

Calculator Model / No.

Name: _____ Class: 13S _____ Reg Number: _____



MERIDIAN JUNIOR COLLEGE
Preliminary Examination
Higher 2

Chemistry

9647/02

Paper 2 Structured Questions

19 September 2014

2 hours

Additional Materials: *Data Booklet*

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Write your calculator brand and model/number in the box provided above.

Answer **all** questions in the spaces provided on the question paper.

All working must be shown clearly.

INFORMATION FOR CANDIDATES

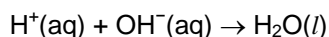
The number of marks is given in brackets [] at the end of each question or part question.

You are reminded of the need for good English and clear presentation in your answers.

Examiner's Use		
Paper 1	MCQ	/ 40
Paper 2	Q1	/ 12
	Q2	/ 12
	Q3	/ 11
	Q4	/ 13
	Q5	/ 14
	Q6	/ 10
Paper 3	/ 80	
Total	/ 192	
Percentage		
Grade		

1 Planning (P)

The enthalpy change of neutralisation is the enthalpy change when one mole of water is formed in the reaction between an acid and a base.



You are required to determine the enthalpy change of neutralisation between a strong base and a carboxylic acid through a series of experiments.

You may assume you are provided with the following:

- **FA 1**, aqueous sodium hydroxide, NaOH
- **FA 2**, 1.50 mol dm⁻³ propanoic acid, CH₃CH₂COOH
- polystyrene (styrofoam) cups
- apparatus normally found in a school laboratory.

In separate experiments, different volumes of **FA 1** and **FA 2** are mixed while keeping the total volume of the reaction mixture constant. In each experiment, the temperature rise, ΔT , is to be determined. When a graph of ΔT against volume of **FA 1** used is plotted, it is observed that the temperature rise will increase, and then decrease when different volumes of **FA 1** are used.

Data from the graph can then be used to determine:

- the concentration of sodium hydroxide, NaOH, in **FA 1**.
- the enthalpy change of neutralisation between NaOH and CH₃CH₂COOH.

It is given that 4.18 J is required to raise the temperature of 1 cm³ of any solution by 1 °C.

- (a) The total volume of the reaction mixture between **FA 1** and **FA 2** is constant. Explain why the temperature rise increases as more **FA 1** is added to the mixture.

As more FA 1 is added to the mixture, with amount of FA 2 being in excess (or FA 1 limiting), the number of moles of water produced increases and amount of heat produced increases in the presence of a same constant volume, hence the temperature rise increases.

[1]

- (b) It is predicted that the maximum temperature change for the neutralisation would occur when the volume of **FA 1** mixed is between 35 cm³ and 40 cm³.

Write a detailed plan on how you could determine the temperature changes for the series of reactions between **FA 1** and **FA 2**. The volume of **FA 1** used should be between 30 cm³ and 45 cm³ while the total volume of any mixture should be kept constant at 70 cm³.

Your plan should contain the following:

- all essential experimental details
- appropriate volumes of solutions to be used
- a tabulation of the experimental data to be collected (on the next page)

Comment [M1]: Shifted the sentence down to make the flow of the question better.

[Turn over

Procedure:

1. Use a 50.00 cm³ burette to transfer 30.00 cm³ of FA 1 into a polystyrene / styrofoam cup labelled FA 1.
2. Use another 50.00 cm³ burette to transfer 40.00 cm³ of FA 2 into another polystyrene/styrofoam cup labelled FA 2. Support this cup in a 250 cm³ beaker.
3. Use a thermometer to stir and measure the initial temperature of the FA 1 and FA 2 solution respectively.
4. Calculate the average temperature of the two solutions.
5. Add the contents of the FA 2 cup to the FA 1 cup. Use the thermometer to stir the mixture and measure the highest temperature of the mixture.
6. Calculate the temperature change of the reaction.
7. Wash and dry both the FA 1 and FA 2 polystyrene / styrofoam cup.
8. Repeat steps 1 to 7 using different volumes of FA 1 and FA 2 as stated in the table below.

