Suggested solutions

DUNMAN HIGH SCHOOL
Preliminary Examination 2018
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Free Response

18 September 2018
2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet
Writing Paper
Cover Sheet
Graph Paper

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page and on the Cover Sheet provided.
2 Write your answers on the separate writing papers provided.
3 Write in dark blue or black pen.
4 You may use an HB pencil for any diagrams or graphs.
5 Start each question on a fresh sheet of paper.
[Marks will be deducted if you fail to do so.]
6 At the end of the examination, fasten all your work securely together with the Cover Sheet on top.
7 Do not use staples, paper clips, glue or correction fluid.

Section A

8 Answer **all** questions

Section B

9 Answer **one** question.

The number of marks is given in brackets [ ] at the end of each question or part question.
You are advised to show all workings in calculations.
You are reminded of the need for good English and clear presentation in your answers.

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Section A

Answer **all** questions.

1 The Williamson ether synthesis is an organic reaction, forming an ether from a halogenoalkane and alcohol in the presence of sodium. This reaction was developed by Alexander Williamson in 1850 and still remains the simplest and most popular method of preparing ethers till today.

The following equation shows the formation of dimethyl ether, a common aerosol propellant.

$$CH_3Cl + CH_3OH \xrightarrow[CH_3OH]{Na} CH_3OCH_3 + HCl$$

(a) **(i)** State the purpose of sodium used in the Williamson ether synthesis.

[1]

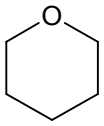
Sodium reacts with CH_3OH to form a **stronger nucleophile, CH_3O^-**

(ii) Hence, name the mechanism of the reaction.

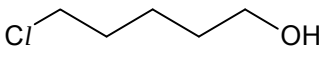
[1]

S_N2 / bimolecular nucleophilic substitution

(iii) Suggest suitable reagent(s) to synthesise each of the following ethers.

- $CH_3CH_2OCH_2CH_3$
- 

[2]

- CH_3CH_2OH (in the presence of Na) and CH_3CH_2Cl
-  (in the presence of Na)

(b) Dimethyl ether is known as a symmetrical ether whereas *tert*-butyl ethyl ether, $CH_3CH_2OC(CH_3)_3$ is an example of an unsymmetrical ether. To prepare *tert*-butyl ethyl ether via the Williamson ether synthesis, there are two possible combinations of reagents, as shown in the table below.

Combination	Reagents
A	CH_3CH_2Br and $(CH_3)_3COH$
B	$(CH_3)_3CBr$ and CH_3CH_2OH

Identify the combination of reagents that might favour the mechanism identified in **(a)(ii)** and justify your choice, with reasoning.

[2]

Combination **A**

CH_3CH_2Br is a **primary alkyl halide**, and hence it will be **less sterically hindered** for the nucleophile / alkoxide ion to **attack from the back** of the halogen as compared to $(CH_3)_3CBr$, a tertiary alkyl halide.

(c) Since the middle of 1990s, dimethyl ether (DME) has been identified as a reliable diesel alternative for cars. The table below compares the physical and chemical properties of DME and diesel fuel.

Property	**Unit**	**DME**	**Diesel Fuel**
Carbon content	mass %	52.2	86
Hydrogen content	mass %	1 – 3	14
Oxygen content	mass %	34.8	0
Liquid density	kg m^{-3}	667	831
*Auto-ignition temperature	K	508	523
^Stoichiometric air/fuel mass ratio	-	9.6	14.6
Normal boiling point	K	248.1	450 – 643
Enthalpy of vaporisation	kJ kg^{-1}	467.1	300
Energy released at burning	MJ kg^{-1}	27.6	42.5

**Auto-ignition temperature is the temperature at which a fuel will ignite spontaneously without an external ignition source.*

^Stoichiometric air/fuel mass ratio is the mass ratio of air to fuel that completely burns the fuel with no excess air.

With reference to the table, suggest one advantage and one disadvantage of using DME as compared to the conventional diesel fuel.

[2]

Advantage: DME has **lower carbon content** than diesel fuel, and thus contribute to **lower carbon dioxide emission** when the same mass is burnt.

Disadvantage: DME releases **less energy at burning** than diesel fuel, and thus is a **less efficient fuel** for the same mass used.

(d) Scientists have recently discovered a new way of synthesising DME by reacting carbon dioxide directly with hydrogen in the presence of Cu-Zn/Al_2O_3 catalyst.

(i) Write the balanced equation for the synthesis of DME from carbon dioxide and hydrogen.

[1]

$2CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O$

(ii) State the type of catalysis that Cu-Zn/Al_2O_3 performs and explain briefly how it promotes the synthesis of DME.

[3]

Heterogeneous catalysis

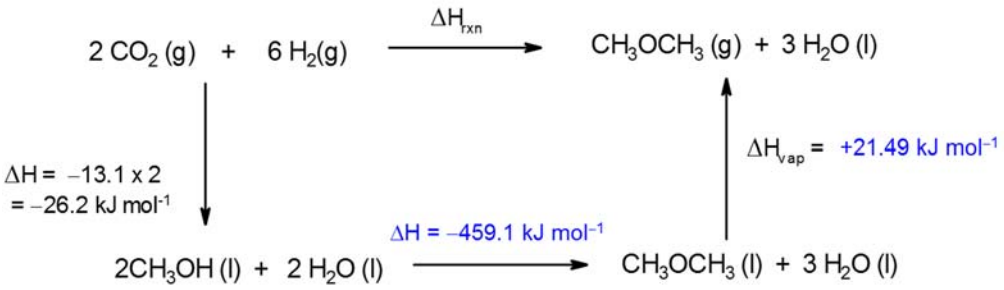
Both H_2 and CO_2 reactants are gases. The solid catalyst provides a surface for the **gaseous molecules to be *adsorbed*** to the surface, **thus increasing the concentration of the reactants / bringing the molecules closer together** and **weakening the bonds of the reactants molecules**, resulting in a lower E_a.

