Anglo-Chinese Junior College

JC2 Preliminary Examination
Higher 2

A Methodist Institution
(Founded 1886)

CANDIDATE NAME	Answers		FORM CLASS	2			
TUTORIAL CLASS	2CH			INDEX NUMBER			

CHEMISTRY

Paper 3 Free Response

9729/03
27 August 2024
2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an 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.
Circle the number of the question you have attempted.

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

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.

For Examiners' use only	
Section A	
1	/ 20
2	/ 20
3	/ 20
Section B	
4 / 5	/ 20
Presentation	
Total	/ 80

This document consists of 28 printed pages and – blank pages.

Section A

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

1	**(a)**	Describe the variation in the behaviour of Period 3 chlorides NaC*l*, $AlCl_3$ and PCl_5 separately with water. Write equations for any reactions described and state the pH of the resultant solutions. [3]	
			NaC*l* hydrates (dissolves) to give a neutral solution (pH 7). There is no hydrolysis. $NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$ $AlCl_3$ undergoes substantial hydrolysis due to the high charge density of Al^{3+}. The resulting solution is acidic. (pH 3-4) Hydration: $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$ Hydrolysis: $[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$ PCl_5 undergoes complete hydrolysis to give an acidic solution. pH 1-2 $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$
			Comments - Students should take note of using the reversible for partial hydrolysis and the irreversible arrow for complete hydrolysis. - Some students were penalised for using the wrong state symbols such as $AlCl_3(aq)$ and $PCl_5(aq)$. - Avoid using the equations that involve limited water as we are unable to give pH of the solid or liquid product: $AlCl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3HCl(g)$ $PCl_5(s) + 2H_2O(l) \rightarrow POCl_3(l) + 2HCl(g)$
	(b)	When soil becomes acidic, aluminium leeches out of minerals into the soil. High aluminium content in soil affects root growth and causes the roots to be brittle. These problems are minimised if the soil pH is maintained above 5.5. In a study of a soil condition, a sample of soil water was titrated with EDTA, a hexadentate ligand, to determine its aluminium ion concentration. equation 1 $[Al(H_2O)_6]^{3+}(aq) + [EDTA]^{4-}(aq) \rightleftharpoons [Al(EDTA)]^-(aq) + 6H_2O(l)$	
		(i)	State the type of reaction in equation 1. [1]
			Ligand exchange.
		(ii)	The concentration of aluminium ions in the soil water sample was found to be 2.90×10^{-5} mol dm^{-3}. Calculate the pH of the water sample, given that the aqueous complex of Al^{3+} has a K_a value of 7.9×10^{-6}. You may assume that the complex of Al^{3+} behaves as a weak monobasic acid, HA. [1]
			$K_a = \frac{[H^+][A^-]}{[HA]}$ $7.9 \times 10^{-6} = [H^+]^2 / (2.90 \times 10^{-5})$ $[H^+] = 1.514 \times 10^{-5}$ pH = 4.82

Comments

Most students were able to use the K_a expression, K_a value and concentration of the weak acid to determine the pH of the weak acid.

(iii) Another 25 cm^3 sample of soil water was found to contain 0.250 mol dm^{-3} of NaH_2PO_4. 20 cm^3 of solution **A** which contains aqueous Na_2HPO_4 was added to the water sample to obtain a solution buffered at pH 6.8.
Calculate the concentration of HPO_4^{2-} in solution **A**, given that the pK_a value of $H_2PO_4^-$ is 7.2. [3]

Final $[H_2PO_4^-] = (0.250 \times \frac{25}{25+20}) = 0.1389$ mol dm^{-3}

$\mathrm{pH} = \mathrm{p}K_a + \lg \frac{[\mathrm{HPO4\ 2-}]}{[\mathrm{H2PO4-}]}$

$6.8 = 7.2 + \lg \frac{[\mathrm{HPO4\ 2-}]}{[\mathrm{H2PO4-}]}$

$\lg \frac{[\mathrm{HPO4\ 2-}]}{[\mathrm{H2PO4-}]} = -0.4$

$\frac{[\mathrm{HPO4\ 2-}]}{[\mathrm{H2PO4-}]} = 0.3981$

$\frac{[\mathrm{HPO4\ 2-}]}{0.1389} = 0.3981$

$[HPO_4^{2-}]_{final} = 5.529 \times 10^{-2}$ mol dm^{-3}

OR

$K_a = \frac{[\mathrm{HPO4\ 2-}][H+]}{[\mathrm{H2PO4-}]}$

$10^{-7.2} = \frac{[\mathrm{HPO4\ 2-}][10^{-6.8}]}{[\mathrm{H2PO4-}]}$

$10^{-7.2} = \frac{[\mathrm{HPO4\ 2-}][10^{-6.8}]}{0.1389}$

$[HPO_4^{2-}]_{final} = 5.529 \times 10^{-2}$ mol dm^{-3}

Amt of HPO_4^{2-} in buffer $= 5.529 \times 10^{-2} \times \frac{25+20}{1000}$
$= 0.002488$ mol

$[HPO_4^{2-}]$ in solution A $= \frac{0.002488 \text{ mol}}{20 \text{ x } 10^{-3}} = \underline{0.124 \text{ mol dm}^{-3}}$

Comments

- Many students were able to use the Henderson-Hesselberg equation (i.e. pH = pK_a + $\lg \frac{[\mathrm{HPO4\ 2-}]}{[\mathrm{H2PO4-}]}$) to relate the pH, pKa and concentrations of the weak acid and salt. They were also able to determine the $[H_2PO_4^-]$ after mixing.
- Common mistakes include:
  - Confusion about the acid and base roles of $H_2PO_4^-$ and HPO_4^{2-} respectively.
  - Failing to recognise that the $[HPO_4^{2-}]$ from the Henderson-Hesselberg equation is the concentration after mixing, not its original concentration in solution A.
  - Using the K_a expression to calculate $[HPO_4^{2-}]$ but failing to recognise that for a buffer, $[H^+] \neq$ [salt] (i.e. $[H^+] \neq [HPO_4^{2-}]$).

(c) The reactions of ethylbenzene to form **H**, **J** and **K** are shown in Fig.1.1.

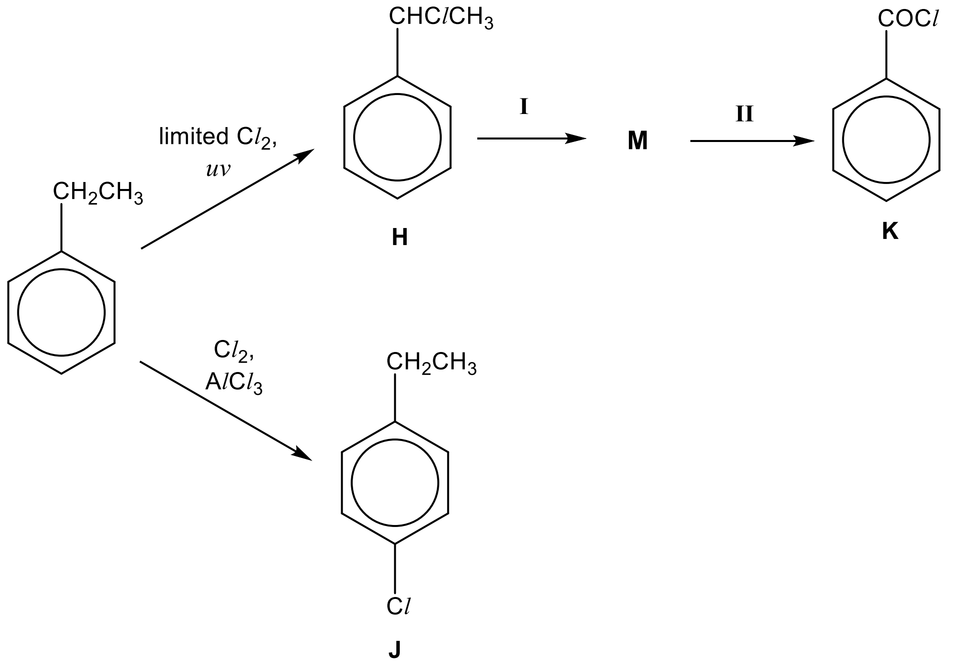


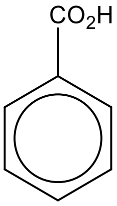
Fig. 1.1

(i) Suggest the reagents and conditions needed for reactions **I** and **II** and suggest the structure of **M** in Fig. 1.1. [3]

I: $KMnO_4$, H_2SO_4(aq), heat under reflux

II: $SOCl_2$ OR PCl_5 OR PCl_3, heat

M:



Comments

- Reaction I is a side-chain oxidation of alkylbenzene. It results in benzoic acid M.
- More students were able to state the correct reagents and conditions to convert M into an acid chloride. However, wrong state symbols such as PCl_5(aq) or $SOCl_2$(aq) would lose this mark.

