NJC H2 Chemistry Prelim Paper 2 Suggested Answers

1 **(a)** Due to **high temperature in the car engine**, **N_2 and O_2 from the air** can react to form NO_2.

NO_2 can be removed from the exhaust gas with the use of a **catalytic converter**, it can be **reduced by CO** to form harmless N_2.

(b) **(i)**

(ii) NO_2, being a **radical**, is **very reactive** and reacts with other gases in the air and gets destroyed more readily, hence a shorter atmospheric residence time

(c) **(i)** $\Delta H^{\ominus} = +9.2 - 2(+33.2) = -57.2$ kJ mol^{-1}

$\Delta S^{\ominus} = +304 - 2(+240) = -176$ J mol^{-1} K^{-1}

(ii) $\Delta H^{\ominus}$ has a negative sign since the dimerization is a **bond formation process**, hence heat is given out / reaction is exothermic.

$\Delta S^{\ominus}$ has a negative sign since the dimerization results in **fewer gas particles**, hence there is a decrease in the disorderliness of the system.

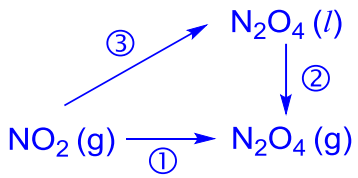
(iii) At equilibrium,

$\Delta G = 0$
$\Delta H^{\ominus} - T\Delta S^{\ominus} = 0$
$-57.2 - T(-176/1000) = 0$

$T = 325$ K

(iv) When N_2O_4 liquefies,
$\Delta G = 0$
$\Delta H_{vap} - T\Delta S_{vap} = 0$
$\Delta H_{vap} = T\Delta S_{vap} = 294 \times 88 = +25.9$ kJ mol^{-1}

(iv) Using Hess's law,



② = ① – ③
For $\Delta H_{rxn} = -57.2 - +25.9 = -83.1$ kJ mol^{-1}
For $\Delta S_{rxn} = -176 - 88 = -264$ J mol^{-1} K^{-1}

2 **(a)** **(i)** H_2O_2 oxidises the I^-, to aqueous I_2, so a **brown solution** / **black solid** would be obtained.
$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$

(ii) $E^{\theta}_{Cl_2/Cl^-}$ = +1.36 V
$E^{\theta}_{H_2O_2/H_2O}$ = +1.77 V
E^{θ}_{cell} = +0.41 V > 0

Since E^{θ}_{cell} is positive, reaction is spontaneous, H_2O_2 can oxidise chloride to chlorine while it itself is reduced to H_2O.

Hence, the oxidation of iodide may not be complete.

(iii) hexane / cyclohexane

The aqueous layer will **decrease in brown intensity** and the colourless organic layer will turn **purple / violet**.

(iv) Organic solvent is **flammable**, and can **cause a fire to break out**.

With higher temperature, iodine may **sublime** and escape.

(v) **Excess aqueous NH_3** should be added.

AgCl is soluble in excess NH_3(aq) but AgI is not. If there was significant amount of silver chloride in the precipitate obtained, most of the precipitate dissolved upon adding excess aqueous NH_3

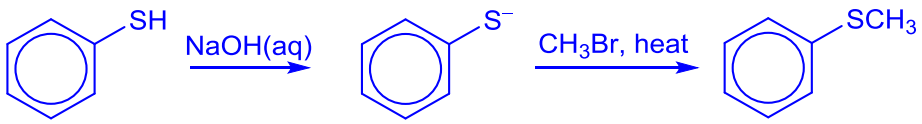
(b) **(i)** Amount of thioanisole used = $\frac{0.9\times1.06}{124.1}$ = 0.007687 mol

Amount of $NaIO_4$ used = $\frac{107\times{}^{15.40}/_{1000}}{214.0}$ = 0.0077 mol

∴ $NaIO_4$ reacts with thioanisole in a 1:1 mol ratio.

