NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME: Teachers' Mark Scheme

CLASS: 1 3 ___ ___ INDEX NO. ___ ___ TUTOR ___

CHEMISTRY

9647/02

Paper 2 Structured

22 September 2014

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.
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 in the spaces provided.
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	P /12	
2	/26	
3	/18	
4	/ 6	
5	/10	/60

This document consists of **17** printed pages and **0** blank page.

[Turn over

For Examiner's Use

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

1 Planning (P)

H*A* is a solid monoprotic acid. It is a weak organic acid with pK_a value of 4.15. Its solubility in water is only about 3.44 g dm^{-3} under normal laboratory temperature. Its sodium salt, Na*A* (M_r = 144.0), is soluble in water.

FA 1 is a fine powder of H*A* with Na*A* as an impurity.

FA 2 is 0.975 mol dm^{-3} aqueous sodium hydroxide.

The reaction between H*A* and NaOH(aq) is exothermic. A preliminary experiment was conducted using 2.50 g of **FA 1** and 40 cm^3 of **FA 2**. The sample of **FA 1** dissolved completely to give a temperature rise of 6.3 °C. The experiment was repeated two more times with different masses of **FA 1**. **FA 1** dissolved completely when 5.00 g were used but only partially when 5.50 g were used.

To determine the percentage by mass of H*A* in **FA 1**, *m* g of **FA 1** can be reacted with *V* cm^3 of **FA 2** to obtain the temperature rise, ΔT. By repeating the experiments for different sets of *m* and *V* values, a suitable graph can be plotted to determine the set of *m* and *V* values required for complete neutralisation (the end-point).

(a) If a series of five experiments is to be carried out, suggest suitable masses and volumes so that ΔT is **at least** 10 °C for each experiment. Show relevant calculations.

Experiment	I	II	III	IV	V
Mass of **FA 1**, *m* / g					
Volume of **FA 2**, *V* / cm^3					

Minimum mass of **FA1** = $\frac{10}{6.3} \times 2.50$ = 3.97 g **[1]**

m / g = 4.00, 4.50, 5.00, 5.50, 6.00 or other suitable sets
V / cm^3 = 40.00 (constant) **[1]**

2/3 points on either side of end-point
Note: For 4.00-5.00 g, NaOH is in excess; 5.50 –6.00 g H*A* is in excess. **[1]**

[3]

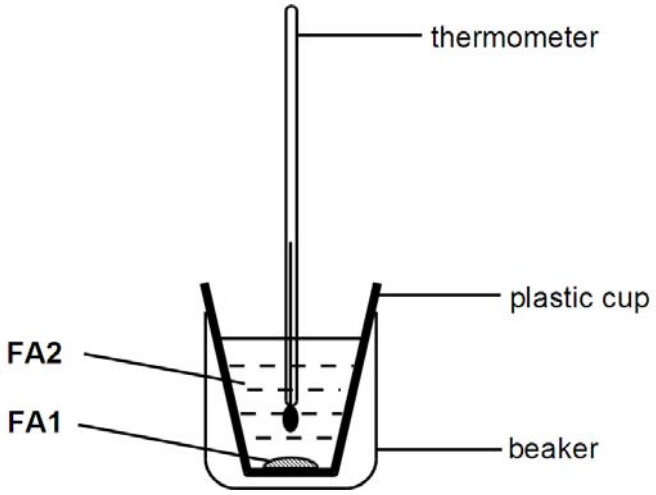
(b) Using the information given above, you are required to write a plan to determine the temperature rise for Experiment **I**.

You may assume that you are provided with:

- **FA 1**;
- **FA 2**;
- polystyrene cup;
- the apparatus and chemicals normally found in a school or college laboratory.

In your plan, you should give essential details and include a labeled diagram of the experimental set-up.

Diagram of experimental set-up:



[2]

Plan for Experiment **I**:

Plan (Accept workable alternative plans.)

1. Place 40.00 cm^3 **FA2** into plastic cup using burette. (Accept 50 cm^3 measuring cylinder.)

2. Measure the initial temperature of the solution using thermometer (0.2 °C graduation).

3. Weigh accurately about 4.00 g of **FA1** in a weighing bottle.

4. Pour **FA1** into the **FA2** in the cup.

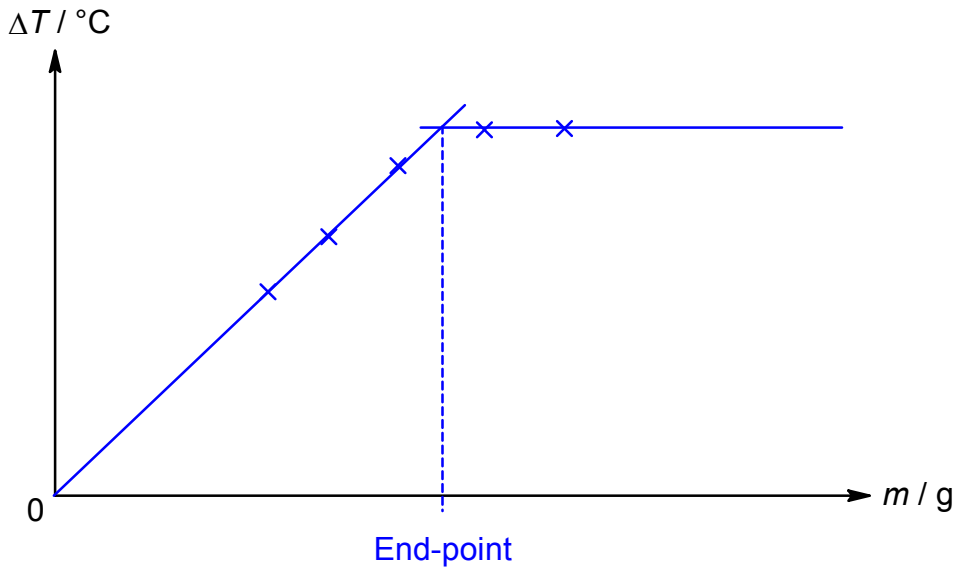
5. Stir with thermometer.

