



CANDIDATE
NAME

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CENTRE
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9701/42

February/March 2022

2 hours

No additional materials are needed.

- 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.

- 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 $\text{H}_2\text{O}_2(\text{aq})$ 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 $\text{H}_2\text{O}_2(\text{aq})$ 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, $\text{CH}_3(\text{CH}_2)_3\text{COCH}_3$, 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]

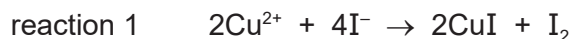
(iii) Suggest the trend in the magnitude of the lattice energies of the Group 1 iodides, LiI, NaI, KI.

Explain your answer.

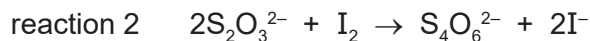
.....

 [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 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.

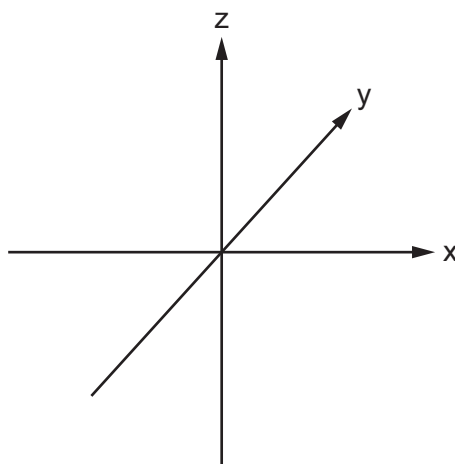
concentration of $\text{Cu}^{2+}(\text{aq}) = \dots\dots\dots \text{mol dm}^{-3}$ [2]

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

$\dots\dots\dots$ [1]

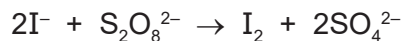
- (iii) Copper(I) and copper(II) both contain electrons in all five 3d orbitals.

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]

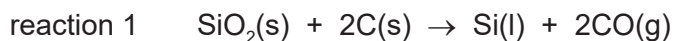
value of K_{sp} = ...

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]

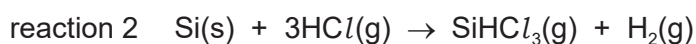
(ii) Reaction 1 is highly endothermic.

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.

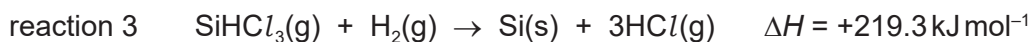
Table 2.1

compound	standard entropy, $S^\circ/\text{JK}^{-1}\text{mol}^{-1}$
$\text{Si}(\text{s})$	19
$\text{HCl}(\text{g})$	187
$\text{SiHCl}_3(\text{g})$	314
$\text{H}_2(\text{g})$	131

Use the data in Table 2.1 to calculate ΔS° for reaction 2.

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

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



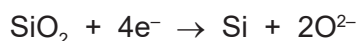
Use this information and your answer to **(b)(i)** to calculate the temperature, in K, at which reaction 3 becomes feasible.

Show your working.

[If you were unable to answer **(b)(i)**, you should use $\Delta S^\circ = -150 \text{ J K}^{-1} \text{ mol}^{-1}$ 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]

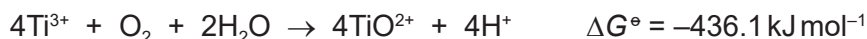
(ii) Give the electronic configuration of an isolated Ti^{3+} ion.

$1s^2$ [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° , 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° , in V, of the $\text{TiO}^{2+}(\text{aq})/\text{Ti}^{3+}(\text{aq})$ half-cell. Show your working.

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

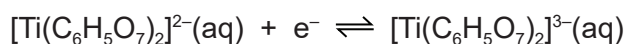
- (ii) When aqueous citrate ions, $\text{C}_6\text{H}_5\text{O}_7^{3-}$, are added to $\text{Ti}^{3+}(\text{aq})$, the $[\text{Ti}(\text{C}_6\text{H}_5\text{O}_7)_2]^{3-}(\text{aq})$ complex forms.

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° , 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.

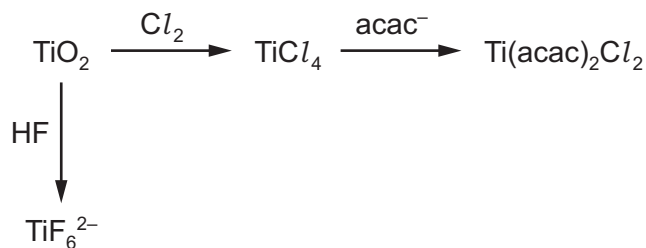


Fig. 3.1

(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.

