PAPER III

1 Penicillin can be made in the laboratory by reacting 6-aminopenicilanic acid with a suitable acyl chloride. For a particular penicillin, the acyl chloride is the $CH_3CH_2CH=CHCH_2COCl$. Since the acyl chloride used can be easily made from the corresponding carboxylic acid, the chemist has decided to work with $CH_3CH_2CH=CHCH_2CO_2H$ because the acyl chloride is more reactive.

(a) (i) The acyl chloride, $CH_3CH_2CH=CHCH_2COCl$, can be obtained by reacting $CH_3CH_2CH=CHCH_2CO_2H$ with PCl_5. Write a balanced equation for the reaction.

[1]

$CH_3CH_2CH=CHCH_2CO_2H + PCl_5 \rightarrow CH_3CH_2CH=CHCH_2COCl + POCl_3 + HCl$

(ii) Using relevant data from the Data Booklet and the bond energies given below, calculate the enthalpy change for the above reaction. [2]

	Bond Energies /kJ mol^{-1}
P-C*l*	322
P=O	423

Bonds Broken		**Bonds formed**	
2 P-C*l*	**2(+322)**	**P=O**	**-423**
C-O	**+360**	**C-C*l***	**-340**
O-H	**+460**	**H-C*l***	**-431**

ΔH = 2(+322)+360+460-423-340-431
= +270 kJ mol^{-1}

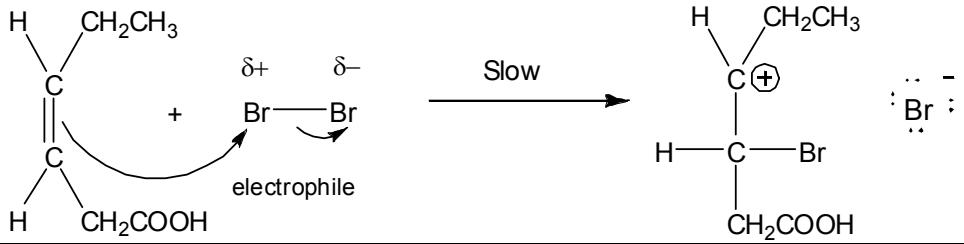
(b) (i) The carboxylic acid, $CH_3CH_2CH=CHCH_2COOH$, can be converted into the hydroxyacid, $CH_3CH_2CH(OH)CHCH_2COOH$. Give the reagent and condition for the reaction. [1]

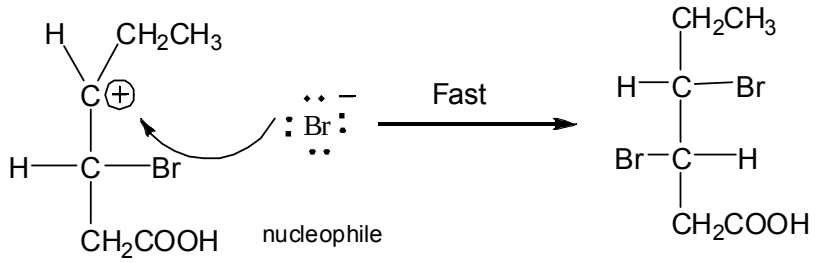
Steam; heat in the presence of H_3PO_4 catalyst 300 ^oC and 65 atm

Alternative: conc H_2SO_4 at 0 ^oC, followed by boiling with H_2O

(ii) The hydroxyacid obtained can be distinguished from its starting material by using bromine. Name and describe the mechanism involved. [4]

Electrophilic Addition

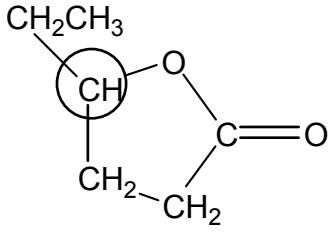




(iii) Suggest another reagent and condition in which the hydroxyacid obtained can be distinguished from its starting material. [2]

Reagent: acidified $K_2Cr_2O_7$ and heat

(c) (i) In the course of preparing the hydroxyacid, an internal chiral ester was also detected. Draw the structure of this ester. Circle the chiral centre(s). [2]

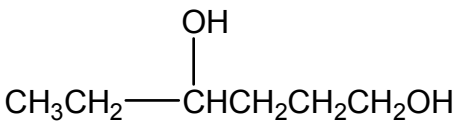


(ii) State the number of sp^2 and sp^3 hybridised carbons in the ester. [2]

sp^2 - 1
sp^3 - 5

(iii) This ester may be made into a diol. Give the reagent and condition for the conversion and draw the structure of this diol. [2]

Reagent and condition: $LiAlH_4$ in dry ether; reflux



(d) (i) An experiment was carried out to determine the enthalpy change of combustion of this diol. Write a balanced equation including state symbols for the combustion of the diol under standard condition. [1]
$CH_3CH_2CH(OH)CH_2CH_2CH_2OH(l) + 17/2O_2(g) \rightarrow 6CO_2(g) + 7H_2O(l)$

(ii) A large beaker of water was placed on the stove and heated. The temperature rise was recorded. The cylinder was weighed before and after the experiment to determine the mass of diol used. The following results were obtained.