(iii) DME can also be synthesised from carbon dioxide via a two-step reaction in the laboratory.

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l) \quad \Delta H = -13.1 \text{ kJ mol}^{-1}$$
$$2CH_3OH(l) \rightarrow CH_3OCH_3(l) + H_2O(l) \quad \Delta H = -459.1 \text{ kJ mol}^{-1}$$

Using the thermochemical equations given and any relevant data in part **(c)**, draw an energy cycle to determine the enthalpy change of reaction for the synthesis of DME from carbon dioxide and hydrogen at room temperature and pressure.

[5]



$\Delta H_{vap} = 467.1/1000 \times 46 = +21.49 \text{ kJ mol}^{-1}$

By Hess' Law,
$\Delta H_{rxn} = -26.2 - 459.1 + 21.49$
$= \underline{\mathbf{-464 \text{ kJ mol}^{-1}}}$

(e) Both dimethyl ether and dimethyl amine have similar hybridisation around the heteroatoms, O and N, respectively.

(i) State the type of hybridisation of the O and N atoms in dimethyl ether and dimethyl amine respectively.

[1]

sp^3

(ii) Dimethyl ether has a solubility of 7.1 g per litre of water but dimethyl amine has a solubility of 3.54 kg per litre of water instead. Using suitable equation(s), explain briefly the difference in the solubilities between the two compounds.

[3]

DME can form **hydrogen bonds with water molecules** whereas dimethyl amine is a weak base and can partially dissociate in water in to form ions which can form **ion-dipole interactions with water molecules**, hence dimethyl amine has a higher solubility in water.

$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$

(iii) A 0.1 mol dm^{-3} solution of dimethyl amine containing an unknown concentration of dimethylamine hydrochloride has a pH of 10.57. Given that the numerical value of K_b of dimethyl amine is 7.4×10^{-4}, determine the concentration of dimethylamine hydrochloride in the solution.

[3]

A buffer system is set up.

$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^- \quad K_b = 7.4 \times 10^{-4}$ mol dm^{-3}

pH = 10.57
pOH = 14 – 10.57 = 3.43
$[OH^-] = 10^{-3.43}$ mol dm^{-3}

$$K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$$

$$7.4 \times 10^{-4} = \frac{[(CH_3)_2NH_2^+][10^{-3.43}]}{0.1}$$

$$[(CH_3)_2NH_2^+] = \frac{7.4\times10^{-4}\times0.1}{10^{-3.43}}$$
$$= 0.199 \text{ mol } dm^{-3}$$

OR

$$pOH = pK_b + \log_{10}\left(\frac{[(CH_3)_2NH_2^+]}{[(CH_3)_2NH]}\right)$$
$$14 - 10.57 = -\log_{10}(7.4 \times 10^{-4}) + \log_{10}\left(\frac{[(CH_3)_2NH_2^+]}{0.1}\right)$$

$[(CH_3)_2NH_2^+] = 0.199$ mol dm^{-3}

(iv) Explain why trimethyl amine has a higher pK_b than dimethyl amine.

[1]

The **lone pair of electrons on N in trimethyl amine is less available for donation** as it is **more sterically hindered with one more $-CH_3$ group** than dimethyl amine, hence decreasing its basicity.

[Total: 25]

2 **(a)** Carbon undergoes combustion in oxygen to form two common oxides, CO and CO_2. These oxides are also formed when solid magnesium oxalate, MgC_2O_4, is heated strongly.

(i) Explain why magnesium oxalate decomposes at a lower temperature than barium oxalate, BaC_2O_4.

[2]

Mg^{2+} has a **smaller ionic radius and a higher charge density** than Ba^{2+}. Therefore, Mg^{2+} has a **greater polarising power** than Ba^{2+}. Mg^{2+} **distorts the electron cloud of $C_2O_4^{2-}$ anion / weakens the bonds in the $C_2O_4^{2-}$ anion to a greater extent.** Hence MgC_2O_4 is less thermally stable.

(ii) ZnC_2O_4 undergoes a similar reaction when heated strongly, even though zinc is not a Group 2 element.

Write an equation, with state symbols, to represent the thermal decomposition of solid zinc oxalate.

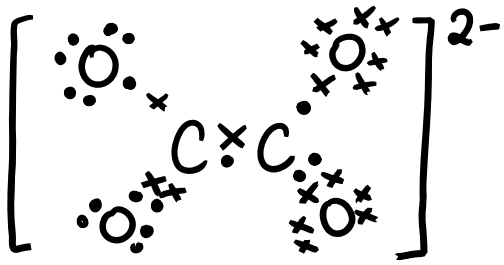
[1]

$ZnC_2O_4(s) \rightarrow ZnO(s) + CO_2(g) + CO(g)$

(iii) Draw the dot–and–cross diagram of $C_2O_4^{2-}$.

State the shape and bond angle around the carbon atoms of the ion.

[3]



Shape: Trigonal Planar about each C atom
Bond Angle: 120°

(b) Zinc can also be used in the manufacturing of rechargeable batteries. Zinc–cerium battery is a type of rechargeable battery using a two–electrolyte system. The overall equation for the discharging process is given below.

$$Zn + 2Ce^{4+} \rightarrow Zn^{2+} + 2Ce^{3+}$$

(i) Given that the typical cell voltage for the cell is 2.2 V, calculate the standard electrode potential of the Ce^{4+}/Ce^{3+} half–cell, using relevant data from the *Data Booklet*.

[1]

From the Data Booklet,
$E^{\ominus}(Zn^{2+}/Zn) = -0.76$ V

$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$
$2.2 = E^{\ominus}(Ce^{4+}/Ce^{3+}) - (-0.76)$
$E^{\ominus}(Ce^{4+}/Ce^{3+}) =$ **+1.44 V**

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(ii) Using relevant data from the *Data Booklet*, deduce if the Ce^{4+}/Ce^{3+} half–cell can be replaced with Br_2/Br^- half–cell.