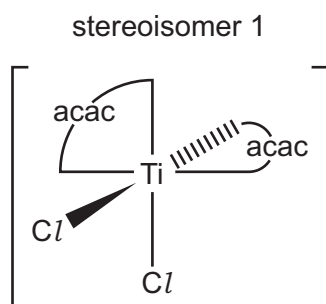
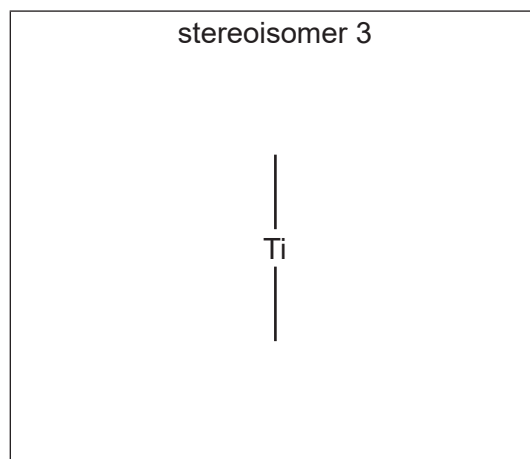
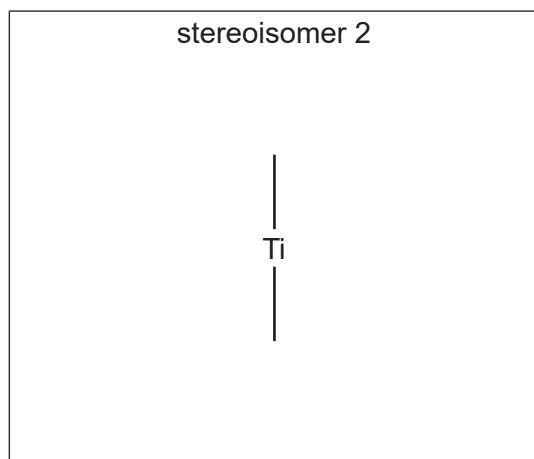


Fig. 3.2

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.

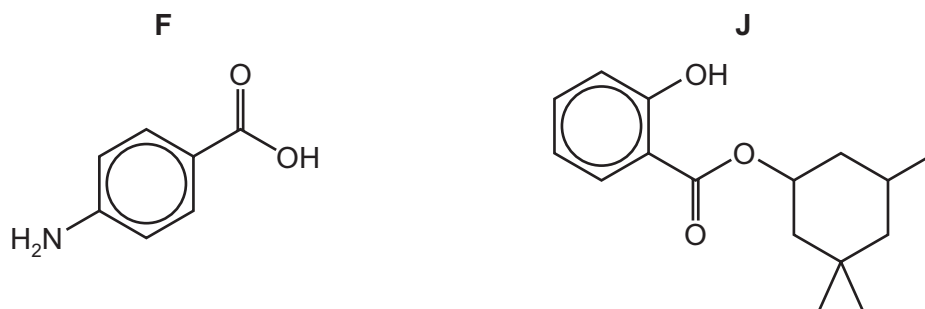


Fig. 4.1

(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_2SO_4	D
3	D	hot alkaline KMnO_4 then dilute H_2SO_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.

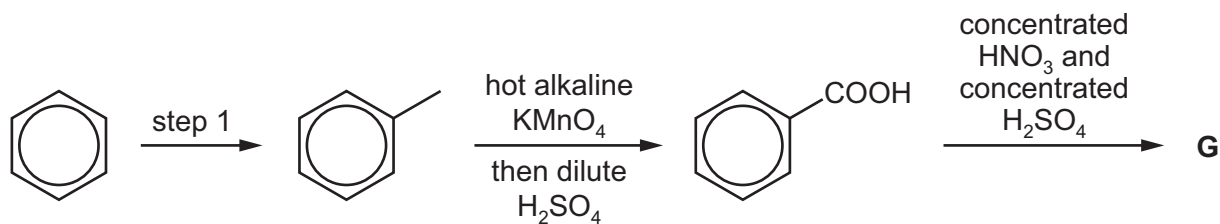


Fig. 4.2

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.

