Index No.	Name	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/02**
Higher 2

Paper 2 Structured Questions **16 August 2018**
2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.
A Data Booklet is provided.

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

For Examiner's Use	
Question no.	**Marks**
1	**/ 14**
2	**/ 6**
3	**/ 9**
4	**/ 13**
5	**/ 12**
6	**/ 9**
7	**/ 12**
TOTAL	**/ 75**

This document consists of **21** printed pages, including this cover page.

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

1 A mixture contains two white solids **X**CO_3 and **Y**SO_4 where **X** and **Y** could be either magnesium, zinc or barium. The following investigations were carried out to determine the identity of **X** and **Y**.

(a) When the mixture of solids was treated with excess dilute hydrochloric acid, a colourless gas was evolved and some, but not all, of the mixture dissolved.

The resulting mixture was filtered. To the filtrate, dilute aqueous ammonia was added dropwise till in excess. The white precipitate formed was insoluble in excess aqueous ammonia.

Deduce the identity of elements **X** and **Y**, showing your reasoning clearly. [3]

- **X- Mg Y- Ba**
- **$BaSO_4$ insoluble in dil HCl ,**
- **filtrate contains Mg^{2+} which ppt to form $Mg(OH)_2$ white ppt insol in excess aq ammonia**
  OR
- **White ppt contains Mg^{2+} as Zn^{2+} forms ppt but it is soluble in excess NH_3**

(b) Group 2 carbonates decompose according to the following equation:

$$ZCO_3\ (s) \longrightarrow ZO\ (s) + CO_2\ (g)$$

element	magnesium	calcium	barium
enthalpy change for the reaction, ΔH_r/ kJ mol^{-1}	+101	+178	+269

(i) Use the data above to state and explain the trend in the thermal stability of the Group 2 carbonates. [3]

- **ΔH_r become more endo, thermal stability increases**
- **increasing ionic radii leading to decreasing charge density/ polarising power and**
- **less distortion of electron cloud of large anion**

(ii) Lithium carbonate, a Group 1 carbonate, decomposes on heating.

Use relevant data from the Data booklet to calculate relative charge densities of the above cations and hence deduce which of the above **ΔH_r** values in the table is likely to be the nearest to that of lithium carbonate. [2]

	Mg^{2+}	Ca^{2+}	Ba^{2+}	Li^{+}
Relative charge density	**2/0.065 =30.8**	**2/0.099 =20.2**	**2/0.135 =14.8**	**1/0.06 =16.7**

ΔH_r of Li_2CO_3 resembles that of $BaCO_3$

(c) Patients with digestive tract problems are sometimes asked to take an x-ray after they have swallowed a "barium meal", consisting of a suspension of $BaSO_4$ in water.

(i) Write an expression for the solubility product, K_{sp}, for $BaSO_4$, including its units.

$K_{sp} = [Ba^{2+}][SO_4^{2-}]$ units: $mol^2\ dm^{-6}$

(ii) The numerical value of K_{sp} is 1.30×10^{-10}. Calculate $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$.

In saturated solution, IP = K_{sp}
$[Ba^{2+}] = \sqrt{1.30 \times 10^{-10}} = 1.14 \times 10^{-5}$ mol dm^{-3}

(iii) Although Ba^{2+} ions are toxic, the $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$ is too low to cause any problems of toxicity.

The numerical value of K_{sp} for $BaCO_3$ (5×10^{-10}) is not significantly higher than that of $BaSO_4$, but $BaCO_3$ is **very** poisonous if ingested. Suggest a reason why this might be so.

$BaCO_3$ reacts with the acid in the stomach to release Ba^{2+} ions.

(iv) $BaSO_4$ is commonly prepared in the laboratory by combining solutions containing Ba^{2+} and SO_4^{2-}.

Determine if $BaSO_4$ will form when equal volumes of 2.00×10^{-2} mol dm^{-3} $Ba(NO_3)_2$ and 4.00×10^{-2} mol dm^{-3} Na_2SO_4 are mixed.

$[Ba^{2+}]$ after mixing = 1.00×10^{-2} mol dm^{-3}
$[SO_4^{2-}]$ after mixing = 2.00×10^{-2} mol dm^{-3}

IP on mixing = $2.00 \times 10^{-4} > K_{sp}$ (1.14×10^{-10})
Hence precipitation will take place.

[2]

[Total: 14]

2 A student conducted two separate electrolysis using inert electrodes under room temperature and pressure.

electrolysis reaction	electrolyte	volume of gas collected at anode / cm^3	duration
1	concentrated hydrochloric acid	150	10 minutes
2	aqueous sodium sulfate	37.5	

(a) (i) Write the half-equation with state symbols for the reaction occurring at the anode for electrolysis reaction **1**. [1]

$2Cl^-$ (aq) → Cl_2 (g)+ $2e^-$

(ii) Calculate the current that was used in electrolysis reaction **1**. [2]

Amt of Cl_2 collected = 150/24000 = 6.25×10^{-3} mol

Amt of electrons passed through = $6.25 \times 10^{-3} \times 2 = 0.0125$ mol

Quantity of charge passed through = 0.0125 x 96500 = 1206.25 C

Current used = 1206.25 / (10 x 60) = 2.01 A

(b) (i) Write the half-equation with state symbols for the reaction occurring at the anode for electrolysis reaction **2**. [1]

$2H_2O$ (l) → O_2 (g) + $4H^+$ (aq) + $4e^-$

(ii) Determine the current used in electrolysis reaction **2**. [2]

