NAME ______________________ CLASS **18S**

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2019

CHEMISTRY

9729/03

Higher 2

23 September 2019

Paper 3 Free Response

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Cover Page for Answer
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a HB pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A *Data Booklet* is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **14** printed pages.

Section A

Answer **all** the questions in this section.

1 **(a)** When a red–hot wire is plunged into separate samples of the gaseous $\mathrm{HC}l$ and HI, a colour change was observed in one of the samples.

Suggest which sample gave the colour change. Use data from the *Data Booklet* to explain your answer. [2]

(b) Chlorine gas can be prepared by reacting concentrated hydrochloric acid with manganese(IV) oxide. Manganese(II) chloride and water are also formed. Chlorine gas evolved is passed through a drying agent.

(i) Write an ion–electron equation for the reduction of manganese(IV) oxide, $\mathrm{MnO_2}$. [1]

(ii) The standard reduction potential, E , of the half–reaction in **(b)(i)** is +1.23 V.

Calculate ΔG , in kJ $\mathrm{mol^{-1}}$, for the overall reaction and use it to explain why the reaction is unlikely to occur. [3]

(iii) Give **two** possible reasons why the reaction does occur. Explain your answer. [2]

(c) Alkenes or alcohols can react with gaseous $\mathrm{HC}l$ to form alkyl chlorides. However, carboxylic acids do not react with gaseous $\mathrm{HC}l$.

(i) Describe the mechanism for the reaction of propene with $\mathrm{HC}l$. [2]

(ii) With reference to your mechanism in **(c)(i)**, suggest how propene can act as a Bronsted–Lowry base. [1]

(iii) State the *type* of reaction that occurs between ethanol and gaseous $\mathrm{HC}l$. [1]

(iv) Explain why ethanoic acid does not react with gaseous $\mathrm{HC}l$. [1]

(d) HC*l* can be used to prepare perchloric acid, $HClO_4$.

In the presence of $HClO_4$, alcohols reacts with nitriles to form *N*–alkylamides. This is known as the *Ritter reaction*, as shown in **Fig. 1.1**.

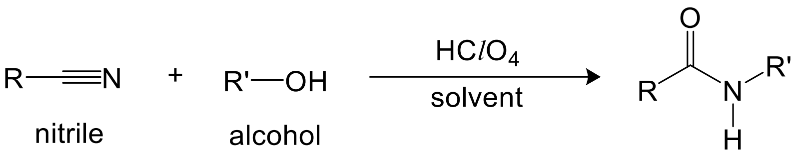


Fig. 1.1

Consider the following reaction which employs the *Ritter reaction* in the last step.

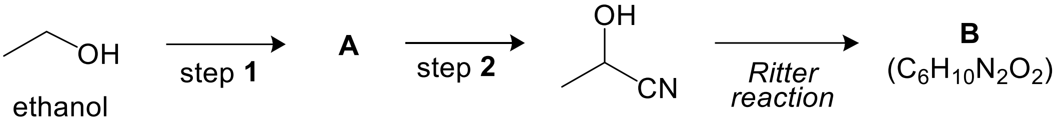


Fig. 1.2

Suggest appropriate reagents and conditions necessary for steps **1** and **2**, and draw the structures of the compounds **A** and **B**. [4]

(e) *Lingzhi* (*Ganoderma lucidum)* is a mushroom that has been used in Chinese medicines for more than 2000 years due to its numerous health benefits.

When *Lingzhi* is ingested, gastric juice in the stomach which comprises mainly hydrochloric acid, activates digestive enzymes to breakdown proteins into smaller peptides and amino acids.

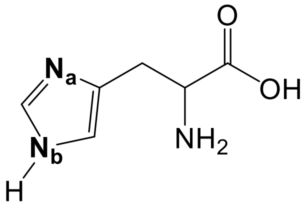
(i) A peptide, isolated from *Lingzhi*, consists of 10 amino acid residues. It is partially hydrolysed into the following tripeptides:

ala–val–ser, leu–gly–val, ser–gly–arg,

val–ala–val, arg–asn–leu, gly–arg–asn

Suggest the primary structure of this peptide. [1]

(ii) Histidine is an amino acid also found in *Lingzhi*.



histidine (his)

Both N_a and N_b are sp^2 hybridised.

By considering the hybridisation state and the orientation of the p orbitals of the two nitrogen atoms, explain why N_a is a stronger base than N_b. [1]

Histamine, which causes allergic reaction such as runny noses and itchy eyes, is synthesised in the body by decarboxylation of histidine with the aid of an appropriate enzyme catalyst.

