CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY
Paper 2 Structured Questions

9647/02
Monday 26 August 2013
2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST
Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper. **[PILOT FRIXION ERASABLE PENS ARE NOT ALLOWED]**
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 all questions.
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 of the question.

	For Examiner's Use		
Paper 1			/40
Paper 2	**Q 1**	/12	
	Q 2	/15	
	Q 3	/4	
	Q 4	/11	
	Q 5	/17	
	Q 6	/13	/72
Paper 3	**Q 1**	/20	
	Q 2	/20	
	Q 3	/20	
	Q 4	/20	
	Q 5	/20	/80
Total			/192

This document consists of **17** printed pages and **1** blank page.

[Turn over

1 Planning (P)

Natural water that contains calcium and magnesium ions is said to be 'hard'. Tap water in England is hard water, which is evident from the limescale found in kettles.

The main source of calcium and magnesium ions in hard water is limestones. However, neither calcium carbonate nor magnesium carbonate is appreciably soluble in water. It is said that the solubility is partly the result of carbon dioxide present in rain water.

You are to design an experiment to investigate whether the presence of carbon dioxide in water, indeed, increases the solubility of magnesium carbonate.

In addition to the standard apparatus available in a school laboratory, you are provided with the following materials,

- magnesium carbonate
- distilled water
- distilled water saturated with carbon dioxide
- methyl orange indicator
- phenolphthalein indicator
- standard hydrochloric acid

(a) Write an expression for the solubility product, K_{sp}, of magnesium carbonate, stating its units.

- **$K_{sp} = [Mg^{2+}]\,[CO_3^{2-}]$ $mol^2\ dm^{-6}$**

……..**[1]**

(b) When a solution is saturated, the undissolved solid is in equilibrium with its aqueous solution.

$$\mathbf{X}(s) + aq \rightleftharpoons \mathbf{X}(aq)$$

Describe briefly how you would prepare a saturated solution of magnesium carbonate at room temperature.

- **Dissolve solid in water until some solid remains undissolved.**
- **Allow solution to stand for few hours (to establish equilibrium).**
- **Filter to remove undissolved solid. The saturated solution is collected as the filtrate.**

……..**[3]**

(c) The concentration of a saturated solution of magnesium carbonate may be determined by titration with standard hydrochloric acid.

(i) Given that, at room temperature, K_{sp} of magnesium carbonate has a numerical value of 6.82×10^{-6}, suggest an appropriate concentration of the standard hydrochloric acid to be prepared. Show your working.

- **for a saturated solution of $MgCO_3$, $[Mg^{2+}][CO_3^{2-}] = K_{sp}$**
- **$\therefore [CO_3^{2-}] = \sqrt{K_{sp}}$ (since $[Mg^{2+}] = [CO_3^{2-}] = [MgCO_3]$)**
  $= \sqrt{6.82 \times 10^{-6}} = 2.61 \times 10^{-3}$ mol dm^{-3}
- **$MgCO_3 + 2HCl \rightarrow MgCl_2 + CO_2 + H_2O$**
- **For volume of analyte to be ≈ volume of titrant at end-point,**
  $\therefore [HCl] = 2 \times [MgCO_3]$
  $= 2 \times 2.61 \times 10^{-3}$
  $= 5.22 \times 10^{-3}$ mol dm^{-3}
  $\therefore$ a suitable $[HCl] = 5.22 \times 10^{-3}$ mol dm^{-3}

OR

$2MgCO_3 + 2HCl \rightarrow MgCl_2 + Mg(HCO_3)_2$
$\therefore [HCl] = [MgCO_3]$
$= 2.61 \times 10^{-3}$ mol dm^{-3}

(ii) Name the indicator used in this titration.

(ii) phenolphthalein indicator

methyl orange indicator

…… **[4]**

(d) Describe what further experiments you would carry out to show that solubility of magnesium carbonate is increased by the presence of carbon dioxide in water. State clearly the volume of solution used and the expected results.

