

Chemistry

Advanced

PAPER 2: Advanced Organic and Physical Chemistry

Monday 19 June 2023 – Afternoon

Time: 1 hour 45 minutes

In the boxes below, write your name, centre number and candidate number.

Surname					
Other names					
Centre Number					
Candidate Number					

YOU MUST HAVE

Scientific calculator, Data Booklet, ruler

YOU WILL BE GIVEN

Diagram Booklet, Periodic Table

INSTRUCTIONS

Answer ALL questions.

Answer the questions in the spaces provided in this Question Paper or in the separate Diagram Booklet – there may be more space than you need.

INFORMATION

The total mark for this paper is 90.

The marks for EACH question are shown in brackets – use this as a guide as to how much time to spend on each question.

For the question marked with an ASTERISK (*), marks will be awarded for your ability to structure your answer logically, showing the points that you make are related or follow on from each other where appropriate.

A Periodic Table is provided as a separate insert.

There may be spare copies of some diagrams.

ADVICE

Read each question carefully before you start to answer it.

Show all your working in calculations and include units where appropriate.

Check your answers if you have time at the end.

Answer ALL questions.

Some questions must be answered with a cross in a box ☐. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☐.

1 This question is about some organic compounds.

- (a) Draw the SKELETAL formula of 1,3-dimethylcyclohexane.
(1 mark)**

(continued on the next page)

1 continued.

(b) What is the general formula for a CYCLOALKENE?
(1 mark)



(continued on the next page)

1 continued.

- (c) A student is asked to devise a laboratory synthesis of 1,2-dichloroethane. The student suggests reacting ethane with chlorine in the presence of ultraviolet radiation.**

**Give TWO reasons why this is not a good method to prepare 1,2-dichloroethane.
(2 marks)**

(Total for Question 1 = 4 marks)

2 This question is about alcohols.

- (a) Ethanol is a fuel and can be made by either the fermentation of carbohydrates or the hydration of ethene.**

How is the ethanol formed by the fermentation of carbohydrates classified?

(1 mark)

- ☐ **A a biofuel and non-renewable**
- ☐ **B a biofuel and renewable**
- ☐ **C a fossil fuel and non-renewable**
- ☐ **D a fossil fuel and renewable**

- (b) Write the equation for the complete combustion of methanol.**

State symbols are not required.

(1 mark)

(continued on the next page)

Turn over

2 continued.

- (c) Identify, by name or formula, the reagent(s) needed to convert propan-1-ol into 1-iodopropane.
(1 mark)
-
-

- (d) A sample of pure propan-2-ol is analysed using infrared and ^{13}C NMR spectroscopy.

- (i) Which of these sets of wavenumber ranges, in cm^{-1} , will be seen in the infrared spectrum of propan-2-ol?
(1 mark)

- ☐ A 1485 – 1365, 2962 – 2853 and 3300 – 2500
- ☐ B 1485 – 1365, 2962 – 2853 and 3750 – 3200
- ☐ C 1669 – 1645, 2962 – 2853 and 3750 – 3200
- ☐ D 1740 – 1720, 3300 – 2500 and 3750 – 3200

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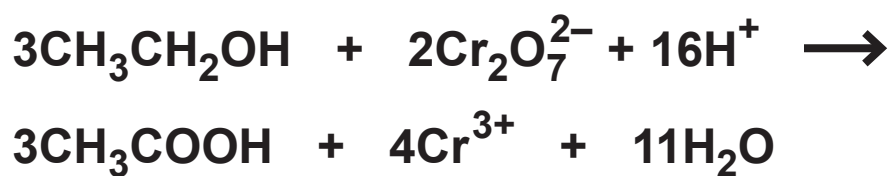
2(d) continued.

- (ii) State the number of peaks in the ^{13}C NMR spectrum of propan-2-ol.
(1 mark)**

(continued on the next page)

2 continued.

- (e) The equation for the oxidation of ethanol by acidified dichromate(VI) ions is shown.**



Deduce the half-equation for the oxidation of ethanol to ethanoic acid.

State symbols are not required.

(1 mark)

(Total for Question 2 = 6 marks)

Turn over

- 3 This question is about the molar masses of three organic compounds, **X**, **Y** and **Z**.

- (a) The accurate relative atomic masses, A_r , of four of the elements that could be present in an organic compound are shown.

Element	A_r
hydrogen, H	1.0078
carbon, C	12.0000
nitrogen, N	14.0031
oxygen, O	15.9949

The mass spectrum of organic compound **X** gives a molecular ion peak at $m/z = 60.0323$

What is compound **X**?
(1 mark)

- ☐ A ethanamide, CH_3CONH_2
- ☐ B ethanoic acid, CH_3COOH
- ☐ C trimethylamine, $(\text{CH}_3)_3\text{N}$
- ☐ D urea, $\text{CO}(\text{NH}_2)_2$

(continued on the next page)

Turn over

3 continued.

