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**DUNMAN HIGH SCHOOL**  
**Preliminary Examination 2016**  
**Year 6**

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**H2 CHEMISTRY**

**9647/03**

Paper 3 Free Response

**20 September 2016**

**2 hours**

Additional Materials: Data Booklet  
Writing Papers  
Graph Paper

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**INSTRUCTIONS TO CANDIDATES**

Write your **name**, **index number** and **class** on this question paper and on the Cover Sheet provided.

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 staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

Start each question on a fresh sheet 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.

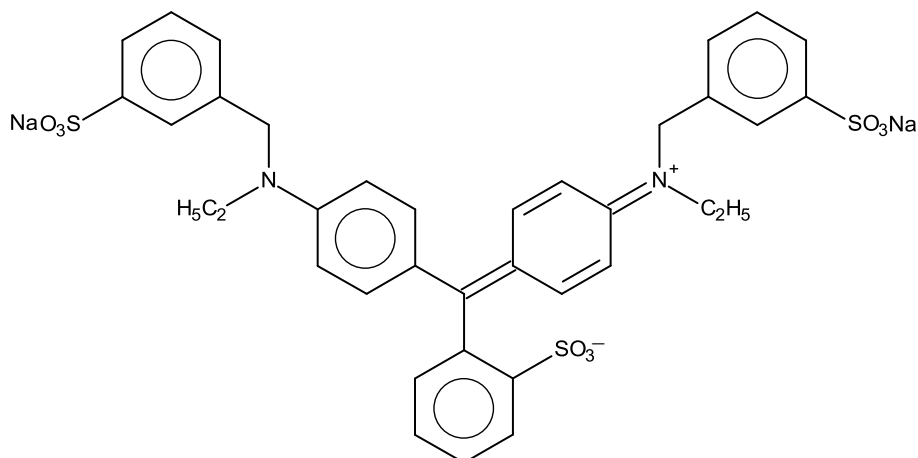
At the end of the examination:

- Fasten all work securely together with the Cover Sheet on top.
- Hand in the question paper separately.

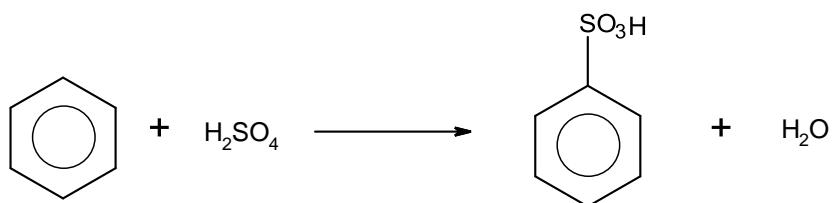
The total marks for this paper is 80 marks.

Answer *any four* questions.

- 1 Blue #1 ( $\text{Na}_2\text{C}_{37}\text{H}_{34}\text{N}_2\text{S}_3\text{O}_9$ ) is a synthetic food colouring often found in ice cream.



- (a) One of the main compounds used to produce Blue #1 is benzenesulfonic acid, which is produced by heating benzene under reflux with concentrated sulfuric acid for several hours.

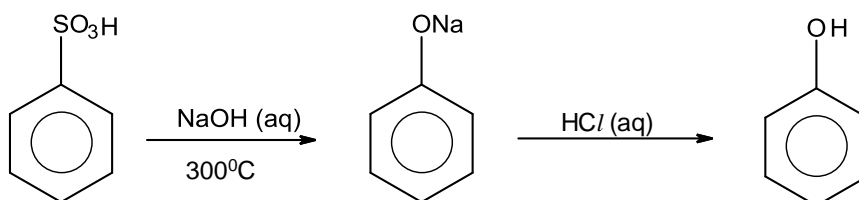


- (i) The first step of the mechanism involves the protonation of one molecule of sulfuric acid by another and the loss of a molecule of water.

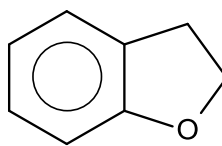
Name the type of reaction and describe the mechanism. In your answer, show relevant lone pairs and charges, and use curly arrows to indicate the movement of electrons.

[4]

- (ii) Benzenesulfonic acid is a useful starting material as it can be easily converted to phenol by heating with  $\text{NaOH(aq)}$  at  $300^\circ\text{C}$  followed by acidification. It also has similar chemical reactivity as nitrobenzene.