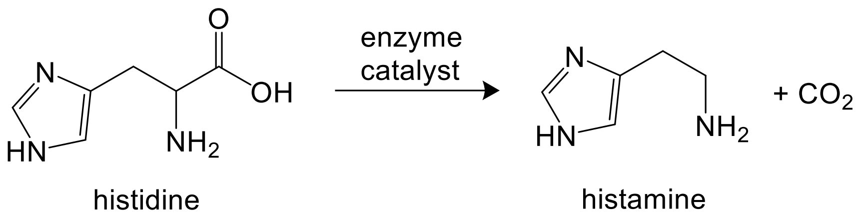


Fig. 1.3

(iii) With the aid of a Boltzmann distribution curve, explain how enzymes speed up the decarboxylation reaction. [3]

(iv) The reaction in **Fig 1.3** has a first–order kinetics.

Sketch a graph to illustrate the relationship between the rate of reaction and [histidine] in the presence of a very small amount of enzyme catalyst. [1]

[Total: 23]

2 **(a)** The kinetic theory of gases makes assumptions about the behaviour of an ideal gas. State **two** assumptions of the kinetic theory of gases. [2]

(b) Ozone, O_3, is produced naturally in the stratosphere when highly energetic solar radiation strikes molecules of oxygen, O_2.

$$3O_2(g) \ll 2O_3(g) \qquad \text{value of } K_p = 6.1 \times 10^{-62} \text{ at } 25\ ^\circ\text{C}$$

(i) Write K_p expression for this reaction. [1]

(ii) Assuming gaseous oxygen and ozone obey the ideal gas equation, use your answer in **(b)(i)** to express K_c in terms of K_p and hence, show that the value of K_c is 1.5×10^{-55}. [2]

(iii) Based on the numerical value of K_c given in **(b)(ii)**, how does the amount of product compare to the amount of reactant in this reaction at equilibrium? [1]

(iv) If a 4 dm^3 flask is initially filled with 10.0 moles of O_2, calculate the equilibrium concentration of ozone.

You may use your conclusion in **(b)(iii)** to make suitable approximation in your calculations. [2]

(c) Ozone reacts with water and sulfur dioxide, SO_2 to form sulfuric acid, H_2SO_4, as the only product.

(i) Construct a balanced equation for this reaction. [1]

H_2SO_4, a dibasic acid, dissociates in two stages.

$$H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+$$

$$HSO_4^- + H_2O \ll SO_4^{2-} + H_3O^+ \qquad K_a = 0.012 \text{ mol}$$

dm^{-3}

(ii) Suggest a reason for the difference in the extent of dissociation of H_2SO_4 and HSO_4^-. [1]

(iii) Calculate the pH of the buffer solution formed when 5 cm^3 of 0.100 mol dm^{-3} HCl solution was added to 10 cm^3 of 0.200 mol dm^{-3} Na_2SO_4 solution. [2]

(d) Concentrated sulfuric acid can be used to form ester by reacting alcohol with ethanoic acid. However, under the same condition, phenol cannot react with ethanoic acid to form ester **E**.

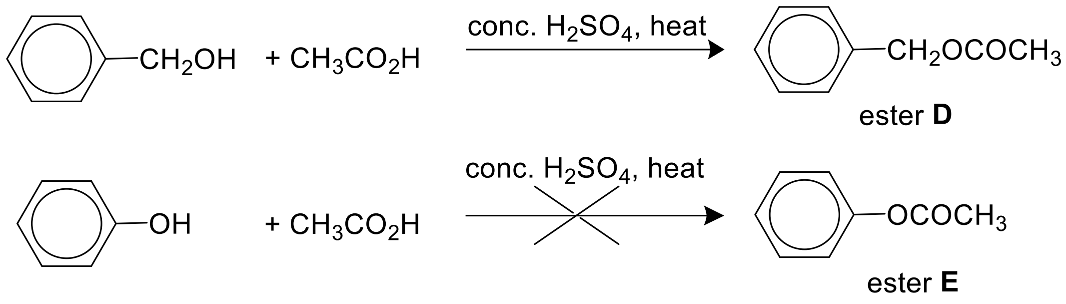


Fig. 2.1

Explain why ester **E** cannot be formed from phenol and ethanoic acid.

