EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2025
General Certificate of Education Advanced Level
Higher 2

Chemistry Paper 3 Suggested Solutions with Marker's comments

Section A

Answer **all** the questions in this section.

1 Indirect calorimetry is used to estimate energy expenditure in humans by measuring the difference in oxygen concentration between inhaled and exhaled air. During aerobic respiration at 37 ºC, glucose, $C_6H_{12}O_6$, is oxidised to carbon dioxide and water while producing energy as shown in reaction 1 below.

reaction 1 $\quad C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \quad \Delta H^{\ominus} = -2818 \text{ kJ mol}^{-1}$

(a) (i) It is assumed that there are negligible intermolecular forces of attraction between gas particles in an ideal gas.

State **two** other basic assumptions of kinetic theory as applied to an ideal gas. [2]

(ii) Air contains about 21% oxygen, by volume. Exhaled air contains 14% oxygen. At complete rest, a typical adult exchanges approximately 500 cm^3 of air per breath at a rate of 12 times per minute at a temperature of 37 ºC at 1 atmospheric pressure.

By assuming oxygen to be an ideal gas, calculate the volume of oxygen gas consumed per minute. Hence, determine amount of oxygen gas used per minute. [3]

(iii) Assuming that the oxygen inhaled is used for respiration directly, use relevant information in reaction 1 and your answer in **(a)(ii)**, calculate the approximate amount of energy released per minute. [1]

(i) The gas particles are in **constant, random motion**,
the volume of ideal gas particles are zero, and
there are **perfectly elastic collisions between gas particles**.

(ii) volume of O_2 consumed per minute $= (21 - 14)/100 \times 500\ cm^3 \times 12$

$= 420\ cm^3 = 4.20 \times 10^{-4}\ m^3$

$pV = nRT$

$(101325)(4.20 \times 10^{-4}) = n(8.31)(37 + 273)$

$n = 0.0165$ mol = **1.65×10^{-2} mol**

(iii) From equation 1, total of 6 mol of O_2 releases 2818 kJ of energy

Amt of energy released per minute $= (2818 \div 6) \times 0.0165 = 7.7495$ kJ

$=$ **7.75 kJ**

(b) Glucose, $C_6H_{12}O_6$, is the ubiquitous source of energy for cells in the body.

(i) Define the standard enthalpy change of formation of glucose, $C_6H_{12}O_6(s)$. [1]

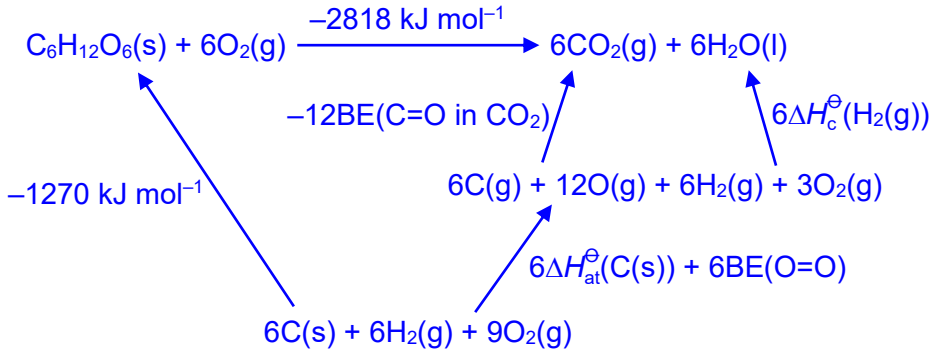
(ii) Use the following data, reaction 1 and appropriate data from the *Data Booklet*, to construct an energy cycle and calculate the standard enthalpy change of atomisation of C(s). Show your working.

enthalpy change of formation of $C_6H_{12}O_6(s)$ = –1270 kJ mol^{-1}
enthalpy change of combustion of $H_2(g)$ = –286 kJ mol^{-1}

[3]

(i) **The energy change when 1 mole of glucose is formed from its constituent elements in their standard states**.

(ii)



$-2818 - 1270 = 6\Delta H^{\ominus}_{at}(C(s)) + 6BE(O=O) - 12BE(C=O \text{ in } CO_2) + 6\Delta H^{\ominus}_{c}(H_2(g))$

$-2818 - 1270 = 6\Delta H^{\ominus}_{at}(C(s)) + 6(+496) - 12(+805) + 6(-286)$

$6\Delta H^{\ominus}_{at}(C(s)) = +4312 \text{ kJ mol}^{-1}$

$\Delta H^{\ominus}_{at}(C(s)) = +$**718.67 kJ mol^{-1}** $\approx$ **+719 kJ mol^{-1}**

(c) Glucose exists in two forms, α-glucose and β-glucose as shown in Fig. 1.1. If a solution of α-glucose is left some time, it will come into dynamic equilibrium with β-glucose.

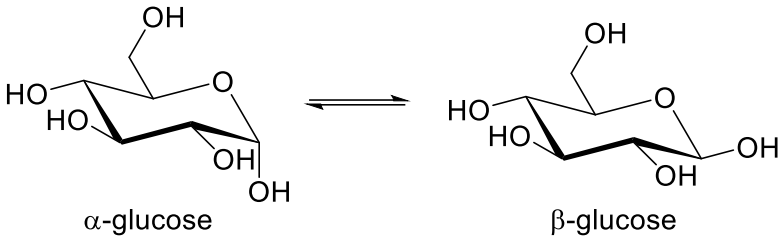


Fig. 1.1

When plane-polarised light is passed through an aqueous solution of glucose, the angle of rotation of the light is dependent upon the structure of the molecule. The angles of rotations of plane-polarised light caused by the two forms of glucose solutions under identical conditions are shown in Table 1.1.