(ii) Describe and explain the relative ease of hydrolysis of **H**, **J** and **K**. [3]

Relative ease of hydrolysis: **K** > **H** > **J**

Due to the presence of the electronegative O and Cl atoms on the acyl chloride in compound **K**, its carbonyl carbon is more electron deficient than that in **H** and more susceptible to attack by the nucleophile. Therefore the hydrolysis of **K** has greater ease than that of **H**.

In aryl chloride **J**, the p orbital of Cl overlaps with the π electron cloud of the benzene ring. As a result the C-Cl bond has partial double bond character which require more energy to break. This makes causes **J** to have the lowest ease of hydrolysis.

Comments

Common misconceptions include:

- Confusing the effect of C=O group in –COCl with that for the base strength of –CONH–.
- Calling the C=O group electron withdrawing without identifying that the cause is the electronegative O atom.
- Thinking that the phenyl group contributes to delocalisation of electron pair from Cl atom.

(d) Graphene is a nanomaterial comprising of a single layer of graphite. Compared with copper, it has higher tensile strength and similar electrical conductivity while having lower mass. An experiment was conducted to electroplate copper onto graphene.

In the experiment, a copper anode and graphene cathode was immersed in aqueous copper(II) sulfate as the electrolyte.

(i) Describe the observations at the cathode and the electrolyte after some time. [1]

- The cathode would increase in size / mass OR show a pink brown colour of copper metal.
- The electrolyte remains the same / remains blue.

Comments

Common mistake include stating that copper is deposited or concentration of $CuSO_4$ remains the same. Students should state the observation changes instead.

(ii) The graphene at the cathode is a square with a length of 0.1 m.

Assume that each copper occupies a cube length of 3.0×10^{-12} m, the graphene has no thickness and there is uniform plating of copper.

Calculate

1. the amount of Cu atoms to cover **both** sides of the graphene with a depth of 500 atoms
2. the time required to achieve this using a current of 5.0 A. [3]

Number of Cu atoms for a depth of 1 atom for both sides
$= 2 \times [0.1^2 \div (3.0 \times 10^{-12})^2] = 2.222 \times 10^{21}$ atoms

Number of Cu atoms for a depth of 500 atoms for both sides
$= 2.222 \times 10^{21} \times 500 = 1.111 \times 10^{24}$ atoms

Amount of Cu to electroplate both sides with a depth of 500 atoms
$= 1.111 \times 10^{24} \div (6.02 \times 10^{23}) = 1.846$ mol

$n(e) = 1.846 \mathbf{\times 2} = 3.692$ mol

$Q = n(e).F = 3.692 \mathbf{\times 96500} = 356278$ C

$t = 356278 \div \mathbf{5.0}$
$= 71255.6$
$= 71300$ s (OR 1190 min OR 19.8 h)

			Comments • Many students had difficulty calculating the correct number of Cu atoms and the amount of Cu deposited. This was usually because they neglect to find the Cu deposited on 2 sides of the sheet. • Some students also forgot to convert the number of Cu atoms into the number of mol of Cu. • However, students were able to apply Q = n(e).F and Q = It correctly.
		(iii)	The student replicated this experiment to electroplate graphene with A*l*. He replaced aqueous $CuSO_4$ with aqueous $Al(NO_3)_3$ and the copper plate with an aluminium plate. Using *E*$^\ominus$ values from the *Data Booklet*, suggest if this experiment will be successful. [2]
			The experiment will not be successful. Al will not be plated at the cathode. Instead, water is preferentially reduced / discharged at the cathode as $E^\ominus(H_2O/H_2)$ is less negative than $E^\ominus(Al^{3+}/Al)$. Cathode: $H_2O + 2e \rightarrow H_2 + 2OH^-$ $E^\ominus(H_2O/H_2) = -0.83V$ OR Al will not oxidized from the anode. Instead, oxidation of water to form O_2 occurs OR $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ occurs. The O_2 produced at the anode reacts with Al to form Al_2O_3. Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E^\ominus(H_2O/O_2) = +1.23V$
			Comments • Students who answered well in this question were able to compare *E*$^\ominus$ values and apply them to the preferential discharge at the cathode. • Students who stated that aluminium would oxidise that the anode did not recognise that there is a layer of Al_2O_3 on the surface of the metal. Similar to the anodising of aluminium, the oxide layer prevents the direct oxidation of Al.
			[Total: 20]

2 The oxime functional group R–C=N–OH undergoes rearrangement to form amide in the presence of aluminium oxide. During the reaction, the alkyl group that is trans to the OH group migrates to the N atom. Fig. 2.1 shows the example of this rearrangement.

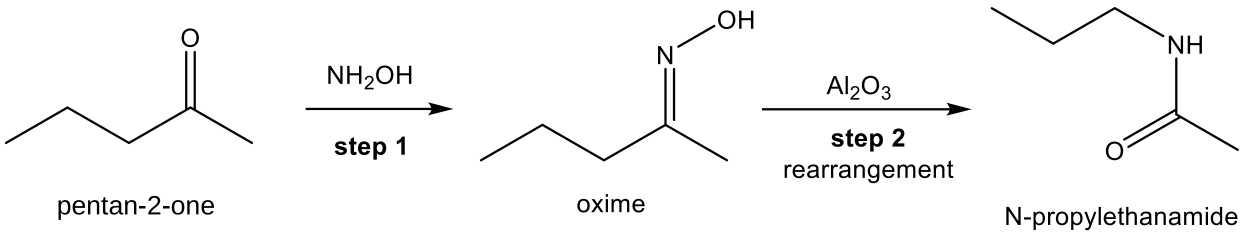
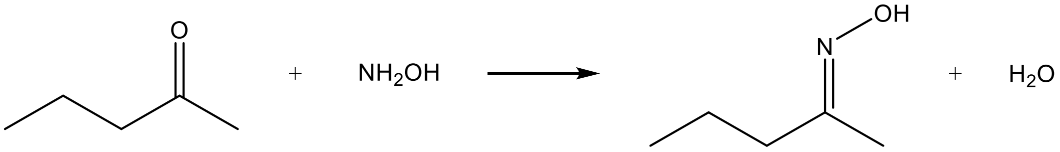


Fig. 2.1

(a) **(i)** Write a balanced equation for step 1 and suggest the type of reaction that occurred. [2]



Condensation OR Nucleophilic acyl substitution OR Addition-elimination

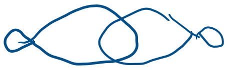
Comments

Students are reminded to use structural formula such as condensed formula or skeletal formula when writing the equation.

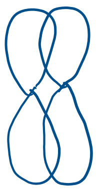
(ii) A molecule of oxime contains both σ bonds and π bonds.
Draw labelled diagrams to show how orbitals of the C atom and N atom overlap to form

- a σ bond
- a π bond [2]

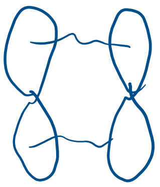
Sigma / σ bond is the head-on overlap between the sp^2 orbitals of C and N atoms.



Pi / π bond is the sideways overlap between the p orbitals of C and N atoms.



or



Comments

- Many students scored well in this question and those who got partial credit usually failed to identify the orbitals involved in the overlap.
- Some students did not show two different sized lobes of the hybridised orbital.
- A smaller number of students lost marks as the head-on overlap was drawn as an angle.

(iii) Oximes may exist as cis-trans isomers. State and explain the feature of the oxime molecule which allows them to show cis-trans isomerism. [1]

Restricted rotation about the C=N bond OR C–N double bond.

Comments
Most students were able to get the correct answer.