- (b) 9.90 g of a gaseous organic compound, Y, occupies a volume of 5.40 dm³ at room temperature and pressure (r.t.p.).**

**Calculate the molar mass of the compound Y.
(2 marks)**

[molar gas volume at r.t.p. = 24.0 dm³ mol⁻¹]

(continued on the next page)

3 continued.

- (c) A quantity of a volatile organic liquid, Z, is placed in a 60.0 cm^3 flask and heated to 95.0°C . When all the liquid has vaporised, the flask is sealed.**

Mass of vapour = 0.170 g

Pressure = 100.6 kPa

Gas constant (R) = $8.31\text{ J mol}^{-1}\text{ K}^{-1}$

Calculate the molar mass of compound Z, giving your answer to an appropriate number of significant figures.

Assume there was no air left in the flask once the liquid Z had vaporised.

(4 marks)

Answer space continues on the next page.

3(c) continued.

Mass of vapour = 0.170 g

Pressure = 100.6 kPa

Gas constant (R) = 8.31 J mol⁻¹ K⁻¹

(Total for Question 3 = 7 marks)

Turn over

4 This question is about some hydrocarbons.

(a) A 2.50 g sample of a hydrocarbon gave 7.59 g of carbon dioxide on complete oxidation.

**Calculate the empirical formula of the hydrocarbon.
(4 marks)**

Answer space continues on the next page.

4(a) continued.

(continued on the next page)

4 continued.

(b) Benzene and ethene react with bromine under different conditions but both reactions involve an electrophile.

**(i) An electrophile is a substance that
(1 mark)**

- ☐ **A accepts a pair of electrons**
- ☐ **B accepts an unpaired electron**
- ☐ **C donates a pair of electrons**
- ☐ **D donates an unpaired electron**

(continued on the next page)

4(b) continued.

(ii) Explain why benzene is resistant to bromination but ethene reacts readily with bromine at room temperature. (4 marks)

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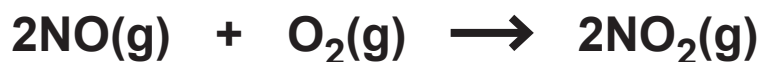
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4(b)(ii) continued.

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(Total for Question 4 = 9 marks)

- 5 Nitrogen monoxide reacts with oxygen to form nitrogen dioxide.



The rate is proportional to the concentration of oxygen and to the square of the concentration of nitrogen monoxide.

- (a) The rate of this reaction can be determined by measuring the change in the total gas pressure.
- (i) Give a reason why this method can be used in this reaction.
(1 mark)

(continued on the next page)

5(a) continued.

- (ii) State TWO factors, other than initial amounts of reactants, that must be kept constant for this method to work.**

(1 mark)

(continued on the next page)

5 continued.

(b) Look at the graph for Question 5(b) in the Diagram Booklet. It shows four lines of a quantity Y plotted against a quantity X.

(i) Which line shows the relationship between the concentration of nitrogen monoxide (Y) and time (X)?
(1 mark)

☐ **A line P**

☐ **B line Q**

☐ **C line R**

☐ **D line S**

(ii) Which line shows the relationship between rate (Y) and concentration of oxygen (X)?
(1 mark)

☐ **A line P**

☐ **B line Q**

☐ **C line R**

☐ **D line S**

5 continued.

- (c) The rate of this reaction is $z \text{ mol dm}^{-3} \text{ s}^{-1}$ under certain conditions.

The concentration of nitrogen monoxide is doubled and the concentration of oxygen is halved. All other conditions remain the same.

What will be the new rate of reaction in $\text{mol dm}^{-3} \text{ s}^{-1}$?
(1 mark)

☐ A $z/2$

☐ B z

☐ C $2z$

☐ D $4z$

(continued on the next page)

5 continued.

- (d) Nitrogen monoxide is formed in car engines. It is removed by the catalytic converter in the car exhaust.**



The reaction is exothermic and the most active catalyst is platinum.

- (i) Look at the diagram for Question 5(d)(i) in the Diagram Booklet. Complete the labelled reaction profile for the CATALYSED reaction. (3 marks)**

- (ii) Catalysts, such as platinum, are very expensive.**

Explain an economic benefit of using a catalyst in an industrial process. (2 marks)

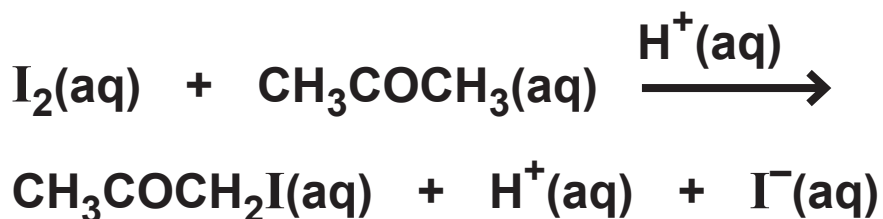
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Turn over

5(d)(ii) continued.

