EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2018
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME							
CIVICS GROUP	1	7	–			INDEX NUMBER	

CHEMISTRY

9729/02

Paper 2 Structured Questions

13 September 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	
2	
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6	
Total	

This document consists of **21** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

For Examiner's Use

1 The table below shows the melting points of some oxides of Period 3 elements.

compound	chemical formula	melting point / ºC
sodium oxide	Na_2O	1132
aluminium oxide	Al_2O_3	2980
sulfur trioxide	SO_3	16

(a) (i) Briefly relate the melting points of these oxides to their structure and bonding.

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(ii) Describe the reactions, if any, of these oxides with water, stating the approximate pH of any solution formed.
Write equations for all the reactions that take place.

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For Examiner's Use

(b) Suggest a reason for each of the following observations:

(i) Effervescence is observed when aqueous sodium carbonate is added to an aqueous solution of aluminium chloride. Write equations for the reactions involved.

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(ii) Silicon tetrachloride, $SiCl_4$, hydrolyses in water while carbon tetrachloride, CCl_4, remains insoluble in water.

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(c) Gaseous N_2O_5 dissociates to form NO_2 and O_2 as shown in the following reaction equilibrium:

$$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$$

The value of the equilibrium constant, K_p, is 1.80×10^4 atm^3 at 750 K and 3.23×10^3 atm^3 at 700 K.

(i) Write an expression for K_p for the above dissociation.

[1]

For Examiner's Use

(ii) Calculate the equilibrium constant in terms of pressure at 700 K for the reaction represented below:

$$\frac{1}{2}O_2(g) + 2NO_2(g) \rightleftharpoons N_2O_5(g)$$

[1]

(iii) Will the enthalpy change for the dissociation be a positive or negative value? Justify your answer briefly.

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(iv) State and justify the effect on the position of equilibrium if the total volume of the system at equilibrium is increased at constant temperature.

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[Total: 15]

For Examiner's Use

2 Halogens have a wide range of uses, such as in water purification and as antiseptics. Halogens form compounds, such as halides and oxoanions which are used in photography and as oxidising agents respectively.

(a) State and explain the variation of the first ionisation energy of the halogens from chlorine to iodine.

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(b) Halogens react with hydrogen gas to form hydrogen halides.
State and explain the trend in the thermal stability of hydrogen halides from HC*l* to HI.

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(c) Halogens react with the thiosulfate ion, $S_2O_3^{2-}$. In acidic medium, bromine reacts with $S_2O_3^{2-}$ to form SO_4^{2-} and bromide ions, while iodine reacts with $S_2O_3^{2-}$ to form $S_4O_6^{2-}$ and iodide ions.

(i) Write an ionic equation for the reaction between iodine with the thiosulfate ion.

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(ii) By quoting suitable values from the *Data Booklet*, explain the difference in the products formed.

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For Examiner's Use

(d) 5.0×10^{-4} mol of a bromate salt containing the BrO_4^{n-} anion was added to 25.0 cm^3 of acidified KI present in excess to yield iodine and bromide ions.

The resultant solution required 40.0 cm^3 of 0.10 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$, for complete reaction.

Determine the value of ***n***.

[2]

(e) When chlorine reacts with magnesium, magnesium chloride, $MgCl_2$ is formed in preference of magnesium(I) chloride, $MgCl$. Attempts to isolate $MgCl$ have not been successful. It is proposed that the $MgCl$ formed undergoes disproportionation to form $MgCl_2$ and Mg.

$$2MgCl\,(s) \rightarrow MgCl_2\,(s) + Mg\,(s)$$

(i) Define the standard enthalpy change of formation of $MgCl$.

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For Examiner's Use

(ii) Using appropriate data from the *Data Booklet* and the information given below, construct a Born-Haber cycle to predict the lattice energy of magnesium(I) chloride, MgC*l*.

Enthalpy change of atomisation of magnesium = +148 kJ mol^{-1}
First electron affinity of chlorine = –349 kJ mol^{-1}
Standard enthalpy change of formation of magnesium(I) chloride = –130 kJ mol^{-1}

[4]

(iii) The preferential formation of MgCl_2 can also be explained through the use of lattice energy of both MgCl_2 and MgCl and the relevant ionisation energies of magnesium.