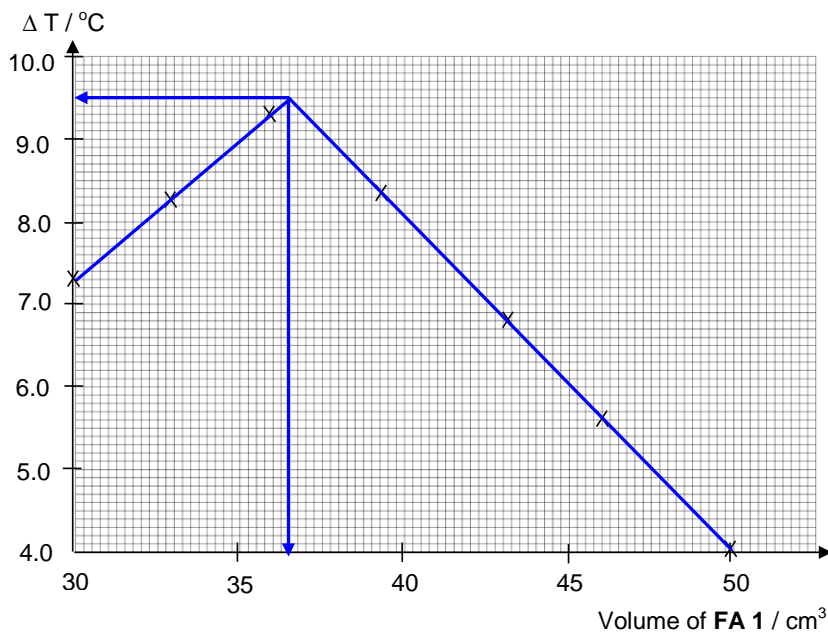
Tabulation:

Volume of FA 1 / cm ³	Volume of FA 2 / cm ³	Initial temperature of FA 1 / °C	Initial temperature of FA 2 / °C	Average temperature of mixture before mixing / °C	Highest temperature of mixture after mixing / °C	ΔT / °C
30.00	40.00					
33.00	37.00					
35.00	35.00					
40.00	30.00					
42.00	28.00					
45.00	25.00					

[6]

[Turn over]

- (c) (i) The following plots were plotted on a grid after an experiment. Draw suitable graphs through the plotted points.



- (ii) By using the graph in (i), calculate:
- the concentration of sodium hydroxide in **FA 1**.
 - the enthalpy change of neutralisation between NaOH and $\text{CH}_3\text{CH}_2\text{COOH}$.

Volume of **FA 1** (NaOH) used when temperature change is maximum
 $= 36.50 \text{ cm}^3$

No of moles of $\text{CH}_3\text{CH}_2\text{COOH}$ used
 $= \frac{70 - 36.5}{1000} \times 1.5$
 $= 0.05025$

$\text{NaOH} \equiv \text{CH}_3\text{CH}_2\text{COOH}$
 No of moles of NaOH (**FA 1**) used $= 0.05025$

Concentration of sodium hydroxide in **FA 1**
 $= \frac{0.05025}{36.5 \times 10^{-3}} = 1.38 \text{ mol dm}^{-3}$

From graph, maximum $\Delta T = 9.5 \text{ }^\circ\text{C}$

Total heat absorbed when ΔT is highest
 $= 70 \times 4.18 \times 9.5$
 $= 2780 \text{ J}$

[Turn over

5

No of moles of water formed = 0.05025

Enthalpy change of neutralisation between NaOH and $\text{CH}_3\text{CH}_2\text{COOH}$

$$\begin{aligned} &= - \frac{2780}{0.05025} \\ &= - 55320 \text{ J mol}^{-1} \\ &= - 55.3 \text{ kJ mol}^{-1} \end{aligned}$$

[4]

- (d) Describe one major source of error for the experiment and suggest an improvement which could significantly increase the accuracy of the experiment.

Error: Heat loss to the surrounding

Suggested Improvement:

Use a lid to cover the styrofoam cup to minimise heat loss.
or Provide lagging for the styrofoam cup to minimise heat loss.

[1]

[Total: 12]

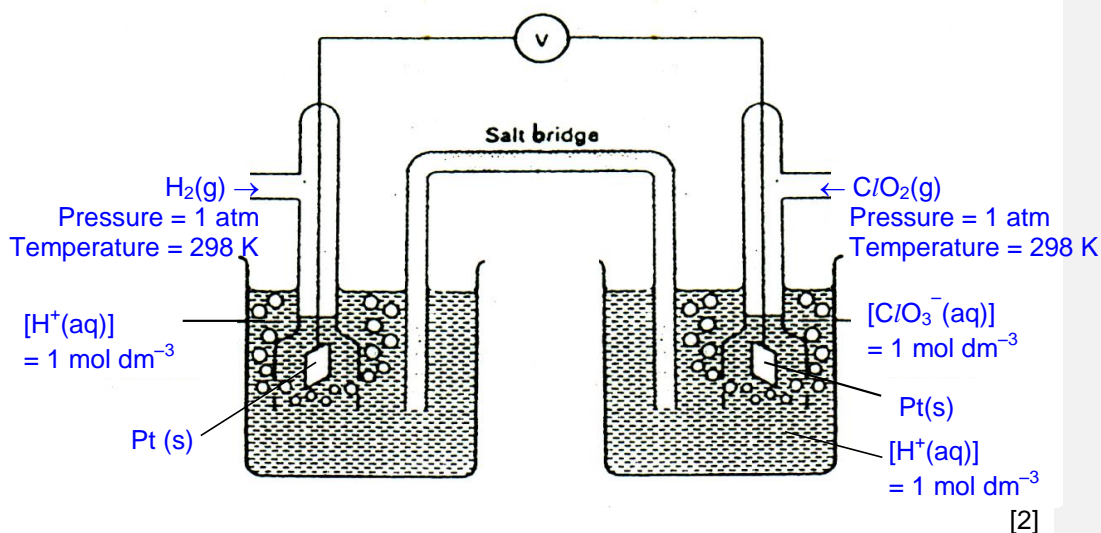
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- 2 Chlorine is a yellow-green gas that was first synthesised around 1630. Nearly all the chlorine in the Earth's crust occurs as chloride in various ionic compounds. It forms a variety of oxides such as chlorate(V), ClO_3^- , chlorate(III), ClO_2^- , and chlorine dioxide, ClO_2 .