6. Record highest temperature reached.

7. Reweigh weighing bottle with any residual solid. **[3]**

.....[5]

(c) The end-point can be determined from a suitable plot of data from the five experiments in **(a)**. Label the axes on the grid below and sketch the graph. Show how the end-point can be determined from the graph.



Axes **[1]**
Shape of graph and end-point **[1]**

[2]

(d) **FA 3** is another solid sample of H*A* and Na*A* with a different percentage composition from **FA 1**.
The following data at the end-point were obtained from a series of eight experiments using **FA 3** and **FA 2**.

Mass of **FA 3** = 4.04 g
Volume of **FA 2** = 30 cm^3
ΔT = 13.1 °C

Calculate the percentage by mass of H*A* in **FA 3**.

$n(HA) = n(NaOH) = \frac{30}{1000} \times 0.975 = 0.02925$ mol

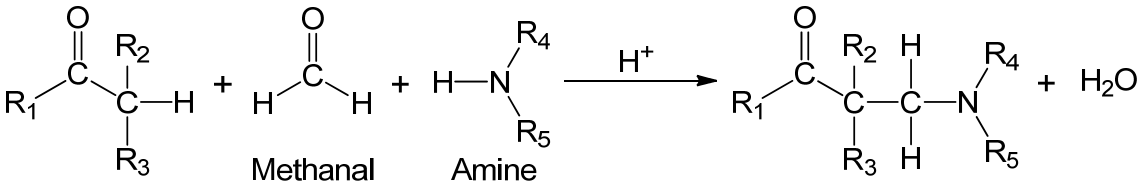
$m(HA) = 0.02925 \times 122.0 = 3.569$ g **[1]**

$\%\ HA = \frac{3.569}{4.04} \times 100 = 88.3\%$ **[1]**

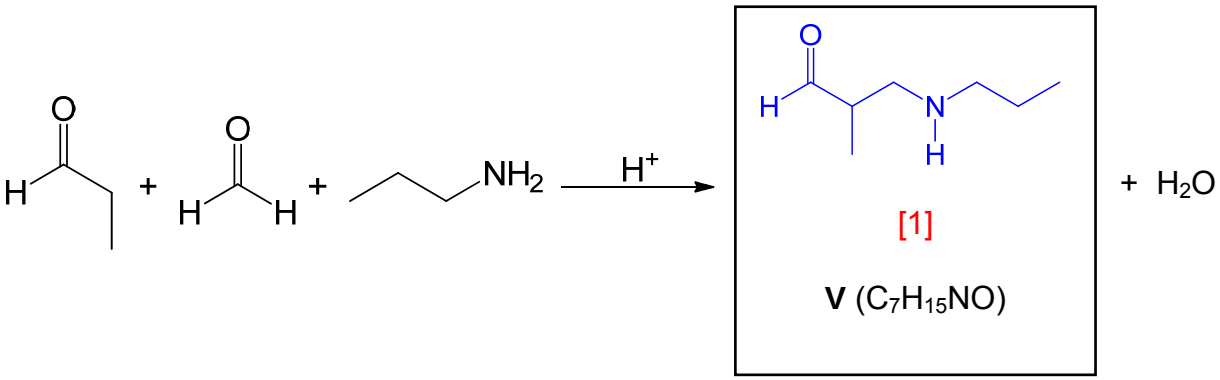
%H*A* = ...[2]

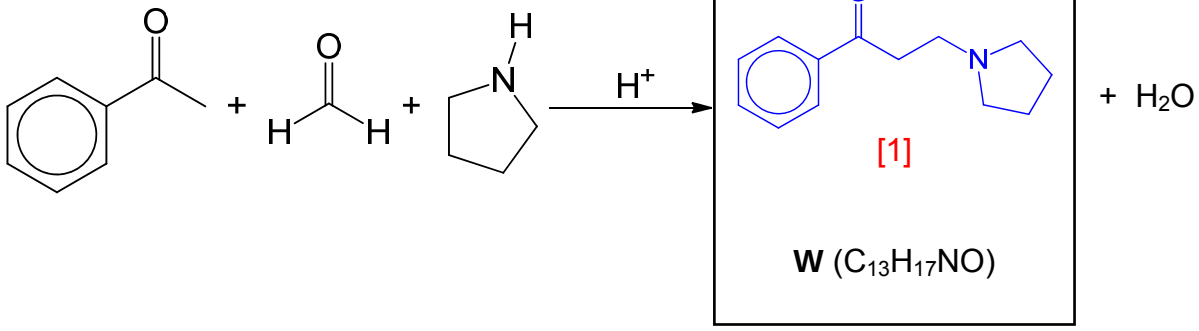
[Total: 12]

2 Mannich reaction is an organic reaction which consists of an amino alkylation of the hydrogen atom adjacent to a carbonyl functional group, by methanal and a primary amine, secondary amine or ammonia, in the presence of acid.