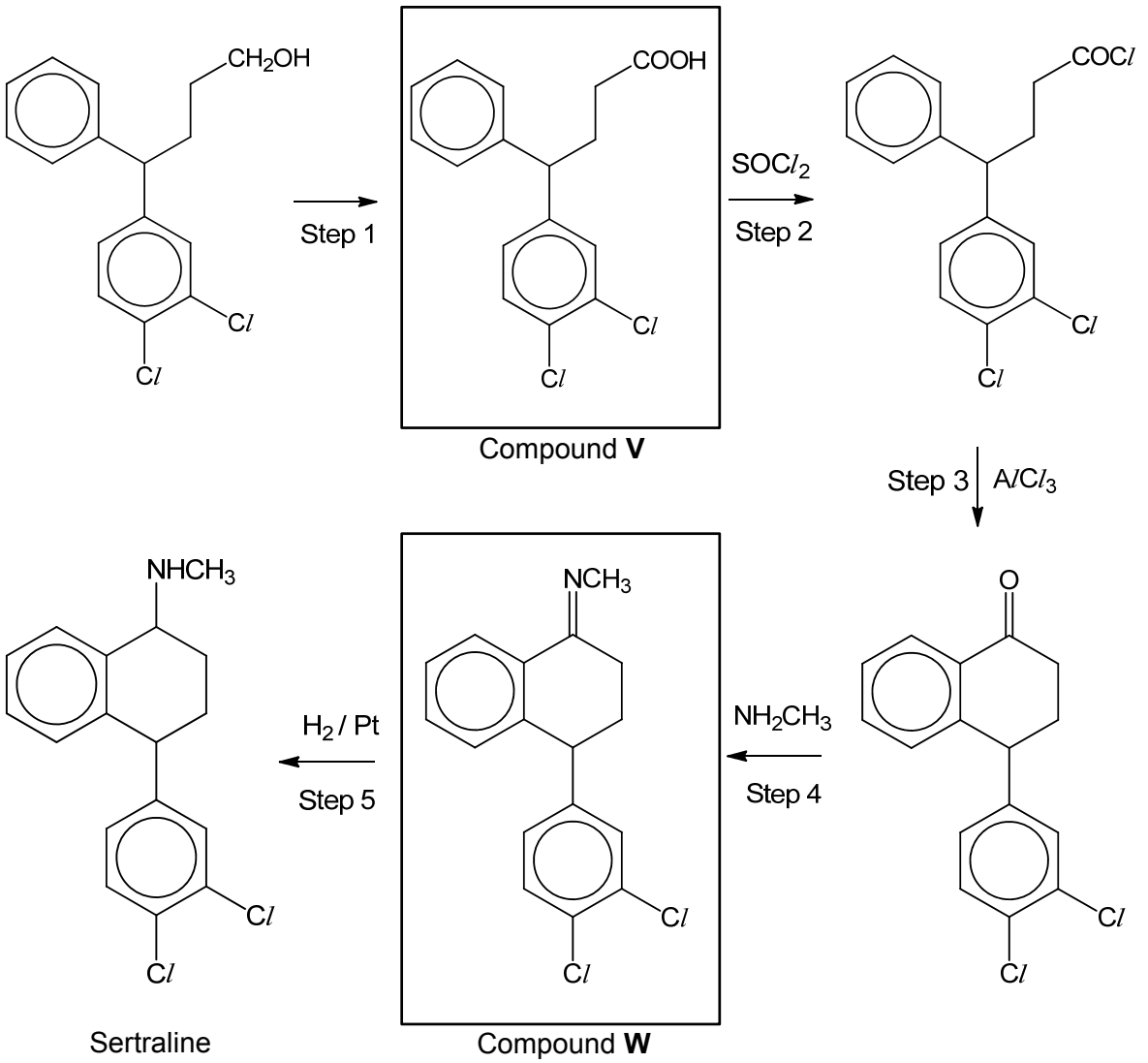
If the current used was the same, the volume of gas obtained in reaction should be halved based on the number of e- required. Since the volume of gas is four times less than that in reaction 1, the current used must be halved.

Current used = ½ x 2.01 =1.005 = 1.01A

[Total: 6]

3 Sertraline is an antidepressant used to treat depression, obsessive compulsive disorder, post-traumatic stress disorder and related conditions. This medication can help to improve mood, mental alertness, energy level and sleep pattern for the patients. Sertraline works by helping to restore the balance of serotonin, a neurotransmitter in the brain which regulates anxiety, mood and happiness.

A proposed synthesis route of sertraline is shown below.

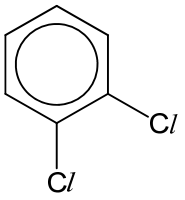


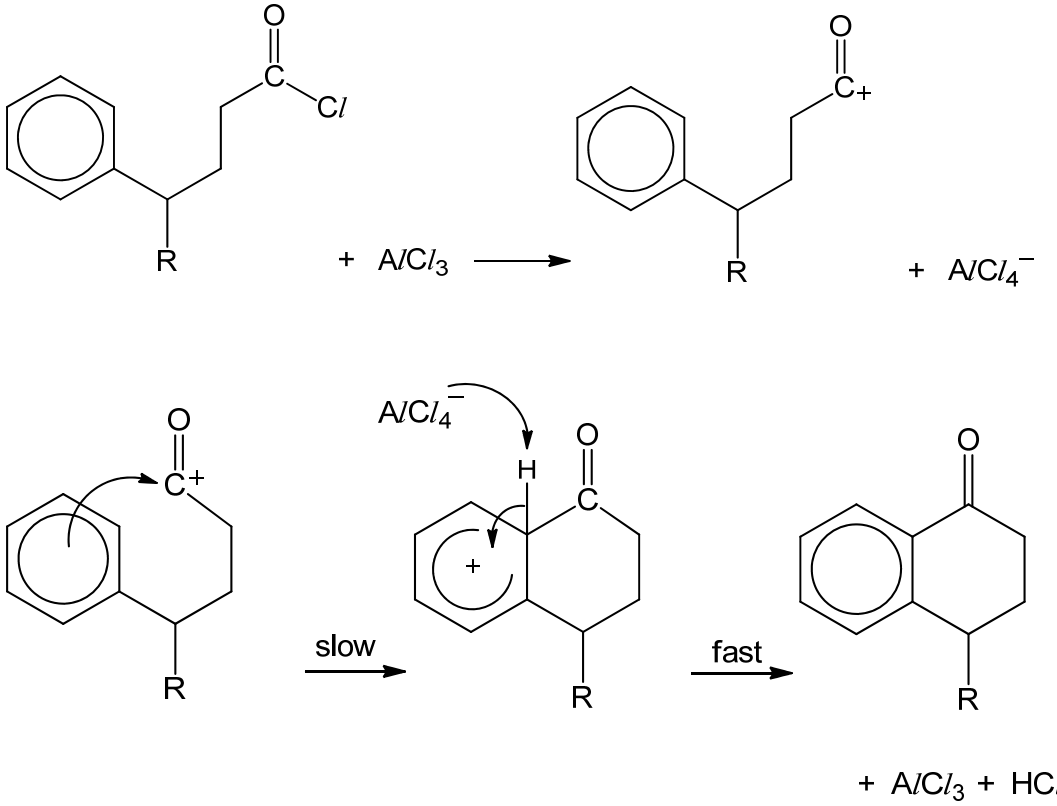
(a) State the reagents and conditions needed for step 1 and draw the structure of compound **V** in the box above.

