Please write clearly in block capitals.

Centre number | | | | | | Candidate number | | | | |

Surname ______________________

Forename(s) ______________________

Candidate signature ______________________

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	
5	
6	
7	
8	
9	
TOTAL	

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

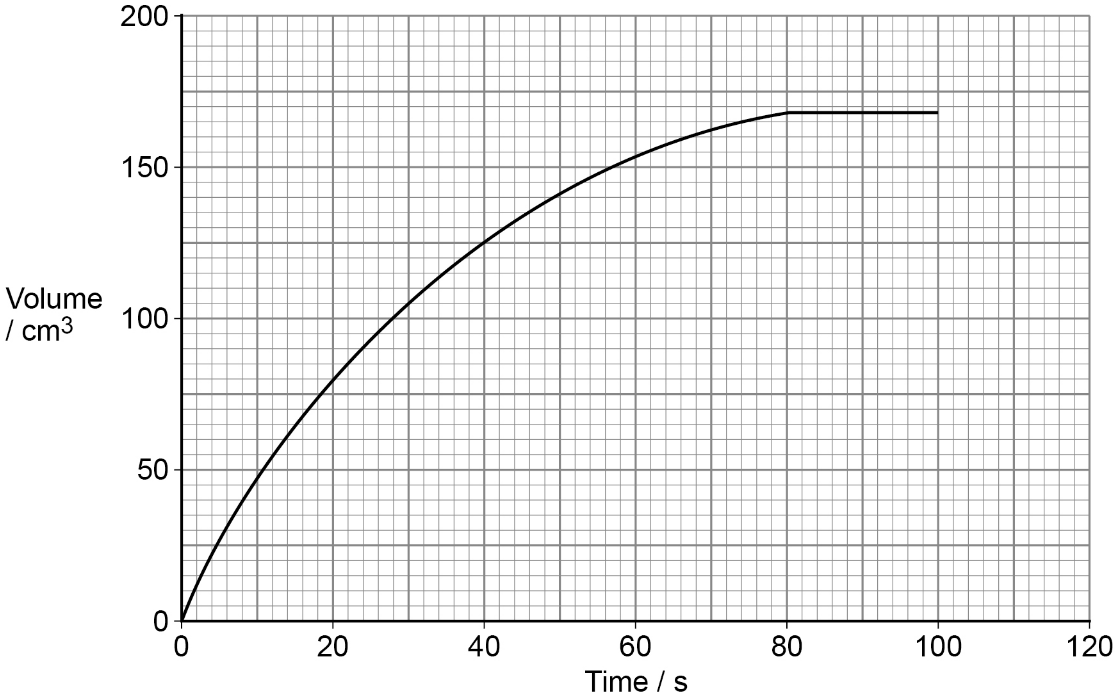
0 1 This question is about rates of reaction.

Phosphinate ions ($H_2PO_2^-$) react with hydroxide ions to produce hydrogen gas as shown.

$$H_2PO_2^- + OH^- \rightarrow HPO_3^{2-} + H_2$$

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]

Rate ______________________________ Units ___________________________

Do not write outside the box

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 cm^3 of hydrogen gas. Each experiment was carried out at the same temperature. **Table 1** shows the results.

Table 1

Initial $[H_2PO_2^-]$ / mol dm^{-3}	***t* / 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 ____

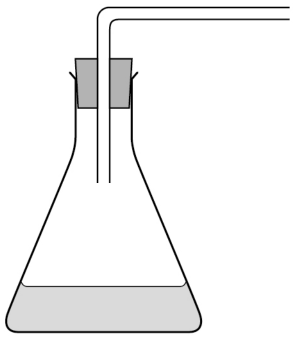
Order ____

Question 1 continues on the next page

0 1 . 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

$$rate = k\,[L]\,[M]^2$$

0 1 . 4 Deduce the overall effect on the rate of reaction when the concentrations of both **L** and **M** are halved.

