Anglo-Chinese Junior College
JC2 Preliminary Examination
Higher 2

A Methodist Institution
(Founded 1886)

CANDIDATE NAME	Answers	FORM CLASS	
TUTORIAL CLASS		INDEX NUMBER	

CHEMISTRY **9729/02**

Paper 2 Structured Questions

21 August 2024
2 hours

Candidates answer on the Question Paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your form class, index number and name in the spaces provided at the top of this page.
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.
The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

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

For Examiner's Use	
Question no.	**Marks**
1	/ 12
2	/ 11
3	/ 10
4	/ 10
5	/ 10
6	/ 22
Presentation of answers	
TOTAL	/ 75

This paper consists of **22** printed pages and **2** blank pages.

Section B: Structured Questions (75 marks)

Answer **all** the questions in the spaces provided.

1 **Y** and **Z** are two elements found in Period 3. Their fifth to eighth ionisation energies are given in Table 1.1.

Table 1.1

successive ionisation energies / kJ mol^{-1}	5th	6th	7th	8th
Y	6530	9353	11019	33606
Z	7004	8496	27107	31719

(a) **(i)** State and explain the group number of **Y**. [1]

Y belongs to Group 17. There is a large jump between the 7th and 8th ionisation energies, so the 8th electron to be removed comes from an inner (principal quantum) shell. [1]

Comments

- Generally well done. However, many students misspelt 'principal' as 'principle'. Also, the terms 'principal quantum shell' and 'subshell' should not be used interchangeably.

(ii) Complete the electronic configurations of **Y**$^+$ and **Z**$^+$.

Y$^+$: $1s^22s^22p^63s^23p^4$
Z$^+$: $1s^22s^22p^63s^23p^3$

Comments

- Students should write out the electronic configuration of elements Y and Z first before removing an electron.

(iii) From your answer in **(a)(ii)**, explain why the second ionisation energy of **Y** is expected to be lower than **Z**. [1]

The second ionisation energy for element Y involves removing a paired electron from the 3p subshell that has interelectronic repulsion while the second ionisation energy for element Z involves removing an unpaired electron from the 3p subshell.

Comments

- A significant number of students were able to identify that there was greater interelectronic repulsion in Y but did not mention this was due to the paired electrons.
- For the 2nd IE of Z, only the electrons in the 3p subshell are unpaired, the inner electrons are still paired so it is incorrect to say that there are no paired electrons in Z.

(iv) However, it turns out that the second ionisation energies of **Y** and **Z** are 2300 kJ mol^{-1} and 2260 kJ mol^{-1} respectively.
Suggest why **Y** has a higher second ionisation energy than **Z**. [1]

The effect of the higher (effective) nuclear charge of Y is more dominant than the interelectronic repulsion between the paired electrons, so the 3p electron to be removed is held more tightly by the nucleus. [1]

Comments

- Many students struggled to adequately account for the higher second IE of Y. Students should recognise that there are two factors to consider: 1. effective nuclear charge and 2. interelectronic repulsion. The predominant factor is determined based on data given. Some managed to identify the predominant factor of higher effective nuclear charge but did not link it to the valence electron being more tightly held by the nucleus.

(b) **(i)** The atomic radii of some Period 4 elements are shown in Fig. 1.1.

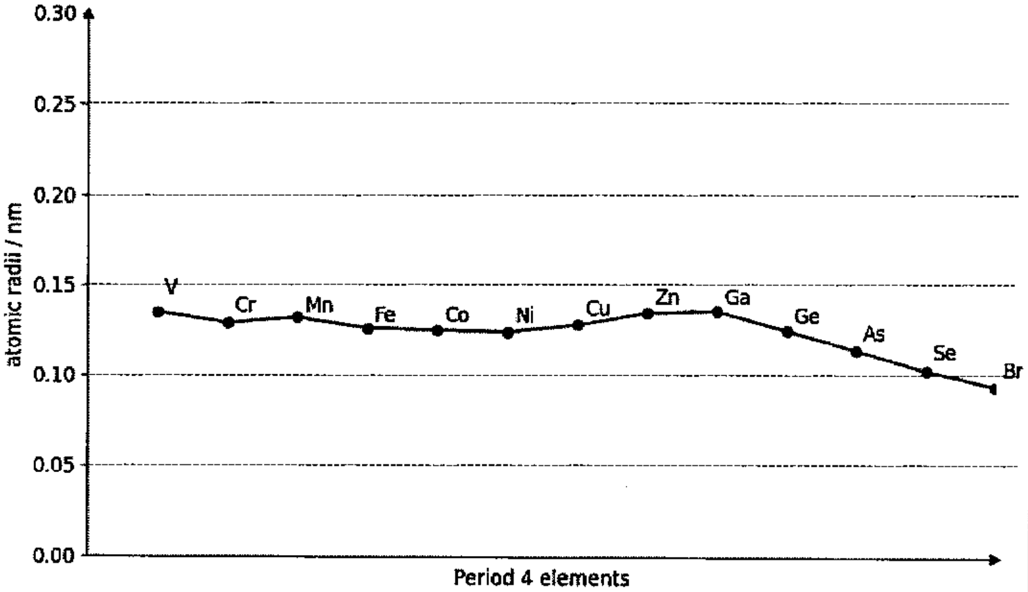


Fig. 1.1

With reference to Fig. 1.1, describe and explain the shape of the graph from

- V to Zn
- Ga to Br

[4]

From V to Zn, the atomic radii remains relatively invariant. While nuclear charge increases from V to Zn, electrons are added to the inner shell / 3d subshell, increasing shielding effect on valence electrons. Increase in effective nuclear charge is minimal/effective nuclear charge remains relatively constant.

From Ga to Br, the atomic radii of the elements decreases across the Period. Across the Period, increasing nuclear charge and approximately constant shielding effect causes effective nuclear charge to increase. The valence electrons experience stronger nuclear attraction and are pulled closer to the nucleus. Hence, atomic radius decreases across the Period.

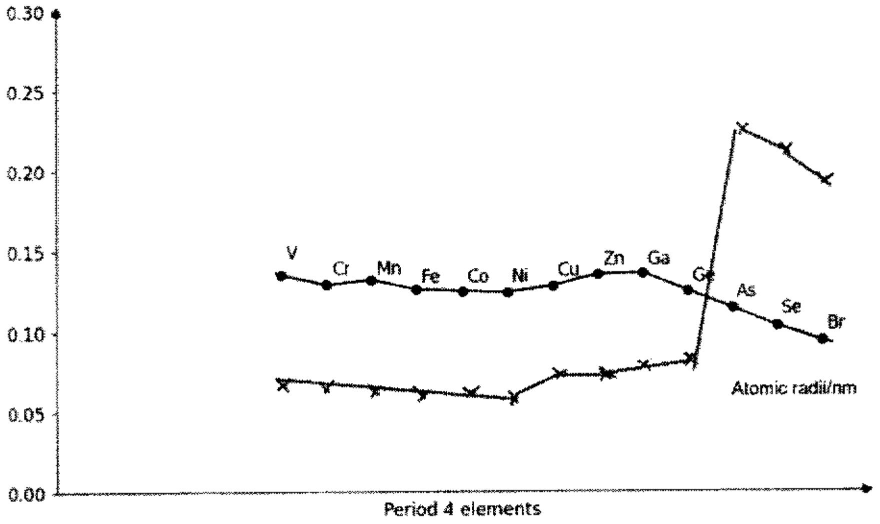
Comments

- This question tested two main learning outcomes:
  1. Describing and explaining the general trend in atomic radius across the Period (Ga to Br) in terms of shielding effect and nuclear charge

2. Explain why atomic radii of transition elements are relatively invariant

- Many students had the general idea of at least one of these learning outcomes, but explanations were lacking.

(ii) With reference to the *Data Booklet* or otherwise, sketch the ionic radii of the Period 4 elements on Fig. 1.1.
You may assume that V to Zn form doubly charged cations. [2]

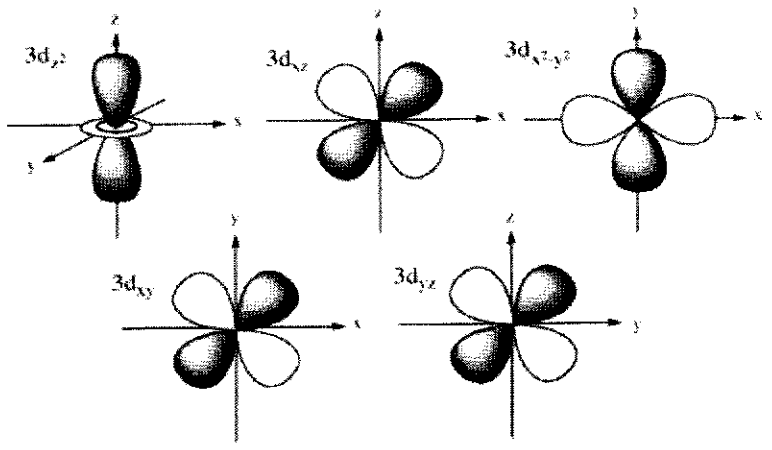


- V to Zn line: lower values of decreasing or constant trend
- Ga to Br line: anions of As, Se and Br must be higher with decreasing trend **&** Ga^{3+} and Ge^{2+}/Ge^{4+} must be lower with decreasing trend

Comments

- Poorly done. Some students only sketched the ionic radii from V to Zn.
- Students should recognise that cationic radii are always smaller than their respective atomic radii as there is one shell of electrons less (V^{2+} to Ge^{2+}/Ge^{4+}). Sharper students extracted the actual cationic radii from the Data Booklet.
- Students should recognise that anionic radii are larger than their respective atomic radii as there is greater interelectronic repulsion when more electrons are added (As^{3-}, Se^{2-}, Br^{-}).