[1]

From the Data Booklet,
$E^{\ominus}(Br_2/Br^-) = +1.07$ V

$E^{\ominus}_{cell} = +1.07 - (-0.76)$
$= +1.83$ V > 0 (feasible)

Since it is feasible for the battery to discharge electricity, the Ce^{4+}/Ce^{3+} half–cell can be replaced with Br_2/Br^- half–cell.

(c) Nickel–metal hydride (Ni–MH) batteries are the most common rechargeable batteries used for devices that require large amounts of energy. Most Ni–MH batteries use an alloy containing mainly lanthanum and nickel.

In one such battery, one of the electrodes is $LaNi_5H_6$ and the other is NiO(OH). The electrolyte is aqueous KOH. During the discharging process, an electrochemical reaction takes place to produce $LaNi_5(s)$ and $Ni(OH)_2(s)$, and releases electrical energy.

(i) Construct a half–equation for the reaction that take place at each electrode during discharging.

[2]

Anode: $LaNi_5H_6(s) + 6OH^-(aq) \rightarrow LaNi_5(s) + 6H_2O(l) + 6e^-$

Cathode: $NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$

(ii) During recharging, an electrical potential is applied across the electrodes to reverse the electrochemical reaction.

Using your answer in **(c)(i)**, write the overall equation for the reaction that occurs during recharging.

[1]

$LaNi_5(s) + 6Ni(OH)_2(s) \rightarrow LaNi_5H_6(s) + 6NiO(OH)(s)$

(iii) Overcharging the Ni–MH battery may result in the electrolyte being discharged at the electrodes to form gaseous products. A safety vent is thus incorporated in the battery to release the excess pressure.

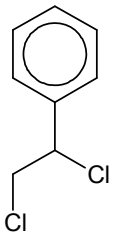
With reference to the *Data Booklet*, suggest a relevant half–equation, with state symbols, for the reaction occurring at one of the electrodes of the Ni–MH battery.

[1]

Anode: $4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-$
OR
Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

[Total: 12]

3 (a) Compounds **X** and **Y** are dichloroalkanes and constitutional isomers of each other. The structure of **Y** is as shown below.



Compound **Y**

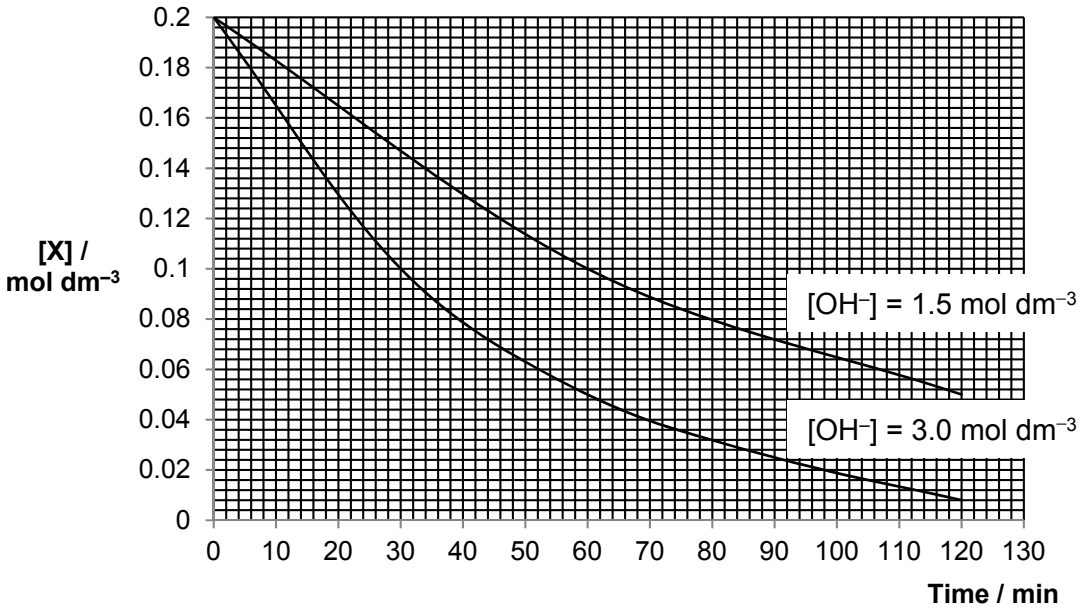
Some additional information is provided about **X**:

- It is not chiral.
- It also contains a benzene ring.
- The two chlorine atoms are not bonded to the same carbon atom.

A series of chemical experiments were also conducted on Compound **X** to further confirm its identity.

Experiment I:

The reaction kinetics of **X** with aqueous sodium hydroxide was determined by monitoring the change in concentration of **X** with time.



Experiment II:

0.25 mol of **X** and **Y** were treated separately with boiling aqueous sodium hydroxide. The products from each compound were then acidified with nitric acid and then treated with silver nitrate solution. The results obtained are shown below.

	Observation upon adding $AgNO_3$	Mass of precipitate / g
X	formation of white precipitate	35.85
Y	formation of white precipitate	71.70

(i) Deduce the rate equation based on the information given in Experiment **I**.

[3]

Using $[OH^-]$ = 3.0 mol dm^{-3} graph,
$t_{1/2}$ is constant at 30 min, order of reaction with respect to X is 1.
OR
Using $[OH^-]$ = 1.5 mol dm^{-3} graph,
$t_{1/2}$ is constant at 60 min, order of reaction with respect to X is 1.

