

Please write clearly in block capitals.

Centre number

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Candidate number

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Surname

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Forename(s)

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Candidate signature

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I declare this is my own work.

# A-level CHEMISTRY

## Paper 2 Organic and Physical Chemistry

Monday 8 June 2020

Afternoon

Time allowed: 2 hours

### Materials

For this paper you must have:

- the Periodic Table/Data Booklet, provided as an insert (enclosed)
- a ruler with millimetre measurements
- a scientific calculator, which you are expected to use where appropriate.

### Instructions

- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do **not** write outside the box around each page or on blank pages.
- If you need extra space for your answer(s), use the lined pages at the end of this book. Write the question number against your answer(s).
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

### Information

- The marks for questions are shown in brackets.
- The maximum mark for this paper is 105.

For Examiner's Use

Question	Mark
1	
2	
3	
4	
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6	
7	
8	
9	
<b>TOTAL</b>	

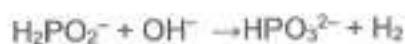


Answer **all** questions in the spaces provided.

0 1

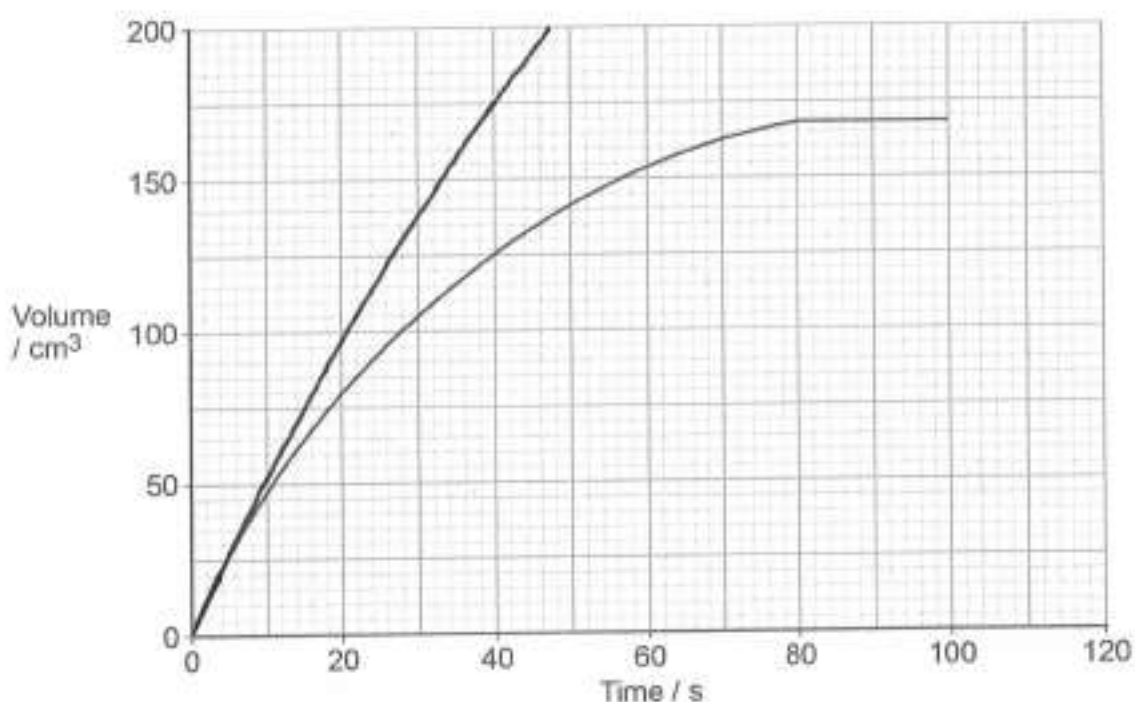
This question is about rates of reaction.

Phosphinate ions ( $\text{H}_2\text{PO}_2^-$ ) react with hydroxide ions to produce hydrogen gas as shown.



A student completed an experiment to determine the initial rate of this reaction. The student used a solution containing phosphinate ions and measured the volume of hydrogen gas collected every 20 seconds at a constant temperature. **Figure 1** shows a graph of the student's results.

**Figure 1**



0 1 . 1

Use the graph in **Figure 1** to determine the initial rate of reaction for this experiment. State its units. Show your working on the graph.

[3 marks]

$$m = \frac{\Delta y}{\Delta x} = \frac{200}{36} = 5.5 \text{ cm}^3 \text{ s}^{-1}$$

Rate 5.5 Units cm<sup>3</sup> s<sup>-1</sup>



0 1 . 2

Another student reacted different initial concentrations of phosphinate ions with an excess of hydroxide ions. The student measured the time ( $t$ ) taken to collect  $15 \text{ cm}^3$  of hydrogen gas. Each experiment was carried out at the same temperature. Table 1 shows the results.