The table below shows the reduction potentials for some oxides of chlorine.

Electrode Reaction	E° / V
$\text{ClO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{ClO}_2^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	+0.33
$\text{ClO}_3^-(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{ClO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	+1.15
$\text{ClO}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Cl}^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.50

- (a) Draw a labelled diagram to show how the redox potential $E^\circ(\text{ClO}_3^- / \text{ClO}_2)$ could be measured in the laboratory.

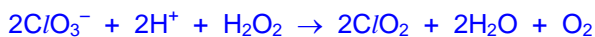
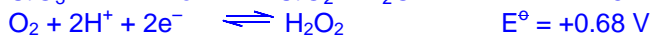
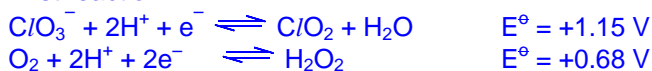


- (b) Use the *Data Booklet* and the above information to predict what might happen when solutions of the two reagents are mixed together. In each case, calculate the E°_{cell} and write an overall equation for any reaction that occurs.

Comment [M2]: Follow A-level phrasing
N2004 P3 Q2

- (i) mixing $\text{ClO}_3^-(\text{aq})$ with excess $\text{H}_2\text{O}_2(\text{aq})$

First reaction:

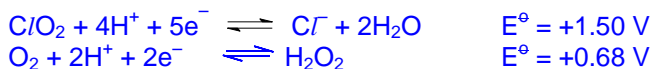


$$E^\circ_{\text{cell}} = 1.15 - 0.68$$

$$= +0.47 \text{ V} > 0 \text{ (feasible)}$$

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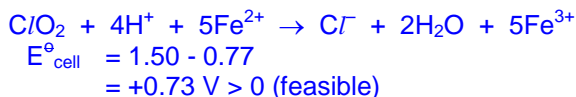
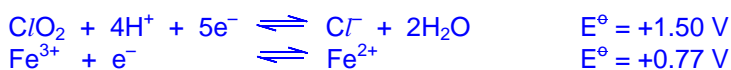
Second consecutive reaction:



$$\begin{aligned} E^\ominus_{\text{cell}} &= 1.50 - 0.68 \\ &= +0.82 \text{ V} > 0 \text{ (feasible)} \end{aligned}$$

Observation: Effervescence of C/O₂ and O₂ gases

(ii) mixing C/O₂ (g) with Fe²⁺ (aq).



Observation:

Pale-green solution of Fe²⁺ solution turns to pale-yellow solution of Fe³⁺.

[4]

(c) It was found that chlorine gas has a density of 3.04 kg m⁻³ at a temperature of 15 °C and a pressure of 1 atm.

(i) Assuming ideal behavior, calculate the relative molecular mass of chlorine.

$$\begin{aligned} PV &= \frac{m}{M}RT \\ \Rightarrow M &= \frac{m}{PV}RT \\ &= \frac{\rho}{P}RT \\ &= \left(\frac{3040}{101000} \right) (8.31)(288) \\ &= 72.0 \end{aligned}$$

(ii) Comment on the theoretical relative molecular mass of chlorine and that obtained in (i). Suggest reason for any discrepancy observed.

Theoretical relative molecular mass of Cl₂ = 71.0

Value obtained in (i) = 72.0

There is discrepancy between the two values; the value obtained in (i) is calculated based on the assumption that chlorine behaves as an ideal gas.

However, there are significant van der Waals' forces of attraction between chlorine molecules. Hence chlorine deviates from ideality.

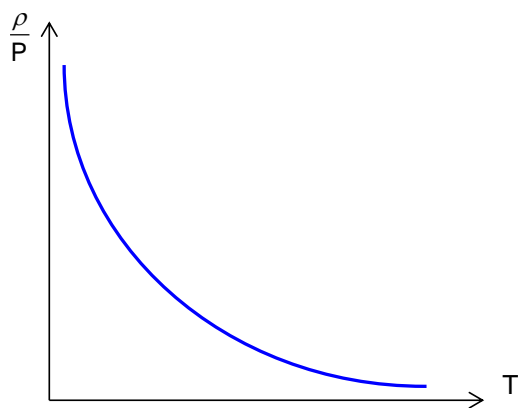
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- (iii) Under what conditions of temperature and pressure would the behaviour of real gases be more ideal?