Mass of diol used = 3.4 g
Mass of water heated = 500 g
Temperature rise = 44 ^{o}C

Using relevant data from the Data Booklet and results given above, calculate the enthalpy change for the combustion of the diol. [3]

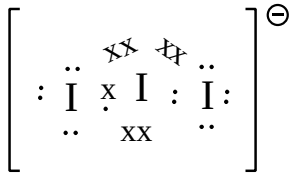
Q = mc∆T
= (500)(4.18)(44)
= -91960 J

Mr of diol = 6(12.0) + 14(1.0) + 2(16.0) = 118.0

∆H = Q/ n
= -91.96/ (3.4/118.0)
= -3191 kJ mol^{-1}
= -3190 kJ mol^{-1}

[Total: 20]

2 (a) The triodide ion, I_3^-, is known to exist as a stable species in aqueous solution. Draw a dot and cross diagram for I_3^- and hence deduce its shape.
[2]



Linear

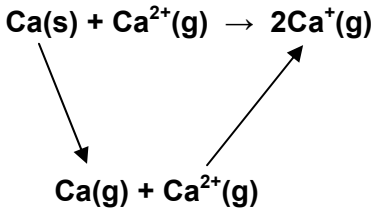
(b) Solid CsI_3 is stable with respect to CsI and I_2 but LiI_3 is not stable with respect to LiI and I_2. Based on your knowledge of the relative stabilities of group II carbonates, rationalize the relative stability of CsI_3 and LiI_3. [3]

Li^+ is much smaller than Cs^+
Charge density of Li^+ is higher than that of Cs^+
I_3^- is polarized to a greater extent by Li^+
CsI_3 is more stable than LiI_3.

(c) (i) Given that the enthalpy of atomization of Ca is +176.4 kJ mol^{-1}, and using relevant ionization energy values from the *Data Booklet*, calculate the enthalpy change for the reaction: [2]

$$Ca(s) + Ca^{2+}(g) \rightarrow 2Ca^+(g)$$

$Ca(g) \rightarrow Ca^+(g) + e$ $\quad$ 1st IE = +590 kJ mol^{-1}
$Ca^+(g) \rightarrow Ca^{2+}(g) + e$ $\quad$ 2nd IE = +1150 kJ mol^{-1}



ΔH = +176.4 - 1150 + 590 = -383. 6 kJ mol^{-1}

(ii) What can you conclude about the relative stability of $Ca^+(g)$ with respect to Ca and Ca^{2+}? [1]

$Ca^+(g)$ is more stable with respect to Ca(s) and $Ca^{2+}(g)$

(d) The energetic relations between the aqueous ions of Ca and the solid Ca metal is given as follows:

$$Ca(s) + Ca^{2+}(aq) \rightarrow 2Ca^+(aq) \qquad \Delta H = +63 \text{ kJ mol}^{-1}$$

In the light of your answer to (c)(ii), account for the differences (if any) noted. [2]

$Ca^+(aq)$ is less stable with respect to Ca(s) and $Ca^{2+}(aq)$
Hydration of Ca^{2+} ion is more extensive than Ca^+

HE of Ca^{2+} >> HE of Ca^{+}

(e) (i) Based on data, the standard electrode potentials of Ca, Sr and Ba are nearly the same, but the enthalpy changes associated with the reactions vary considerably.

	Mg	Ca	Sr	Ba
E^{θ} (M^{2+} / M) / V	-2.38	-2.87	-2.89	-2.90
ΔH / kJ mol^{-1} $M^{2+}(aq) + 2e \rightarrow M(s)$	-403.2	-256.2	-289.8	-365.4

.

Although there is found to be a good correlation between the ΔH for $M^{2+}(aq) + 2e \rightarrow M(s)$ and the corresponding E^{θ} (M^{2+}/M), the degree of similarity between the E^{θ} (M^{2+}/M) is greater whilst that for the ΔH is noticeably lower. What factor is responsible for the dissimilarity of the set ΔH values? [1]

Entropy changes during hydration are neglected and hence ΔH is not a good measure of the spontaneity / tendency of the reaction.

(ii) For Mg, ΔH deviates so greatly, that no good correlation can be observed between ΔH and E^{θ}. Suggest a reason for this inconsistency between the two values for Mg. [2]

Mg^{2+} is relatively smaller with a high charge density compared with the other ions which are much larger. Hence a greater degree of hydration of Mg^{2+} leads to greater orderliness in the solution thus affecting the entropy change significantly.

(iii) In the light of your answers to (e)(i) and (e)(ii), what energy term will give a more exact correlation with the E^{θ}? Why? [2]

ΔG for $M^{2+}(aq) + 2e \rightarrow M(s)$
ΔG^{θ} accounts for entropy changes in the reaction

(f) HF(aq) is the weakest acid compared with the other aqueous hydrogen halides. One factor relevant to its weakness is that the entropy change that accompanies its dissociation is the most negative. What other factor is relevant in explaining the weakness of HF(aq) as an acid? [1]

The dissociation of aqueous hydrogen halides as represented by the equation: $HX(aq) \rightarrow H^{+}(aq) + X^{-}(aq)$, is least favourable energetically for HF due to high BE.