$K_2Cr_2O_7$, dilute H_2SO_4, heat under reflux

(b) Electrophilic substitution takes place in step 3 where $AlCl_3$ acts as a Lewis acid catalyst and reacts with the acyl chloride functional group to generate the electrophile.

Write an equation to show the generation of the electrophile and hence draw the mechanism for the reaction that occurs in step 3.

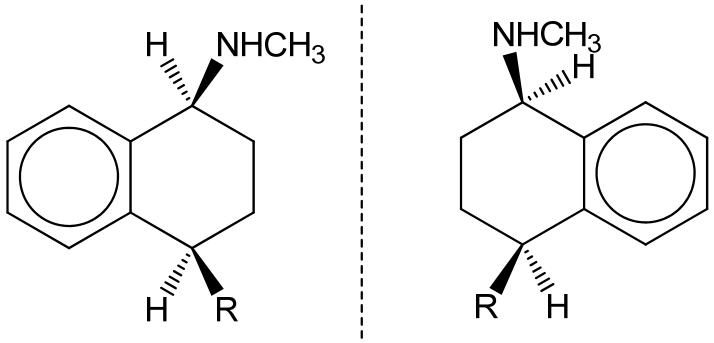
You may use R to represent  in Sertraline for part **(b)** and part **(d)**.

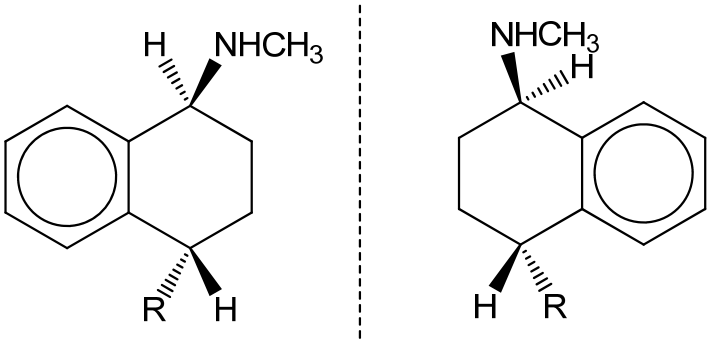


(c) State the type of reaction taking place in step 4 and draw the structure of compound **W** in the box above.

Condensation

(d) Sertraline exists as a mixture of stereoisomers. Draw the structures of the stereoisomers of Sertraline.





[Total: 9]

4 (a) The change in colour from blue to pink of the cobalt complexes has been the basis of cobalt chloride indicator papers for the detection of the presence of water.

The two differently coloured cobalt(II) complex ions, $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$, exist together in equilibrium in solution in the presence of chloride ions. This is represented by the equation below.

$$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$$

An experiment is conducted to investigate the effects on the equilibrium position by imposing a series of changes on the system. The shift in equilibrium position can be indicated by any colour change of the solution.

species	colour
$Co(H_2O)_6^{2+}$ (aq)	pink
$CoCl_4^{2-}$ (aq)	blue
initial equilibrium mixture containing $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$	purple

After a 3.00 cm^3 sample of an initial equilibrium mixture was placed in three separate boiling tubes, a different substance was added to each tube, as indicated in Table 4.1.

(i) Complete Table 4.1 by predicting:

- the change in concentration, if any, of each ions in solution compared to the initial solution, after a new equilibrium position is reached.
- the colour change, if any, that takes place from the initial purple-coloured solution.

Table 4.1

Substance added	Change in concentration from initial solution to new equilibrium (increase, decrease, unchanged)			Colour change (pink, blue or unchanged)
	$[Co(H_2O)_6]^{2+}$	Cl^-	$[CoCl_4]^{2-}$	
$H_2O(l)$				
Concentrated HCl				

$AgNO_3(aq)$				

[3]

Substance added	Change in concentration from initial equilibrium to final equilibrium (increase, decrease, unchanged)			Colour favoured (pink, blue or unchanged)
	$[Co(H_2O)_6]^{2+}$	Cl^-	$[CoCl_4]^{2-}$	
$H_2O(l)$	**decrease**	**decrease**	**decrease**	**pink**
Concentrated HCl	**decrease**	**increase**	**increase**	**blue**
$AgNO_3(aq)$	**increase**	**decrease**	**decrease**	**pink**

[3]

(ii) Another experiment was conducted to investigate the effect of temperature on the same equilibrium mixture. When 3.00 cm^3 of the original equilibrium mixture in a test tube was placed in an ice bath, the solution became pink.

Determine whether the forward reaction, as illustrated by the equation above, is exothermic or endothermic. Use Le Châtelier's Principle to justify your answer.

A decrease in temperature shifts position of equilibrium to the left (pink colour) and a decrease in temperature favours exothermic reaction to release heat.

Hence the reverse reaction is exothermic and the forward reaction is endothermic.

(b) At room temperature, a solution of sodium tartrate, $Na_2C_4H_4O_6$, does not react with hydrogen peroxide. When heated in a water bath, the reaction mixture reacts giving a very slow stream of carbon dioxide.

When a few drops of an aqueous pink cobalt(II) salt are added, the colour of the solution soon turns green and a vigorous effervescence of carbon dioxide takes place.

When the reaction stops, the pink colour is restored.

