ST ANDREW'S JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME

CLASS	2	2	S		

CHEMISTRY 9729/03

Paper 3 Free Response **14 September 2023**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work that you hand in.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the **spaces provided** on the Question Paper.

If additional space is required, you should use the pages at the end of this booklet.

The question number must be clearly shown.

Section A

Answer **all** questions.

Section B

Answer **one** question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Q1		21
Q2		20
Q3		19
Q4 or Q5		20
Total		80

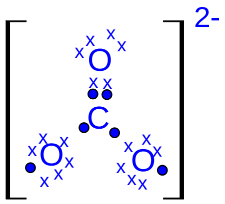
This document consists of XX printed pages (including this cover page).

Section A

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

1 In the manufacture of tinted glass for chapels, a variety of carbonates including calcium carbonate were smelted together to form the needed colourations.

(a) **(i)** Draw a 'dot-and-cross' diagram to show the bonding present within a carbonate ion, CO_3^{2-}. **[1]**



Accept x instead of • for the added e on the O

(ii) State and explain, with reference to the VSEPR theory, the shape of the carbonate ion. **[2]**

The carbonate ion has 3 bond pairs and 0 lone pairs around the central C. To minimise (electrostatic) repulsion (between the electron pairs, the shape of carbonate ion will be trigonal planar.

(iii) When sodium carbonate was added to water, a weakly alkaline solution is produced. **[1]**

Write an equation for this reaction.

$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

(b) **(i)** Write a balanced equation, with state symbols, for the thermal decomposition of calcium carbonate under standard conditions. **[1]**

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

(ii) Construct a fully labelled energy cycle to show that the standard enthalpy change of formation of carbon dioxide is –399 kJ mol^{-1}. **[2]**

Your cycle should include relevant data from the *Data Booklet* together with the following data.

Standard enthalpy change of atomisation of carbon = +715 kJ mol^{-1}

$$\begin{tikzcd}
C(s) + O_2(g) \arrow[r, "\Delta H_f"] \arrow[d, "+715"] & CO_2(g) \\
C(g) + O_2(g) \arrow[r, "+496"] & C(g) + 2O(g) \arrow[u, "-805 \times 2"']
\end{tikzcd}$$

[1]

$\Delta H_f = +715 + 496 - 805 \times 2$

$= -399$ kJ mol^{-1}

(iii) The standard enthalpy changes of formation for these species are shown in the following table. **[1]**

Species	$CaCO_3(s)$	CaO (s)	$CO_2(g)$
ΔH_f^o / kJ mol^{-1}	–1207	–635	–399

Using your answer in **(b)(i)** and **(ii)**, calculate the standard enthalpy change of decomposition of calcium carbonate.

$\Delta H_{reaction} = \Delta H_f^o(CaO(s)) + \Delta H_f^o(CO_2(g)) - \Delta H_f^o(CaCO_3(s))$

$= -635 + (-399) - (-1207)$

$= +173$ kJ mol^{-1}

(iv) By considering the entropy change, ΔS, and enthalpy change, ΔH,, in the decomposition of calcium carbonate, predict if the reaction is spontaneous at high or low temperature. **[2]**

$\Delta S > 0$ as the number of gaseous particles increases.

Hence, at high temperature, $|T\Delta S| > |\Delta H|$ (or words to the effect),

$\Delta G < 0$ and reaction is spontaneous.

(v) Using relevant data from the *Data Booklet*, suggest how the decomposition temperature of nickel (II) carbonate would compare with calcium carbonate. Explain your reasoning. **[2]**

Ionic radii of Ca^{2+} = 0.099 nm and ionic radii of Ni^{2+} = 0.069 nm

Since the radii of Ni^{2+} is smaller as compared to Ca^{2+}, Ni^{2+} would have a stronger polarising power / higher charge density as compared to Ca^{2+}.

This would result in a stronger extent of polarisation / distortion of the electron cloud of the carbonate anion and

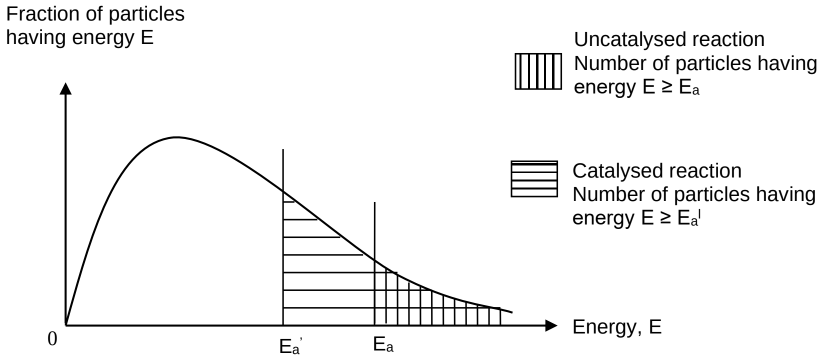
a stronger weakening of the covalent bonds within carbonate anion.

Hence less energy would be required to break such covalent bonds and a lower decomposition temperature is expected for $NiCO_3$ as compared to $CaCO_3$.

(c) The reaction of propanone with iodine can be catalysed by an acid. **[3]**

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$$

Sketch a Boltzmann distribution curve for the reaction and use it to explain the effect on the rate of the reaction when the catalyst is removed by adding $CaCO_3$.



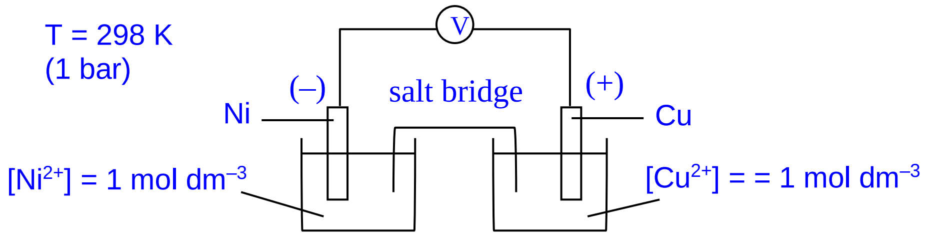
where $E_a{}'$ is the original activation energy and E_a is the new higher activation energy.

- Removal of the catalyst / H^+ ions results in the removal of the **alternative reaction pathway with a lower activation energy, E_a'**. Or removal of H^+ catalyst means the reaction proceeds in a reaction pathway with higher activation energy, E_a.
- The **number of reactant particles having energy greater than or equal to the activation energy decreases**.
- **Frequency** of **effective collisions** decreases.
- Rate **decreases**.