(iv) Suggest a simple chemical test to distinguish pentan-2-one and N-propylethanamide shown in Fig. 2.1. [2]

Test: NaOH(aq), heat
Observation: The amide releases a gas that turns moist red litmus paper blue, but pentan-2-one does not form a gas that turns moist red litmus blue.

OR Test: aqueous I_2, NaOH, heat
Observation: Pentan-2-one give yellow ppt but amide does not.

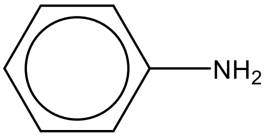
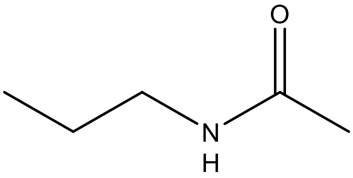
OR Test: 2, 4-dinitrophenylhydrazine
Observation: Pentan-2-one give orange/yellow ppt but amide does not form any orange or yellow ppt.

Comments

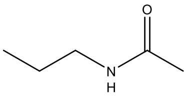
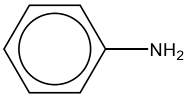
- Students are reminded that the differentiation should be carried out using only 1 chemical test.
- The test that is chosen must also have different observable changes.
- The observation for both compounds must be stated.

(b) The pK_b values of three nitrogen containing compounds are given in Table 2.1.

Table 2.1

name	structure	pK_b
phenylamine		9.4
ethylamine	$CH_3CH_2NH_2$	3.4
N-propylethanamide		14.4

Rank the compounds in order of increasing basicity and explain your reasoning. [3]

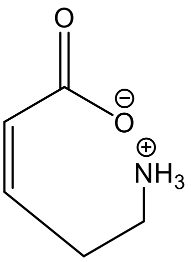
Increasing basicity:  <  < $CH_3CH_2NH_2$

Phenylamine and amide are less basic than $CH_3CH_2NH_2$ as the p orbitals of NH_2 overlap with the pi electron cloud of benzene OR C=O groups.

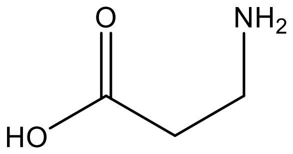
As O is more electronegative, the lone pair on N of the amide is more effectively delocalised into the C=O as compared to benzene ring of phenylamine thus the lone pair on N of amide is not available for donation to H^+.

Thus the lone pair on N is delocalised into the benzene ring and less available for donation to H^+.

		$CH_3CH_2NH_2$ has an electron donating alkyl group so the lone pair on N is more available for donation to H^+.	
		Comments • Students have a good understanding of the different strength of base, but could improve on the use of terminology in their explanation. • Wrong / poor phrasing include: ○ Donation of lone pair instead of donation of lone pair of electrons to H+. ○ Phenyl group is electron withdrawing instead of lone pair of electron delocalises into the phenyl group due to the overlap of p orbital on N and pi e cloud of phenyl group. • Some students did not credit the different extent of delocalisation in amide and phenylamine to the electronegative O atom in the amide.	
	(c)	Zwitterion **A** $C_5H_9NO_2$ reacts with hot acidified potassium manganate(VII) to form compound **B** $C_3H_7NO_2$ and compound **C**, $C_2H_2O_4$. Compound **C** further oxidises to form a gas that forms white precipitate in limewater. **B** does not rotate plane polarised light. Compound **A** also reacts with $SOCl_2$ to form **D** C_5H_8NOCl which further reacts to form a neutral compound **E** C_5H_7NO. **E** is also formed when the oxime **F** C_5H_7NO reacts in the presence of aluminium oxide.	
		(i)	Describe the formation of a *zwitterion*. [1]
			The carboxylic acid and the amine functional groups undergo ionisation to form a $-COO^-$ group and a $-NH_3^+$ group on the same molecule / compound.
			Comments Many students recognised that presence of -COOH and $-NH_2$ exchanging proton to forms 2 oppositely charged groups, but did not state that the two groups are on the same molecule.
		(ii)	Suggest possible structures for **A**, **B**, **C**, **D, E** and **F**. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. [9]
			A undergoes oxidative cleavage / oxidation of an alkene functional group. **A** has 2 degrees of unsaturation. **B** does not have a chiral centre / has internal plane of symmetry as it does not rotate plane polarised light. Carboxylic acid in compound **A** also undergoes substitution / nucleophilic substitution with $SOCl_2$ to form an acyl chloride. The acyl chloride in compound **D** undergoes intramolecular condensation with the amine functional group to form amide **E**. **E** is a cyclic amide as it forms from the rearrangement of oxime **F**. or **F** is a cyclic structure.

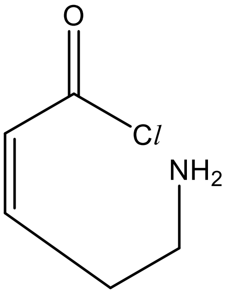


A

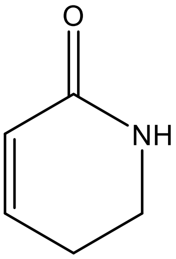


B

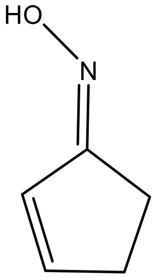
(Accept B as a zwitterion)



D



E



F

C is $(COOH)_2$

Comments

- Weaker answers recognised only the presence of alkene on **A**, carboxylic acid on **B**, acyl chloride on **D** and the absence of a chiral centre on **B**.
- Almost all could suggest the structure of **C**
- Stronger students would observe that **D** also has a amine group. This allows it to undergo intramolecular condensation with the acyl chloride. The resulting product is a cyclic amide **E**.
- Among the students who drew the correct structure of **E**, some were able to use Fig. 2.1 to deduce the structure of oxime **F**.

[Total: 20]

3	**(a)**	**(i)**	Using relevant $E^\ominus$ values from the *Data Booklet*, describe the trend in reactivity of Group 2 metals as reducing agents. [2]
			Down the group: $Mg^{2+} + 2e^- \rightleftharpoons Mg$ $E^\ominus = -2.38$ V $Ca^{2+} + 2e^- \rightleftharpoons Ca$ $E^\ominus = -2.87$ V $Ba^{2+} + 2e^- \rightleftharpoons Ba$ $E^\ominus = -2.90$ V (do not need to quote the values) The relative reactivity of Group 2 metals as reducing agents increases down the group OR stronger / better reducing agent OR 'more reactive' from Mg to Ca to Ba. This is shown by the reduction potential/$E^\ominus$ value of Group 2 cations becoming more negative/ less positive down the group. Hence the tendency of Group 2 metals to get oxidised increases down the group/tendency of Group 2 metals to lose electrons increases down the group.
			Comments - While question did not ask to quote values from Data Booklet, students should note that trend can only be seen with more than 3 pieces of data. To only mention 2 metals is merely a comparison. Phrases like 'down the group' should be used in the responses. - A handful of responses gave contradictory conclusions.
		(ii)	Using the *Data Booklet* or otherwise, explain another property of Group 2 metals that supports this trend. [2]
			Down the group, the valence electrons are further from the nucleus / larger atomic radius (Not accepted: ionic radius) OR the sum of the first and second ionisation energies decrease down the group, and experiences weaker nuclear attraction. The tendency of Group 2 metals to lose the 2 electrons increases down the group OR less energy required / it is easier to lose electrons.
			Comments - Quite a number of students were able to identify the correct property. However for IE, students should contextualise the question to Group 2 metals, hence it should be highlighted that it is the sum of the first and second IE that should be looked at to determine the trend. - Incorrect responses included description of trend of nuclear charge, shielding effect and effective nuclear charge.
	(b)	Thermogravimetric analysis, TGA, is an analytical technique primarily used to characterise materials by measuring the change in mass that occurs as a sample is heated at a constant rate. A thermogram from the TGA of calcium carbonate and magnesium carbonate is shown in Fig. 3.1.	

