Q1. The rate of hydrolysis of an ester **X** ($HCOOCH_2CH_2CH_3$) was studied in alkaline conditions at a given temperature. The rate was found to be first order with respect to the ester and first order with respect to hydroxide ions.

(a) (i) Name ester **X**.

.....

(1)

(ii) Using **X** to represent the ester, write a rate equation for this hydrolysis reaction.

.....

(1)

(iii) When the initial concentration of **X** was 0.024 mol dm^{-3} and the initial concentration of hydroxide ions was 0.035 mol dm^{-3}, the initial rate of the reaction was
8.5×10^{-5} mol dm^{-3} s^{-1}.
Calculate a value for the rate constant at this temperature and give its units.

Calculation .....

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Units .....

.....

(3)

(iv) In a second experiment at the same temperature, water was added to the original reaction mixture so that the total volume was doubled.
Calculate the initial rate of reaction in this second experiment.

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(1)

(v) In a third experiment at the same temperature, the concentration of **X** was half that used in the experiment in part (a) (iii) and the concentration of hydroxide ions was three times the original value.
Calculate the initial rate of reaction in this third experiment.

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(1)

(vi) State the effect, if any, on the value of the rate constant *k* when the temperature is lowered but all other conditions are kept constant. Explain your answer.

Effect ….....

Explanation .....

(2)

(b) Compound **A** reacts with compound **B** as shown by the overall equation

$$A + 3B \rightarrow AB_3$$

The rate equation for the reaction is

$$\text{rate} = k[A][B]^2$$

A suggested mechanism for the reaction is

Step **1** $A + B \rightarrow AB$

Step **2** $AB + B \rightarrow AB_2$

Step **3** $AB_2 + B \rightarrow AB_3$

Deduce which one of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step .....

Explanation .....

.....

(2)
(Total 11 marks)

Q2. A reaction mechanism is a series of steps by which an overall reaction may proceed. The reactions occurring in these steps may be deduced from a study of reaction rates. Experimental evidence about initial rates leads to a rate equation. A mechanism is then proposed which agrees with this rate equation.
Ethanal dimerises in dilute alkaline solution to form compound **X** as shown in the following equation.

$$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$$
X

A chemist studied the kinetics of the reaction at 298 K and then proposed the following rate equation.

$$\text{Rate} = k\,[CH_3CHO][OH^-]$$

(a) Give the IUPAC name of compound **X**.

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(1)

(b) The initial rate of the reaction at 298K was found to be 2.2×10^{-3} mol dm^{-3} s^{-1} when the initial concentration of ethanal was 0.10 mol dm^{-3} and the initial concentration of sodium hydroxide was 0.020 mol dm^{-3}.
Calculate a value for the rate constant at this temperature and give its units.

Calculation .....

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Units .....

(3)

(c) The sample of **X** produced consists of a racemic mixture (racemate). Explain how this racemic mixture is formed.

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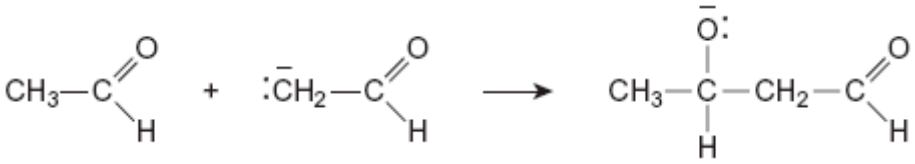
(2)

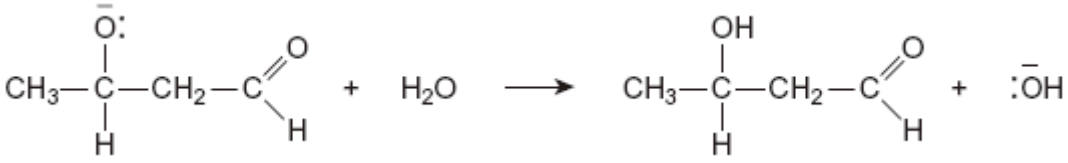
(d) A three-step mechanism has been proposed for this reaction according to the following equations.

Step **1**

Step **2**



Step **3**



(i) Using the rate equation, predict which of the three steps is the rate-determining step. Explain your answer.

Rate-determining step .....

Explanation .....

.....

(2)

(ii) Deduce the role of ethanal in Step **1**.

.....

