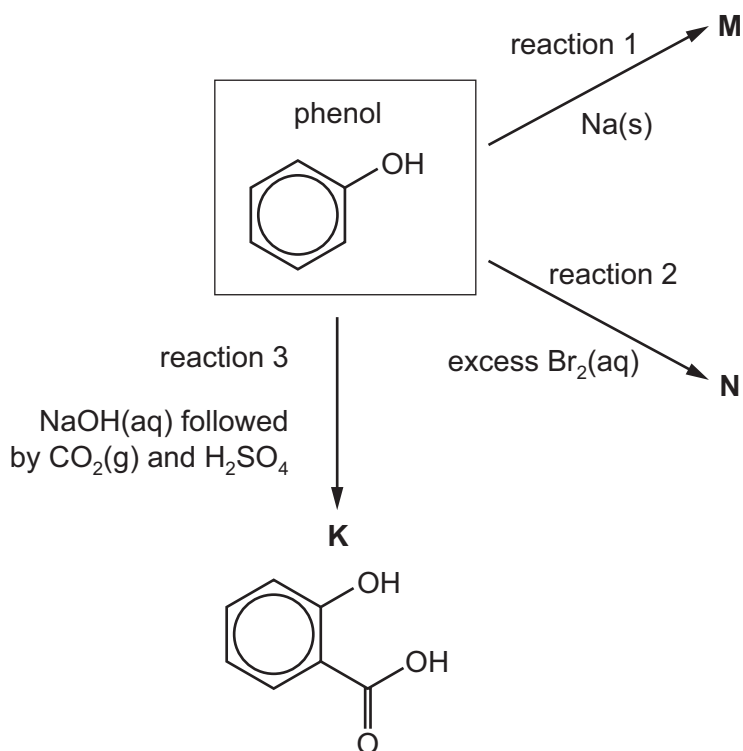


Fig. 4.4

(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.

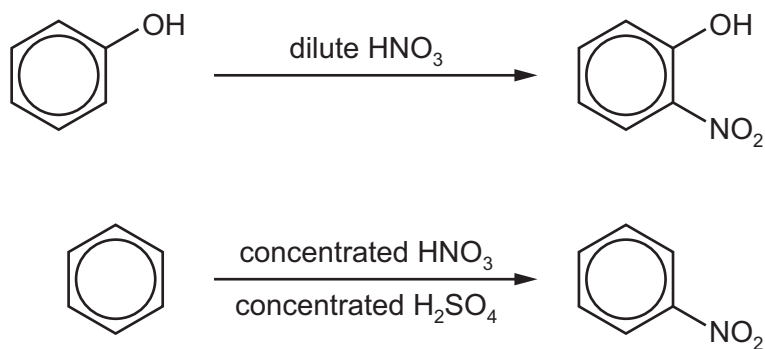


Fig. 4.5

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 cm^3 of distilled water to produce a solution of pH 1.51.

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

$\text{p}K_a = \dots\dots\dots$ [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 NH_3 , alanine forms.

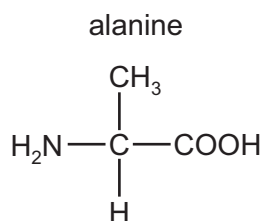


Fig. 5.1

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.