The half equation for the oxidation of tartrate ions is given as shown:

$$C_4H_4O_6^{2-}(aq) + 8OH^-(aq) \longrightarrow 4CO_2(g) + 6H_2O(l) + 10e^-$$

(i) In alkaline medium, H_2O_2 exists as hydroperoxide ions, HO_2^-. Construct a balanced half equation for the reduction of HO_2^- to OH^-.

$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$

(ii) Write a balanced ionic equation for the reaction between tartrate ions and hydroperoxide ions.

Oxidation half-equation
$C_4H_4O_6^{2-} + 8OH^- \rightarrow 4CO_2 + 6H_2O + 10e^-$

Reduction half-equation

$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$

Balanced eqn:
$C_4H_4O_6^{2-} + 5\ HO_2^- \rightarrow 4CO_2 + H_2O + 7OH^-$

(iii) Suggest why there is no reaction observed when tartrate ions and hydroperoxide ions are mixed at room temperature even though the reaction is energetically feasible.

The activation energy is high due to electrostatic repulsion between the two negatively charged ions.

(iv) Explain why a slow stream of carbon dioxide is observed when reaction mixture is heated in a water bath.

As temperature increases, more particles have energy more than or equal to the activation energy and
hence frequency of effective collision increases and rate increases.

(v) State the identity of the aqueous ions responsible for the green colour.

Aqueous cobalt (III) ions

(vi) Use your answer in **(b)(v)** to describe the catalysed two-step reactions involving aqueous cobalt ions with the tartrate ions and hydroperoxide ions.

New mechanism:

Step 1- pink cobalt(II) ions is oxidised by hydroperoxide ions to green cobalt(III) ions

Step 2-green cobalt(III) ions are reduced by tartrate ions back to pink cobalt(II) ions, thus regenerating the catalyst.

Or
Step 1
$2Co^{2+} + HO_2^- + H_2O \rightarrow 2Co^{3+} + 3OH^-$

Step 2
$C_4H_4O_6^{2-} + 8OH^- + 10Co^{3+} \rightarrow 4CO_2 + 6H_2O + 10Co^{2+}$

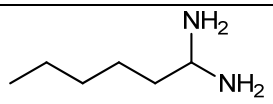
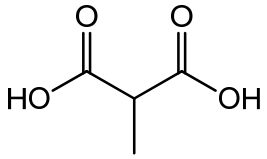
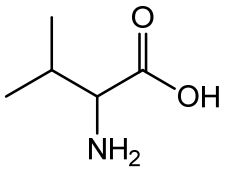
[Total: 13]

5 (a) Amino acids are biologically-important organic compounds containing both amine ($-NH_2$) and carboxylic acid (-COOH) functional groups.

To consider the effect of having both an amine and a carboxylic acid functional group on the same molecule, amino acids can be compared with other organic compounds such as diamines and dicarboxylic acids.

Amino acids have significantly higher melting points than diamines and dicarboxylic acids of similar mass and structure as shown in Table 5.1 below.

Table 5.1

compound type	example	molar mass / g mol^{-1}	melting point / ^{o}C
diamine	 hexane-1,1-diamine	116.2	39
dicarboxylic acid	 methylpropanedioic acid	118.1	184
amino acid	 2-amino-3-methylbutanoic acid (valine)	117.2	298

Explain why the melting points show an increasing trend from diamine to amino acid in terms of structure and bonding.

Diamine and dicarboxylic acid have simple molecular structures with hydrogen bonds between polar molecules.

Dicarboxylic acid has stronger hydrogen bonds than diamine as O-H bond is more polarised and has more extensive hydrogen bonds than diamines.

Hence more energy is needed to break hydrogen bonds in dicarboxylic acid than in diamine, hence it has higher m.p.

Valine has a giant ionic lattice with strong electrostatic forces of attraction(or ionic bonds) between the zwitterions.

More energy is needed to break stronger ionic bonds compared to hydrogen bonds, hence it has the highest m.p.

(b) When 50.0 cm^3 of hexane was shaken with 20.0 cm^3 of an aqueous solution containing 1.10 g of 2-amino-3-methylbutanoic acid (valine), it was found that 0.050 g of valine was extracted into the hexane. At equilibrium, the ratio of the concentration of valine in the two immiscible solvents is a constant called partition coefficient where

$$K_{partition} = \frac{[valine]_{hexane}}{[valine]_{aq}}$$

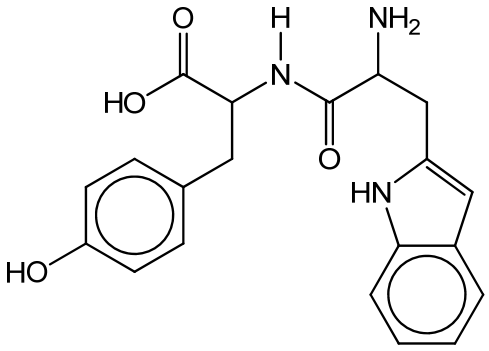
(i) Calculate the partition coefficient, $K_{partition}$, of valine between hexane and water.

$K_{partition}$ = $[valine]_{hexane}/[valine]_{aq}$
= (0.05/50)/(1.05/20) = 0.0190

(ii) State which is a better solvent for valine and explain the reason for its solubility in that solvent.

Water is a better solvent as valine exists as zwitterion and forms ion-dipole interactions with water.

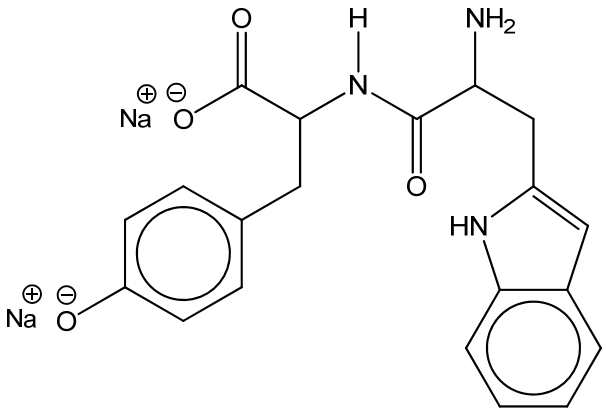
(c) Tryptophan is an essential amino acid found in foods such as chicken, eggs, cheese and milk. It is needed to create the neurotransmitter serotonin which promotes sleep. Two amino acids, tyrosine (tyr) and tryptophan (trp), form a dipeptide, tyr-trp, as shown by the following structure.



