

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
 Higher 2

CANDIDATE
NAME

SUBJECT
CLASS

REGISTRATION
NUMBER

CHEMISTRY

Paper 2 Structured Questions

9729/02

28 August 2023

2 hours

Candidates answer on Question Paper.
 Additional Materials: Data Booklet

READ THE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a soft pencil for any diagrams, graphs or rough working.

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

Answers **all** questions.

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

For Examiner's Use	
1	/9
2	/10
3	/12
4	/13
5	/13
6	/18
Paper 2 Total	/75

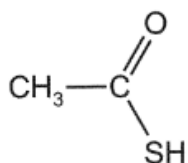
	Marks	Weightings
Paper 1	/30	15%
Paper 2	/75	30%
Paper 3	/80	35%
Paper 4	/55	20%

Overall Percentage	
Grade	

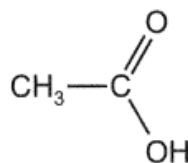
This document consists of **23 printed pages and 1 blank page.**

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

- 1 (a) Thioacetic acid, CH_3COSH and ethanoic acid, CH_3COOH , both act as weak acids in solution.

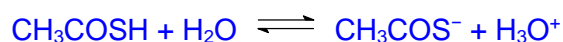


thioacetic acid

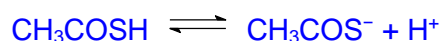


ethanoic acid

- (i) An equilibrium is set up when CH_3COSH is added to water.
Write the equation for this equilibrium.



or



*Partial dissociation (reversible arrow)

[1]

- (ii) 0.150 mol of CH_3COSH dissolves in 250 cm^3 of distilled water to produce a solution of pH 1.79.

Calculate the $\text{p}K_a$ of CH_3COSH .

$$\text{Initial } [\text{CH}_3\text{COSH}] = \frac{0.150}{250/1000} = 0.600 \text{ mol dm}^{-3}$$

$$\text{Equilibrium } [\text{H}^+] = 10^{-1.79} = 1.6218 \times 10^{-2} \text{ mol dm}^{-3}$$

	CH_3COSH	+ H_2O	\rightleftharpoons	CH_3COS^-	+ H_3O^+
Initial / mol dm^{-3}	0.600			0	0
Change / mol dm^{-3}	-1.6218×10^{-2}			$+1.6218 \times 10^{-2}$	$+1.6218 \times 10^{-2}$
Eqm / mol dm^{-3}	0.58378			1.6218×10^{-2}	1.6218×10^{-2}

$$K_a = \frac{[\text{CH}_3\text{COS}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COSH}]} = \frac{(1.6218 \times 10^{-2})^2}{0.58378} = 4.5055 \times 10^{-4}$$

$$\text{p}K_a = -\lg(4.5055 \times 10^{-4}) = 3.346 = 3.35$$

[2]

- (iii) CH_3COOH has a $\text{p}K_{\text{a}}$ value of 4.76. With reference to the *Data Booklet*, explain the difference in the $\text{p}K_{\text{a}}$ values of CH_3COOH and CH_3COSH .

The O–H bond (460 kJ mol^{-1}) in CH_3COOH is stronger than S–H bond (347 kJ mol^{-1}) in CH_3COSH , thus it is harder for O–H bond to break to release H^+ and CH_3COOH has a smaller extent of dissociation, it has a smaller K_{a} than CH_3COSH and hence a larger $\text{p}K_{\text{a}}$ than CH_3COSH .

[2]

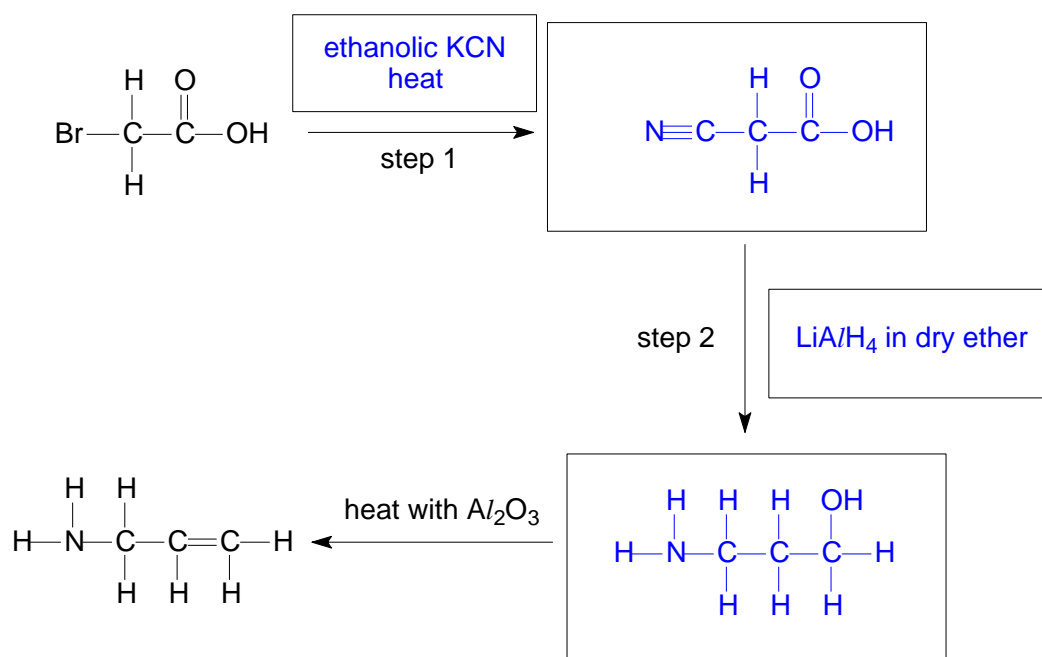
- (b) (i) State the type of reaction involved when CH_2ClCOOH and CH_2BrCOOH are synthesized from CH_3COOH .