Given that the experimental lattice energy of MgCl_2 is –2526 kJ mol^{-1}, explain why MgCl_2 is formed preferentially and MgCl is not.

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[Total: 15]

For Examiner's Use

3 The Haber Process is one of the landmark discoveries that converts nitrogen from the atmosphere to ammonia via a reversible reaction with hydrogen gas. This allows the agricultural industry to flourish due the increased accessibility of ammonia to synthesise nitrogen-containing fertilisers.

(a) (i) Write an equation, including state symbols, for the Haber Process.

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(ii) Using the information in **(a)(i)**, predict and explain the sign of the entropy change for the conversion of nitrogen to ammonia.

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(b) Often the behaviour of gases can be estimated using the ideal gas equation, which is based on the laws of Boyle, Charles and Avogadro. However, this is assuming that all gases behave ideally. These assumptions are based on the kinetic theory of gases.

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

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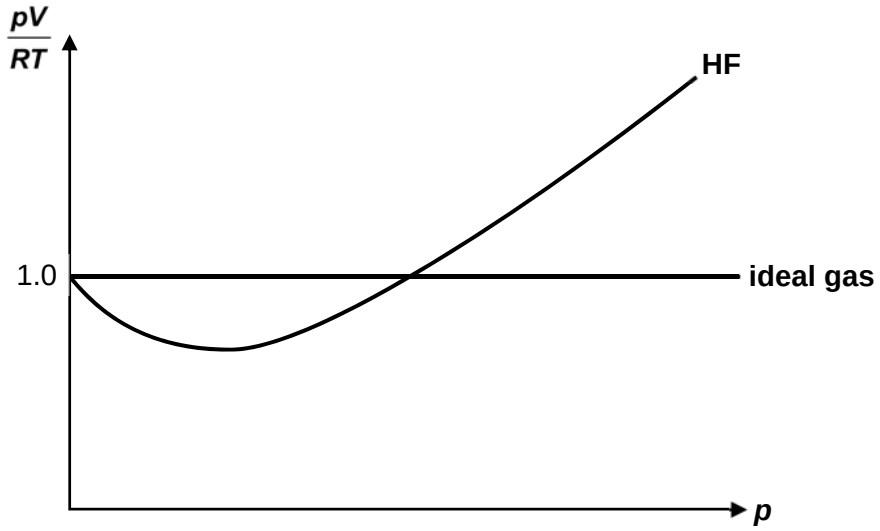
For Examiner's Use

(ii) The plot of $\frac{pV}{RT}$ against p for one mole of an ideal gas and one mole of hydrogen fluoride gas at 300 K is given below.



Sketch on the graph above to show how one mole of ammonia gas (NH_3) will behave at 300 K. Explain your answer.

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(iii) Under what conditions of temperature and pressure would ammonia behave like an ideal gas? Explain your answer.

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[Total: 10]

For Examiner's Use

4 Trimethylamine, $(CH_3)_3N$, is a base which is used as a starting material for the preparation of insecticides and pharmaceuticals.

(a) A 10.0 cm^3 of an aqueous solution of trimethylamine was placed in a conical flask. The pH of the solution was found to be 11.85. When a titration was performed, 16.00 cm^3 of 0.250 mol dm^{-3} dilute sulfuric acid was required to neutralise this base.

(i) Calculate the concentration of trimethylamine in the conical flask.

[1]

(ii) Use your answer in **(a)(i)** and the above data to show that trimethylamine is a weak base. Explain your answer.

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(iii) Write an expression for the base dissociation constant, K_b, for trimethylamine. Hence determine its pK_b value.

[2]

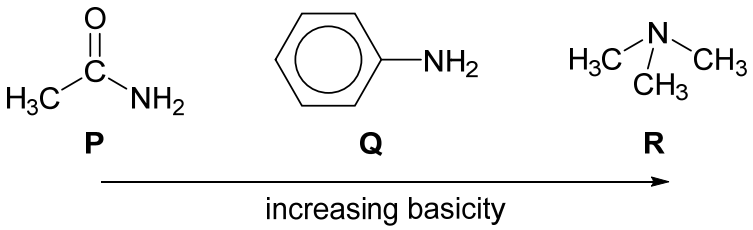
(b) Sketch the pH curve that would be obtained for the titration reaction mentioned in **(a)**. Label clearly **any significant co-ordinates** on your sketch.

