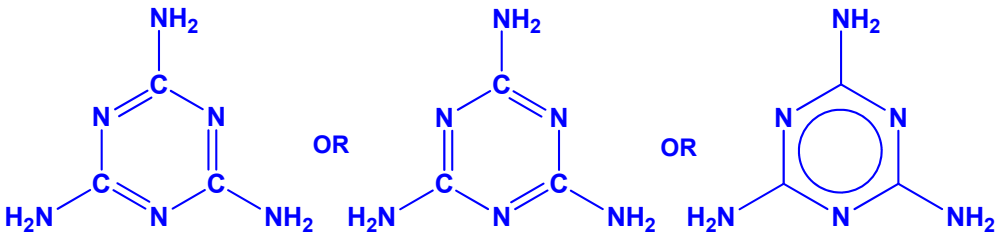
Victoria Junior College
2017 H2 Chemistry Prelim Exam 9729/2
Suggested Answers

1 This question concerns some unusual nitrogen compounds.

(a) Heating monomer **X** to 150 °C produces the trimer, melamine, $C_3H_6N_6$. Melamine is a cyclic planar molecule and is symmetrical.

(i) Suggest a structure for melamine.



[1]

(ii) The average C–N bond length is 0.145 nm and the average C=N bond is 0.125 nm. Suggest why all the carbon-nitrogen bonds in melamine are intermediate in length between the given C–N and C=N values.

The structure of melamine is resonance–stabilised due to delocalisation of p orbital electrons between carbon and nitrogen atoms. Hence all carbon-nitrogen double bonds are partial double bonds.

[1]

(iii) Deduce the structure of **X**. Calculate the number of protons, neutrons and electrons in a monomer of **X**.

$H_2N—C\equiv N$

22p, 20n, 22e⁻

[2]

(b) Group 1 metal azides, **M**N_3, can be formed by passing heated dinitrogen oxide, N_2O over their corresponding amines, **M**NH_2.

(i) Explain why lattice energies of Group 1 azides become less exothermic down the group.

Lattice energy α $|q^+.q^- / (r^+ + r^-)|$. Down Group 1, cationic radius increases, thus lattice energy becomes less exothermic.

[1]

(ii) Suggest why the azides become thermally more stable down the group.

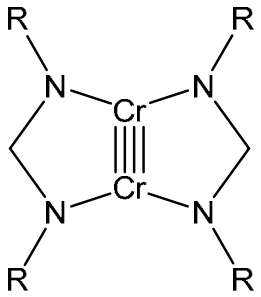
Down Group 1, cationic radius increases while charge remains the same. The charge density and polarising power of cations decrease. Extent of polarisation of anionic charge cloud N_3^- is less. More energy is required to decompose and break the N-N bonds within N_3^- down Group 1. Hence azides become more stable to heat.

[2]

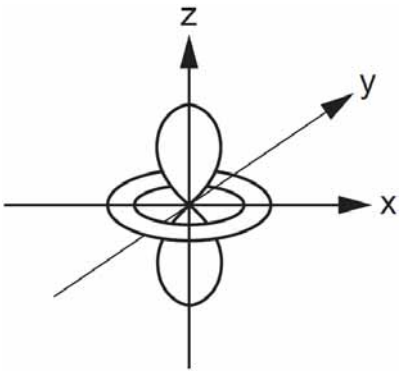
(c) Nitrogen has been used extensively in the research of compounds involving quadruple (bond order of 4) and quintuple (bond order of 5) bonds.

These compounds typically involve transition metal atoms that are able to form bonds between themselves using their d orbitals.

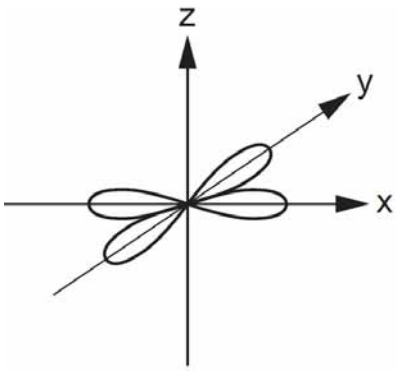
An example is given below:



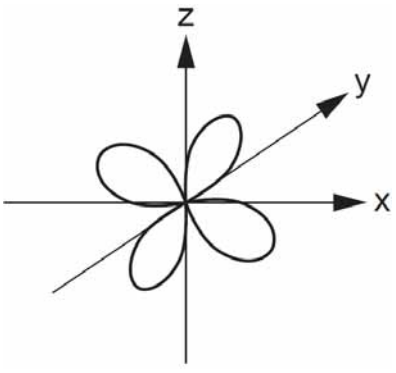
(i) Sketches of the shapes of the atomic orbitals from the d subshells are shown below, in random order. Name and label **each** orbital.