Table 1.1

solution	angle of rotation of plane-polarised light
1.0 mol dm^{-3} of α-glucose	+111°
1.0 mol dm^{-3} of β-glucose	+19°

(i) When 1 dm^3 of a freshly prepared solution of 1.0 mol dm^{-3} α-glucose is left till equilibrium is achieved, the measured rotation is +53°. Assuming that the angle of rotation due to each glucose is directly proportional to its concentration, calculate a value for the equilibrium constant, K_c, for the conversion of α-glucose into β-glucose. [2]

(ii) The conversion of α-glucose into β-glucose is catalysed by acids. State and explain the effect on the final measured rotation if the conversion is now carried out in the presence of dilute sulfuric acid. [2]

(i)

	α-glucose	⇌	β-glucose
initial conc / mol dm^{-3}	1		–
change in conc / mol dm^{-3}	$-y$		$+y$
eqm conc / mol dm^{-3}	$1-y$		y

At equilibrium,

optical rotation due to α-glucose + optical rotation due to β-glucose = 53°

$(1-y)(111°) + (y)(19°) = 53°$

$92y = 58$

$y = 58/92 = 0.63$

K_c = [β-glucose] / [α-glucose]

= y / (1–y)

= 0.63 / (1– 0.63)

= **1.71**

(ii) **The dilute sulfuric acid catalyst does not affect on the final measured rotation since a catalyst does not affect the equilibrium position since the rates of both forward and reverse reactions are increased to the same extent.**

It only enables the equilibrium (i.e. the final rotation) to be established at an earlier time.

(d) Oxygen used in respiration binds to haemoglobin in red blood cells, which can undergo ligand exchange with water in tissues to regulate oxygen delivery. Both deoxyhaemoglobin and oxyhaemoglobin contain iron atoms in the +2 oxidation state. The oxygen-containing ligand is H_2O in deoxyhaemoglobin, Hb, and O_2 in oxyhaemoglobin, $Hb(O_2)_4$.

One molecule of deoxyhaemoglobin, Hb, can bind with four molecules of oxygen, as shown in equilibrium 1.

equilibrium 1 $\quad Hb(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq) \quad \Delta H^{\ominus} = -630.9 \text{ kJ mol}^{-1}$, $\Delta G^{\ominus} = -160.7 \text{ kJ mol}^{-1}$

(i) State *Le Chatelier's Principle*. [1]

(ii) During the initial stage of vigorous exercise, rapid muscle contractions generate heat that spreads through the body, raising core temperature.

Using Le Chatelier's Principle, explain how the initial increase in temperature affects equilibrium 1. [1]

(iii) Suggest how the magnitude of K_c for equilibrium 1 is likely to be and explain its significance. [2]

(iv) Carbon monoxide, CO, can bind to haemoglobin at the same binding site as oxygen. Explain why CO is poisonous. [2]

[Total: 20]

(i) Le Chatelier's principle states that if **a system in equilibrium is subjected to a change which disturbs the equilibrium, the system responds in such a way to counteract the effect of the change imposed, in order to re-establish the equilibrium of the system**.

(ii) **The equilibrium position shifts to the left** in order **to favour the endothermic reaction to absorb excess heat**.

(iii) **The magnitude of K_c is likely to be very large**. **Hence, the extent of this reaction is effectively complete or equilibrium position lies mostly on the right since $\Delta G^{\ominus}$ is highly negative implying that the forward reaction is thermodynamically spontaneous.**

2 **(a)** The Williamson ether synthesis involves nucleophilic substitution between a halogenoalkane (RX) and alkoxides (RO^-), the conjugate base of an alcohol. The alkoxide serves as the nucleophile in the reaction. An example of the reaction can be seen below:

$$RO^- + R'X \longrightarrow ROR' + X^-$$

A solution containing CH_3ONa, is reacted separately with 1-bromopropane and 2-bromo-2-methylpropane.

(i) Predict the predominant mechanism for:

I) the reaction of 1-bromopropane with CH_3ONa

II) the reaction of 2-bromo-2-methylpropane with CH_3ONa

Explain your reasoning. [3]

(ii) For each mechanism, state and explain the stereochemical outcome of the nucleophilic substitution reaction. [2]

(i) **I**) 1-bromopropane is a primary halogenoalkane. If it were to undergo substitution **via S_N1, the intermediate produced is a highly unstable primary carbocation**. **Rear-side attack by the nucleophile is relatively unhindered**. Hence, 1-bromopropane will react **via S_N2 mechanism**.

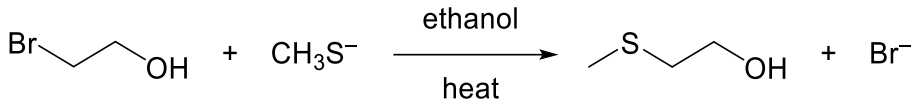
II) 2-bromo-2-methylpropane is a tertiary halogenoalkane. **Steric hinderance for the rear-side attack via S_N2 is severe due to the presence of three bulky alkyl groups**. However, the **formation of tertiary carbocation, stabilised by three electron-donating alkyl groups will be favourable**. Hence, 2**-bromo-2-methylpropane will react via S_N1 mechanism**.