Real gases tend towards ideal gas behavior under:

- (1) temperature is very high.
(2) pressure is very low.

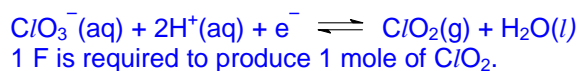
- (iv) On the axes below, sketch the expected graph of density/pressure, $\frac{\rho}{P}$, against temperature, T, for an ideal gas.



[4]

- (d) Chlorine dioxide, ClO_2 , is a useful agent in water treatment. Very pure chlorine dioxide is produced by electrolysis of aqueous sodium chlorate(V), NaClO_3 .

Calculate the current needed to produce 1 tonne of ClO_2 gas per day.
(1 tonne = 1000 kg)



$$\text{Hence, no of moles of } \text{ClO}_2 \text{ evolved} = \frac{1.0 \times 10^6}{67.5} = 1.48 \times 10^4$$

$$\text{current needed, } I = \frac{1.48 \times 10^4}{24 \times 60 \times 60} \times 96500 = 1.65 \times 10^4 \text{ A}$$

[2]

[Total: 12]

[Turn over

3 Copper and cobalt are common transition elements.

(a) By quoting appropriate data from the *Data Booklet*,

(i) comment and account for the atomic radii of copper and cobalt.

Cu (0.117 nm) have similar atomic radii / is slightly larger than Co (0.116 nm).

For Cu, as electrons are added to the inner 3d orbitals which are provide better shielding to the valence 4s electrons even as nuclear charge increases.

Effective nuclear charge decreases only slightly / remains approximately constant.

(ii) suggest an element in Period 2 that requires approximately similar energy to produce its ion in the +2 oxidation state as that of copper.

Be

Ionisation energy required to form $\text{Cu}^{2+} = 745 + 1960 = 2705 \text{ kJ mol}^{-1}$

Ionisation energy required to form $\text{Be}^{2+} = 900 + 1760 = 2660 \text{ kJ mol}^{-1}$

[3]

[Turn over

- (b) Various potassium salts are known, some of which include anions containing cobalt complexed with cyanide ions, CN^- .

Salt **A** has an empirical formula of $\text{K}_4\text{CoC}_4\text{N}_4$. Salt **B** has a composition by mass of K, 35.3%; Co, 17.7%; C, 21.7%; N, 25.3%.

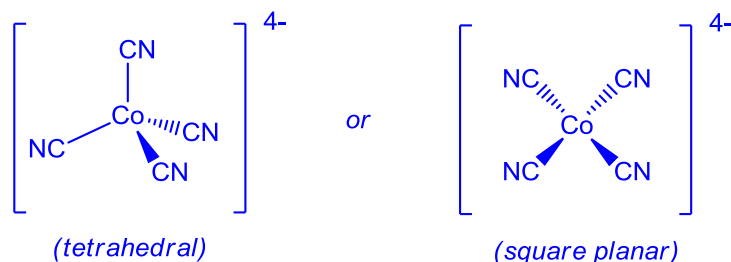
- (i) Determine the empirical formula of Salt **B**.

Element	K	Co	C	N
% by mass	35.3	17.7	21.7	25.3
Ar	39.1	58.9	12.0	14.0
No. of mol	$\frac{35.3}{39.1}=0.903$	$\frac{17.7}{58.9}=0.301$	$\frac{21.7}{12.0}=1.81$	$\frac{25.3}{14.0}=1.81$
Simplest ratio	3	1	6	6

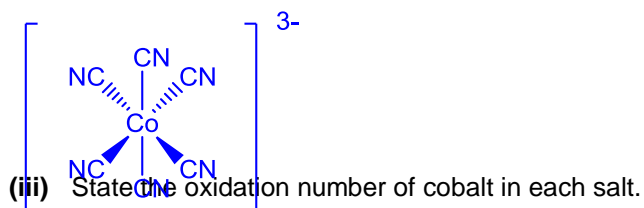
Salt **B**: $\text{K}_3\text{CoC}_6\text{N}_6$

- (ii) Suggest, by means of a diagram, the shape for the cobalt-containing anion of each salt.

Anion of Salt **A**



Anion of Salt **B**



Salt **A**: 0

Salt **B**: +3

- (iv) Write the electronic configuration for cobalt in Salt **B**.



[6]

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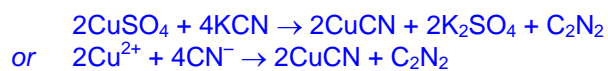
- (c) Some salts of copper(I) such as CuCl or CuCN are insoluble in water. Solutions of other copper(I) salts generally convert readily into copper metal and copper(II) ions when left to stand.

When a solution of copper(II) sulfate, CuSO_4 , is added to an excess of potassium cyanide, KCN , the corresponding copper(I) compound is formed, together with cyanogen, C_2N_2 .