(Total for Question 5 = 10 marks)

6 Iodine reacts with propanone in acidic conditions.



A student was asked to investigate the kinetics of this reaction.

The student predicted that the rate equation for the reaction would be

$$\text{rate} = k[\text{I}_2(\text{aq})][\text{CH}_3\text{COCH}_3(\text{aq})][\text{H}^+(\text{aq})]^0$$

because the balanced equation shows that one molecule of iodine reacts with one molecule of propanone and the acid is a catalyst.

(a) The student first determined the order of reaction with respect to iodine by keeping the concentrations of propanone and acid constant. The student used the outline procedure shown.

- mix 25 cm^3 of aqueous propanone with 25 cm^3 of dilute sulfuric acid in a conical flask
- add 25 cm^3 of aqueous iodine, immediately start a stopwatch and swirl the mixture in the conical flask
- use a pipette to remove a 10.0 cm^3 sample of the solution and place it in a clean conical flask

(continued on the next page)

Turn over

6(a) continued.

- add a spatula measure of sodium hydrogencarbonate and note the exact time it is added
 - take four more 10.0 cm^3 samples of the mixture and add sodium hydrogencarbonate to each of them at regular time intervals
 - titrate the unreacted iodine in the samples with sodium thiosulfate solution using starch indicator.
- (i) State how the student could ensure that the concentrations of propanone and acid are effectively constant throughout the experiment.
(1 mark)

(continued on the next page)

6(a) continued.

- (ii) Explain why sodium hydrogencarbonate is added.
(2 marks)**

(continued on the next page)

6 continued.

(b) The student obtained these results.

Time / min	5	10	15	20	25
Volume of thiosulfate / cm ³	15.0	13.8	12.6	11.4	10.2

- (i) Give a reason why it is not necessary to calculate the concentration of iodine at each time to work out the order of reaction with respect to iodine.
(1 mark)

(continued on the next page)

6(b) continued.

(ii) Look at the grid for Question 6(b)(ii) in the Diagram Booklet. Plot a graph to show that the order of reaction with respect to iodine is zero.

(2 marks)

(iii) Give a reason why the graph shows that the order of reaction with respect to iodine is zero.

(1 mark)

(continued on the next page)

6 continued.

- (c) Further experiments showed that the correct overall rate equation is**

$$\text{rate} = k[\text{CH}_3\text{COCH}_3(\text{aq})][\text{H}^+(\text{aq})][\text{I}_2(\text{aq})]^0$$

- (i) Deduce a possible rate determining step in the mechanism of this reaction.
Curly arrows are not required.
(2 marks)**

(continued on the next page)

6(c) continued.

- (ii) Look at the table for Question 6(c)(ii) in the Diagram Booklet. Data from two experiments carried out at the same temperature are shown.

What is the rate, in $\text{mol dm}^{-3} \text{s}^{-1}$,
in Experiment 2?
(1 mark)

☐ A 2.24×10^{-5}

☐ B 3.36×10^{-5}

☐ C 4.48×10^{-5}

☐ D 8.96×10^{-5}

(continued on the next page)

6(c) continued.

- (iii) The experiment in (a) is repeated but using aqueous bromine instead of aqueous iodine. All other conditions are kept the same.**

Explain how you would expect the rate of reaction of bromination of propanone to compare with the rate of iodination of propanone.

**Assume that the reaction between bromine and propanone in acidic conditions has the same rate equation as that between iodine and propanone in acidic conditions.
(2 marks)**

Answer space continues on the next page.

6(c)(iii) continued.

(Total for Question 6 = 12 marks)

7 This question is about carbonyl compounds.

- (a) Ethanal, CH_3CHO , and ethanoic acid, CH_3COOH , are both soluble in water but ethanoic acid has a much higher boiling temperature than ethanal.**

Explain these physical properties of ethanal and ethanoic acid in terms of intermolecular forces.

Include a labelled diagram to show why ethanal is soluble in water.

(4 marks)

Answer space continues on the next 2 pages.

7(a) continued.

[illegible]

Turn over

7(a) continued.

(continued on the next page)

7 continued.

(b) Look at the structure for Question 7(b) in the Diagram Booklet. Propanal reacts with hydrogen cyanide in the presence of potassium cyanide to form 2-hydroxybutanenitrile.

- (i) Draw the mechanism for this reaction. Include curly arrows and any relevant lone pairs and dipoles.
(4 marks)**

7(b) continued.