(a) Predict the structures of **V** and **W** for each of the following Mannich reactions.





[2]

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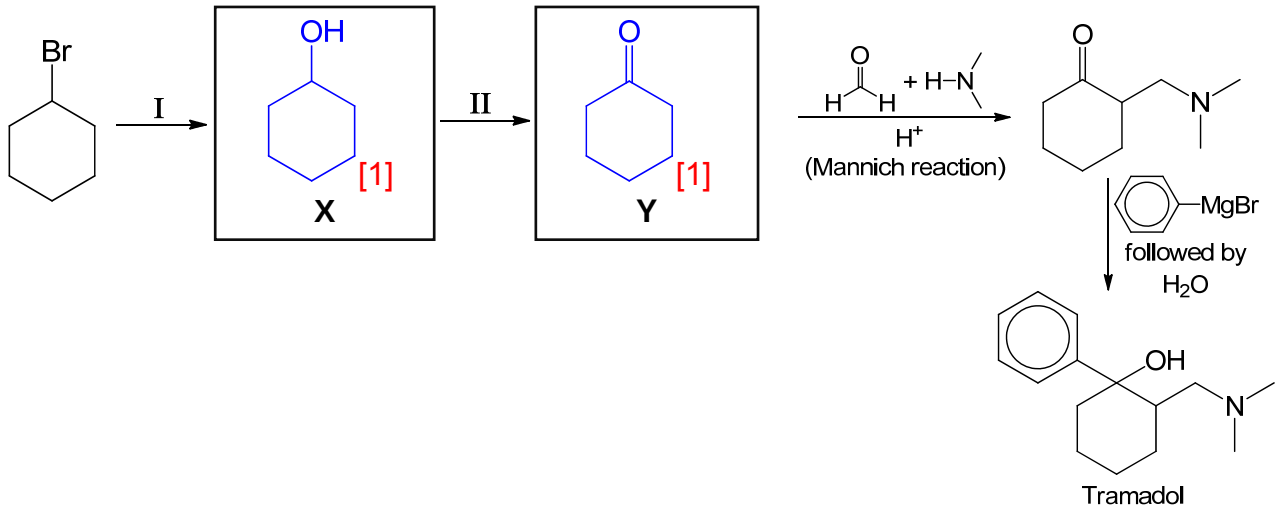
(b) Tramadol is a narcotic-like pain reliever. It could be synthesised from bromocyclohexane via a four step synthetic route. The third step of the reaction scheme involves a Mannich reaction.



(i) Draw the structures of **X** and **Y** in the space above.

(ii) Suggest the reagents and conditions for **I** and **II**.

I Aqueous NaOH, heat under reflux [1] .....

II $KMnO_4(aq)$ or $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat under reflux [1] .....

[4]

(c) When aqueous silver nitrate is added to a solution containing sodium chloride, a white precipitate is formed. When excess aqueous ammonia is added to the resulting solution, the white precipitate dissolves to give solution **Z**.

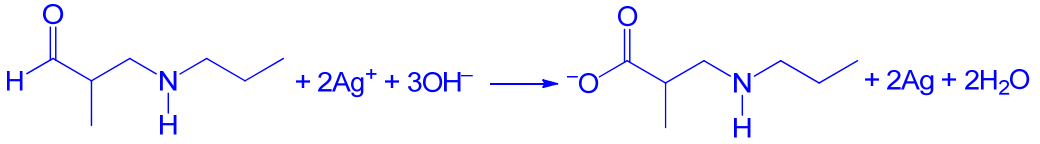
(i) Suggest the identity of the white precipitate and complex ion found in solution **Z**.

white precipitate AgCl [1].....

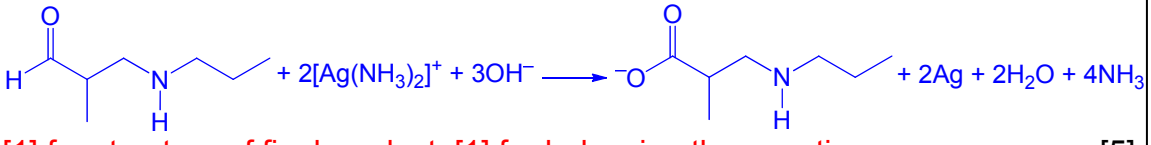
complex ion $[Ag(NH_3)_2]^+$ [1].....

(ii) Solution **Z** is added separately to compounds **V** and **W** from **(a)** and warmed. State the observation and write equations for any reactions that occur.