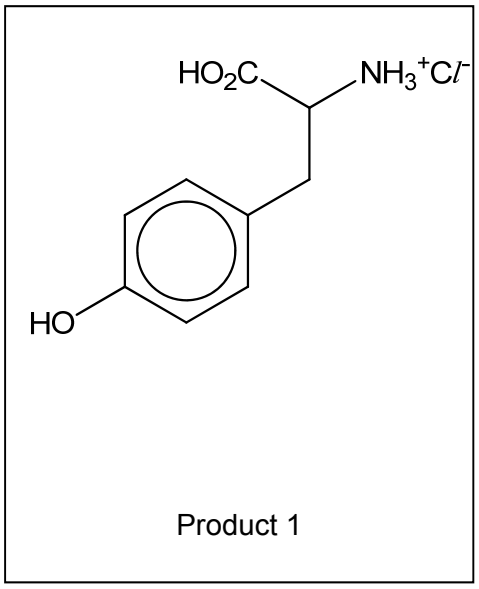
tyr–trp

Draw the structures of the products of the reactions of tyr-trp with an excess of each of the following reagents.

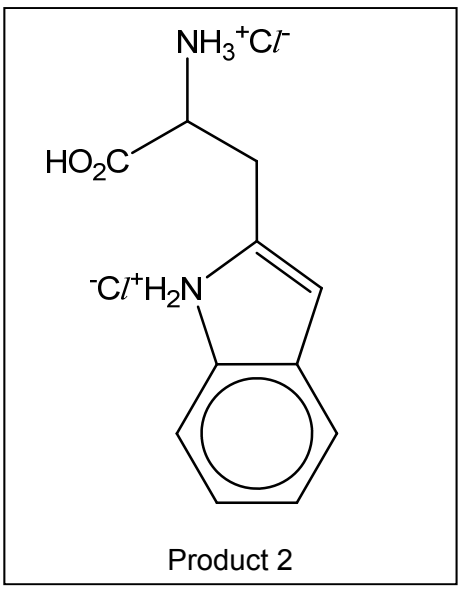
(i) NaOH(aq) at room temperature



(ii) HC*l*(aq) and heat under reflux

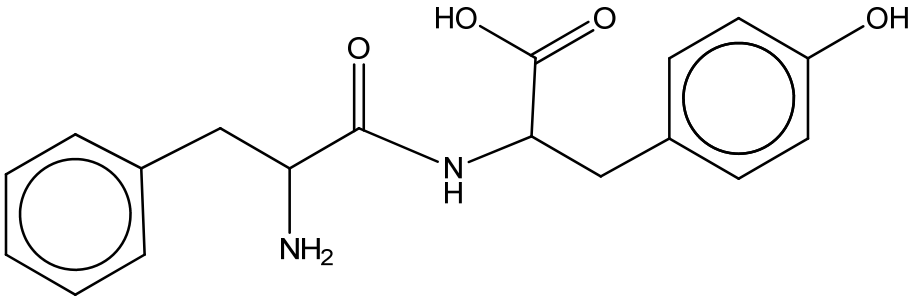


Product 1



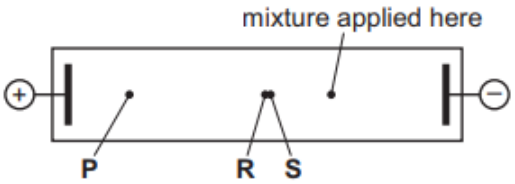
Product 2

(d) Phenylalanine and tyrosine form another dipeptide (phe-tyr) as shown below.



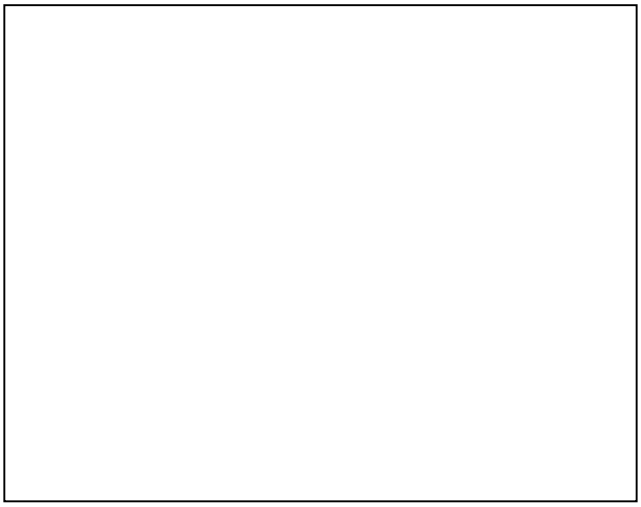
phe-tyr

A mixture of the dipeptide (phe-tyr) and its two constituent amino acids (phenylalanine and tyrosine) was subjected to electrophoresis in a buffer at pH 12. At the end of the experiment the following results were seen. Spots **R** and **S** remained very close together.



The three spots are due to the three species phenylalanine, tyrosine and the dipeptide, phe-tyr.

