HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**13S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9647/03

Paper 3 Free Response

22 September 2014

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

INSTRUCTIONS TO CANDIDATES

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

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

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

Answer any **four** questions.

Begin each question on a **new** piece of paper.

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers.

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

At the end of the examination, fasten all your work securely together.

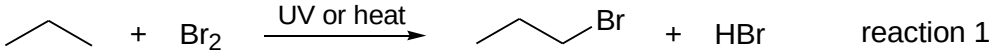
Write down the **question numbers** for the questions that you have attempted on the **cover page** provided.

Answer any **four** questions.

1 **(a)** Describe and explain the trend observed for the reactions of chlorine, bromine and iodine with hydrogen.

[2]

(b) Bromoalkanes can be synthesised by reacting alkanes and bromine in the presence of UV light or heat. One example of such reaction is shown below:



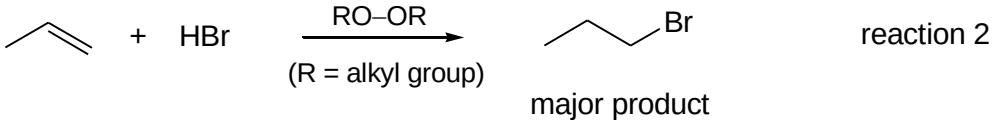
reaction 1

(i) Describe the mechanism for reaction 1. Indicate any unpaired electrons using a dot (•).

(ii) State how monosubstituted product can be favoured for reaction 1.

[4]

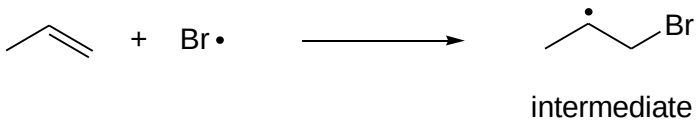
(c) Another way to synthesise bromoalkanes is by reacting alkenes with hydrogen bromide, as shown in reaction 2 below. This is known as a radical addition reaction, where HBr is added across the alkene in a reaction involving radicals.



reaction 2

(i) By considering the electrophilic addition of HBr on alkenes, suggest why the major product of reaction 2 is unusual.

The compound RO–OR in reaction 2 is used to generate a bromine radical, which will attack the alkene C=C bond to produce a radical intermediate as shown below:

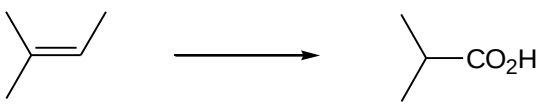


The radical intermediate will then abstract a hydrogen atom from HBr to form the major product in a subsequent step.

(ii) Explain why the bromine radical would attack the C=C bond.

(iii) Draw the structure of another possible radical intermediate. Compare the relative stabilities of the two radical intermediates to account for the major product formed.

(iv) Hence, propose a three-stage reaction scheme for the following transformation, naming the reagents and conditions used in each step. Draw the structures of the intermediate compounds.



[7]

(d) In the atmosphere, the ozone gas O_3 absorbs UV light and undergoes gas phase decomposition through the following mechanism:

Step 1: $O_3 = O_2 + O$

Step 2: $O_3 + O \rightarrow 2O_2$

The rate equation for the decomposition of ozone has the following form,

$$\text{rate} = k[O_3]^2[O_2]^{-1}$$

where k is the rate constant.

(i) State the units of k.

(ii) With an appropriate sketch of the Boltzmann distribution, explain how a rise in temperature affects the value of k.

The presence of a chlorine radical accelerates the gas phase decomposition of ozone through the following mechanism:

$$O_3 + Cl\bullet \rightarrow ClO\bullet + O_2$$
$$ClO\bullet + O \rightarrow Cl\bullet + O_2$$

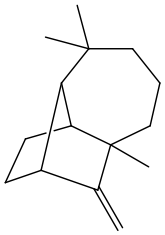
(iii) State the role of the chlorine radical in the mechanism above. Explain your answer.

(iv) Explain how chlorofluoroalkanes (CFCs) destroy the ozone layer.

[7]

[Total: 20]

2 Longifolene is a naturally occurring oily liquid found in pine trees.

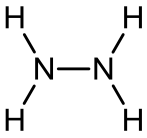


longifolene

(a) Explain why longifolene is not miscible with water.