Free radical substitution

[1]

- (ii) Prop-2-en-1-amine, $\text{CH}_2=\text{CHCH}_2\text{NH}_2$, commonly used as a pharmaceutical intermediate, can be synthesized from CH_2BrCOOH .

Complete the following synthetic route for the conversion of CH_2BrCOOH into $\text{CH}_2=\text{CHCH}_2\text{NH}_2$. Suggest the structure of the intermediate compounds, and reagents and conditions for step 1 and 2.

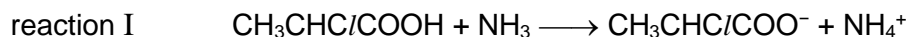


Note: Step 2 must use LiAlH_4 in dry ether as we need to reduce BOTH $-\text{CN}$ and $-\text{COOH}$ groups to obtain the amine and primary alcohol.

[3]

[Total: 9]

- 2 (a) A student studies the reaction of $\text{CH}_3\text{CHCl}/\text{COOH}$ with aqueous NH_3 to determine the reaction mechanism. The student finds that when $\text{CH}_3\text{CHCl}/\text{COOH}$ and NH_3 are added in a 1:1 stoichiometric ratio, the conjugate acid and base of the reactants are quickly formed.



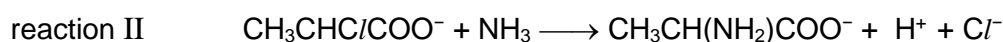
Identify the conjugate acid-base pairs in reaction I.

conjugate acid-base pair 1: $\text{CH}_3\text{CHCl}/\text{COOH}$ and $\text{CH}_3\text{CHCl}/\text{COO}^-$

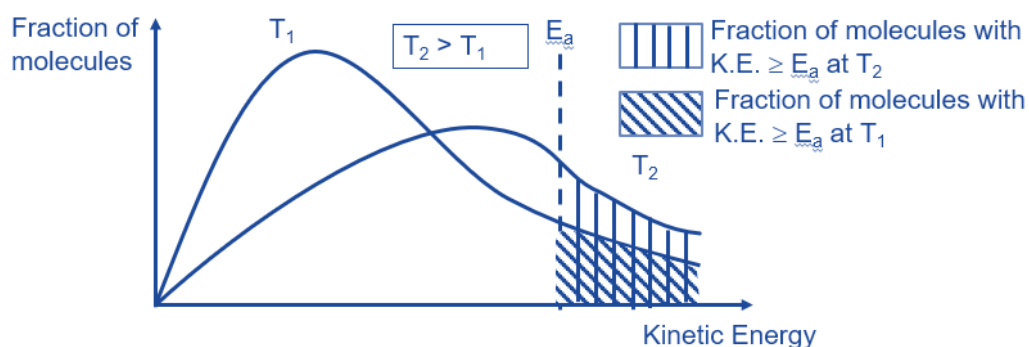
conjugate acid-base pair 2: NH_4^+ and NH_3

[1]

- (b) In an excess of NH_3 , $\text{CH}_3\text{CHCl}/\text{COO}^-$ undergoes a nucleophilic substitution reaction.



- (i) Describe the effect of an increase in temperature on the rate of reaction of $\text{CH}_3\text{CHCl}/\text{COO}^-$ and NH_3 , illustrating your answer using the Boltzmann distribution curve.



As the temperature increases, the average kinetic energy of the particles increases.

There are more particles with kinetic energy equal or greater than the activation energy, E_a .

This results in higher frequency of effective collisions. Hence rate of reaction increases.

[3]

A student mixes $\text{CH}_3\text{CHClCOO}^-$ with a large excess of NH_3 and monitored the $[\text{CH}_3\text{CHClCOO}^-]$ with time. The graph in Fig. 2.1 shows the results obtained.