Using initial rate method,
Initial rate for graph where $[OH^-]$ = 1.5 mol dm^{-3}
= 0.2/110 = 0.001818 mol dm^{-3} min^{-1}
Initial rate for graph where $[OH^-]$ = 3.0 mol dm^{-3}
= 0.2/52 = 0.003846 mol dm^{-3} min^{-1}

As $[OH^-]$ increases 2 times, initial rate also increases 2 times
Hence, order of reaction with respect to OH^- is 1.

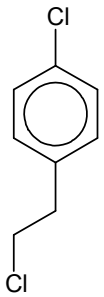
Rate = k [X] $[OH^-]$

(ii) Using your answer in **(a)(i)** and the information given in Experiment **II**, deduce, with reasoning, a possible structure of **X**.

[2]

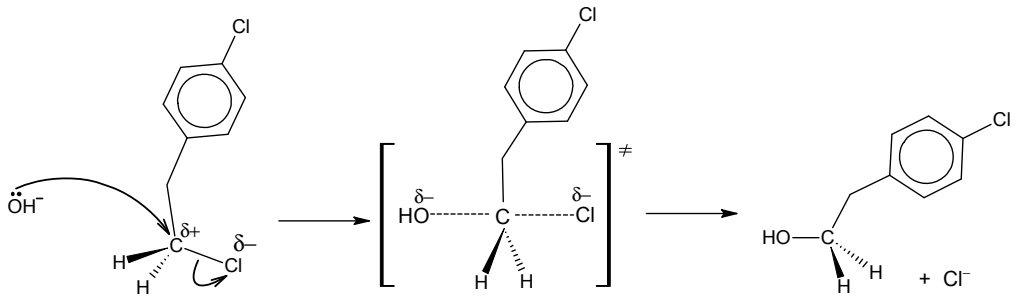
From (a)(i), X undergoes S_N2 mechanism
$\Rightarrow$ X is a primary chloroalkane.

From expt II, 0.25 mol of X forms 0.25 mol of AgCl
$\Rightarrow$ There is only one Cl atom in the alkyl side chain OR there is only one Cl atom bonded to the benzene ring



(iii) Draw the mechanism for the reaction of **X** with aqueous sodium hydroxide. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

[3]



(b) Depending on the mechanism, the solvent affects the stability of nucleophile and/or reaction intermediates in the nucleophilic substitution of halogenoalkanes (RX). The table below shows the rates of reaction when different halogenoalkanes and solvents are used.

Solvent	Type	Relative rates of reaction with OH^-	
		1° RX in S_N2	3° RX in S_N1
CH_3OH	Protic	1	4
H_2O	Protic	7	150 000
CH_3COOH	Protic	1	1
CH_3COCH_3	Aprotic	5000	–

(i) Suggest, using **only** structure and bonding, the difference between *protic* and *aprotic* solvents, in terms of solvent-solvent interactions.

[1]

Protic solvent refers to molecules with **H atoms that can be used to form hydrogen bonds**. Aprotic solvents can only form **permanent dipole-permanent dipole interactions between molecules/ have no H atoms that can form hydrogen bonds**.

(ii) Suggest an explanation for the effect of solvent on the relative rate of S_N2 reactions.

[2]

For S_N2 reactions, protic solvents like water can form **hydrogen bond with OH^-** and hence, slowing down the rate of reaction. Aprotic solvents like CH_3COCH_3, do not form hydrogen bond and hence **the lone pair of electron on OH^- is more available to attack the electron deficient C on 1° RX.**

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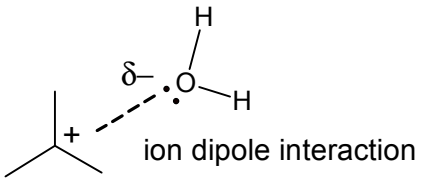
(iii) Explain, with an aid of a diagram, how water increases the rate of S_N1 reaction.
[2]



ion dipole interaction

The ion dipole interaction **stabilised the carbocation**.

(iv) Would the rate of S_N1 reaction be faster or slower if hexane was used in place of ethanoic acid?
[1]

Slower.

(c) Silver forms a series of halides of general formula AgX. The chloride, bromide and iodide of silver are sparingly soluble in water at room temperature.

Data about the solubilities in water and the solubility products of the chloride, bromide and iodide of silver at 298 K are given below.

Salt	Solubility / mol dm^{-3}	Solubility product / mol^2 dm^{-6}
AgC*l*	1.4×10^{-5}	2.0×10^{-10}
AgBr	7.1×10^{-7}	5.0×10^{-13}
AgI	8.9×10^{-9}	to be calculated

(i) Write an expression for the solubility product, K_{sp} of silver iodide.
[1]

$K_{sp} = [Ag^+]\,[I^-]$

(ii) From the data above, calculate a value for K_{sp} of silver iodide.
[1]

$[Ag^+] = [I^-]$
$K_{sp} = (8.9 \times 10^{-9})^2$
$= \underline{\mathbf{7.92 \times 10^{-17}\ mol^2\ dm^{-6}}}$

(iii) Using your answer in **(c)(ii)**, calculate the solubility of AgI in 0.0125 mol dm^{-3} $AgNO_3$.
[2]

Let solubility of AgI in 0.0125 mol dm^{-3} $AgNO_3$ be x mol dm^{-3}.

$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$

$K_{sp} = [Ag^+][I^-] = (0.0125 + x)\,(x) = 7.92 \times 10^{-17}$

It can be assumed that $x << 0.0125$ such that $(0.0125 + x) \approx 0.0125$

$(0.0125)\,(x) = 7.92 \times 10^{-17}$

$x = 6.34 \times 10^{-15}$ mol dm^{-3}

Solubility of AgI in 0.0125 mol dm^{-3} $AgNO_3$ = **6.34×10^{-15} mol dm^{-3}**

(iv) When silver nitrate is added to solution containing chloride ions, a white precipitate is observed. The white precipitate dissolves when aqueous ammonia was added. Upon adding of aqueous sodium bromide to the resultant mixture, a cream precipitate is obtained.