- **Prepare a saturated solution of $MgCO_3$ in water saturated with CO_2.**
- **Pipette 25.0 cm^3 of the saturated solution of $MgCO_3$ prepared above (into a 250 cm^3 conical flask). Add (3 drops of) methyl orange indicator. Titrate with standard / 5.22×10^{-3} mol dm^{-3} HCl (placed in a 50 cm^3 burette) until the solution in the conical flask changed from yellow to orange.**
  Expected results: vol of HCl > that for saturated solution of $MgCO_3$.

[3]

(e) Recently phenolphthalein is classified as a carcinogen and is banned from use in the school laboratory. Suggest a suitable replacement for phenolphthalein indicator from the list below.

indicator	colour (lower pH)	pH range	colour (upper pH)
congo red	blue	3.0 – 5.0	red
methyl red	red	4.8 – 6.0	yellow
phenol red	yellow	6.4 – 8.2	red-violet
cresol red	yellow	7.1 – 8.8	violet

cresol red

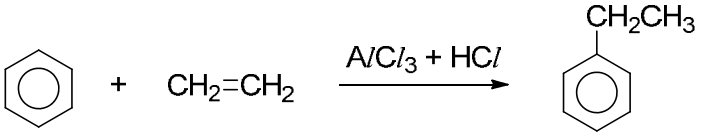
…… **[1]**

[Total: 12]

2 Ethylbenzene is a highly flammable and colourless liquid. It is important in the petrochemical industry as an intermediate in the production of styrene which is a precursor for polystyrene, a common plastic material.

Ethylbenzene has a characteristic gasoline odour with an odour threshold, which is the lowest concentration of a compound detectable by smell, of 2.3 parts per million (ppm). It also has density of 0.866 g cm^{-3} and boiling point of 136 °C.

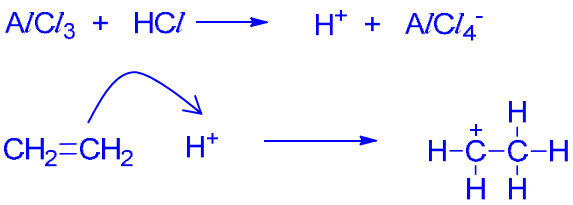
(a) Ethylbenzene can be produced by combining ethene with benzene in an acid-catalysed reaction as shown below.



(i) Name the mechanism for this reaction.

Electrophilic substitution

(ii) The first step of the mechanism involves the reaction between $AlCl_3$ and HCl. Show clearly how ethene interacts with the species formed from the first step to generate the attacking species for subsequent reaction with benzene. You should include in your answer curly arrows to depict electron movement and all charges.



(iii) Suggest why 1,4-diethylbenzene is also formed in the overall reaction.

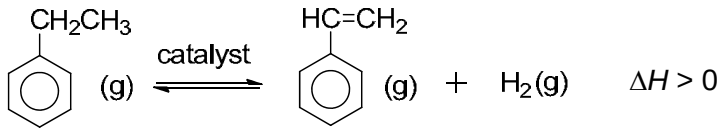
Presence of electron donating / activating ethyl group makes ethylbenzene even more susceptible to further electrophilic attack at position 4 on benzene, thereby forming the disubstituted compound.

(iv) If a room has dimensions of 5 m x 4 m x 3 m, calculate the minimum mass of ethylbenzene that would be present before its odour is detected.

Volume of room = 5 x 4 x 3 = 60 m^3
For odour detection,
minimum vol of ethylbenzene = $\frac{2.3}{10^6}$ x 60
= 1.38 x 10^{-4} m^3
∴ minimum mass of ethylbenzene = (0.866 x 10^6) x 1.38 x 10^{-4} **[6]**
= 119.5 g

5

(b) Ethylbenzene can reversibly undergo catalytic dehydrogenation at 600 ^{o}C and 0.5 bar in the presence of a solvent to form styrene. [1 bar = 1 x 10^5 Pa]



(i) State **two** main assumptions of the kinetic theory of gases.