[1]

(b) Hydrazine, ethylamine and ammonia are common bases used in chemical syntheses. The structure of hydrazine is shown below.

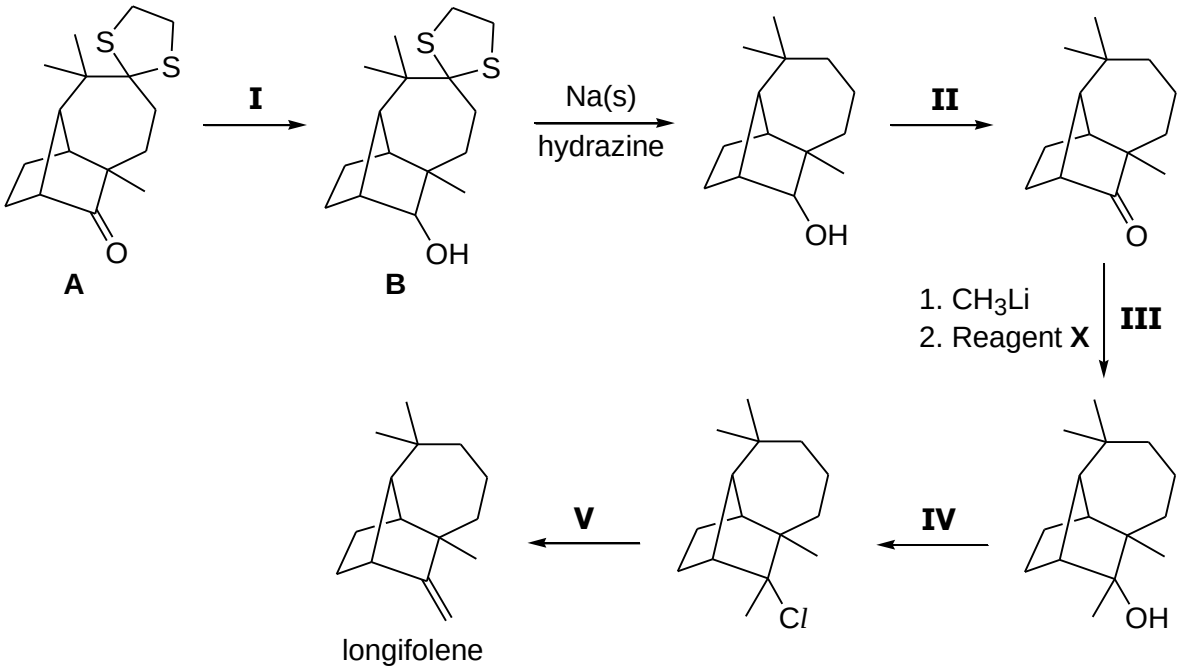


hydrazine

Describe and explain the relative basicities of hydrazine, ethylamine and ammonia.

[3]

(c) Part of the laboratory synthesis of longifolene by American Nobel Laureate Elias James Corey is shown below.



(i) Suggest reagents and conditions needed for reactions **I**, **II**, **IV** and **V**.

(ii) Suggest a simple chemical test to distinguish between compounds **A** and **B**.

[6]

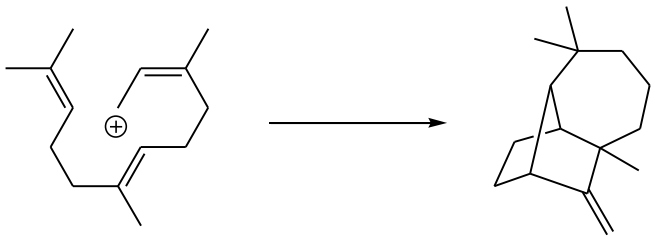
(d) **(i)** In reaction **III**, CH_3Li can be treated as a source of a CH_3^- anion. Draw a dot-and-cross diagram for the CH_3^- anion and state the geometry of the anion.

(ii) Suggest the identity of reagent **X** used in reaction **III**.

(iii) Name and draw out the full mechanism of reaction **III**. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.
(You may use **R** to represent parts of the molecule not involved in the reaction.)

[6]

(e) The natural synthesis of longifolene in pine trees involves the folding of a long chain farnesyl carbocation into longifolene.



farnesyl carbocation longifolene

(i) Deduce whether the ΔS of the folding process is positive or negative.