(ii) **S_N1 mechanism will result in a racemic mixture** since the alpha-carbon become a positively charged carbocation carbon which is **trigonal planar**. **Attack of the nucleophile occurs with equal probability from both sides of the plane, leading to an equimolar mixture of two enantiomerically pure product**.

S_N2 mechanism will result in a single enantiomer since attack takes place from **opposite side of the C-X bond, forming a new C-Nu bond and cleaving the C-X bond resulting in an inversion of stereochemistry**.

(b) Thiolates such as methyl thiolate, CH_3S^-, act similarly to alkoxides in the nucleophilic substitution of halogenoalkanes, forming a sulfide.

The synthesis of 2-hydroxyethyl methyl sulfide from 2-bromoethanol using CH_3S^- can be seen from the following reaction scheme:



(i) Describe a simple chemical test to distinguish between 2-bromoethanol and 2-hydroxyethyl methyl sulfide. [2]

The kinetics of the reaction was studied with the results given in Table 2.1.

Table 2.1

experiment	$[CH_3S^-]$ / mol dm^{-3}	$[CH_2BrCH_2OH]$ / mol dm^{-3}	relative rate
1	0.100	0.150	1.00
2	0.150	0.150	1.50
3	0.200	0.200	2.67

(ii) Define the term *order of reaction*. [1]

(iii) Use the data to determine the order of reaction with respect to both CH_3S^- and CH_2BrCH_2OH. [2]

(iv) Hence, write a rate equation for the reaction. [1]

(v) Using your answer in **(b)(iv)**, describe the mechanism for the reaction. [3]

(i) **Test**: Add to the reactant and product separately, **$AgNO_3$ in ethanol and heat**, (or the longer 3-step way: NaOH(aq) + heat, HNO_3, $AgNO_3$(aq))

Observation: The reactant **will form a cream precipitate of AgBr** while the product will **not form any precipitate**.

(ii) The order of reaction with respect to a particular reactant is the **power to which the concentration of that reactant is raised in the experimentally determined rate equation.**

(iii) Comparing experiment 1 and 2,

When **[CH_3S^-] increases to 1.5 times**, while keeping [CH_3BrCH_2OH] constant, the **relative rate increases to 1.5 times**.

Order of reaction with respect to CH_3S^- is **one**.

Let rate equation be rate = $k[CH_3S^-][BrCH_2CH_2OH]^b$

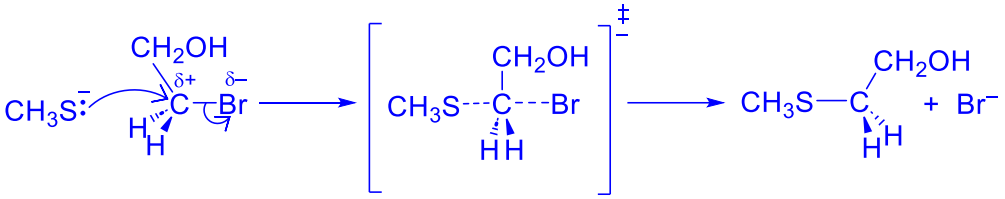
Comparing experiment 1 and 3,

$$\frac{2.67}{1.50} = \frac{k(0.200)^1(0.200)^b}{k(0.150)^1(0.150)^b} \Rightarrow b = 1$$

Order of reaction with respect to $BrCH_2CH_2OH$ is **one**.

(iv) rate = $k[CH_3S^-][BrCH_2CH_2OH]$

(v) **S_N2 Nucleophilic substitution**

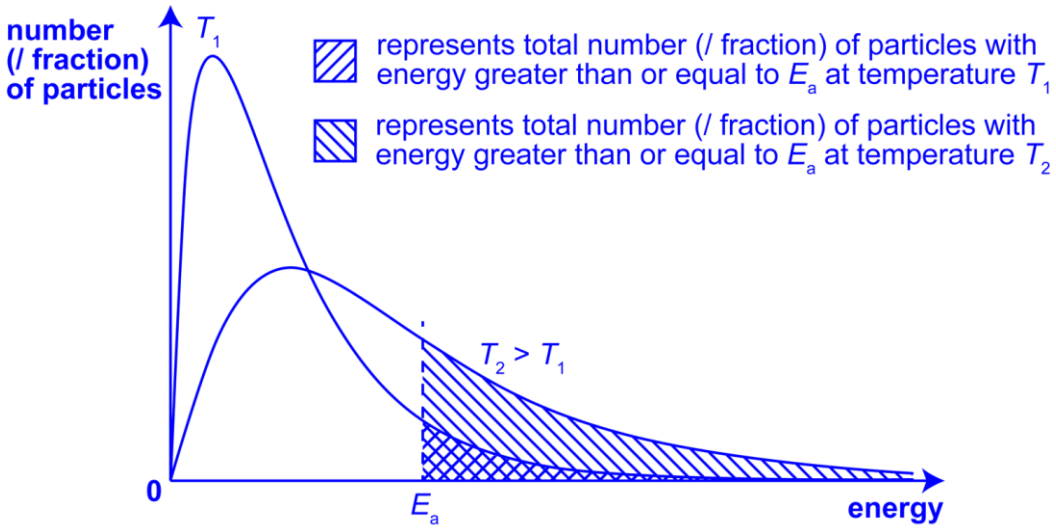


(c) Sodium methoxide, CH_3ONa, can also be used to synthesis 2-hydroxyethyl methyl sulfide from 2-bromoethanol. The rate of reaction was found to be slower than when sodium methanethiol, CH_3SNa, is used.