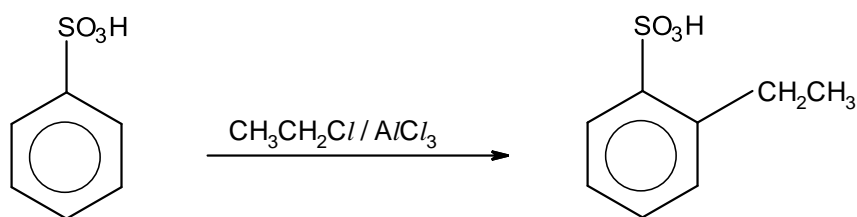
Compound **A** can be synthesised from either benzenesulfonic acid or ethylbenzene in not more than 4 steps.



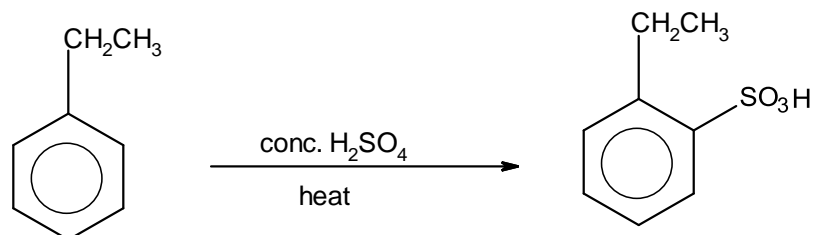
**A**

The first step of the synthesis using either benzenesulfonic acid or ethyl benzene is as shown below in Scheme 1 and 2 respectively:

**Scheme 1:**



**Scheme 2:**



Identify the correct scheme that will give compound **A** and copy the synthetic scheme in your answer.

Using information in **(a)(ii)**, suggest the next three steps to synthesise compound **A**. Show all intermediates, reagents and conditions clearly in your synthetic route.

[4]

- (b) Blue #1 can be oxidised by household bleach to form colourless products, as represented by the equation below.



To study the kinetics of the reaction, a student used an UV spectrophotometer to study the absorbance of Blue #1 over time during the bleaching process.

In experiment 1, the student mixes 3.0 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> Blue #1, 1.0 cm<sup>3</sup> of water and 0.5 cm<sup>3</sup> of 3.5 mol dm<sup>-3</sup> bleach together. The results of experiment 1 are as shown below.

Time (s)	15	30	45	60	75	90	105	120	135
Absorbance	0.495	0.424	0.371	0.328	0.285	0.251	0.218	0.191	0.170

- (i) Explain why bleach is used in large excess as compared to that of Blue #1. [1]
- (ii) Given that absorbance measured varies linearly with the concentration of Blue #1, use a suitable graphical method to determine the order of reaction with respect to the blue food colouring, Blue #1. [3]
- (iii) The student subsequently conducted a few more experiments using other volumes of Blue #1 and bleach. The table below shows the results obtained.

Experiment	Volume of Blue #1 / cm <sup>3</sup>	Volume of distilled water / cm <sup>3</sup>	Volume of bleach / cm <sup>3</sup>	Rate constant
1	3.0	1.0	0.5	
2	4.0	0.0	0.5	0.00882
3	3.0	0.5	1.0	0.01698

Using results from (b)(ii), determine the rate constant for experiment 1. Hence, deduce the overall order of reaction, showing your reasoning clearly.

[3]

- (c) (i) Household bleach is also often known as “chlorine water”. The active chemical responsible for the bleaching action in household bleach is the anion, OCl<sup>-</sup>, which is easily formed by the disproportionation of chlorine in water.

Write a balanced equation between chlorine and water, and hence, suggest the identity of the other compound formed.