For Examiner's Use

[2]

(c) The basicity of trimethylamine is different in comparison with other nitrogen organic compounds.

Account for the trend in basicity as shown below.



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[Total: 10]

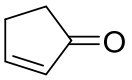
For Examiner's Use

5 (a) This question is about Grignard reagents, compounds that are of great use in organic synthesis for forming carbon–carbon bonds.

Grignard reagents are compounds of general formula RMgX where X = Br or I. They are very reactive, giving rise to the highly nucleophilic ion R^-. When a solution of a Grignard reagent in dry ether is added to a carbonyl compound, the R^- attacks the carbonyl group.

The mechanism of this reaction involves **two steps**:

- The first step is the rate determining step which involves a nucleophilic attack of nucleophilic ion **R^-** on the carbonyl carbon to form a tetrahedral intermediate.
- The second step involves an acid-base reaction with water.

(i) 2-cyclopentenone,  , is treated with the Grignard reagent ethyl magnesium bromide, CH_3CH_2MgBr, followed by water. An organic compound **W**, $C_7H_{12}O$, is formed.

Name and draw the mechanism of the above reaction.

[3]

(ii) Does 2-cyclopentenone exhibit *cis-trans* isomerism? Explain your answer.

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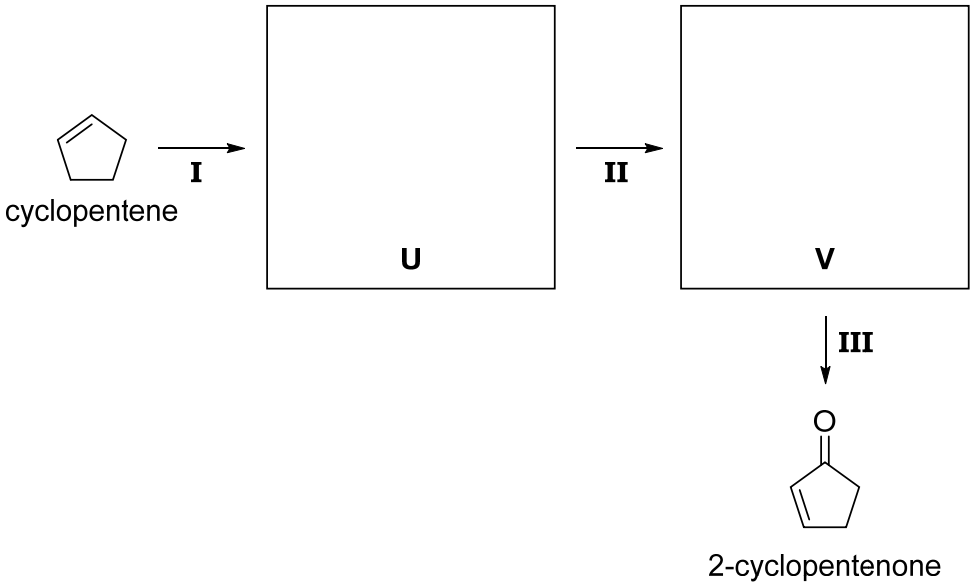
For Examiner's Use

(iii) 2-cyclopentenone can be formed from cyclopentene. Propose a three-step synthetic route to obtain 2-cyclopentenone from cyclopentene. State the reagents and conditions required, and draw the structures of the intermediates **U** and **V** obtained in the boxes below.



Step I: .....

Step II: .....

Step III: ..... [3]

For Examiner's Use

(b) A six-membered cyclic compound **X**, an isomer of **W**, $C_7H_{12}O$, reacts with gaseous HBr at room temperature to form chiral compounds with molecular formula $C_7H_{13}OBr$. Compound **X** is readily oxidised by hot acidified potassium manganate(VII) to form an acidic compound **Y**, $C_7H_{12}O_5$. 1 mole of **Y** is exactly neutralised by 2 moles of sodium hydroxide. When **Y** is warmed with concentrated sulfuric acid, a sweet-smelling compound **Z**, $C_7H_{10}O_4$ is isolated.