(g) (i) The enthalpy of vaporisation of the hydrogen halides is markedly different for one of the HX as compared with the others. Identify the hydrogen halide and suggest what phenomenon is responsible for this deviation. [2]

HF
Hydrogen bonds between HF molecules

(ii) The values of entropies of vaporization (ΔS_b), that is the molar latent enthalpy of evaporation (ΔH_{vap}) divided by the boiling point (T_b/ K) is approximately constant for HC*l*, HBr and HI, but very different for HF. How would you expect the entropies of vaporization for HF to compare with the other three? Why? [2]

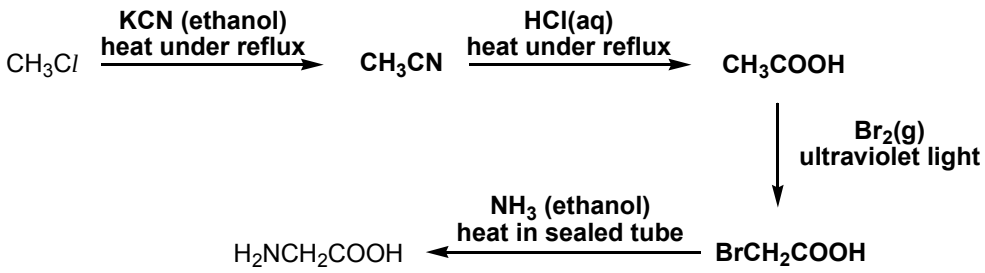
Higher. Hydrogen bonds impose an extra degree of order on HF at its boiling point which results in the higher value of entropy of vaporization as a consequence of the extra degree of order being lost.

[Total: 20]

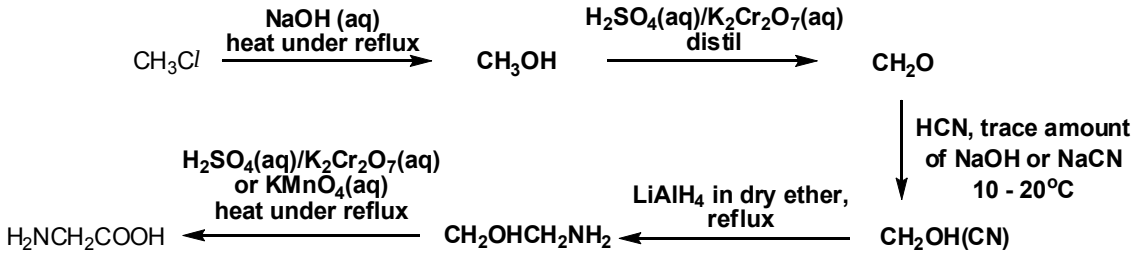
3 Glycine, H_2NCH_2COOH, is the smallest of the 20 amino acids commonly found in proteins.

(a) Propose a synthesis pathway to obtain glycine starting from chloromethane. State clearly all intermediates, reagents and conditions. [7]