1. Gas particles have negligible size/volume compared to the volume of its container.

2. There is negligible intermolecular forces of attraction between gas particles.

(ii) Under the conditions used for the reaction, 0.0200 g of the equilibrium mixture occupies 38.0 cm^3. Calculate the average relative molecular mass of the gaseous mixture, giving your answer to 1 decimal place.

using ideal gas equation, pV = nRT

$$(0.5 \times 10^5)(38.0 \times 10^{-6}) = \frac{0.0200}{\text{average } M_r}(8.31)(600 + 273)$$

∴ Average M_r = 76.4

(iii) Assuming the mole fraction of styrene and hydrogen gas is the same at equilibrium, and using your answer in **(b)(ii)**, calculate the proportion of ethylbenzene, styrene and hydrogen gas present in the equilibrium mixture.

Let fraction of styrene in mixture be *x*.
Hence, fraction of hydrogen gas would also be *x*, and
fraction of ethylbenzene would be (1–2*x*).

$$(1-2x)\,M_{r\ ethylbenzene} + x\,M_{r\ styrene} + x\,M_{r\ hydrogen} = 76.4$$
$$106\,(1-2x) + 104x + 2x = 76.4$$
$$\therefore \quad x = 0.279$$

Hence in the mixture,
Fraction of styrene = fraction of hydrogen = 0.279
Fraction of ethylbenzene = 0.442

(iv) Hence, calculate the value of K_p for the dehydrogenation of ethylbenzene at 600 °C, giving its units.

$$K_p = \frac{P_{styrene} \times P_{hydrogen}}{P_{ethylbenzene}}$$
$$= \frac{(0.279 \times 0.5)^2}{0.442 \times 0.5}$$
= 0.0881 bar OR 8.81 x 10^3 Pa

(v) State and explain the effect of an increase in temperature on the K_p for the dehydrogenation of ethylbenzene.

Dehydrogenation of ethylbenzene is an endothermic process.

According to Le Chatelier's Principle, increasing temperature favours endothermic reaction. Thus, position of equilibrium shifts to the right. There will be a greater proportion of styrene and hydrogen gas in the reaction mixture, causing the K_p to increase.

[9]

[Total: 15]

3 "Every drop of Evian Natural Spring Water begins as rain and snow falling high in the pristine and majestic French Alps."

Bottled water has become big business due to a growing number of consumers preferring bottled water to tap water. Statements advertising bottled water tends to convey images of purity and natural processes.

The label of an Evian mineral water bottle shows the following:

pH = 7.1	
Mineral content	**Amount per L (mg dm^{-3})**
Aluminium	trace
Calcium	80
Magnesium	26
Potassium	1
Bicarbonate	360
Chloride	6.8
Nitrate	3.7
Sulfate	35

(a) Suggest the ions which will be precipitated when excess alkali is added to the mineral water.

Mg^{2+} and Ca^{2+} ..... **[1]**

(b) Describe, with the use of suitable equations, what happens to the aluminium ions in the water sample as alkali is added slowly until in excess.

Formation of white ppt of $Al(OH)_3$ when alkali is added initially.

$Al^{3+} + 3\ OH^- \rightarrow Al(OH)_3$

White precipitate dissolves in excess alkali forming colourless solution of $[Al(OH)_4]^-$.

$Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$

[2]

(c) A student carried out an electrolysis using a sample of Evian water. Write an ion-electron equation for the reaction at the cathode assuming an inert electrode was used.

$2H_2O + 4e^- \rightarrow H_2 + 2OH^-$ ..... **[1]**

[Total: 4]

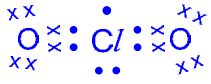
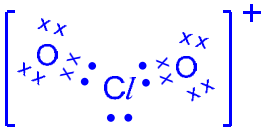
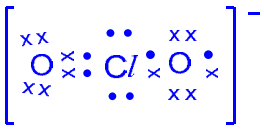
4 Chlorine containing inorganic compounds have often been used as bleaching or disinfecting agent. An example is chlorine dioxide, ClO_2.