(d) When aqueous Cu^{2+} and Ni are mixed, an equilibrium is set up.

$$Ni + Cu^{2+} \rightleftharpoons Ni^{2+} + Cu$$

(i) Draw a fully labelled diagram of the experimental set-up used to measure the standard cell potential for this equilibrium. **[2]**



(ii) Calculate the standard cell potential in **(d)(i)** and hence calculate the standard free energy change, $\Delta G^\ominus$, per mole of Cu formed. **[2]**

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ +0.34 V

$Ni^{2+} + 2e^- \rightleftharpoons Ni$ -0.25 V

$E^\ominus_{cell} = +0.34 - (-0.25) = +0.59$ V

$\Delta G^\ominus = -(2)(96500)(+0.59)$

$= -\ 113879$ J mol^{-1}

$= -114$ kJ mol^{-1}

(iii) Use the *Data Booklet* to suggest how the position of equilibrium would change when concentrated NH_3 is added to the Ni^{2+}/Ni half cell. Explain your answer and write a balanced equation for this reaction. **[2]**

$Ni^{2+} + 2e^- \rightleftharpoons Ni$ – 0.25 V

$[Ni(NH_3)_6]^{2+} + 2e^- \rightleftharpoons Ni + 6NH_3$ – 0.51 V

[Ni^{2+}] drops / E_{anode}(Ni^{2+}/Ni) becomes more negative / increases the reducing ability of Ni / decreases the oxidising ability of Ni^{2+} / [Ni^{2+}] decreases.

Hence, position of equilibrium would shift right

$$Ni + 6NH_3 + Cu^{2+} \rightarrow [Ni(NH_3)_6]^{2+} + Cu$$

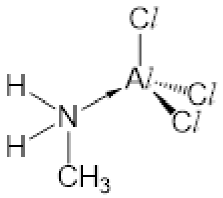
[Total: 21 marks]

2 **(a)** Methylamine, CH_3NH_2, can function as a *Lewis base*.

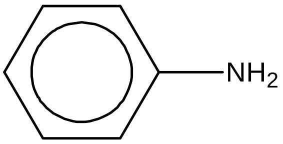
(i) Explain what is meant by this statement and illustrate your answer with an equation. **[2]**

N in methylamine can serve as **electron pair donors**.

$CH_3NH_2 + AlCl_3 \rightarrow$



(ii) Describe and explain the relative basicities of the following compounds.

Compound	**formula**
A	CH_3NH_2
B	$CH_3CH_2CH_2CONHCH_3$
C	

[3]

Order of increasing basic strength: **B** < **C** < **A**

B is an amide and is the least basic (effectively neutral) because the lone pair of electrons on N is delocalised over the N-C-O bond, hence unavailable for donation to a proton.
C is more basic **B** as the delocalisation effect in **C** is less extensive.

A is the most basic as the electron donating -CH_3 group makes the lone pair of electrons on N in **A** more available for donation to a proton.
C is less basic than **A** because the lone pair of electrons on N can delocalise into the benzene ring.

(b) Methylamine can also serve as a *monodentate ligand*.

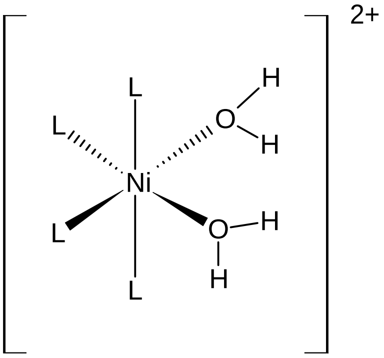
(i) State what is meant by *monodentate ligand.* **[2]**

A monodentate ligand is an ion or molecule (or species) which can donate one lone pair of electrons to the vacant orbitals of a (central) metal atom/ion to form **one** dative/coordinate bond.

(ii) In the presence of aqueous methylamine, $[Ni(H_2O)_6]^{2+}$ reacts to form a mixture of two isomeric octahedral complexes.

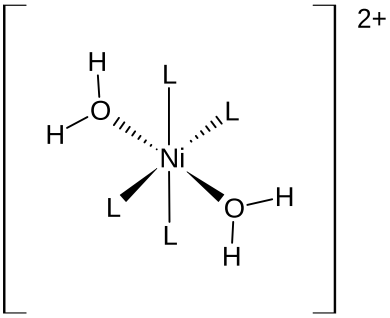
$[Ni(H_2O)_6]^{2+} + 4CH_3NH_2 \rightleftharpoons [Ni(CH_3NH_2)_4(H_2O)_2]^{2+} + 4H_2O$ ---- ***Reaction 2.1***

One of the isomeric octahedral complexes has the *cis* configuration as shown below where L is the CH_3NH_2 ligand.



Draw the **3-dimensional** structure of the *trans* isomer of $[Ni(CH_3NH_2)_4(H_2O)_2]^{2+}$.

You may also use L to represent CH_3NH_2. **[1]**



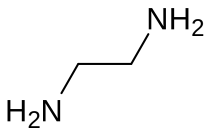
Trans

(iii) Predict the effect of plane-polarised light on the solution containing the *cis* isomer of the $[Ni(CH_3NH_2)_4(H_2O)_2]^{2+}$ complex. Explain your reasoning. **[2]**

No effect on plane-polarised light

as the *cis* isomer has an internal plane of symmetry/no chiral centre/is a meso compound and is achiral.

(c) Ethane-1,2-diammine, en, is another ligand that reacts with $[Ni(H_2O)_6]^{2+}$ to form octahedral nickel(II) complexes.

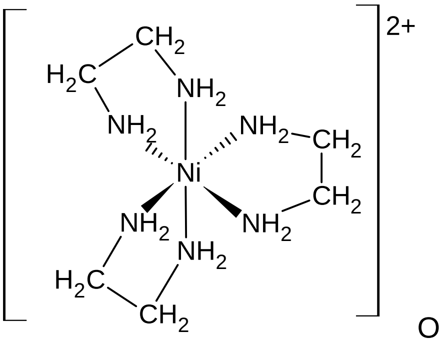


ethane-1,2-diammine

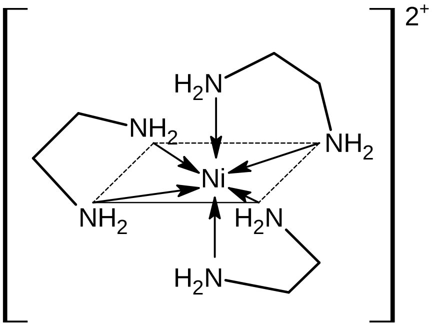
When an excess of ethane-1,2-diammine is added to an aqueous solution of $[Ni(H_2O)_6]^{2+}$,the following equilibrium is established.