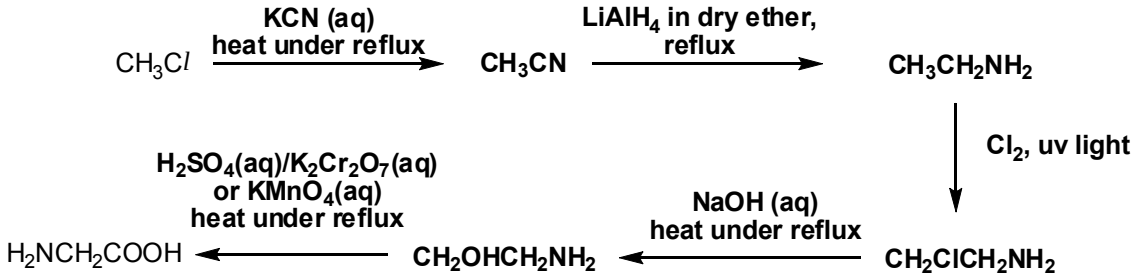
Possible synthetic route 1



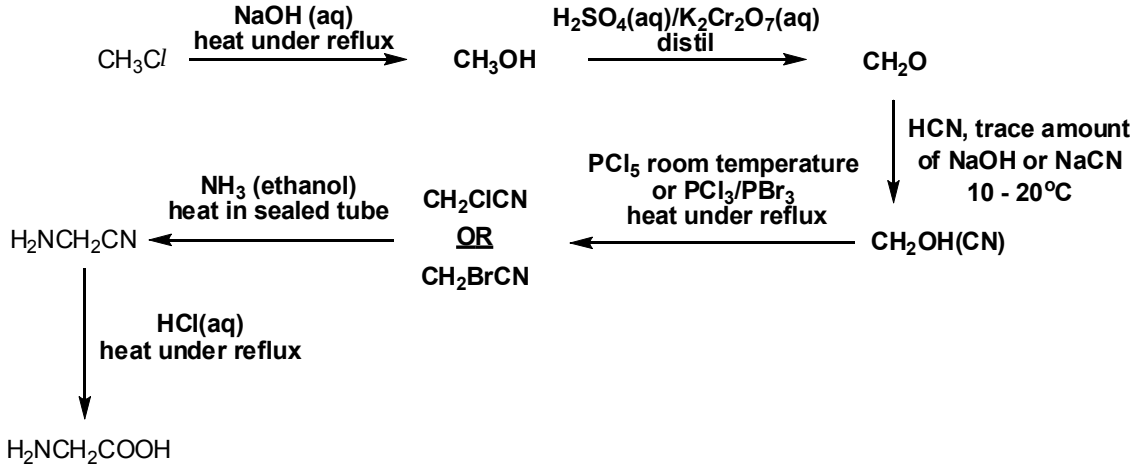
Possible synthetic route 2



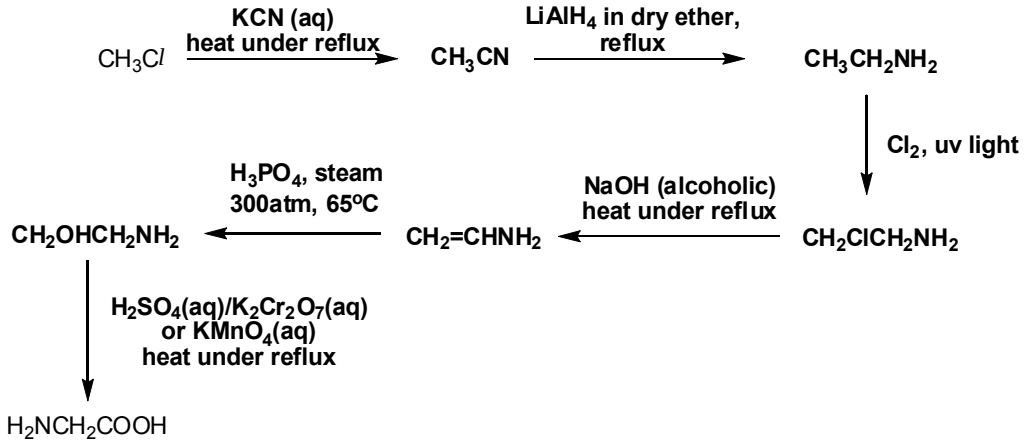
Possible synthetic route 3



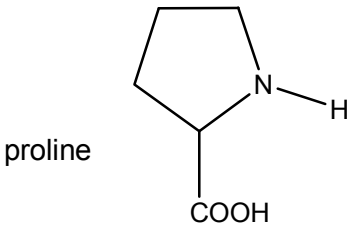
Possible synthetic route 4



Possible synthetic route 5



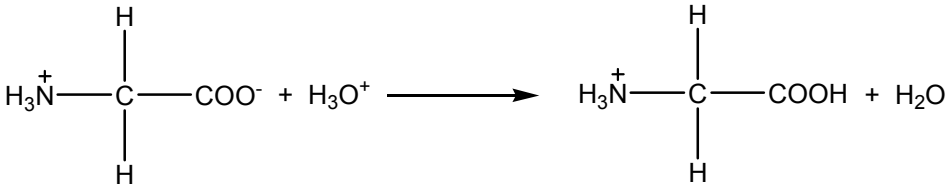
(b) Would you expect the amine group in glycine to have a bigger or smaller K_b than that in proline? Explain your answer briefly.
[2]



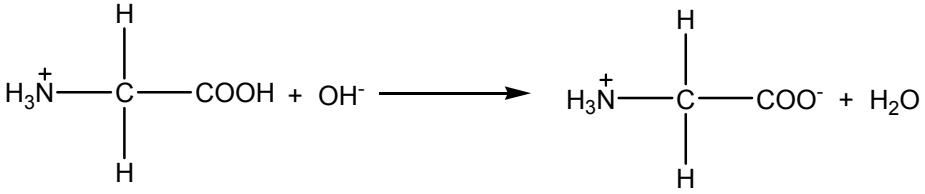
Smaller K_b.
Proline has a secondary amine with 2 electron donating alkyl groups. This makes the lone pair in N more available for co-ordination to a proton compared to the amine in glycine which has only 1 electron donating alkyl group.

(c) Glycine has many uses. For example it can serve as a buffering agent in antacids, analgesics, antiperspirants, cosmetics, and toiletries. With the use of equations, show how glycine can acts as a buffer. [2]