By considering the strength of the nucleophile, suggest why the rate of reaction is slower when using sodium methoxide. [1]

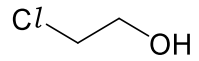
The O atom on the methoxide anion has **a stronger electronegativity** as compared to the S atom on the methyl thiolate. Hence, the **lone pair of electrons is less available, making it a weaker nucleophile**, resulting in a slower rate of reaction.

(d) The rate of reaction for the synthesis increases when the temperature is increased. With the aid of a clearly labelled Maxwell-Boltzmann distribution curve, explain this observation. [3]

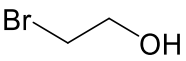


As temperature increases, **average kinetic energy of the particles increases**, and this results in an increase in frequency of collisions. In addition, **the number (/ fraction) of particles with energy equal to or greater than E_a increases**. Both factors result in **frequency of effective collision increases**, and the rate constant increases, hence the rate of reaction increases.

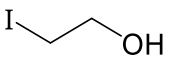
(e) Another series of experiments were done to study the difference in the rates of nucleophilic substitution for the following compounds using methyl thiolate.



2-chloroethanol



2-bromoethanol



2-iodoethanol

Deduce the order of increasing rate of reaction of the following compounds. Explain your answer. [2]

[Total: 20]

2-chloroethanol < 2-bromoethanol < 2-iodoethanol

Down the group, the **C-X bond strength decreases due to the decreasing effective overlap of the halogen orbitals with the C orbitals**. Thus, the bond becomes easier to break.

3 Hydroformylation shown in Fig. 3.1 is one of the largest homogeneous catalytic reactions used to manufacture aldehydes industrially. The aldehydes are subsequently hydrogenated to alcohols or oxidised to carboxylic acids.

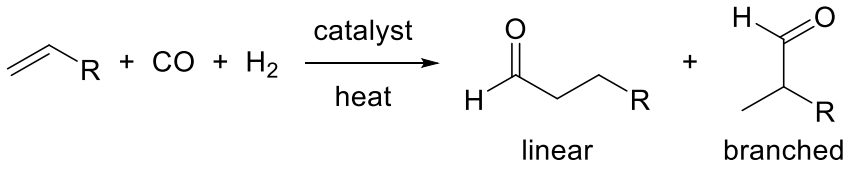


Fig. 3.1

The phosphine-modified cobalt catalyst, $HCo(CO)_3(PR_3)$, was developed to increase the linear : branched aldehyde selectivity. This catalyst also functions as an effective aldehyde hydrogenation catalyst to produce the corresponding alcohol.

The proposed mechanisms for the hydroformylation cycle are shown in Fig. 3.2.

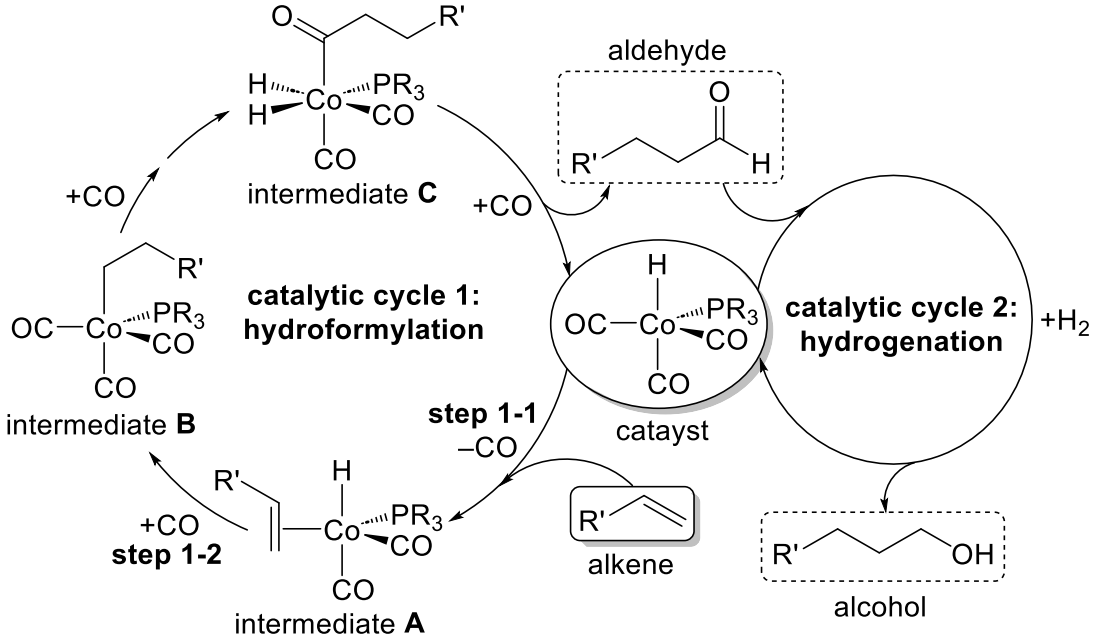


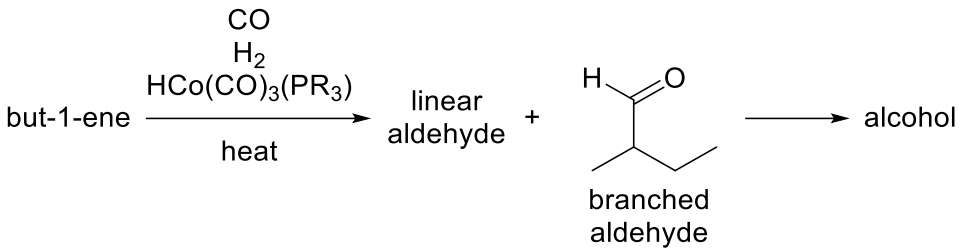
Fig. 3.2

An important step in catalytic cycle 1 is **step 1-2**, which involves addition of a Co–H bond adds across the C=C double bond within intermediate **A**, with binding of a carbon monoxide ligand, to give intermediate **B**.