- (ii) Explain whether or not the 2-hydroxybutanenitrile formed will be a racemic mixture.
(3 marks)**

(continued on the next page)

Turn over

7 continued.

(c) Carbonyl compounds can be identified by reacting them with 2,4-dinitrophenylhydrazine (2,4-DNPH) to form a solid derivative.

These derivatives have characteristic melting temperatures.

**(i) Look at the diagram for Question 7(c)(i) in the Diagram Booklet. Identify the steps required to prepare a sample of a pure, dry derivative of a carbonyl compound X.
(3 marks)**

STEP 1

STEP 2

(continued on the next page)

Turn over

7(c)(i) continued.

STEP 3

(continued on the next page)

7(c) continued.

- (ii) Look at the table for Question 7(c)(ii) in the Diagram Booklet. The melting temperature ranges of the derivatives of some carbonyl compounds that could be **X** are shown in the table.

The melting temperature of the derivative of carbonyl compound **X** is 156–158 °C and **X** has an absorption at 1717 cm⁻¹ in its infrared spectrum.

Deduce the identity of **X**. Justify your answer.
(2 marks)

7(c) continued.

(iii) These carbonyl compounds may also be identified using modern methods such as proton NMR spectroscopy.

Look at the diagram for Question 7(c)(iii) in the Diagram Booklet. The structure of the pentan-3-one derivative formed with 2,4-DNPH is shown.

Label the different proton environments that would give rise to the peaks in the low resolution proton NMR spectrum.

(2 marks)

(Total for Question 7 = 18 marks)

8 This question is about isomerism in organic compounds.

(a) How many structural isomers are there with the formula C_5H_{12} ?
(1 mark)

☐ A 2

☐ B 3

☐ C 4

☐ D 5

(continued on the next page)

8 continued.

- (b) Propene reacts with bromine to form 1,2-dibromopropane as the only product.**

Draw the mechanism for the reaction between propene and bromine.

Include curly arrows and any relevant lone pairs and dipoles.

(3 marks)

Answer space continues on the next page.

8(b) continued.

(continued on the next page)

8 continued.

(c) When propene reacts with a mixture of bromine and sodium chloride, it forms 1,2-dibromopropane, 1-bromo-2-chloropropane and 2-bromo-1-chloropropane but no 1,2-dichloropropane.

**(i) Explain, by reference to your mechanism in (b), why no 1,2-dichloropropane forms.
(2 marks)**

Answer space continues on the next page.

Turn over

8(c)(i) continued.

(continued on the next page)

8(c) continued.

- (ii) Explain why far more 1-bromo-2-chloropropane forms than 2-bromo-1-chloropropane.
(2 marks)**

(continued on the next page)

Turn over

8 continued.

***(d) Discuss the different types of stereoisomerism that occur in organic compounds. Use only molecules **A** and **B** as examples.**



A



B

Include in your answer:

- **how the different types of isomerism arise**
- **the naming of alkenes with the formula **A****
- **the properties of isomers with the formula **B****
- **diagrams of the different isomers.**

(6 marks)

Answer space continues on the next 5 pages.

8(d) continued.

8(d) continued.

8(d) continued.

8(d) continued.

[illegible]

Turn over

8(d) continued.

(Total for Question 8 = 14 marks)

9 This question is about the analysis of some organic compounds.

(a) A compound **A** ($\text{C}_3\text{H}_7\text{Cl}$) reacts with dilute aqueous sodium hydroxide to produce **B** ($\text{C}_3\text{H}_8\text{O}$). **B** can be oxidised to **C** ($\text{C}_3\text{H}_6\text{O}$), which cannot be oxidised any further.

A reacts with magnesium in dry ether to give **D** ($\text{C}_3\text{H}_7\text{MgCl}$). When carbon dioxide is passed through the solution of **D**, followed by acidification, **E** ($\text{C}_4\text{H}_8\text{O}_2$) is formed.

Identify the structures of **A** to **E**.
(5 marks)

Answer space continues on the next page.

9(a) continued.

9 continued.

- (b) An organic compound, Q, contains carbon, hydrogen and nitrogen only.**

When a 1.19 g sample of the compound was heated with sodium hydroxide solution, all of the nitrogen was converted into ammonia. The ammonia was passed into 100.0 cm³ of 0.225 mol dm⁻³ hydrochloric acid.



25.0 cm³ portions of the resulting solution containing unreacted hydrochloric acid required a mean titre of 15.5 cm³ of 0.100 mol dm⁻³ sodium hydroxide for neutralisation.

**Calculate the percentage of nitrogen in Q.
(5 marks)**

Answer space continues on the next page.

9(b) continued.

(Total for Question 9 = 10 marks)

TOTAL FOR PAPER = 90 MARKS

END OF PAPER