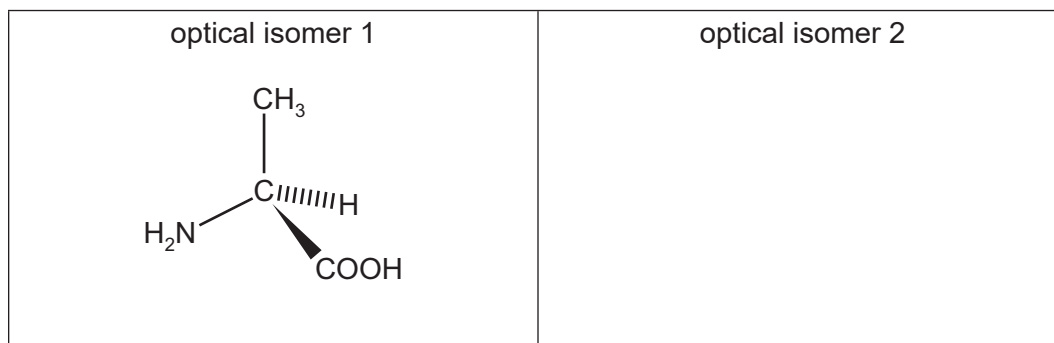


Fig. 5.2

[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]

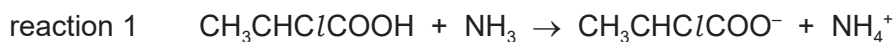
- (vi) Scientists are investigating **C** as a replacement for poly(propene) in packaging.

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 NH_3 to determine the reaction mechanism.

The student finds that when $\text{CH}_3\text{CHClCOOH}$ and NH_3 are added in a 1 : 1 stoichiometric ratio, the conjugate acid and base of the reactants are quickly formed.



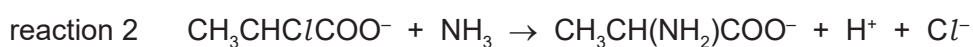
- (i) Identify the conjugate acid–base pairs in reaction 1.

conjugate acid–base pair I and

conjugate acid–base pair II and

[1]

In an excess of 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 NH_3 . The graph in Fig. 5.3 shows the results obtained.