(1)

(iii) Use your knowledge of reaction mechanisms to deduce the type of reaction occurring in Step **2**.

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(1)

(iv) In the space below draw out the mechanism of Step **2** showing the relevant curly arrows.

(2)

(e) In a similar three-step mechanism, one molecule of **X** reacts further with one molecule of ethanal. The product is a trimer containing six carbon atoms.

Deduce the structure of this trimer.

(1)
(Total 13 marks)

Q3. (a) The following table shows the results of three experiments carried out at the same temperature to investigate the rate of the reaction between compounds **P** and **Q**.

	Experiment 1	Experiment 2	Experiment 3
Initial concentration of **P**/mol dm^{-3}	0.50	0.25	0.25
Initial concentration of **Q**/mol dm^{-3}	0.36	0.36	0.72
Initial rate/mol dm^{-3} s^{-1}	7.6×10^{-3}	1.9×10^{-3}	3.8×10^{-3}

Use the data in the table to deduce the order with respect to **P** and the order with respect to **Q**.

*Order with respect to **P*** .....

*Order with respect to **Q*** .....

(2)

(b) In a reaction between **R** and **S**, the order of reaction with respect to **R** is one, the order of reaction with respect to **S** is two and the rate constant at temperature T_1 has a value of 4.2×10^{-4} mol^{-2} dm^6 s^{-1}.

(i) Write a rate equation for the reaction. Calculate a value for the initial rate of reaction when the initial concentration of **R** is 0.16 mol dm^{-3} and that of **S** is 0.84 mol dm^{-3}.

Rate equation .....

Calculation .....

(ii) In a second experiment performed at a different temperature, T_2, the initial rate of reaction is 8.1×10^{-5} mol dm^{-3}s^{-1} when the initial concentration of **R** is 0.76 mol dm^{-3} and that of **S** is 0.98 mol dm^{-3}. Calculate the value of the rate constant at temperature T_2.

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(iii) Deduce which of T_1 and T_2 is the higher temperature.

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(6)
(Total 8 marks)

Q4. The initial rate of the reaction between the gases NO and H_2 was measured in a series of experiments at a constant temperature and the following rate equation was determined.

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

(a) Complete the table of data below for the reaction between NO and H_2

Experiment	Initial [NO] / mol dm^{-3}	Initial [H_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	3.0×10^{-3}	1.0×10^{-3}	1.8×10^{-5}
2	3.0×10^{-3}		7.2×10^{-5}
3	1.5×10^{-3}	1.0×10^{-3}	
4		0.50×10^{-3}	8.1×10^{-5}

(3)

(b) Using the data from experiment 1, calculate a value for the rate constant, *k*, and state its units.

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(3)
(Total 6 marks)

Q5. The hydrolysis of methyl propanoate was studied in acidic conditions at 25°C and the rate equation was found to be

$$\text{rate} = k[CH_3CH_2COOCH_3][H^+]$$

(a) Use the data below to calculate the value of the rate constant, *k*, at this temperature.
Deduce its units.

Initial rate of reaction / mol dm^{-3} s^{-1}	Initial concentration of methyl propanoate / mol dm^{-3}	Initial concentration of hydrochloric acid / mol dm^{-3}
1.15×10^{-4}	0.150	0.555

Rate constant .....

.....

.....

Units .....

.....

(3)

(b) The reaction in part (a) was repeated at the same temperature, but water was added so that the volume of the reaction mixture was doubled. Calculate the initial rate of reaction under these conditions.

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(1)

(c) A third experiment was carried out at a different temperature. Some data from this experiment are shown in the table below.

Initial rate of reaction / mol dm^{-3} s^{-1}	Value of rate constant at this different temperature	Initial methyl propanoate / mol dm^{-3}
4.56×10^{-5}	8.94×10^{-4}	0.123

Calculate the initial pH of the reaction mixture. Give your answer to two decimal places.

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(3)
(Total 7 marks)

Q6. Kinetic studies enable chemists to suggest mechanisms for reactions.

(a) The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Experiment	Initial concentration of **A**/mol dm^{-3}	Initial concentration of **B**/mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
1	0.12	0.15	0.32×10^{-3}
2	0.36	0.15	2.88×10^{-3}
3	0.72	0.30	11.52×10^{-3}

(i) Deduce the order of reaction with respect to **A**.

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.....

(ii) Deduce the order of reaction with respect to **B**.

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.....