$[Ni(H_2O)_6]^{2+}(aq) + 3en(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) + 6H_2O(l)$ ------ ***Reaction 2.2***

(i) Draw a diagram of the structure of $[Ni(en)_3]^{2+}$, showing the **3-dimensional** arrangement around the Ni(II) ion. **[1]**



OR



(ii) The K_c value for ***Reaction 2.2*** is 6.76×10^{17}. Hence, suggest the sign and magnitude of $\Delta G^{\ominus}$ for ***Reaction 2.2*** and identify the more stable complex for the reaction. **[1]**

$\Delta G^{\ominus}$ is less than zero and has a large magnitude, thus $[Ni(en)_3]^{2+}$ is more stable.

(iii) With reference to ***Reactions 2.1*** and ***2.2***, suggest why ethane-1,2-diammine forms a more stable nickel(II) complex than with methylamine. **[1]**

Ethane-1,2-diammine serves as a bidentate ligand /which forms 2 dative bonds to Ni^{2+} per molecule. The "chelate effect" allows it to bind more strongly to the Ni^{2+} ion compared to the monodentate methylamine ligand.

OR The stability of a complex increases as the entropy change of the system becomes more positive when monodentate ligands are exchanged with bidentate ligands.

(d) Nickel complexes often exhibit a range of colours as shown in Table 2.1.

Complex	**Colour**
$[Ni(H_2O)_6]^{2+}$	Green
$[Ni(en)_3]^{2+}$	Blue
$[Ni(H_2O)_6]^{3+}$	Pink

Table 2.1

(i) The five d orbitals in a gas–phase Ni^{2+} ion are degenerate, but are split into two levels when Ni^{2+} ion is in an octahedral complex.

State and explain how the energy of the d subshell of Ni^{2+} ion in an octahedral complex compares with the energy of the d subshell in the gas-phase Ni^{2+} ion. State and explain why the d orbitals split into two levels in an octahedral complex, including which of the d orbitals are in each level. **[3]**

The energy of the d subshell of Ni^{2+} ion octahedral complex is higher than the energy of the d subshell in the gas-phase Ni^{2+} ion. This is due to the (electronic / electrostatic) repulsion between the (lone pair of) electrons of the ligands and the electrons in the d orbitals / Ni^{2+}.

The splitting into 2 energy levels is due to the ligands that approach Ni^{2+} ion along the axes, resulting in greater repulsion with the d_{z^2} and the $d_{x^2-y^2}$ orbitals . Hence, these orbitals have a higher energy than the d_{xy}, d_{xz} and d_{yz} orbitals.

(ii) Explain the following:

- $[Ni(H_2O)_6]^{2+}$ has a different colour from $[Ni(H_2O)_6]^{3+}$.
- $[Ni(en)_3]^{2+}$ has a different colour from $[Ni(H_2O)_6]^{2+}$. **[2]**

There is a difference in electronic configuration / different number of electrons between Ni^{2+} and Ni^{3+}. Whereas, there is a difference in ligand between $[Ni(en)_3]^{2+}$ and $[Ni(H_2O)_6]^{2+}$. Hence in both cases, this results in a difference in the energy gap, ΔE, between lower energy and higher energy d orbitals.

(iii) When concentrated hydrochloric acid is added to a green solution containing $[Ni(H_2O)_6]^{2+}$, a yellow solution of $[NiCl_4]^{2-}$ is formed and the following equilibrium is established. **[2]**

$$[Ni(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [NiCl_4]^{2-} + 6H_2O \quad \text{--------} \textbf{\textit{ Reaction 2.3}}$$

Suggest the expected observation when silver nitrate solution is added dropwise to the yellow solution of $[NiCl_4]^{2-}$. Explain your answer.

When Ag^+ is added, white ppt of AgC*l* is observed.

As $[Cl^-]$ decrease, according to Le Chatelier's principle, position of equilibrium shift left to increase the concentration of $[Cl^-]$.

The yellow solution becomes more green in colour due to formation of more $[Ni(H_2O)_6]^{2+}$.

[Total: 20 marks]

3 1,3-butadiene is a colourless gas at room temperature. It undergoes a reaction with an equimolar amount of HBr to produce a mixture of products as shown in Fig. 3.1

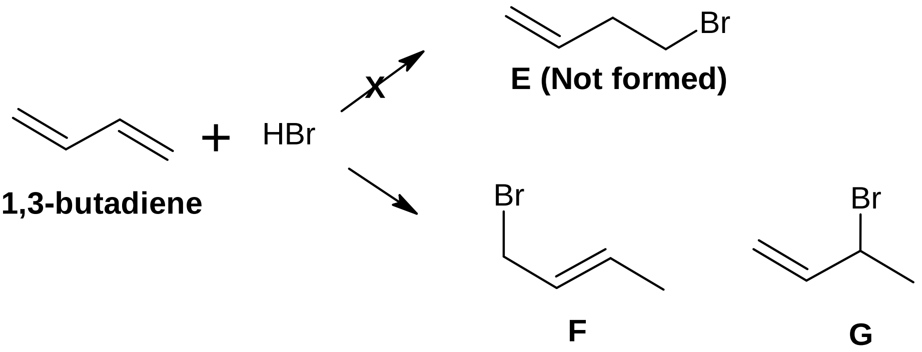
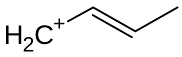


Fig. 3.1

(a) **(i)** The reaction between 1,3-butadiene and HBr to form compound **F** involves the shifting of the π electrons and the generation of the carbocation,  in the first step.

Complete Fig. 3.2 to name and suggest the mechanism for this reaction. Draw curly arrows to show the movement of electron pairs, showing relevant lone pairs and dipoles to describe the mechanism.