Table 1

Initial $[\text{H}_2\text{PO}_2^-] / \text{mol dm}^{-3}$	$t / \text{s}$
0.25	64
0.35	32
0.50	16
1.00	4

State the relationship between the initial concentration of phosphinate and time ( $t$ ).

Deduce the order of the reaction with respect to phosphinate.

[2 marks]

Relationship  $[\text{H}_2\text{PO}_2^-]^{-2} \propto 1/t$

Order 2

Question 1 continues on the next page

Turn over ►



- 01.3 Complete the diagram in Figure 2 to show how the hydrogen gas could be collected and measured in the experiments in Questions 01.1 and 01.2.

[1 mark]

Figure 2



The rate equation for a different reaction is

$$\text{rate} = k [\text{L}] [\text{M}]^2$$

- 01.4 Deduce the overall effect on the rate of reaction when the concentrations of both L and M are halved.

[1 mark]

The rate will fall by a factor  
of 8



- 0 1 . 5 The rate of reaction is  $0.0250 \text{ mol dm}^{-3} \text{ s}^{-1}$  when the concentration of L is  $0.0155 \text{ mol dm}^{-3}$

Calculate the concentration of M if the rate constant is  $21.3 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$

[3 marks]

$$\begin{aligned}
 [M]^2 &= \frac{\text{Rate}}{k[L]} = \frac{0.0250}{21.3 \times 0.0155} \\
 &= 7.57 \times 10^{-2} \text{ mol dm}^{-3} \\
 m &= \sqrt{7.57 \times 10^{-2}} \\
 &= 0.275 \text{ mol dm}^{-3}
 \end{aligned}$$

Concentration of M 0.275 mol dm<sup>-3</sup>

- 0 1 . 6 Define the term overall order of reaction.

[1 mark]

The sum of the powers to which the concentrations of reactions are raised in the rate equation.

11

Turn over for the next question

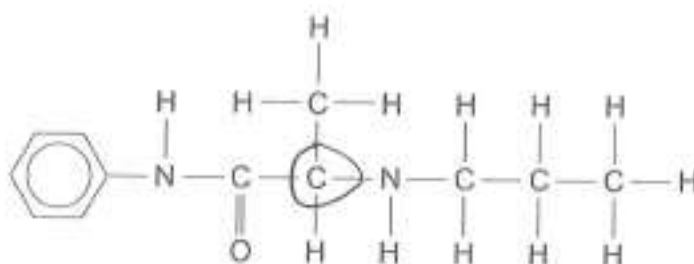
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0 2

Prilocaine is used as an anaesthetic in dentistry.  
Figure 3 shows the structure of prilocaine.

Figure 3



0 2 . 1

Draw a circle around any chiral centre(s) in Figure 3.

[1 mark]

0 2 . 2

Identify the functional group(s) in the prilocaine molecule.

[1 mark]

Tick (✓) the box(es) corresponding to the functional group(s).

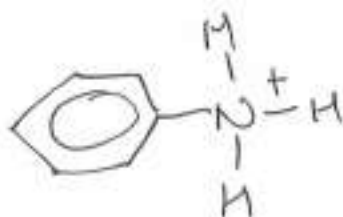
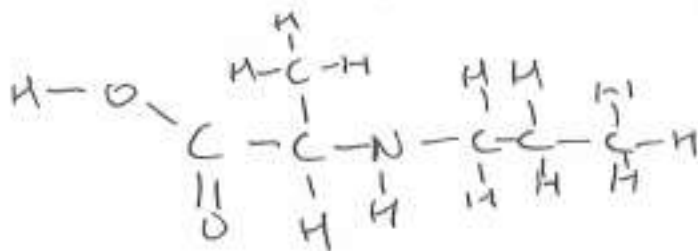
Amide	Amine	Ester	Ketone
✓	✓		

0 2 . 3

Prilocaine is completely hydrolysed in the human body to give a mixture of products.

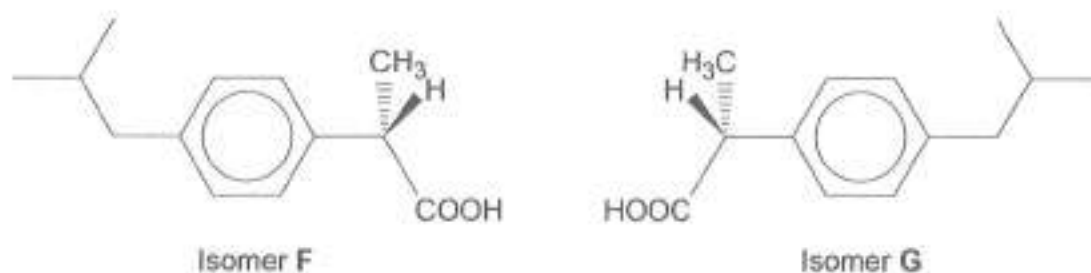
Draw the structures of the two organic products formed in the complete hydrolysis of prilocaine in acidic conditions.