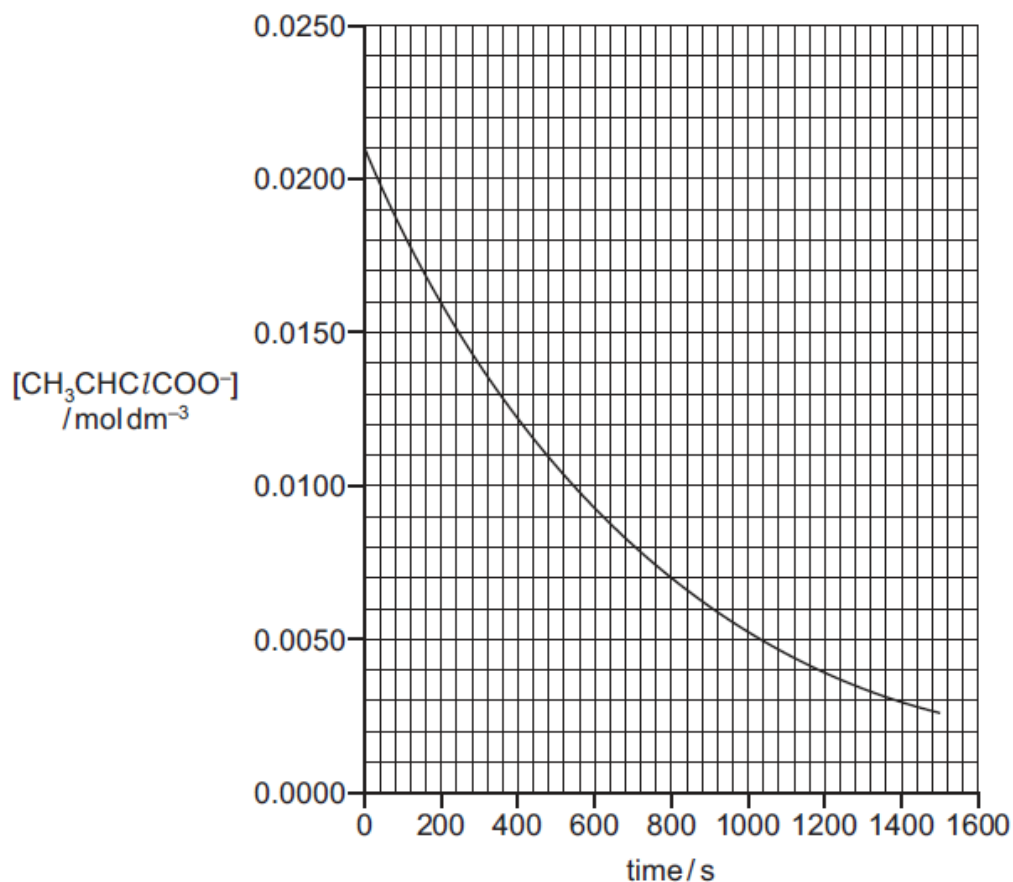


Fig. 2.1

- (ii) Use the graph in Fig. 2.1, deduce the order of reaction II with respect to $\text{CH}_3\text{CHClCOO}^-$.

As the reaction proceeds, $[\text{NH}_3]$ remains approximately constant while $[\text{CH}_3\text{CHClCOO}^-]$ decreases. It is observed that rate of reaction (gradient of conc vs time graph) decreases with a constant half-life of 500s.

Reaction II is 1st order with respect to $\text{CH}_3\text{CHClCOO}^-$.

Show working for the following (either in words or on the graph)

Time taken for $[\text{CH}_3\text{CHClCOO}^-]$ to decrease from $0.0210 \text{ mol dm}^{-3}$ to $0.0105 \text{ mol dm}^{-3}$ is 500s;

Time taken for $[\text{CH}_3\text{CHClCOO}^-]$ to decrease from $0.0105 \text{ mol dm}^{-3}$ to $0.00525 \text{ mol dm}^{-3}$ is 500s

[2]

- (iii) Explain why a large excess of NH_3 needs to be used to obtain the results in Fig. 2.1.

To ensure that concentration of NH_3 remains relatively constant throughout the reaction and does not affect the rate of reaction II.

[1]

- (iv) The student measured the effect of changing concentration of NH_3 on the rate of reaction II. Table 2.1 shows the results obtained.

Table 2.1

experiment	$[\text{CH}_3\text{CHC}/\text{COO}^-]$ / mol dm^{-3}	$[\text{NH}_3]$ / mol dm^{-3}	Initial rate of reaction / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.00120	0.00300	1.47×10^{-5}
2	0.00120	0.00450	2.21×10^{-5}

Use the information in Table 2.1 and your answer in **b(ii)** to determine whether the nucleophilic substitution reaction proceeds via $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ mechanism.

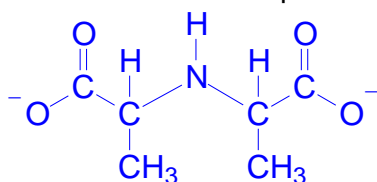
Explain your answer.

Comparing experiment 1 & 2, when $[\text{CH}_3\text{CHC}/\text{COO}^-]$ is constant and $[\text{NH}_3]$ increases 1.5 times, initial rate of reaction increases 1.5 times. Hence, reaction is 1st order with respect to NH_3 .

$\text{S}_{\text{N}}2$ mechanism since rate is 1st order with respect to $[\text{CH}_3\text{CHC}/\text{COO}^-]$ and 1st order with respect to $[\text{NH}_3]$.

[2]

- (v) When an excess of $\text{CH}_3\text{CHC}/\text{COO}^-$ is used in reaction II, further substitution reactions occur. One product has the formula $\text{C}_6\text{H}_9\text{NO}_4^{2-}$, suggest its structure.



Thinking process: N atom of $\text{CH}_3\text{CH}(\text{NH}_2)\text{COO}^-$ acts as the nucleophile and reacts with C-C/ of another $\text{CH}_3\text{CHC}/\text{COO}^-$. N will be bonded to two C atoms.

[1]

[Total: 10]

3 This question is related to the properties of Group 17 elements and their compounds.

(a) Table 3.1 shows the reactions between concentrated sulfuric acid and sodium halides.

Table 3.1

halide	reaction
NaCl	$\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{HCl} + \text{NaHSO}_4$
NaBr	$2\text{NaBr} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{Br}_2 + \text{SO}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
NaI	$8\text{NaI} + 5\text{H}_2\text{SO}_4 \longrightarrow 4\text{I}_2 + \text{H}_2\text{S} + 4\text{Na}_2\text{SO}_4 + 4\text{H}_2\text{O}$

(i) Suggest the role of concentrated sulfuric acid in its reaction with NaCl.

Acid (proton/ H^+ donor)

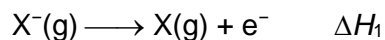
[1]

(ii) By considering the changes in oxidation states of S, deduce whether NaBr or NaI is a stronger reducing agent.

With NaBr, the oxidation state of S decreases from +6 in H_2SO_4 to +4 in SO_2
 With NaI, the oxidation state of S decreases from +6 in H_2SO_4 to -2 in H_2S .
 Hence, NaI is a stronger reducing agent as it causes the oxidation number of S to decrease by a larger extent.

[2]

- (iii) ΔH_1 is defined as the energy required to remove one mole of electrons from one mole of gaseous halide ions to form one mole of gaseous halogen atom.



With reference to the ionic radii in the *Data Booklet*, suggest a reason for the trend of ΔH_1 shown in Table 3.2.

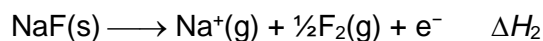
Table 3.2

halide ion	$\Delta H_1 / \text{kJ mol}^{-1}$
$\text{Cl}^-(g)$	+349
$\text{Br}^-(g)$	+324
$\text{I}^-(g)$	+295

Down Group 17, the anionic radii of the halides increase from Cl^- (0.181nm) to Br^- (0.195 nm) to I^- (0.216 nm). Hence, the most loosely held electron is further away from the nucleus and experience weaker nuclear attraction. Hence, they become easier to remove/requires less energy down the group.