(ii) $C_6H_5SCH_3 + NaIO_4 \rightarrow C_6H_5SOCH_3 + NaIO_3$

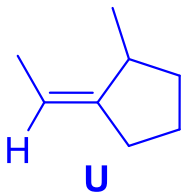
(iii)



(c) As a reducing agent, H_2O_2 will be oxidized.
Quote both eqns and $E^{\ominus}$
(In acidic) $O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $E^{\ominus}$ = +0.68 V
(In alkaline) $O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$ $E^{\ominus}$ = –0.08 V

Due to a more negative $E^{\ominus}$ value, HO_2^- is more likely to be oxidised than H_2O_2. H_2O_2 is a better reducing agent in alkaline condition.

3 **(a)**



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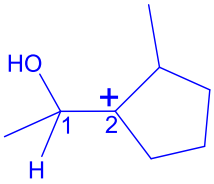
(b) Reagents : Dilute $KMnO_4$, NaOH(aq)

Conditions : cold

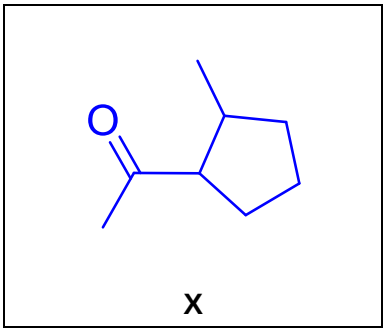
(c) Structure of carbocation intermediate



The carbocation ion would be formed at C_2 as it will form a more highly substituted carbocation than if the C+ is formed on C_1. OR

The carbocation would be formed at C_2 as it will have **<u>more</u>** electron donating alkyl group attached to C_2 than if the C+ is formed at C_1

(d)



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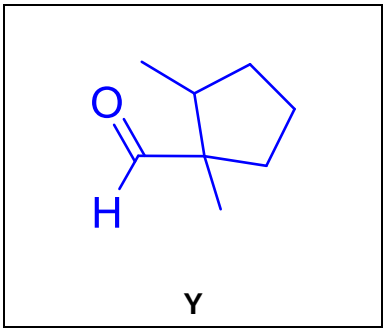

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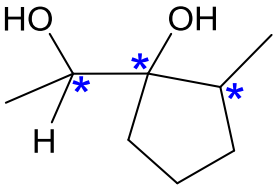
(e) **(i)**



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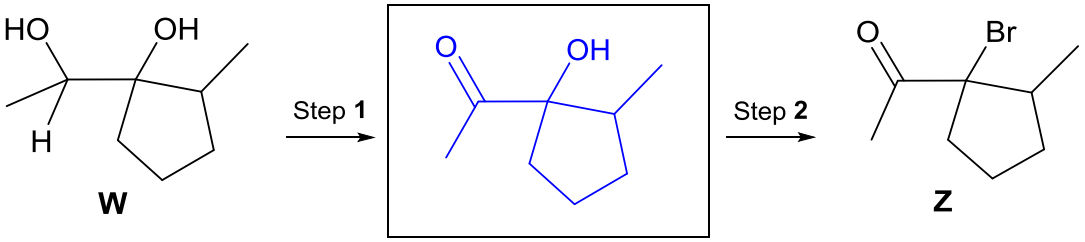
(ii) $2^3 = 8$

(f)



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Reagents and Conditions

Step **1** $KMnO_4$, H_2SO_4(aq), heat (or $K_2Cr_2O_7$, H_2SO_4, Heat [under reflux])

Step **2** Anhydrous PBr_3 (or $SOBr_2$ or HBr(g))

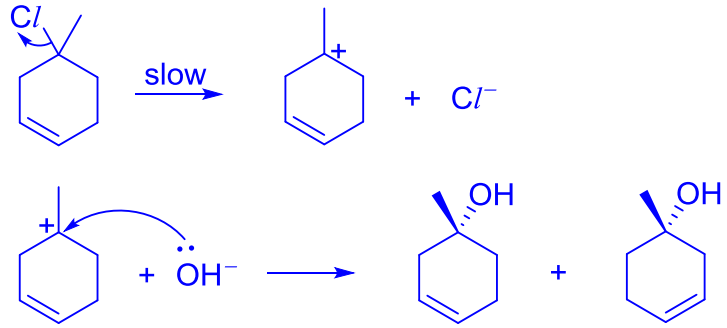
4 **(a)** **(i)** NaOH(aq), heat

(ii) Since the [OH^-] decreases linearly over time with fixed gradient, rate of reaction remains the same throughout the whole experiment, the order or reaction with respect to OH^- is 0.