(i) Draw the structural formula of the species responsible for spot **P.**



[1]

(ii) Suggest why the other two species give spots **R** and **S** that are so close together.

dipeptide / phe-tyr) has 2– and its M_r is about double that of phe with 1

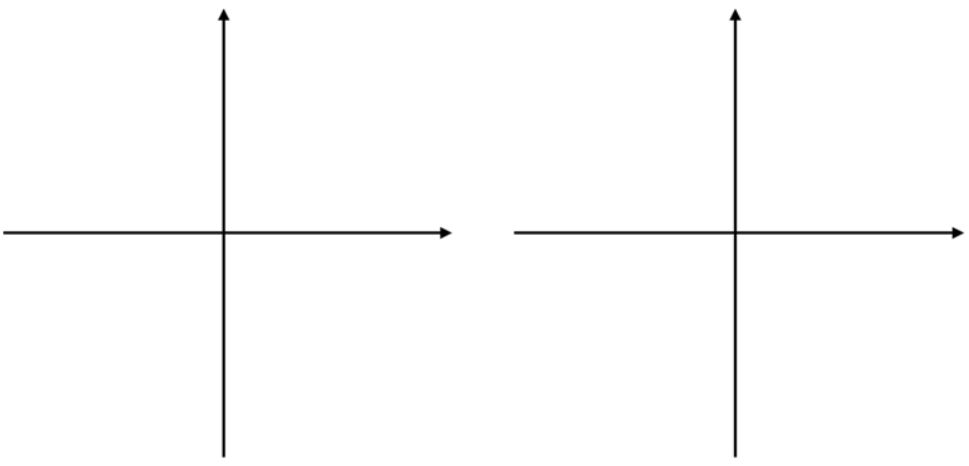
OR

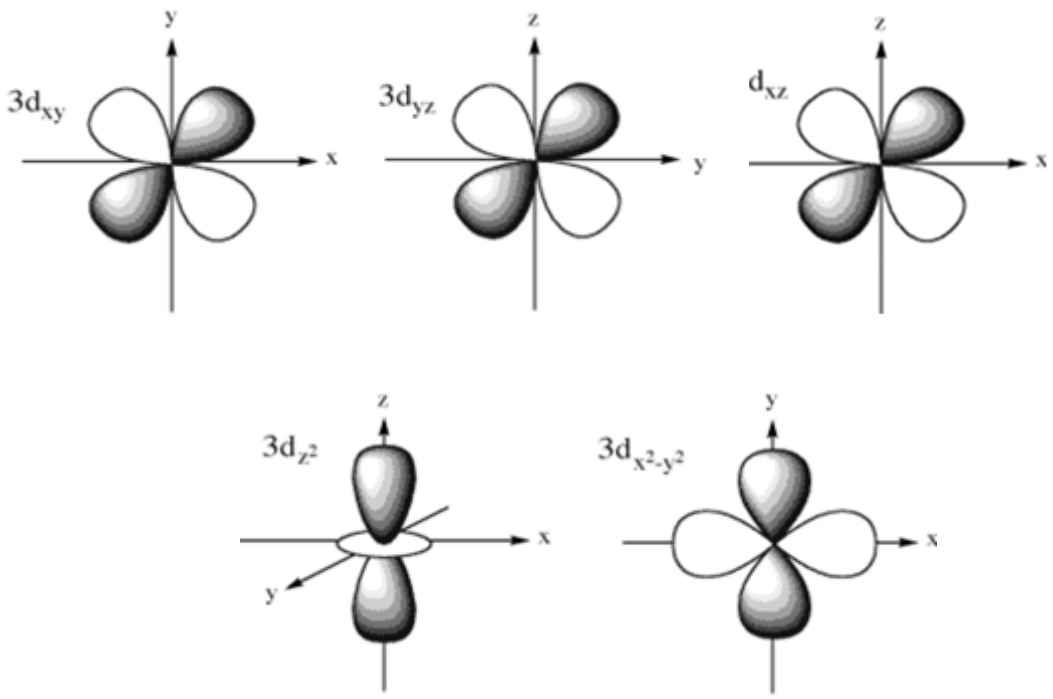
charge / mass ratios are about the same for the dipeptide (phe-tyr) and phe

[Total: 12]

6 In an isolated transition metal atom, the five 3d-orbitals are degenerate. However, in an octahedral complex ion, the presence of ligands splits the five orbitals into a group of three and a group of two. These two groups have slightly different energies.

(a) Using the axes provided below, draw and label the shape of **one** d-orbital in **each** of the two groups mentioned above.





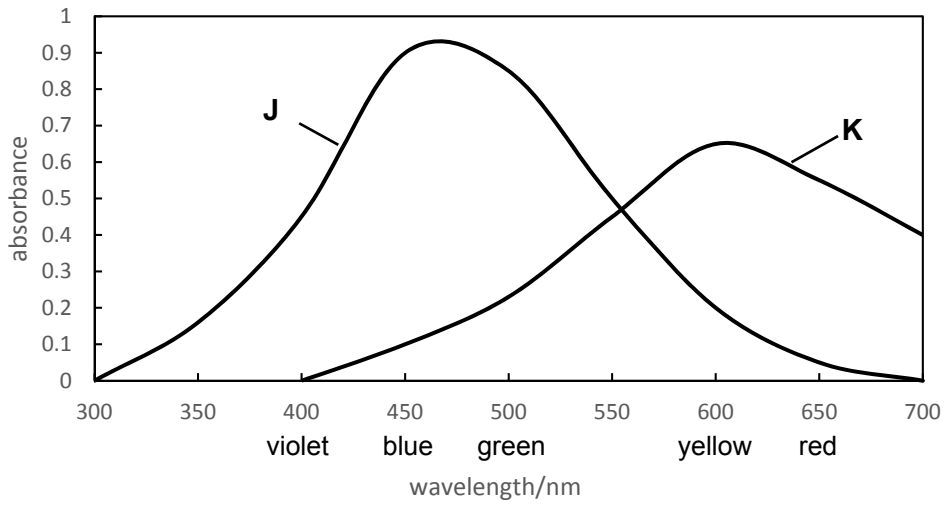
(b) Explain how the presence of the six ligands, L, in $[NiL_6]^{2+}$ splits the five 3d orbitals into two groups of different energy, and explain whether the two-orbital group or the three-orbital group has the higher energy.

Ligands have lone pairs of electrons and they approach the metal ion along the primary axes.

The d electrons in the orbitals pointing towards the ligands experience repulsion and hence of a higher energy level.

Since the d(x^2-y^2) and dz^2 orbitals point towards the ligands, the two-orbital group is higher in energy.

(c) The absorbance spectra of solutions of two transition metal complexes **J** and **K** are shown in the diagram below.



A list of possible colours for these complexes is as follows.

yellow red green blue

Choose one of the colours above to describe the observed colour of each solution.
Solution **J** …….. Solution **K** ……..