[2]

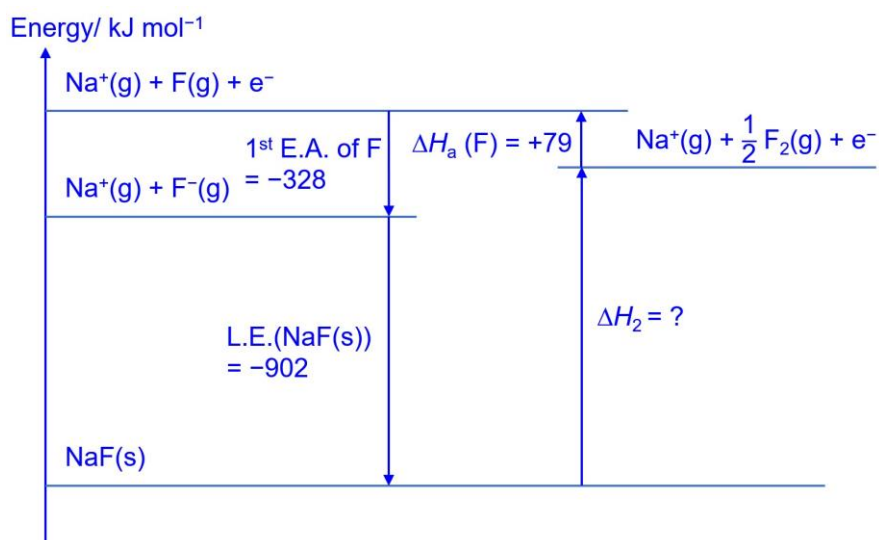
- (iv) Given the following data, construct an energy level diagram and calculate ΔH_2



1st electron affinity of fluorine = -328 kJ mol^{-1}

enthalpy change of atomisation of fluorine = $+79 \text{ kJ mol}^{-1}$

lattice energy of sodium fluoride = -902 kJ mol^{-1}



By Hess' law,

$$\begin{aligned} \Delta H_2 \text{ for NaF} &= -\text{L.E. (NaF)} - 1\text{st E.A. of F} - \Delta H_a \text{ for F} \\ &= -(-902) - (-328) - (+79) \\ &= +1151 \text{ kJ mol}^{-1} \end{aligned}$$

[3]

- (b) Chlorofluoroalkanes, CFCs, were once used as refrigerant fluids. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer.

- (i) Suggest one reason why CFCs were originally used for these purposes.

C-F bonds are strong and this leads to CFCs being unreactive and stable.

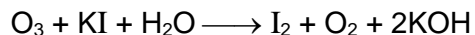
[1]

- (ii) Briefly explain how CFCs destroy the ozone layer.

In the atmosphere, the C-Cl bonds in CFCs are broken to release chlorine radicals. These radicals then react with ozone and destroy the ozone layer.

[1]

- (iii) The percentage of O_3 in a gaseous mixture can be determined by its reaction with aqueous KI.



The iodine formed can be determined by its reaction with sodium thiosulfate.



When 250 cm^3 of a gaseous mixture containing O_3 at s.t.p. was passed into an excess of aqueous KI, 15.0 cm^3 of 0.050 mol dm^{-3} sodium thiosulfate was required to react with the iodine produced.

Calculate the percentage of O_3 in the gaseous mixture.

$$\text{amount of } S_2O_3^{2-} = \left(\frac{15.0}{1000} \right) \times 0.050 = 7.50 \times 10^{-4} \text{ mol}$$

$$\text{amount of } I_2 = \frac{1}{2} \times (7.50 \times 10^{-4}) = 3.75 \times 10^{-4} \text{ mol}$$

$$\text{amount of } O_3 = 3.75 \times 10^{-4} \text{ mol}$$

$$\text{volume of } O_3 = (3.75 \times 10^{-4}) \times 22.7 = 8.51 \times 10^{-3} \text{ dm}^3 = 8.51 \text{ cm}^3$$

$$\text{percentage of } O_3 = \frac{8.51}{250} \times 100\% = 3.40\%$$

[2]

[Total: 12]

- 4 (a) Compound **G** has the molecular formula $C_7H_{14}O$. Treating **G** with hot acidified $KMnO_4(aq)$ produces two compounds **H**, C_4H_8O , and **J**, $C_3H_4O_3$. These three compounds were tested using the reagents shown in the Table 4.1 below.

Table 4.1

test reagent	result of test with		
	compound G	compound H	compound J
$Br_2(aq)$	Br_2 decolourises	no reaction	no reaction
$Na(s)$	effervescence observed	no reaction	effervescence observed
alkaline aqueous iodine, warm	no reaction	yellow precipitate	yellow precipitate
2,4-dinitrophenylhydrazine	no reaction	orange precipitate	orange precipitate

- (i) Name the type of reaction occurring when compounds **H** and **J** react with 2,4-dinitrophenylhydrazine.

condensation

[1]

- (ii) Based on the results of the tests in the table, suggest the structure for compounds **H** and **J**.

compound H	compound J
$ \begin{array}{c} O \\ \\ H_3C - C - CH_2CH_3 \\ C_4H_8O \end{array} $	$ \begin{array}{c} O \quad O \\ \quad \\ H_3C - C - C - OH \\ C_3H_4O_3 \end{array} $

Thinking process:

H and **J** are products of vigorous oxidation with acidified $KMnO_4$

From reaction with 2,4-DNPH, **H** and **J** contains carbonyl group (aldehyde/ketone)

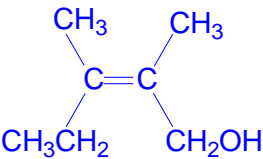
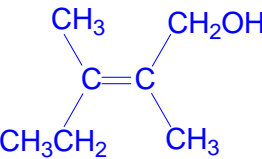
From reaction with alkaline I_2 , **H** and **J** contains methyl carbonyl group. (cannot be methyl carbinol group as the alcohol would have been oxidised by $KMnO_4$ in the earlier reaction)

From reaction with $Na(s)$, **J** contains a carboxylic group or 3° alcohol (cannot be 1° or 2° alcohol due to earlier oxidation by $KMnO_4$)

[2]

- (iii) Compound **G** exists as two stereoisomers, **G1** and **G2**.