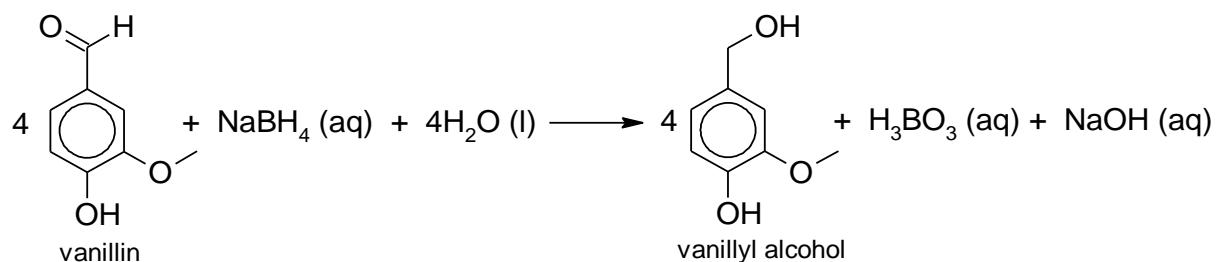
[1]

- (ii) Chlorine reacts with Period 3 elements, Mg and Si, to give chlorides. The two chlorides differ in their reaction with water. Describe their differences, and explain them in terms of the different structures and types of chemical bonding. Write an equation for the reaction, if any.

[4]

[Total: 20]

- 2 Vanillin and vanillyl alcohol (derived from vanillin) are both used as flavouring, usually in sweet foods such as chocolate. Vanillyl alcohol is commonly synthesised via the reduction of vanillin using sodium borohydride, as shown below.



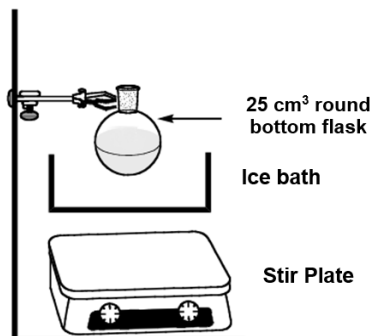
- (a) (i) Draw a 'dot-and-cross' diagram to show the bonding in sodium borohydride. [1]
- (ii) Suggest why sodium borohydride is used in this reduction instead of lithium aluminium hydride. [1]
- (iii) Given that the melting points of vanillin and vanillyl alcohol are 355 K and 388 K respectively, predict and explain the sign of the entropy change of reaction at 360 K. [1]
- (iv) A higher temperature leads to a faster rate of reaction. However, thermodynamic factors must also be taken into consideration when considering appropriate conditions for a reaction.

Explain how higher temperatures will affect the thermodynamic outcome.

[2]

**(b)** The procedure for the reduction of vanillin to vanillyl alcohol is as follows:

1. Place 2 g of vanillin in a 25 cm<sup>3</sup> round bottom flask followed by 4 cm<sup>3</sup> ethanol. Add a magnetic stirrer, clamp the flask above a stir plate and commence stirring at room temperature to dissolve vanillin.
2. After the vanillin dissolves, add an ice bath under the flask to cool the solution.



3. In a separate reaction vial, dissolve 0.5 g of NaBH<sub>4</sub> in 3.8 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> NaOH solution.
4. Using a glass pipette, slowly add the NaBH<sub>4</sub> solution dropwise to the vanillin solution over a period of 10 minutes.
5. Only after the addition is complete, remove the ice bath. This is because NaBH<sub>4</sub> decomposes at high temperatures.
6. Stir the resulting mixture for 10 minutes at room temperature.
7. Add 6 mol dm<sup>-3</sup> HCl dropwise until the evolution of hydrogen gas stops.
8. Stir to allow the product to precipitate from solution.

**(i)** State a reason why sodium borohydride must be added dropwise to the reaction mixture (in Step 4).

[1]

**(ii)** In Step 7, hydrochloric acid was added to react with excess sodium borohydride present in the reaction mixture. Write an equation for this reaction, given that boric acid (H<sub>3</sub>BO<sub>3</sub>) is one of the products formed.

[1]