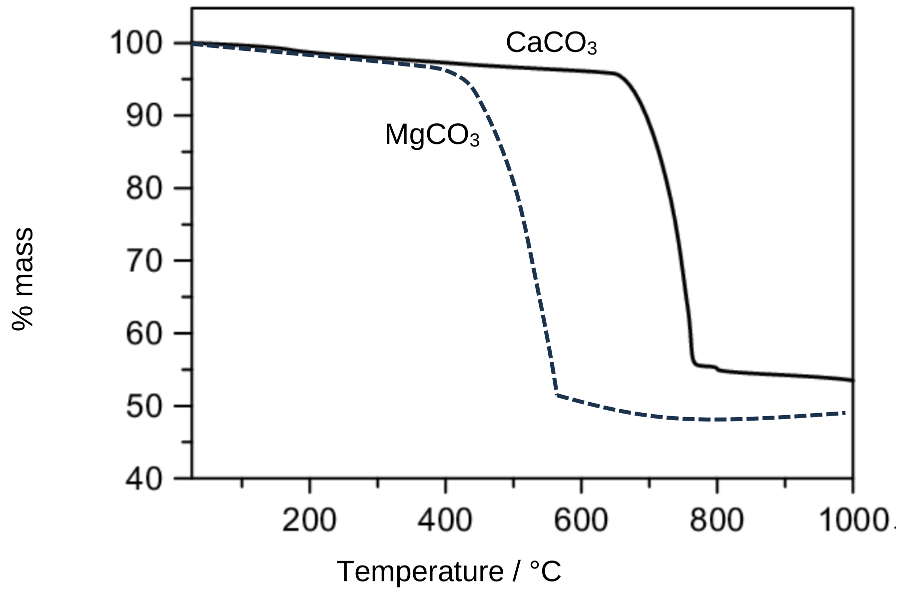


Fig. 3.1

(i) For both samples, the thermogram shows significant loss in mass when the temperature is high enough.
Write an equation for the heating of calcium carbonate at about 800°C. [1]

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

Not accepted: reversible arrow

Comments

- Generally well done. Some students wrote an equation representing combustion instead.

(ii) With reference to the equation in **(b)(i)**, explain the differences between the thermogram of calcium carbonate and magnesium carbonate in terms of

- the temperature when the carbonate starts to have significant decrease in mass
- the final mass of product obtained, given that the same initial mass is used for both carbonates. [4]

Magnesium carbonate has a smaller ionic radius of Mg^{2+} than Ca^{2+}, giving rise to a larger charge density and OR larger polarising power of Mg^{2+},

allowing it to polarise/distort electron cloud of carbonate OR weaken the C-O bond within carbonate anion to a larger extent. (Not accepted: ionic or intermolecular bond)

Less energy is needed to break the weaker covalent bonds within carbonate anion of $MgCO_3$, hence $MgCO_3$ starts to decompose at a lower temperature.

Magnesium has a smaller atomic mass than calcium, hence the amount of $MgCO_3$ used is larger.

The amount / mass of CO_2 lost from $MgCO_3$ is larger, hence the mass of product left is smaller than that of $CaCO_3$.

Comments

- The first part of the question was generally well done. A number of responses were careless in their phrasings, eg. polarise the carbonate anion, weaken the carbonate bond.

- The second part of the question was poorly done. While many recognised that Mg has a smaller A_r than Ca, students were unable to properly explain why final mass of CaO is higher than MgO.
- Many incorrect responses also misinterpreted the question and described the differences instead of explain.

(iii) Explain the difference in melting points of calcium carbonate and magnesium carbonate in terms of structure and bonding. [2]

$CaCO_3$ and $MgCO_3$ have giant ionic lattice structures and strong electrostatic forces of attraction/ionic bonds between the oppositely charged ions.

The charges of Mg^{2+} and Ca^{2+} are the same, and the ionic radius of Ca^{2+} is larger than that of Mg^{2+}.

Since LE α $\left|\frac{q_+q_-}{r_+ + r_-}\right|$, more energy is required to overcome to stronger ionic bond / more exothermic or higher LE between Mg^{2+} and CO_3^{2-} than between Ca^{2+} and CO_3^{2-}.

Therefore, the melting point of $MgCO_3$ is greater OR the melting point of $CaCO_3$ is smaller.

Comments

- This question was poorly attempted. Most of the incorrect responses gave similar answers to the first part of (b)(ii).

(c) **(i)** Explain what is meant by the term *standard enthalpy change of combustion*. [1]

It is the energy evolved when one mole of substance is burned completely in excess oxygen at 298 K and 1 bar.

(Not accepted: energy required / absorbed, standard conditions)

Comments

- This question was poorly answered.
- Wrong answers 'energy change', '273K' or did not state the temperature and pressure of standard conditions.

A bomb calorimeter consists of a thermally-insulated sealed metal container immersed in water. A sample of calcium is placed into the metal container, after which the container is filled with high pressure of excess oxygen. The sample is then ignited and the temperature change in the surrounding water is recorded.
Some data is recorded in Table 3.1.

Table 3.1

mass of calcium / g	1.41
mass of water / g	150
temperature of water before ignition / °C	28.6
temperature of water after ignition / °C	56.0
heat capacity of calorimeter, C_p / J K^{-1}	191
specific heat capacity of water, c / J g^{-1} K^{-1}	4.18

(ii) The heat released, q, can be found using the following relationship.

$$q = (C_p + mc)\,\Delta T$$

Together with the information in Table 3.1, calculate the enthalpy change of combustion of calcium. [2]

$q = (191 + (150 \times 4.18))\,(56.0 - 28.6)$

$= 22413$ J

Amount of calcium ignited = 1.41 / 40.1

= 0.0352 mol

$\Delta H_{\text{combustion}} = -22413/0.0352$

$= -637419 \text{ J mol}^{-1}$

$= -637 \text{ kJ mol}^{-1}$

Comments

- Generally well done. Most common mistake was forgetting to include the negative sign for ΔH.

(iii) The experiment was repeated with 1 bar pressure of oxygen gas. The value of the enthalpy change of combustion obtained was smaller than that in **(c)(ii)**.

Suggest a reason for the discrepancy. [1]

The lower pressure of O_2 in the bomb calorimeter may have resulted in incomplete combustion OR Ca is not fully reacted of calcium, hence less heat is evolved, resulting in less exothermic enthalpy change of combustion calculated.

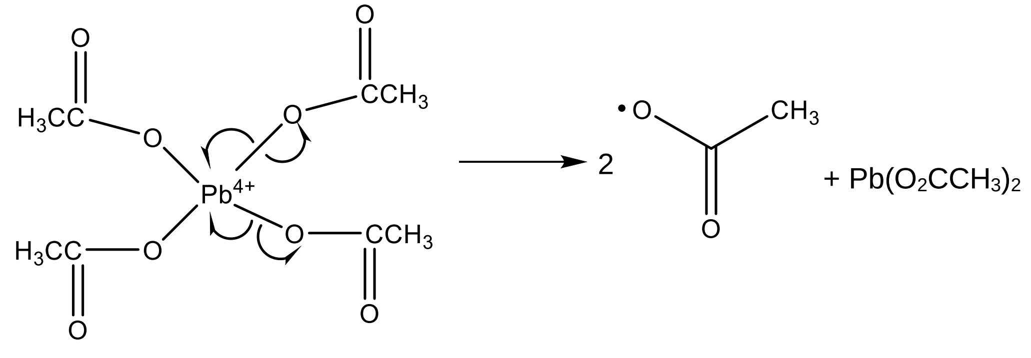
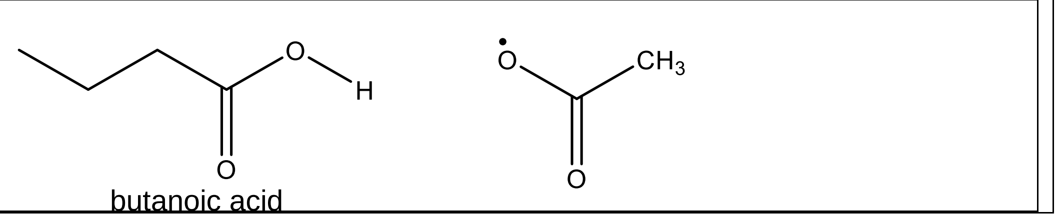
Comments

- This question was generally well done. Incorrect responses focused on rate of reaction.