With the aid of suitable equations, explain the chemistry of the reactions occurring.

[3]

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
White ppt is formed due to the formation of insoluble AgCl.

$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + Cl^-$
White ppt dissolves due to the formation of a complex ion.

$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
Cream ppt is obtained when NaBr is added to the resultant mixture because K_{sp} of AgBr < K_{sp} of AgCl so ionic product still exceeds K_{sp} of AgBr

(v) When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$ is given by the following equation.

$$\Delta G^{\ominus}_{ppt} = 2.303\ RT \log_{10} K_{sp}$$

For silver fluoride, its K_{sp} value is 1.006 at 298 K.

Use the equation given above to deduce if silver fluoride is soluble in water at 298 K. Explain your answer.

[2]

$\Delta G^{\ominus}_{ppt} = 2.303\ RT \log_{10} K_{sp}$
$= 2.303(8.31)(298)(\log_{10} 1.006)$
$= +14.8$ J mol^{-1}

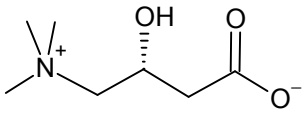
Since $\Delta G^{\ominus}_{ppt} > 0$, precipitation will not occur.
Therefore, AgF is soluble in water at 298 K.

[Total: 23]

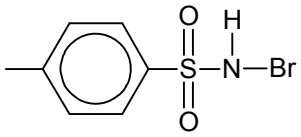
Section B

Answer **one** question from this section.

4 Levocarnitine is a quaternary ammonium compound involved in metabolism in most mammals.



levocarnitine



bromamine-T

(a) A kinetic study on the reaction between levocarnitine and bromamine-T, in the presence of $RuCl_3$, was carried out in aqueous hydrochloric acid.

The following equilibrium exists for $RuCl_3$ in aqueous hydrochloric acid.

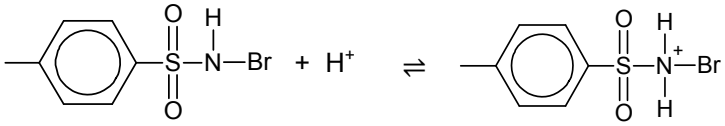
$$[RuCl_5(H_2O)]^{2-} + Cl^- \rightleftharpoons [RuCl_6]^{3-} + H_2O$$

Explain why $[RuCl_6]^{3-}$ is likely to be the reactive species instead of $[RuCl_5(H_2O)]^{2-}$ in this study.

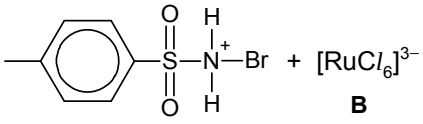
[1]

By Le Chatelier's Principle, the presence of **chloride ions from aqueous HCl** will shift the **position of equilibrium to the right**, favouring the formation of $[RuCl_6]^{3-}$.

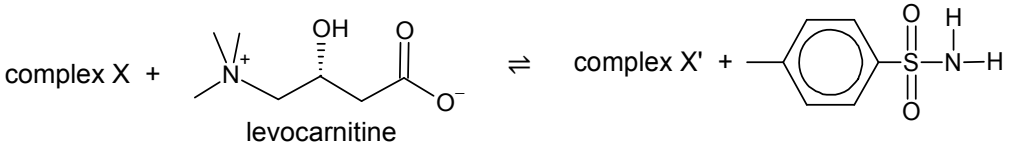
(b) The mechanism for the reaction between levocarnitine and bromamine-T was proposed as follows.



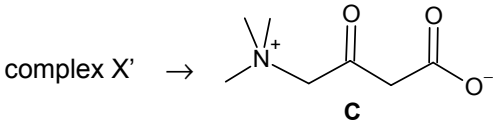
bromamine-T **A** step 1



B complex X step 2



levocarnitine complex X' step 3



C step 4

(i) Use the Lewis theory of acids and bases to identify and explain the role of bromamine-T in step 1.

[1]

Bromamine-T acts as a **Lewis base** in step 1 as it **donates its lone pair of electrons** on N atom to H^+.

(ii) The species in the equations shown have various roles. They can be reactants, products, catalysts or intermediates.

Suggest, with a reason in each case, the roles of the species **A**, **B** and **C**.

[3]

A is an **intermediate** as it was **formed in step 1 and then reacted in step 2**.

B is a **catalyst** as it **reacted in step 2 and was regenerated in step 4**.

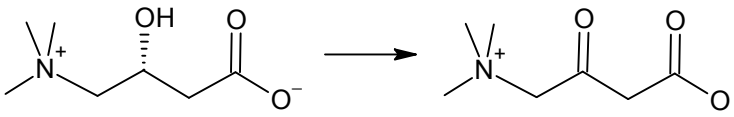
C is a **product** as it was **formed in step 4 and not reacted in other steps**.

(iii) State the type of reaction that levocarnitine had undergone with bromamine-T. Explain your answer in terms of changes in oxidation number.

[2]

Oxidation

The oxidation number of **carbon** (bonded to -OH group) **increased from 0 in levocarnitine** to **+2 in species C**.



levocarnitine **C**

(c) A series of experiments were carried out at different temperatures under pseudo-first order conditions with respect to bromamine-T.

The value of the observed rate constant, *k'*, for the catalysed reaction was determined at each temperature and the results are summarised in the table below.

k' / 10^4 s^{-1}	temperature, T / K
1.82	293
3.00	303
4.62	313
7.30	323

The activation energy, E_a, and the pre-exponential factor, *A*, which is a constant, for the reaction can be determined from the equation.

$$k' = Ae^{\frac{-E_a}{RT}}$$

R is the molar gas constant.
T is the reaction temperature in Kelvin.
k' is the observed rate constant at a chosen temperature.