Name of Mechanism: Electrophilic addition

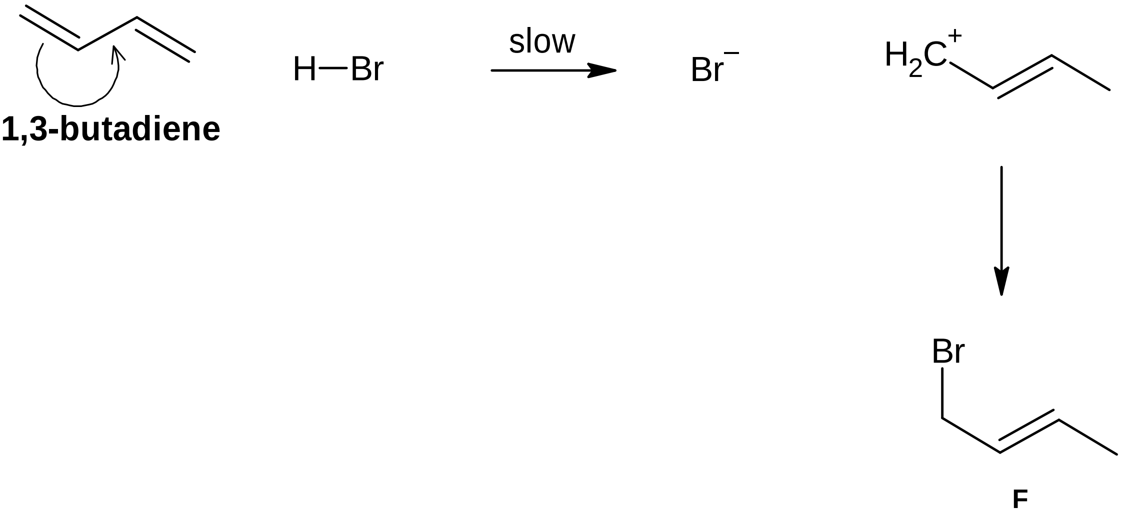
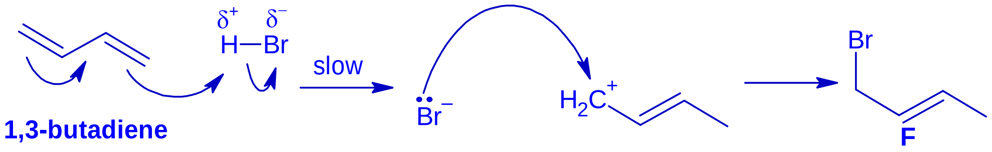
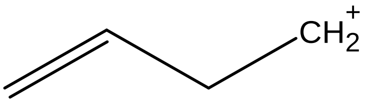


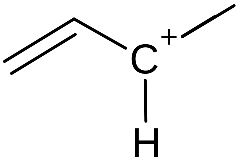
Fig. 3.2

[3]



(ii) Draw the structures of the carbocation intermediates that would result in compounds **E** and **G** respectively. **[2]**





(iii) Using the structures of the carbocation intermediates of **E**, **F** and **G**, suggest reasons to explain Fig. 3.1. Use concepts of electronic effect and delocalisation in your answer. **[2]**

The intermediate in forming compound **E** is a primary carbocation which is very unstable since there is only one electron-donating alkyl group bonded to the positively charged carbon present to disperse the positive charge. Hence this carbocation does not form.

The carbocations in forming compounds **F** and **G**, the delocalisation of π-electron cloud of the C=C bond to the carbon with the positive charge carbocation, dispersing the positive charge, thus stabilising the carbocation.

(b) 1,3-butadiene can be reduced with hydrogen gas in the presence of a nickel catalyst. Explain why $LiAlH_4$ cannot be used. **[1]**

Alkene functional group in 1,3-butadiene will repel the nucleophile, H^-, in $LiAlH_4$.

(c) Compound **R** ($C_{13}H_{16}O_3$) contains a 1,4-disubstituted benzene ring and does not contain any chiral centre.

R does not react with 2,4-dinitrophenylhydrazine and PCl_5. When treated with neutral $FeCl_3$, **R** forms a violet solution.

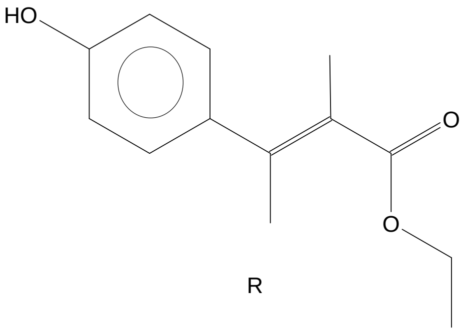
R also reacts with hot aqueous sulfuric acid to form ethanol as one of the products.

When treated with hot acidified $KMnO_4$, **R** forms compounds **S**, $C_8H_8O_2$, **T**, $C_3H_4O_3$ and **U**, $C_2H_4O_2$.

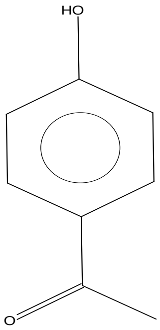
Compound **S** forms a yellow precipitate with alkaline aqueous iodine. **T** and **U** reacts with sodium carbonate to give effervescence.

Suggest possible structures of **R**, **S**, **T** and **U**. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. **[8]**

Observations	**Deductions**
Compound **R** does not react with 2,4-dinitrophenylhydrazine and phosphorus pentachloride	√There is **no carbonyl compound, alcohol and carboxylic acid groups** in **R**.
R forms a violet solution with neutral $FeCl_3$	√**Complex formation** reaction √**R** contains a **phenol**
R also reacts with hot aqueous sulfuric acid to form ethanol as one of the products.	√R could contain an **ester** based on the number of oxygen. R (ester) undergoes basic √**hydrolysis**
When treated with hot acidified $KMnO_4$, **R** forms compounds **S**, $C_8H_8O_2$, **T**, $C_3H_4O_3$ and **U**, $C_2H_4O_2$.	√**R undergoes oxidation** √**R contains a C=C** √ R (ester) undergoes acidic **hydrolysis**
Compound **S** give a yellow precipitate with alkaline aqueous iodine	√**S undergoes oxidation** √**S contains methyl ketone**
T and **U** reacts with sodium carbonate to give effervescence	√**Both T and U contain RCOOH** √ **They undergo acid-carbonate reaction**



R



S

T: $CH_3COCOOH$

U: CH_3COOH

Note: For structure S, students are to respond to data given the molecular formula that they are to stop at methyl ketone and also that it reacted with alkaline aq iodine. N2016 P3 Q3(d)

(d) Copper is one of the oldest transition metals to be used in synthetic organic chemistry. The reduction of a particular copper ore produced an alloy which was mainly copper with silver and zinc as minor impurities. It contained no other metal. In order to purify it, this alloy was the anode of an electrolysis cell, with a pure copper cathode and aqueous $CuSO_4$ as electrolyte.