Intermediate **B** reacts with more carbon monoxide, eventually giving intermediate **C**. Finally, intermediate **C** breaks down to give the aldehyde with regeneration of the catalyst.

The aldehyde formed from catalytic cycle 1 then enters catalytic cycle 2 and is reduced to give the corresponding alcohol.

(a) But-1-ene was reacted with CO and H_2 using $HCo(CO)_3(PR_3)$ as catalyst.



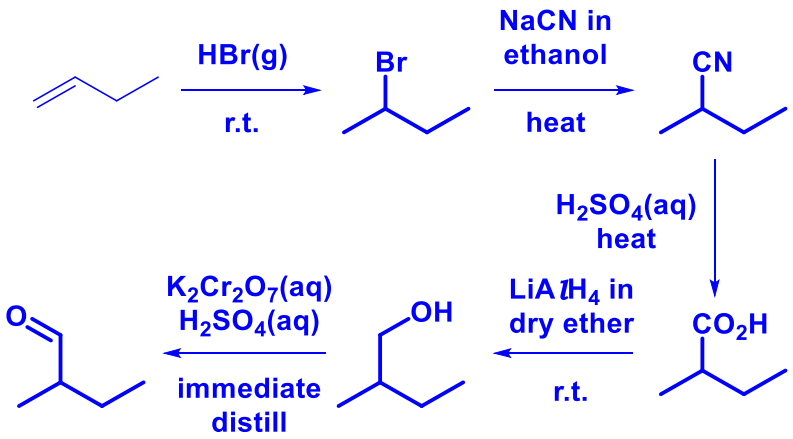
(i) Draw the skeletal structure of the linear aldehyde. [1]

(ii) Starting from but-1-ene, suggest an alternative 5-step synthesis to form the branched aldehyde. The synthesis involves a nitrile intermediate. [5]

(iii) Suggest a simple chemical test to confirm that all the aldehydes have been hydrogenated to the corresponding alcohols. [2]

(i)

(ii)



(iii) Test: Add **2,4-dinitrophenylhydrazine** to the product mixture at room temperature

Observation: **No orange ppt observed;** accept Tollens' and Fehling's

(b) (i) State the type of reaction in **step 1-1**. [1]

(ii) State the type of bond between the alkene and Co in intermediate **A** and suggest how it is formed. [2]

(iii) State the shapes of intermediate **B** and intermediate **C** about Co. [1]

(iv) Given that the Co in intermediate **C** is in the +3 oxidation state. State its full electronic configuration. [1]

(i) ligand exchange reaction

(ii) Dative / coordinate bond formed then alkene **donates its pair of π electrons** to the Co

(iii) intermediate **B** : trigonal bipyramidal

Intermediate **C** : octahedral

(iv) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

(c) The linear and branched product arises in **step 1-2** as the addition of Co–H across the C=C double bond can occur in two ways as shown in Fig. 3.3.

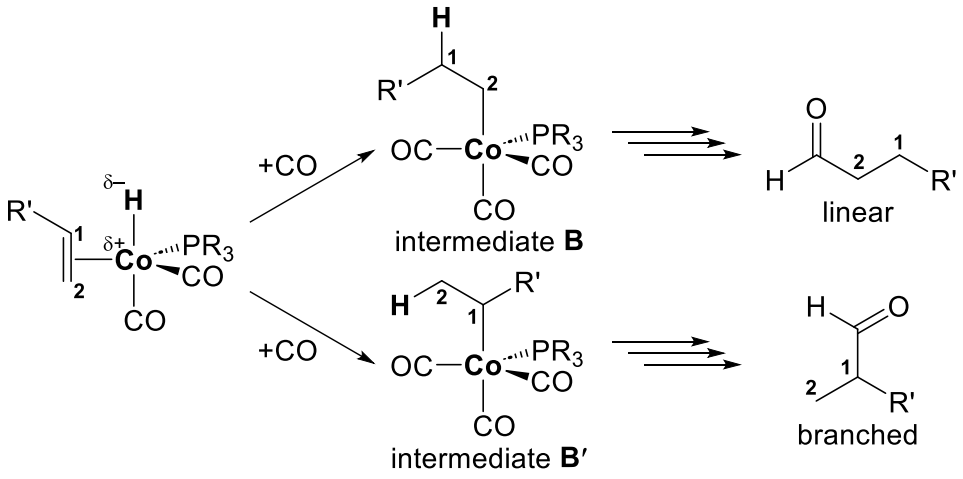


Fig. 3.3

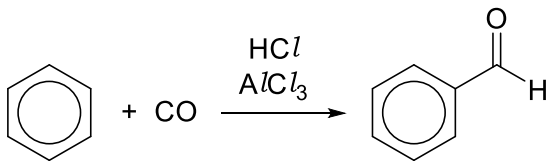
(i) Based on your understanding of the mechanism of electrophilic addition, explain why intermediate **B** is formed preferentially over intermediate **B′**. [2]