**(iii)** State one way you could modify the procedure to increase the isolated yield.

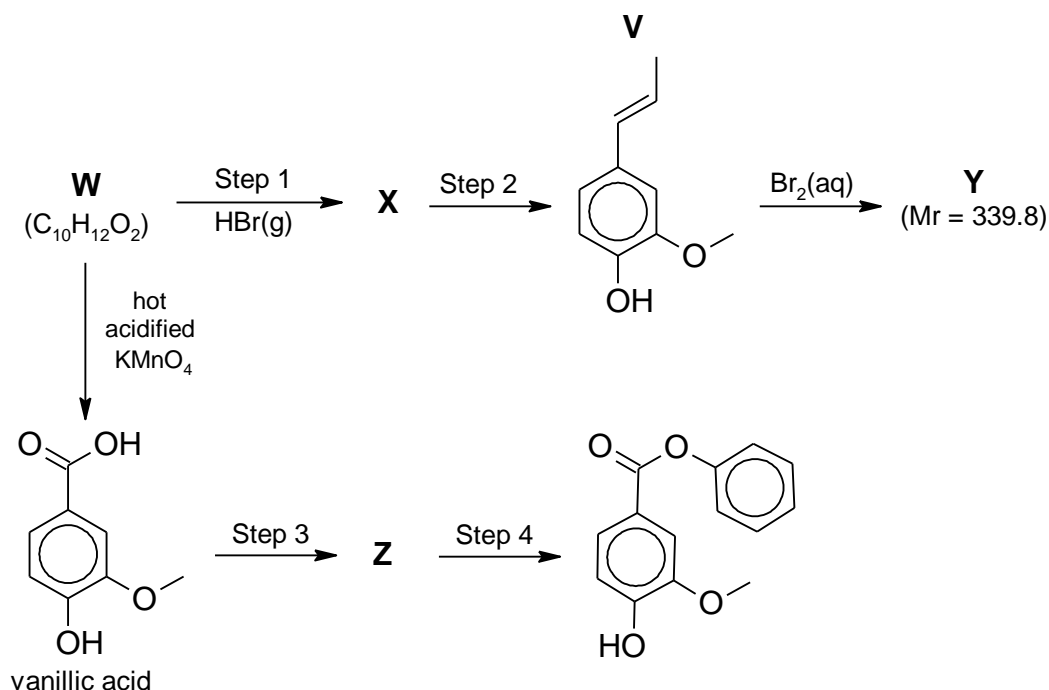
[1]

**(iv)** A preliminary way to determine whether the reaction has gone to completion is to draw out aliquots of the reaction mixture and test for the presence of vanillin in it.

Describe a simple chemical test to test for the presence of vanillin. Give the expected observations and write a balanced equation for the reaction with vanillin.

[2]

- (c) Compound **W**, an isomer of **V**, can also be used as a starting reagent to synthesise vanillic acid and other organic compounds shown in the reaction scheme below.



- (i) Draw the structures of compounds **W**, **X** and **Y**, and state the reagents and conditions for Steps 2 and 4.

[4]

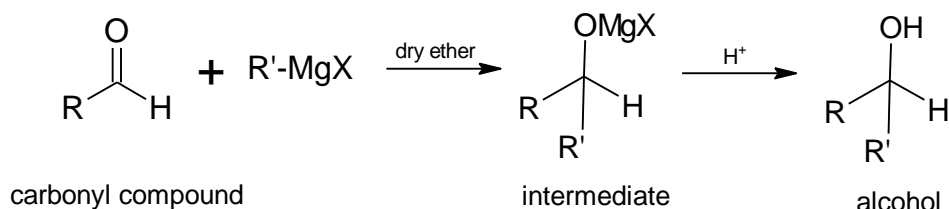
- (ii) Vanillic acid (4-hydroxy-3-methoxybenzoic acid) has an isomer, 2-hydroxy-3-methoxybenzoic acid.

State which of the two isomers has a higher boiling point. Explain your answer.

[2]

- (d) Organometallic compounds, usually a metal attached to an R group, can be used to convert carbonyl compounds to alcohols.

A common type of organometallic compound are Grignard reagents. They have the formula  $RMgX$ , where X is a halogen and R is an alkyl or aryl group.



Draw the structure of the intermediate formed when vanillin reacts with ethylmagnesium bromide.

[1]

- (e) The chemistry of lithium and its compounds differs significantly from the rest of the Group I metals. In fact, lithium shows many similarities to magnesium exemplifying the so-called “diagonal relationship” because of their positions in the periodic table.

In an experiment, a sample of solid magnesium amide,  $\text{Mg}(\text{NH}_2)_2$  and lithium amide,  $\text{LiNH}_2$  are heated separately.

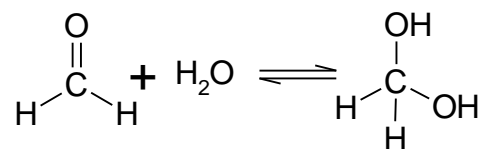
Magnesium amide decomposes when heated to give magnesium nitride,  $\text{Mg}_3\text{N}_2$  and ammonia gas.