Explain with relevance to relevant $E^{\ominus}$ values, what happens to the silver and zinc impurities during this purification procedure. **[3]**

$Ag^+ + e^- \rightleftharpoons Ag$ (+0.80V)
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ (+0.34V)
$Zn^{2+} + 2e^- \rightleftharpoons Zn$ (–0.76V)

At the anode
Cu is preferentially oxidised to Cu^{2+} and dissolve in the electrolyte. Zn will be oxidised to Zn^{2+} and dissolve in the electrolyte as well since $E^{\ominus}(Zn^{2+}/Zn)$ is more negative than $E^{\ominus}(Cu^{2+}/Cu)$.

Ag will not be oxidised to Ag^+ as $E^{\ominus}(Ag^+/Ag)$ is more positive than $E^{\ominus}(Cu^{2+}/Cu)$ and will be collected as anode sludge.

At the cathode
Cu^{2+} is preferentially reduced to Cu and deposited at electrode S as $E^{\ominus}(Cu^{2+}/Cu)$ is more positive than $E^{\ominus}(Zn^{2+}/Zn)$. Zn^{2+} have less positive $E^{\ominus}$ than $E^{\ominus}(Cu^{2+}/Cu)$, Zn^{2+} will remain dissolve in the electrolyte.

[Total: 19 marks]

Section B

Answer **one** question from this section.

4 **(a)** Describe and explain the trend in acidity of the hydrogen halides, HF, HC*l*, HBr and HI. Include equations to illustrate the acidic strength of HF and HI. [3]

Down the group, the atomic size of F to I increases.

There is less effective orbital overlap between the hydrogen atom and the halogen atom. Bond strength decreases from HF to HI and energy required to break the HX bond is lesser. Hence more H^+ ions will be dissociated from HF to HI.

Acidity increases from HF to HI .

$HF + H_2O \rightleftharpoons F^- + H_3O^+$

$HI + H_2O \rightarrow I^- + H_3O^+$

(b) The Koch reaction, as shown in Fig. 4.1, is an organic reaction for the synthesis of tertiary carboxylic acids from alkenes. On treatment with sulfuric acid, the mechanism begins by protonation of the alkene to form a carbocation. This is followed by an attack on the resulting carbocation by carbon monoxide. The subsequent acylium cation is then hydrolysed to the tertiary carboxylic acid.

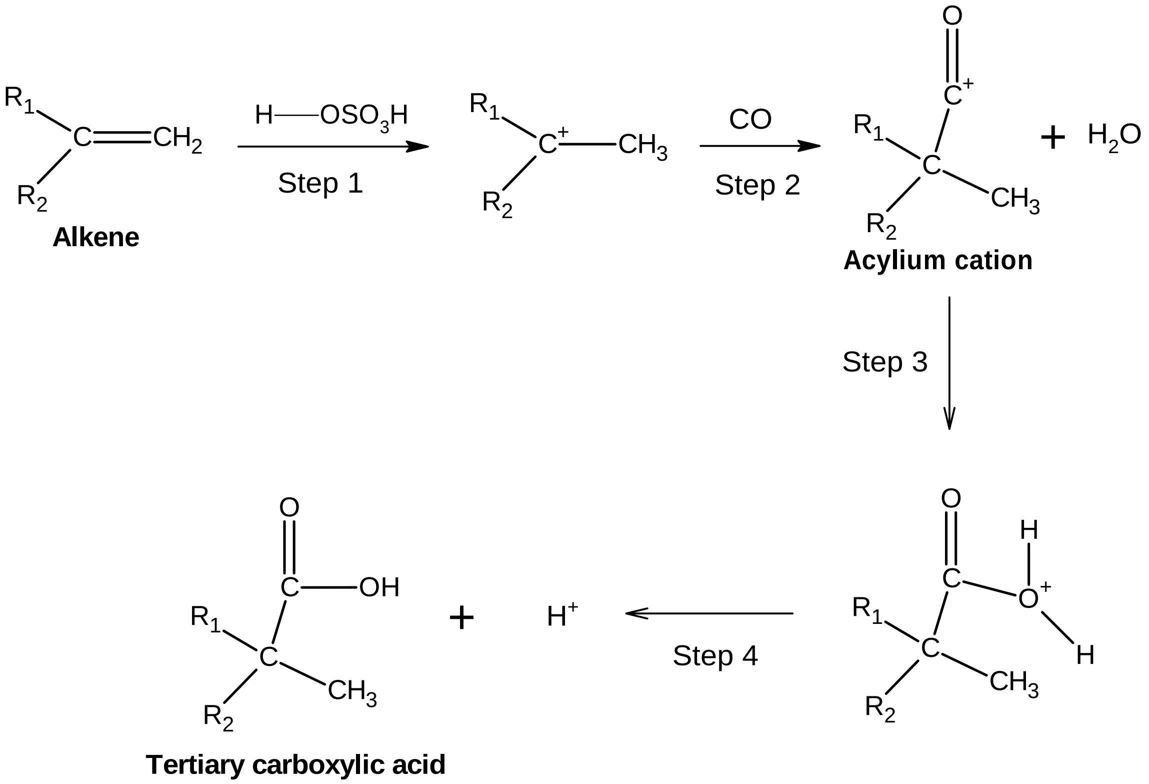
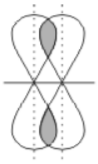


Fig. 4.1

(i) With reference to the hybridisation of the carbon atoms and orbital overlap, describe the covalent bonding in an alkene, C=C. Draw labelled diagram(s) to illustrate your answer. **[2]**

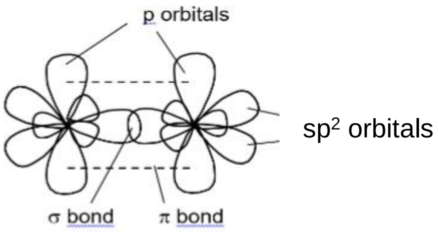
Two sp^2 orbitals overlap head-on to form sigma bond.

Two unhybridised p orbitals overlap side-on to form pi bond.