Solution **Z** containing $[Ag(NH_3)_2]^+$ is Tollen's reagent.
V will give a silver mirror. **W** will not give a silver mirror. [1]

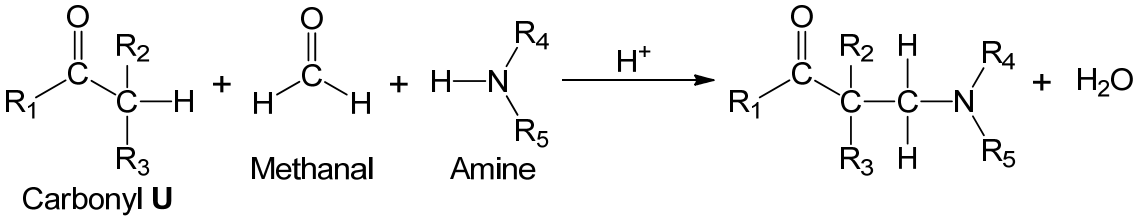


or



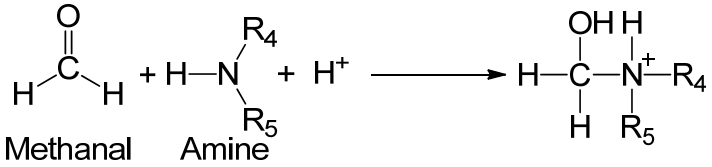
[1] for structure of final product; [1] for balancing the equation [5]

This equation for Mannich reaction is repeated from *page 6*.

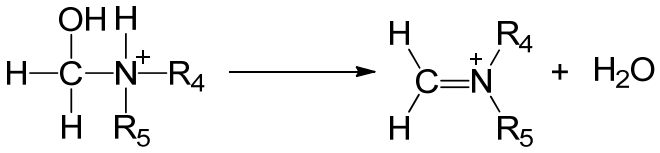


The proposed mechanism for Mannich reaction:

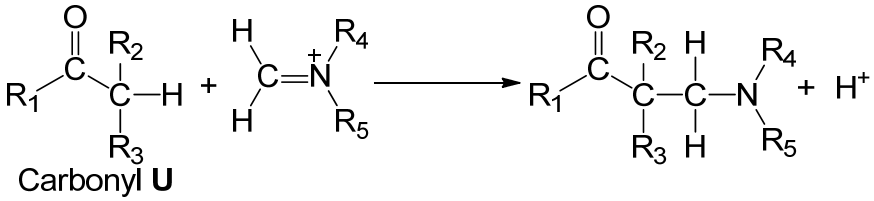
Step 1:



Step 2:



Step 3:



(d) Suggest the types of reaction that occurred in steps 1 and 2.

Step 1 Nucleophilic addition [1].....

Step 2 Elimination [1].....

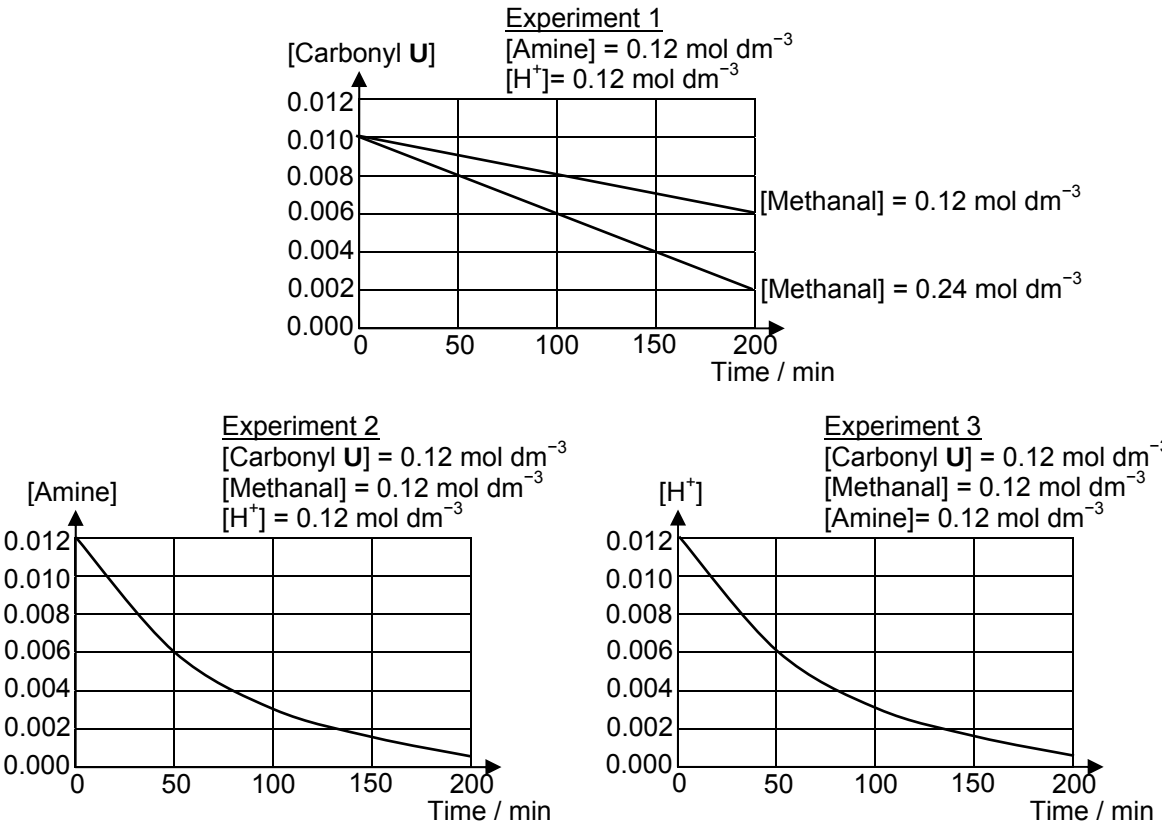
[2]