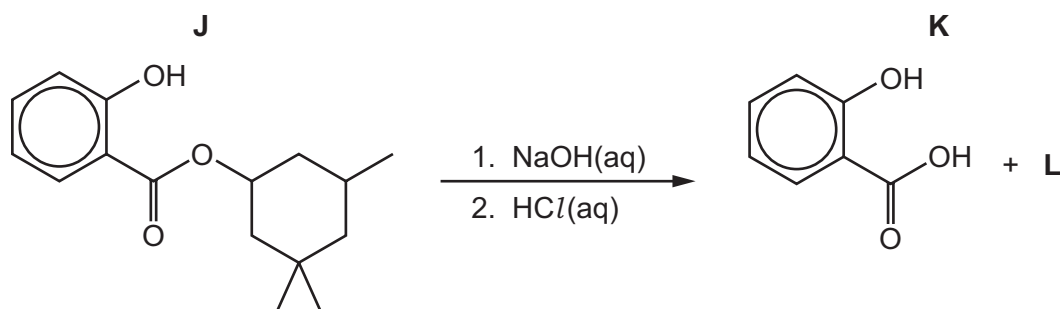


Fig. 4.3

- (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.

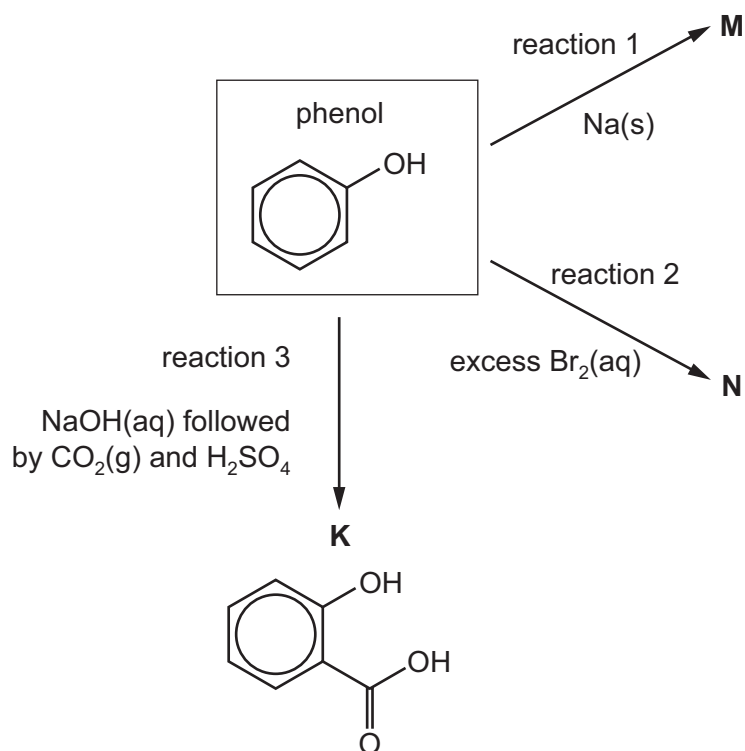


Fig. 4.4

(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.

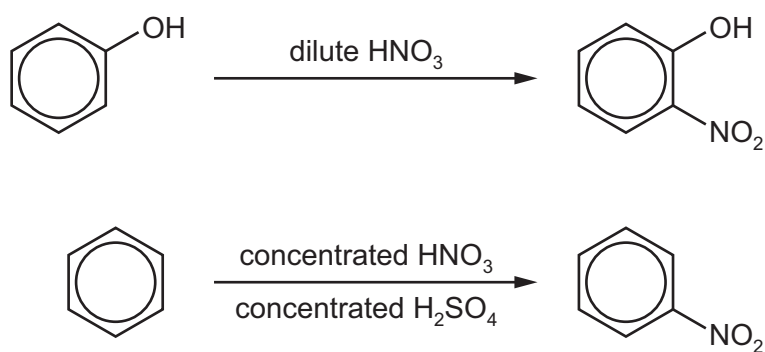


Fig. 4.5

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 $\text{p}K_{\text{a}}$ 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 NH_3 , alanine forms.

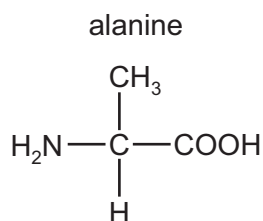


Fig. 5.1

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.