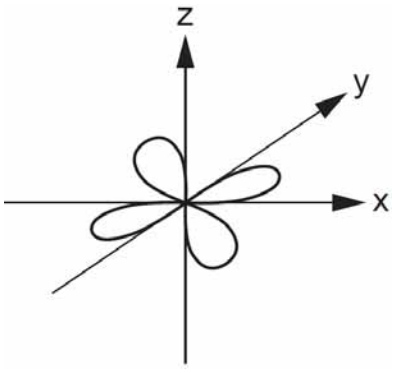
d_{z^2}



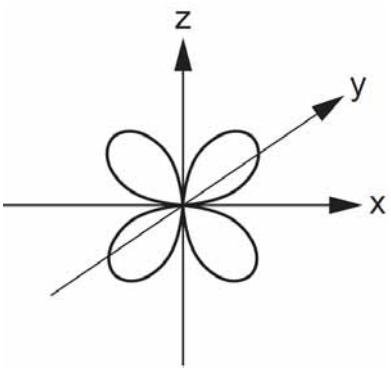
$d_{x^2 - y^2}$



d_{yz}



d_{xy}



d_{xz}

[2]

(ii) The d orbitals of an atom can overlap with d orbitals of the same type to form pi (π) and delta (δ) bonds. While a single sigma (σ) bond involves the overlap of two orbital lobes in total, and a single pi (π) bond four lobes, a single delta (δ) bond involves the overlap of eight lobes in total. When two atoms overlap, the z-axis is used to define the internuclear axis.

Suggest two different d orbitals that could be involved in delta bonds (δ).

$d_{x^2 - y^2}$ and d_{xy}

[1]

[Total: 10]

2 *Use of Data Booklet is relevant to this question.*

Aerozine 50 is a 50/50 mix of UDMH, $(CH_3)_2N_2H_2$ and hydrazine, N_2H_4. It is used as a rocket fuel, and is typically mixed with dinitrogen tetroxide, N_2O_4, as the oxidising agent.

The equation for the reaction between UDMH and dinitrogen tetroxide under standard conditions is given as follows:

$$(CH_3)_2N_2H_2(l) + 2N_2O_4(g) \rightarrow 2CO_2(g) + 3N_2(g) + 4H_2O(l) \quad \text{---------- } \textbf{reaction 1}$$

(a) Suggest an equation, including state symbols, for the reaction between hydrazine and dinitrogen tetroxide under standard conditions.

$2N_2H_4(l) + N_2O_4(g) \rightarrow 3N_2(g) + 4H_2O(l)$

[1]

(b) An experiment was set up such that hydrazine in a spirit burner was combusted beneath a copper can filled with water. It was found that 0.50 g of hydrazine was required to raise the temperature of 100 cm^3 of water in the can by 15 ºC.

Using relevant data from the *Data Booklet* and the information given below, calculate the efficiency of the system, expressed as a percentage.

- The heat capacity of the copper can be taken to be 96.0 J K^{-1}
- The density of water can be taken to be 1.00 g cm^{-3}.
- The standard enthalpy change of combustion of hydrazine, found using a bomb calorimeter, has a value of –628 kJ mol^{-1}.

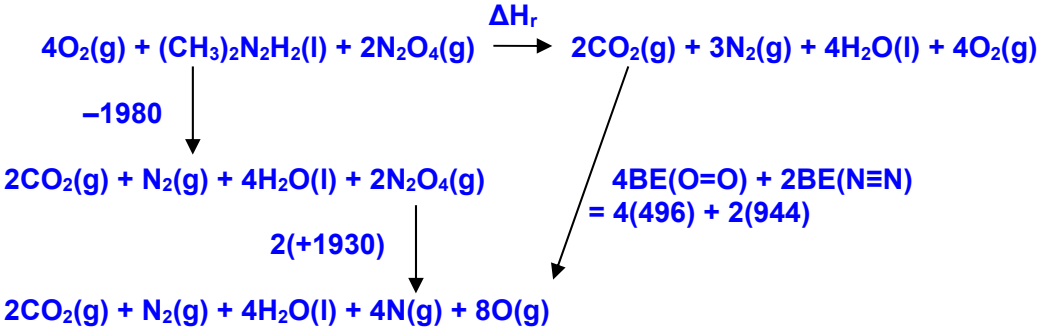
$Q_{absorbed}$ = (100)(4.18)(15) + (96.0)(15)
= 7710 J
$Q_{released}$ = 628000 x (0.5/32.0)
= 9813 J
Efficiency = 7710/9813 x 100 %
= 78.6 %

[3]

Pure UDMH, $(CH_3)_2N_2H_2$, can be used as an alternative to *Aerozine 50* in thruster rockets.