[3 marks]



0 2 . 4 Figure 4 shows optical isomers F and G.

Figure 4



Isomer F is the active compound in the medicine ibuprofen.

In the manufacture of ibuprofen both isomers F and G are formed. An enzyme is then used to bind to isomer G and catalyse its hydrolysis.

After the products of hydrolysis of G are removed, a pure sample of isomer F is collected.

Explain how a structural feature of this enzyme enables it to catalyse the hydrolysis of isomer G but not the hydrolysis of isomer F.

[2 marks]

The enzyme has an active site that matches the stereochemistry of only the G isomer

7

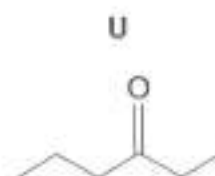
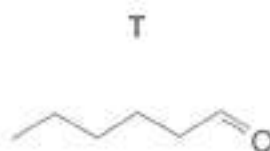
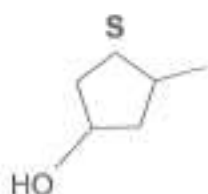
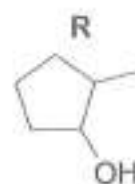
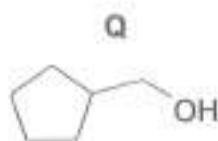
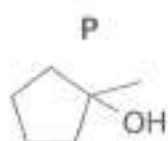
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0 3

This question is about the structural isomers shown.



0 3 . 1

Identify the isomer(s) that would react when warmed with acidified potassium dichromate(VI).

State the expected observation when acidified potassium dichromate(VI) reacts.

[2 marks]

Isomer(s) Q, R, S, TExpected observation Orange solution turns green

0 3 . 2

Identify the isomer(s) that would react with Tollens' reagent.

State the expected observation when Tollens' reagent reacts.

[2 marks]

Isomer(s) TExpected observation silver mirror



- 0 3 . 3 Separate samples of each isomer are warmed with ethanoic acid and a few drops of concentrated sulfuric acid. In each case the mixture is then poured into a solution of sodium hydrogencarbonate.

Identify the isomer(s) that would react with ethanoic acid.

Suggest a simple way to detect if the ethanoic acid reacts with each isomer.

Give a reason why the mixture is poured into sodium hydrogencarbonate solution.

[3 marks]

Isomer(s) P, Q, R, S

Suggestion

Sweet smelling liquid

Reason To react with any excess acid

- 0 3 . 4 State the type of structural isomerism shown by isomers P, Q, R and S.

[1 mark]

Position

- 0 3 . 5 Describe fully how infrared spectra can be used to distinguish between isomers R, S and T.

Use data from Table A in the Data Booklet in your answer.

[4 marks]

R and S would show peaks at  
3230 - 3550  $\text{cm}^{-1}$  for the O-H bond  
T has a C=O peak at 1680 - 1750  $\text{cm}^{-1}$

R and S will have unique fingerprint  
regions below 1500  $\text{cm}^{-1}$  that can be  
compared to a data base

- 0 3 . 6 State why mass spectrometry using electrospray ionisation is not a suitable method to distinguish between the isomers.

[1 mark]

All have the same  $M_r$



0 4

Aspirin can be produced by reacting salicylic acid with ethanoic anhydride. An incomplete method to determine the yield of aspirin is shown.

1. Add about 6 g of salicylic acid to a weighing boat.
2. Place the weighing boat on a 2 decimal place balance and record the mass.
3. Tip the salicylic acid into a 100 cm<sup>3</sup> conical flask.
4. Re weigh the empty boat
5. Add 10 cm<sup>3</sup> of ethanoic anhydride to the conical flask and swirl.
6. Add 5 drops of concentrated phosphoric acid.
7. Warm the flask for 20 minutes.
8. Add ice-cold water to the reaction mixture and place the flask in an ice bath.
9. Filter off the crude aspirin from the mixture and leave it to dry.
10. Weigh the crude aspirin and calculate the yield.

0 4 . 1

Describe the instruction that is missing from step 4 of the method.

Justify why this step is necessary.

[2 marks]

Instruction re weigh the empty boat

Justification Allows calculation of exact mass of salicylic acid added to reaction mixture

0 4 . 2

Suggest a suitable piece of apparatus to measure out the ethanoic anhydride in step 5.