- (i) Write a balanced chemical equation for the decomposition of lithium amide. [1]
- (ii) With reference to *Data Booklet*, predict the decomposition temperature of  $\text{LiNH}_2$  when compared to  $\text{Mg}(\text{NH}_2)_2$ , given that the ionic radius of  $\text{Li}^+$  is 0.060 nm. Explain your answer. [2]

[Total: 20]



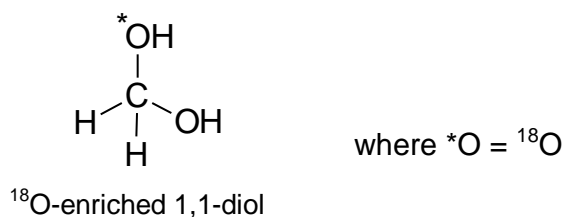
- 3 (a) Methanal undergoes reaction with water to yield 1,1–diol. The reaction is reversible and the 1,1–diol can eliminate water to regenerate methanal.



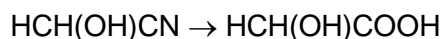
- (i) State the type of reaction for the above reaction. [1]
- (ii) The reaction is slow but the rate is increased by the addition of a small amount of NaOH as catalyst. Suggest why NaOH is needed to initiate the reaction in the mechanism. [1]

The oxygen in water is primarily 99.8%  $^{16}\text{O}$  but water enriched with the heavy isotope,  $^{18}\text{O}$ , is also available. When methanal is dissolved in  $^{18}\text{O}$ –enriched water, the isotopic label becomes incorporated into the 1,1–diol which regenerates methanal.

- (iii) Using your answer to (a)(ii), suggest how  $^{18}\text{O}$  is incorporated into the 1,1–diol.



- [1]
- (iv) The addition of water to aldehydes proceeds more rapidly than it does to ketones. Suggest a reason why. [1]
- (b) Methanal also reacts with HCN to form 2–hydroxyacetonitrile,  $\text{HCH}(\text{OH})\text{CN}$ . The 2–hydroxyacetonitrile formed can be further converted to 2–hydroxyethanoic acid, as shown below.



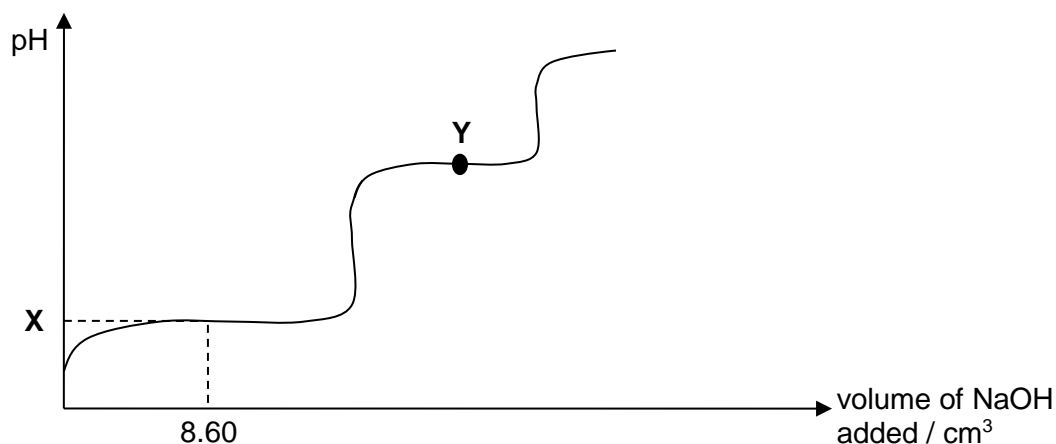
- (i) Explain whether 2–hydroxyethanoic acid has a larger or smaller  $K_{\text{a}}$  than ethanoic acid. [2]

Phenol and 2–hydroxyethanoic acid are weak Brønsted acids with  $\text{p}K_{\text{a}}$  values of 9.80 and 3.86 respectively.

A mixture of  $20.0 \text{ cm}^3$  of phenol and 2–hydroxyethanoic acid was titrated against a solution of  $1 \text{ mol dm}^{-3}$  of sodium hydroxide. Only 1 to 2 drops of phenolphthalein and bromothymol blue indicators are used in this titration.