(c) Draw and label the d orbitals in cobalt ion. [2]



Comments

- Most students were able to get at least 1m. When labelling orbitals, students should follow the convention (e.g. d_{yz} and not d_{zy}).

[Total: 12]

2 The hydroboration-oxidation reaction of an alkene bond using borane, BH_3, provides a useful method for hydration. Using this reaction, 1-methylcyclohexene can be converted to trans-2-methylcyclohexanol as shown in Fig. 2.1.

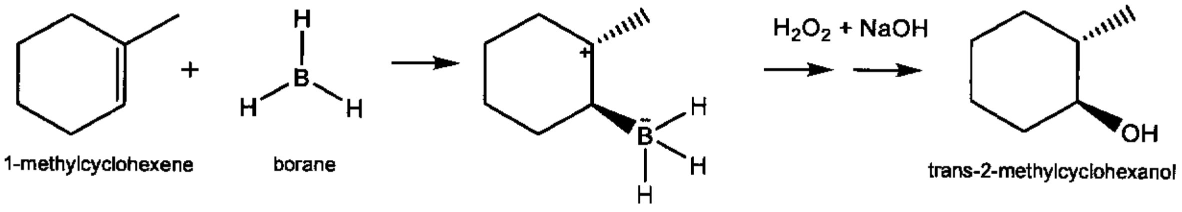


Fig. 2.1

(a) (i) Explain the role of borane in Fig. 2.1. [1]

BH_3 is a lewis acid as it accepts an electron pair from the alkene.
OR
BH_3 is an electrophile as borane is electron-deficient OR alkene is electron-rich.

Comments

- Some students merely stated the role of borane without any explanation.

(ii) Suggest why the *trans* configuration is favoured in the product formed in Fig. 2.1. [1]

Steric hindrance is minimised/ There is less interelectronic repulsion when the bulky methyl and BH_3^- groups are at opposite sides of the ring.
OR
Cis configuration is not favoured because the bulky methyl and BH_3^- groups are on the same side, hence there is more steric hinderance.

Comments

- Students should always explain what they understand by 'steric hindrance'.

(b) Suggest a chemical test that would allow you to distinguish between 2-methylcyclohexanol and ethanol. Include a relevant equation in your answer. [2]

To separate test tubes containing each sample, add I_2(aq), NaOH(aq) and heat/warm. Yellow ppt observed for ethanol but not for 2-methylcyclohexanol.

$CH_3CH_2OH + 4I_2 + 6NaOH \rightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$

DNA: Iodoform test. Must state R&C used.
DNA: if 2 tests were applied. Qn asked for 1 chemical test only.

Comments

- Some students did not mention 'heat' for iodoform test.
- Some students did not read the question properly and missed out on giving an equation.

- A significant number of students were unable to give the correct balanced equation for iodoform test. A common mistake was to give CH_3COO^- as one of the products.
- A minority of students thought that cyclohexanol was the same as phenol which is a big misconception.

(c) Borane dimerises to form the more stable diborane, B_2H_6, shown in Fig 2.2.

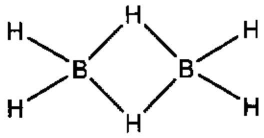


Fig 2.2

(i) Suggest **two** unusual features about the bonding shown in Fig 2.2. [2]

Bridging hydrogen forms two bonds when it has only one valence electron.
OR
Hydrogen should not be able to accept a lone pair of electrons as it does not have an empty orbital.

Boron forms four bonds when it has only three valence electrons.
OR
Boron/hydrogen should not be able to form dative bonds since it does not have a lone pair of electrons.

Comments

- Most students could score at least 1m.

(ii) Fig 2.3 depicts another equivalent representation of the bonding in diborane. The bridging B-H-B bonds are curved, giving it the name 'banana bonds'.

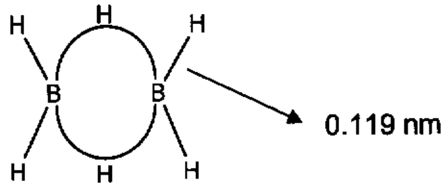


Fig 2.3

The 'banana bonds' consist of three-centre-two-electron bonds, which are electron-deficient chemical bonds where three atoms share two electrons.
State the total number of bonding electrons in diborane. [1]

12

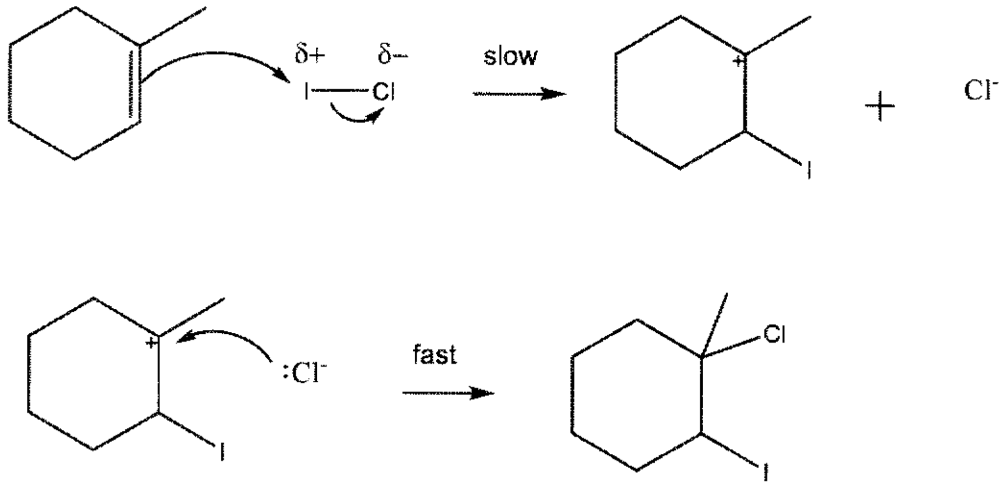
Comments

- 6, 8, 14 electrons were given in students' responses.

(iii) The B–H bonds in diborane have different bond lengths. The terminal B–H bonds are 0.119 nm in length.

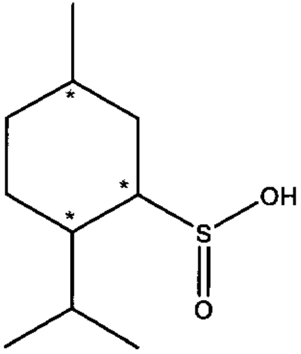
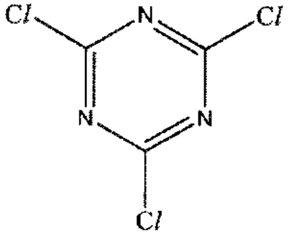
Explain how the bond length of the bridging B–H bonds compares with the terminal B–H bonds.

Note: Fig 2.3 is not drawn to scale. [1]

			Since 3 atoms share a pair of electrons instead of 2 atoms, the bond length is expected to be longer.
			Comments • Poorly done. Those who identified that the bond length is expected to be longer did not give an adequate explanation.
	(d)		1-methylcyclohexene can react with iodine monochloride, IC*l*. Name and describe the mechanism of this reaction, showing curly arrows, charges, dipoles and any relevant lone pairs. [3]
			
			Comments • A minority of students did not use 1-methylcyclohexene as the starting structure even though it was already given in the question. • A significant number of students did not draw the curly arrows correctly, or drew the wrong intermediate. Slow step was also not labelled and some did not give the name of the mechanism.
			[Total: 11]

3	Cyanogen chloride, C*l*CN, exists as a highly toxic gas and reacts rapidly with hydroxide ions. equation 1 $ClCN + OH^- \rightarrow HOCN + Cl^-$		
	(a)	**(i)**	State the hybridisation of the carbon atom in cyanogen chloride. [1]
			sp
			Comments • A minority of students were penalised for notation (sp^1).
		(ii)	Name the *type of reaction* occurring in equation 1. [1]
			Nucleophilic substitution / hydrolysis
			Comments • Generally well done.

	(b)	**(i)**	0.06 g of cyanogen chloride was fully dissolved in 100 cm^3 of 2 mol dm^{-3} aqueous sodium hydroxide. The rate constant for the reaction is k = 4.2 mol^{-1} dm^3 s^{-1}. Construct the rate equation for equation 1. [1]
			rate = k[C*l*CN][OH$^-$]
			Comments - Students should use the units of the rate constant to identify the overall order of the reaction.
		(ii)	Calculate the concentration of cyanogen chloride in the solution. [1]
			$[ClCN] = \frac{0.06}{61.5} \div \frac{100}{1000} = 9.76 \times 10^{-3}$ mol dm^{-3}
			Comments - Mostly well done.
		(iii)	Using your answer in **(b)(ii)** and the information in **(b)(i)**, deduce the half-life of the reaction. [1]
			Since [C*l*CN] << [OH$^-$], this is a pseudo first-order reaction. rate = k'[C*l*CN], where k' = k[OH$^-$] k' = 4.2 × 2 = 8.4 s^{-1} $t_{\frac{1}{2}} = \frac{\ln 2}{8.4} = 0.0825$ s
			Comments - Poorly done. Many students did not identify that [OH$^-$] is in large excess compared to the calculated value of [C*l*CN] in (b)(ii), making this a pseudo first-order reaction.
	(c)	**(i)**	In a separate experiment, 0.15 g of gaseous cyanogen chloride was found to occupy a volume of 72.3 cm^3 at 127 °C and a pressure of 102.7 kPa. Calculate the relative molecular mass of cyanogen chloride using the experimental data. [1]
			$M = \frac{mRT}{pV}$ $= \frac{0.15 \times 8.31 \times (127 + 273)}{102700 \times 72.3 \times 10^{-6}}$ = 67.1 g mol^{-1} The relative M_r is 67.1.
			Comments - Relative molecular mass has no units. Only molar mass has units of g mol^{-1}.
		(ii)	Pure cyanogen chloride was used in the experiment. Suggest why there is a difference between the theoretical value of its relative molecular mass and the value obtained in **(c)(i)**. [2]