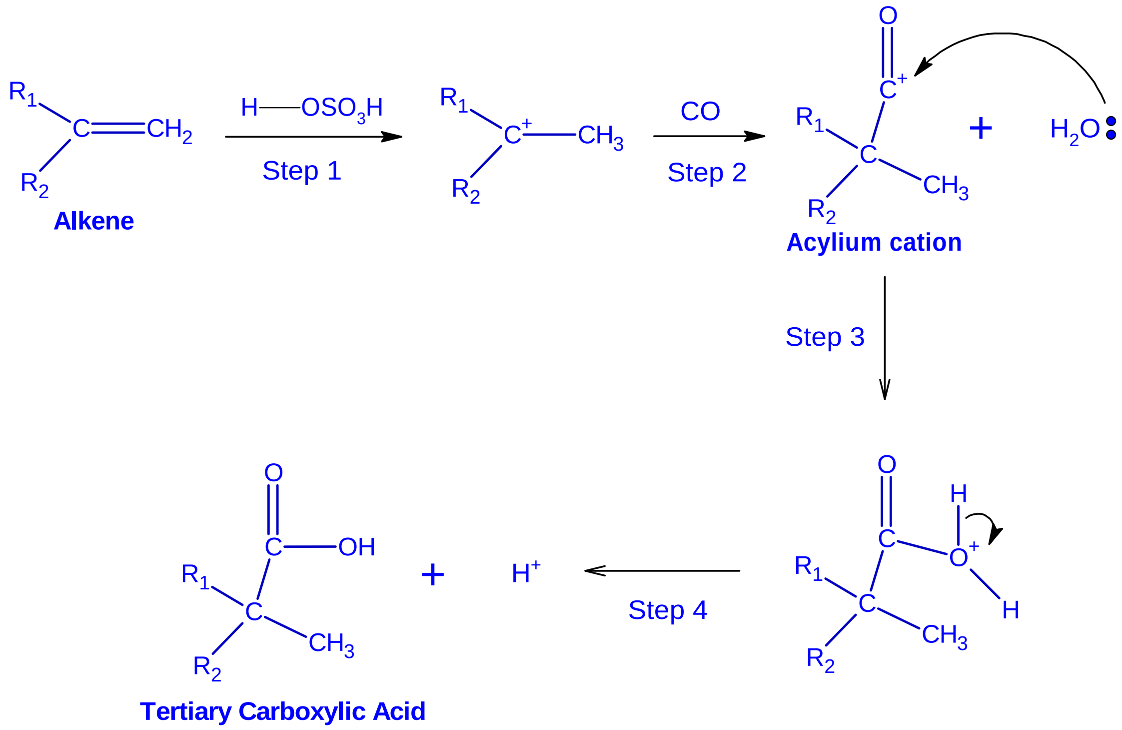
Side on overlap between p orbitals to form π bond

OR

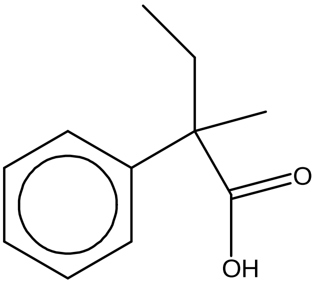


Head on overlap between sp^2 orbitals to form σ bond and side on overlap to form π bond.

(ii) On Fig. 4.1, draw curly arrows in **Steps 3** and **4**, to show the mechanism for the reaction. Show all relevant lone pairs of electrons in your answer. **[1]**

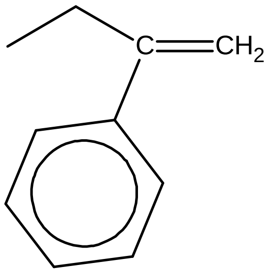


(iii) Draw the structure of the alkene that produces carboxylic acid **A** from the Koch reaction.



Carboxylic acid A

[1]

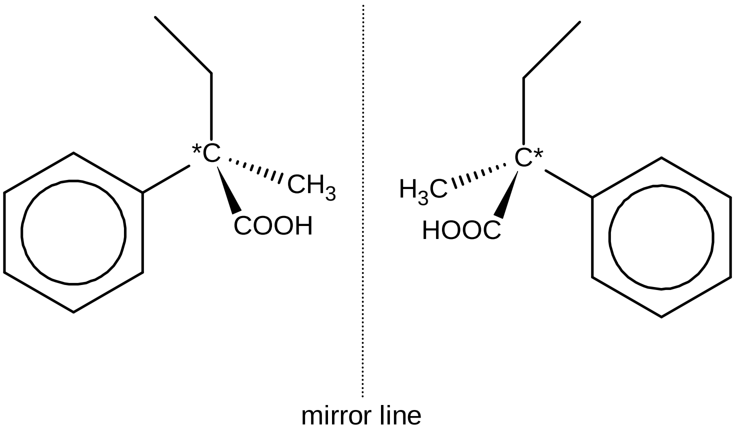


(c) **(i)** Describe the type of stereoisomerism shown by carboxylic acid **A** and draw the structures to illustrate your answer. **[2]**

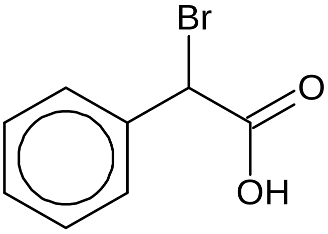
Enantiomerism

Enantiomers have the same molecular and structural formulae. They are **non-superimposable mirror images** of each other. Enantiomerism occurs when a molecule has

- a chiral centre and
- no internal plane of symmetry



(ii) Carboxylic acid **A** and carboxylic acid **B** have different pK_a values. State which compound, **A** or **B**, has a smaller pK_a value. Explain your answer. **[2]**



Carboxylic acid B

B has a smaller pK_a, as it is a stronger acid.

The electronegative/ electron withdrawing Br disperses the negative charge of O, stablising the conjugate base of B.

(d) Alkenes can react with an excess of hydrogen in the presence of a catalyst to form alkanes. Outline the mode of action of the nickel catalyst in the reaction of alkenes with hydrogen. **[2]**

The availability of 3d and 4s electrons in Ni allows the ready exchange of electrons between Ni and the alkene to form weak bonds. Alkenes and hydrogen **adsorbs** on the catalyst surface by **forming weak interactions**.

This **weakens the bonds in the reactants**, while **lowering the activation energy** and **increasing the surface concentration of reactants** on the catalyst. The products formed then **desorb** from the surface of catalyst.

(e) 40.00 cm^3 of 0.595 mol dm^{-3} of aqueous sodium hydroxide is added to 25.0 cm^3 of 0.500 mol dm^{-3} of $(CH_3)_3CCOOH$ that was formed from the Koch reaction.