It was found that the first colour change occurs at 17.20 cm<sup>3</sup> and the second colour change occurs at 26.80 cm<sup>3</sup> of sodium hydroxide used.

A sketch (not drawn to scale) of the pH titration curve is shown below.



- (ii) Both phenolphthalein and bromothymol blue are weak acids. State the effect on the volume of sodium hydroxide used for titration, if both indicators are added in larger amount.

[1]

- (iii) State the value of point X.

[1]

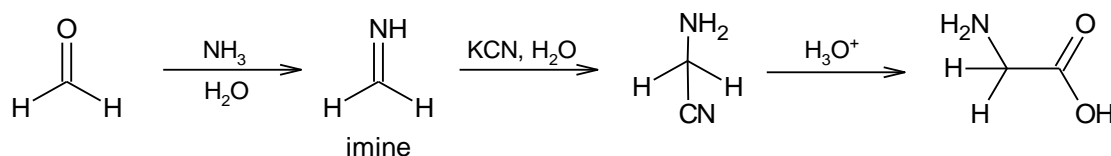
- (iv) Write an equation to illustrate how the species found in point Y can maintain the pH of a solution when a small amount of H<sup>+</sup>(aq) is added.

[1]

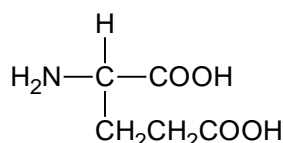
- (v) Calculate the concentration of phenol and 2-hydroxyethanoic acid in the original mixture.

[2]

- (c) The Strecker synthesis is a route to preparing amino acids. Methanal can be used to synthesise glycine, 2-aminoethanoic acid, in this way.



The amino acid shown below is glutamic acid.

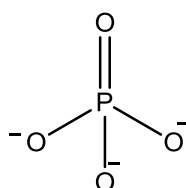


- (i) Identify the aldehyde-containing compound and the imine intermediate which are needed to synthesise glutamic acid via the Strecker synthesis. [2]

- (ii) Suggest, with a reason, if there is any difference in the optical activity of a sample of glutamic acid synthesised by Strecker's method and that of natural occurring glutamic acid. [1]

- (d) Glycine and glutamic acid are among the many amino acids which constitute the long amino acid sequence of *protein kinase*. *Protein kinase* is an enzyme which plays a major role in protein regulation. It modifies other proteins by chemically adding phosphate groups to them. This process is called phosphorylation.
- (i) In phosphorylation, a phosphate group ( $\text{PO}_4^{3-}$ ) from adenosine triphosphate (ATP) is transferred to and replaces a free hydroxyl group of amino acid. Shown below are the structures of three amino acids and phosphate group.

serine (ser)	glycine (gly)	glutamic acid (glu)
$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{N}-\text{C}-\text{COOH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{N}-\text{C}-\text{COOH} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{N}-\text{C}-\text{COOH} \\   \\ \text{CH}_2\text{CH}_2\text{COOH} \end{array}$



phosphate group ( $\text{PO}_4^{3-}$ ):

Draw the structure of the tripeptide, ser-gly-glu, after phosphorylation.

[2]

- (ii) The secondary structure of *protein kinase* consists of segments of  $\alpha$ -helix. Describe the bonding which holds the  $\alpha$ -helix in place. [2]

- (iii) The *protein kinase* is destroyed during the process of denaturation. Explain how this can occur by heating. [2]

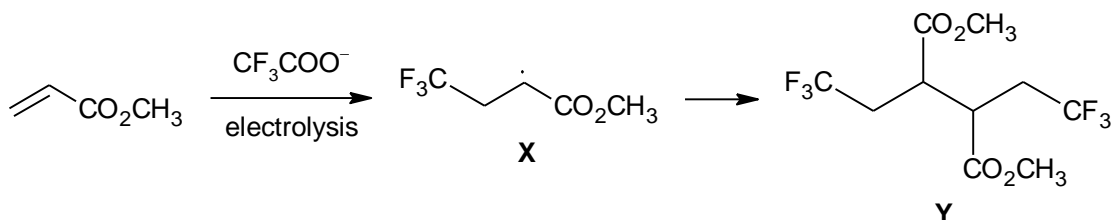
[Total: 20]

- 4 In 1849, the German chemist Adolf Kolbe reported his investigations into the electrolysis of aqueous solutions of some carboxylate anions, using inert platinum electrodes. The Kolbe electrolysis of trifluoroacetate ( $\text{CF}_3\text{CO}_2^-$ ), for example, is known to produce trifluoromethyl radical ( $\cdot\text{CF}_3$ ,  $M_r = 69$ ) and a gas at the anode.