(ii) Phosphine ligand, PR_3, with different R groups gives different linear : branched product ratio. State and explain one characteristic of the alkyl group, R, which will further favour formation of intermediate **B**. [2]

(i) Since the Co–H bond is polarised with Co carrying the partial positive charge and H carrying the partial negative charge, during addition of the Co–H across the C=C, the pair of C=C **π electrons** will preferentially **attack the electrophilic Co atom** leading to a **more stable secondary carbocation at carbon 1 than a primary carbocation at carbon 2** and **H:⁻**, which then combine to give intermediate **B**.

(ii) A **sterically bulky R group** will further favour formation of intermediate **B**.
This is because a bulky PR_3 will render intermediate **B′ more unstable / less stable** compared to intermediate **B** due to **steric repulsion between PR_3 and R′**. *or*
The bulky PR_3 will render **electrophilic attack** of the $Co(CO)_2(PR_3)$ fragment **faster at carbon 2** compared to carbon 1 due to **steric hindrance by R′ at carbon 1**

The Friedel-Crafts formylation of benzene using carbon monoxide can be achieved by the Gatterman-Koch reaction in which CO(g) and HCl(g) are used *in-situ* with a Lewis acid catalyst such as $AlCl_3$.



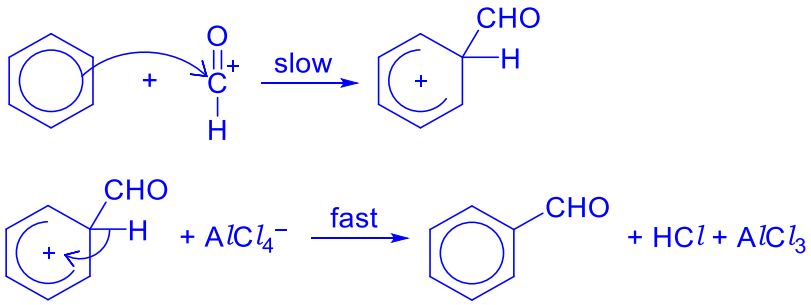
Assuming that CO(g) and HCl(g) reacts in the presence of $AlCl_3$ as shown.

$$CO + HCl + AlCl_3 \rightarrow {}^{+}CHO + AlCl_4^{-}$$

(d) Describe the mechanism for the Friedel-Crafts formylation of benzene to give benzaldehyde. Show the displayed structure of the electrophile, the structure of the intermediate and the movement of electron pairs by using curly arrows.

[3]
[Total: 20]

Electrophilic substitution



Section B

Answer **one** question from this section.

4 **(a)** Glycolic acid, $CH_2(OH)COOH$, is an α-hydroxy acid used in some skincare products.

Sodium glycolate can be prepared by adding disodium hydrogen phosphate to a solution of glycolic acid in a cosmetic formulation. The reaction establishes the following equilibrium in water:

equilibrium 1 $\quad CH_2(OH)COOH + HPO_4^{2-} \rightleftharpoons CH_2(OH)COO^- + H_2PO_4^-$

The K_a values for $CH_2(OH)COOH$ and $H_2PO_4^-$ are given in Table 4.1.

Table 4.1

acid	K_a
$CH_2(OH)COOH$	1.48×10^{-4}
$H_2PO_4^-$	6.20×10^{-8}

(i) Write down the IUPAC name for glycolic acid. [1]

(ii) Identify the two different conjugate acid-base pairs in equilibrium 1. [1]

(iii) Use the K_a values in Table 4.1 to calculate the equilibrium constant, K_c, for equilibrium 1. [2]

(iv) In an experiment, a buffer solution of pH 4.00 is prepared using 50.0 cm^3 of 0.0500 mol dm^{-3} glycolic acid and x cm^3 of 0.100 mol dm^{-3} NaOH.

$$CH_2(OH)COOH + NaOH \rightarrow CH_2(OH)COONa + H_2O$$

Assume that all NaOH reacts with glycolic acid, what is the volume, x cm^3, of 0.100 mol dm^{-3} NaOH required to make the buffer? [4]

(i) 2-hydroxyethanoic acid

(ii) Acid: **$CH_2OHCOOH$** Conjugate base: **$CH_2(OH)COO^-$**

Base: **HPO_4^{2-}** Conjugate acid: **$H_2PO_4^-$**

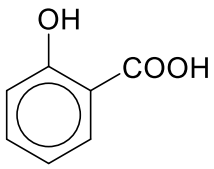
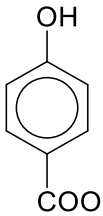
(iii) $$K_c = \frac{[CH_2(OH)COO^-][H_2PO_4^-]}{[CH_2(OH)COOH][HPO_4^{2-}]}$$

$$= \frac{[CH_2(OH)COO^-]}{[CH_2(OH)COOH]} \times \frac{[H_2PO_4^-]}{[HPO_4^{2-}]}$$

$$= \frac{[CH_2(OH)COO^-][H^+]}{[CH_2(OH)COOH]} \times \frac{[H_2PO_4^-]}{[HPO_4^{2-}][H^+]}$$

(b) Table 4.2 shows the pK_a values of two isomeric benzoic acids: salicylic acid and 4-hydroxybenzoic acid.