[Turn over

(e) The rate equation for the Mannich reaction can be expressed as

$$\text{rate} = k\,[\text{Carbonyl } \mathbf{U}]^p\,[\text{Methanal}]^q\,[\text{Amine}]^r\,[\text{H}^+]^s$$

A chemist carried out a series of experiments to investigate the order of reaction with respect to each of the reactants.



(i) Determine the values of *p*, *q*, *r* and *s*. *(You may make use of the space provided on the next page.)*

p: 0
From experiment 1, the graph of [Carbonyl **U**] against time is a straight line with constant negative gradient (i.e. rate of reaction is independent of [Carbonyl **U**]). Hence, zero order with respect to Carbonyl **U**. [1]

q: 1
From experiment 1, when [methanal] increase by 2 times, the magnitude for the gradient of straight line increase by 2 times. Hence, first order with respect to methanal. [1]

r: 1
From experiment 2, the graph of [Amine] against time shows a constant half-life of 50 min. Hence, first order with respect to amine. [1]

s: 1
From experiment 3, the graph of $[H^+]$ against time shows a constant half-life of 50 min. Hence, first order with respect to H^+. [1]

(ii) State and explain which step of the mechanism is the rate-determining step.

rate-determining step: Step 1 [1] .....

explanation: One molecule of methanal collides with one molecule of amine ..

and H^+ ion, which corresponds to the rate equation. [1] .....

(iii) Suggest why such a reaction is unusual.

The rate determining step involves collision of three particles (overall 3rd order reaction).
The probability of effective collision between the three particles with energy greater or equals to activation energy is low and hence such reaction is unusual. [1]

(iv) Using data from experiment 2, calculate the rate constant *k*, stating its units.

Half life from experiment 2 = 50 min
rate = k [Methanal] [Amine] $[H^+]$
since [Methanal] and $[H^+]$ is in large excess,
➔ rate = k' [Amine], where k' = k [Methanal]$[H^+]$

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[\text{Methanal}][H^+]}$$

$$50 = \frac{\ln 2}{k(0.12)(0.12)}$$

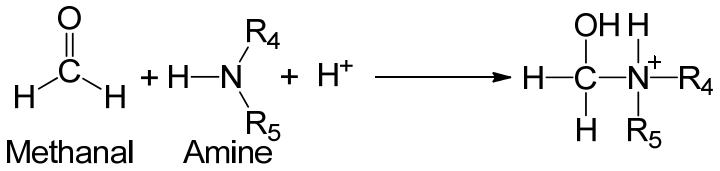
k = 0.9627
= 0.963 $mol^{-2}\ dm^6\ min^{-1}$ [1] for method and answer + [1] for units

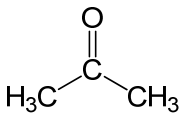
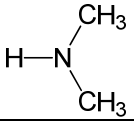
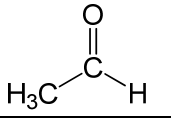
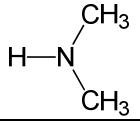
rate constant k = ...

[9]

(f) The chemist decides to further investigate step 1 of the mechanism by replacing methanal with other carbonyl compounds, and using different amines. The concentrations of all the reactants are kept constant for all experiments.

Step 1:



experiment	*carbonyl compound*	*amine*	*initial rate / ×10^{-4} mol dm^{-3} min^{-1}*
4			0.55
5			1.02

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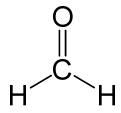
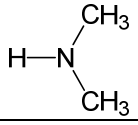
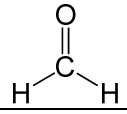
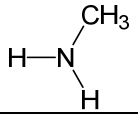
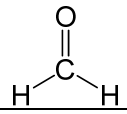
6			1.98
7			1.01
8		NH_3	0.33

Suggest an explanation of the trend in the initial rate for

(i) Experiments 4, 5 and 6

In experiment 4, 5 and 6, the amines used are the same but the carbonyl compound have two, one and no electron donating alkyl groups bonded to the C=O group respectively. [1]

Hence, the carbonyl carbon atom becomes more electron-deficient (higher partial positive charge) from the ketone and aldehyde in experiment 4 and 5 respectively to methanal in experiment 6, making it more susceptible towards nucleophilic attack. Thus, the initial rate increases. [1]
or

From experiment 4 to 6, the amines used are the same but the number of alkyl groups bonded to the C=O group decrease from two to zero, causing a decrease in steric hinderance for the nucleophile to approach the carbonyl carbon. [1]

Hence, the attacking nucleophile is able to approach carbonyl carbon of methanal in experiment 6 more readily than that of aldehyde and ketone in experiment 5 and 4 respectively. Thus, the initial rate increases. [1]