[1 mark]

Do not write outside the box

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

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

[3 marks]

Concentration of **M** ____________________ mol dm^{-3}

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

[1 mark]

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11

Turn over for the next question

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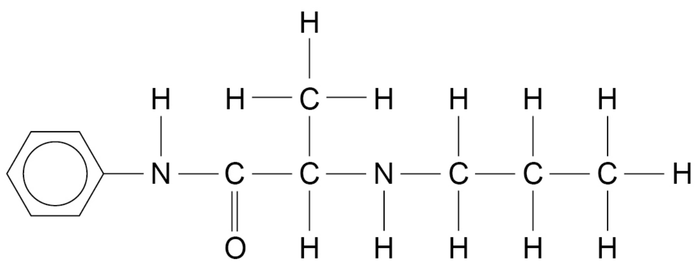
0 2 Prilocaine is used as an anaesthetic in dentistry.
Figure 3 shows the structure of prilocaine.

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.

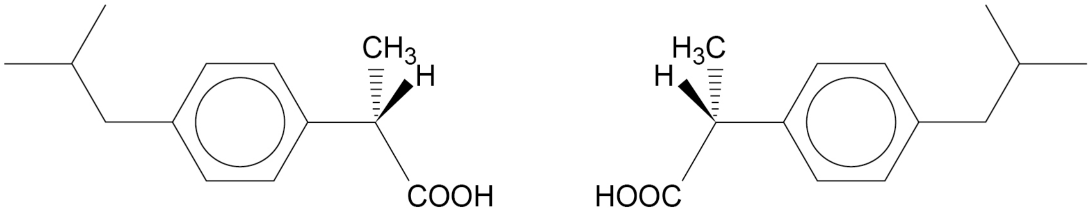
Draw the structures of the two organic products formed in the complete hydrolysis of prilocaine in acidic conditions.

[3 marks]

Do not write outside the box

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

Figure 4



Isomer **F** Isomer **G**

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]

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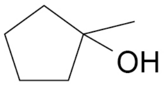
7

Turn over for the next question

0 3 This question is about the structural isomers shown.

P



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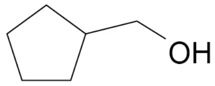

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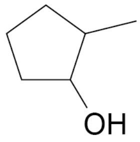

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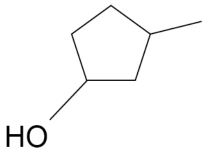

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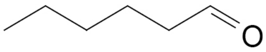

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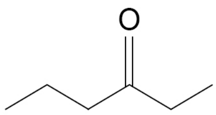

0 3 . 1 Identify the isomer(s) that would react when warmed with acidified potassium dichromate(VI).

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

[2 marks]

Isomer(s) ____________________

Expected observation ____________________

____

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) ____________________

Expected observation ____________________

____

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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) ____________________

Suggestion ____________________

____

____

Reason ____________________

____

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

[1 mark]

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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]

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

[1 mark]

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13

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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^3 conical flask.

4. ____

5. Add 10 cm^3 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 ____

Justification ____

____

____

0 4 . 2 Suggest a suitable piece of apparatus to measure out the ethanoic anhydride in step **5**.

[1 mark]

____

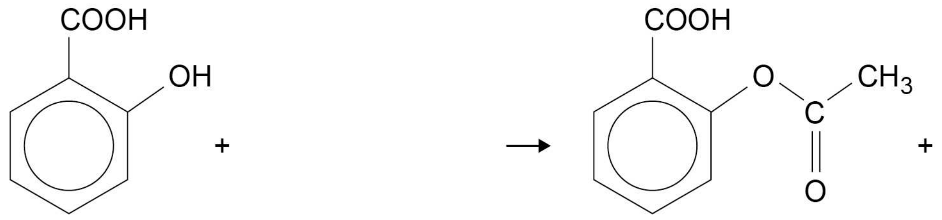
0 4 . 3 Identify a hazard of using concentrated phosphoric acid in step **6**.

[1 mark]

____

0 4 . 4 Complete the equation for the reaction of salicylic acid with ethanoic anhydride to produce aspirin.