(c) Using relevant data from the *Data Booklet* and the information given below, construct an energy cycle to calculate the enthalpy change for **reaction 1**.

$(CH_3)_2N_2H_2(l) + 4O_2(g) \rightarrow 2CO_2(g) + N_2(g) + 4H_2O(l)$	–1980 kJ mol^{-1}
$N_2O_4(g) \rightarrow 2N(g) + 4O(g)$	+1930 kJ mol^{-1}



By Hess Law
$\Delta H_r + 4(496) + 2(944) = -1980 + 2(+1930)$
$\Delta H_r = -1990$ kJ mol^{-1}

[3]

(d) The total mass of propellant (UDMH and dinitrogen tetroxide, N_2O_4) used in the thruster rockets in the ascent stage of a lunar module was 366 kg.

Assuming that UDMH (M_r = 60.0) and dinitrogen tetroxide (M_r = 92.0) were mixed according to the stoichiometric ratio, calculate the mass of UDMH in the propellant mixture.

Let amount of UDMH be x mol and amount of N_2O_4 be 2x mol
$x(60.0) + 2x(92.0) = 366000$
$x = 1500$ mol
$m_{UDMH} = 1500 \times 60.0$
$= 90000$ g
$= 90$ kg

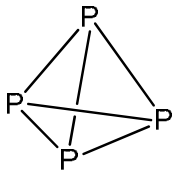
[1]

[Total: 8]

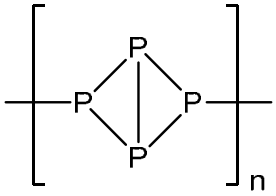
3 Use of the *Data Booklet* is relevant to this question.

Phosphorus and sulfur are elements in Period 3 in the Periodic Table and each can exist in various allotropic forms.

Phosphorus can exist as white phosphorus and red phosphorus. White phosphorus exists as a tetrahedron with bond angle 60° while red phosphorus exists as a polymeric chain of regular tetrahedrons.

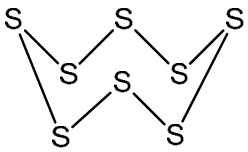


white phosphorus



red phosphorus

Sulfur, on the other hand is thermodynamically most stable at room temperature as rhombic sulfur, which consists of puckered S_8 rings.



Both elements form a wide range of compounds with the halogens.

(a) (i) By considering the bond angles involved, suggest why white phosphorus is less stable than red phosphorus.

The bond angle of 60° in white phosphorus, P_4 is smaller than 107° in red phosphorus. Hence there will be high angular strain in the bonding / strong electronic repulsion between the bond pairs. Thus, white phosphorus is less stable than red phosphorus.

[1]

(ii) The phosphorus halides fume in air because of reaction with water vapour.

Explain briefly why phosphorus(V) chloride can react with water. Write a balanced equation for its reaction.

PCl_5 undergoes hydrolysis in water due to the presence of energetically accessible vacant 3d orbitals on phosphorus which can accommodate lone pair of electrons from oxygen atoms of water molecules.

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

[2]

(b) When sulfur is heated under pressure with chlorine, the major product is SCl_2.

$$S_8(g) + 8Cl_2(g) \rightarrow 8SCl_2(g)$$

(i) Using data from the *Data Booklet*, calculate the enthalpy change, ΔH, for this reaction.

ΔH = Bonds broken – Bonds formed
= 8 x BE(S-S) + 8 x BE (C*l*-C*l*) – 16 x BE(S-C*l*)
= (8 × 264) + (8 × 244) – (16 × 250)
= +64 kJ mol^{-1}

[2]

Under suitable conditions, SCl_2 reacts with water to produce a yellow precipitate and a solution **X**. Solution **X** contains a mixture of SO_2(aq) and compound **Y**.

(ii) By constructing an equation for the hydrolysis of SCl_2, work out how the oxidation number of sulfur changes during the reaction.

$2SCl_2 + 2H_2O \rightarrow S + SO_2 + 4HCl$
Oxidation number of sulfur increases from +2 (in SCl_2) to +4 (in SO_2), and also decreases from +2 (in SCl_2) to 0 (in S).