Comparing the time taken for 0.4 mol dm^{-3} of OH^- being reacted, it takes a half the time for sample with 0.5 mol dm^{-3} of **P** (13 mins) than that of 0.25 mol dm^{-3} of **P** (26.5 mins). This means when the [**P**] is doubled, the rate is also doubled. The order of reaction with respect to **P** is 1.

Rate Equation : Rate = k [Compound **P**]

(iii) Nucleophilic Substitution (S_N1)



(iv) There is no optical activity present in the products.

Trigonal planar carbocation intermediate allows nucleophile to approach from top and bottom of the plane at equal probability producing equimolar of enantiomers forming a racemic mixture. The effect of rotation of plane polarised light by one enantiomer is completely cancel by the other enantiomer resulting in lack of optical activity.

(v) Trend: R–I, R–Br, R–C*l*

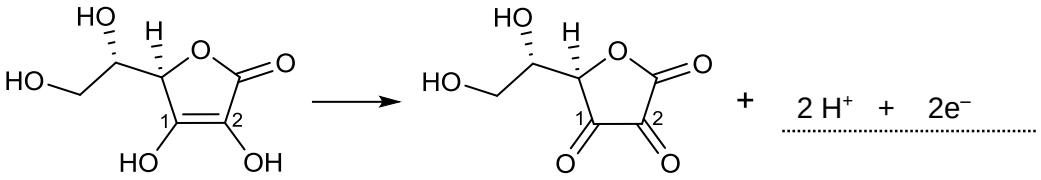
Rate of this nucleophilic reaction depends on the breaking of the C–X bond. C–I bond (240 kJ mol^{-1}) is the weakest as compared to C–Br (280 kJ mol^{-1}) and C–C*l* (340 kJ mol^{-1}). C–I bond is the easiest to be broken and hence would take the shortest time to complete the substitution (highest rate). C–Br bond is weaker than C–C*l*, so C–Br would be easier to break and take shorter time than C–C*l*.

(b) **(i)** 75% yield = 20 g
100% yield = 20 x 4/3 = 26.67g
Amount of diphenylethandioate = 26.67 ÷ 242 = 0.11021 mol
Amount of phenol = 0.11021 x 2 = 0.22042 mol
Mass of phenol used = 0.22042 x 94 = 20.7 g

(ii) Add neutral $FeCl_3$ (aq). Reaction is completed when there is no formation of violet complex, indicating that all phenol have been reacted.
OR
Add aqueous Br_2. Reaction is completed when orange aqueous Br_2 do not decolourise upon addition, indicating all phenol have been reacted. Reaction is incomplete when orange aqueous Br_2 decolorised and white precipitate formed.
OR
Add Br_2 in CCl_4. Reaction is completed when orange-red Br_2 do not decolourise upon addition, indicating all phenol have been reacted. Reaction is incomplete when orange-red Br_2 decolorised.

5 (a) (i) Oxidation state of C_1 in vitamin C : +1
Oxidation state of C_1 after oxidation : +2

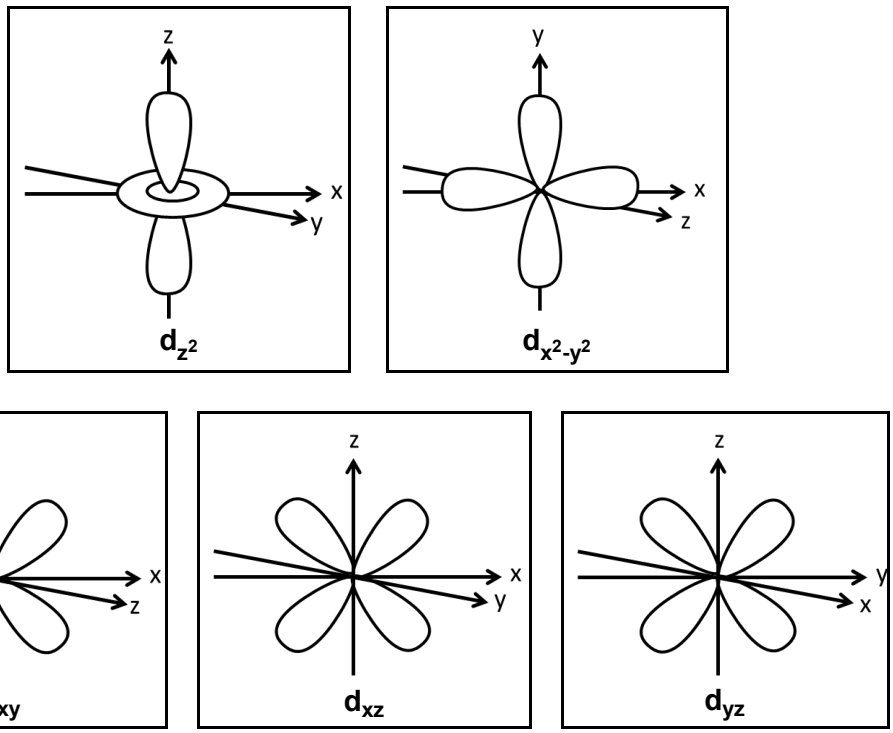
(ii)