Table 4.2

acid	pK_{a1}	pK_{a2}
 salicylic acid	3.0	13.4
 4-hydroxybenzoic acid	4.1	9.7

Explain the following:

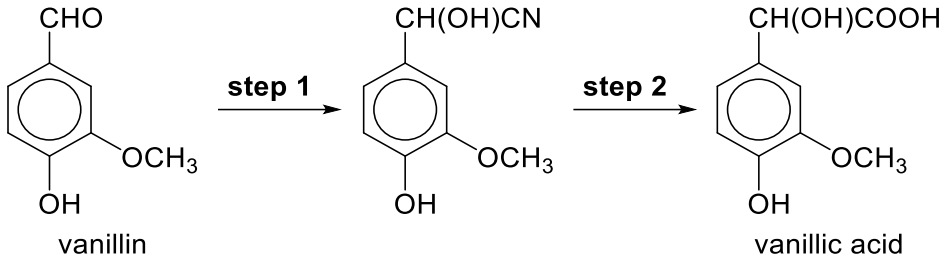
(i) pK_{a2} is larger than pK_{a1} of salicylic acid. [1]

(ii) pK_{a1} of salicylic acid is smaller than pK_{a1} of 4-hydroxybenzoic acid. [1]

(i) **Electrostatically unfavourable / more difficult to remove H^+ from a negatively charged anion,** conjugate base less likely to dissociate a secpmd H^+.

(ii) This is because the **conjugate base of salicylic acid is stabilised by intramolecular hydrogen bonding**. In 4-hydroxybenzoic acid, the −OH and $-COO^-$ groups are too far away for hydrogen bonding to form.

(c) Vanillin, a common flavor and fragrance ingredient, can be converted into vanillic acid by a two-step laboratory synthesis.



vanillin vanillic acid

(i) State the reagent and conditions used in **step 1**. [1]

(ii) State the type of reaction that occurs in **step 1** and **2**. [2]

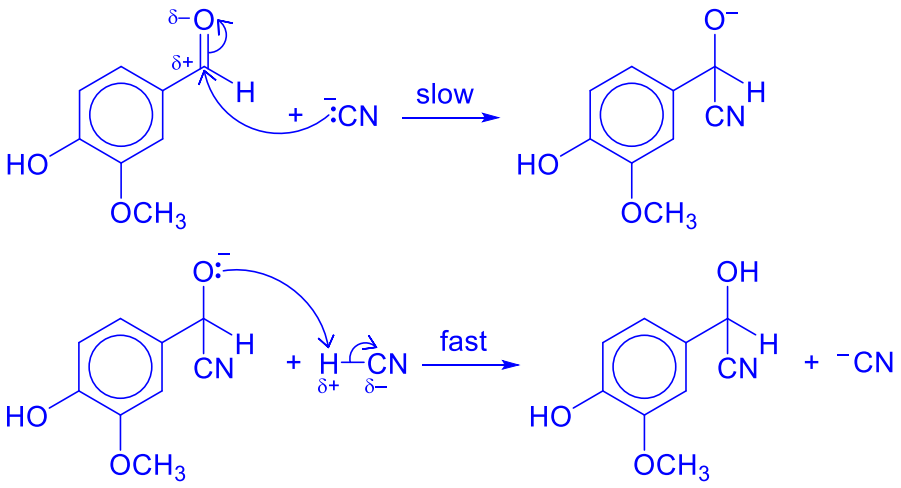
(iii) Draw the mechanism of the reaction in **step 1**. Show clearly all charges and the ntermediate formed and use curly arrows to indicate the movement of electron pairs. [3]

(i) HCN, trace amount of NaCN/NaOH, cold

(ii) Step 1: nucleophilic addition

Step 2: acidic hydrolysis

iii) $NaCN \rightarrow Na^+ + CN^-$



(d) Hexagonal boron nitride, h-BN, consist of planar sheets of alternate boron and nitrogen atoms, similar in arrangement to the carbon atoms in graphite. Its softness and sheen make powdered h-BN widely used in cosmetics.

(i) h-BN is often referred to as "white-graphite'. With reference to chemical bonding and structure, explain why both h-BN and graphite have a soft and slippery feel. [2]

(ii) Explain, with reference to electronegativity, why h-BN does not conduct electricity readily, whereas graphite does. [2]

(i) Both are **giant covalent structure,** with strong covalent bonds found within the **layer/plane.** In both h-BN and graphite, the atoms are in trigonal planar arrangements. Each plane/sheet are held by **weak instantaneous dipole-induced dipole interactions**. Hence the layers can **slide over each other easily.**

[Total: 20]

(ii) In both compounds, since the C, B and B atoms are sp^2 hybridised each with a unhybridised **p orbital** that can **overlap sideway** to give a **delocalised** π electron cloud.

For graphite, **each carbon atom** has **one lone electron that can move freely** through the structure, enabling electrical conduction.

In h-BN, **lone pair of electrons are more localised on more electronegative nitrogen atom**, and so there are no free electrons to carry charge, making it an electrical insulator.

5 In an effort to address pollution caused by industrial nitroaromatics and agricultural nitrates, researchers have developed a dual-function electrochemical system that converts these nitrogen-containing wastes into useful products. At the cathode, the electrolytic reduction of nitrobenzene to phenylamine is described in Fig. 5.1.