(d) The decarboxylation of carboxylic acids to obtain alkenes can be achieved in a series of steps.
The overall balanced equation of the reaction process is shown as follows.

$$\text{R–COOH} + Pb(O_2CCH_3)_4 \xrightarrow{Cu(O_2CCH_3)_2} \text{alkene} + CO_2 + 2CH_3COOH + Pb(O_2CCH_3)_2$$

The process of decarboxylation of butanoic acid, $CH_3CH_2CH_2COOH$, with lead tetraethanoate, $Pb(O_2CCH_3)_4$ in the presence of catalytic amounts of $Cu(O_2CCH_3)_2$ is shown in Fig. 3.2.

step 1	
step 2	

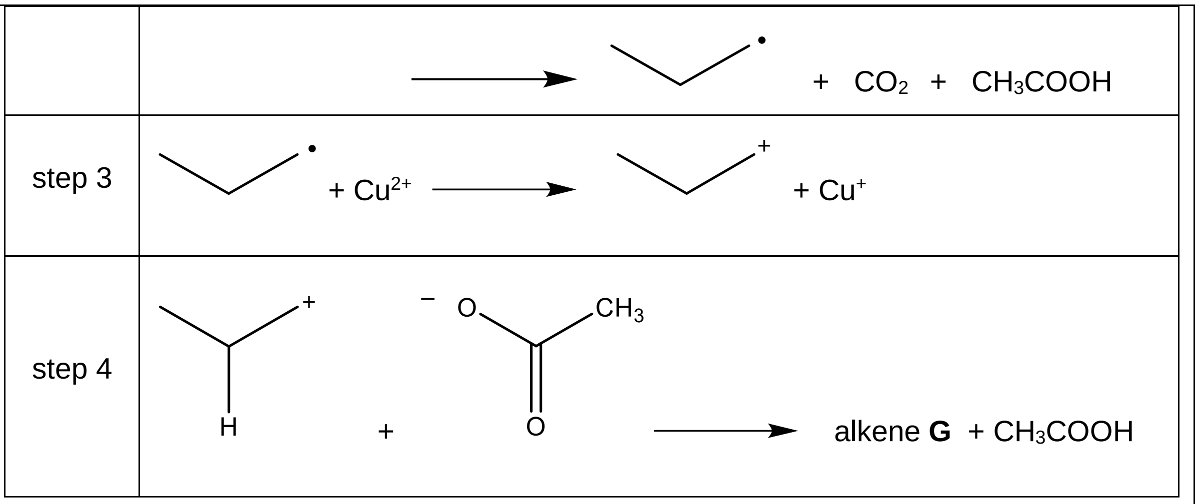
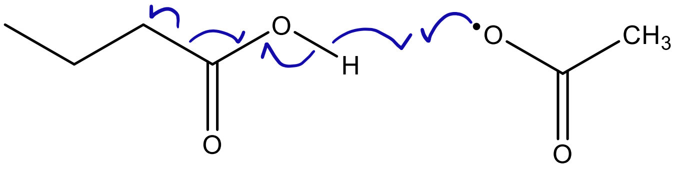
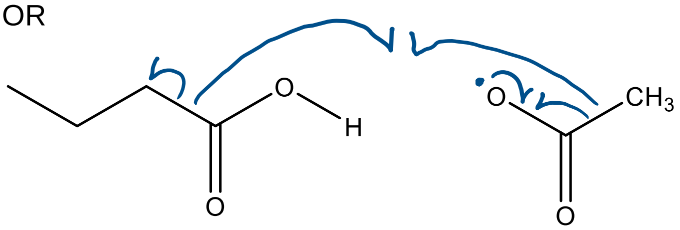


Fig. 3.2

(i) Steps 1 and 2 of the decarboxylation process involve the generation of free radicals. The mechanism of step 1 has been drawn in Fig. 3.2. Complete the mechanism on step 2 on Fig. 3.2 by adding **five** half arrows. [1]



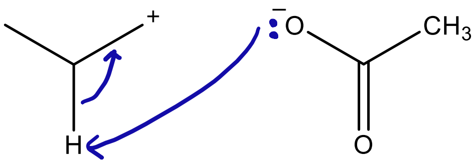
OR



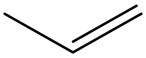
Comments

- Students should take note that converging half arrows should point towards each other to show new bond formed.

(ii) Complete the mechanism of step 4 on Fig. 3.2 by adding **two** full arrows, hence deduce the structure of **G**. [2]



G:



Comments

- Many students did not take guidance from the products to be formed when generating their answer.

			- A number of responses formed 2-methylpropene for alkene G.
		(iii)	Name the *types of reaction* for steps 3 and 4. [2]
			Step 3: redox (Not accepted: [O]) Step 4: acid-base
			Comment - Elimination is the overall reaction, not step 4.
		[Total: 20]	

Section B

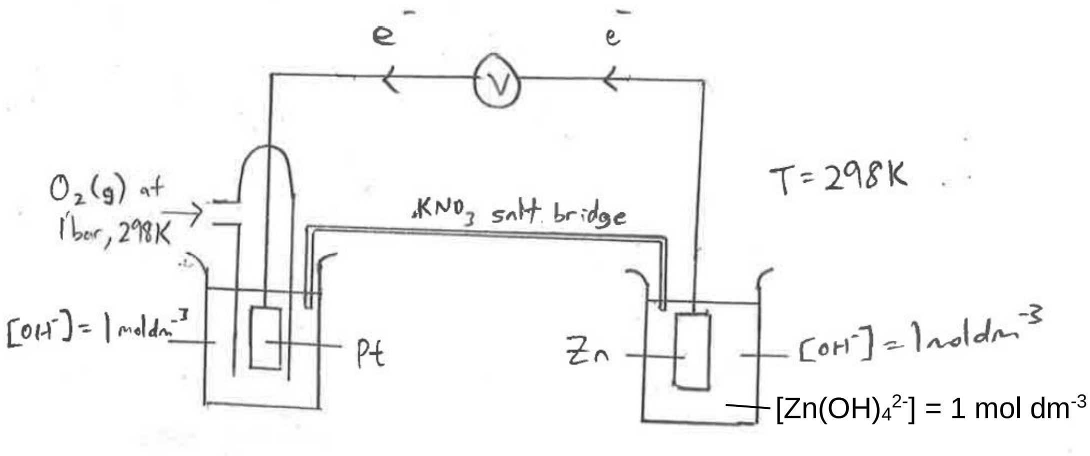
Answer **one** question from this section.

4 **(a)** The zinc-air battery involves a porous zinc electrode that reacts to form zincate, $Zn(OH)_4^{2-}$.

$$Zn(OH)_4^{2-}(aq) + 2e^- \rightleftharpoons Zn(s) + 4OH^-(aq) \qquad E^\theta = -1.25\text{ V}$$

The other electrode in the battery is the oxygen electrode in an alkaline medium.

(i) Draw a fully labelled diagram of the experimental set-up used to measure this E^θ_{cell} and indicate the direction of electron flow. [3]



Correct answers should include:

- Correct electron flow (Zn to Pt)
- O_2 at 1 bar, 298K
- $[OH^-] = 1$ mol dm^{-3} at cathode
- Salt bridge and voltmeter
- Both Pt and Zn electrodes
- $[Zn(OH)_4]^{2-} = 1$ mol dm^{-3} at anode
- $[OH^-] = 1$ mol dm^{-3} at anode

Comments

- This is a galvanic cell. Some students wrongly drew an electrolytic cell instead.
- Some students did not know how to draw the half-cell for oxygen electrode in alkaline medium. The correct half-equation can be taken from Data Booklet.
- A large number of students were unable to fully show standard conditions on their diagram (T=298K, concentration of any aqueous species at 1 mol dm^{-3}, Pt electrode if electrode not specified, pressure of any gas at 1 bar).