[2]

(iii) Hence, suggest a pH value of the resultant solution formed.

pH = 1 [OR 2]

[1]

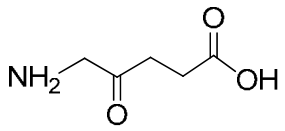
(iv) Using relevant data from the *Data Booklet*, suggest what would be observed when acidified potassium dichromate is added to a sample of solution **X**.

$E^\ominus(Cr_2O_7^{2-} \mid Cr^{3+}) = +1.33$ V > $E^\ominus(SO_4^{2-} \mid SO_2) = +0.17$ V
$E^\ominus_{cell} = +1.33 - 0.17 = +1.16$ V (spontaneous)
Thus $K_2Cr_2O_7$(aq), solution changes from orange to green.

[2]

[Total: 10]

4 Aminolevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.

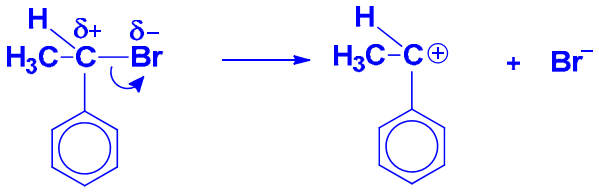


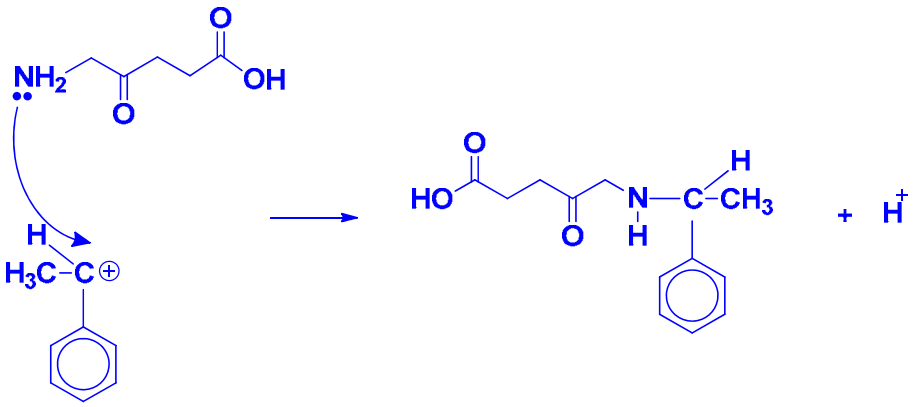
aminolevulinic acid

(a) Aminolevulinic acid reacts readily with (1-bromoethyl)benzene.

Name and outline the mechanism for the reaction of aminolevulinic acid with (1-bromoethyl)benzene.

S_N1 mechanism

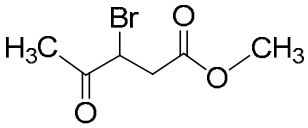




Note:
Dipole on C-Br and lone pair on N
Carbocation intermediate
Arrow drawn from lone pair on N to C+ AND arrow indicating heterolytic fission of C-Br bond
Product

[3]

(b) Compound **A** is a precursor in the synthesis of aminolevulinic acid.



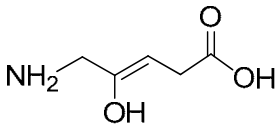
compound **A**

Suggest a simple chemical test to distinguish between compound **A** and aminolevulinic acid. Include clearly the reagents, conditions and observations for each compound. Write a balanced equation for any positive test.

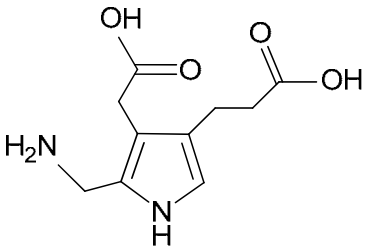
I_2(aq)/NaOH(aq), heat < 70°C
Observation for compound A: pale yellow ppt formed
$CH_3CO_2CH_2CH(Br)COCH_3 + 3I_2 + 6OH^- \rightarrow$
$^-O_2CCH_3CH_2CH(OH)CO_2^- + CHI_3 + 3I^- + 3H_2O + CH_3OH + Br^-$
Observation for aminolevulinic acid: no ppt formed
[Alternative tests accepted: Na_2CO_3 OR Na OR $KMnO_4/H_2SO_4$]

[3]

(c) Porphobilinogen is a pyrrole involved in porphyrin metabolism. It is generated from a reduced form of aminolevulinic acid, compound **B** by the enzyme ALA dehydratase.