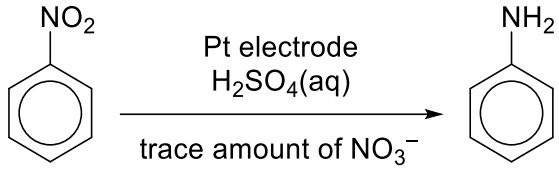


Fig 5.1

(a) State the reagents and conditions for the conversion of nitrobenzene to phenylamine in a laboratory. [1]

Sn, conc HCl, heat (followed by NaOH)

(b) **(i)** Given the nitrogen in nitrobenzene has an oxidation state of +3, describe the change in oxidation state of the nitrogen, in Fig. 5.1. [1]

(ii) Hence or otherwise, write the half-equation for this reaction. [1]

(iii) During a 4-hour electrolysis, a steady current of 2 A was passed. However, only 2.79 g of phenylamine was formed.

Using your answer to **(b)(ii)**, calculate the theoretical amount of electrons required to form 2.79 g of phenylamine. [1]

(iv) Faradaic efficiency describes the efficiency with which charge is transferred in an electrolysis system and is given by the equation below.

$$\text{Faradaic efficiency} = \frac{\text{charge required}}{\text{charge passed}} \times 100\%$$

Hence, calculate the Faradaic efficiency of the electrolysis in **(b)(iii)**. [3]

(i) The oxidation state of the N decreases from +3 in nitrobenzene to –3 in phenylamine.

(ii) $\mathbf{C_6H_5NO_2 + 6H^+ + 6e^- \rightarrow C_6H_5NH_2 + 2H_2O}$

(iii) $n_{\text{phenylamine}} = \dfrac{2.79}{12.0\times6+1.0\times5+14.0+1.0\times2} = 0.0300 \text{ mol}$

$n_{\text{electrons}}$ required = 0.0300 × 6 = **0.180 mol**

(iv) (theoretical) charge required, $Q = n_eF = 0.180 \times 96500 = 17370$ C

(actual) charge passed = 2 × 4 × 60 × 60 = 28800 C

Faradaic efficiency $= \dfrac{17370}{28800}\times100\% =$ **60.3%**

(c) The use of the *Data Booklet* is relevant to this question.

(i) A student suggests that the trace amounts of NO_3^- ions at the cathode could also be reduced to NH_4^+ ions. Discuss how electrode potential and concentration might influence this competition.
(The $E^{\ominus}$(nitrobenzene | phenylamine) is +0.79 V.) [3]

(ii) Suggest other possible side products at the cathode. [1]

(i) The reduction of NO_3^- has a **more positive $E^{\ominus}$** (+0.87 V) than that of nitrobenzene (+0.79 V), indicating its reduction is thermodynamically more favourable.

However, since NO_3^- ion is present in trace amount, by LCP, the position of the equilibrium $NO_3^- + 10H^+ + 8e^- \rightleftharpoons NH_4^+ + 3H_2O$ is **shifted to the left**, **favouring oxidation**, making the electrode potential **less positive**.

Since the electrode potential for both competing reactions are similar, it is possible for the $E(NO_3^-|NH_4^+)$ to be **less positive than *E*(nitrobenzene | phenylamine)**.

(ii) **HNO_2 or NO_2**

(d) Rank the following compounds in order of increasing basicity and explain your reasoning.

phenylamine, methylamine, ethanamide [4]

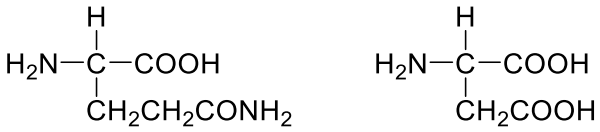
Increasing basicity: $CH_3CONH_2 < C_6H_5NH_2 < CH_3NH_2$

Phenylamine and ethanamide are less basic than CH_3NH_2 as the **p orbitals of N overlap with the π electron cloud of benzene and the C=O groups respectively**.

For ethanamide, the **lone pair of electrons on N atom is delocalized into the π electron cloud of the C=O bond**, thus this lone pair of electrons is **not available for donation** to a proton, hence it is **neutral.**

For phenylamine, the **lone pair of electrons on N atom is delocalized into the π electron cloud in the benzene ring**. This **reduces the availability of the lone pair of electrons** on N atom **for donation** to a proton. **CH_3NH_2 has an electron donating alkyl group** so the lone pair on N is **more available** for donation to H^+. Hence, it is the most basic.

(e) The structures of two amino acids, glutamine and aspartic acid are given below.



glutamine

aspartic acid

(i) Suggest a simple chemical test to distinguish between glutamine and aspartic acid. [2]

(ii) The three pK_a values associated with aspartic acid are 1.99, 3.90 and 9.90.

Draw the structures of the predominant species of aspartic acid at

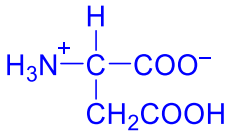
- pH 3
- pH 8
- pH 11

[3]

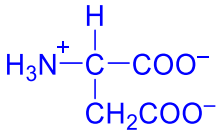
[Total: 20]

(i) Add **NaOH(aq)** to the separate samples and **heat** them in water bath.
Glutamine will produce ammonia which turns moist red litmus paper blue but **aspartic acid does not produce a gas that turns moist red litmus paper blue**.

(ii) pH 3 :



pH 8 :



pH 11 :