(ii) Calculate the standard Gibbs free energy change, ΔG^θ, for the oxidation of one mole of zinc in the zinc-air battery. [2]

$$E^\theta_{cell} = +0.40 - (-1.25) = +1.65\ V$$

$$\Delta G^\theta = -(2)(96500)(+1.65)$$

$$= -3.18 \times 10^5\ Jmol^{-1}$$

$$= -318\ kJmol^{-1}$$

Comments

			A significant number of students incorrectly used n=4. The question has already specified that this is for the oxidation of one mole of zinc, which involves 2 moles of electrons.
		(iii)	Predict how the E_{cell} will change when water is added into the $Zn(OH)_4^{2-}$/Zn half-cell. [2]
			Addition of water/dilution decreases the total number of particles per unit volume. Position of equilibrium shifts right for $Zn(OH)_4^{2-}(aq) + 2e^- \rightleftharpoons Zn(s) + 4OH^-(aq)$/ tendency for reduction of $[Zn(OH)_4]^{2-}$ decreases as there are more aqueous products than reactants/more ions on RHS. $E(Zn(OH)_4^{2-}/Zn)$ will become more positive/less negative./E_{anode} increase E_{cell} will become less positive/decrease.
			Comments Poorly done. This explanation is analogous to the decrease in total pressure exerted by gases when volume increases. POE will shift to favour the side which has more gaseous particles to increase pressure.
		(iv)	The zinc-air battery can be recharged and is relatively cheaper to produce. Suggest one **other** advantage of using the zinc-air battery. [1]
			Advantage: Zinc-air fuel cells have high energy densities. Alternative answers: Less flammable/Less explosive/Does not produce greenhouse gases/portable (Not accepted: does not produce harmful / polluting / toxic gases, more environmentally friendly to dispose)
			Comments A significant number of students provided vague responses which were not accepted.
	(b)	**(i)**	In the Contact Process, vanadium oxide catalyses the formation of sulfur trioxide, which is eventually converted to sulfuric acid through further reactions. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ State the type of catalyst in this reaction and describe how vanadium oxide speeds up this gaseous reaction. [3]
			Heterogeneous catalyst. As the gaseous reactants diffuse toward the solid catalyst surface, they are adsorbed/form bonds with the active sites or the catalyst/donate electrons to vacant orbitals of catalyst on the active sites on the catalyst surface via van der Waal's forces. The surface concentration of SO_2 and O_2 increases. This weakens the intramolecular covalent bonds in the reactant molecules. Adjacent reactants can then react to form products at a lower activation energy, which leads to increased rate. The products desorb/diffuse away/dissociate from the catalyst surface and diffuse away, thus allowing the vacant active sites to be available for adsorption of other reactant molecules.

(ii) In aqueous solution, vanadium ions form complexes of which the colours are lilac $[V(H_2O)_6]^{2+}$, green $[V(H_2O)_6]^{3+}$ and blue $[VO(H_2O)_5]^{2+}$.

Explain why vanadium ions are often coloured in aqueous solutions. [3]

In the presence of water ligands, the 3d orbitals of vanadium are split into two sets of slightly different energy levels.

Vanadium ions has partially filled 3d orbitals.

(Not accepted: empty or vacant)

An electron from the lower 3d energy level can absorb a specific frequency of light from the visible spectrum and be promoted/excited to a higher energy level

The colour observed is complementary to the colour of light absorbed.

OR wavelengths of light not absorbed/reflected are observed.

(c) In the nitration of benzene, sulfuric acid and nitric acid are used to generate the highly reactive nitronium ion.
Fig. 4.1 shows the incomplete mechanism for the formation of the nitronium ion.

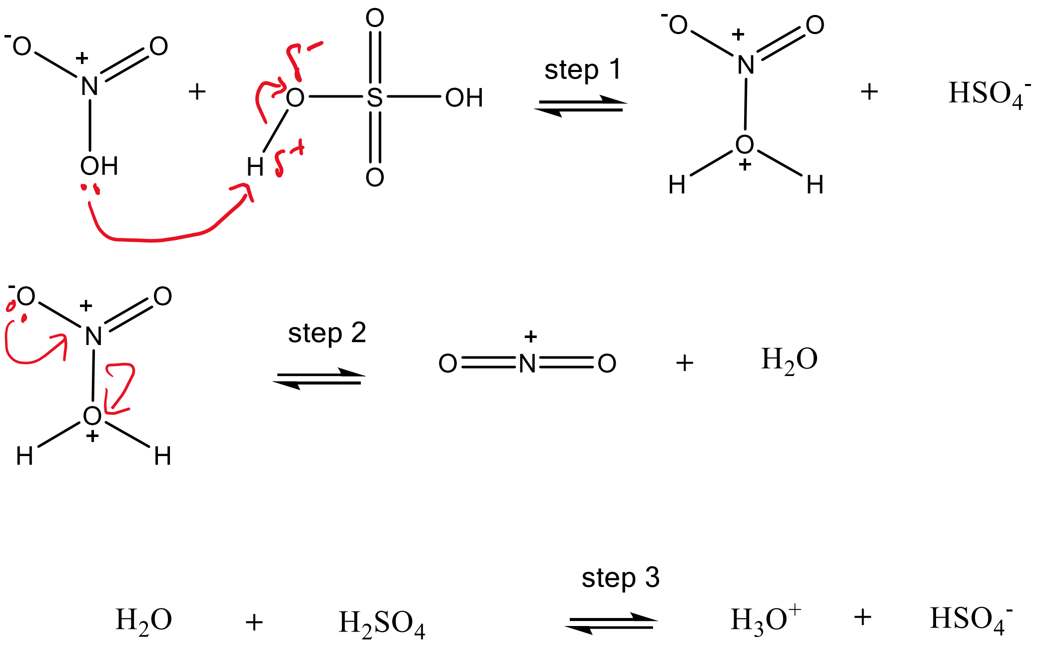


Fig. 4.1

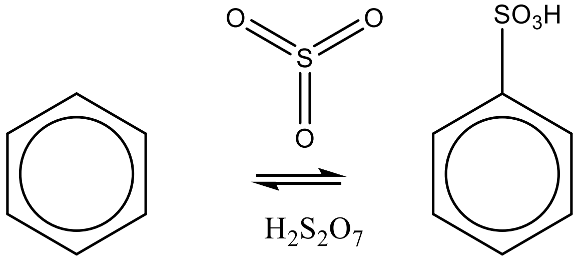
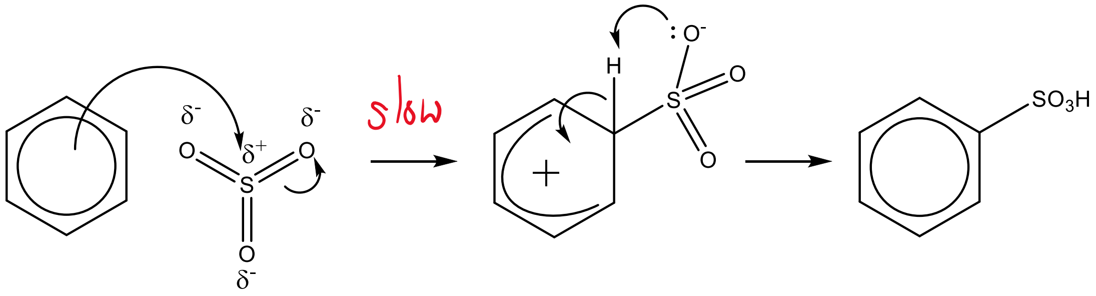
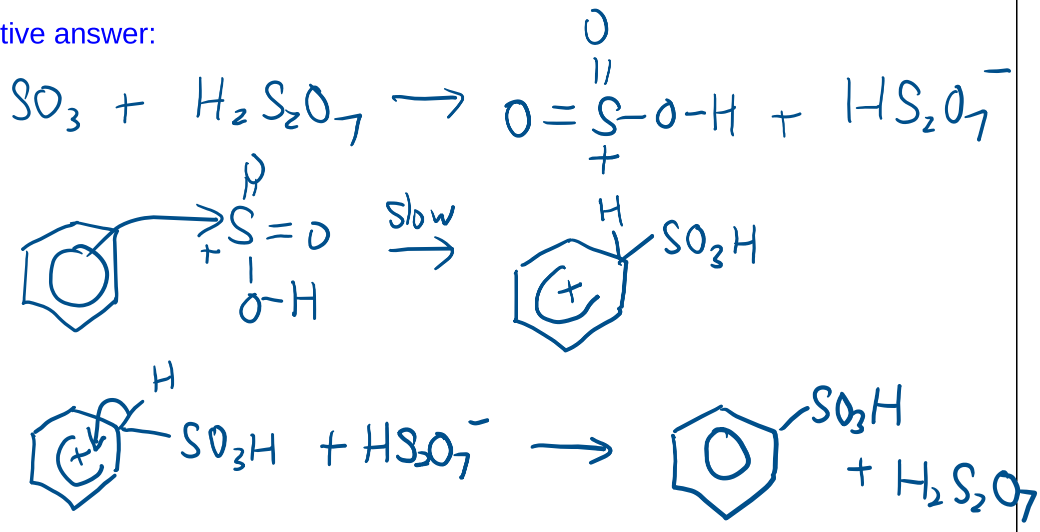
(i) On Fig. 4.1, draw curly arrows, partial charges and insert relevant lone pairs in steps 1 and 2 to complete the mechanism for the formation of the nitronium ion. [2]

(ii) State the role of sulfuric acid in step 1. [1]

Brønsted-Lowry acid / Bronsted acid / proton donor

(Not accepted: catalyst or acid or Lewis acid)

(d) **(i)** Benzene can also undergo electrophilic substitution with sulfur trioxide in the presence of fuming sulfuric acid.