When small amount of strong acid is added,

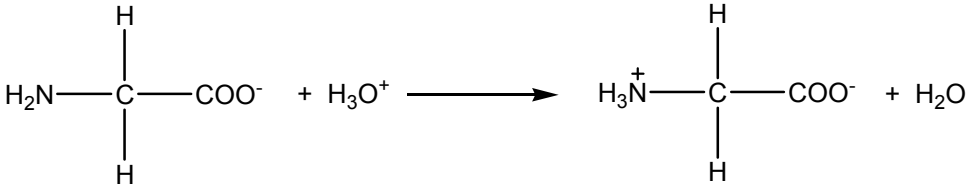


When small amount of strong base is added,

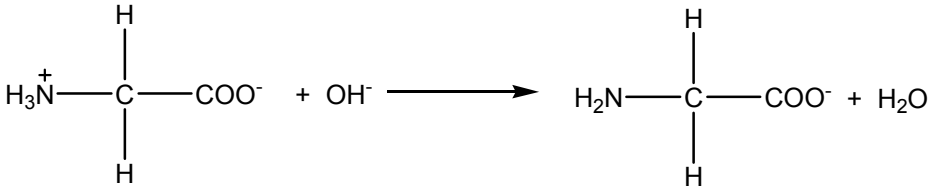


OR

When small amount of strong acid is added,

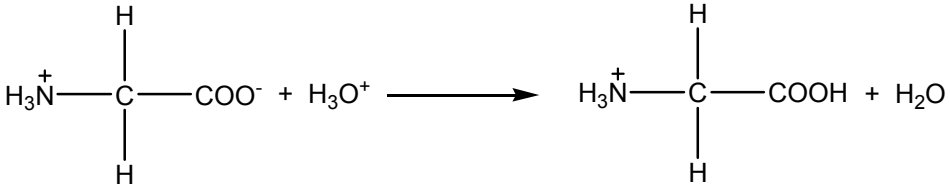


When small amount of strong base is added,

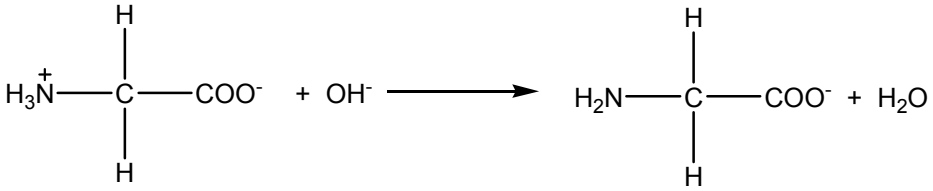


OR

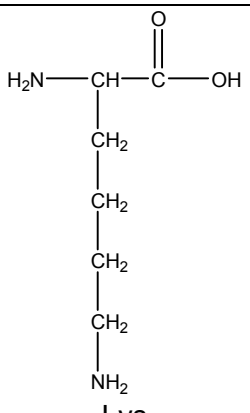
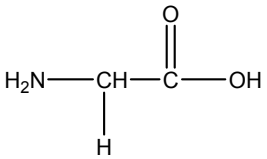
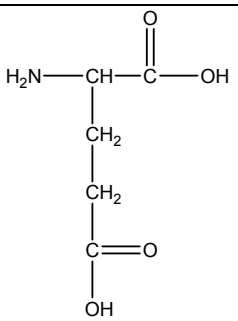
When small amount of strong acid is added,



When small amount of strong base is added,



(d) In a reaction, tripeptide **S** produces the following amino acids in equimolar amounts. The resulting solution was added to an excess of a buffer solution of pH 4.0 and placed at the centre of the plate. A potential difference was then applied across the plate.

Amino Acid	 Lys	 Gly	 Glu
pI	9.7	6.0	3.2

(i) Draw a possible structure of tripeptide **S**. [1]

Any structure of the following combinations:

- **Lys-Gly-Glu**

- **Lys-Glu-Gly**
- **Gly-Lys-Glu**
- **Gly-Glu-Lys**
- **Glu-Lys-Gly**
- **Glu-Gly-Lys**

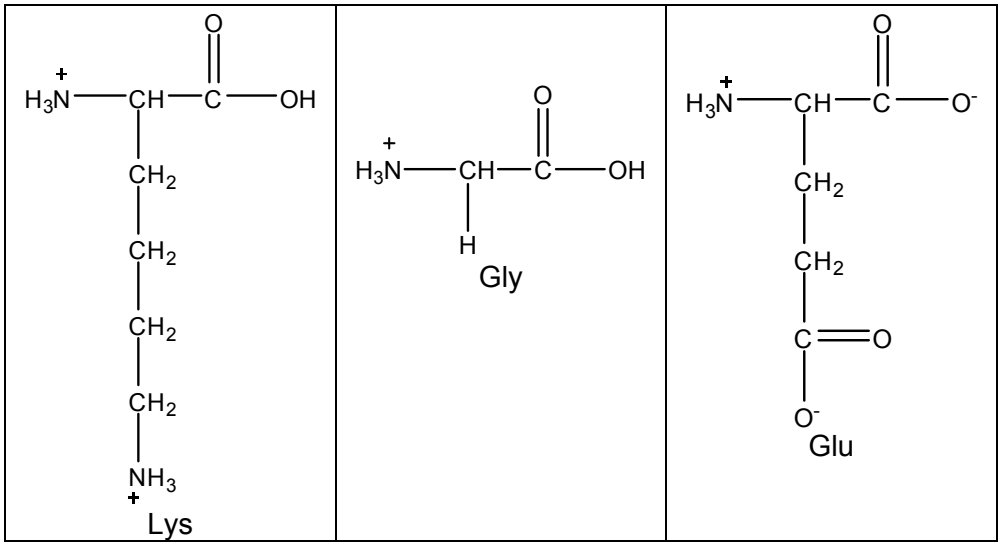
(ii) What reagent and condition are needed break tripeptide **S** into its constituent amino acids? What is the name given to this type of reaction? [2]

HCl(aq) <u>OR</u> NaOH(aq) heat.

Hydrolysis.

(iii) Draw the predominant form of the three amino acids in the buffer solution and hence explain how they can be separated. [6]

Predominant Form



They can be separated by gel electrophoresis. Lys and Gly being positively charged will be attracted to the cathode. Glu being negatively charged will be attracted to the anode. Considering that Lys has a greater charge: mass ratio than Gly, Lys will be nearer to the cathode than Gly.

[Total: 20]

4 (a) Hard water is water that has higher calcium and magnesium content. Using hard water results in sediments accumulating in electrical appliances such as water heaters and washing machines. This raises the electricity consumption rate and shortens the lifespan of the appliances. Hard water is treated through a softening process, where the metal ions are removed, before it is used for consumption.

A sample of hard water containing Mg^{2+} (aq) was collected. The presence of Mg^{2+} is to be tested by precipitating $MgCO_3$.

(i) Write an expression for the solubility, K_{sp}, of magnesium hydroxide. [1]

$K_{sp} = [Mg^{2+}][OH^-]^2$

(ii) The solubility of $Mg(OH)_2$ in pure water at 25 ^oC is 9.08 x 10^{-3} g dm^{-3}. For a saturated aqueous solution of $Mg(OH)_2$ at 25 ^oC, calculate the concentrations of Mg^{2+} and OH^- and prove that the solubility product, K_{sp}, of $Mg(OH)_2$ is 1.5 x 10^{-11} mol^3 dm^{-9}. [2]

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

Solubility of $Mg(OH)_2$ = $\frac{9.08 \times 10^{-3}}{58.3}$ = 1.55 x 10^{-4} mol dm^{-3}

$[Mg^{2+}]$ = 1.55 x 10^{-4} mol dm^{-3}

$[OH^-] = 2 \times 1.55 \times 10^{-4} = 3.10 \times 10^{-4}$ mol dm^{-3}

$K_{sp} = [Mg^{2+}][OH^-]^2$
$= 1.55 \times 10^{-4} \times (3.10 \times 10^{-4})^2$
$\approx 1.5 \times 10^{-11}$ mol^3 dm^{-9} (rounded off to 2 sig. fig.)