[1 mark]

10 cm<sup>3</sup> Measuring Cylinder

0 4 . 3

Identify a hazard of using concentrated phosphoric acid in step 6.

[1 mark]

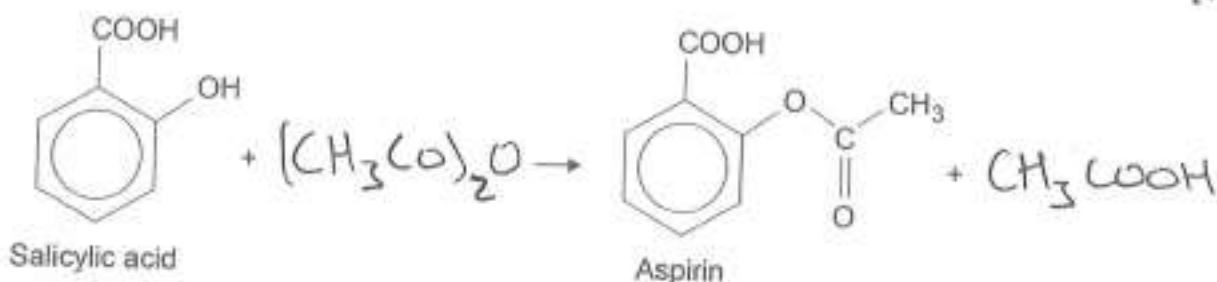
phosphoric acid is corrosive.



0 4 . 4

Complete the equation for the reaction of salicylic acid with ethanoic anhydride to produce aspirin.

[1 mark]



0 4 . 5

A 6.01 g sample of salicylic acid ( $M_r = 138.0$ ) is reacted with  $10.5 \text{ cm}^3$  of ethanoic anhydride ( $M_r = 102.0$ ). In the reaction the yield of aspirin is 84.1%

The density of ethanoic anhydride is  $1.08 \text{ g cm}^{-3}$

Show by calculation which reagent is in excess.

Calculate the mass, in g, of aspirin ( $M_r = 180.0$ ) produced.

[5 marks]

$$n \text{ Salicylic acid} = \frac{6.01}{138} = 4.36 \times 10^{-2} \text{ moles}$$

$$m (\text{CH}_3\text{CO})_2\text{O} = 10.5 \times 1.08 = 11.34 \text{ g}$$

$$n = \frac{11.34}{102} = 1.11 \times 10^{-1} \text{ moles } (\text{CH}_3\text{CO})_2\text{O} \text{ in excess}$$

$$\text{Mass aspirin} = 0.841 \times 180 \times 4.36 \times 10^{-2}$$

$$= 6.59 \text{ g} \quad \text{Reagent in excess } \underline{(\text{CH}_3\text{CO})_2\text{O}}$$

Mass of aspirin 6.59 g

Turn over ►



- 0 4 . 6 Suggest **two** ways in which the melting point of the crude aspirin collected in step 9 would differ from the melting point of pure aspirin.

[2 marks]

Difference 1 The value would be lower

Difference 2 Crude aspirin would melt over a range of values

- 0 4 . 7 The crude aspirin can be purified by recrystallisation using hot ethanol (boiling point = 78 °C) as the solvent.

Describe **two** important precautions when heating the mixture of ethanol and crude aspirin.

[2 marks]

Precaution 1 Ethanol is flammable. Use a water bath or electric heater to heat

Precaution 2 Heat to a temp below 78°C so ethanol does not boil off

- 0 4 . 8 The pure aspirin is filtered under reduced pressure. A small amount of cold ethanol is then poured through the Buchner funnel.

Explain the purpose of adding a small amount of cold ethanol.

[1 mark]

To remove any soluble impurities

- 0 4 . 9 A sample of the crude aspirin is kept to compare with the purified aspirin.

Describe **one** difference in appearance you would expect to see between these two solid samples.

[1 mark]

The pure product will be lighter in colour



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ANSWER IN THE SPACES PROVIDED

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1 3

0 5 This question is about 2-bromopropane.

0 5 . 1 Define the term electronegativity.

Explain the polarity of the C-Br bond in 2-bromopropane.