(i) Write an expression for K_a of $(CH_3)_3CCOOH$, giving its units.
Hence, calculate K_a of $(CH_3)_3CCOOH$ given that the initial pH of $(CH_3)_3CCOOH$ is 2.8. **[2]**

$K_a = \frac{[(CH_3)_3CCOO^-][H^+]}{[(CH_3)_3CCOOH]}$ **mol dm^{-3}**

Expression & units

$= \frac{[H^+]^2}{[(CH_3)_3CCOOH]} = \frac{(10^{-2.8})^2}{0.5} = \underline{\mathbf{5.02 \times 10^{-6}}}$

(ii) Write two equations to show how a solution containing $(CH_3)_3CCOO^-(aq)$ and $(CH_3)_3CCOOH(aq)$ behaves as a buffer when small amounts of $OH^-(aq)$ and $H_3O^+(aq)$ are separately added to the solution. **[2]**

$(CH_3)_3CCOO^- + H_3O^+ \rightarrow (CH_3)_3CCOOH + H_2O$

$(CH_3)_3CCOOH + OH^- \rightarrow (CH_3)_3CCOO^- + H_2O$

(iii) Calculate the $[(CH_3)_3CCOO^-]$ / $[(CH_3)_3CCOOH]$ ratio when the pH of the solution is 5.6. Hence, comment, with reason, on the effectiveness of the mixture as a buffer in removing H_3O^+ compared to in removing OH^-. **[2]**

$\text{pH} = \text{p}K_a + \lg \frac{[(CH_3)_3CCOO^-]}{[(CH_3)_3CCOOH]}$

$5.6 = -\lg 5.02 \times 10^{-6} + \lg \frac{[(CH_3)_3CCOO^-]}{[(CH_3)_3CCOOH]}$

$\frac{[(CH_3)_3CCOO^-]}{[(CH_3)_3CCOOH]} = 2.00$

At pH of 5.6, there is a higher concentration of $(CH_3)_3CCOO^-$ than $(CH_3)_3CCOOH$. Hence, the buffer is more effective in removing H_3O^+.

(iv) Write an equation to show that the pH of the equivalence point is more than 7 in this titration. **[1]**

$(CH_3)_3CCOO^- + H_2O \rightleftharpoons (CH_3)_3CCOOH + OH^-$

[Total: 20]

5 **(a)** Describe the reactions of Period 3 oxides with water by reference to the reactions of Na_2O, Al_2O_3 and P_4O_{10}.

Write equations for any reactions described. **[3]**

Na_2O reacts **vigorously** with water to form a colourless and strongly alkaline solution.

$Na_2O\ (s) + H_2O\ (l) \rightarrow 2\ NaOH\ (aq)$

Al_2O_3 does not react with water / insoluble in water, due to its highly exothermic lattice energy .

P_4O_{10} reacts **vigorously** with water to form a colourless and acidic solution.

$P_4O_{10}\ (s) + 6\ H_2O\ (l) \rightarrow 4\ H_3PO_4\ (aq)$

(b) Table 5.1 gives the melting points, in °C, of the oxides and chlorides of two elements in the Periodic Table.

	Magnesium	Aluminium
Oxide	2900	2000
Chloride	714	190

Table 5.1

Explain, in terms of structure and bonding, the differences in melting point between

- $MgCl_2$ and $AlCl_3$
- MgO and Al_2O_3 **[2]**

$MgCl_2$ is a giant ionic lattice structure with strong ionic bonds. Aluminium chloride is a simple covalent molecule with weaker instantaneous dipole-induced dipole interaction which requires lesser energy to overcome.

Both MgO and Al_2O_3 has a giant ionic lattice structure. Since, Al^{3+} has a high charge density, it can polarise the electron cloud of oxide anion causing covalent character in Al_2O_3 which requires lesser energy to overcome.

(c) Values of two solubility products are given in Table 5.2.

Compound	K_{sp}
$Hg_2C_2O_4$	6.5×10^{-7}
$Ag_2C_2O_4$	5.4×10^{-12}

Table 5.2

(i) Write the expression for the solubility product, K_{sp}, of $Hg_2C_2O_4$, stating its units. [2]

$K_{sp} = [Hg^+]^2[C_2O_4^{2-}]$

mol^3dm^{-9}

(ii) Solid mercury oxalate, $Hg_2C_2O_4$, is shaken with water. The remaining solid is filtered off, leaving a saturated solution, **X**.

Drops of dilute silver nitrate are added to **X** until silver oxalate, $Ag_2C_2O_4$, just precipitates. Using Table 5.2, calculate the concentration of $[C_2O_4^{2-}(aq)]$ in **X** and the concentration of $[Ag^+(aq)]$ when $Ag_2C_2O_4$ just precipitates. [2]

When solid mercury oxalate dissolves to form a saturated solution,

$Hg_2C_2O_4\,(s) \rightleftharpoons 2Hg^+(aq) + C_2O_4^{2-}\,(aq)$

Let solubility of $Hg_2C_2O_4$ be s, then $K_{sp} = [Hg^+]^2[C_2O_4^{2-}] = (2s)^2(s) = 4s^3 = 6.5 \times 10^{-7}$

$\therefore$ s = **5.46×10^{-3}** mol dm^{-3} = $[C_2O_4^{2-}]$

When $Ag_2C_2O_4$ just precipitates, $[Ag^+]$ increase in the solution such that

ionic product of $Ag_2C_2O_4$= K_{sp} of $Ag_2C_2O_4$

Thus $[Ag^+]^2[C_2O_4^{2-}] = [Ag^+]^2(5.46 \times 10^{-3}) = 5.4 \times 10^{-12}$

$[Ag^+]$ = **3.15×10^{-5}** mol dm^{-3}

(iii) Suggest and explain how the solubility of $Ag_2C_2O_4$ is affected by adding $NH_3(aq)$. [2]

$Ag_2C_2O_4$ is soluble in $NH_3(aq)$ to form silver (I) diammine complex, $[Ag(NH_3)_2]^+$

$\therefore$ $[Ag^+]$ is reduced such that I.P. (AgC*l*) < K_{sp} ($Ag_2C_2O_4$),

$\therefore$ $Ag_2C_2O_4$ ppt. dissolves .