Suggest the structures for compound **X**, **Y** and **Z**.

X	
Y	
Z	

[3]

[Total: 10]

For Examiner's Use

6 Halogenoalkanes are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine and iodine). They serves as important intermediates in organic synthesis due to the ease of cleavage of the polar C–X bond (X = C*l*, Br or I), leading to substitution of the halogen atom by a wide variety of nucleophiles.

(a) The reaction between the primary halogenoalkane, benzyl chloride, $C_6H_5CH_2Cl$, and sodium hydroxide is known follow the rate equation:

rate = *k* [benzyl chloride]

(i) Draw the mechanism of the reaction which is consistent with the rate equation.

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(ii) Suggest a possible reason why despite being a primary halogenoalkane, benzyl chloride adopts the mechanism you have drawn in **(a)(i)**.

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(b) Unlike halogenoalkanes, halogenoalkenes such as vinyl bromide, CH_2=CHBr, are inert towards nucleophilic substitution. Suggest a possible explanation for this inertness.

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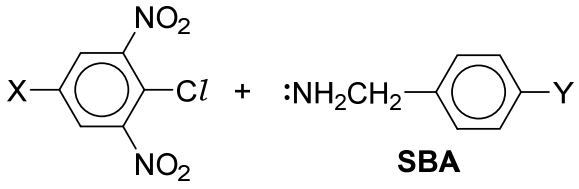
For Examiner's Use

Like halogenoalkenes, halogenoarenes are also usually inert towards nucleophilic substitution reaction.

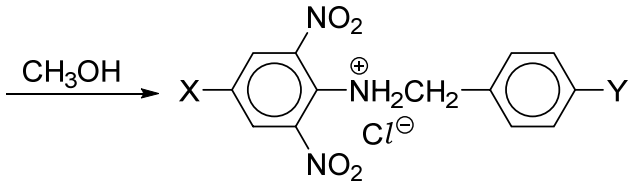
Nonetheless, when suitably tuned, halogenoarenes can be made to undergo nucleophilic substitution too, although the mechanism is different from the S_N1 and S_N2 mechanisms of aliphatic halogenoalkanes.

(c) 4-X-Substituted-2,6-dinitrochlorobenzenes (SDCB) react with 4-Y-substituted-benzylamines (SBA) in methanol to give benzylammonium chloride salt:



SDCB

SBA



benzylammonium chloride

In the reaction, SDCB is regarded as the substrate, while SBA is the nucleophile.

(i) Suggest how it can be shown *chemically* that substitution reaction had indeed taken place with SDCB?

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(ii) Suggest, with reason, one physical property which may be used to follow the progress of the reaction.

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For Examiner's Use

The reaction was found to follow overall second-order kinetics, with rate equation:

$$\text{rate} = k[\text{SDCB}][\text{SBA}]$$

The rate constant, k ($\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$), for the reaction of three 4-X-substituted-2,6-dinitrochlorobenzenes with four 4-Y-substituted-benzylamines in pure methanol at 25 ºC is given in Table 6.1 below.

Table 6.1

X (SDCB substrate)	**4-Y-benzylamine (SBA nucleophile)**			
	4-OCH_3	**4-CH_3**	**H**	**4-C*l***
NO_2	3.12	2.47	2.34	1.66
CN	0.748	0.563	0.498	
CF_3	0.100	0.0902	0.0744	0.0479

The values of the rate constant, k, can be obtained from suitable concentration–time plots such as those shown in Figure 6.1 on the next page.

Figure 6.1 is obtained by monitoring changes in the concentration of the nucleophile, 4-chlorobenzylamine, with time, using an **excess** of the three substrates separately. The initial concentrations of the three substrates are indicated on Figure 6.1.

(iii) With the aid of Figure 6.1, determine the rate constant, k, when X = CN, using 4-chlorobenzylamine as nucleophile, and fill in the blank in Table 6.1.