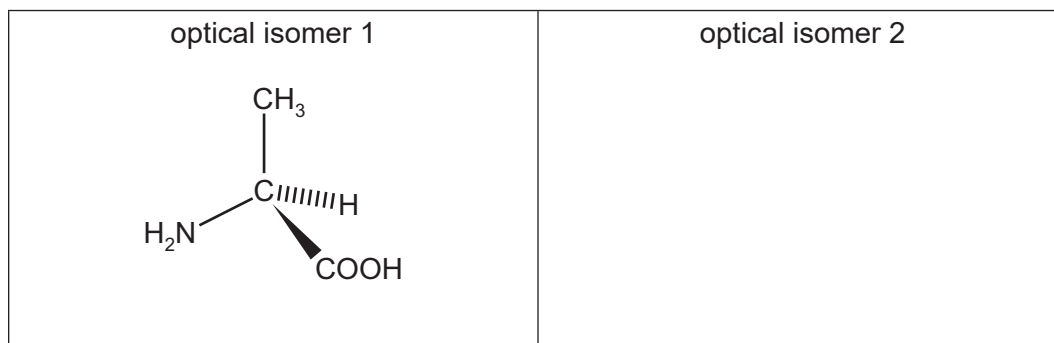


Fig. 5.2

[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.

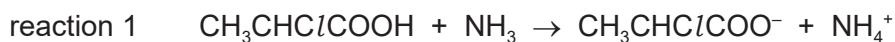
Suggest an advantage of using **C** instead of poly(propene).

.....

..... [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.



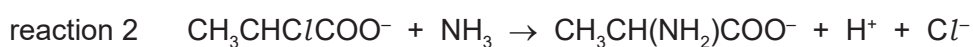
- (i) Identify the conjugate acid–base pairs in reaction 1.

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.

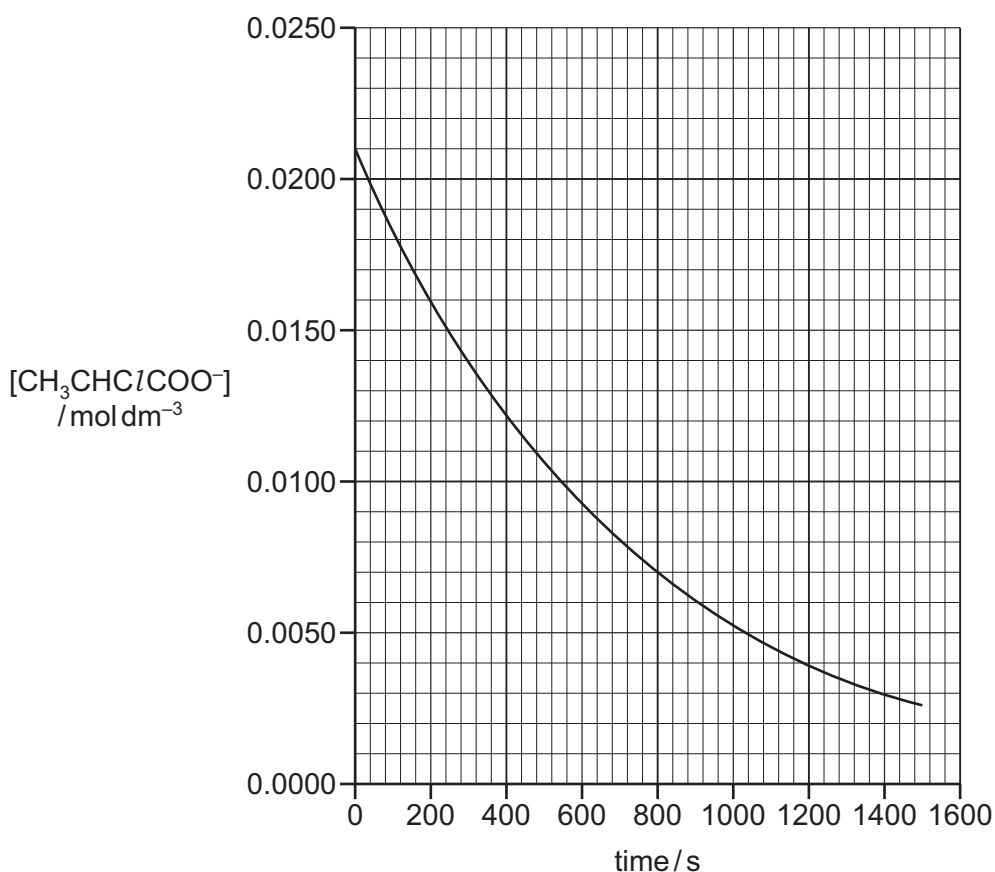


Fig. 5.3

- (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.