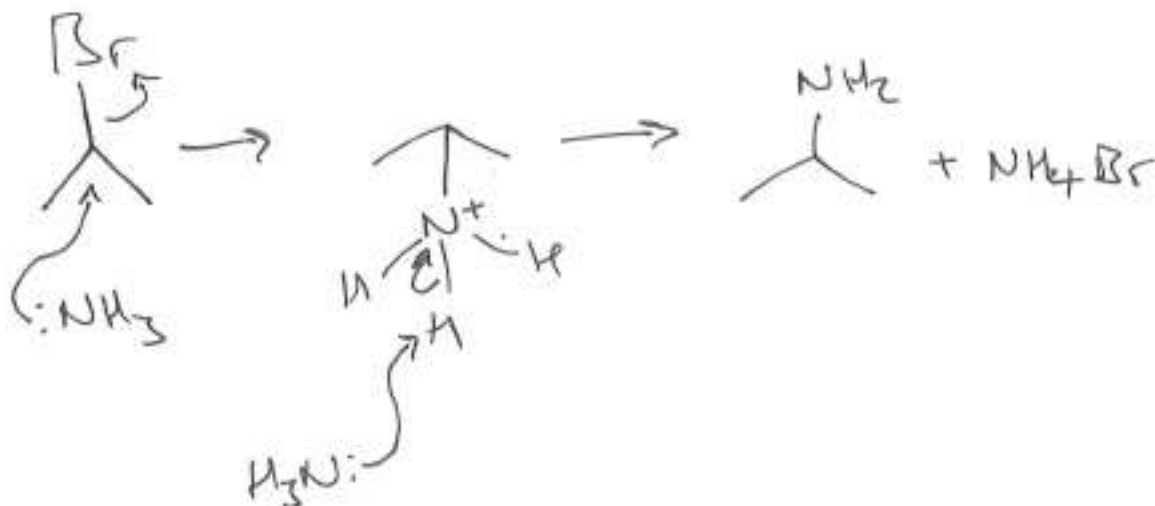
[3 marks]

Electronegativity The relative tendency of an atom to attract a pair of electrons in a bond to itself in a covalent bond

Explanation Br is more electronegative than carbon so Br is  $\delta^-$  and C is  $\delta^+$

0 5 . 2 Outline the mechanism for the reaction of 2-bromopropane with an excess of ammonia.

[4 marks]

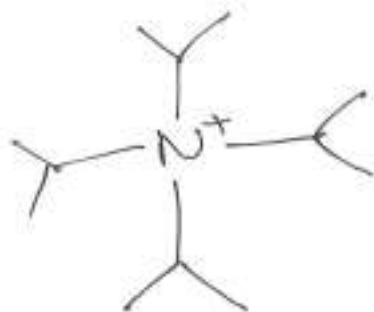


0 5 3 Draw the skeletal formula of the main organic species formed in the reaction between a large excess of 2-bromopropane and ammonia.

Give a use for the organic product.

[2 marks]

Skeletal formula



Use

Shampoo and conditioner

3

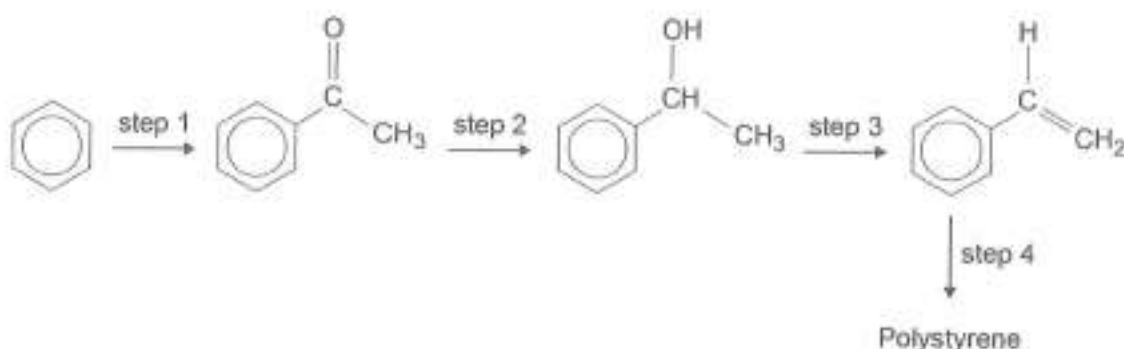
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0 6

Polystyrene can be made from benzene in the series of steps shown.



0 6 . 1

State the type of reaction in step 1.

Identify the reagent(s) and conditions needed for step 1.

[3 marks]

Type of reaction Acylation

Reagent(s) CH<sub>3</sub>COCl

Conditions AlCl<sub>3</sub>

0 6 . 2

State the name of the mechanism for the reaction in step 2.

Identify the inorganic reagent needed for step 2.

Name the organic product of step 2.