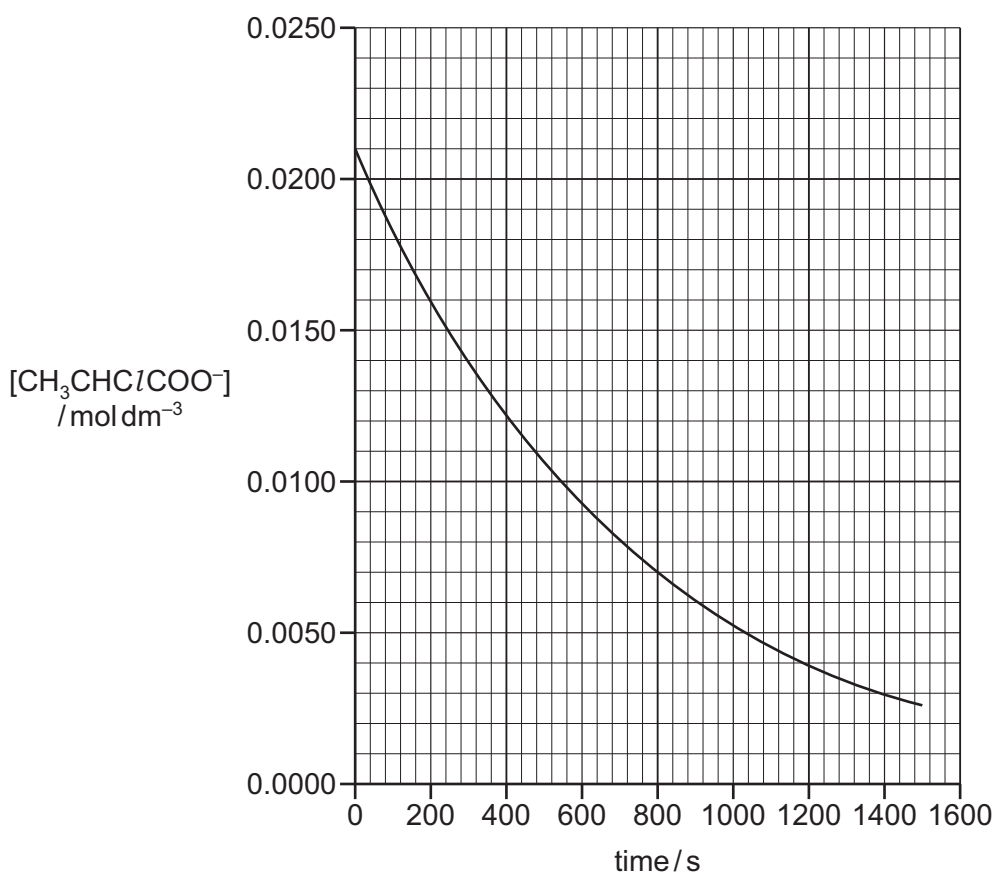


Fig. 5.3

- (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 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 NH_3 on the rate of reaction 2. Table 5.1 shows the results obtained.

Table 5.1

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

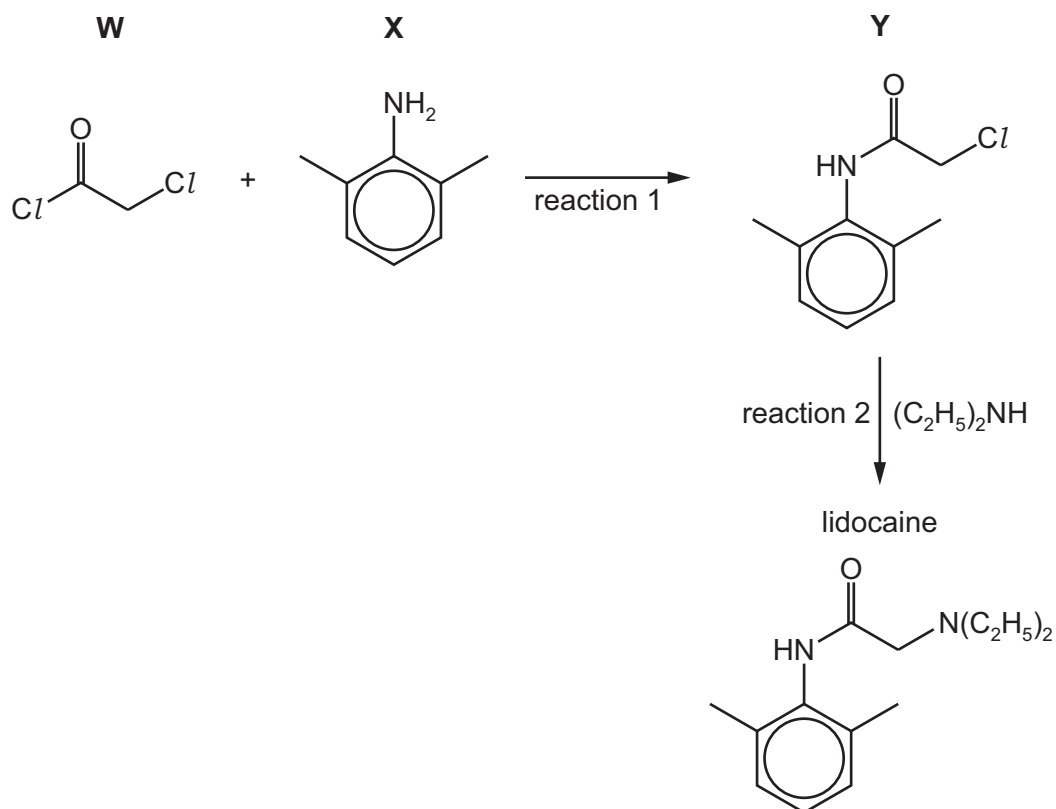


Fig. 6.1

- (a) **W** can be formed by reacting HOCH_2COOH with an excess of SOCl_2 .

Write an equation for this reaction.

..... [1]

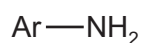
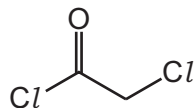
- (b) After **W** and **X** have reacted together, an excess of $\text{CH}_3\text{COONa}(\text{aq})$ is added to the reaction mixture.