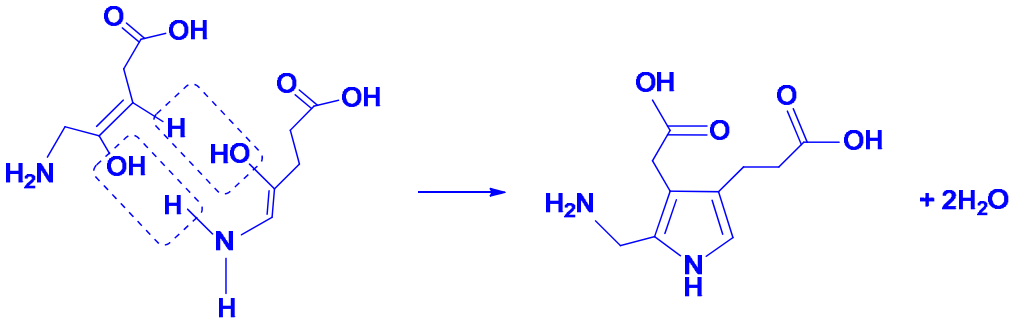


compound **B**



porphobilinogen

Show how porphobilinogen may be formed from the condensation of two molecules of compound **B**, with the help of a balanced equation. Indicate clearly with dotted lines how the non-organic by-products are formed.



Note:
2 molecules of A aligned as above
2 x dotted lines showing formation of $2H_2O$

[2]

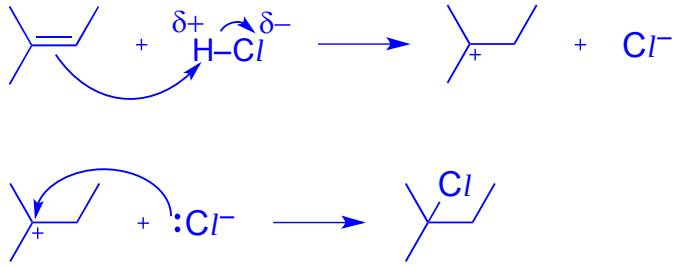
[Total: 8]

5 The formation of carbon-carbon bonds is important in the synthesis of large organic compounds. This question discusses the chemistry of some carbon-carbon bond forming reactions.

(a) Most of the starting reagents of such reactions typically involve a halogenoalkane. Halogenoalkanes can be obtained by reacting alkenes with hydrogen halides.

(i) Name and outline the mechanism of the reaction between 2-methylbut-2-ene and hydrogen chloride, showing the major product formed.

Electrophilic Addition



pair of arrows and partial charges (step 1)
correct intermediate & major product
balanced equations

[2]

(ii) 2-methylbut-2-ene can also react with hydrogen bromide and hydrogen iodide to form its respective halogenoalkane.

Suggest and explain, with reference to the mechanism of the reaction, how the rate of reaction changes from HC*l* to HI.

The **first step of the mechanism is the rate-determining step**.

From C*l* to I, **atomic radius increases**, **H–X bond length increases due to less effective overlap of orbitals**. **Bond strength decreases** and **less energy is required** to break H–X bond.

Hence rate of reaction increases in the following order.
Rate of reaction: HC*l* < HBr < HI

[2]

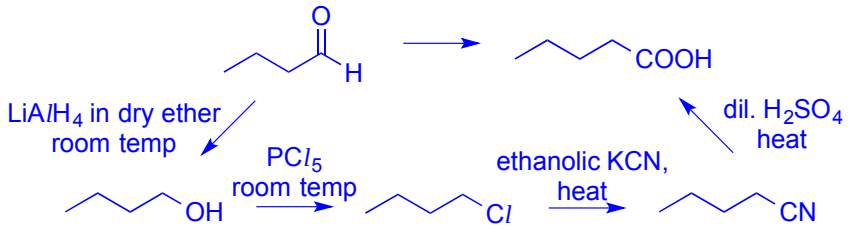
(b) Depending on the conditions of the reaction, a nitrile group can be introduced into an organic compound through either a halogenoalkane or a carbonyl, forming carbon-carbon bonds in the process.

(i) Suggest why alkenes are unable to react to form nitriles in the same way as carbonyls.