(a) Chlorine dioxide can exist in both the anionic form, ClO_2^-, as well as the cationic form, ClO_2^+.

(i) Calculate the oxidation state of chlorine in each of the species.

ClO_2: ……**+4**…… ClO_2^+: ……**+5**…… ClO_2^-: ……**+3**……

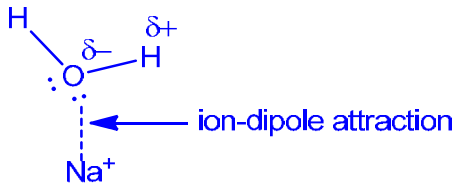
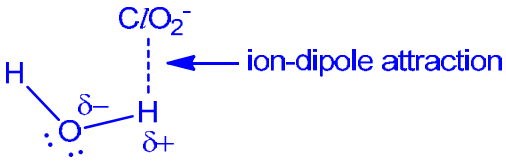
(ii) Given that chlorine is the central atom, draw the dot-and-cross diagram for each of the species. For ClO_2 and ClO_2^+, predict the O–Cl–O bond angle.

	ClO_2	ClO_2^+	ClO_2^-
Dot-and-cross diagram			
Bond angle	**115°** ***Accept any value between 105° and 118°***	**118°**	105°

[6]

(b) When a sample of solid sodium chlorite, $NaClO_2$, is dissolved in water, the cations and anions are each surrounded by water molecules.

Draw suitable diagrams to illustrate how a water molecule is attached to a sodium ion and a chlorite ion. Include labels in your answer to show the types of interaction involved.

Na^+	ClO_2^-
	

[2]

9

Organic compounds containing halogen atoms such as chlorine are very useful in organic reactions.

(c) Halogenoalkanes can undergo the Wurtz reaction, a coupling reaction where two halogenoalkanes are reacted with sodium to form a new carbon-carbon bond.

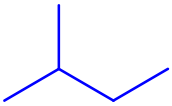
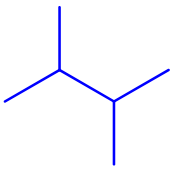
$$2R–X + 2Na \rightarrow R–R + 2Na^{+}X^{-}$$

(i) Explain why the reaction does not occur readily when chlorobenzene is used.

Strong C-C*l* bond present in chlorobenzene due to the overlap of the p orbitals of C*l* with the delocalised π electron system of benzene that gives the C-C*l* a partial double bond character.

(ii) When a 1:1 molar mixture of 2-chloropropane and chloroethane is reacted in the presence of sodium, a mixture of three alkanes is formed.

Suggest the structures of these alkanes and the ratio in which they are formed.

Alkane formed			
Ratio	**1**	**2**	**1**

[3]

[Total: 11]

5 Methanoic acid can be oxidised by bromine to form carbon dioxide gas.

$$HCO_2H(aq) + Br_2(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

A student carried out an experiment to determine the rate of this reaction using a large excess of methanoic acid. During the reaction, reddish-brown colour of bromine fades as it is used up. The change in colour intensity, measured by a colorimeter, can be used to determine the concentration of bromine.

The experimental data obtained is shown in the table below

Time / min	0	1	2	3	4	6	8	10
$[Br_2]$ / mol dm^{-3}	0.010	0.008	0.007	0.0054	0.0046	0.0029	0.0020	0.0013

(a) In the experiment, the initial concentration of methanoic acid used was 0.50 mol dm^{-3}. Explain why a large amount of methanoic acid was used in the experiment.

A large amount was used to ensure that the concentration of methanoic acid is effectively constant throughout the experiment. Thus, the rate of reaction is independent of the concentration of methanoic acid/the reaction will be of pseudo zero order with respects to methanoic acid. **[1]**

(b) **(i)** On the grid provided on the next page, plot a suitable graph which you can use to determine the order of reaction with respect to bromine.