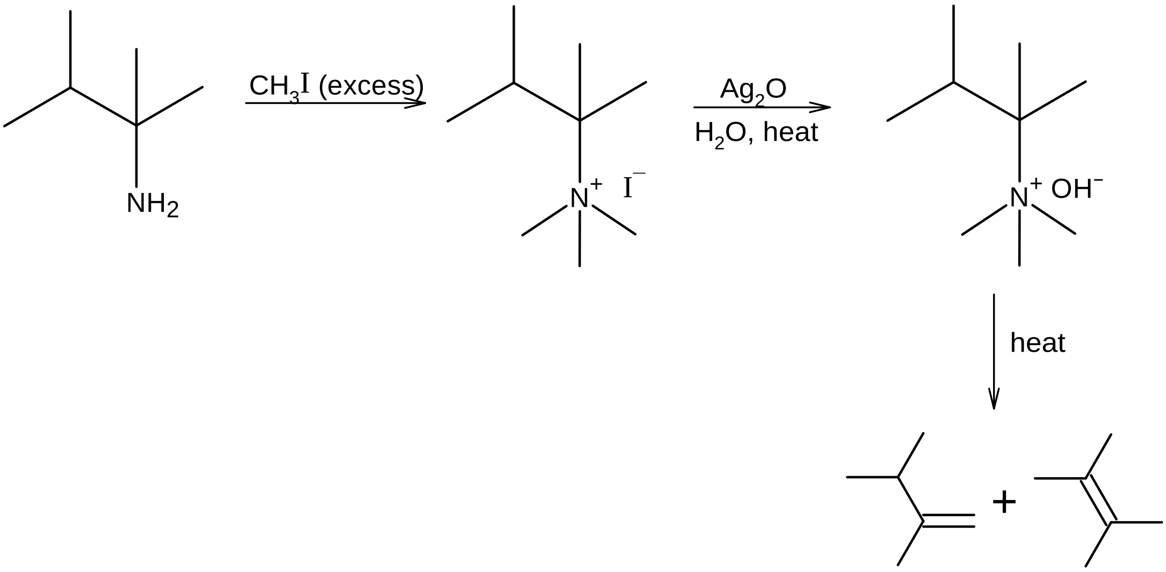
OR

$Ag_2C_2O_4\,(s) \rightleftharpoons 2Ag^+(aq) + C_2O_4^{2-}\,(aq)$

the decrease in $[Ag^+]$ shifts the position of equilibrium to the right to dissolve solid $Ag_2C_2O_4$.

(d) Hofmann elimination is an elimination reaction of an amine to form alkenes. The least stable alkene, which contains the fewest substituents on the carbons of the double bond, known as the Hofmann product, is preferentially formed.

The reaction starts with the formation of a quaternary ammonium iodide salt by treatment of the amine with excess iodomethane, CH_3I, followed by treatment with silver oxide and water to form a quaternary ammonium hydroxide. When this salt undergoes decomposition by heat, the Hofmann product, **Y**, and another alkene, **Z**, are formed.

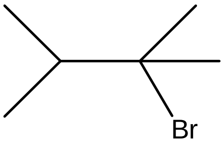


Y **Z**

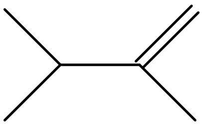
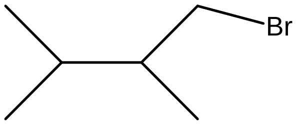
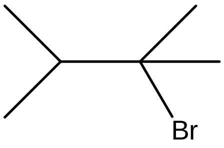
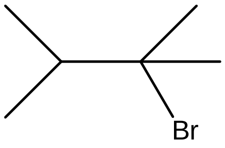
Hofmann product

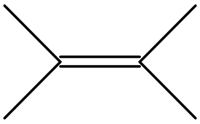
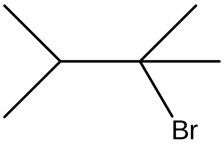
Fig. 5.1

(i) Both alkenes, **Y** and **Z**, are reacted separately with gaseous HBr. In both reactions, 2-bromo-2,3-dimethylbutane is obtained as either the only product or the major product. Explain why.



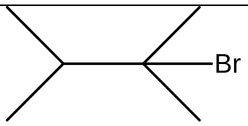
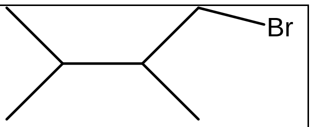
2-bromo-2,3-dimethylbutane [2]

 will form a mixture of  and . However, the carbocation that forms  is a tertiary carbocation which is more stable due to greater number of electron-donating groups / that disperses the positive charge on the carbocation.

 is a symmetrical alkene (or draw out the structure or words to the effect), hence only one product of  will be formed.

(ii) The Hofmann product, **Y**, produced in Fig. 5.1 undergoes a reduction reaction, followed by reaction with Br_2 in ultraviolet light to form two mono-brominated products. Draw the structures of these products.

Hence, state the mole ratio in which the products are formed. Explain your answer. **[3]**

Products formed		
Number of identical H atoms	2	12
Ratio of products	1	6

(iii) It is found by experiment that during free radical substitution, primary, secondary and tertiary hydrogen atoms are replaced by bromine atoms at different rates, as shown in Table 5.3.

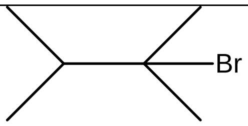
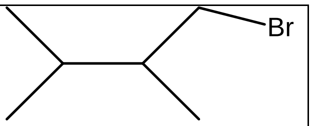
Reaction	relative rate
$RCH_3 \rightarrow RCH_2Br$	1
$R_2CH_2 \rightarrow R_2CHBr$	7
$R_3CH \rightarrow R_3CBr$	21

Table 5.3

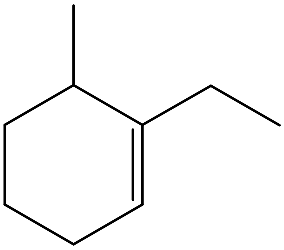
Explain why the relative rate of substitution of a tertiary hydrogen atom is faster than that of a primary hydrogen atom. **[1]**

Tertiary radical is more stable than a primary radical due to more electron donating groups that stabilises the electron deficient radical.

(iv) Predict the relative ratio of the two possible products from **(d)(ii)** using the information in Table 5.3, together with the number of hydrogen atoms of each type (primary, secondary or tertiary) within the molecule. **[1]**

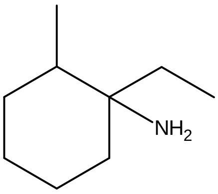
Products formed		
Ratio of products	1 x 21 = 21	6 x 1 = 6
	7	2

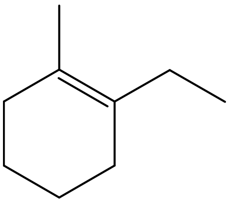
(v) Draw the structure of the amine that produces the following Hofmann product from the Hofmann elimination reaction. **[2]**



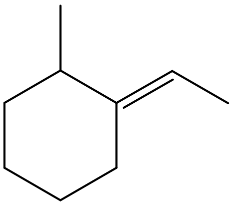
Hofmann product

Hence, suggest another possible alkene that could be formed from the Hofmann elimination reaction.





OR



[Total: 20]

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