(ii) State the number of chiral carbons on longifolene.

(iii) Suggest why the smell of chemically synthesised longifolene in the laboratory is different from the samples of longifolene extracted from pine trees.

[4]
[Total: 20]

3 **(a)** The wide temperature range over which water is a liquid (m.p. 0 °C, b.p. 100 °C) and its polarity have given it a dominant position as a solvent for ionic species. In the search for alternative polar solvents, ammonia (m.p. –78 °C, b.p. –33 °C) is a logical choice.

(i) Explain in terms of electronegativity and the shape of the molecule, why the water molecule is polar.

(ii) Give two reasons why the boiling point of water is higher than that of ammonia.

[4]

(b) Solid copper(II) hydroxide dissolves readily in excess aqueous ammonia as well as in liquid ammonia, forming similar complex ions.

(i) Explain what is meant by the term *complex ion*.

(ii) Give one reason why transition metal ions have a strong tendency to form complex ions.

(iii) Suggest an equation for the reaction between solid copper(II) hydroxide and liquid ammonia, and the colour of the solution formed.

[5]

(c) Like pure water, pure liquid ammonia is weakly ionised.

The ionic product of water, K_w, is 1.0×10^{-14} mol^2 dm^{-6} at 25 °C while that of liquid ammonia, K_{NH_3}, is 1.0×10^{-30} mol^2 dm^{-6} at –33 °C.

Write an equation for the auto-ionisation of liquid ammonia and use it to calculate a value for the concentration (in mol dm^{-3}) of ammonium cations in liquid ammonia at –33 °C.

[2]

(d) A student plans to prepare an ammonia / ammonium chloride buffer with pH 9.
He is given the following solutions.

- 100 cm^3 of an aqueous solution containing 0.28 mol of ammonia
- 1.00 mol dm^{-3} dilute hydrochloric acid

Determine the volume of hydrochloric acid he could add to the 100 cm^3 aqueous ammonia to obtain the required buffer.
(K_b of NH_3 = 1.8×10^{-5} mol dm^{-3})

[2]

(e) Phenylamine and benzene both undergo substitution reactions with bromine.

State the reagents and conditions needed to carry out each of these reactions. Comment on and explain why there is a difference in the conditions used and the number of bromine atoms in the organic product.

[4]

(f) When one mole of the dichloride **A**, $ClCH_2COCl$, is treated with $H_2N–CH_2CH_2–NH_2$ at room temperature, compound **B**, $C_4H_9ClON_2$, is obtained.

Treating **A** again with $H_2N–CH_2CH_2–NH_2$ but with heating produces **C**, $C_4H_8ON_2$.

Draw the structures of **B** and **C**, and explain the difference in the reactivity of the two chlorine atoms in **A**.

[3]
[Total: 20]

4 **(a)** Phosphorus pentachloride, PCl_5, is a white, moisture-sensitive solid. It is a dangerous substance as it reacts violently with water

(i) Write a balanced equation for the reaction between PCl_5 and a small amount of water.

(ii) The above reaction of PCl_5 with water involves the replacement of –Cl with –OH twice, followed by a loss of water. Step 1 of the reaction is shown below.

Step 1: $PCl_5 + H_2O \rightarrow PCl_4OH + HCl$

Write equations to show the next two steps for the formation of the products in **(a)(i)** from PCl_5.

[3]

(b) **(i)** PCl_5 reacts completely with a large excess of water to form phosphoric acid, H_3PO_4. Write a balanced equation for this reaction. State the type of reaction taking place and the approximate pH value of the resultant solution.

(ii) State the oxidation number of phosphorus in phosphoric acid.

(iii) Given that H_3PO_4 has three hydroxyl groups, draw its displayed formula.

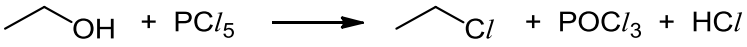
Two moleules of phosphoric acid can undergo a condensation reaction producing diphosphoric acid, $H_4P_2O_7$, and water. The reaction involves an –OH group from each H_3PO_4 molecule forming an oxygen bridge between the two phosphoric acid units.

(iv) Draw the structure of diphosphoric acid.