[2]

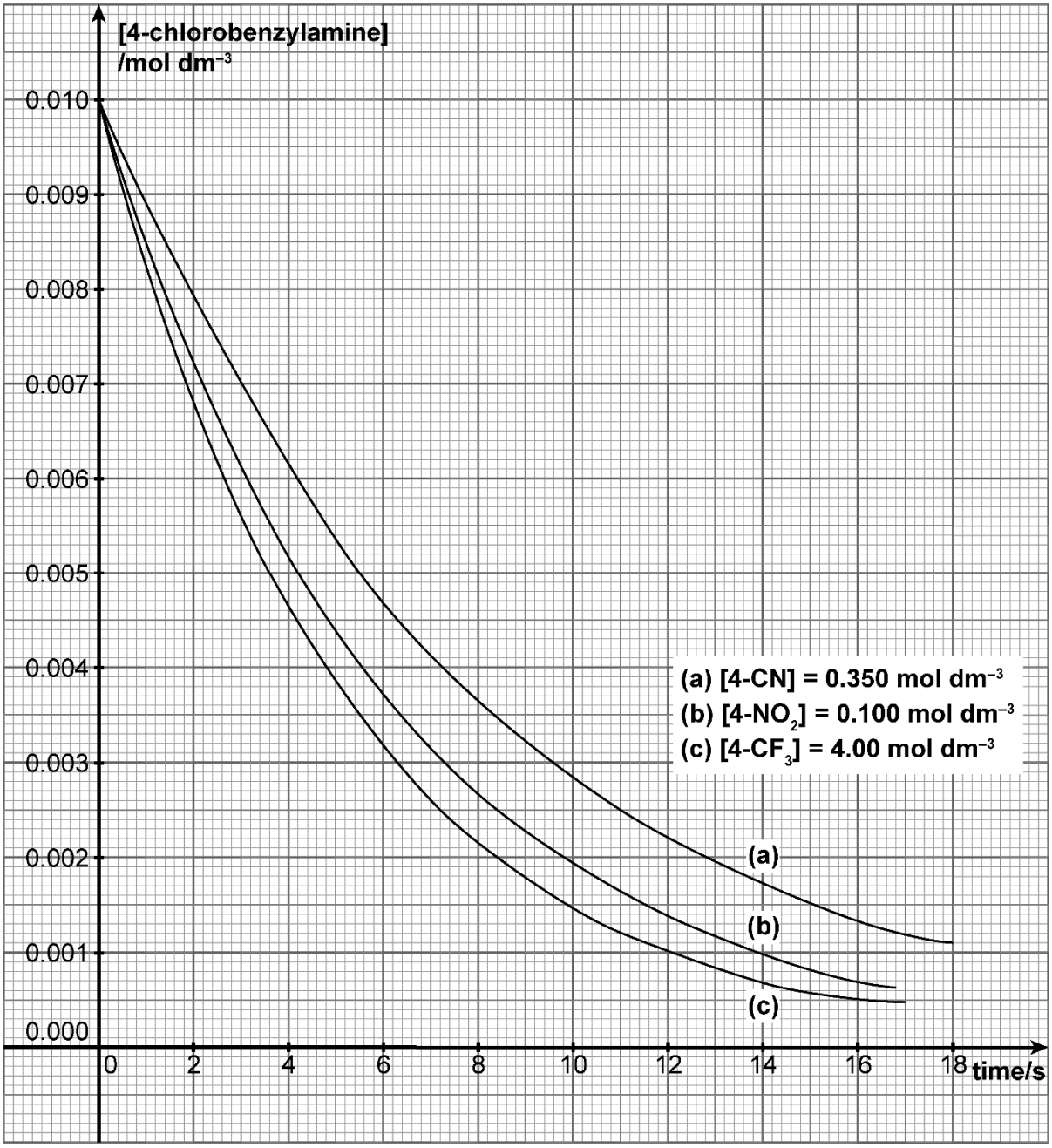
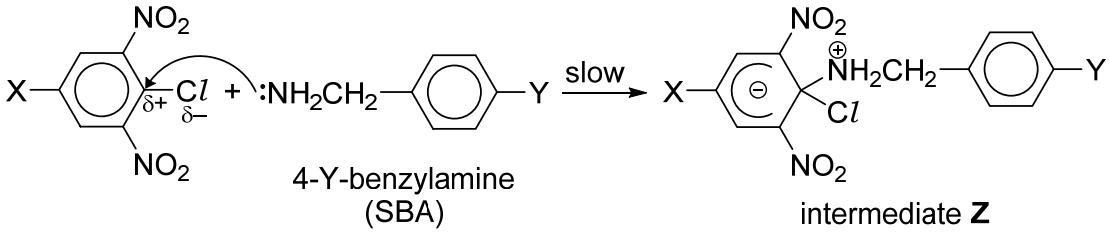