(iii) How would you expect the solubility of magnesium hydroxide in aqueous magnesium nitrate to compare with that in pure water? Discuss this effect using Le Chatelier's Principle. [2]

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

By Le Chatelier's Principle, presence of Mg^{2+} in aqueous magnesium nitrate shifts the equilibrium to the left to reduce $[Mg^{2+}]$.
Solubility is lowered due to common ion effect.

(iv) The concentration of Mg^{2+} in the water sample was found to be 3.2×10^{-4} mol dm^{-3}. A 50 cm^3 sample was used in this test. To this sample, 30 cm^3 of a 5.0×10^{-4} mol dm^{-3} aqueous sodium hydroxide was added. Using the K_{sp} value in (ii), deduce if a precipitate would appear when the two solutions were added. [2]

New $[Mg^{2+}] = \left(\frac{50}{1000} \times 3.2 \times 10^{-4}\right) \div \left(\frac{50}{1000} + \frac{30}{1000}\right) = 2.00 \times 10^{-4}$ mol dm^{-3}

New $[OH^-] = \left(\frac{30}{1000} \times 5.0 \times 10^{-4}\right) \div \left(\frac{50}{1000} + \frac{30}{1000}\right) = 1.875 \times 10^{-4}$ mol dm^{-3}

Ionic product $= 2.00 \times 10^{-4} \times (1.875 \times 10^{-4})^2 = 7.03 \times 10^{-12}$ mol^3 $dm^{-9} < K_{sp}$
Hence precipitation will not occur.

(b) Compound **A**, $C_9H_{10}NOCl$, is a basic compound. It reacts with 2,4-dinitrophenylhydrazine to form a orange precipitate **B**, but does not react with Tollens' reagent. **A** does not react with aqueous bromine. When **A** was heated with bromine and iron(III) bromide, it was found that **A** reacts with 2 moles of bromine. Compound **C**, $C_9H_{11}NO_2$, is formed when **A** is heated under reflux with aqueous sodium hydroxide. **C** reacts with acidified potassium dichromate to produce **D**. 0.10 mole of **D** reacts completely in the presence of 0.05 moles of sodium carbonate. Upon heating **A** with ethanol in a sealed tube, a single organic compound **E**, C_9H_9NO, is obtained.

Deduce the structures of compounds **A**, **B**, **C**, **D** and **E**, giving reasons for your answer. [13]

<u>Marking scheme</u>

EXPLANATIONS:

A has high C : H ratio, showing the presence of a aromatic ring.

A has a carbonyl group (i.e. it is a ketone or an aldehyde) as it forms orange ppt with

2,4 - dinitrophenylhydrazine.

A is a ketone and not an aldehyde as it does not react with Tollens' reagent.

A is an amine as it is a basic compound.

A is not phenylamine as it does not undergo electrophilic substituion with aqueous bromine.

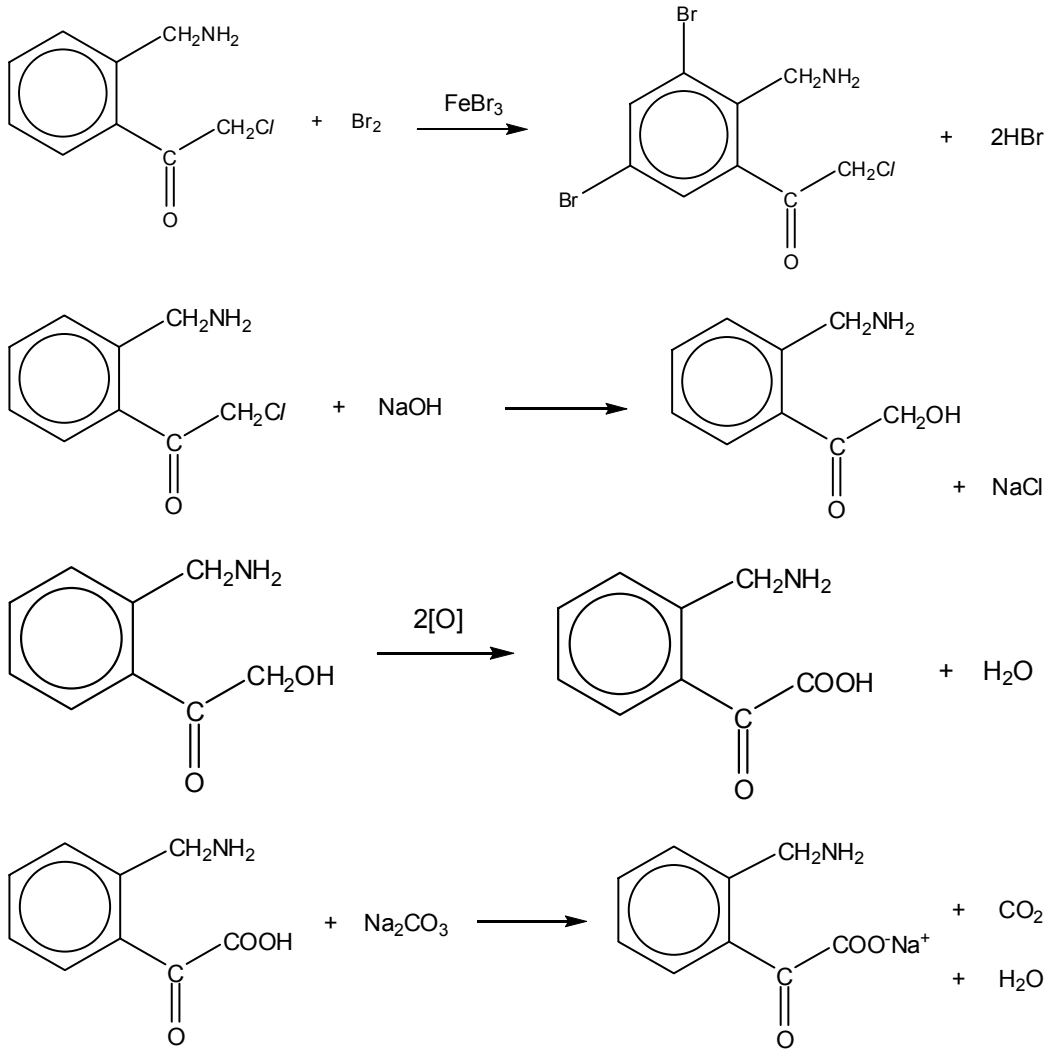
A is does not have C=C bond(s) as it does not decolourise aqueous bromine.