(a) Suggest the identity of the gas and hence construct a half-equation for the reaction at the anode.

[2]

When the Kolbe electrolysis of trifluoroacetate was carried out in the presence of alkenes such as  $\text{CH}_2=\text{CHCO}_2\text{CH}_3$ , the radical intermediate **X** was formed which further dimerised to yield product **Y** shown below.



(b) State the oxidation number of the carbonyl carbon atom in  $\text{CH}_2=\text{CHCO}_2\text{CH}_3$ .

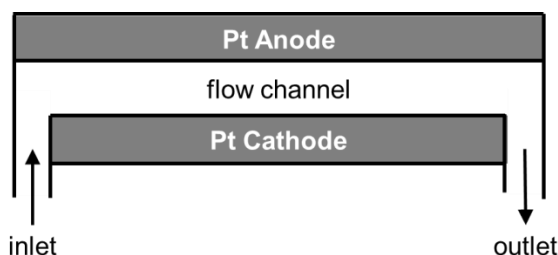
[1]

(c) Suggest a two-step mechanism for the reaction above to form **Y**, starting from the reaction between trifluoromethyl radical ( $\cdot\text{CF}_3$ ) and the alkene. Use curly arrows to indicate the movement of single electrons and indicate any unpaired electrons by a dot ( $\bullet$ ).

[3]

The Kolbe electrolysis in (c) was performed by continuous introduction of a water/ $\text{CH}_3\text{CN}$  solution containing trifluoroacetate and the alkene into an electrochemical microreactor at constant current and room temperature.

The electrochemical microreactor has a flow channel sandwiched between two platinum electrodes as shown in the figure below.



(d) (i) Given that the flow channel has a volume of  $23\ \mu\text{L}$  and reaction mixture was injected at a rate of  $20\ \mu\text{L}\ \text{min}^{-1}$ , calculate the time (in seconds) in which the current was passed through the solution.

( $1\ \mu\text{L} = 10^{-3}\ \text{cm}^3$ )

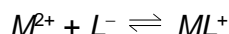
[1]

(ii) The purified product **Y** ( $M_r = 310$ ) was obtained as a colourless solid weighing  $0.401\ \text{g}$ . Using your answers from (a) and (d)(i), calculate the current (in ampere) that would have been applied to the microreactor.

[2]

- (e) (i) How many stereoisomers does **Y** have? [1]
- (ii) Draw the isomer of **Y** that is **not** optically active, showing clearly the stereochemistry of the molecule using wedged  $\blacktriangleleft$  and dashed bonds  $\cdots$ . [1]
- (f) When the Kolbe electrolysis of trifluoroacetate was carried out in the presence of another alkene,  $\text{CH}_2=\text{CHCONH}_2$  ( $M_r = 71$ ), a non-dimer product ( $M_r = 209$ ) was formed instead. Suggest the structure of the product obtained. [1]
- (g) The trifluoromethyl ( $-\text{CF}_3$ ) group is regarded as an important structural feature in many pharmaceutically relevant molecules because it is known to enhance chemical inertness. Suggest an explanation for its property. [1]
- (h) (i) Deduce the structure of the radical intermediate formed when Kolbe electrolysis of difluoroacetate,  $\text{CHF}_2\text{CO}_2^-$ , was carried out in the presence of the alkene,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$ . [1]
- (ii) The yield of the dimer product for this electrolysis was much poorer than that for trifluoroacetate and  $\text{CH}_2=\text{CHCO}_2\text{CH}_3$ . Use your answer in (h)(i) to suggest a reason for the difference in yield. [2]

Some carboxylate anions,  $\text{L}^-$ , are also known to form 1:1 complexes with divalent metal ions,  $\text{M}^{2+}$ , according to the following equilibrium.