Draw the structure of the two isomers and state the type of stereoisomerism involved. Hence, explain how this type of stereoisomerism arises.

isomer G1	isomer G2
	

Shows the pair of cis-trans isomerism with trigonal planar shape around each C

Type of stereoisomerism: cis-trans isomerism

The molecule exhibits cis-trans isomerism due to restricted rotation about the C=C bond AND two different groups attached to each C atom of the C=C

Thinking Process:

From reaction with alkaline I₂, G does not contain methyl carbinol/methyl carbonyl group.

From reaction with 2,4-DNPH, G does not contain carbonyl group.

From reaction with Br₂(aq), G contains C=C

From reaction with Na, G contains alcohol (cannot be carboxylic acid as G only has 1 O atom).

[4]

- (iv) Compound **G** reacts with H₂(g) in the presence of Ni catalyst but not with LiAlH₄. Explain why.

The alkene functional group in Compound **G** is electron-rich and hence repels the nucleophile H⁻ in LiAlH₄.

[1]

- (b) Compound **K**, an alcohol, has a relative molecular mass of 60.0. The mass ratio of carbon to hydrogen to oxygen is 9 : 2 : 4.

- (i) Deduce the molecular formula of compound **K**.

$$\text{Amount of C} = \frac{9}{12.0} = 0.75 \text{ mol}$$

$$\text{Amount of H} = \frac{2}{1.0} = 2 \text{ mol}$$

$$\text{Amount of O} = \frac{4}{16.0} = 0.25 \text{ mol}$$

$$\text{Mol ratio of C : H : O} = 3 : 8 : 1$$

Empirical formula of compound **K** is $\text{C}_3\text{H}_8\text{O}$.

Let the molecular formula be $(\text{C}_3\text{H}_8\text{O})_n$.

$$M_r \text{ of } (\text{C}_3\text{H}_8\text{O})_n = 60.0$$

$$[(3(12.0) + 8(1.0) + 16.0)] \times n = 60.0$$

$$n = 1$$

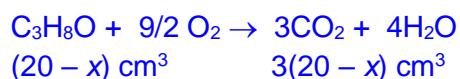
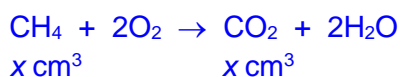
Molecular formula of compound **K** is $\text{C}_3\text{H}_8\text{O}$.

[2]

- (ii) A 20 cm³ mixture containing CH₄ and compound **K**, was burnt completely in excess oxygen. On passing the residual gas through aqueous sodium hydroxide, there was a reduction in volume by 25 cm³. All volumes were measured at room temperature and pressure.

Calculate the percentage by mass of CH₄ in the mixture.

Let volume of CH₄ be x cm³, then vol of compound C₃H₈O = $(20 - x)$ cm³



$$\text{Total volume of CO}_2 \text{ produced} = x + 3(20 - x) = 25$$

$$60 - 2x = 25$$

$$\Rightarrow x = 17.5$$

$$\text{Amount of CH}_4 = \frac{17.5}{24000} = 7.29 \times 10^{-4} \text{ mol}$$

$$\text{Mass of CH}_4 = 7.29 \times 10^{-4} \times 16.0 = 0.01167 \text{ g}$$

$$\text{Amount of C}_3\text{H}_8\text{O} = \frac{2.5}{24000} = 1.04 \times 10^{-4} \text{ mol}$$

$$\text{Mass of C}_3\text{H}_8\text{O} = 1.04 \times 10^{-4} \times 60.0 = 0.00625 \text{ g}$$

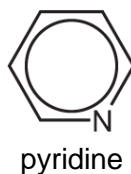
Percentage by mass of CH₄ in the mixture

$$= \frac{0.01167}{0.01167 + 0.00625} \times 100\% = 65.1 \%$$

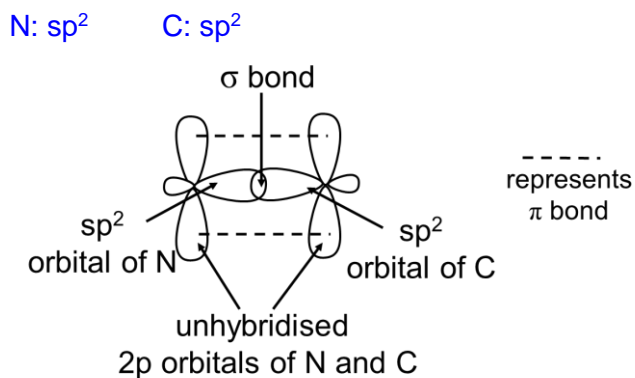
[3]

[Total: 13]

- 5 (a) Pyridine, C_5H_5N , and benzene, C_6H_6 , have similar structures.



- (i) Identify the hybridization of orbitals in C and N atoms in pyridine and use a labelled diagram to show how the orbitals overlap to form the bonds between C and N in pyridine.



Sigma bond is formed by head-on overlap of sp^2 orbitals of C and N.

Pi bond is formed by sideways overlap of unhybridized p orbitals of C and N.

[3]

- (ii) Pyridine reacts with Cl_2 in the presence of AlCl_3 as shown in Fig. 5.1.