Graph of $[Br_2]$ (y-axis) vs time (x-axis) should be drawn.

Axes should be correctly labelled and a smooth curve should be drawn.

(ii) Using the graph you have drawn in **(b)(i)**, determine the order of reaction with respect to bromine and the initial rate of the reaction. All relevant working should be shown on the graph or in the space provided below.

constant half-life, $t_{½}$ = 3.4 – 3.6 min

Order of reaction with respect to Br_2: **1**

Initial rate of reaction: **2.06×10^{-3} mol dm^{-3} min^{-1}**

11

[4]

(c) Write the rate equation for the reaction between bromine and methanoic acid given that the overall order of reaction is 2. Hence, calculate the rate constant for the reaction including its units.

Since the overall order is 2,

∴ order w.r.t. to methanoic acid is 1.

Hence, rate equation is rate = *k* [Br_2] [HCO_2H]

Method 1: Use rate equation to solve for *k*

$$k = \frac{\text{rate}}{[Br_2][HCO_2H]} = \frac{2.06\times10^{-3}}{(0.010)(0.50)}$$

$$= 0.412\ \text{mol}^{-1}\,\text{dm}^3\,\text{min}^{-1}$$

Method 2: Use half-life from graph to find *k*'

At constant [HCO_2H], rate = *k*' [Br_2] where *k*' = *k* [HCO_2H]

$$k' = \frac{\ln 2}{t_{½}} = \frac{\ln 2}{3.6} = 0.193$$

$$\Rightarrow k\,[HCO_2H] = 0.193$$

$$k\,(0.50) = 0.193$$

$$\therefore k = 0.385\ \text{mol}^{-1}\,\text{dm}^3\,\text{min}^{-1}$$

[2]

(d) Suggest an alternative method which can be used to determine the order of reaction with respect to bromine.

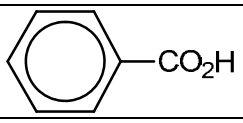
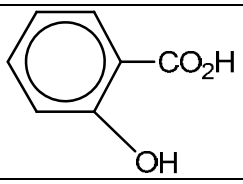
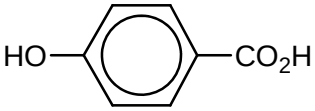
Measure volume of CO_2 evolved at fixed time interval (gas collection)

***(Titration is not likely to work here as both methanoic acid and product* (H^+)**

***can be neutralised.*)** **[1]**

13

(e) The following table gives the pK_a values of some carboxylic acids.

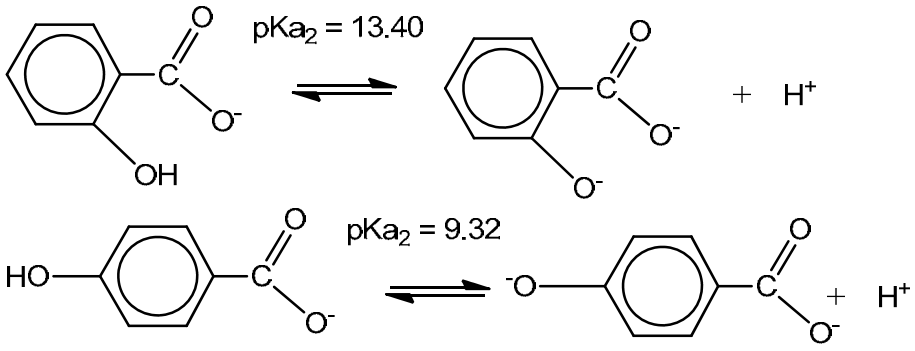
Carboxylic Acids	Formula	pK_{a1}	pK_{a2}
ethanoic acid	CH_3CO_2H	4.74	-
2-fluoroethanoic acid	FCH_2CO_2H	2.65	-
2-chloroethanoic acid	$ClCH_2CO_2H$		-
benzoic acid		4.20	-
2-hydroxybenzoic acid		2.97	13.40
4-hydroxybenzoic acid		4.48	9.32

(i) Suggest the value for the pK_a of 2-chloroethanoic acid.

pK_a of 2-chloroethanoic acid is ……**2.86**……..