- (i) The table below gives the values of  $\log K$  for some 1:1 metal-carboxylate complexes.

metal ion	acetate ( $\text{CH}_3\text{COO}^-$ )	chloroacetate ( $\text{CH}_2\text{ClCOO}^-$ )
$\text{Cd}^{2+}$	1.30	0.99
$\text{Cu}^{2+}$	1.76	1.07
$\text{Ni}^{2+}$	0.72	0.23

Using relevant data from the table, deduce

- I the relative stabilities of the metal complexes formed with the acetate ligand. [1]
- II the relative magnitude of the  $\log K$  values of 1:1  $\text{Cu}^{2+}\text{-CH}_3\text{COO}^-$  and  $\text{Cu}^{2+}\text{-HCOO}^-$  complexes and suggest a reason for your answer. [3]

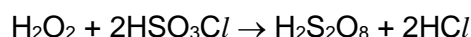
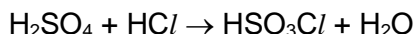
[Total: 20]

5 This question is about Period 3 elements and the uses of its compounds.

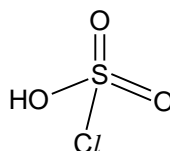
- (a) A sample of magnesium oxide is suspected to be contaminated with a substantial amount of aluminium oxide. Describe a simple gravimetric method to prove that the contamination has taken place. Include equation(s) for the chemical reaction(s) involved, if any.

[3]

- (b) Another Period 3 oxide, sulfur trioxide dissolves in water to form sulfuric acid,  $\text{H}_2\text{SO}_4$  which can be converted into peroxodisulfuric acid,  $\text{H}_2\text{S}_2\text{O}_8$  via the two-step process below, with chlorosulfonic acid,  $\text{HSO}_3\text{Cl}$ , as an intermediate:



- (i) The structure of  $\text{HSO}_3\text{Cl}$  is given below.



The boiling point of  $\text{H}_2\text{SO}_4$  is  $290^\circ\text{C}$  whereas that of  $\text{HSO}_3\text{Cl}$  is  $152^\circ\text{C}$ . By making reference to the structures of the two compounds, explain the difference in the boiling points.

[2]

- (ii) Draw the structure of a  $\text{H}_2\text{S}_2\text{O}_8$  molecule, showing the spatial arrangement and estimated bond angle around any one sulfur atom. The  $\text{H}_2\text{S}_2\text{O}_8$  molecule contains a  $\text{O}-\text{O}$  bond.

[2]

- (c) Chlorine forms an oxide,  $\text{Cl}_2\text{O}_7$ , with the structure  $\text{O}_3\text{Cl}/\text{OCl}/\text{O}_3$  and a boiling point of  $82^\circ\text{C}$ . Its standard enthalpy change of formation is  $-546 \text{ kJ mol}^{-1}$ .

- (i) Write the equation which corresponds to the standard enthalpy change of formation of  $\text{Cl}_2\text{O}_7$ .

[1]

- (ii) Given that the bond energy of  $\text{Cl}-\text{O}$  bond is  $269 \text{ kJ mol}^{-1}$  and using relevant data from the *Data Booklet*, estimate the average bond energy of the  $\text{Cl}=\text{O}$  bond.

[2]

- (iii) The bond energy calculated in (c)(ii) could have been more accurate if the value of an additional enthalpy change is known. State what process this enthalpy change corresponds to.

[1]

- (iv) Given that the value of the enthalpy change in (c)(iii) is  $+45 \text{ kJ mol}^{-1}$ , construct an energy level diagram to calculate the enthalpy change of formation of gaseous  $\text{Cl}_2\text{O}_7$ .

[3]

- (d) Aluminium oxide is used extensively in organic synthesis as a dehydrating agent.

An organic compound **A**,  $C_{12}H_{18}O$ , contains a benzene ring with 2 substituents on the 1- and 4- positions on the ring. **A** is optically active. When it is treated with  $Al_2O_3$ , compound **B** is formed. **B** can be converted into another optically active compound **C** by reacting with dry gaseous  $HCl$ . When **C** is heated under reflux with acidified  $KMnO_4$ , compound **D**,  $C_{11}H_{14}O_2$ , is produced. Treatment of **D** with  $PCl_5$  produces compound **E**. When **E** is heated with gaseous  $NH_3$ , a neutral compound **F** is formed.

Identify the six compounds **A – F**.

[6]

[Total: 20]

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