Suggest suitable reagent and conditions for the formation of ester **E** from phenol. [2]

(e) **Fig. 2.2** shows the reaction scheme for the conversion of a diester into salbutamol, a drug used to treat asthma.

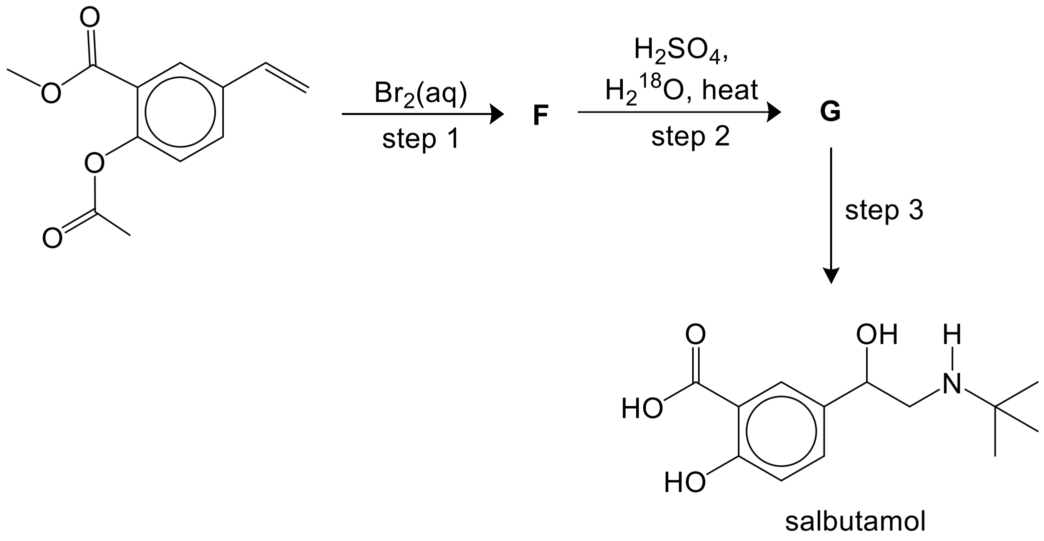


Fig. 2.2

(i) Draw the structure of **F**. [1]

(ii) Isotopic labelling experiment is often used to elucidate the mechanism of organic reaction. In step 2 of **Fig 2.2**, the water used in the hydrolysis of **F** was labelled using the oxygen isotope ^{18}O.

Draw the structure of **G**, stating clearly the ^{18}O isotope if present. [2]

(iii) Suggest the reagent and conditions necessary for step 3. [1]

(iv) Suggest why step 2 cannot be carried out before step 1. [1]

(v) Explain why the reaction in step 3 is likely to give a low yield of salbutamol. [1]

[Total: 20]

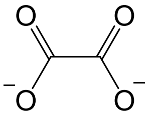
3 **(a)** **(i)** Write the full electronic configurations for a Cr atom. [1]

(ii) Transition elements exhibit a range of different oxidation states.

Describe and explain the pattern of **maximum** oxidation states for the elements from Sc to Zn. [2]

(iii) Explain why iron(III) salts are usually coloured while scandium(III) salts are white or colourless. [3]

(iv) When a solution of cobalt(II) sulfate is warmed with potassium ethanedioate, $K_2C_2O_4$, sulfuric acid and hydrogen peroxide, a complex with the formula $K_3[Co(C_2O_4)_3]$ is formed. The structure of ethanedioate ion is given below.



ethanedioate ion

Draw the three–dimensional diagram to show the shape of the cobalt–containing anion. [1]

(b) Copper in oxidation state of +1 is unstable in aqueous solution but can be stabilised as insoluble salts and in some complexes.

Step 1: On boiling with copper metal, 1 mole of blue aqueous $CuCl_2$ reacts with 2 moles of dilute HCl to give a colourless solution **P**, which contains complex ion of copper and chlorine.

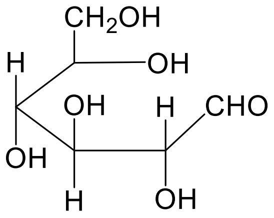
Step 2: After filtering off the excess copper metal and diluting the solution with water, a white solid **Q**, containing copper and chlorine only, is formed. The oxidation number of copper in **P** and **Q** are the same.

(i) Explain the observations in step 1.