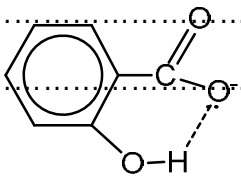
(ii) With the aid of equations, explain why 2-hydroxybenzoic acid has a higher pK_{a2} than 4-hydroxybenzoic acid.

For the 2nd ionisation:



2-hydroxybenzoate ion is a weaker acid than its counterpart as the OH group and the O^- in the carboxylate ion form intramolecular hydrogen bonding due to the close proximity between the two groups.

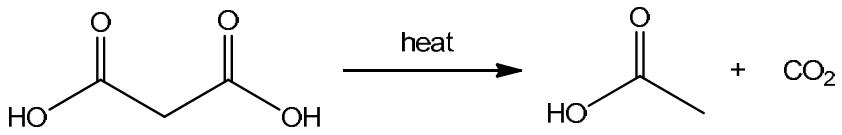
~~This limits the dissociation of the hydroxyl group, resulting in a larger pK_{a2}~~ **value. (diagram not needed)**



[3]

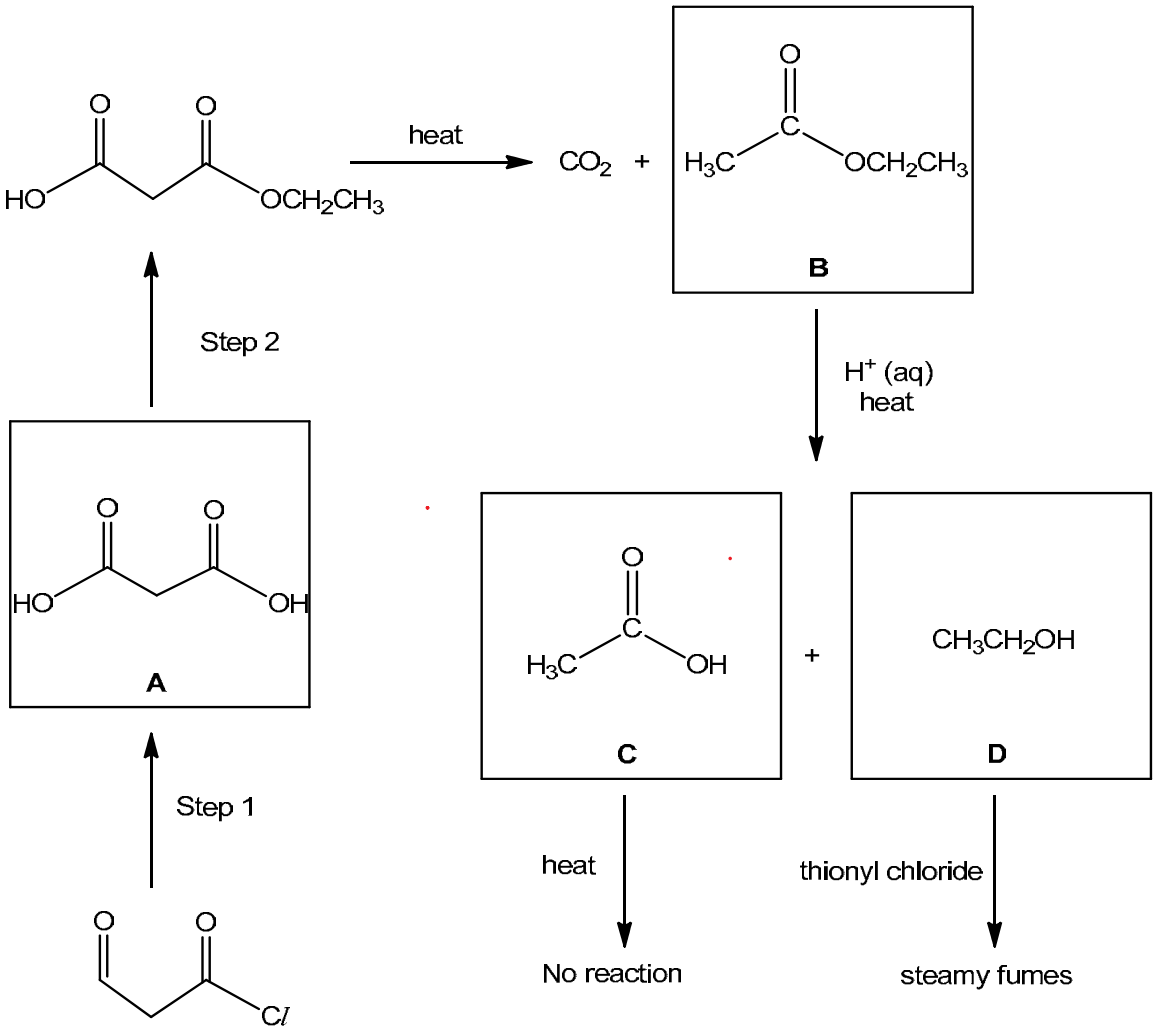
(f) Oxidation of carboxylic acids involves the removal of the carbonyl carbon atom as carbon dioxide in a process known as decarboxylation.