			 Explain why sulfur trioxide can act as an electrophile. [1]
			Sulfur is bonded to three highly electronegative oxygen atoms, making sulfur electron deficient OR partial positive charge.
			Comments Students who did not score in this question usually did not explain why S is electron deficient.
		(ii)	Suggest a mechanism for the reaction between benzene and sulfur trioxide. Show the displayed structure of the electrophile, the structure of the intermediate and the movement of electron pairs by using curly arrows. [2]
			 Alternative answer: 
		[Total: 20]	

5 The “OXO” reaction is industrially important in making aldehydes and ketones from alkenes. For example, propanal can be synthesised from ethene, C_2H_4, as shown in the following equation.

$$CH_2{=}CH_2(g) + CO(g) + H_2(g) \rightleftharpoons CH_3CH_2CHO(g) \qquad \Delta H < 0$$

(a) An equimolar mixture of C_2H_4, CO and H_2 is added to a sealed vessel and heated to 500 K in the presence of rhodium catalyst. At equilibrium, 99% of C_2H_4 has reacted. The total pressure in the vessel is 40.8 atm at equilibrium.

(i) Write the expression for the equilibrium constant, K_p, for this reaction. Use your expression to calculate the value of K_p for this reaction. Include its units. [4]

$$K_p = \frac{P_{CH_3CH_2CHO}}{P_{CH_2=CH_2}P_{CO}P_{H_2}}$$

	C_2H_4	+	CO	+	H_2	$\rightleftharpoons$	CH_3CH_2CHO
Initial/atm	x		x		x		0
Change/atm	-0.99x		-0.99x		-0.99x		+0.99x
Final/atm	0.01x		0.01x		0.01x		0.99x

0.01x + 0.01x + 0.01x + 0.99x = 40.8

1.02x = 40.8

x = 40

Partial pressure of C_2H_4 = CO = H_2 = 0.01 x 40

= 0.4 atm OR 4.053×10^4 Pa

Partial pressure of CH_3CH_2CHO = 0.99 x 40

= 39.6 atm OR 4.01×10^6Pa

$$K_p = \frac{39.2}{(0.4)(0.4)(0.4)}$$

$= 619\ atm^{-2}$

OR $= 6.03 \times 10^{-8}\ Pa^{-2}$

Comments:

- Even though the question did not specify the units, it is better to leave the units according to the units given in the question to minimise conversion errors.
- The K_p expression should not have square brackets or contain multiplication signs.

(ii) The conditions used for the manufacturing of propanal in the OXO process is 480 K and 100 atm in the presence of a rhodium based catalyst.

Explain the conditions used for the manufacture of propanal. [2]

As the reaction is exothermic, a low temperature will shift the position of equilibrium to the right to release heat. However, a moderate temperature is used as too low a temperature would lead to a slow rate of reaction.

A high pressure would shift the position of equilibrium to the right as there are less moles of gases on the right and this would also increase rate of reaction. However, a moderate pressure is used as too high a pressure would incur high costs.

A catalyst is used to increase the rate of reaction.

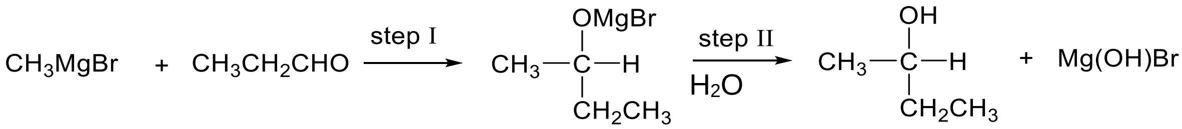
Comments:

For these types of questions, you need to cover the following points:

- Considerations of rate (wrt pressure, temperature)
- Slow rate when low temperature and pressure used/increase temperature and pressure to increase rate
- Catalyst: to increase rate
- Considerations of POE (wrt pressure and temperature)
- Temperature: discuss about POE by considering that production of propanal is exothermic
- Pressure: discuss about POE by considering that there is less moles of gas on the product side
- Costs considerations to maintain high pressure
- It is **not necessary to discuss about why** the use of a catalyst, higher temperature and pressure increases rate of reaction (i.e. the collision theory) as this is not the focus of the question.

(b) The Grignard reagent is a class of covalent compounds involving magnesium. One example of a Grignard reagent is CH_3MgBr which is prepared by treating magnesium metal with bromomethane in an ether solvent.

A typical example of the use of a Grignard reagent is the two-step reaction of CH_3MgBr with propanal, CH_3CH_2CHO, to form butan-2-ol.



$$CH_3MgBr + CH_3CH_2CHO \xrightarrow{\text{step I}} CH_3-\overset{OMgBr}{\underset{CH_2CH_3}{C}}-H \xrightarrow[H_2O]{\text{step II}} CH_3-\overset{OH}{\underset{CH_2CH_3}{C}}-H + Mg(OH)Br$$

(i) State the types of reaction for steps I and II. [2]

step I: Nucleophilic addition

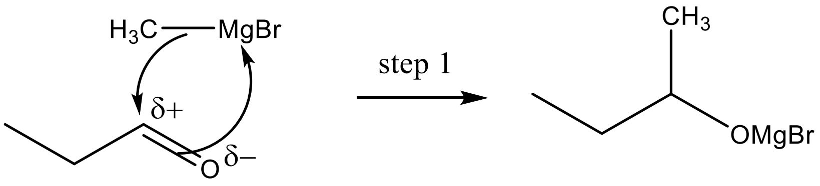
step II: Hydrolysis

Comments:

The question already stated that Grignard reagent are covalent compounds involving Mg.

Hence, we can assume the bond between C and Mg and also between O and Mg is covalent.

For step I, we observe that CH_3MgBr "adds" across the C=O bond in CH_3CH_2CHO, where CH_3 goes to C and MgBr goes to O (just like for HCN, the CN goes to C and H goe to O)



Since step II involves water breaking the covalent bond beteeen O and Mg, it is hydrolysis.

Acid base is only when the oxygen is a free RO^{-} ion, i.e. a conjugate base then the reaction with H_2O will be acid base as the free RO^{-} ion will accept H^{+} to become ROH.

(ii) State the reagents and conditions to convert butan-2-ol to 2-bromobutane. [1]

NaBr, concentrated H_2SO_4 OR HBr OR PBr_3, heat

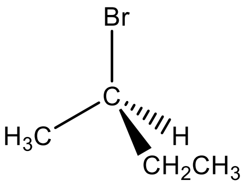
Comments

Any aq state symbols are not accepted as HBr will dissociate into H_3O^{+} and Br^{-} thus no longer able to react with butan-2-ol.

Likewise, PBr_3 (like PCl_5) will react with water in aq medium thus is no longer able to react with butan-2-ol.

"R" and "S" are used to denote enantiomers. R and S isomers rotate plane polarised light in opposite directions.

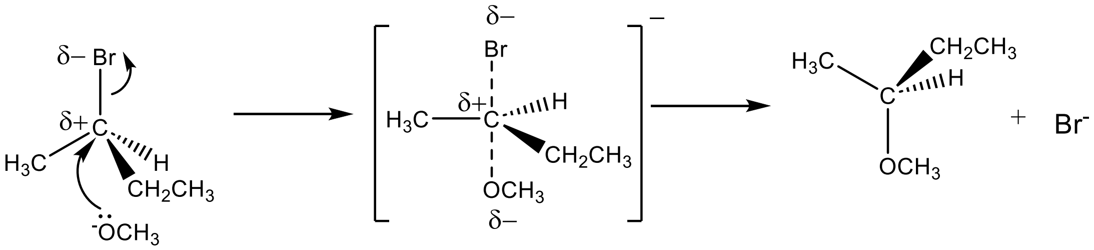
The R isomer of $CH_3CH_2CHBrCH_3$ is shown below.