- (i) State the type of reaction when a solution of copper(I) ions is left standing for a while.

Disproportionation

- (ii) Suggest an equation for the reaction between copper(II) sulfate and excess potassium cyanide.



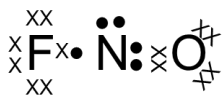
[2]

[Total: 11]

[Turn over

4 The general formula of nitrosyl halide is NOX, where X is F, Cl or Br.

- (a) (i) Draw a dot-and-cross diagram for nitrosyl fluoride, NOF, and hence use the Valence Shell Electron Pair Repulsion, VSEPR, theory to predict the shape of nitrosyl fluoride.



There are 2 bond pairs and 1 lone pair around N atom.

To minimise repulsion and maximise stability, the 3 electron pairs are repel furthest possible.

Lone pair – bond pair repulsion > bond pair – bond pair repulsion.

Shape of NOF is bent / v-shaped.

- (ii) Arrange, in ascending order, the bond angle of NOF, NOCl and NOBr. Explain your answer.

Bond angle: NOF < NOCl < NOBr

The electronegativity decreases from F to Br

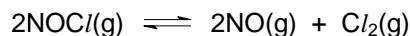
Going from NOF to NOBr:

- The bond pairs are increasingly drawn closer to central N atom.
- Hence the bond pairs experience increasing repulsion with one another.
- This will result in them being pushed further away and hence an increase in the bond angle.

[5]

[Turn over

- (b) Nitrosyl chloride undergoes dissociation according to the following equation.



Different amount of the three gases, nitrosyl chloride, NOCl, nitrogen monoxide, NO, and chlorine, Cl₂, were introduced into a closed vessel at 230 °C. At 10 minutes, the concentration of the three gases were determined and provided in the table below.

Temperature / °C	[NOCl] / mol dm ⁻³	[NO] / mol dm ⁻³	[Cl ₂] / mol dm ⁻³
230	2.00×10^{-3}	1.10×10^{-3}	9.00×10^{-3}

- (i) Write the expression for the equilibrium constant, K_c , for this reaction.

$$K_c = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2}$$

- (ii) Given that the value of K_c at 230 °C is 4.50×10^{-2} , explain quantitatively if the system has attained equilibrium at 10 minutes.

By substitute the concentration values into the K_c expression,

$$K_{t=10\text{min}} = \frac{(1.10 \times 10^{-3})^2 (9.00 \times 10^{-3})}{(2.00 \times 10^{-3})^2} \\ = 2.73 \times 10^{-3} \text{ mol dm}^{-3}$$

Since this is not equal to the K_c value, system has not attained equilibrium.

- (iii) Hence, deduce which direction the reaction will proceed in order for the system to attain equilibrium.

The net reaction will proceed towards the right, since reaction quotient is lesser than K_c .

- (iv) Suggest a reason why nitrosyl fluoride has the least tendency to dissociate.

Among the N–X bond, N–F bond is the strongest / bond energy of N–F is the highest hence it requires the largest amount of energy to break.

[4]

[Turn over

- (c) The experiment was repeated at 465 °C and the initial concentrations of the three gases are given in the table below.

Temperature / °C	[NOC] / mol dm ⁻³	[NO] / mol dm ⁻³	[Cl ₂] / mol dm ⁻³
465	4.00×10^{-4}	7.60×10^{-3}	1.98×10^{-4}

- (i) At equilibrium, the [NOC] was found to be 3.68×10^{-4} mol dm⁻³. Calculate the value of K_c at 465 °C.

	2NOC (g)	\rightleftharpoons	2NO (g)	+	Cl ₂ (g)
Initial conc / mol dm ⁻³	4.00×10^{-4}		7.60×10^{-3}		1.98×10^{-4}
Change in conc / mol dm ⁻³	-3.20×10^{-5}		$+3.20 \times 10^{-5}$		$+1.60 \times 10^{-5}$
Equilibrium conc / mol dm ⁻³	3.68×10^{-4}		7.63×10^{-3}		2.14×10^{-4}

$$K_c = \frac{(7.63 \times 10^{-3})^2 (2.14 \times 10^{-4})}{(3.68 \times 10^{-4})^2}$$

$$= 9.20 \times 10^{-2} \text{ mol dm}^{-3}$$

- (ii) Hence, explain whether the forward reaction is exothermic or endothermic.

At higher temperature, by Le Chatelier's Principle, the equilibrium position will shift towards the endothermic reaction to absorb the heat.

Since K_c increases with temperature, indicating that the forward reaction proceeds to a larger extent. Therefore, the forward reaction is endothermic.

[4]

[Total: 13]

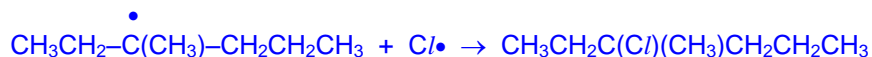
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5 This question is about C_7H_{16} and the organic products that could be obtained from it.