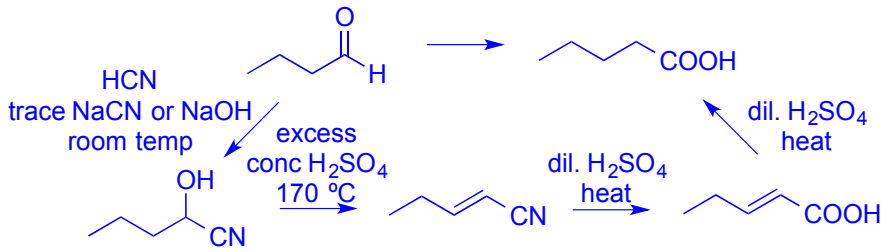
CN^- acts as a nucleophile due to the presence of a lone pair of electrons available for donation. **Alkenes have high electron density in the C=C** and hence **would repel CN^-**.

[1]

(ii) Propose a synthetic route that is **less than 5 steps** to convert butanal to pentanoic acid. State the reagents and conditions you would use for each step and draw the structures of the intermediate compounds.



OR



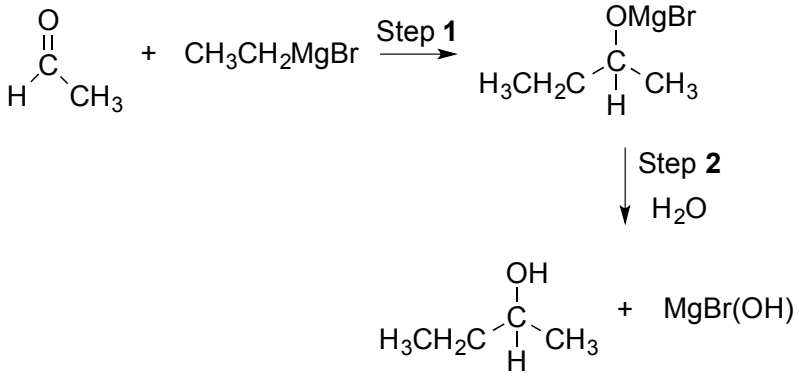
note: elimination of water and hydrolysis of nitrile are interchangeable

[5]

(c) A classic carbon-carbon bond formation reaction is the Grignard reaction. First, the Grignard reagent, an alkylmagnesium halide, is formed by reacting a halogenoalkane with magnesium.

$$CH_3CH_2Br + Mg \rightarrow CH_3CH_2MgBr$$

The reaction then proceeds with a reaction between the alkylmagnesium halide with a carbonyl to give an alcohol in a 2-step reaction.

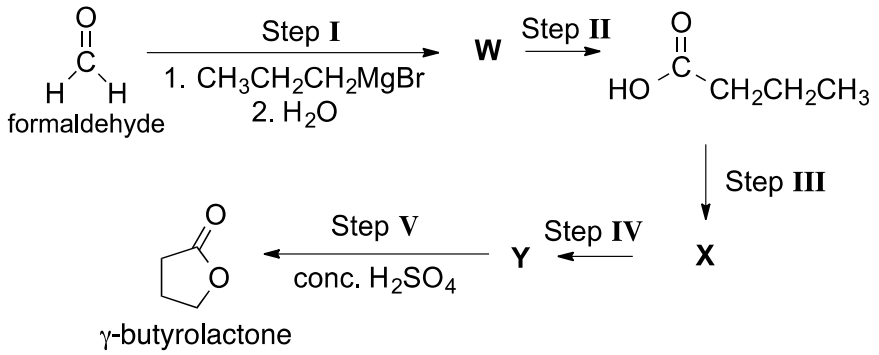


(i) Suggest the type of mechanism for Step **1**.

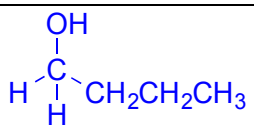
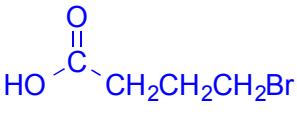
Nucleophilic addition

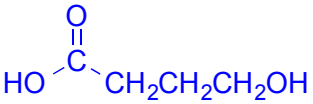
[1]

(ii) The synthesis of γ-butyrolactone, a common solvent from formaldehyde, involves the Grignard reaction as follows.



Propose structures of **W**, **X**, **Y** and **Z**.

	
W	**X**


Y

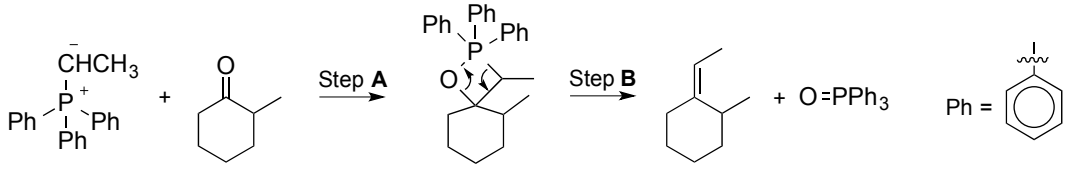
[3]

(iii) State the reagents and conditions required for steps **II**, **III** and **IV**.