Your answer should include the type of reactions that have occurred and give the formula of any insoluble salt and complex formed. Write an equation for the reaction that occurred. [2]

(ii) Identify the white solid **Q** formed in step 2. [1]

(c) Fehling's solution can be used to screen for glucose in urine, thus detecting diabetes. It gives a positive test due to the presence of an aliphatic aldehyde functional group in the open structure of glucose.

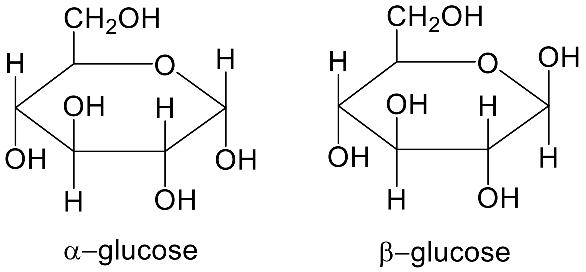


open structure of glucose

Fehling's solution is prepared by mixing $CuSO_4$(aq) and an alkaline solution of Roselle salt. The resulting solution contains a deep blue copper–containing complex ion, $[CuL_2]^{2-}$.

(i) State what would you observe when Fehling's solution is added to glucose. Draw the structure of the organic product formed. [2]

However, the open structure made up a very small amount of the glucose molecules in aqueous solution. The glucose molecules are present predominantly in cyclic ring structures, namely α–glucose and β–glucose, as shown in **Fig. 3.1**.



α–glucose β–glucose

Figure 3.1

(ii) This cyclic form of glucose exhibits both enantiomerism and cis–trans isomerism. One way of labelling the stereochemical configuration of α–glucose is (trans, cis) while that of β–glucose is (trans, trans).

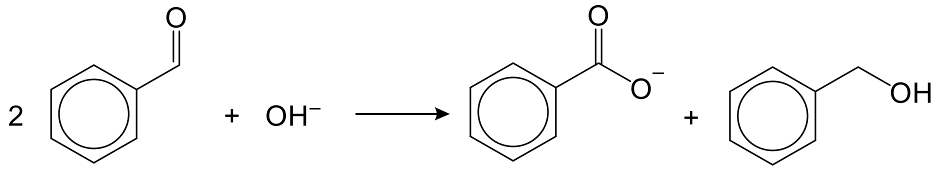
Explain why glucose can exhibit both enantiomerism and cis–trans isomerism. [2]

(iii) A 1.0 mol dm^{-3} α–glucose solution has an optical rotation angle of +113.4 ° while a 1.0 mol dm^{-3} β–glucose solution has an optical rotation angle of +19.0 ° at 298 K.

An equilibrium mixture containing both α–glucose and β–glucose has an optical rotation angle of +52.2 °.

Determine the percentage of α–glucose in the mixture. [2]

(iv) On the other hand, the complex ion in Fehling's solution has no reaction with benzaldehyde, which is an aromatic aldehyde. This is because under the influence of the alkaline medium, benzaldehyde reacts according to the below equation.



Suggest the type of reaction that has occurred. [1]

[Total: 17]

Section B

Answer **one** question from this section.

4 **(a)** There is said to be a 'diagonal relationship' between elements of the second and third periods of the Periodic Table, exemplified by lithium and magnesium, and by beryllium and aluminium. This relationship leads to diagonal pairs of elements having similar properties.

(i) By considering the trends in electronegativity across the period and down the group, suggest why beryllium and aluminium have similar properties. [1]

(ii) In terms of structure and bonding, explain why the boiling point of beryllium chloride is much lower than that of beryllium oxide. [2]

(iii) Beryllium chloride dissolves in water to give $[Be(H_2O)_4]^{2+}$.

Predict and explain the effect of adding beryllium chloride to a beaker of litmus solution. [2]

(b) Beryllium oxide was heated with a mixture of potassium fluoride and hydrogen fluoride. An ionic compound was formed, which dissolved in water. When the resultant solution was added to aqueous lead(II) nitrate, a white precipitate, **A**, containing only beryllium, fluorine and lead was obtained. The white precipitate contained 3.08 % by mass of beryllium.

(i) Given that the relative formula mass of **A** is approximately 290 and the empirical formula of **A** is $PbBe_xF_y$, determine the values of x and y.

Shows all working clearly. [2]

(ii) The anion in compound **A** is also formed when 1 mole of beryllium difluoride reacts with 2 moles of potassium fluoride.