Solution J red **Solution K blue**

(d) Ligands are classified based on their ability to split the five 3d orbitals into two groups with an energy difference (ΔE). Strong field ligands produce a large ΔE while weak field ligands produce a small ΔE.

The energy of a photon can be obtained by Planck's equation:

$$E = \frac{hc}{\lambda}$$

where:

E is the energy of the photon
λ is the wavelength of the photon
h is Planck's constant
c is the speed of light in vacuum

Use the data below as well as data from the *Data Booklet*, complete the table and arrange the ligands in order of increasing field strength.

species	$[M(CN)_6]^{2-}$	$[M(F)_6]^{4-}$	$[M(H_2O)_6]^{2+}$
λ / nm	430	650	600
ΔE / J			

Increasing field strength: ……<……<…… [2]

species	**$[M(CN)_6]^{2-}$**	**$[M(F)_6]^{4-}$**	**$[M(H_2O)_6]^{2+}$**
λ/nm	**430**	**650**	**600**
ΔE/ J	**4.63×10^{-19}**	**3.06×10^{-19}**	**3.32×10^{-19}**

Increasing field strength: $F^- < H_2O < CN^-$

[Total: 9]

7 The oxidising power of our atmosphere has been well-studied and is of importance as many environmental trace gases, such as methane, are removed.

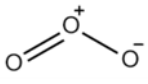
The most abundant oxidants in the atmosphere are oxygen and ozone molecules. These molecules have strong bonds and are hence relatively unreactive except towards radicals. Research in the 1950s suggested that the hydroxyl radical, •OH, is a strong oxidant.

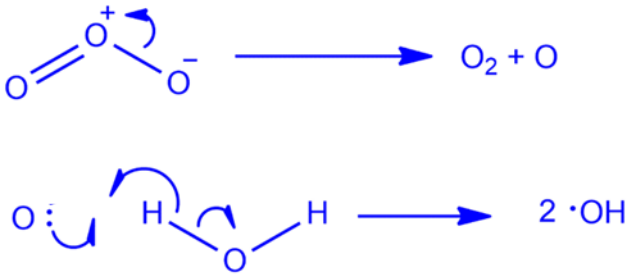
In the stratosphere, UV light from the sun heterolytically breaks ozone molecules into oxygen molecules and oxygen atoms. The oxygen atoms react homolytically with water vapour to produce hydroxyl radicals, •OH.

$$O_3 \xrightarrow{UV} O_2 + O \qquad \text{----------(1)}$$

$$O + H_2O \longrightarrow 2{\bullet}OH \qquad \text{----------(2)}$$

(a) Use equations (1) and (2) to draw the mechanism for the formation of the hydroxyl radical, •OH. Include in your mechanism the necessary curly arrows and electrons. [2]

Use  as the structure of ozone.



(b) Hydroxyl radicals are particularly reactive towards H-containing molecules due to H-abstraction converting •OH back to H_2O.

$$\bullet OH + CH_4 \longrightarrow H_2O + \bullet CH_3 \qquad \text{----------(3)}$$

Some information about an elementary reaction (3) was obtained.

[•OH] / molecules cm^{-3}	1.0×10^6
[CH_4] / molecules cm^{-3}	4.4×10^{13}
rate constant, k / cm^3 $molecule^{-1}$ s^{-1}	1.4×10^{-5}

Source: Jacob, D. J. Introduction to Atmospheric Chemistry; Princeton University Press: 1999

(i) Use information in the table to write an equation to represent the rate equation for the pseudo-first-order reaction with respect to the concentration of the hydroxyl radical, •OH.

rate = k' [•OH]

(ii) Calculate the half-life of the hydroxyl radical, •OH to the nearest **2 significant figures**.

rate = k' [•OH], k' = k [CH_4]

k' = 1.4 x 10^{-5} x 4.4 x 10^{13} = 6.16 x 10^8 s^{-1}

$t_{1/2}$ = $\frac{ln2}{k'}$ = $\frac{ln2}{6.16\times10^8}$ = 1.1 x 10^{-9} s

(c) The relative rates of disappearance in air at 305 K for a series of hydrocarbons were measured in an environmental chamber under simulated atmospheric conditions. Absolute rate constants obtained from the reaction are as follows.

hydrocarbon	k / × 10^9 mol^{-1} dm^3 s^{-1}
butane	1.8
hexane	3.8
cis-but-2-ene	39.2

Source: J. Phys. Chem. 80, 8, 789-794

(i) Use the information given in **(b)** and refer to the bonding within butane and hexane to suggest a reason for the difference in their reactivity.

There are more C–H bonds in hexane than butane, leading to a faster rate of H-abstraction.

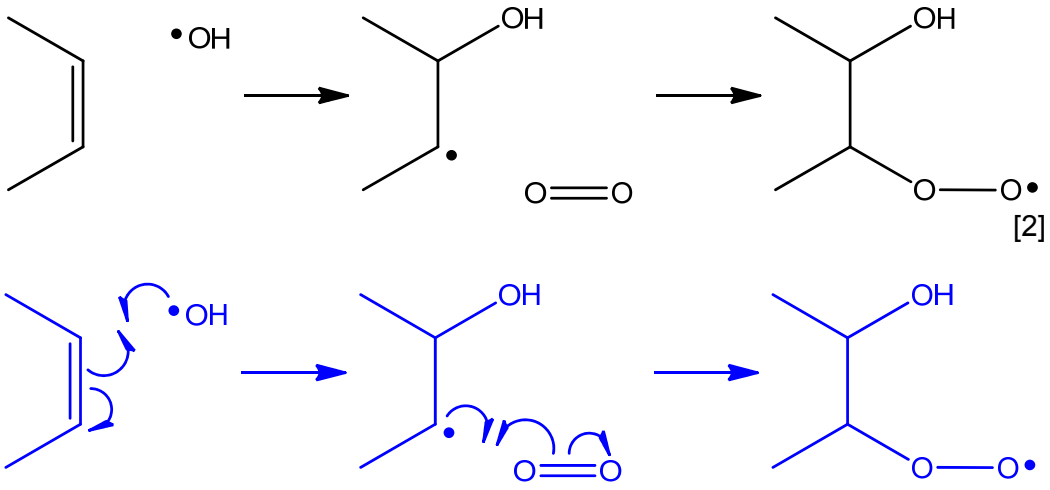
(ii) The reaction between hydroxyl radicals and alkenes proceed via a different mechanism and this increases the rate of reaction.