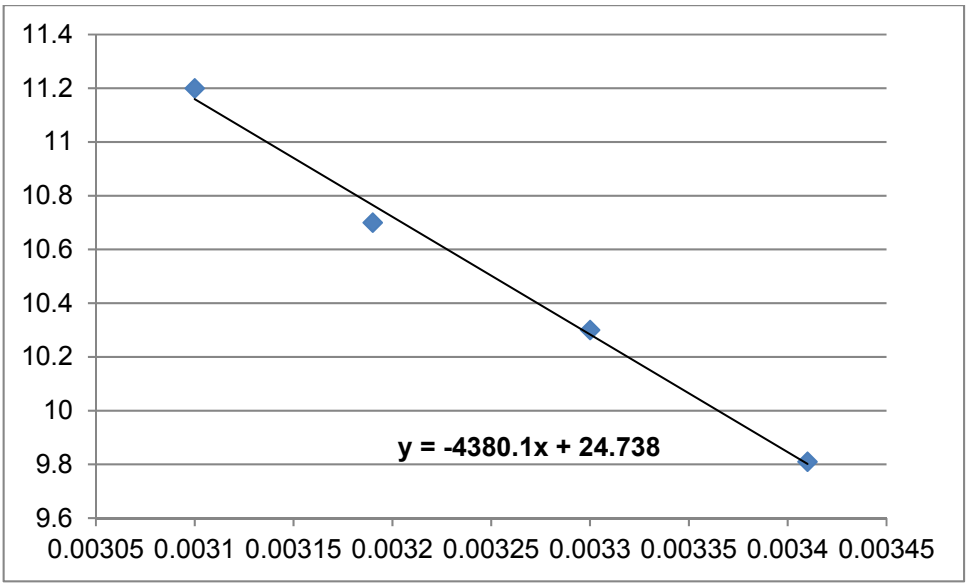
(i) Calculate the values of ln *k*' and $\frac{1}{T}$ for each of the experiments above.

[2]

k' / 10^4 s^{-1}	ln *k*'	temperature, T / K	$\frac{1}{T}$ / K^{-1}
1.82	9.81	293	0.00341
3.00	10.3	303	0.00330
4.62	10.7	313	0.00319
7.30	11.2	323	0.00310

(ii) Hence plot a graph of ln *k*' against $\frac{1}{T}$ and determine E_a from the gradient of the best-fit line which is $\frac{-E_a}{R}$.

[4]

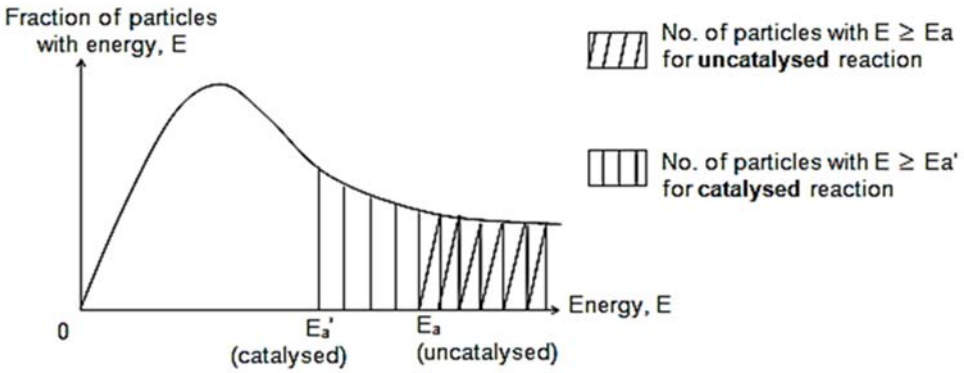


Gradient = $\frac{-E_a}{R}$ = –4380.1 K

Hence E_a = 36399 J mol^{-1} = **36.4 kJ mol^{-1}**

(iii) How would you expect the activation energy and rate of the reaction to be different if the reaction was uncatalysed? Explain your answer with the aid of a Boltzmann distribution curve.

[3]



The activation energy will be **higher** and the rate of reaction **slower** if the reaction was uncatalysed.

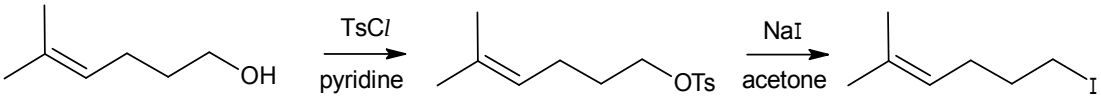
When a catalyst is used,

- reaction takes place via an alternative pathway that requires a lower activation energy
- there are more reactant particles with energy ≥ E_a and frequency of effective collisions increases
- rate of reaction increases, since the rate of reaction is proportional to the frequency of effective collisions.

(d) Tosyl chlorides (TsC*l*) are often used to convert alcohols (ROH) into alkyl tosylates (ROTs) as shown below.

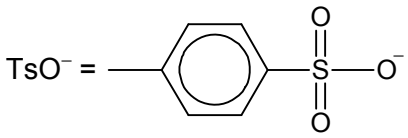
$$\text{ROH} \xrightarrow[\text{pyridine}]{\text{TsC}l} \text{ROTs}$$

This conversion allows alcohols to undergo nucleophilic substitution reactions by converting the poor leaving group (OH) into a good leaving group (OTs). An example of this application is given below.



(i) The tosylate group is a better leaving group than the alcohol group due the greater stability of the TsO^- ion formed compared to OH^-.

Suggest an explanation for the stability of the TsO^- ion.