Draw a 'dot–and–cross' diagram of this anion, showing the outer shell electrons only. In your diagram, use the symbols '•' and '×' to distinguish electrons from different atoms, and the symbol '☐' for any additional electrons responsible for the overall negative charge. [1]

Aryl esters can be converted to aryl ketones by a reaction known as the Fries rearrangement.

In the presence of $AlCl_3$, the acetyl group, $-COCH_3$, is transferred to the 2–position to form 2–hydroxyacetophenone, depending on the reaction conditions used. A proposed mechanism for the Fries rearrangement of phenyl ethanoate is shown **Fig. 4.1.**

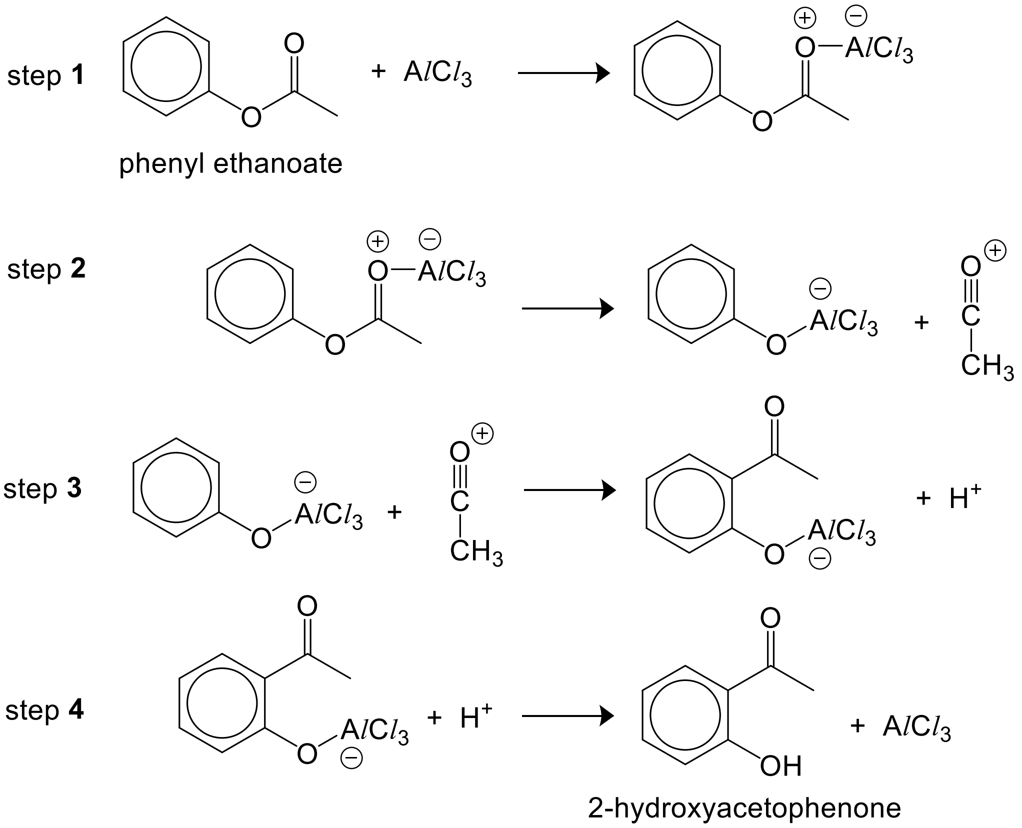


Fig. 4.1

(c) **(i)** Write an overall equation for the Fries rearrangement of phenyl ethanoate. [1]

(ii) Considering the mechanism in **Fig. 4.1** and your overall equation in **(c)(i)**, state and explain the roles of $AlCl_3$ in Fries rearrangement. [2]

(iii) Step **3** of the mechanism in **Fig. 4.1** occurs in two stages.

- In stage 1, benzene attacks the electron–deficient carbon atom of CH_3CO^+ to form an intermediate with delocalised positive charge.
- In stage 2, the loss of a proton restores the aromaticity of the compound.

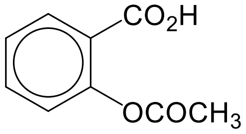
Using curly arrows to show the movement of electron pairs, complete the mechanism. Show all charges and relevant lone pairs. [3]

(iv) Describe a simple chemical test to confirm that 2–hydroxyacetophenone is formed during the reaction. State what you would observe. [2]

(v) 4–hydroxyacetophenone was also formed during the Fries rearrangement of phenyl ethanoate. However, 2–hydroxyacetophenone is likely to be formed in larger proportion than 4–hydroxyacetophenone due to the formation of favourable interactions between the ketone and alcohol functional groups.