[3 marks]

Name of mechanism Nucleophilic addition

Inorganic reagent NaBH<sub>4</sub>

Name of organic product 1-phenylethanol

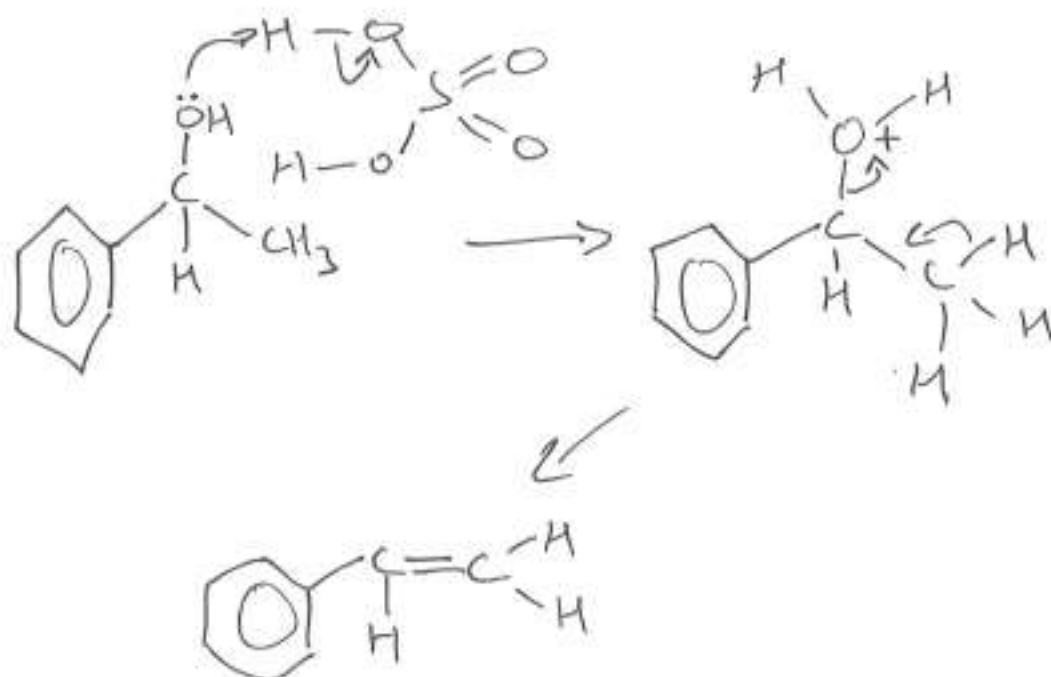




06.3 The organic product of step 2 is reacted with concentrated sulfuric acid in step 3.

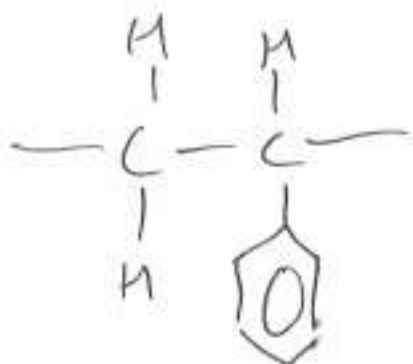
Outline the mechanism for step 3.

[3 marks]



06.4 Draw the repeating unit of polystyrene.

[1 mark]



Turn over for the next question



07

This question is about NMR spectroscopy.

07.1

A compound is usually mixed with  $\text{Si}(\text{CH}_3)_4$  and either  $\text{CCl}_4$  or  $\text{CDCl}_3$  before recording the compound's  $^1\text{H}$  NMR spectrum.

State why  $\text{Si}(\text{CH}_3)_4$ ,  $\text{CCl}_4$  and  $\text{CDCl}_3$  are used in  $^1\text{H}$  NMR spectroscopy.

Explain how their properties make them suitable for use in  $^1\text{H}$  NMR spectroscopy.

[6 marks]

$\text{CCl}_4$  and  $\text{CDCl}_3$  are used as solvents in  $^1\text{H}$  NMR spectroscopy. They are used for solvents as neither of them have any H atoms and so do not give any signal in the NMR spectrum. This means that they do not swamp the molecules that are being studied.

$\text{CCl}_4$  is a non-polar solvent and so it is used for the analysis of non-polar species.  $\text{CDCl}_3$  is polar and as such is used for polar compounds.

$\text{Si}(\text{CH}_3)_4$  is used as a set reference.  $\text{Si}(\text{CH}_3)_4$  (TMS) is used as it will give only 1 signal as all hydrogens are in an identical environment. This signal is also far away from other typical  $^1\text{H}$  signals, avoiding confusion.

Lastly, all compounds are inert and volatile, avoiding reaction with other



other compounds and making them  
easy to remove

Question 7 continues on the next page

Turn over ►



- 0 7 . 2 Deduce the splitting pattern for each of the peaks given by the H atoms labelled x, y and z in the  $^1\text{H}$  NMR spectrum of the compound shown.



[3 marks]

x doublet

y Quartet

z doublet

- 0 7 . 3 Suggest why it is difficult to use Table B in the Data Booklet to predict the chemical shift ( $\delta$  value) for the peak given by the H atom labelled y.

[1 mark]

The H atom is bonded to a C-Cl group and adjacent to a C=O group. It does not fit with the data in table B.