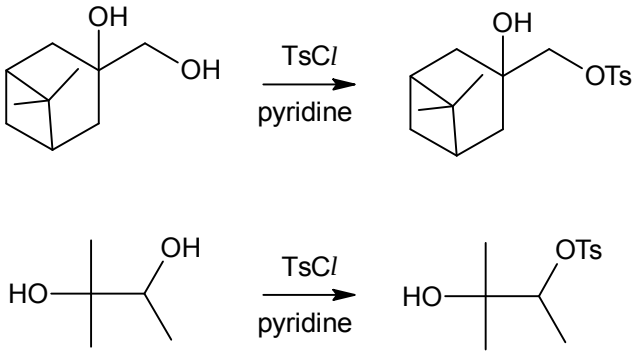


[1]

TsO^- is **resonance stabilised** as the **negative charge on oxygen is delocalised into the adjacent S=O bond**.

(ii) The conversion of alcohols into alkyl tosylates using tosyl chlorides is selective in nature.

Consider the following examples involving diols and suggest a factor that affects the selectivity of the conversion. Explain your answer.

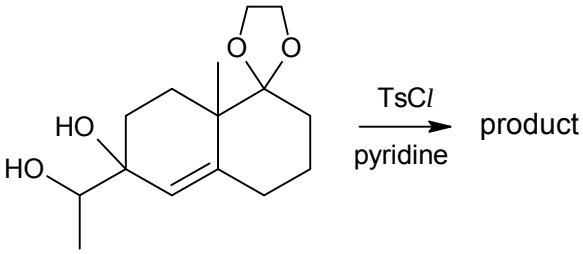


[2]

Degree of substitution of alcohol OR degree of **steric hindrance around alcohol** group.

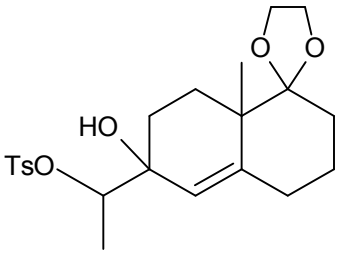
Tosyl group is a **bulky group** so TsCl can **approach the less hindered/ less substituted alcohol more easily**.

(iii) Predict the product of the following conversion.



The  ring remains unaltered in the reaction.

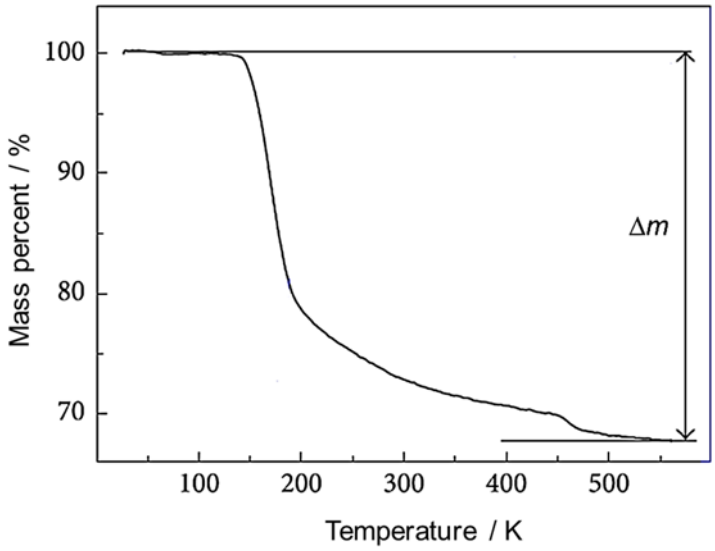
[1]



[Total: 20]

5 (a) Thermogravimetric analysis (TGA) is a technique where the mass of a sample in a controlled atmosphere is recorded as a function of temperature as the temperature of the sample is increased.

A sample of lithium pentaborate pentahydrate ($LiB_5O_8.5H_2O$) was subject to TGA and the graph obtained is shown below.



Suggest an explanation, supported with relevant calculations, for the loss in mass (Δm) of $LiB_5O_8.5H_2O$ observed in the graph.

[M_r ($LiB_5O_8.5H_2O$) = 278.9]

[2]

The mass loss is likely due to the **loss of the five water molecules** in $LiB_5O_8.5H_2O$.

% mass loss = $\frac{5 \times 18}{278.9} \times 100$ = **32.3 %** which agrees well with the value obtained from the graph (≈ 32.5 %).

(b) The sample of $LiB_5O_8.5H_2O$ used in **(a)** was synthesised as a system of Li_2O, B_2O_3 and H_2O in the laboratory.

(i) Deduce the molar ratio of Li_2O : B_2O_3 : H_2O in a pure sample of $LiB_5O_8.5H_2O$.

[1]

Since $LiB_5O_8.5H_2O \equiv \frac{1}{2} Li_2O \equiv \frac{5}{2} B_2O_3 \equiv 5H_2O$,

molar ratio of Li_2O : B_2O_3 : H_2O = **1 : 5 : 10**

(ii) Aqueous sodium hydroxide can be used to react with B_2O_3 to determine its actual amount in the sample.

Given that B_2O_3 and Al_2O_3 have similar reactions with aqueous sodium hydroxide under appropriate conditions, write a balanced equation for the reaction between B_2O_3 and aqueous sodium hydroxide.

[1]

$B_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[B(OH)_4]$

(c) Li_2O can be produced from the thermal decomposition of lithium peroxide, Li_2O_2.

(i) State and explain how the lattice energies of Li_2O and Li_2O_2 would differ.

[2]

$\Delta H_{latt}^{\ominus}(Li_2O)$ will be **more exothermic** than that of $\Delta H_{latt}^{\ominus}(Li_2O_2)$

For ionic compounds, $|\Delta H_{latt}| \propto \left|\frac{q_+ q_-}{r_+ + r_-}\right|$

cationic charge (q_+) and radius (r_+) are the **same** for both compounds.
anionic charge (q_-) is the **same** for both compounds.
Anionic radius (r_-): $O^{2-} < O_2^{2-}$

(ii) Lithium peroxide reacts with carbon dioxide according to the equation shown below.

$$2Li_2O_2(s) + 2CO_2(g) \rightarrow 2Li_2CO_3(s) + O_2(g)$$

State the change in oxidation number of oxygen as Li_2O_2 is converted into the products.