(2)

(b) The following data were obtained in a series of experiments on the rate of the reaction between NO and O_2 at a constant temperature.

Experiment	Initial concentration of NO/mol dm^{-3}	Initial concentration of O_2/mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
4	5.0×10^{-2}	2.0×10^{-2}	6.5×10^{-4}
5	6.5×10^{-2}	3.4×10^{-2}	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[NO]^2[O_2]$$

(i) Use the data from Experiment **4** to calculate a value for the rate constant, *k*, at this temperature, and state its units.

Value of k .....

.....

Units of k .....

.....

(ii) Calculate a value for the initial rate in Experiment **5**.

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.....

(iii) Using the rate equation, a scientist suggested a mechanism for the reaction which consisted of the two steps shown below.

Step 1 $NO + NO \rightarrow N_2O_2$

Step 2 $N_2O_2 + O_2 \rightarrow 2NO_2$

Which did the scientist suggest was the rate–determining step?

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(5)
(Total 7 marks)

Q7. Propanone and iodine react in acidic conditions according to the following equation.

$$CH_3COCH_3 + I_2 \rightarrow ICH_2COCH_3 + HI$$

A student studied the kinetics of this reaction using hydrochloric acid and a solution containing propanone and iodine. From the results the following rate equation was deduced.

$$\text{rate} = k[CH_3COCH_3][H^+]$$

(a) Give the overall order for this reaction.

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(1)

(b) When the initial concentrations of the reactants were as shown in the table below, the initial rate of reaction was found to be 1.24×10^{-4} mol dm^{-3} s^{-1}.

	initial concentration / mol dm^{-3}
CH_3COCH_3	4.40
I_2	5.00×10^{-3}
H^+	0.820

Use these data to calculate a value for the rate constant, *k*, for the reaction and give its units.

Calculation .....

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Units .....

(3)

(c) Deduce how the initial rate of reaction changes when the concentration of iodine is doubled but the concentrations of propanone and of hydrochloric acid are unchanged.

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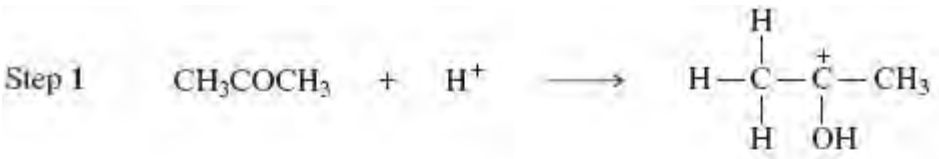
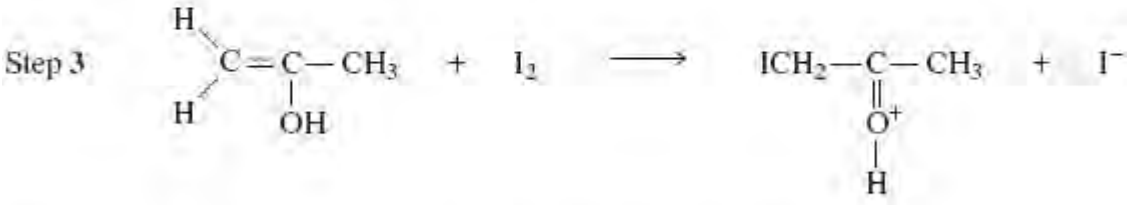
(1)

(d) The following mechanism for the overall reaction has been proposed.

Step 1 

Step 2 

Step 3 

Step 4 

Use the rate equation to suggest which of the four steps could be the rate-determining step. Explain your answer.

Rate-determining step .....

Explanation .....

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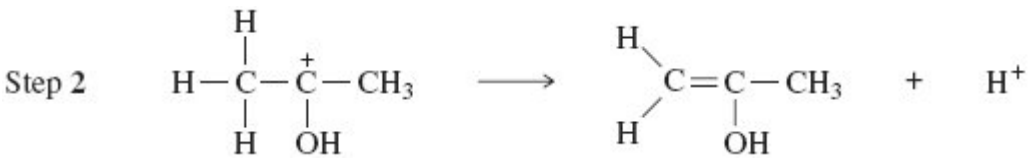
(2)

(e) Use your understanding of reaction mechanisms to predict a mechanism for Step **2** by adding one or more curly arrows as necessary to the structure of the carbocation below.

Step 2 

(1)
(Total 8 marks)