Step **II**: **$KMnO_4$, H_2SO_4(aq), heat**
Step **III**: **Br_2, excess $CH_3CH_2CH_2CO_2H$, uv light**
Step **IV**: **NaOH(aq), heat**

[3]

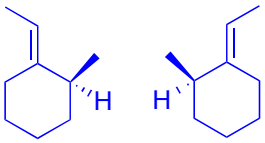
(d) Another common carbon-carbon bond formation reaction is the Wittig reaction. A phosphorus-containing reagent reacts with a carbonyl to form an intermediate, which then cleaves quickly to give an alkene.



(i) Identify, with the aid of a diagram, the type of stereoisomerism that the product can show.

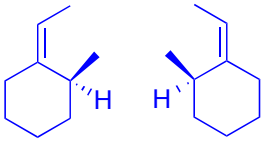
cis-trans isomerism (OR enantiomerism)

trans



(+) (–)

cis



Note: since the question asked for "can show", students only need to identify one, even though there were 2

[2]

(ii) By considering the hybridisation of relevant carbon atoms, suggest a reason why step **B** is a fast reaction.

The carbon centres in the 4-membered cyclic ring are **sp^3 hybridised**. There is **high ring strain** due to angles being less than the ideal 109.5º. This results in the ring being **unstable**, which will then collapse quickly.

[2]

[Total: 21]

6 **(a)** 1.0 cm^3 of 0.10 mol dm^{-3} solution of sodium iodide was added to 1.0 cm^3 of 0.050 mol dm^{-3} $AgNO_3(aq)$. 3.0 cm^3 of 1.0 mol dm^{-3} $NH_3(aq)$ was then added. The resulting precipitate formed is virtually insoluble.

(i) Show that the number of moles of $I^-(aq)$ that is **not** used to form the precipitate is 5.0 x 10^{-5} mol.

Amount of I^- originally = 1.0 / 1000 x 0.10 = 1.0 x 10^{-4} mol
Amount of Ag^+ originally = 1.0 / 1000 x 0.050 = 5.0 x 10^{-5} mol
Amount of I^- left = 1.0 x 10^{-4} – 5.0 x 10^{-5} mol
= 5.0 x 10^{-5} mol (the rest of I^-has been precipitated as AgI)

[1]

(ii) Show that under these conditions $[I^-(aq)]$ = 0.010 mol dm^{-3} and hence $[Ag^+(aq)]$ which would just allow the precipitate to dissolve.

$K_{sp}(AgI)$ = 8.0 x 10^{-17} mol^2 dm^{-6}

$[I^-(aq)]$
= (5.0 x 10^{-5}) / (1.0 + 1.0 + 3.0) x 1000 = 0.010 mol dm^{-3}

For AgI to just dissolve, ionic product < K_{sp}(AgI)
$[Ag^+(aq)]$ = 8.0 x 10^{-17} / 0.010 = 8.0 x 10^{-15} mol dm^{-3}

[1]

(iii) Under the conditions of the experiment, $[Ag^+(aq)]$ = 1.9 x 10^{-9} mol dm^{-3}. Use your answer in **(a)(ii)** to justify why the precipitate is virtually insoluble.

The value of $[Ag^+]$ calculated in (a)(ii) is <u>less</u> than 1.9 x 10^{-9} mol dm^{-3},
Hence <u>ionic product > K_{sp}(AgI)</u>, precipitation still occurs and will not be soluble.

[1]

(iv) When the above experiment is repeated using sodium chloride instead of sodium iodide, different observations were made. Briefly describe and explain the differences with the aid of equations. **No** calculations are required.

$Ag^+(aq) + X^-(aq) \rightleftharpoons AgX(s)$ X = Cl or I …… (1)

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
Formation of white ppt of silver chloride and yellow ppt of silver iodide
Silver chloride will dissolve in aqueous NH_3 but silver iodide will not.
Aqueous NH_3 will form a complex with Ag^+ ions,
thus <u>equilibrium (1) will shift left</u> to restore the Ag^+ ions that were removed.
Hence <u>ionic product of $[Ag^+][Cl^-] < K_{sp}$ (AgCl) so ppt dissolves</u>
AgI is less soluble <u>with a much lower K_{sp}</u> hence ionic product of $[Ag^+][I^-] > K_{sp}$(AgI) so ppt remains.