[1 mark]



Salicylic acid   Aspirin

0 4 . 5 A 6.01 g sample of salicylic acid (M_r = 138.0) is reacted with 10.5 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 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]

Reagent in excess ____________________________

Mass of aspirin _________________ g

Turn over ►

Do not write outside the box

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 ______________________________

____

Difference 2 ______________________________

____

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 ______________________________

____

Precaution 2 ______________________________

____

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]

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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]

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16

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Turn over for the next question

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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 ______________________________

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Explanation ______________________________

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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 ______________________________

9

Turn over for the next question

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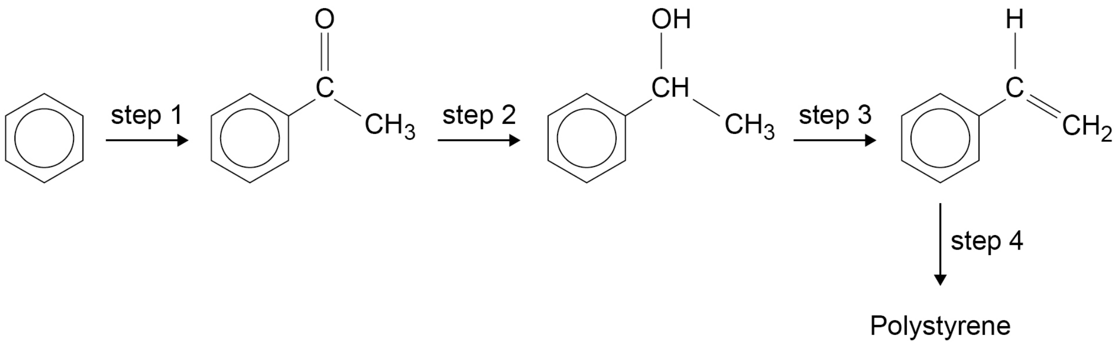
0 6 Polystyrene can be made from benzene in the series of steps shown.



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 ____________________

Reagent(s) ____________________

Conditions ____________________

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 ____________________

Inorganic reagent ____________________

Name of organic product ____________________

Do not write outside the box

0 6 . 3 The organic product of step **2** is reacted with concentrated sulfuric acid in step **3**.

Outline the mechanism for step **3**.

[3 marks]

0 6 . 4 Draw the repeating unit of polystyrene.

[1 mark]

10

Turn over for the next question

Do not write outside the box

0 7 This question is about NMR spectroscopy.

0 7 . 1 A compound is usually mixed with $Si(CH_3)_4$ and either CCl_4 or $CDCl_3$ before recording the compound's ^1H NMR spectrum.

State why $Si(CH_3)_4$, CCl_4 and $CDCl_3$ are used in ^1H NMR spectroscopy.

Explain how their properties make them suitable for use in ^1H NMR spectroscopy.

[6 marks]

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Question 7 continues on the next page

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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]H NMR spectrum of the compound shown.

$$\underset{\boldsymbol{x}}{CH_3}\underset{\boldsymbol{y}}{CH}ClCO\underset{\boldsymbol{z}}{CH}(CH_3)_2$$

[3 marks]

x ______________________________

y ______________________________

z ______________________________

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

[1 mark]

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0 7 . 4 Two isomers of $CH_3CHClCOCH(CH_3)_2$ each have two singlet peaks only in their [1]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

12

Do not write outside the box

0 8 This question is about citric acid, a hydrated tricarboxylic acid. Its formula can be represented as $H_3Y.xH_2O$

0 8 . 1 A 1.50 g sample of $H_3Y.xH_2O$ 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]

0 8 . 2 A 3.00 g sample of $H_3Y.xH_2O$ (M_r = 210.0) is heated to constant mass.
The anhydrous H_3Y that remains has a mass of 2.74 g

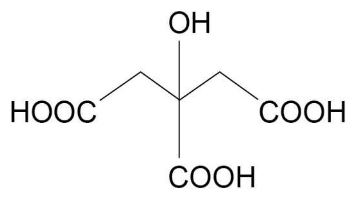
Show, using these data, that the value of x = 1

[2 marks]

Do not write outside the box

Figure 5 shows the structure of H_3Y

Figure 5



0 8 . 3 Complete this IUPAC name for H_3Y

[1 mark]

____________________________ propane-1, 2, 3-tricarboxylic acid

0 8 . 4 State the number of peaks you would expect in the ^{13}C NMR spectrum for H_3Y

[1 mark]

____

9

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0 9 **A** and **B** react together to form an equilibrium mixture.

$$A(aq) + 2B(aq) \rightleftharpoons C(aq)$$

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**.