Figure 6.1

For Examiner's Use

(d) Although the reaction is second-order, however, it is **not** a single-step reaction. Instead, SBA performs a rate-determining nucleophilic attack at the electrophilic C–C*l* carbon of SDCB, leading to the formation of resonance-stabilised intermediate **Z**:

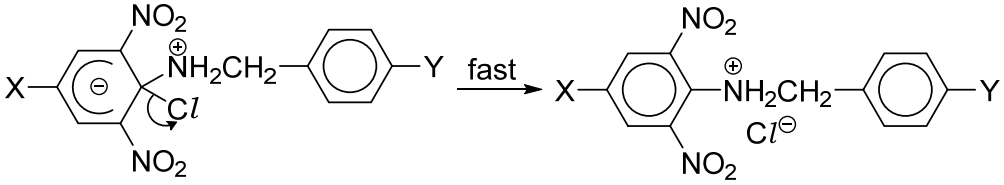
For Examiner's Use



4-Y-benzylamine (SBA)

intermediate **Z**

Subsequently, intermediate **Z** rapidly expels a chloride ion to give the desired benzylammonium chloride:



intermediate **Z** benzylammonium chloride

This two-step mechanism is known as the S_NAr mechanism.

Using the mechanism given above and the data in Table 6.1, explain which of the three substituents X = NO_2, CN or CF_3, is the strongest electron-withdrawing group.

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(e) The magnitude of the rate constant *k* can be used as a direct measure of the nucleophilicity of the 4-Y-benzylamine (SBA) nucleophile, that is, the larger the rate constant *k*, the more nucleophilic is the 4-Y-benzylamine.

Using the mechanism of the S_NAr mechanism described, explain why there is a positive correlation between the magnitude of the rate constant *k* and the nucleophilicity of the 4-Y-benzylamine.

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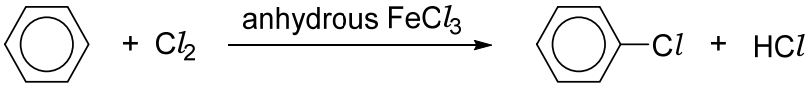
For Examiner's Use

Chloroarenes can be prepared by the reaction of benzene and chlorine in the presence of anhydrous $FeCl_3$ as a Lewis acid catalyst:



(f) Describe the role of anhydrous $FeCl_3$ in the reaction, illustrating with an equation.

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Anhydrous iron(III) chloride, $FeCl_3$, is an almost black crystalline solid and is very hygroscopic; it forms a series of hydrates when exposed to moist air. The common hydrate is yellow $FeCl_3 \cdot 6H_2O$, which contains $[FeCl_2(H_2O)_4]^+$. This is very soluble in water, and gives a strongly acidic solution.

The $[Fe(H_2O)_6]^{3+}$ ion exist only in strongly acidic solution in the absence of coordinating anion. The ion is violet in solution, although some hydrolysis may colour the solution yellow-brown.

(g) (i) Explain why $[FeCl_2(H_2O)_4]^+$ and $[Fe(H_2O)_6]^{3+}$ have different colours despite both containing iron(III).

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(ii) Explain why the violet $[Fe(H_2O)_6]^{3+}$ ion is stable only in highly acidic solution.

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For Examiner's Use

(h) On the other hand, anhydrous iron(III) iodide, FeI_3, had only been prepared recently in non-aqueous medium via the reaction of 6-coordinated $Fe(CO)_4I_2$ in hexane:

$$Fe(CO)_4I_2 + \tfrac{1}{2}I_2 \xrightarrow[\text{hexane}]{\text{uv light}} FeI_3 + 4CO$$

(i) State and explain the type of reaction involved in the synthesis of iron(III) iodide.

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A non-aqueous medium is required for the above synthesis as iron(III) iodide is completely decomposed in aqueous solution.

(ii) Using the *Data Booklet*, suggest possible products from the decomposition of iron(III) iodide in water.

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[Total: 15]

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