			Cyanogen chloride does not behave ideally, due to <u>strong permanent dipole-permanent dipole (pd-pd) interactions OR instantaneous dipole-induced dipole (id-id) interactions</u> between cyanogen chloride molecules. This leads to a <u>smaller p (or V or pV)</u> due to particles colliding with the walls of the container with reduced force, hence <u>larger value of calculated relative molecular mass</u>.
			<u>Comments</u> • The assumption of volume of gas particles being significant as compared to the volume of gas was not a valid consideration because this would result in the pV value being larger than that of an idea gas (calculated M_r value would be smaller than expected)
	(d)	Cyanogen chloride can react with sulfinic acids to form sulfonyl cyanides. An example of a sulfinic acid is shown in Fig.3.1.  **Fig. 3.1**	
		Chiral centres have four different substituent groups bonded to it. The lone pair of electrons on atoms can also be considered as a distinct group. Identify the chiral carbons of sulfinic acid shown on Fig. 3.1 by marking them with an asterisk (*). [1]	
		<u>Comments</u> • Generally well done. Students should note that sulfur is also chiral.	
	(e)	Cyanogen chloride can trimerise to form a 6-membered cyclic molecule with molecular formula, $(ClCN)_3$. This molecule has no overall dipole moment. Suggest a possible structure of the trimer. [1]	
			
		<u>Comments</u> • Students should pay attention to the number of bonds that carbon and nitrogen can form. Where possible, avoid having 4 bonds for N atom as this would create a positive charge.	
		[Total: 10]	

4 Pyrite, FeS_2, is often referred to as "Fool's Gold" because it resembles gold to the untrained eye. It is one of the most abundant sulfide mineral available.

Table 4.1 shows some physical properties of pyrite and gold against other substances.

Table 4.1

compound	gold	FeS_2 (pyrite)	steel
melting point / °C	1064	1177	1425
Mohs hardness	2.5	6.3	6.5
Density / g cm^{-3}	19.0	5.0	7.9

(a) (i) Explain the high melting points of gold and pyrite. [2]

Gold has giant metallic structure, FeS_2 has giant ionic lattice structure. Large amounts of energy are required to overcome the strong metallic bonds / electrostatic forces of attraction between gold ions and its sea of delocalised electrons, and strong ionic bonds / electrostatic forces of attraction between Fe^{2+} and S_2^{2-} ions.

Comments

- This was generally well done. A small number of responses identified both gold and FeS_2 as having giant metallic structures and metallic bonding.
- Some students misinterpreted the question as having to compare between the melting points of gold and FeS_2.

(ii) Mohs Hardness Scale is a measure of a substance's resistance to scratching. The substance's hardness is measured against another substance of known hardness on the Mohs Hardness Scale. A substance can only scratch a substance of equal or lower Mohs hardness value.

Suggest a simple way to distinguish between gold and pyrite. [1]

Scratch the two samples against each other. The mineral that is scratched is gold, the mineral that is not scratched is pyrite.

OR Cut/Obtain the same volume of both substances, weigh the substances using a mass balance. The heavier sample is gold.

OR take a sample of gold and pyrite and calculate their densities.

Comments

- Some responses were vague in their description of how the results of their method would allow both materials to be distinguished.
- Some responses proposed using another material of Mohs Hardness value between 2.5 and 6.3. Students should keep in mind that specific examples should be used as far as possible.

(iii) Pyrite and steel have similar values on the Mohs Hardness Scale that are relatively higher than that of metals. Explain this phenomenon, making reference to their lattice structure. [2]

The lattice structure of pyrite is made up of alternating Fe^{2+} and S_2^{2-} ions of different sizes. OR Pyrite has strong ionic bonds / high lattice energy.

Steel is an alloy composed of different metals, hence its lattice structure is made up of different sized metal atoms.

The distortion in both lattice structures require larger force for the layers to slide/shift over one another, hence both pyrite and steel are relatively hard.

Comments

- Most responses stopped after identifying the structure of pyrite and steel. Some responses identified steel as being ionic. This awards no marks.
- Students should take note to ensure the identified structure and bonding are correctly matched. There were responses which mentioned the giant ionic lattice structures had weaker id-id between its molecules.
- A handful of responses were able to identify that having high Mohs Hardness value meant difficulty for layers to slide over one another.

(b) Due to its shiny and gold-like appearance, pyrite is widely used in decorative items. However, over time, items with pyrite were found to be cracked and discoloured. When exposed to air and moisture, the iron-containing mineral can form rust, Fe_2O_3, along with a toxic gas, SO_2, and corrosive acid.

(i) Construct a balanced equation of the formation of rust from pyrite. [1]

$2FeS_2 + 6O_2 + H_2O \rightarrow Fe_2O_3 + 3SO_2 + H_2SO_4$

$2FeS_2 + 7O_2 + 3H_2O \rightarrow Fe_2O_3 + SO_2 + 3H_2SO_4$

$2FeS_2 + \frac{13}{2}O_2 + 2H_2O \rightarrow Fe_2O_3 + 2SO_2 + 2H_2SO_4$

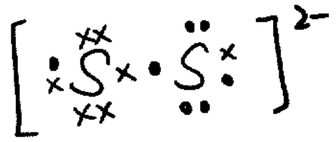
$2FeS_2 + \frac{11}{2}O_2 + H_2O \rightarrow Fe_2O_3 + 3SO_2 + H_2SO_3$

Any equation for 1m

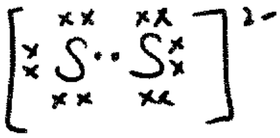
Comments

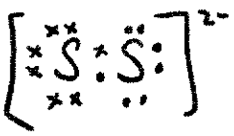
- Despite having multiple possible answers, this question was poorly done.
- Incorrect responses left out either O_2 or H_2O as one of the required reactants for rusting to occur.

(ii) Draw the 'dot-and-cross' diagram of the disulfide ion, S_2^{2-}. [1]



Accept :





Comments

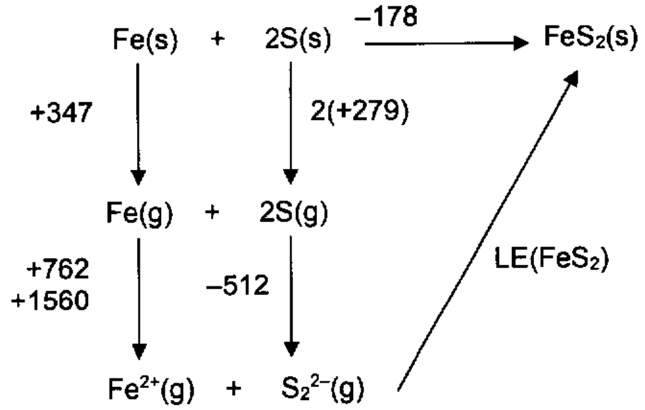
- In general the cohort performed below expectations for this question.
- Incorrect responses included forming double bonds or dative bond between the 2 S atoms, as well as when one S atom gains both electrons.
- Students should take note to show the distinction between the electrons of two adjacent atoms clearly.

(c) Iron(II) compounds are generally only stable in neutral, non-oxidising conditions. It is difficult to determine the lattice energy of FeS_2 experimentally.

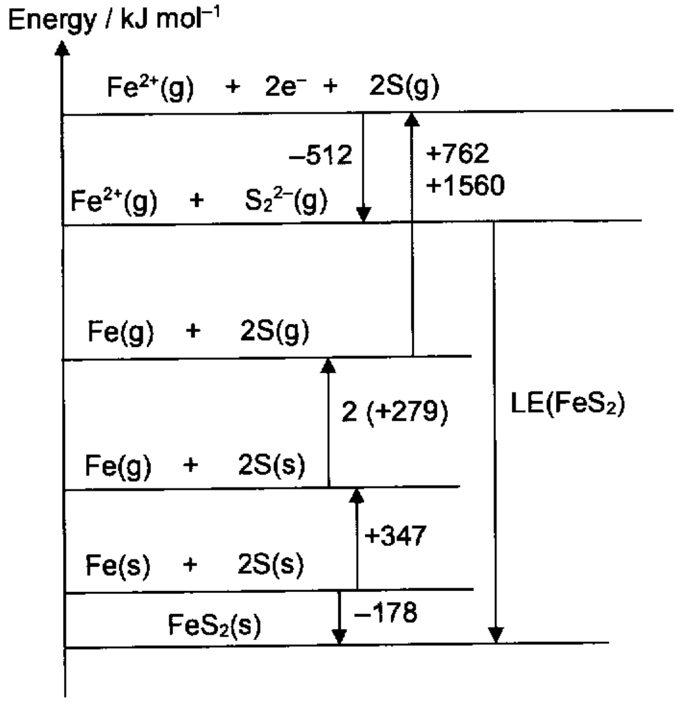
Table 4.2

	value / kJ mol^{-1}
standard enthalpy change of formation of $FeS_2(s)$	–178
standard enthalpy change of atomisation of Fe(s)	+347
standard enthalpy change of atomisation of S(s)	+279
$2S(g) + 2e^- \rightarrow S_2^{2-}(g)$	–512

Use the data given in Table 4.2, together with data from the *Data Booklet* to calculate the lattice energy of FeS_2.
Show your working. [3]



OR



By Hess' Law,

$-178 = 347 + 762 + 1560 + 2(279) + (-512) + \text{LE}(FeS_2)$
$\text{LE}(FeS_2) = -2890 \text{ kJ mol}^{-1}$ (3 s.f.)