- (a) Of all the isomers of C_7H_{16} , only **C** and **D** can react with chlorine in the presence of ultraviolet light, each giving a tertiary monosubstituted halogenoalkane which is optically active.

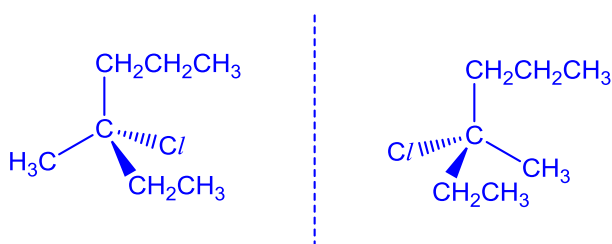
The reaction between **C** and chlorine produced 3-chloro-3-methylhexane, $CH_3CH_2CCl(CH_3)CH_2CH_2CH_3$.

- (i) Write an equation for the termination step of the reaction involving **C** to produce 3-chloro-3-methylhexane, showing clearly the structural formulae of all reactants and products involved.



- (ii) When only one form of enantiomers of **C** is reacted with chlorine, it was found that the termination step to produce 3-chloro-3-methylhexane resulted in a mixture that could **not** rotate plane-polarised light.

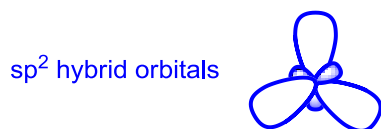
Draw the structures of the isomers formed in this mixture.



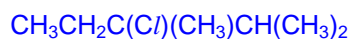
- (iii) Suggest the type of hybridisation of the carbon atom containing a lone electron produced during the reaction in (ii).

Draw the hybridised orbitals for this carbon atom.

The carbon is sp^2 hybridised.



- (ii) Suggest the structural formula of the monosubstituted halogenoalkane formed by **D**.



[4]

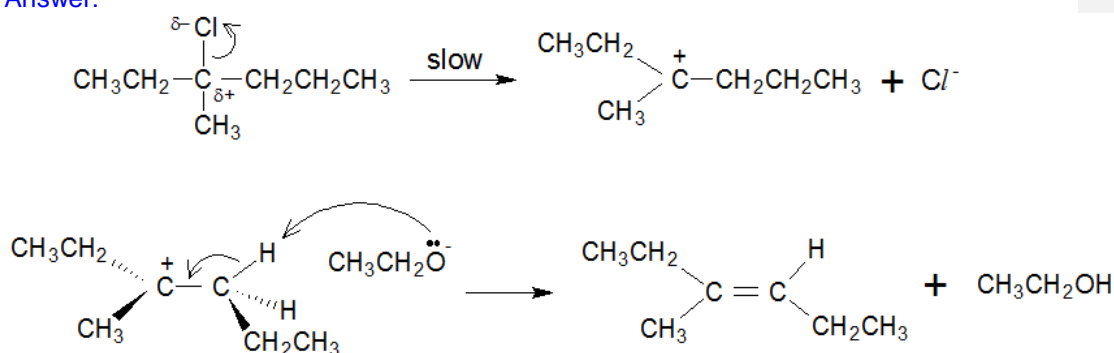
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- (b) 3-chloro-3-methylhexane can undergo elimination to produce 3-methylhex-3-ene. Such an elimination reaction usually involves a strong base such as an ethoxide ion, $\text{CH}_3\text{CH}_2\text{O}^-$.

- (i) The following shows the incomplete mechanism for the elimination reaction.

Complete the mechanism by drawing any missing lone pair, curly arrows and charges.

Answer:



- (ii) If 1-chloro-3-methylhexane is used instead of 3-chloro-3-methylhexane in (i), the mechanism shown would take place in one step instead of two steps.

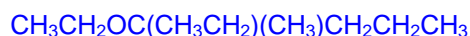
Suggest a reason for this observation.

For 1-chloro-3-methylhexane, the primary carbocation would not be less stable than the tertiary carbocation produced from 1-chloro-3-methylhexane. Less electron-donating alkyl group causes the intensity of the positive charge to be higher (or causes the positive charge to be less dispersed).

OR 1-chloro-3-methylhexane is a primary halogenoalkane with less steric hindrance. There are less bulky alkyl group around the C of C-Cl which could prevent the ethoxide ion from approaching the H atom during elimination.

- (iii) In (i), besides the elimination product for 3-chloro-3-methylhexane, it is possible that other unintended organic side products may be formed through other types of reaction.

Suggest the identity of a possible organic side product.



[4]

[Turn over

(c) Another isomer of C_7H_{16} is heptane. Heptane can reform to produce methylbenzene and hydrogen gas.