(b) (i) 5 million red blood cells contain 150 mg of haemoglobin.
Mass of haemoglobin in 10000 million red blood cells
$= \frac{10000}{5} \times 150 = 300000$ mg
Mass of iron in 10000 million red blood cells
$= \frac{4}{100} \times 300000$ mg $= 12000$ mg $= 12$ g
Amount of iron required $= \frac{12}{55.8} = 0.215$ mol

(ii) Red blood cell has a lifespan of 120 days. However, even when the red blood cells dies, some of the **iron still remains in the body for further use.**

(c) (i)



(ii) In the presence of ligands, the d-orbitals of the transition element ion are split into two different energy levels with a small energy gap, ΔE**.**

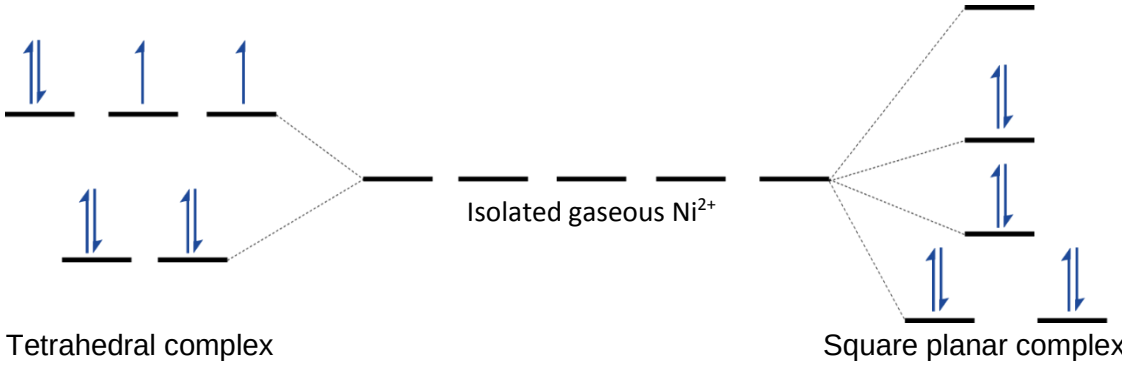
Electrons in the lower energy d-orbitals can absorb light of a certain wavelength with energy corresponding to the energy gap, ΔE, and be promoted to the higher energy d-orbitals **(d-d transition).**

The light not absorbed would be reflected and the colour of the complex is the **complementary** of the wavelength absorbed.

(d)

(i) $1s^2\ 2s^2\ 2p^6\ \ 3s^2\ 3p^6\ 3d^8$

(ii)



Tetrahedral complex Square planar complex

(iii) Square planar [only contains paired electrons in the d orbitals]

(e) **(i)** Condensation (also accept nucleophilic substitution or nucleophilic acyl substitution)

(ii) Heating under reflux with conc HC*l* will cause the hydrolysis of the amide group in luminol.

(iii) Luminol is less basic as compared to N_2H_4.
The lone pair on all N of luminol are involved in delocalization with the neighbouring benzene and C=O groups. As such, they are less available for donation to H^+ and act as a base. The lone pair on N of N_2H_4 do not undergo such delocalization and is more available for donation to H^+.