Comments

- Some responses included the S−S bond energy in their calculation, showing a lack of understanding of the term enthalpy change of atomisation of S(s).
- Some students formed S_2^{2-} first, before removing electrons from Fe atom to form Fe^{2+}. This is conceptually wrong.
- There were careless mistakes in the application of Hess' Law, or correct application but incorrect calculation carried out.

[Total: 10]

5 2-(2-chloroethyl)phenol can be used in a synthesis pathway shown in Fig. 5.1.

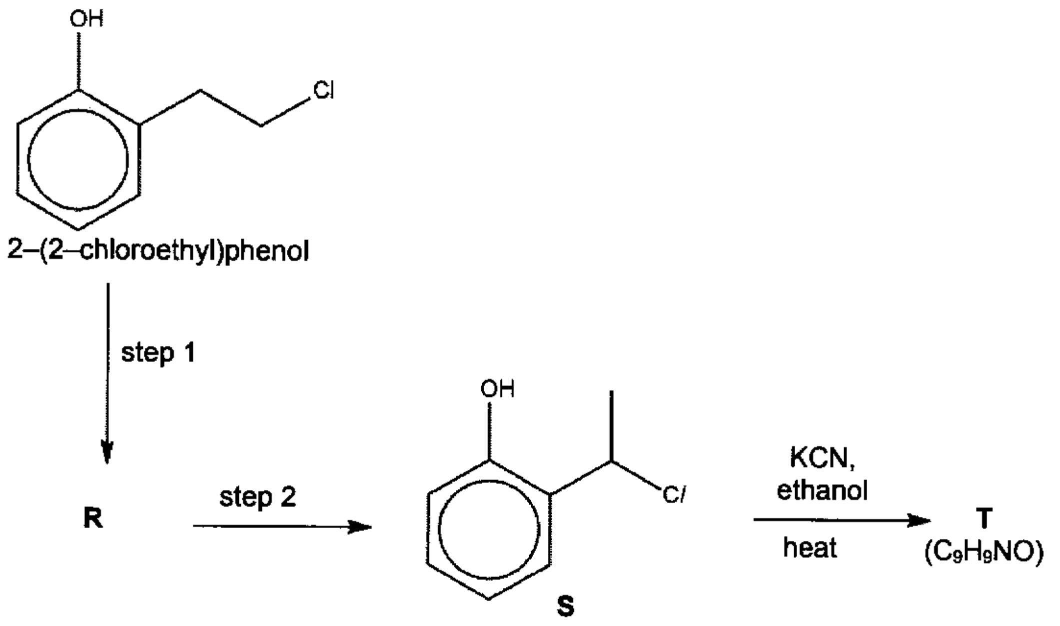


Fig. 5.1

1 mol of compound **R** reacts with 3 mol of aqueous Br_2 to give a white precipitate.

(a) (i) Suggest what this observation indicate about the functional groups in **R**. [1]

There is 1 phenol (with a substitution on position 2) and 1 alkene on R.

Comments

- Many responses only identified one functional group.
- Some identified benzene instead of phenol. Students should recognise that benzene does not react with aqueous Br_2 to give a white precipitate.

(ii) Describe the reagents and conditions needed for steps 1 and 2. [2]

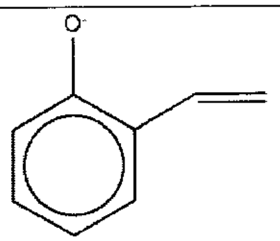
Step 1: Ethanolic NaOH, heat under reflux [1]
Step 2: HC*l* (g) (no need (g) state symbol, but penalise for (aq)) [1]

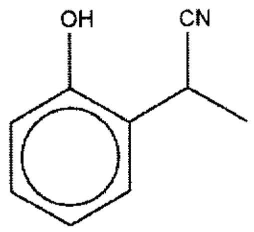
DNA: hydrochloric acid, HC*l* (aq)

Comments

- Most responses scored either 2 or 0 for this question.
- Incorrect responses included using aqueous NaOH/KOH for step 1, or aqueous HCl for step 2.

(iii) Suggest the structures of **R** and **T**. [2]

R: 

T: 

Comments

- Most responses showed correct structure for T, less so for R.
- Note that as strong base is used in step 1, the acidic proton of phenol should be removed.

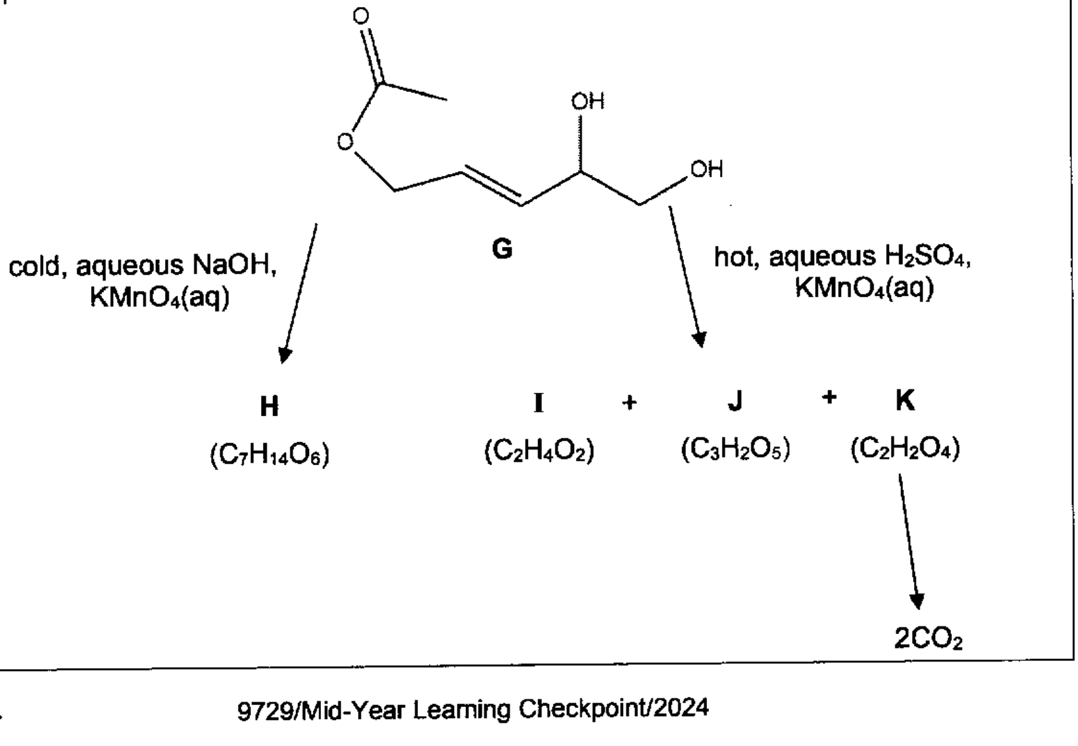
(iv) Describe the relationship between 2–(2–chloroethyl)phenol and compound **S**. [1]

Positional isomerism.
OR Constitutional/structural isomerism

Comments

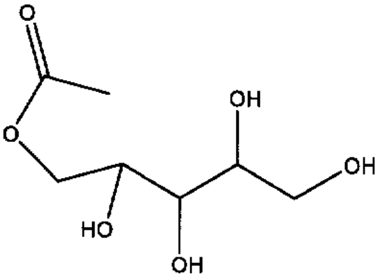
- This question was generally well done.

(b) Hot, concentrated potassium manganate(VII) oxidises several classes of organic compounds to ketones, carboxylic acids or carbon dioxide. By this means, the structures of compounds can be determined. Some compounds are easily oxidized, while others require longer heating.
Compound **G** can be oxidized by $KMnO_4$ under different conditions to give various products.



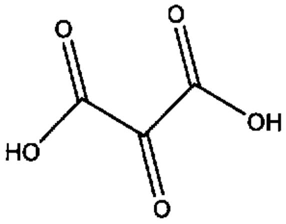
Suggest the structures of the compounds **H**, **I**, **J** and **K**. [4]

H:



I: CH_3COOH

J:



K: $(COOH)_2$

Comments

- This question was generally well done.

[Total: 10]

6 The salinity of seawater is due to the many dissolved molecules and ions present in it. Table 6.1 shows some significant species present in seawater, some of which play a role in maintaining the pH of seawater.

Table 6.1

species	concentration in parts per million (ppm)
Cl^-	19300
Na^+	10800
Ca^{2+}	420
HCO_3^-	116
CO_3^{2-}	9.54
$Si(OH)_4$	9.32
CO_2	0.660
$SiO(OH)_3^-$	0.285

The concentration of dissolved species is measured in parts per million. This refers to the mass of the species dissolved in a million grams of water.

Oceans serve as a natural sink for carbon, by absorbing about 30% of carbon dioxide emissions from the atmosphere. The processes, and their associated equations, involved in the absorption of carbon dioxide by seawater are numbered 1 to 4 in Table 6.2.

Table 6.2

process	equation	K_a at 25 °C
1	$CO_2(g) \rightleftharpoons CO_2(aq)$	-
2	$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$	-
3	$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$	4.5×10^{-7}
4	$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$	4.7×10^{-11}

Process 3 and 4 represent the first and second acid dissociation constant of carbonic acid respectively.

(a) Some species in Table 6.1 form Brønsted-Lowry conjugate acid-base pairs which are responsible for buffering the pH of seawater.

(i) Identify two Brønsted-Lowry conjugate acid-base pairs in Table 6.1.

conjugate acid-base pair 1: ....HCO_3^- and CO_3^{2-} ....

conjugate acid-base pair 2: .... $Si(OH)_4$ and $SiO(OH)_3^-$.................. [1]

Comments
- Students generally recognized the characteristics of a Brønsted-Lowry conjugate acid-base pair.
- A significant portion of answers include H_2CO_3 / HCO_3^- as a response, even though H_2CO_3 was not found in Table 6.1.