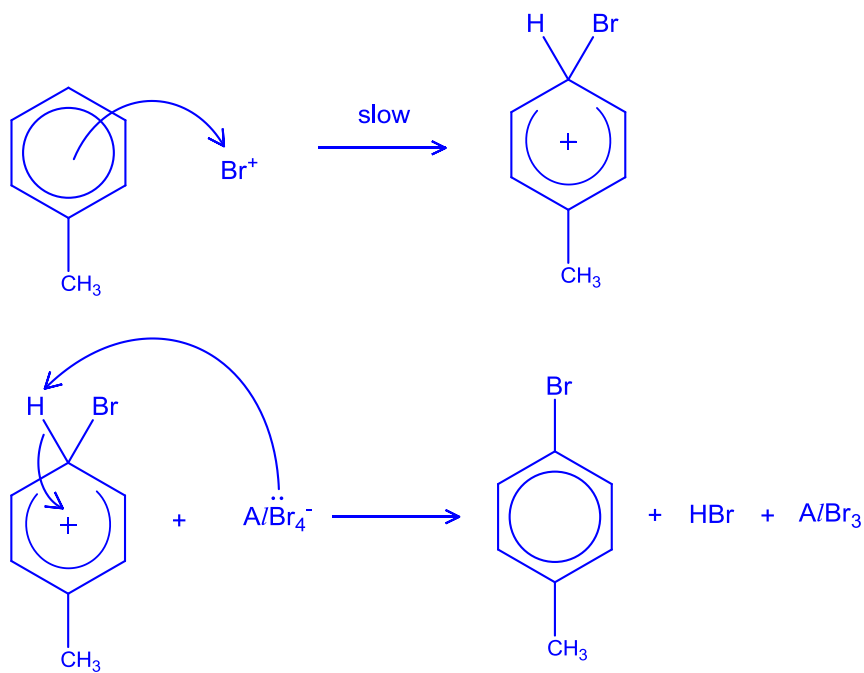
- (i) Write a balanced equation for the reformation reaction to produce methylbenzene, showing clearly the structures of all reactants and products.



- (ii) The methylbenzene formed in (i) is reacted with bromine as well as other appropriate reagents and conditions to produce 4-bromomethylbenzene.

Describe the mechanism for this reaction.

Electrophilic substitution



[4]

[Turn over

(d) Some bromine used in part (c)(ii) was accidentally contaminated with an excess of hot potassium hydroxide. A student attempted two different methods to deduce the amount of bromine contaminated.

- (i) In Experiment 1, the student poured an excess of aqueous silver nitrate into the contaminated solution in an attempt to precipitate silver bromide.

Briefly explain how silver(I) nitrate would not allow the student to deduce the amount bromine contaminated.

Excess OH^- would cause brown Ag_2O / AgOH solid to be produced.
 $\text{HNO}_3(\text{aq})$ should have been added first to neutralize $\text{KOH}(\text{aq})$ before adding silver nitrate.

- (ii) In Experiment 2, the student evaporated the contaminated solution to dryness. Then he reacted the resulting residual solid with concentrated sulfuric acid.

Briefly explain why this method would not be able to obtain the accurate amount of bromine contaminated.

Some HBr / Br_2 evolved would be lost and hence not all bromine is recovered.
The remaining KOH can also react with the concentrated sulfuric acid.

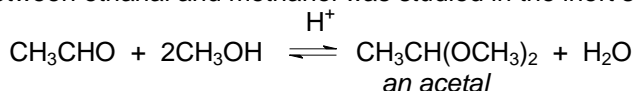
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[Turn over

- 6 Acetals are compounds formed when aldehydes or ketones are reacted with an alcohol and an acid catalyst.

The reaction between ethanal and methanol was studied in the inert solvent dioxan.



- (a) When the initial rate of this reaction was measured at various starting concentrations of the two reactants with H^+ concentration of 0.05 mol dm^{-3} , the following results were obtained.

Experiment	$[\text{CH}_3\text{CHO}] / \text{mol dm}^{-3}$	$[\text{CH}_3\text{OH}] / \text{mol dm}^{-3}$	Relative rate
1	0.20	0.10	1.00
2	0.25	0.10	1.25
3	0.25	0.16	2.00

- (i) Determine the order of reaction with respect to the following reactants, explaining how you arrive at your answer.

- CH_3CHO

Comparing Expt 1 & 2,
when concentration of CH_3CHO was increased 1.25 times, keeping the concentration of CH_3OH constant, the relative rate was 1.25 times the original value.

Hence order of reaction wrt CH_3CHO is 1.

- CH_3OH

Comparing Expt 2 & 3,
when concentration of CH_3OH was increased 1.6 times, keeping the concentration of CH_3CHO constant, the relative rate was 1.6 times the original value.

Hence order of reaction wrt CH_3OH is 1.