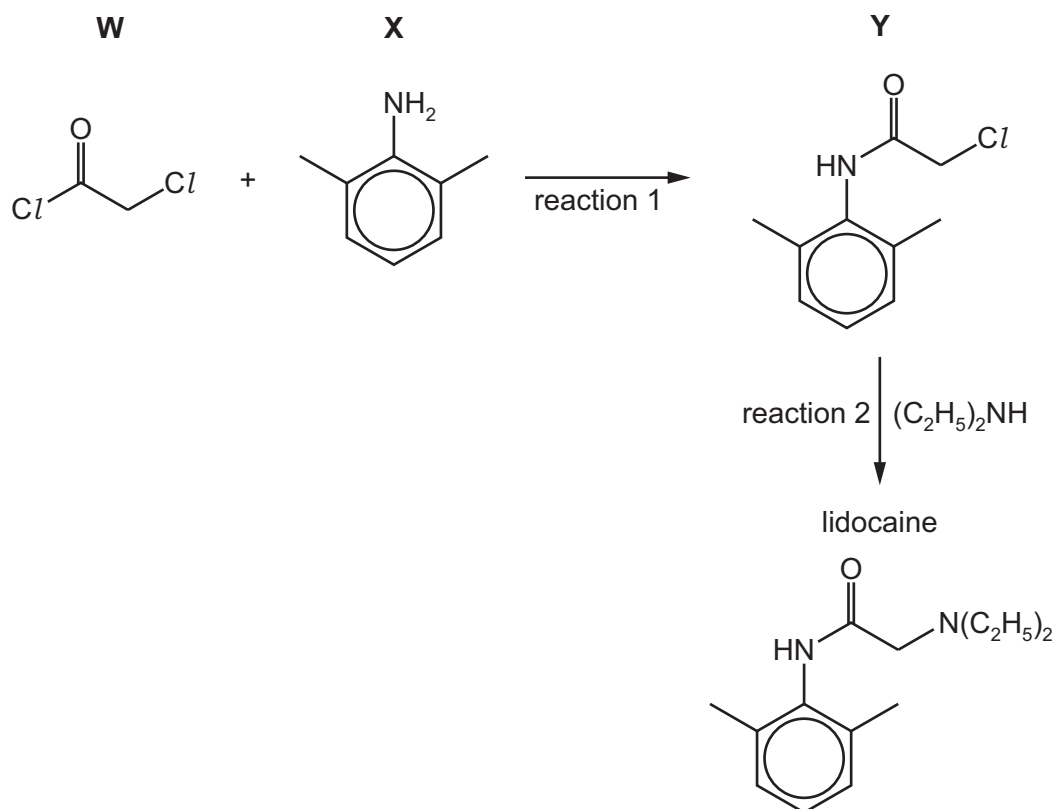


Fig. 6.1

- (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.

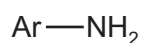
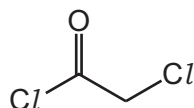
Suggest why.

.....

..... [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-NH_2 to represent **X**.



[4]

(d) $(\text{C}_2\text{H}_5)_2\text{NH}$ reacts with **Y** in reaction 2.

Explain why $(\text{C}_2\text{H}_5)_2\text{NH}$ 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
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.