(ii) Using one of the conjugate acid-base pairs in **(a)(i)**, write equation(s) to show how the buffer system helps to maintain the pH of seawater. [1]

$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$
$CO_3^{2-} + H^+ \rightarrow HCO_3^-$
OR
$Si(OH)_4 + OH^- \rightarrow SiO(OH)_3^- + H_2O$
$SiO(OH)_3^- + H^+ \rightarrow Si(OH)_4$

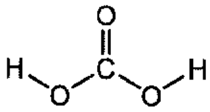
Comments
- Students should use a full arrow to illustrate the action of a buffer in overcoming small amounts of H^+ or OH^- added.
- Balanced equations should be written.

(b) The carbon–oxygen bond length in some compounds is given in Table 6.3.

Table 6.3

species containing carbon–oxygen bond	bond length / nm
CH_3OH	0.143
HCHO	0.123
H_2CO_3	0.134

(i) Draw the displayed formula for H_2CO_3. [1]



Comments

- Some students thought that the species was ionic in nature.
- All bonds in the species must be shown in a displayed formula. The bond between oxygen and hydrogen atom was not shown in some answers.

(ii) Considering the overlap of atomic orbitals, suggest why all the carbon – oxygen bonds in H_2CO_3 have a bond length that is in between that of CH_3OH and HCHO. [2]

The p orbital of O atom can overlap with the π system of C=O bond.

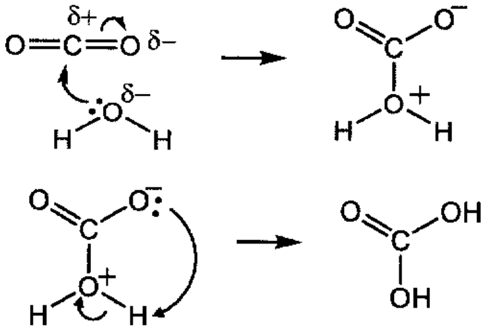
This allows for delocalisation / resonance of electrons across the C–O bond.
OR There is partial double bond character in the C–O bond.

Comments

- Some answers which described the number of single and double bonds in each species or referred to the number of sigma and pi bonds, were not given credit.
- Other weak responses described the overlap of atomic orbitals to give sigma and pi bonds but did not link this to the bond length.
- Strong responses demonstrated clearly the structure (atomic orbitals) to property (bond length) relationship.

Process 2 is thought to proceed via the two steps described below.
step 1: Water behaves as nucleophile and attacks a carbon dioxide molecule.
step 2: An intramolecular proton transfer occurs within the intermediate to form carbonic acid.

(iii) Draw a mechanism for process 2. Show relevant curly arrows, dipoles, charges and lone pairs of electrons in your answer. [2]



Comments

- Students should make use of the displayed formula of H_2CO_3 to help them identify the bonds broken and formed in each step.
- Most students could identify that the carbon atom in CO_2 behaves as the electrophile (through the polarity of the C=O bond) but did not break the C=O bond when H_2O attacked.
- The curly arrows for step 2 as well as the structure of the intermediate proved to be challenging for many students

		(iv)	Hence, suggest and explain which step is likely to be the rate determining step in the mechanism of **(b)(iii)**. [1]
			Step 1 because this step is endothermic. OR Step 1 involves bond breaking of the stronger C=O π bond. / breaking a stronger bond OR The second step involves a charged species, hence it reacts faster.
			Comments • Weak responses merely restated the question, e.g. step 1 is the slow step, without any attempts to explain. • Strong responses linked the rate of reaction to the energy required to break bonds (activation energy) or the frequency of collision between charged species (rate constant).
	(c)	**(i)**	Write the K_a expression for process 3. [1]
			$K_a = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$ Accept $[H_3O^+]$ for $[H^+]$
			Comments • This question is generally well done.
		(ii)	The concentration of CO_2 is assumed as the concentration of H_2CO_3 while the density of water is 1 g cm^{-3}. The pH of seawater is 8.0. Use this information and that from Table 6.1 to calculate another value for the first acid dissociation of H_2CO_3. [2]
			There is 0.66 g of CO_2 in 10^6 g of water. $[CO_2] = [H_2CO_3] = \frac{0.66}{44} \times 10^{-3} = 1.50 \times 10^{-5}$ mol dm^{-3} $[HCO_3^-] = \frac{116}{61} \times 10^{-3} = 1.90 \times 10^{-3}$ mol dm^{-3} $K_a = \frac{[1.90 \times 10^{-3}][1 \times 10^{-8}]}{[1.50 \times 10^{-5}]} = 1.267 \times 10^{-6}$ $= 1.27 \times 10^{-6}$ mol dm^{-3}
			Comments • Many students struggled to convert concentration from ppm to mol dm^{-3}. • Some responses assumed $[HCO_3^-]$ to be equal to $[H^+]$. • Strong responses recognised that $[H_2CO_3]$, $[HCO_3^-]$ and $[H^+]$ are different.
		(iii)	Suggest a reason why the K_a value calculated in **(c)(ii)** differs from that in Table 6.2. [1]
			The temperature at which the pH of seawater was measured was not at 25 °C (non-standard conditions). OR Density of seawater is not 1 g cm^{-3}.
			Comments • Weak responses discussed shifts in POE which do not affect the value of K_a.

- Strong responses referenced ideas discussed in **6(a)(i)** and **6(a)(ii)**.

Corals are soft bodied organisms that build their skeletons by precipitating calcium carbonate from seawater, allowing for the storage of large amounts of carbon in the corals' skeleton. This is done by bringing seawater into a calcifying space between the existing coral skeleton and the coral body, where protons are pumped out to increase the concentration of carbonate ions. The carbonate ions are then precipitated together with calcium ions as calcium carbonate on the surface of the existing coral skeleton.

With rising carbon dioxide emissions into the atmosphere due to human activities, the pH levels of seawater are decreasing. This has led to an acidification of the oceans and corals find it increasing challenging to build their calcium carbonate skeletons.

(d) State one human activity that is increasing the emission of carbon dioxide into the atmosphere. [1]

Burning of petroleum / fossil fuels / natural gas (CH_4).

Comments

- Answers should draw reference to the activities which involve carbon – based fuels.

(e) The K_{sp} values and relative solubilities of $CaCO_3$, $Ca(OH)_2$ and $Ca(HCO_3)_2$ are given below.

Table 6.4

species	K_{sp} value	solubility
$CaCO_3$	6.0×10^{-9}	sparingly soluble
$Ca(OH)_2$	5.02×10^{-6}	sparingly soluble
$Ca(HCO_3)_2$	–	soluble

When carbon dioxide is bubbled into a saturated solution of calcium hydroxide, a white precipitate is observed.

(i) Write the K_{sp} expression for calcium hydroxide and state its units. [1]

$K_{sp} = [Ca^{2+}][OH^-]^2$, units: $mol^3\ dm^{-9}$

Comments

- This question was generally well done. There were occasional slips in determining the units of K_{sp}.

(ii) Calculate the concentration, in $mol\ dm^{-3}$, of $Ca^{2+}(aq)$ in a saturated solution of calcium hydroxide. [1]

Let x be the solubility of $Ca(OH)_2$.

$x(2x)^2 = 5.02 \times 10^{-6}$

$[Ca^{2+}] = 1.0787 \times 10^{-2}$

$= \underline{1.08 \times 10^{-2}}\ mol\ dm^{-3}$

Comments

- There were some errors in determining the solubility of $Ca(OH)_2$.

(iii) Calculate the concentration of $CO_3^{2-}(aq)$ present in solution when calcium carbonate begins to precipitate. [1]

			$[CO_3^{2-}] = \frac{6\times10^{-9}}{1.08\times10^{-2}}$ $= 5.556 \times 10^{-7}$ $= 5.56 \times 10^{-7}$ mol dm^{-3}
			Comments • Many responses assumed $[CO_3^{2-}] = [Ca^{2+}]$ but they did not realise this was in a saturated calcium hydroxide solution.
		(iv)	The following reaction occurs when carbon dioxide is continuously bubbled through a saturated solution of calcium hydroxide. $H_2CO_3 + CO_3^{2-} \rightleftharpoons 2HCO_3^-$ $\quad K_c$
			Use information from Table 6.2 to calculate a value for K_c and state what the K_c value indicates about the position of equilibrium. [1]
			$K_c = \frac{4.5\times10^{-7}}{4.7\times10^{-11}} = 9.57 \times 10^3$ Position of equilibrium lies to the right.
			Comments • Strong responses quickly recognised how to manipulate the identified equations in Table 6.2 correctly while weak responses struggled with the manipulation.
		(v)	Using the equation provided in **(e)(iv)** and information from Table 6.4, predict and explain the likely observations made when carbon dioxide is continuously bubbled through a saturated solution of calcium hydroxide. [2]
			$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$ --- (1) The white precipitate of $CaCO_3$ dissolves, giving a colourless solution when CO_2 is continuously bubbled through. The $[CO_3^{2-}]$ decreases, favouring the position of equilibrium of (1) to shift right, increasing its solubility OR the $[CO_3^{2-}]$ decreases, resulting in the IP < K_{sp}, hence the precipitate dissolves. OR When more CO_2 is present, $[H_2CO_3]$ increases and POE shifts to the right resulting in higher $[HCO_3^-]$. $Ca(HCO_3)_2$ that is formed is soluble.
			Comments • Some responses thought the white precipitate was $Ca(OH)_2$. • Many responses did not include the likely observations to be seen. • Some answer presented inaccuracies or contradictions regarding the changes of $[H_2CO_3]$, $[HCO_3^-]$ and $[CO_3^{2-}]$. Students are advised to think through their answer first, before crafting a clear and logical response that is free from contradictions.