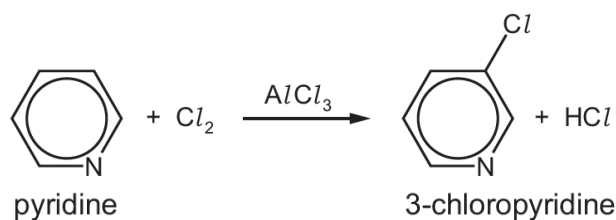
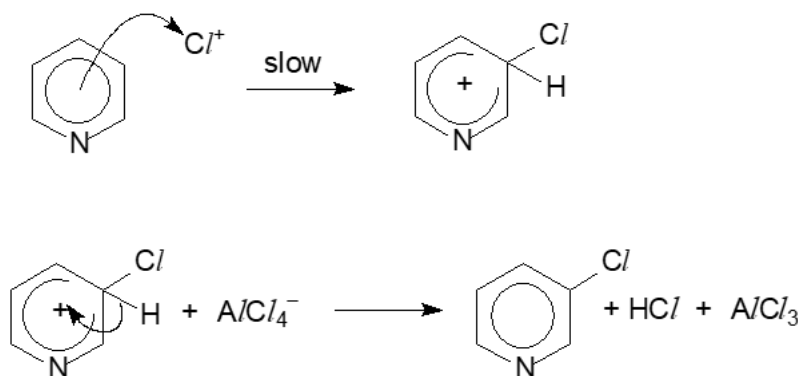


Fig. 5.1

The mechanism of this reaction is similar to that of the chlorination of benzene.

Describe the mechanism for the above reaction of pyridine with Cl^+ . Include all relevant charges, dipoles, lone pairs of electrons and curly arrows as appropriate.

Electrophilic substitution



[3]

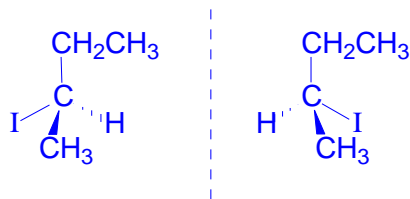
- (iii) Suggest how the basicity of 3-chloropyridine might compare to that of pyridine. Give a reason for your answer.

The electron withdrawing chlorine group will cause the lone pair of electrons on the nitrogen atom to be less available to accept a proton/ H^+ . Hence, 3-chloropyridine is a weaker base than pyridine.

[2]

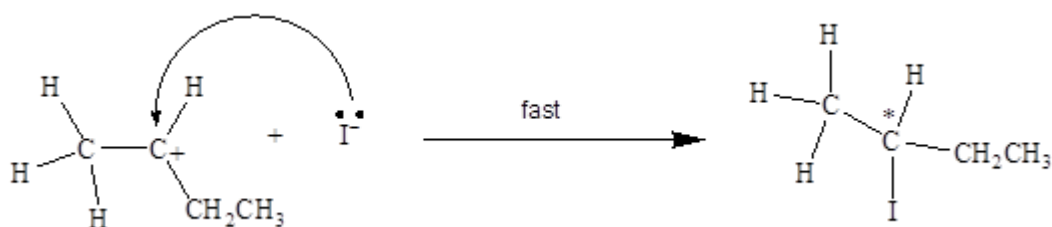
- (b) (i) Addition of hydrogen iodide gas to but-1-ene gives a racemic mixture.

Draw the 2 enantiomers and explain how a racemic mixture is obtained in this reaction.



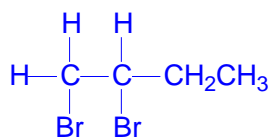
The **product contains a chiral carbon that is produced in Step 2 of the electrophilic addition mechanism where the I^- can attack the trigonal planar carbocation from either side with equal probability.** The two enantiomers are produced in equal amount.

For reference:

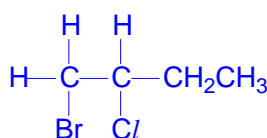


- (ii) Reaction of but-1-ene with bromine in the presence of aqueous sodium chloride gives a mixture of products. [2]

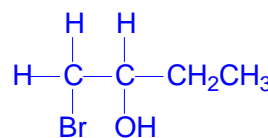
Draw the structure of three possible products and name the compounds.



1,2-dibromobutane



1-bromo-2-chlorobutane

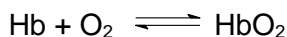


1-bromobutan-2-ol

[3]

[Total: 13]

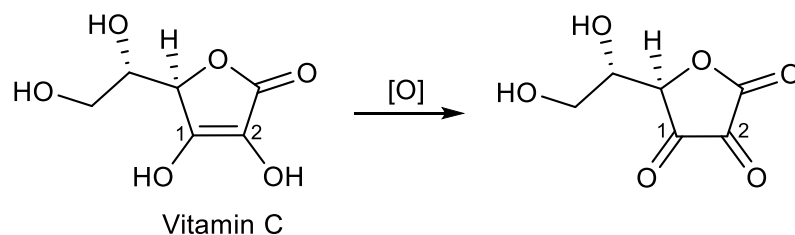
- 6 Haemoglobin reacts with oxygen to form oxyhaemoglobin as follows.



In order for haemoglobin to absorb oxygen, iron must be present. Iron makes up 4% by mass of the haemoglobin molecule. A healthy person should have 30 mg of haemoglobin per million red blood cells.

Approximately 10,000 million new blood cells are formed in the bone marrow daily. Components of the red blood cells are recycled by the liver at the end of their life cycle.

Iron is taken into the body in the diet as Fe^{3+} . In the presence of vitamin C, Fe^{3+} is converted to Fe^{2+} and incorporated into the haemoglobin structure. Vitamin C itself is oxidized in the process as follows.



- (a) (i) State the oxidation state of C_1 of vitamin C before and after oxidation.