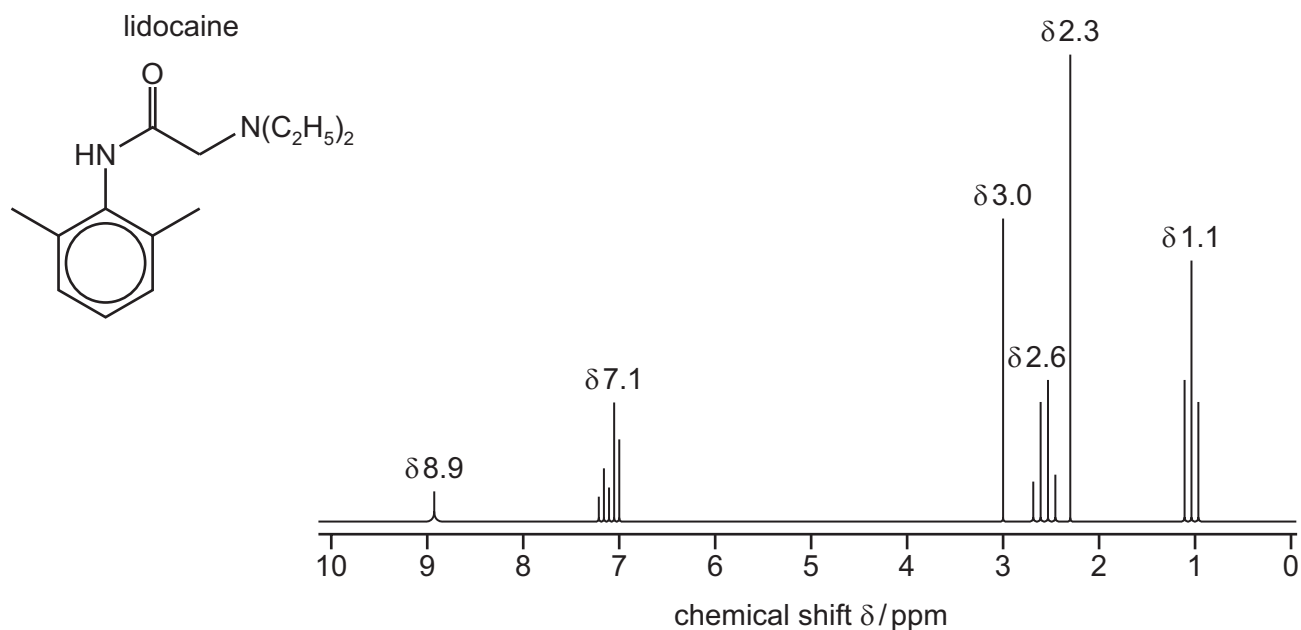


Fig. 6.2

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 $\delta 2.6$ 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 ^1H 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}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 J g ⁻¹ K ⁻¹)

The Periodic Table of Elements

Group																		
1	2	Key										13	14	15	16	17	18	
		1Hhydrogen1.0																
		atomic number atomic symbol name relative atomic mass																
3Li lithium 6.9	4Be beryllium 9.0																	
11Na sodium 23.0	12Mg magnesium 24.3																	
19K potassium 39.1	20Ca calcium 40.1	21Sc scandium 45.0	22Ti titanium 47.9	23V vanadium 50.9	24Cr chromium 52.0	25Mn manganese 54.9	26Fe iron 55.8	27Co cobalt 58.9	28Ni nickel 58.7	29Cu copper 63.5	30Zn zinc 65.4	31Ga gallium 69.7	32Ge germanium 72.6	33As arsenic 74.9	34Se selenium 79.0	35Br bromine 79.9	36Kr krypton 83.8	
37Rb rubidium 85.5	38Sr strontium 87.6	39Y yttrium 88.9	40Zr zirconium 91.2	41Nb niobium 92.9	42Mo molybdenum 95.9	43Tc technetium —	44Ru ruthenium 101.1	45Rh rhodium 102.9	46Pd palladium 106.4	47Ag silver 107.9	48Cd cadmium 112.4	49In indium 114.8	50Sn tin 118.7	51Sb antimony 121.6	52Te tellurium 127.6	53I iodine 126.9	54Xe xenon 131.3	
55Cs caesium 132.9	56Ba barium 137.3	57–71lanthanoids	72Hf hafnium 178.5	73Ta tantalum 180.9	74W tungsten 183.8	75Re rhenium 186.2	76Os osmium 190.2	77Ir iridium 192.2	78Pt platinum 195.1	79Au gold 197.0	80Hg mercury 200.6	81Tl thallium 204.4	82Pb lead 207.2	83Bi bismuth 209.0	84Po polonium —	85At astatine —	86Rn radon —	
87Fr francium —	88Ra radium —	89–103actinoids	104Rf rutherfordium —	105Db dubnium —	106Sg seaborgium —	107Bh bohrium —	108Hs hassium —	109Mt meitnerium —	110Ds darmstadtium —	111Rg roentgenium —	112Cn copernicium —	113Nh nihonium —	114Fl flerovium —	115Mc moscovium —	116Lv livermorium —	117Ts tennessine —	118Og oganesson —	

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.4	61 Pm promethium —	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
	89 Ac actinium —	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium —	94 Pu plutonium —	95 Am americium —	96 Cm curium —	97 Bk berkelium —	98 Cf californium —	99 Es einsteinium —	100 Fm fermium —	101 Md mendelevium —	102 No nobelium —	103 Lr lawrencium —

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