(vi) Using the equation provided in **(e)(iv)** and your answer in **(e)(v)**, describe how the increasing carbon dioxide emissions in the atmosphere makes it challenging for corals to build their calcium carbonate skeleton. [1]

With increasing CO_2 emissions, $[HCO_3^-]$ is increased / $[CO_3^{2-}]$ is decreased. Corals will have to pump out more H^+ for $[CO_3^{2-}]$ to be increased to the saturation point for precipitation of $CaCO_3$ to occur.

Comments

- Students are required to draw concepts related to ionic product and precipitation.
- Strong answers were contextualised, referenced points mentioned in **6(e)(v)** or discussed the idea of 'pumping protons out of the calcifying space to increase $[CO_3^{2-}]$' from the text.

(f) Aragonite and calcite are two different solid forms of calcium carbonate that can be precipitated by corals.

Some information about these two forms of calcium carbonate is provided below.

Table 6.5

form of calcium carbonate	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	$\Delta S_f^{\ominus}$ / J mol^{-1} K^{-1}
aragonite	−1207.8	+88.0
calcite	−1207.6	+91.7

(i) The entropy change, $\Delta S_{rxn}^{\ominus}$, of a reaction, can be determined using the following formula:

$$\Delta S_{rxn}^{\ominus} = \sum m\Delta S_f^{\ominus}(\text{products}) - \sum n\Delta S_f^{\ominus}(\text{reactants})$$

where m and n are the coefficients of the products and reactants in the balanced equation.

Use information from Table 6.5 to show that the conversion of aragonite to calcite is a spontaneous process under standard conditions.

$$CaCO_3\ (\text{aragonite}) \rightarrow CaCO_3\ (\text{calcite})$$

[2]

$\Delta H_{rxn}^{\ominus} = -1207.6 + 1207.8$
$= +0.2$ kJ mol^{-1}
$\Delta S_{rxn}^{\ominus} = 91.7 - 88.0$
$= +3.70$ J mol^{-1} K^{-1}
$\Delta G_{rxn}^{\ominus} = \Delta H_{rxn}^{\ominus} - T\Delta S_{rxn}^{\ominus}$
$= 200 - 298(+3.7)$
$= -903$ J mol^{-1} OR -0.903 kJ mol^{-1}

Comments

- Various errors were made in the calculation of ΔH, ΔS and ΔG. A common one was the lack of conversion from J to kJ in the calculation of ΔG.
- Some students could not remember the temperature for standard conditions

[Total: 22]

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
9729/03

Paper 3 Free Response

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

Section A

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

1 (a) Describe the variation in the behaviour of Period 3 chlorides $NaCl$, $AlCl_3$ and PCl_5 separately with water.
Write equations for any reactions described and state the pH of the resultant solutions. [3]

$NaCl$ 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}

$$\text{pH} = \text{p}K_a + \lg \frac{[\text{HPO4 2−}]}{[\text{H2PO4−}]}$$
$$6.8 = 7.2 + \lg \frac{[\text{HPO4 2−}]}{[\text{H2PO4−}]}$$
$$\lg \frac{[\text{HPO4 2−}]}{[\text{H2PO4−}]} = -0.4$$
$$\frac{[\text{HPO4 2−}]}{[\text{H2PO4−}]} = 0.3981$$
$$\frac{[\text{HPO4 2−}]}{0.1389} = 0.3981$$
$[HPO_4^{2-}]_{\text{final}} = 5.529 \times 10^{-2}$ mol dm^{-3}

OR

$$K_a = \frac{[\text{HPO4 2−}][H+]}{[\text{H2PO4−}]}$$
$$10^{-7.2} = \frac{[\text{HPO4 2−}][10^{-6.8}]}{[\text{H2PO4−}]}$$
$$10^{-7.2} = \frac{[\text{HPO4 2−}][10^{-6.8}]}{0.1389}$$
$[HPO_4^{2-}]_{\text{final}} = 5.529 \times 10^{-2}$ 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 $= \frac{0.002488 \text{ mol}}{20 \times 10^{-3}} = \underline{0.124 \text{ mol dm}^{-3}}$

Comments

- Many students were able to use the Henderson-Hesselberg equation (i.e. pH = pK_a + lg $\frac{[\text{HPO4 2−}]}{[\text{H2PO4−}]}$) 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.

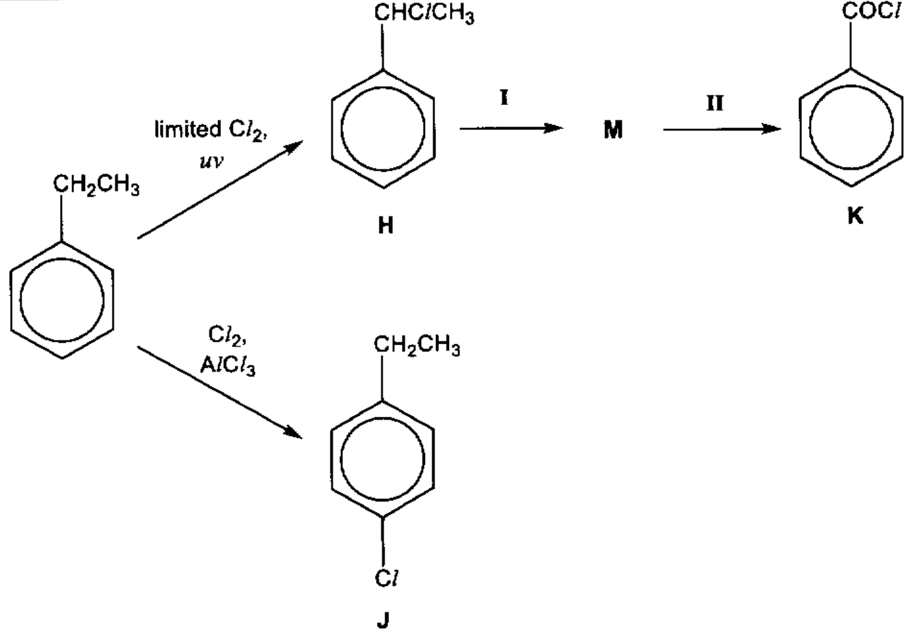


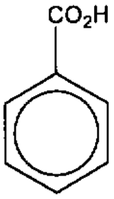
Fig. 1.1

(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 C*l* 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

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

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

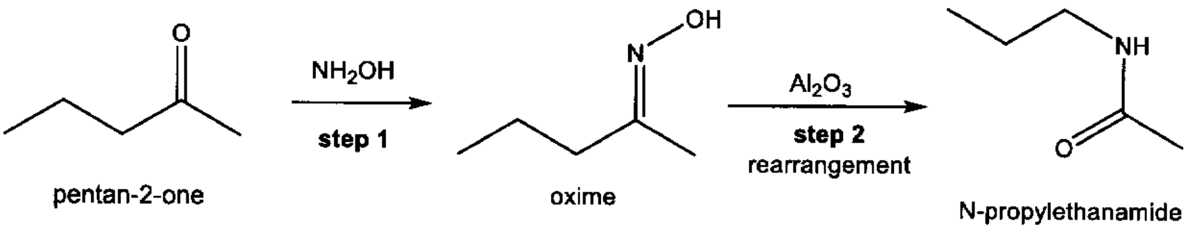
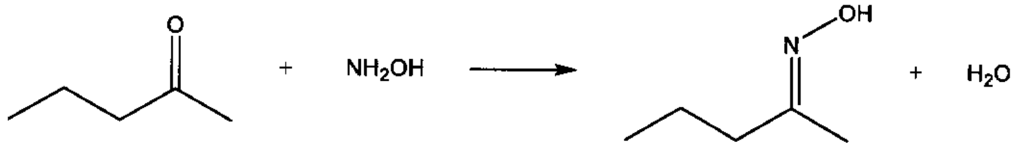


Fig. 2.1

(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.

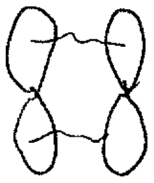
(ii) A molecule of oxime contains both σ bonds and π bonds.
Draw labelled diagrams to show how orbitals of the C atom and N atom overlap to form

- 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.

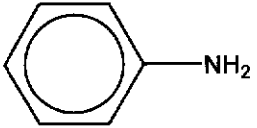
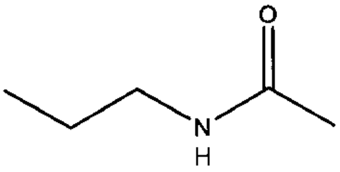
OR Test: 2, 4-dinitrophenylhydrazine
Observation: Pentan-2-one give orange/yellow ppt but amide does not form any orange or yellow ppt.

Comments

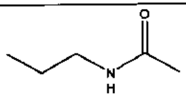
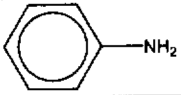
- Students are reminded that the differentiation should be carried out using only 1 chemical test.
- The test that is chosen must also have different observable changes.
- The observation for both compounds must be stated.

(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.

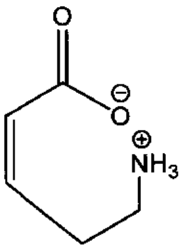
A has 2 degrees of unsaturation.

B does not have a chiral centre / has internal plane of symmetry as it does not rotate plane polarised light.

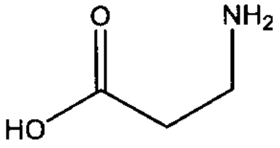
Carboxylic acid in compound **A** also undergoes substitution / nucleophilic substitution with $SOCl_2$ to form an acyl chloride.

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.