[2]

The oxidation number of O **increases from –1 in Li_2O_2 to 0 in O_2**.

The oxidation number of O **decreases from –1 in Li_2O_2 to –2 in Li_2CO_3**.

(iii) Calculate the highest temperature reached when the 2.50 g of lithium carbonate was dissolved in 30 cm^3 of water at room temperature. The standard enthalpy change of solution of lithium carbonate is –18.2 kJ mol^{-1}.

[2]

Moles of Li_2CO_3 = $2.50 / (6.9 \times 2 + 12 + 16 \times 3) = 0.033875$ mol
$q = 18.2 \times 10^3 \times 0.033875 =$ **616.53 J**

$\Delta T = q / mc = 616.53 / (30 \times 4.18) = 4.9165$ °C/K
Highest temperature = 20 + 4.9165 = **24.9 °C** OR **298 K**

(iv) Calculate the pH of the resulting solution formed in **(c)(iii)** given that the K_b of carbonate ion is 1.995×10^{-4} mol dm^{-3}.

[3]

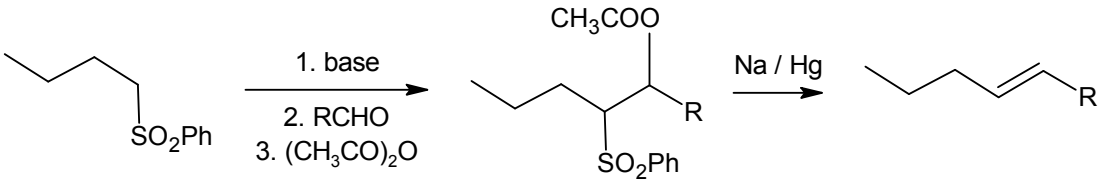
$[CO_3^{2-}] = \frac{0.033875}{0.030} = 1.129$ mol dm^{-3}

$[OH^-] = \sqrt{\left(K_b \times \left[CO_3^{2-}\right]\right)}$
$= \sqrt{(1.995 \times 10^{-4} \times 1.129)}$
$= 0.01501$ mol dm^{-3}

$pH = 14 - pOH = 14 + \log_{10}(0.01501) =$ **12.2**

(d) Phenylsulfonyl ($PhSO_2$) and acetate (CH_3COO) groups on adjacent carbons in a starting material can be lost to form an alkene via Julia olefination.

An example of Julia olefination is as follows.

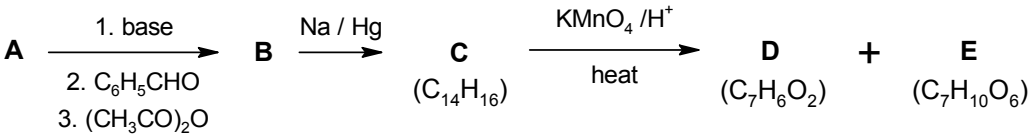


(i) Suggest the type of reaction occurring in the final step of Julia olefination.

[1]

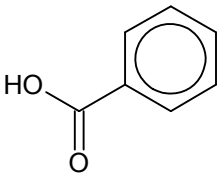
Elimination

Consider the reaction scheme below involving Julia olefination.



(ii) Compound **D** effervesces with sodium carbonate. Suggest the structure of **D**.

[1]



D

$(C_7H_6O_2)$

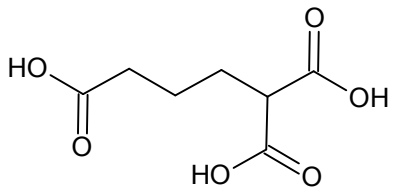
(iii) Compound **E** is non-cyclic and has six carbons in the longest continuous carbon chain. It also does **not** contain any chiral carbon.

One mole of **E** reacts with three moles of thionyl chloride ($SOCl_2$) to liberate acidic gas.

Identify the functional group present in **E** and suggest its structure.

[2]

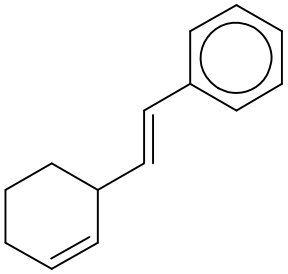
Functional group: **carboxylic acid**



E
($C_7H_{10}O_6$)

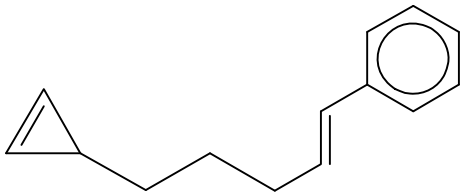
(iv) Hence suggest the structures of compounds **A** to **C**.

[3]

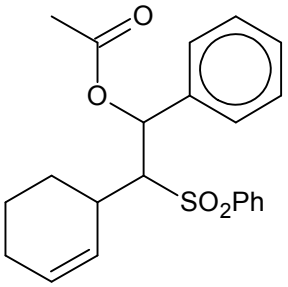


C
($C_{14}H_{16}$)

OR

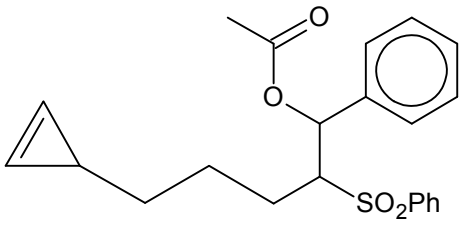


C
($C_{14}H_{16}$)

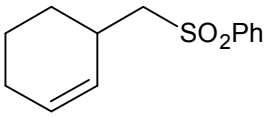


B

OR

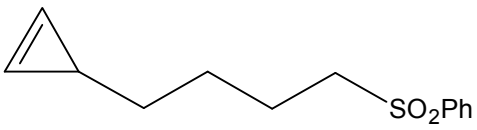


B



A

OR



A

[Total: 20]