Carboxylic acids with a carbonyl carbon at position 3 readily undergo thermal decarboxylation as illustrated by malonic acid.



Malonic acid

Simple carboxylic acids such as ethanoic acid rarely undergo such decarboxylation. By using this information and your knowledge of the reactions of carboxylic acids and its derivatives, complete the reaction scheme shown below by drawing the structures of compounds **A** to **D** in the boxes provided. State the reagents and conditions for step 1 and step 2.



Step 1: Reagents: **$KMnO_4/H^+$ or $K_2Cr_2O_7/H^+$**

Conditions: **heat under reflux**

Step 2: Reagents: **limited CH_3CH_2OH**

Conditions: **conc H_2SO_4 and heat under reflux**

[6]

[Total: 17]

6 Chromium is a typical transition element and it forms many stable coloured complexes that are capable of exhibiting various types of isomerism.

(a) Chromium(III) chloride with the general formula $CrCl_3 \cdot 6H_2O$ can exist as hydrated isomers which differs in the number of water molecules attached as ligands to the metal ion.

(i) One of the hydrated isomers is $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$. Explain why an aqueous solution of this isomer is green.

Cr^{3+} has d^3 electronic configuration/ incompletely/ partially filled d-orbitals In the presence of ligands, the incompletely filled d-orbitals become non-degenerate / split into two groups of slightly different energy/ split into a lower and higher energy level. When a d-electron from the lower energy level (3d) is promoted/excited to the higher energy level (3d*), a process known as d-d* electronic transition occurs.

Radiation (red light) in visible light region of the electromagnetic spectrum is absorbed. The green light transmitted (not absorbed) will be seen as the colour of the complexes.

(ii) Suggest the formulae of **two** other possible hydrated isomers of chromium(III) chloride.

$[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ or $[Cr(H_2O)_6]Cl_3$ or $[CrCl_3(H_2O)_3] \cdot 3H_2O$

(iii) When aqueous ammonia is added gradually to a solution containing $[Cr(H_2O)_6]^{3+}$, a grey-green precipitate is formed. When aqueous ammonia is added in excess, the precipitate dissolves to give a purple solution. Explain the observations with the aid of relevant equations, including state symbols.