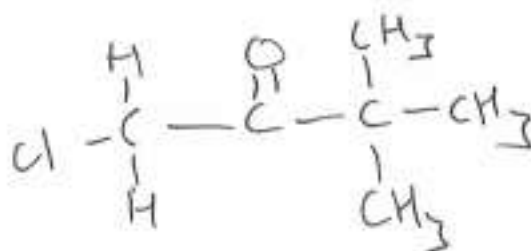
- 0 7 . 4 Two isomers of  $\text{CH}_3\text{CHClCOCH}(\text{CH}_3)_2$  each have two singlet peaks only in their  $^1\text{H}$  NMR spectra.

In both spectra the integration ratio for the two peaks is 2:9

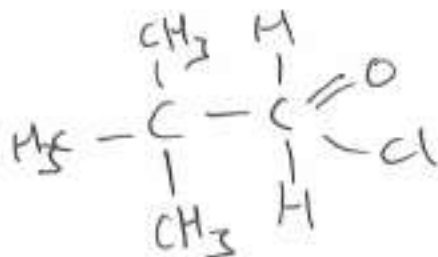
Deduce the structures of these two isomers.

[2 marks]

Isomer 1



Isomer 2



0 8

This question is about citric acid, a hydrated tricarboxylic acid. Its formula can be represented as  $H_3Y \cdot xH_2O$

0 8

. 1

A 1.50 g sample of  $H_3Y \cdot xH_2O$  contains 0.913 g of oxygen by mass.  
The sample burns completely in air to form 1.89 g of  $CO_2$  and 0.643 g of  $H_2O$ .

Show that the empirical formula of citric acid is  $C_3H_5O_4$

[5 marks]

$$n CO_2 = \frac{1.89}{44} = 0.043 \text{ moles}$$

$$n H_2O = \frac{0.643}{18} = 0.0357 \text{ moles}$$

$$n H = 0.036 \times 2 = 0.0714 \text{ moles}$$

$$n O = \frac{0.913}{16} = 0.057$$

C	H	O	
$\frac{0.043}{0.043}$	$\frac{0.0714}{0.043}$	$\frac{0.057}{0.043}$	$\Rightarrow C_3H_5O_4$
1	1.66	1.33	

0 8

. 2

A 3.00 g sample of  $H_3Y \cdot xH_2O$  ( $M_r = 210.0$ ) is heated to constant mass.  
The anhydrous  $H_3Y$  that remains has a mass of 2.74 g

Show, using these data, that the value of  $x = 1$

[2 marks]

$$n H_2O = \frac{0.26}{18} = 0.014 \text{ moles}$$

$$n H_3Y \cdot xH_2O = \frac{3}{210} = 0.014 \text{ moles}$$

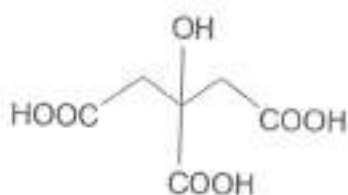
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Figure 5 shows the structure of H<sub>3</sub>Y

Figure 5



0 8 . 3 Complete this IUPAC name for H<sub>3</sub>Y

[1 mark]

2 - Hydroxy propane-1, 2, 3-tricarboxylic acid

0 8 . 4 State the number of peaks you would expect in the <sup>13</sup>C NMR spectrum for H<sub>3</sub>Y

[1 mark]

4

9



09

A and B react together to form an equilibrium mixture.



An aqueous solution containing 0.25 mol of A is added to an aqueous solution containing 0.25 mol of B.

When equilibrium is reached, the mixture contains 0.015 mol of C.

09

1

Calculate the amount of A and the amount of B, in moles, in the equilibrium mixture.

[2 marks]

$$n A_{Eqm} = 0.25 - 0.015 = 0.235 \text{ moles}$$

$$n B_{Eqm} = 0.25 - (2 \times 0.015) = 0.22 \text{ moles}$$

Amount of A 0.235 mol

Amount of B 0.220 mol

09

2

At a different temperature, another equilibrium mixture contains 0.30 mol of A, 0.25 mol of B and 0.020 mol of C in  $350 \text{ cm}^3$  of solution.

Calculate the value of the equilibrium constant  $K_c$ .

Deduce the units of  $K_c$ .

[4 marks]

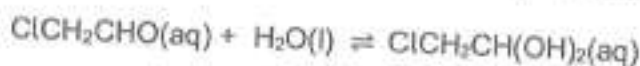
$$\frac{0.02}{0.35} \div \left( \frac{0.30}{0.35} \times \left( \frac{0.25}{0.35} \right)^2 \right) = 0.13 \text{ mol}^{-2} \text{ dm}^6$$

$K_c$  0.13

Units  $\text{mol}^{-2} \text{ dm}^6$



When an excess of water is added to chloroethanal, an equilibrium mixture is formed.