(ii) Experiments 6, 7 and 8

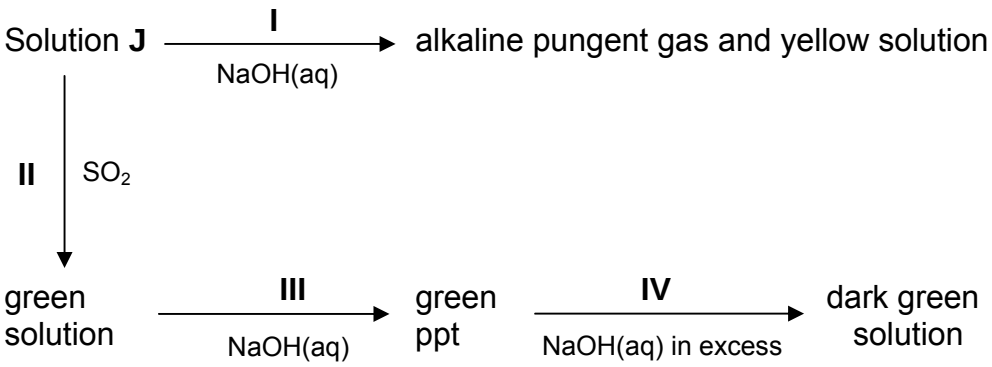
From experiment 6 to 8, the same carbonyl compound (methanal) was used, but the number of electron donating alkyl groups bonded to the nitrogen atom of amine group decrease from two to zero, causing a decrease in electron density around the nitrogen atom (decrease in nucleophilicity). [1]

Hence, the amine becomes less nucleophilic to attack the carbonyl carbon of methanal and approach the carbonyl carbon of methanal less readily. Thus, the initial rate decreases. [1]

[4]

[Total: 26]

3 **J** is ionic with an empirical formula of $Cr_2H_8N_2O_7$. One formula unit of **J** contains one type of anion and one type of cation in a ratio 1:2. **J** is an orange crystalline solid that is readily soluble in sulfuric acid to give an orange solution.



(a) **(i)** Suggest the formulae of each of the ions present in **J**.

anion $Cr_2O_7^{2-}$ [1]..... cation NH_4^+ [1].....

(ii) What is the alkaline pungent gas and yellow solution that is formed in reaction **I**?

alkaline pungent gas NH_3..... yellow solution CrO_4^{2-}.....[1 for both]

(iii) Explain if reaction **I** is a redox reaction.

This is not a redox reaction. Oxidation no. of Cr remains at +6 in $Cr_2O_7^{2-}$ and CrO_4^{2-}. Oxidation no. of N remains as –3 in NH_4^+ and NH_3. [1].....

(iv) Write a balanced ionic equation for the reaction of solution **J** with SO_2 in reaction **II**.

$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$ [1] .....

(v) Suggest ionic equations to explain the formation of green precipitate and dark green solution in reactions **III** and **IV** respectively.

III $Cr^{3+}(aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s)$ [1]..... .

IV $Cr(OH)_3(s) + 3OH^-(aq) \rightarrow Cr(OH)_6^{3-}(aq)$ [1] ..... .

(vi) State and explain clearly if there is any change in observation if NaOH(aq) is replaced by Na_2CO_3(aq) in reaction **III**.

Green ppt formed with effervescence of CO_2. [1] ..... .

Cr^{3+} has high charge density and undergoes hydrolysis to give acidic solution.

$[Cr(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Cr(H_2O)_5(OH)]^{2+} + H_3O^+$ [1]..... .

$CO_3^{2-} + H_3O^+ \rightarrow CO_2 + 3H_2O$ ..... .

[9]

[Turn over

On heating a sample of **J**, a violent reaction takes place with the evolution of steam and a diatomic gas **M** (M_r = 28.0). The residue from the reaction is a green powder that does not dissolve in water but dissolves in sulfuric acid to give a green solution. The addition of aqueous sodium hydroxide to this green solution gives the precipitate that had been produced in reaction **III**.

(b) Suggest the identity of gas **M** hence write a balanced equation for the action of heat on **J**.

M N_2 [1] .....

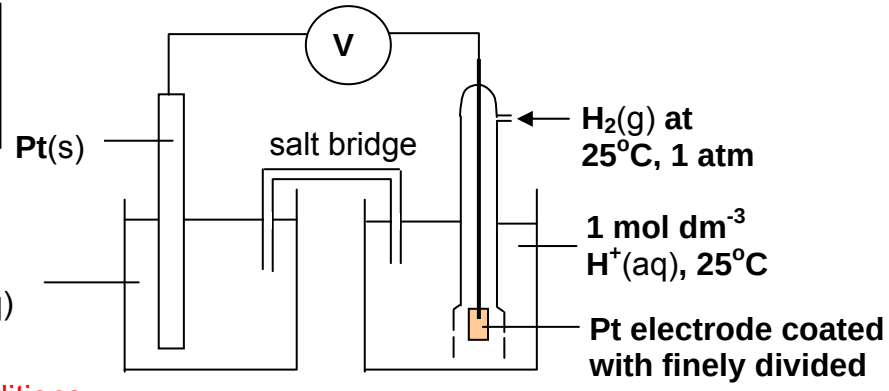
$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s) + N_2(g) + H_2O(g)$ [1] .....