Oxidation state of C_1 in vitamin C :

Oxidation state of C_1 after oxidation :

[1]

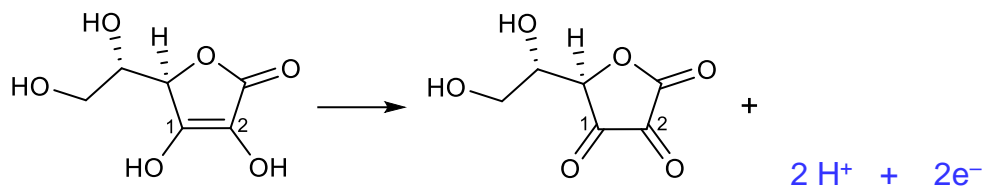
Oxidation state of C_1 in vitamin C : +1
 Oxidation state of C_1 after oxidation : +2

To determine the oxidation state of C at C_1 , the oxidation states of the atoms attached to C_1 are to be considered.

Before oxidation, C_1 is bonded to two adjacent carbon atoms and one oxygen atom. Since C_1 and the adjacent two carbon atoms have the same electronegativity, zero oxidation state is assigned to these two carbon atoms. $-\text{O}$ (single bond O) is assigned an oxidation state of -1 as O is more electronegative than C, the oxidation state of C_1 must be $+1$.

After oxidation, C_1 is bonded to two adjacent carbon atoms and one oxygen atom. Since C_1 and the adjacent two carbon atoms have the same electronegativity, zero oxidation state is assigned to these two carbon atoms. $=\text{O}$ (double bond O) is assigned an oxidation state of -2 as O is more electronegative than C, the oxidation state of C_1 must be $+2$.

- (ii) Hence or otherwise, complete the half equation for the oxidation of vitamin C below.



Note: Oxidation state of C₁ increases by 1 unit after oxidation, hence 1e⁻ is lost. Similarly, oxidation state of C₂ also increases by 1 unit after oxidation, 1 e⁻ is lost as well.

Overall, vitamin C loses 2 e⁻ during oxidation.

[1]

- (b) (i) Calculate the mass of iron, that needs to be available each day within the bone marrow for the production of new red blood cells.

1 million red blood cells contain 30 mg of haemoglobin.

Mass of haemoglobin in 10000 million red blood cells

$$= 10000 \times 30 = 300000 \text{ mg}$$

Mass of iron in 10000 million red blood cells

$$= \frac{4}{100} \times 300000 \text{ mg} = 12000 \text{ mg} = 12 \text{ g}$$

To calculate the amount of iron needed for the production of new red blood cells, the relevant information below must be sieve out from the reading of the question.

New blood cells formed daily: 10,000 million

1 million red blood cells contain 30 mg of haemoglobin.

iron in haemoglobin molecule: 4% by mass

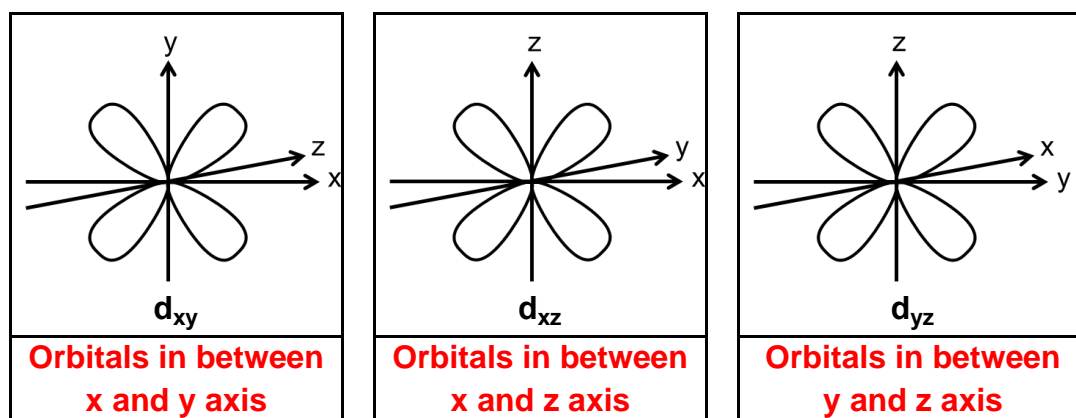
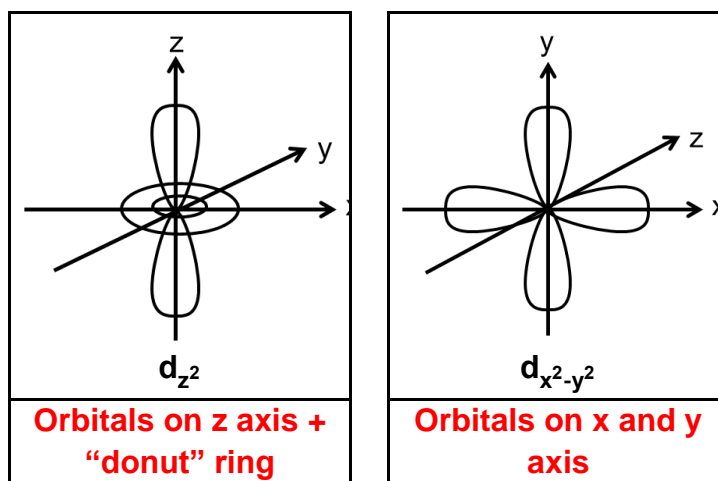
[2]

- (ii) According to Health Science Authority, the recommended daily dietary intake of iron is lower than the value calculated in (b)(i). Suggest a reason for this.

Components of the red blood cells are recycled by the liver at the end of their life cycle, the iron are recycled and available to produce new red blood cell.

[1]

- (c) (i) In the space provided below, draw the shapes of all the 3d orbitals. Label the axes clearly.



Note the drawing of the position of the 3rd axis for d_{xy} / d_{xz} / d_{yz} orbitals. It should not look like the orbital is ON the 3rd axis.

[3]

- (ii) Account for the red colouration of blood.

In the presence of ligands, electronic repulsion between lone pair electrons of ligands and the electrons in d orbitals causes the degenerate **d-orbitals of the transition metal ion to split into two different energy levels with a small energy gap, ΔE .** (d splitting)

Electrons in the lower energy d-orbitals can absorb light from the visible spectrum and be promoted to the higher energy d-orbitals (d-d transition).