In aqueous ammonia, hydroxide ions are produced.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

or

$$[Cr(H_2O)_6]^{3+}(aq) \rightarrow [Cr(OH)(H_2O)_5]^{2+}(aq) + H^+(aq)$$

$$NH_3(aq) + H^+(aq) \rightleftharpoons NH_4^+(aq)$$

The hydroxide ions produced react with $Cr^{3+}(aq)$ and a grey-green precipitate of $Cr(OH)_3$ is formed.

$$Cr^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Cr(OH)_3(s)$$

$$[Cr(H_2O)_6]^{3+}(aq) + 3\ NH_4OH\ (aq) \rightarrow Cr(OH)_3(s) + 6H_2O\ (l) + NH_4^+(aq)$$

The grey-green precipitate dissolves in excess $NH_3(aq)$ to give a purple solution due to the formation of the complex ion, $[Cr(NH_3)_6]^{3+}(aq)$.

$$Cr(OH)_3(s) + 6NH_3(aq) \rightleftharpoons [Cr(NH_3)_6]^{3+}(aq) + 3OH^-(aq)$$

$$[Cr(H_2O)_6]_3^+(aq) + 6NH_3(aq)) \rightarrow [Cr(NH_3)_6]^{3+}(aq) + 6H_2O\ (l)$$

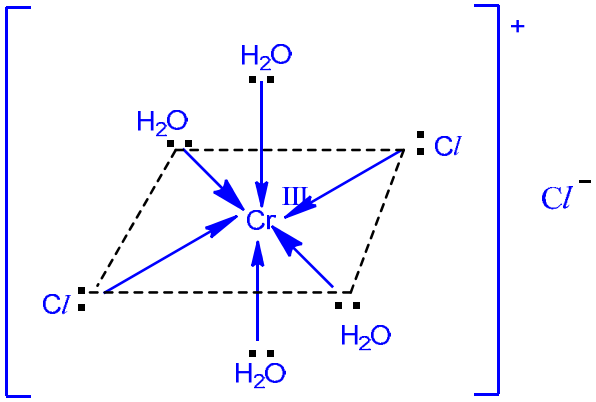
[8]

(b) Certain octahedral transition metal complexes are able to exhibit both geometric (*cis-trans*) and optical isomerism.

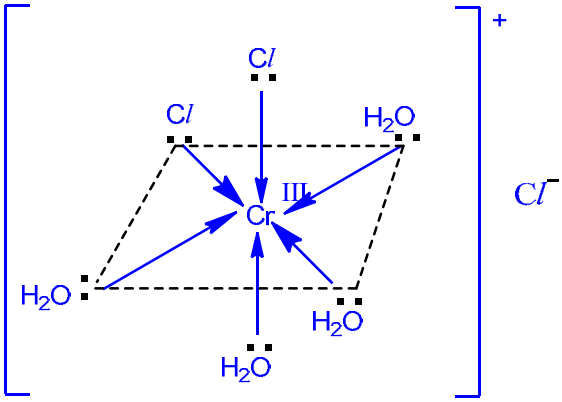
Cis-trans isomers are isomers which differ in the arrangement of two ligands.

Cis- isomers are isomers where the two ligands are 90° apart from one another in relation to the central metal ion, whereas *trans*-isomers are isomers where the two ligands are 180° apart in the complex.

(i) Select a suitable hydrated isomer of chromium(III) chloride which contains a complex ion capable of exhibiting *cis-trans* isomerism. Draw the structures of the two isomers and label clearly which is the *cis-* and *trans-* isomers.



Trans isomer



Cis isomer

17

(ii) Another chromium-containing complex, $[CrCl(NH_3)(en)_2]^{2+}$, exists as three isomers. [en: ethylenediamine, $H_2NCH_2CH_2NH_2$]

Isomer **A** rotates plane-polarised light to the right.

Isomer **B** rotates plane-polarised light to the left.

Isomer **C** has no effect on the plane-polarised light.

Draw the structures of isomers **A** to **C**.

You may use  to represent ethylenediamine.

[5]

[Total: 13]