[3]

(b) The standard electrode potential values for reactions **(I)** and **(II)** are +1.21 V and +0.54 V respectively.

$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$ **(I)**

$\frac{1}{2}I_2 + e^- \rightleftharpoons I^-$ **(II)**

(i) Find the standard Gibbs free energy change for **each** of the reactions **(I)** and **(II).**

For reaction (I),
$\Delta G^\ominus = -5 \times 96\,500 \times 1.21 = -5.84 \times 10^5$ J mol^{-1}
For reaction (II),
$\Delta G^\ominus = -1 \times 96\,500 \times 0.54 = -5.21 \times 10^4$ J mol^{-1}

[1]

(ii) Use your answers from **(b)(i)** to find the standard Gibbs free energy change for the following reaction, and hence its standard electrode potential.

$IO_3^- + 6H^+ + 6e^- \rightleftharpoons I^- + 3H_2O$

$\Delta G^\ominus = -5.21 \times 10^4 + (-5.84 \times 10^5) = -6.36 \times 10^5$ J mol^{-1}
$E^\ominus(IO_3^-/I^-) = -6.36 \times 10^5 / (-6 \times 96\,500) = +1.10$ V

[2]

(c) When 0.530 g of potassium iodide was completely reacted with an aqueous solution of XeF_2, all the iodide is converted into the iodate anion. A student proposed that the anion could be either iodate(V), IO_3^-, or iodate(VII), IO_4^-.

(i) Show that the number of moles of iodate that were involved in the reaction is 3.19×10^{-3} mol.

Amount of iodate = Amount of KI
= 0.530 / 166.0
= 3.19×10^{-3} mol

[1]

(ii) The equation involving the reaction of iodate(VII), IO_4^- with excess acidified potassium iodide is given below:

$$IO_4^- + 8H^+ + 7I^- \rightarrow 4I_2 + 4H_2O$$

For the reaction involving iodate(V), IO_3^- with excess acidified potassium iodide, write the corresponding half equations and hence the overall **ionic** equation.

Reduction: **$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$**
Oxidation: **$2I^- \rightarrow I_2 + 2e^-$**
Overall ionic equation: **$IO_3^- + 6H^+ + 5I^- \rightarrow 3I_2 + 3H_2O$**

[3]

(iii) 3.19 x 10^{-3} mol of iodate anion, which is either iodate(V), IO_3^-, or iodate(VII), IO_4^- is acidified, and added to excess potassium iodide solution where iodine is formed. It is found that 28.40 cm^3 of 0.900 mol dm^{-3} of $Na_2S_2O_3$ is required to discharge the colour of iodine.

It is given that $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$.

By using the information and your answers in **(c)(ii)**, determine whether the anion is iodate(V), IO_3^-, or iodate(VII), IO_4^-.

Since $I_2 : S_2O_3^{2-} = 1 : 2$,
assuming anion is IO_3^-, $IO_3^- : S_2O_3^{2-} = 1 : 6$
assuming anion is IO_4^-, $IO_4^- : S_2O_3^{2-} = 1 : 8$

If anion is IO_3^-,

volume of $S_2O_3^{2-}$ required = $\dfrac{6 \times 3.19 \times 10^{-3} \times 10^3}{0.900} = 21.30$ **cm^3**

If anion is IO_4^-,

volume of $S_2O_3^{2-}$ required = $\dfrac{8 \times 3.19 \times 10^{-3} \times 10^3}{0.900} = 28.40$ **cm^3**

(or any reasonable method of elimination is accepted)
Hence the anion is IO_4^-.

[2]

(d) Nitrogen trifluoride was first prepared in the electrolysis of a molten mixture of ammonium fluoride and hydrogen fluoride using inert electrodes.

(i) It is given that at one of the electrodes, the following reaction occurs:
$NH_4^+ + 3F^- \rightarrow NF_3 + 4H^+ + 6e^-$

State the electrode that is involved in the above reaction and its polarity.

Anode
positive

[1]

(ii) When the above electrolysis was set up using a current of 0.50 A, 0.276 g of nitrogen trifluoride was liberated. Calculate the time taken for the electrolysis to occur.

Amount of NF_3 collected = 0.276 / (14.0 + 19.0 x 3) = 3.89 x 10^{-3} mol
Amount of electrons needed to liberate NF_3
= 3.89 x 10^{-3} x 6 = 2.33 x 10^{-2} mol

Total quantity of charge used = 2.33 x 10^{-2} x 96 500 = 2250 C

Time taken = 2250 / 0.50 = 4500 s = 75 min

[2]

[Total: 18]