The colour observed (red) is the complementary colour of the wavelength of light absorbed (green).

[3]

- (d) Complexes of Ni^{2+} are commonly found to have coordination number of 4, and exist either as tetrahedral or square planar complexes.

Fig 6.1 shows the splitting of the energy levels of d orbitals for tetrahedral and square planar complexes.

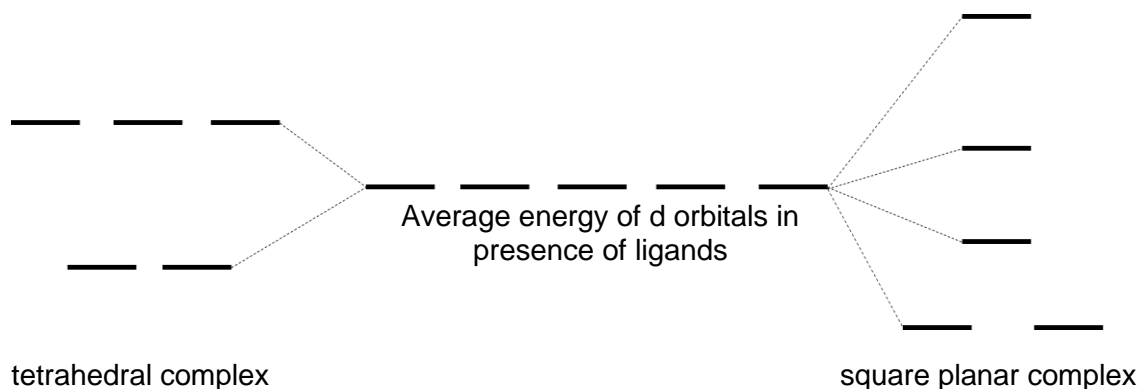


Fig 6.1

- (i) Complete the electronic configuration for Ni^{2+} .

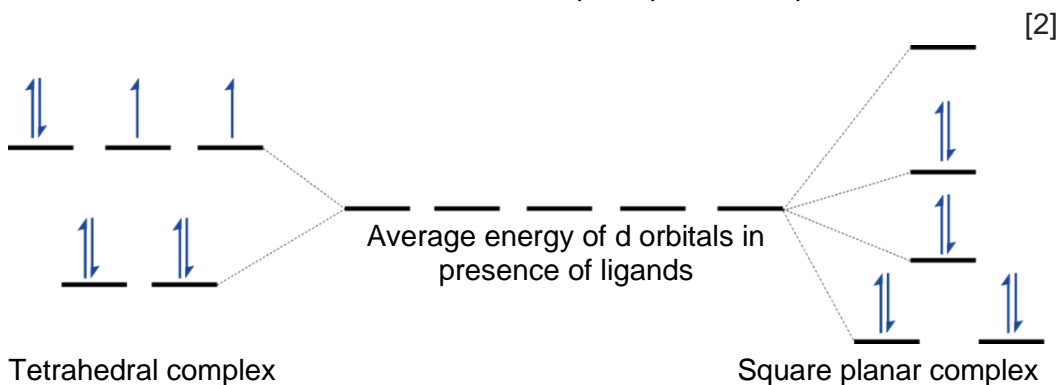
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$

Note: for transition metal cations, electrons are removed from 4s subshell first.

[1]

- (ii) The Aufbau principle states that in the ground state of an atom or ion, electrons fill atomic orbitals of the lowest available energy levels before occupying higher levels.

On the energy levels provided in Fig 6.1, show the electronic arrangement of the 3d electrons of Ni^{2+} in the tetrahedral and square planar complex.



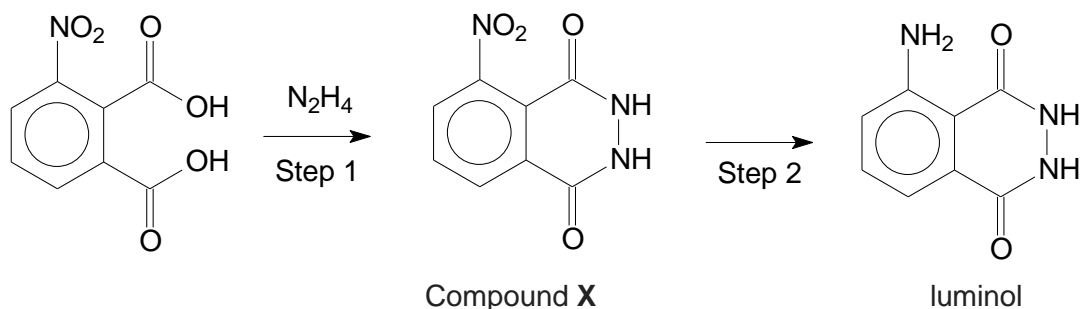
- (iii) Complex ions with only paired electrons are considered to be diamagnetic while those with at least one unpaired electron are considered to be paramagnetic.

A Ni^{2+} complex $[\text{NiX}_4]^{2-}$ is found to be diamagnetic, with reference to your answer in (d)(ii), state the shape of this complex ion.

Square planar [only contains paired electrons in the d orbitals]

[1]

- (e) Forensic investigators use luminol to detect traces of blood at crime scenes, as it reacts with the iron in haemoglobin. Luminol can be synthesized using the following route.



- (i) State the type of reaction for Step 1 and Step 2.

Step 1: Condensation (also accept nucleophilic substitution or nucleophilic acyl substitution) It is observed that 2 mol of H_2O are lost after step 1.

Step 2: Reduction

[2]

- (ii) A research student used the following reagent for Step 2.

Sn, conc HCl, heat, followed by excess NaOH(aq)

Suggest a reason why his method will not give luminol as the product.

Heating with conc HCl will cause the hydrolysis of the amide group in luminol.

[1]

[Total : 18]