A has a substituent on position 2 and/or 4 relative to the amine group, hence it only reacts with 2 moles of Br_2 and not 3 moles.

D contains one carboxyl group (-COOH) per molecule as it reacts with half equivalent amount of sodium carbonate.

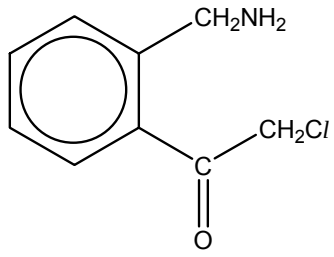
A is a primary alkyl halide as it is hydrolysed and oxidised to carboxylic acid D.

A undergoes intramolecular nucleophilic substitution between its amine and alkyl halide to give a single product **E**. Hence the substituents are in position 1 and 2 on the aromatic ring.

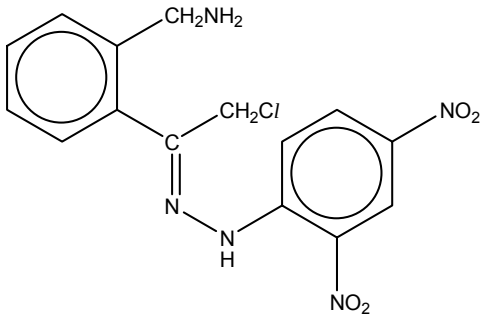


STRUCTURES:

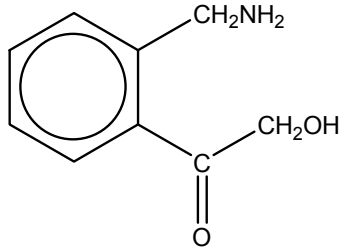
A



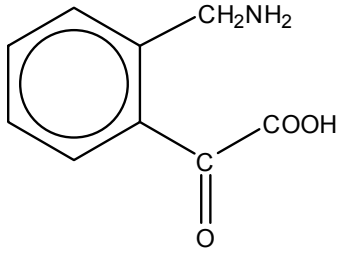
B



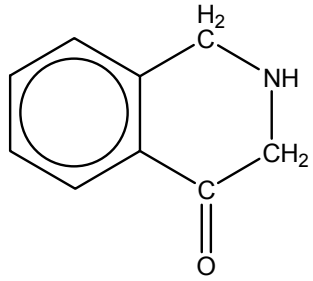
C



D

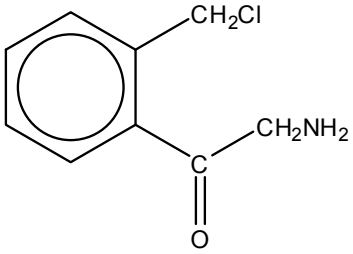


E

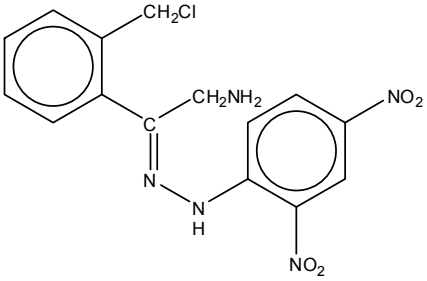


Alternative answer:

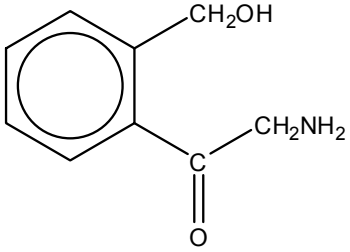
A



B



C



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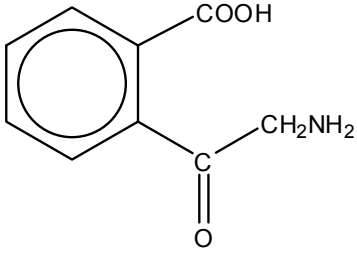
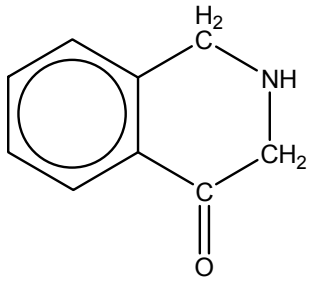


E



[Total 20]

5 (a) It is often stated that, compared to the (III) oxidation state of the adjacent elements, Mn(III) is a stronger oxidizing agent and that Fe(III) is a weaker oxidizing agent than expected. Show how relevant data from the data booklet can be used to illustrate this statement. What explanation can you offer for this? [4]

Mn^{3+} + e^- ⇌ Mn^{2+} 1.49V
Fe^{3+} + e^- ⇌ Fe^{2+} 0.77V

From the above standard electrode potential values, it is seen that Mn^{3+} is more easily reduced to Mn^{2+} than the corresponding Fe^{3+} to Fe^{2+}.