An expression for an equilibrium constant ( $K$ ) for the reaction under these conditions is

$$K = \frac{[\text{ClCH}_2\text{CH}(\text{OH})_2]}{[\text{ClCH}_2\text{CHO}]}$$

- 09.3 Suggest why an expression for  $K$  can be written without the concentration of water. [1 mark]

The concentration of water is effectively constant because it is so much in excess

- 09.4 Distilled water is added to 4.71 g of chloroethanal ( $M_r = 78.5$ ) to make 50.0 cm<sup>3</sup> of solution. The mixture is allowed to reach equilibrium.

The value of the equilibrium constant ( $K$ ) is 37.0

Calculate the equilibrium concentration, in mol dm<sup>-3</sup>, of ClCH<sub>2</sub>CH(OH)<sub>2</sub>

[5 marks]

$$n_{\text{chloroethanal}} = \frac{4.71}{78.5} = 0.06 \text{ moles}$$

$$n_{\text{eqm}} = 0.06 - x$$

$$n_{\text{ClCH}_2\text{CH}(\text{OH})_2} = x$$

$$37 = \frac{x}{\frac{0.06 - x}{x}}$$

$$-37(0.06 - x) = x$$

$$2.22 = 38x$$

$$[\text{ClCH}_2\text{CH}(\text{OH})_2] = \frac{0.058421}{0.05} \quad x = 0.058421$$

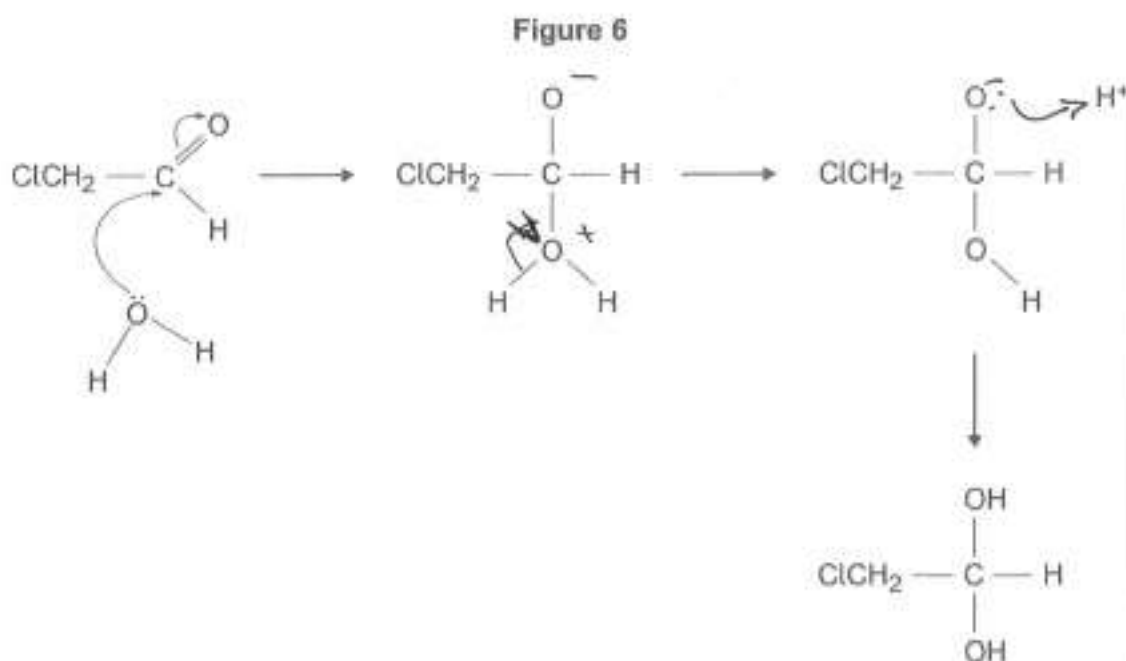
Concentration  $\rightarrow$  1.17 mol dm<sup>-3</sup>





09.5

Figure 6 shows an incomplete nucleophilic addition mechanism for the reaction of water with chloroethanal.



Complete the mechanism in **Figure 6** by adding **two** curly arrows, all relevant charges and any lone pairs of electrons involved.

[3 marks]

09.6

When an excess of water is added to ethanal a similar nucleophilic addition reaction occurs.



Suggest why this reaction is slower than the reaction in Question 09.5.

[3 marks]

The C in the C=O bond is less  $\delta^+$  as the attached CH<sub>3</sub> is less electron donating so the E<sub>a</sub> of the reaction is higher.

END OF QUESTIONS