[2]

(c) Draw a labelled diagram to show how you could measure the standard electrode potential of the $Cr^{3+}(aq)/Cr^{2+}(aq)$ system.

-1 mk if battery is included in the diagram.

[1] for EACH half cell drawn and labelled correctly.



1 mk for salt bridge and conditions

[3]

(d) Chrome plating is a technique of electroplating a thin layer of chromium onto a metal or plastic object. The electrolyte is a solution of $CrCl_3(aq)$. In a given electroplating experiment, a current of 4.0 A was passed through the circuit. How long would it take to plate a 20 cm^2 area of an object with 0.10 mm thickness?
[Density of chromium = 7.15 g cm^{-3}]

Volume of Cr = 20 x 0.10 x10^{-1} = 0.2 cm^3;
Mass of Cr = 7.15 x 0.2 = 1.43 g;
Amount of Cr = 1.43 / 52.0 = 0.0275 mol [1]
Cr^{3+} +3e → Cr

Q = n_eF = It
Hence Q = 3 x 0.0275 x 96500 C

Time = 3 x 0.0275 x 96500 / 4.0 = 1990s (or = 33.2 min) [1]

[2]

(e) Manganese and iron are adjacent elements in the d block elements.

$Mn^{3+} + e \rightleftharpoons Mn^{2+}$ $\quad E^{\ominus} = +1.49$ V
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $\quad E^{\ominus} = +0.77$ V

The electrode potentials show that Mn(III) is a stronger oxidising agent than Fe(III). Using electronic configurations, suggest a possible reason for this observation.

Mn^{3+}: [Ar] $3d^4$ $\quad Mn^{2+}$: [Ar] $3d^5$
Fe^{3+}: [Ar] $3d^5$ $\quad Fe^{2+}$: [Ar] $3d^6$

Fe^{3+} has a d^5 ie half-filled configuration which is stable, reduction to Fe^{2+} (with d^6 configuration) poses some destabilization due to inter-electron repulsion. [1]

On the other hand, oxidation of Mn^{3+} (d^4) to Mn^{2+} (d^5) results in extra stability due to half-filled configuration. [1]

.....

.....

.....

.....

.....

.....

.....

.....

.....[2]

[Total:18]

[Turn over

4(a) When chlorine is bubbled through potassium iodide, a brown solution is formed. On shaking the mixture in tetrachloromethane, a purple layer is observed.

(i) Write an equation for the reaction between chlorine and potassium iodide.

$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$ .....

(ii) What is the ion responsible for the brown solution?

I_3^-.....

(iii) Explain why the purple layer is observed.

I_2 is a non-polar molecule. It forms dispersion forces with CCl_4 molecule. .....

I_3^- is soluble in water due to ion-dipole interaction.....

.....

.....

.....

[3]

(b) In an experiment, H_2S was reacted with 12.00 cm^3 of 0.30 mol dm^{-3} of an unknown bromate ion, BrO_x^- in acidic medium to form sulfur of mass 0.289 g as well as bromine solution.

Deduce the oxidation state of Br in BrO_x^-, and hence the value of **x**.

$H_2S \rightarrow S + 2H^+ + 2e$

n(e transferred) = 2 x n(S) = 0.289/32.1= $2(9.00 \times 10^{-3})$

$n(BrO_x^-) = (12.00/1000) \times 0.300 = 0.0036$ mol

0.0036 mol BrO_x^- gains $2(9.00 \times 10^{-3})$ mol [1]

Hence 1 mol BrO_x^- gains 5 mol e to be reduced to Br_2.

Original oxidation state of Br in BrO_x^- is +5.[1]

Value of x : 5 + x(-2) = -1; solving for x = 3 [1]

[3]

[Total: 6]

5(a) Insulin is a peptide hormone that is essential in regulating carbohydrates and fat metabolism in the body. It is composed of two peptide chains (e.g. chain A and chain B). Both the chains are joined together by two disulfide linkages, and another disulfide linkage is formed within chain A. In most species, the insulin is composed of 51 amino acids, where chain A consists of 21 amino acids while chain B consists of 30 amino acids.

(i) Which amino acid forms the disulfide linkages? Illustrate this process by means of an equation.

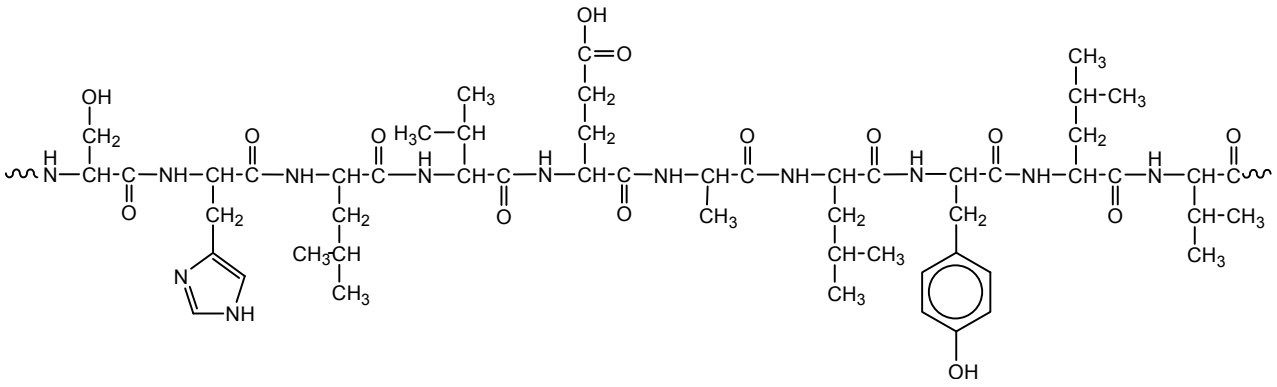
Cysteine [1] both amino acid and equation

$$–CH_2–SH \quad + \quad HS–CH_2– \quad + \quad [O] \rightarrow \quad –CH_2–S–S–CH_2– \quad + \quad H_2O$$