- (ii) Hence, write the rate equation for the reaction, including the units of the rate constant.

$$\text{Rate} = k [\text{CH}_3\text{CHO}][\text{CH}_3\text{OH}]$$

Units of k : $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ or $\text{mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ or $\text{mol}^{-1} \text{ dm}^3 \text{ h}^{-1}$

[Turn over

- (iii) When the H^+ concentration used in Experiment 2 was increased to 0.10 mol dm^{-3} , the relative rate had a value of 2.50.

State the value of the relative rate when the concentrations of CH_3CHO , CH_3OH and H^+ used are 0.20 mol dm^{-3} each.

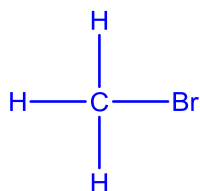
relative rate = 8

[4]

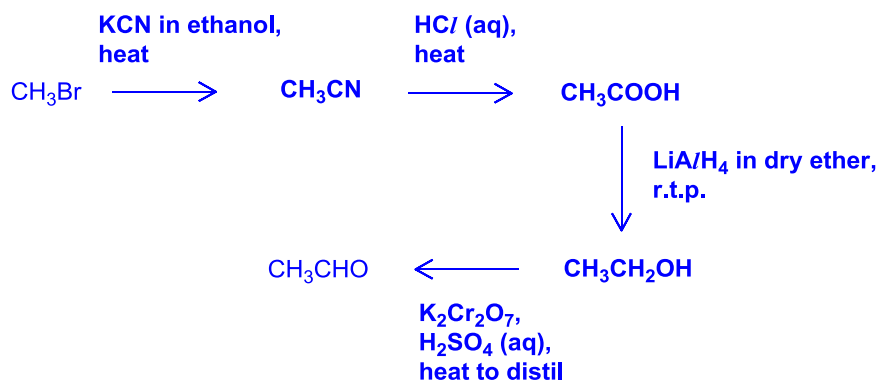
- (b) The reactants CH_3CHO and CH_3OH can be synthesised from the same bromoalkane.

Draw the full structural formula of this bromoalkane, and provide a suitable synthesis route, of **not** more than four steps, to form CH_3CHO .

Structure of bromoalkane



CH_3CHO

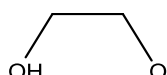


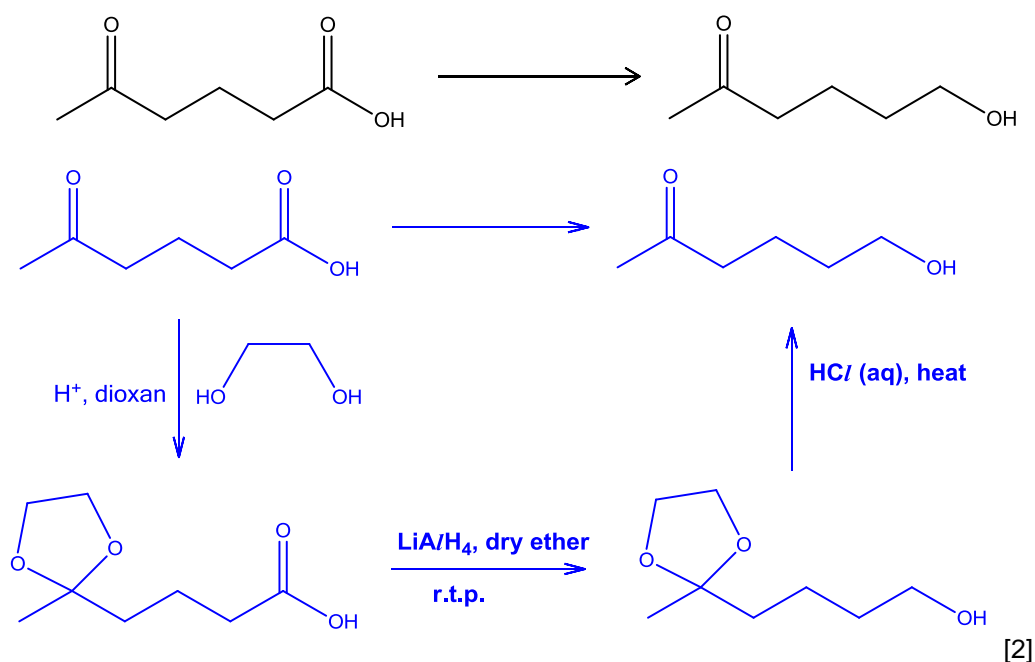
[4]

[Turn over

- (c) The acetal group does not react with bases or reducing agents, which the carbonyl group is susceptible to. For instance, both NaBH_4 and LiAlH_4 do not react with the acetal group.

Hence it is possible to use the formation of acetals from carbonyl compounds as a way to protect the carbonyl groups from these reagents. Subsequently one can restore the carbonyl functional group by acidic hydrolysis since the formation of acetals is a reversible reaction.

By using  as the alcohol to form an acetal group in the inert solvent dioxan as a first step, suggest a suitable synthesis route for the following conversion.



[Total: 10]

End of Paper 2