Account for this difference referring to the terms 'sigma' and 'pi'.

The pi electrons in the alkene C=C bond are less tightly bound to the nucleus
OR
weaker as compared to the sigma electrons in the C–H bond and hence reaction with alkenes proceed faster.

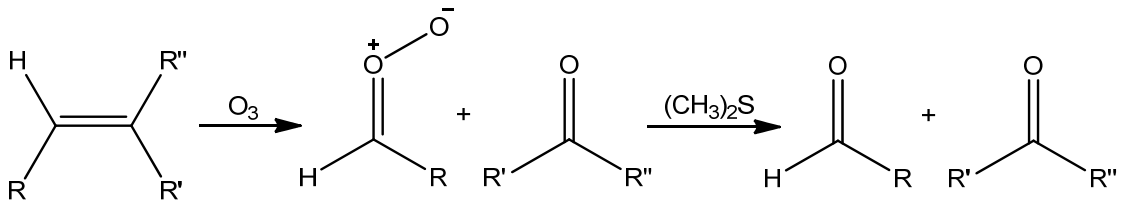
After the attack of the hydroxyl radical on cis-but-2-ene, the intermediate is now reactive enough to react with molecular oxygen.

(iii) Complete the diagram to suggest a mechanism to show how the hydroxyperoxyl radical is formed. Show the movement of electrons by using curly arrows.

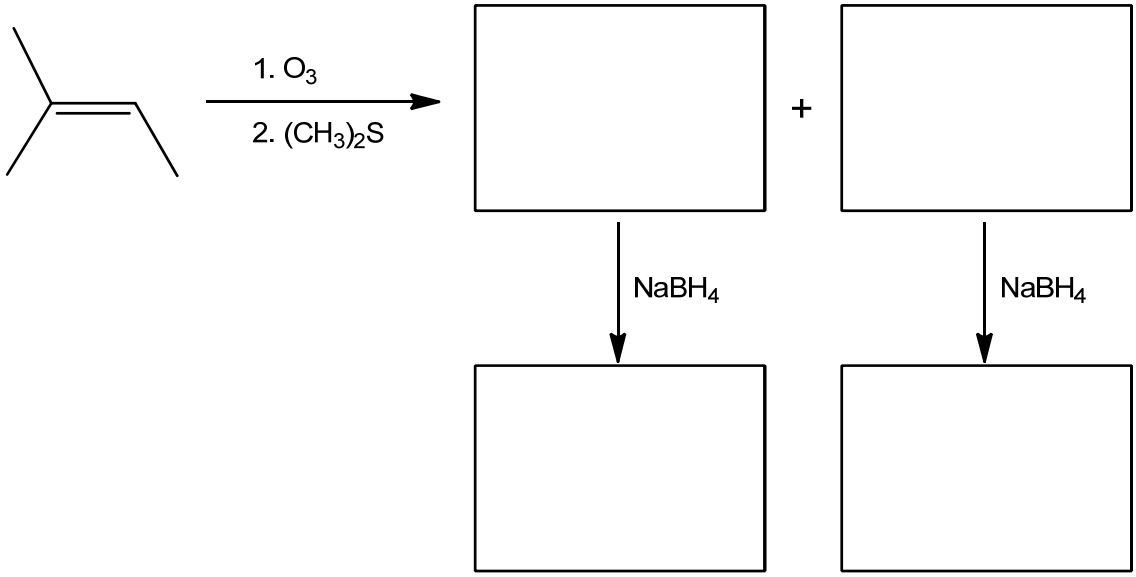


[2]

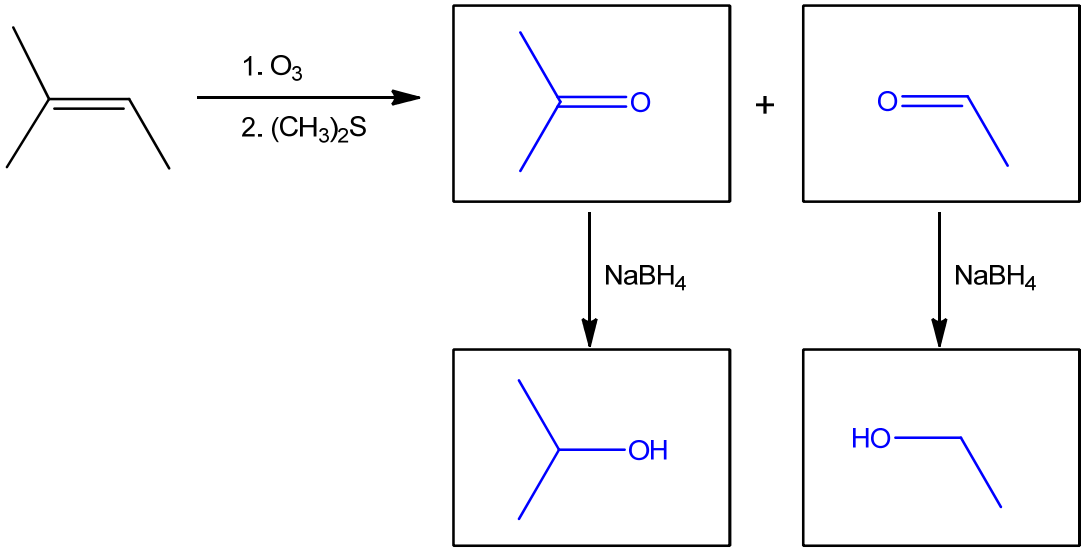
(d) Alkenes can also react with ozone directly via a process known as ozonolysis and the first step produces a carbonyl oxide and a carbonyl compound. Quenching with dimethyl sulfide produces two carbonyl compounds.



Complete the reaction scheme below.



[3]



[Total: 12]

~ End of Paper~