Draw an appropriate diagram to illustrate the type of interactions formed, stating the interactions clearly. [2]

(d) Aryl ester **B** is an analog of phenyl ethanoate.



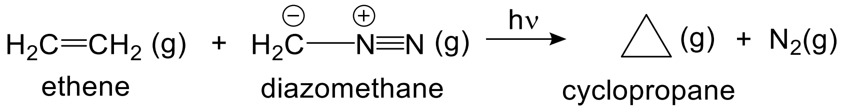
aryl ester **B**

Considering the mechanism in **(c)(iii)**, explain how the rate of Fries rearrangement might compare with phenyl ethanoate if aryl ester **B** was used instead. [2]

[Total: 20]

5 **(a)** **(i)** Explain what is meant by the term *bond energy*. [1]

(ii) In the presence of light, diazomethane gas reacts with ethene to give cyclopropane.



Use relevant bond energies data from the *Data Booklet* to calculate the standard enthalpy change of the reaction between diazomethane gas and ethene. [2]

(iii) Other than average bond energies in the *Data Booklet*, suggest why the theoretical value calculated in **(a)(ii)** is likely to be *significantly* less exothermic than the actual value. [1]

(b) Alkenes can be formed from alkyl halide, via elimination process, in the presence of a suitable base such as potassium hydroxide. Like nucleophilic substitution of alkyl halides, there are two possible mechanisms for the elimination reaction, namely E1 and E2.

E1 reaction is an unimolecular reaction which occurs via a two-step mechanism.

- In the first step which is also the rate–determining step, the alkyl halide undergoes a dissociation process to yield a carbocation and halide ion.
- The carbocation then reacts with hydroxide ion where a C–H bond is broken to give the alkene in the second step.

On the other hand, E2 reaction is a bimolecular elementary reaction.

Using 2–bromo–2–methylpropane as an example, **Fig. 5.1** shows the overall equation for the elimination reaction of alkyl halide.

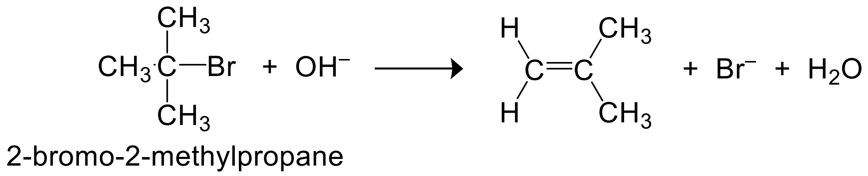


Fig. 5.1

(i) Using 2–bromo–2–methylpropane as an example, write the rate equations for the E1 reaction **and** the E2 reaction. [2]

(ii) Using the information on E1 mechanism given above, outline the E1 mechanism for 2–bromo–2–methylpropane.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

(iii) Explain how the rate of E1 reaction of 2–bromo–2–methylpropane would change if $CH_3CH_2O^-$ is used as the base instead of OH^-. [2]

(c) Since both mechanisms proceed via the same carbocationic intermediate, there is usually competition between E1 reaction and S_N1 reaction.

(i) Write a balanced chemical equation for the nucleophilic reaction of 2–bromo–2–methylpropane with potassium hydroxide. [1]

(ii) Considering the equation in **Fig. 5.1** and your answer in **(c)(i)**, explain, in thermodynamic terms, why E1 reaction predominates over S_N1 reaction when a higher temperature was used. [2]

(iii) When benzyl bromide, $C_6H_5CH_2Br$, is reacted with potassium hydroxide, it was found that it does not undergo elimination reaction. Also, benzyl bromide undergoes substitution via S_N1 instead of the usual S_N2 mechanism, typical for a primary alkyl halide.

Explain the above observations. [3]

(iv) In comparing the reactivity between different alkyl halides towards nucleophilic substitution, there are two main factors at work: the strength of C–X bond and the stability of the leaving group X^-.

One way of measuring the stability of the leaving group X^- ion is to use the pK_a values of HX acids in **Table 5.2**.

Table 5.2

HX	HF	HC*l*	HBr	HI
pK_a of HX	+3	–7	–9	–10

By relating the pK_a values given in **Table 5.2** to the position of equilibrium and the stability of X^- ion, explain how the reactivity of alkyl halide towards nucleophilic substitution vary from fluorine to iodine. [3]

[Total: 20]