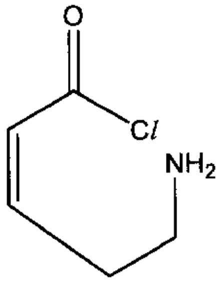


A

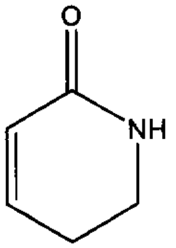


B

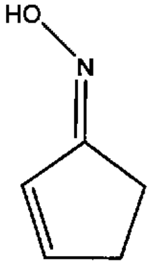
(Accept B as a zwitterion)



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:

$Mg^{2+} + 2e^- \rightleftharpoons Mg \quad E^\ominus = -2.38\ V$

$Ca^{2+} + 2e^- \rightleftharpoons Ca \quad E^\ominus = -2.87\ V$

$Ba^{2+} + 2e^- \rightleftharpoons Ba \quad E^\ominus = -2.90\ V$ (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.

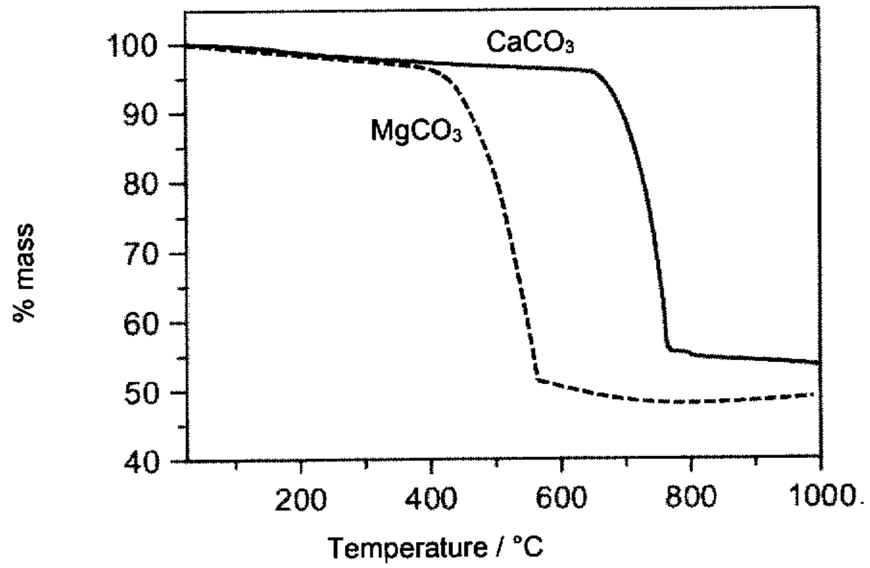


Fig. 3.1

(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 $|\frac{q_+q_-}{r_++r_-}|$, 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

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

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

$= -637$ 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

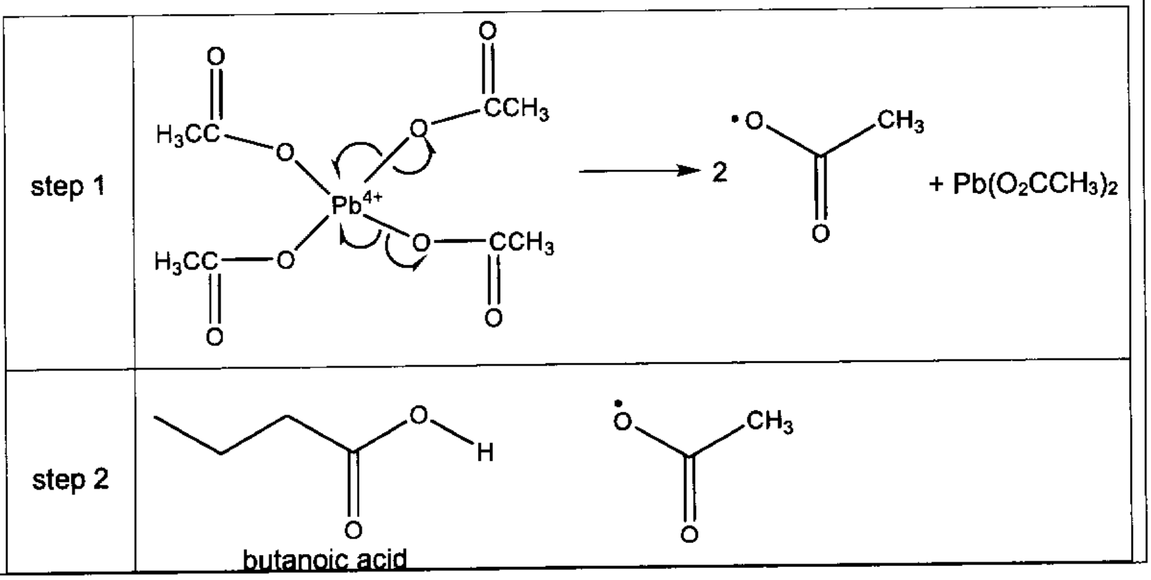
- This question was generally well done. Incorrect responses focused on rate of reaction.

(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.

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

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.



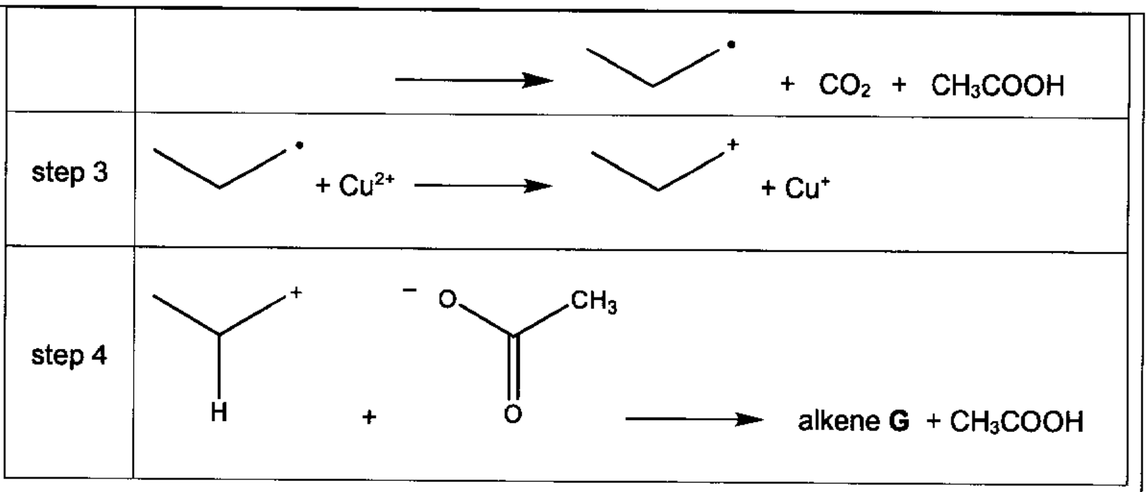
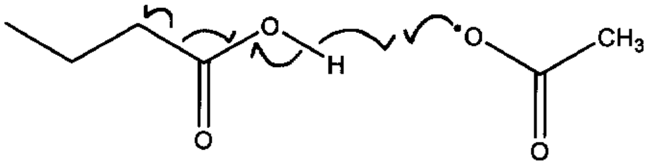
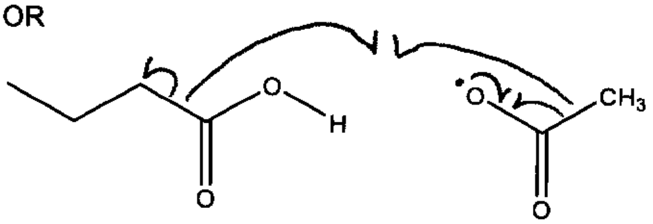


Fig. 3.2

(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]



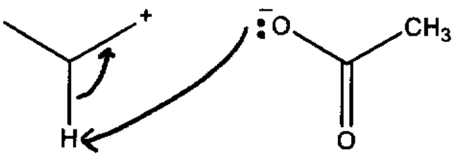
OR

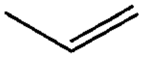


Comments

- 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

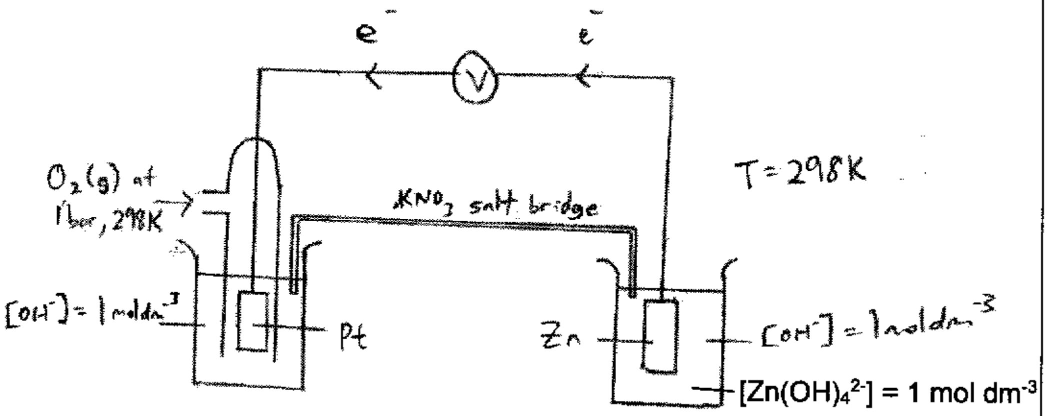
Answer **one** question from this section.

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

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

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.