When a sample of the R isomer of $CH_3CH_2CHBrCH_3$ is heated with $CH_3O^{-}Na^{+}$ in methanol, the S isomer of $CH_3CH_2CH(OCH_3)CH_3$ is obtained.

(iv) Name and draw the reaction mechanism for this reaction using the given structure of the R isomer of $CH_3CH_2CHBrCH_3$. Show relevant lone pairs of electrons, dipoles and curly arrows. [3]

Nucleophilic substitution S_N2



Comments

Since the question stated that when the "R" enantiomer is reacted with the nucleophile, the "S" enantiomer is formed, this implies an inversion of configuration, thus the mechanism MUST be S_N2.

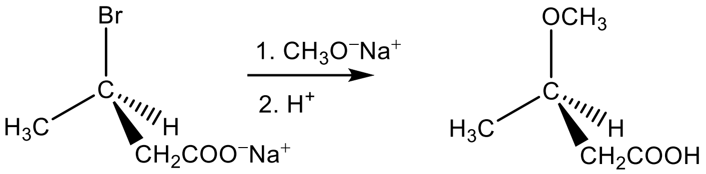
Note that the mechanism must have the following:

- Title must include S_N2
- Partial charges on C and Br
- Lone pair on O
- Curly arrows x 2

- Inversion about the chiral C (the OCH_3 must be bonded to the C on the opposite side of the original Br)

(v) In the presence of $CH_3O^-Na^+$, the R isomer of 3-bromobutanoic acid, $CH_3CH(Br)CH_2COOH$ is converted to $CH_3CH(Br)CH_2COO^-Na^+$.

When the R isomer of $CH_3CH(Br)CH_2COO^-Na^+$ is reacted with $CH_3O^-Na^+$ followed by acidification, the R isomer of $CH_3CH(OCH_3)CH_2COOH$ was obtained.

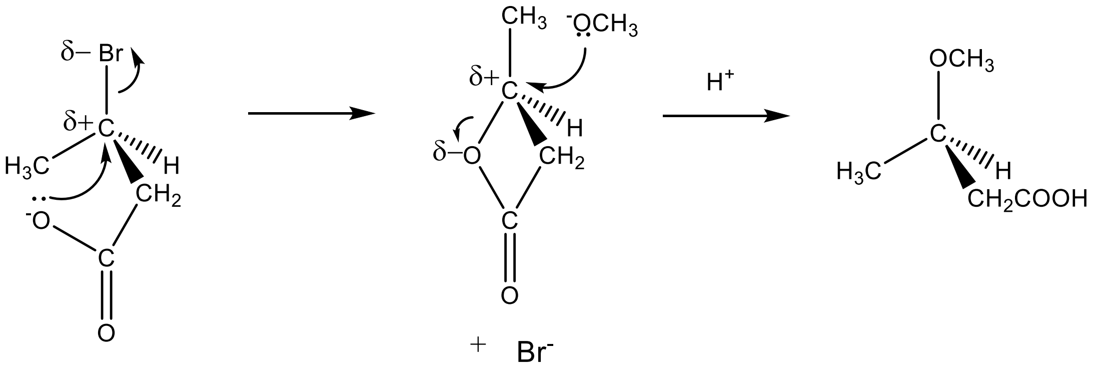


Explain why this is so. [1]

The COO⁻ group substitutes/attacks/displace the Br resulting in the S isomer, then the $^-OCH_3$ substitutes/attacks/displace the COO⁻ group resulting in the R isomer again. (or wtte)

OR S_N2 occurred twice

Comments



In step 1, an S_N2 attack by the COO⁻ and inverts the stereochemistry around the alkyl bromide and forms the S isomer.

In step 2, another S_N2 attack by the $^-OCH_3$ inverts the stereochemistry again and forms the R isomer.

We cannot state the S_N1 reaction occurred since S_N1 results in a racemic mixture of R and S isomers due to the planar carbocation intermediate that can be attacked by the nucleophile from either side. However, in this case, the R isomer is formed, not a racemic mixture.

(vi) Explain why 3-bromobutanoic acid is a stronger acid than butanoic acid. [2]

The bromine group is electron withdrawing and electronegative, hence it disperses the negative charge, of $CH_3CH(Br)CH_2COO^-$ to a greater extent, hence $CH_3CH(Br)CH_2COO^-$ is more stable than $CH_3CH_2CH_2COO^-$ or conjugate base of 3-bromobutanoic acid is more stable.

Comments

Do not state that 3-bromobutanoic acid is more stable than butanoic acid as it is the conjugate base, $CH_3CH(Br)CH_2COO^-$ that is more stable than $CH_3CH_2CH_2COO^-$.

	(c)	Butanoic acid can be converted to calcium butanoate, $(CH_3CH_2CH_2COO)_2Ca$ when reacted with calcium hydroxide. Calcium butanoate supplements are sometimes used to support digestive health as it is known to have anti-inflammatory properties and supports the health of the colon.	
		(i)	Write an equation for the reaction between butanoic acid and calcium hydroxide. [1]
			$Ca(OH)_2 + 2CH_3CH_2CH_2COOH \rightarrow (CH_3CH_2CH_2COO)_2Ca + 2H_2O$
			Comments • The equation should not be written where butanoic acid or calcium butanoate is the molecular form, $C_4H_8O_2$ or $(C_4H_7O_2)Ca$ as it is important to show where the proton is dissociated from in butanoic acid. And it is only possible to show if the structural formula is used. • You should also not represent butanoic acid as C_3H_7COOH as C_3H_7 can be straight or branched chain. • Note that calcium hydroxide is $Ca(OH)_2$, since there is two OH^-, the mole ratio with butanoic acid is 1:2, not 1:1. • Do note that state symbols are NOT required, but any incorrect state symbols will still be penalised.
		(ii)	Given that the solubility of calcium butanoate is 0.0161 mol dm^{-3}, calculate the K_{sp} of calcium butanoate stating its units. [2]
			$[Ca^{2+}] = 0.0161$ mol dm^{-3} $[CH_3CH_2CH_2COO^-] = 2 \times 0.0161 = 0.0322$ mol dm^{-3} $K_{sp} = [Ca^{2+}][CH_3CH_2CH_2COO^-]^2$ $= 0.0161 \times (0.0322)^2$ $= 1.67 \times 10^{-5}$ mol^3 dm^{-9}
			Comments • A common mistake is to equate K_{sp} to $(0.0161)^3$ • Note that $[CH_3CH_2CH_2COO^-]$ is twice that of $[Ca^{2+}]$
		(iii)	Calculate the solubility of calcium butanoate in a solution containing 0.1 mol dm^{-3} of calcium chloride. [1]
			Let the solubility = x $[Ca^{2+}] = x + 0.1$ (x from calcium butanoate, 0.1 from $CaCl_2$) $[CH_3CH_2CH_2COO^-] = 2x$ (only from calcium butanoate) $(x+0.1)(2x)^2 = 1.67 \times 10^{-5}$ (assume $x+0.1 = 0.1$) $4x^2 = 1.67 \times 10^{-4}$ $x = 6.46 \times 10^{-3}$ mol dm^{-3}
			Comments • A common error was to assume that $[CH_3CH_2CH_2COO^-]$ is twice that of $[Ca^{2+}]$. This is incorrect as $CH_3CH_2CH_2COO^-$ only comes from $(CH_3CH_2CH_2COO)_2Ca$ but Ca^{2+} comes from $(CH_3CH_2CH_2COO)_2Ca$ and $CaCl_2$.
		(iv)	The $\Delta G^\ominus_{sol}$ of an ionic compound in J mol^{-1}, is given by the following expression. $\Delta G^\ominus_{sol} = -RT \ln K_{sp}$

			Calculate the $\Delta G^\ominus_{sol}$ in kJ mol^{-1}, for calcium butanoate. [1]
			$\Delta G^\ominus_{sol} = -8.31 \times 298 \times \ln(1.67 \times 10^{-5})$ $= +27240$ J mol^{-1} $= +\underline{27.2}$ kJ mol^{-1}
			Comments • Do note that temperature should be 298K as it is standard conditions, not 293K or 273K • You should also put the + sign in front of your answer.
		[Total: 20]	