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–NH₂ to represent **X**.



[4]

(d) (C₂H₅)₂NH reacts with **Y** in reaction 2.

Explain why (C₂H₅)₂NH 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
X	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 (^1H) NMR spectrum of lidocaine is shown in Fig. 6.2.

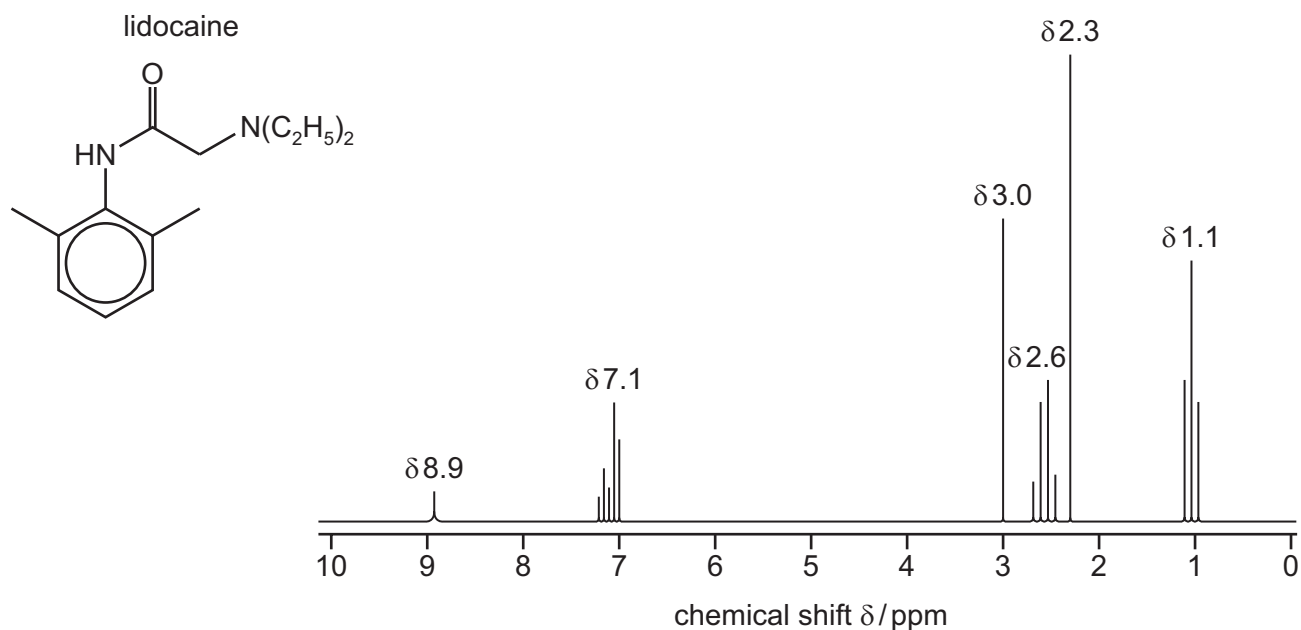


Fig. 6.2

Table 6.2

environment of proton	example	chemical shift range δ /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	CH_3-Ar , $-\text{CH}_2-\text{Ar}$, $>\text{CH}-\text{Ar}$	2.3–3.0
alkyl next to electronegative atom	CH_3-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	HCOR	9.3–10.5
alcohol	ROH	0.5–6.0
phenol	$\text{Ar}-\text{OH}$	4.5–7.0
carboxylic acid	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	RCONHR	5.0–12.0

(i) Name the splitting patterns at δ 2.6 and δ 1.1.

δ 2.6 δ 1.1 [1]

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

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

δ 7.1

δ 3.0

δ 2.3 [2]

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

..... [1]

[Total: 14]

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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 $\text{J g}^{-1} \text{ K}^{-1}$)

The Periodic Table of Elements

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		Key																			
		atomic number																			
		atomic symbol																			
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