(v) This condensation reaction may continue to give triphosphoric acid, $H_5P_3O_{10}$, and tetraphosphoric acid. Give the molecular formula of tetraphosphoric acid.

[7]

(c) Phosphorus pentachloride can be used to convert alcohols into chloroalkanes. For example,



The mechanism of converting ethanol into chloroethane is thought to involve the following steps:

- The initial formation of a P−O bond, which is a result of a nucleophilic substitution on P by the lone pair of electrons on the ethanol's oxygen atom, together with a loss of Cl^-.
- This is followed by Cl^- acting as a base, abstracting a proton from the –OH group.
- Lastly, a nucleophilic substitution on the carbon atom by another Cl^- ion takes place, resulting in the formation of a P=O bond and the breaking of a P−Cl bond simultaneously.

(i) Use the information given above to draw out the three-step full mechanism for the reaction of ethanol with PCl_5, showing all charges and using curly arrows to show the movement of electron pairs.

(ii) Considering the bonds formed, suggest **one** reason that drives this reaction to completion.

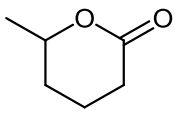
(iii) Ethanol can be converted to both ethanal and ethanoic acid. State the reagents and conditions you could use to obtain **each** product.

[6]

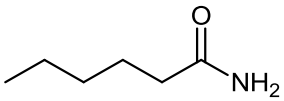
(d) Suggest methods by which the following compounds **X**, **Y** and **Z** could be distinguished from each other by chemical tests.

The distinguishing of the compounds may rely on a preliminary breaking-up of the compounds and subsequent testing of the reaction products.

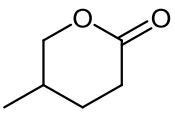
State any observations you would make with each compound.



X



Y



Z

[4]
[Total: 20]

5 **(a)** State the electronic configuration of chromium.

[1]

(b) A black oxide CrO, dissolves readily in dilute acid to form a sky blue solution **A**. When left in the air, the solution changes to a green solution **B**. When a small amount of sodium hydroxide is added to **B**, a grey green precipitate **C** is formed. Upon the addition of excess sodium hydroxide, a complex $[Cr(OH)_6]^{3-}$ is formed which reacts with H_2O_2 to form a yellow solution **D**.

(i) Identify the unknown chromium containing species, **A**, **B**, **C** and **D**.

(ii) State the reaction that has occurred in the conversion of $[Cr(OH)_6]^{3-}$ to **D**.

[5]

(c) In an acidic medium, chromium(VI) exists as $Cr_2O_7^{2-}$.

(i) State one reason why aqueous Cr^{6+} ion does not exist.

(ii) Write the equation for the conversion of solution **D** to $Cr_2O_7^{2-}$ and use Le Chatelier's Principle to explain the effect of increasing $[H^+]$ on this equilibrium.

[3]

(d) A hydrated salt **E** contains 13.0 % of Cr, 27.0 % of H_2O and 60.0 % of Br by mass. An aqueous solution containing 0.400 g of **E** immediately gives 0.188 g of cream precipitate when treated with aqueous silver nitrate.

(i) Calculate the mole ratio of Cr: H_2O: Br in the hydrated salt **E**.

(ii) Identify the cream precipitate and hence, determine the formula of the complex cation in the hydrated salt **E**.

(iii) Hence, draw the structure of the complex ion present in **E**, showing clearly how the ligands are arranged around chromium.

[4]

(e) Fifty years ago, most sulfuric acid was manufactured by the "lead chamber process". Sulfur dioxide was mixed with air, steam and nitrogen dioxide in lead-lined chambers.

With the aid of $E^{\ominus}$ values from the *Data Booklet*, explain the following observations.

(i) The chamber used in the process must not be made of steel as iron rapidly dissolves in concentrated sulfuric acid, whereas lead is only superficially attacked.

(ii) A colour change is observed when SO_2 is bubbled into $K_2Cr_2O_7(aq)$.

[4]

(f) The equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is reached fairly quickly.

When 4.60 g of N_2O_4 is placed in an evacuated 0.740 dm^3 flask at 300 K, the equilibrium pressure is 2.00 atm.

(i) Calculate the total number of moles of gas at equilibrium, assuming that the gases behave ideally.

(ii) Write an expression for K_p for the reaction and calculate its value at 300 K.

[3]

[Total:20]