(ii) Suggest a method by which the disulfide linkage can be broken and how it brings about denaturation.

Adding heavy metal ions such as Ag^+, Hg^{2+}, Pb^{2+} and Cu^{2+}.
Heavy metal ions disrupt disulfide bonds because they have high affinity for sulfur and leads to formation of precipitates. [1]

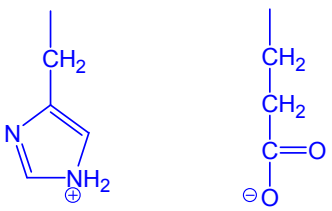
The structure of a portion of chain B is shown below.



(iii) How many different amino acid residues are present in this portion of chain B?

7 [1] .....

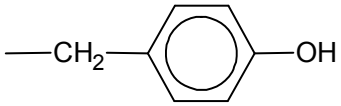
(iv) Using the above portion of chain B, draw the structures of the R groups that give rise to ionic bonds.



[1]

[4]

(b) A nonapeptide **P** was analysed and it contained the following amino acids:

amino acid	*abbreviation*	*formula of R-group*	*number of residues*
Aspartic acid	Asp	$-CH_2CO_2H$	3
Lysine	Lys	$-(CH_2)_4NH_2$	2
Tyrosine	Tyr		3
Valine	Val	$-CH(CH_3)_2$	1

An enzyme **C** digests proteins or polypeptides at the carboxylic acid end of the amino acid tyrosine, Tyr. The following peptides were identified after digestion of **P** with **C**, and subsequent separation.

Asp –Val
Lys – Asp – Tyr
Tyr

Another enzyme **D** digests at the amino end of aspartic acid, Asp. The following peptides were identified after digestion of the same polypeptide **P** with **D**, and subsequent separation.

Asp-Tyr
Asp-Tyr-Lys
Asp-Val
Tyr-Lys

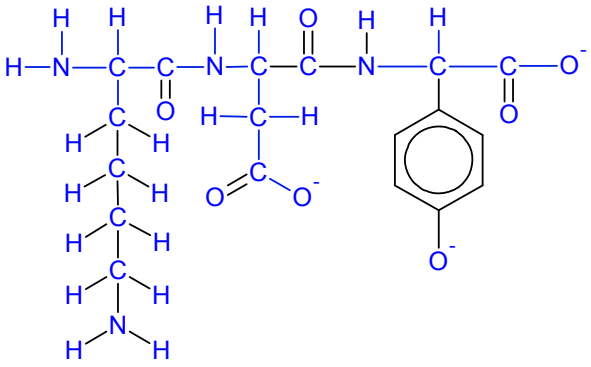
(i) Use the above information to deduce the amino acid sequence of peptide **P** and explain your reasoning.

Complete Sequence:

Tyr
Tyr-Lys
Lys-Asp-Tyr
Asp-Tyr-Lys
Lys-Asp-Tyr
Asp-Tyr
Asp-Val [2] for working

Nonapeptide: Tyr-Lys-Asp-Tyr-Lys-Asp-Tyr-Asp-Val [1]

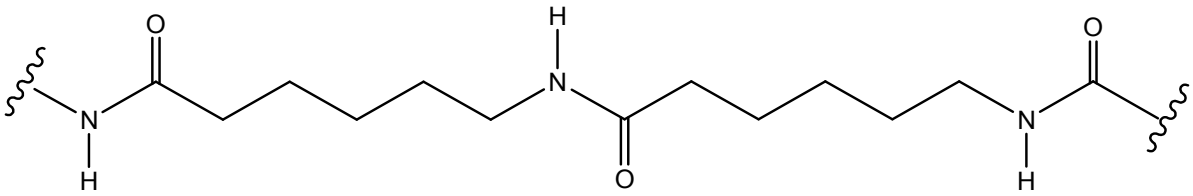
(ii) Draw the displayed formula of the Lys-Asp-Tyr tripeptide at pH 11.



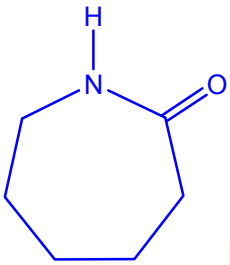
[1] 2 X COO^- and phenoxide
[1] displayed formula

[5]

(c) Nylon 6 is synthesised by ring opening polymerisation of caprolactam molecules. When caprolactam molecule polymerises, the ring breaks and the molecules join up in a continuous chain as shown below.



Suggest the structure of caprolactam.



[1]

[1]

[Total: 10]

[End of Paper]