This can be explained by the d^5 configuration.
Mn^{2+} ⟶ Mn^{3+}
d^5 d^4

half-filled 3d orbitals a more stable configuration
Fe^{2+} ⟶ Fe^{3+}
d^6 d^5

Inter-electronic repulsion decreased stability Therefore, Mn^{3+} is a stronger oxidizing agent than Fe^{3+}.

(b) Manganese(IV) oxide is used in the manufacture of dry cell batteries. A particular dry cell, consisting of a sodium anode and a graphite cathode immersed in a polymer electrolyte, has been developed to detect gases like fluorine and chlorine. The graphite cathode is coated with manganese(IV) oxide which will be converted to MnO(OH) solid and hydroxide ions during discharge.

(i) Write the ion-electron equations for the reaction which occurs at the anode and cathode respectively. [2]

Anode : $Na \rightarrow Na^+ + e^-$
Cathode : $MnO_2 + H_2O + e^- \rightarrow MnO(OH) + OH^-$

(ii) The voltage of this sodium-carbon dry cell is found to be 1.0 V. With reference to the data booklet, estimate approximately the E^o of the manganese half cell and state any assumptions you make. [2]

E^θ_3 (MnO_2/Mn(OH)) = -1.71V. Assumptions: 25^{o}C & solution of 1.0 moldm$^-$

(c) Hadfield steel which is used in situation where very hard steel is required contains manganese and iron together with very little carbon.

When a 0.2 g sample of steel was dissolved in dilute acid and suitably oxidized, a purple solution containing iron(III) ions and manganate(VII) was formed. Titration of this solution required 24.5 cm^3 of 0.100 mol dm^{-3} iron(II) sulphate to discharge the colour.

Calculate the percentage of manganese in the Hadfield steel sample. [4]

Fe^{2+} reduces MnO_4^- only (1 mol MnO_4^- = 5 mol Fe^{2+})

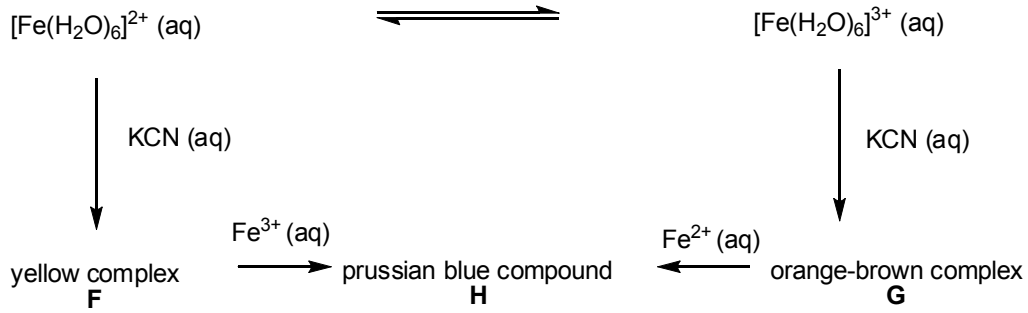
Number of moles of Fe^{2+} = 0.1 x $\frac{24.5}{1000}$ = 2.45 x 10^{-3}

Number of moles of MnO_4^- = 1/5 x 2.45 x 10^{-3}
= 4.9 x 10^{-4}

Mass of Mn = 54.9 x 4.9 x 10^{-4}
= 2.69 x 10^{-2} g

% by mass of Mn = $\frac{2.69 \times 10^{-2}}{0.20}$ x 100 = 13.5 %

(d) Aqueous Fe(II)/Fe(III) undergo the following reactions.



(i) Suggest the formulae of the anions of **F** and **G**. [2]

F : $[Fe(CN)_6]^{4-}$
G : $[Fe(CN)_6]^{3-}$

(ii) The anions of **F** and **G** are complex ions. They are formed between a transition metal ion and ligands. What do you understand by the term ligand? Why do transition metal ions have strong tendency to form complex ions? [4]

Ligands are molecules or ions that possess at least one <u>lone pair electrons</u> that can form <u>dative covalent bonds</u> to the central metal ion.

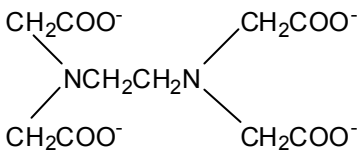
Transition elements have strong tendency to form complexes as their cations are small and highly charged.

Central metal ion have <u>empty low-lying 3d orbitals</u> to accommodate the lone pair electrons from the ligands.

(iii) Suggest a formula for the compound **H**. [1]

$Fe_3[Fe(CN)_6]_2$ / $Fe_4[Fe(CN)_6]_3$

(iv) The deterioration in the air of some organic substances, such as cosmetics, is accelerated by iron(II) ions Suggest why the deterioration can be slowed down by a small quantity of EDTA. [1]



EDTA

Hexadentate ligand EDTA can form a very stable complex with Fe^{2+}, thus removing the catalytic effect of Fe^{2+}

[Total: 20]