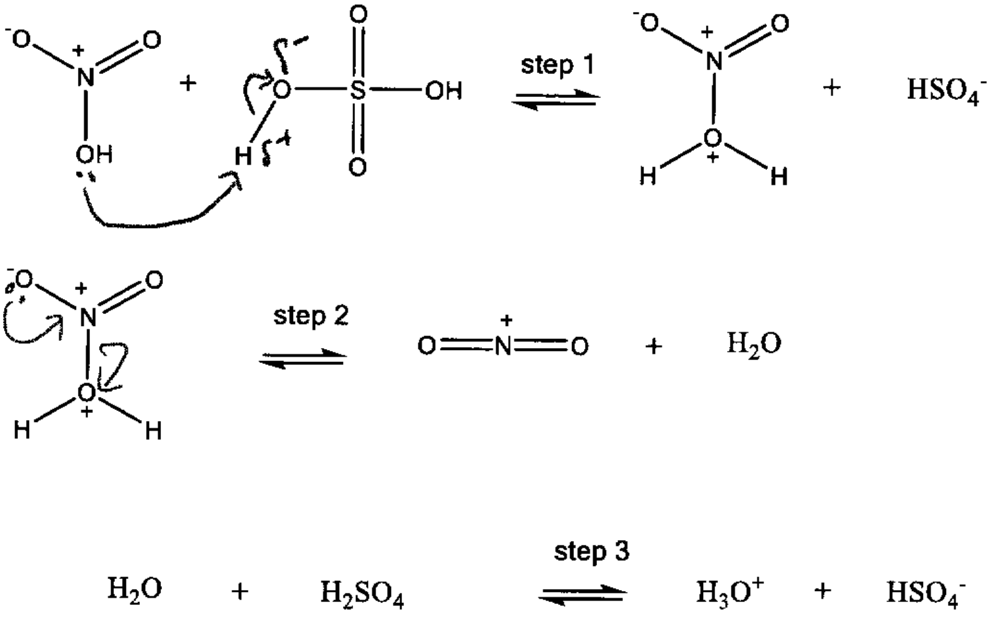


Fig. 4.1

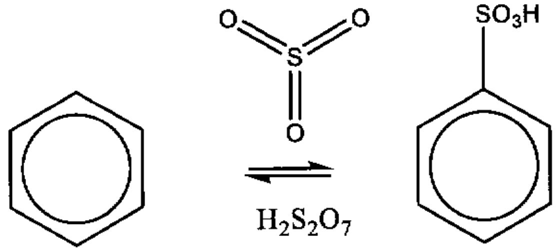
(i) On Fig. 4.1, draw curly arrows, partial charges and insert relevant lone pairs in steps 1 and 2 to complete the mechanism for the formation of the nitronium ion. [2]

(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.



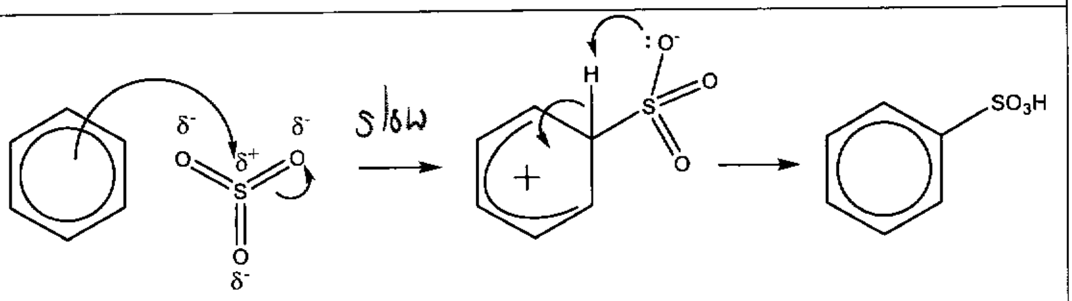
Explain why sulfur trioxide can act as an electrophile. [1]

Sulfur is bonded to three highly electronegative oxygen atoms, making sulfur electron deficient OR partial positive charge.

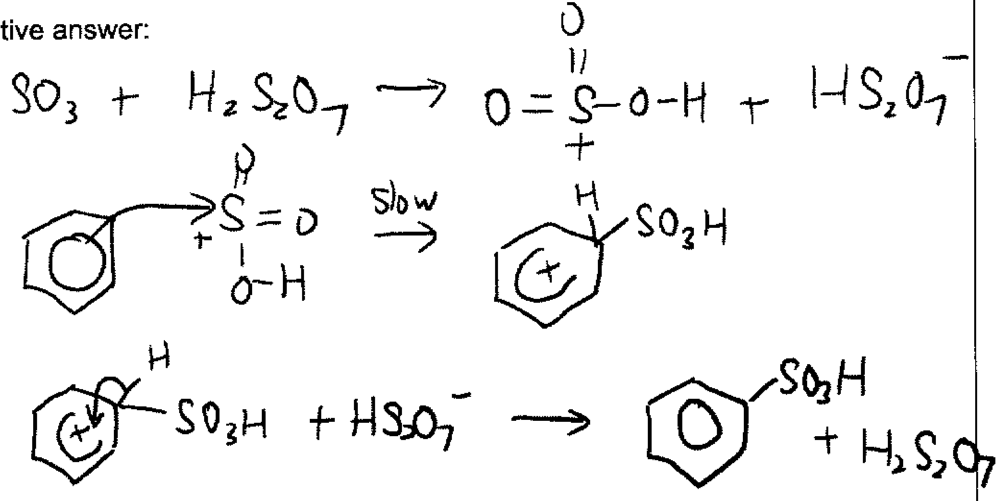
Comments

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 x 10^4 Pa

Partial pressure of CH_3CH_2CHO = 0.99 x 40

= 39.6 atm OR 4.01 x 10^6Pa

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

= 619 atm^{-2}

OR = 6.03 x 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.

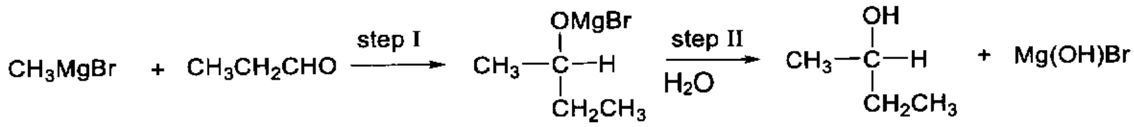
Comments:

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.



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

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

step I: Nucleophilic addition

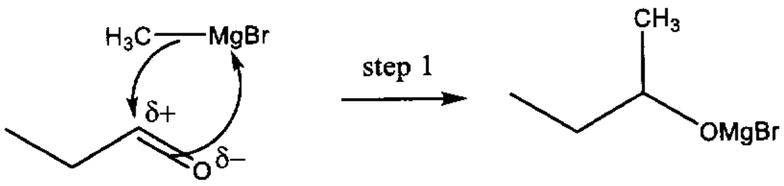
step II: Hydrolysis

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

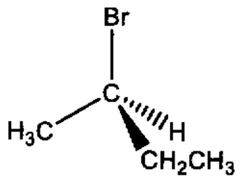
Comments

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.

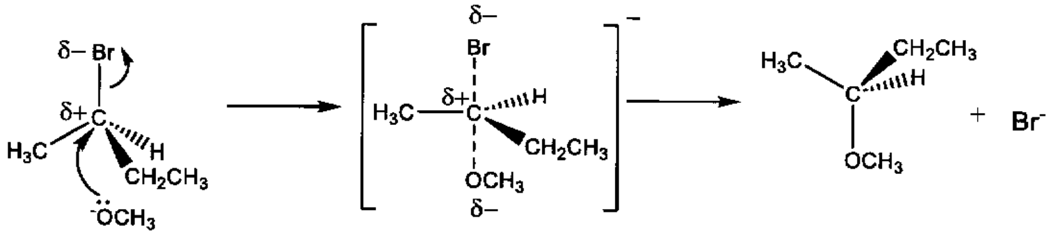
The R isomer of $CH_3CH_2CHBrCH_3$ is shown below.



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 SN2



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.

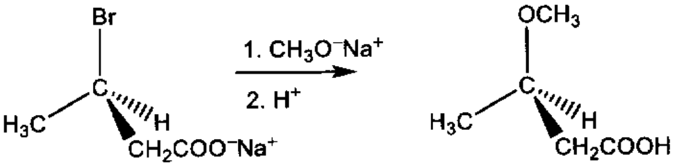
Note that the mechanism must have the following:

- 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.

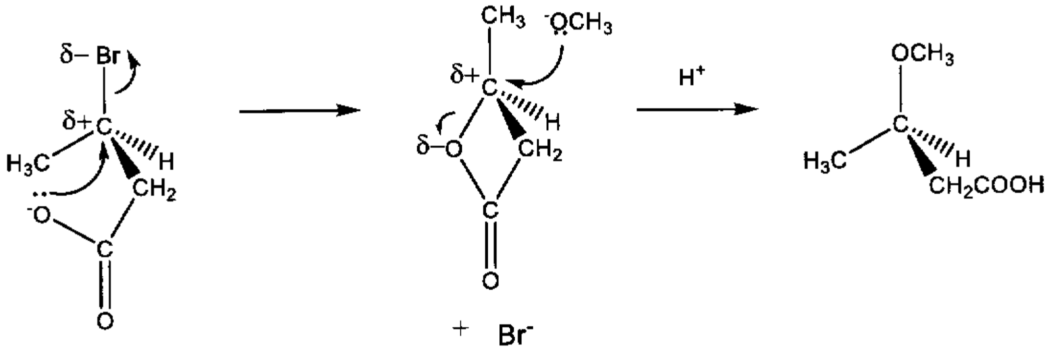


Explain why this is so. [1]

The <u>COO⁻ group substitutes/attacks/displace the Br resulting in the S isomer</u>, then the <u>⁻OCH₃ substitutes/attacks/displace the COO⁻ group resulting in the R isomer</u> again. (or wtte)

OR S_N2 occurred twice

<u>Comments</u>



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

<u>Comments</u>

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 ΔG°_{sol} of an ionic compound in J mol^{-1}, is given by the following expression.

$$\Delta G^\circ_{sol} = -RT \ln K_{sp}$$

			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]