0 9 . 1 Calculate the amount of **A** and the amount of **B**, in moles, in the equilibrium mixture.

[2 marks]

Amount of **A** ________________ mol

Amount of **B** ________________ mol

0 9 . 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 cm^3 of solution.

Calculate the value of the equilibrium constant K_c

Deduce the units of K_c

[4 marks]

K_c ________________

Units ________________

Turn over ►

Do not write outside the box

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

$$ClCH_2CHO(aq) + H_2O(l) \rightleftharpoons ClCH_2CH(OH)_2(aq)$$

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

$$K = \frac{[ClCH_2CH(OH)_2]}{[ClCH_2CHO]}$$

0 9 . 3 Suggest why an expression for *K* can be written without the concentration of water.

[1 mark]

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0 9 . 4 Distilled water is added to 4.71 g of chloroethanal (M_r = 78.5) to make 50.0 cm^3 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^{-3}, of $ClCH_2CH(OH)_2$

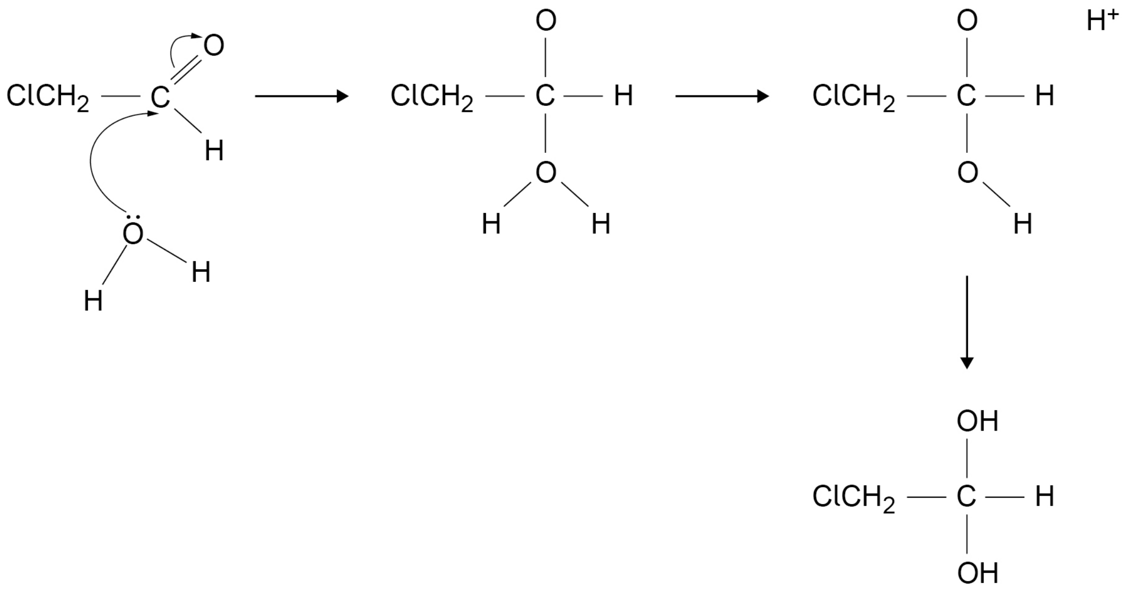
[5 marks]

Concentration ____________________ mol dm^{-3}

Do not write outside the box

0 9 . 5 **Figure 6** shows an incomplete nucleophilic addition mechanism for the reaction of water with chloroethanal.

Figure 6



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

[3 marks]

0 9 . 6 When an excess of water is added to ethanal a similar nucleophilic addition reaction occurs.

$$CH_3CHO(aq) + H_2O(l) \rightleftharpoons CH_3CH(OH)_2(aq)$$

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

[3 marks]

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18

END OF QUESTIONS

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Question number	**Additional page, if required. Write the question numbers in the left-hand margin.**