Hwa Chong Institution
2011 Prelim Paper 3 Answers

1 (a) (i) At the water surface, the surfactants are orientated such that the hydrophilic heads are exposed to water for favourable ion-dipole interactions, whereas the hydrophobic tails are exposed above the water surface, maintained by dispersion forces.

(ii) Mechanical agitation during washing causes oil or grease to be surrounded by surfactant molecules and broken into small droplets so that relatively small micelles are formed. The charged surfaces of the micelles prevent the oil or grease droplets from coalescing again and the micelles are easily washed away.

(b) (i) PCl_5 (s), room temperature

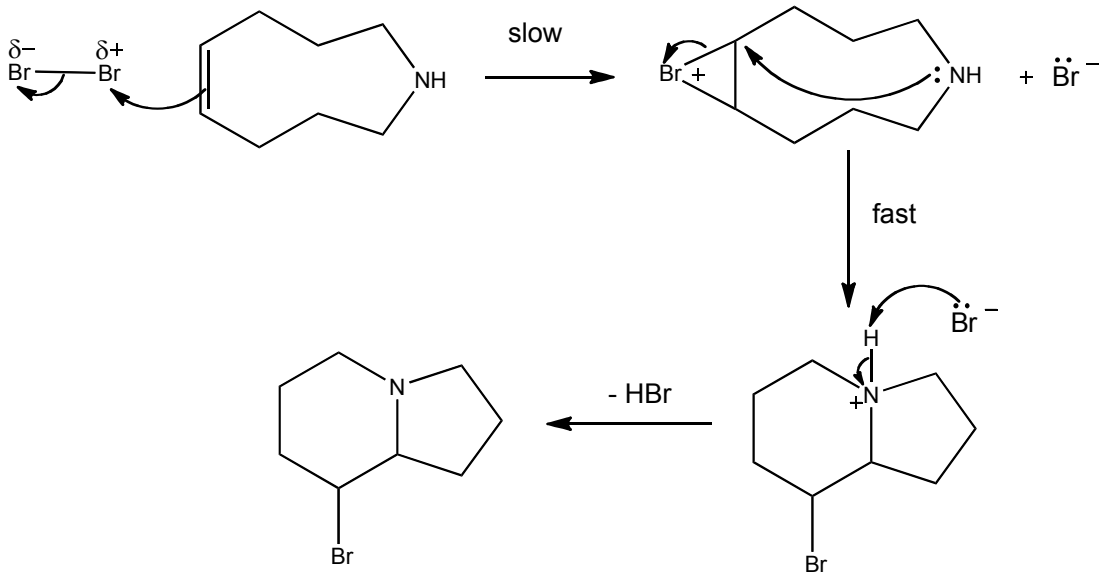
(ii) acid-base reaction

(iii) $H_2NCH_2CH_2OH$ is bifunctional and the acid chloride would be able to react with both the amine and the alcohol to give side products ($C_{11}H_{23}CO_2CH_2CH_2NH_2$ or $C_{11}H_{23}CONHCH_2CH_2OCOC_{11}H_{23}$).

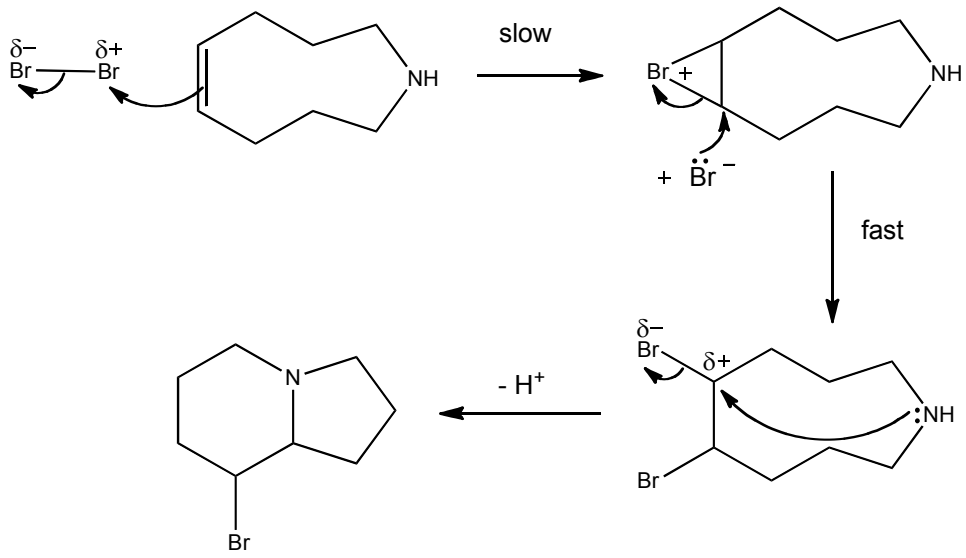
(iv)

$$CH_3CH_2Cl \xrightarrow[\text{heat}]{\text{ethanolic NaOH}} CH_2{=}CH_2 \xrightarrow{Br_2\,(aq)} CH_2BrCH_2OH \xrightarrow[\text{heat in a sealed tube}]{\text{conc } NH_3} H_2NCH_2CH_2OH$$

(c) Electrophilic Addition



Alternatively,
Electrophilic Addition (followed by nucleophilic substitution)



(d) **(i)** $$K_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 \times P_{O_2}}$$

P_{SO2} = 0.15 atm
P_{O2} = 0.075 atm
P_{SO3} = 8 – 0.15 – 0.075 = 7.775 atm

$$K_p = \frac{7.775^2}{0.15^2 \times 0.075} = 3.58 \times 10^4 \text{ atm}^{-1}$$

(ii) V_2O_5 acts as a heterogeneous catalyst.

It is in a different phase from the reacting mixture. **The reactant molecules readily adsorb onto the surface of the catalyst**.

The adsorption process brings the reactant molecules closer thus **increasing their concentrations at the catalyst surface**; **adsorption also weakens the strong S=O and O=O bonds**; and allows these **molecules to be orientated in the right positions for reaction**. The catalysed pathway thus involves **lower activation energy.**

When the reaction is complete, the molecules will **desorb and diffuse away from catalyst surface so that the active sites are exposed for further reaction**.

2 (a) Liquid fuels must be vaporized before combustion can take place.

As diesel oil has more C atoms than gasoline and hence a **larger electron cloud**, the **dispersion forces between its molecules are stronger**.

Its boiling point is higher and hence **vaporizes much less easily** and therefore is not easily ignited.

(b) (i) $C_2H_5OH\ (l) + H_2O\ (l) + O_2\ (g) \rightarrow 4H_2\ (g) + 2CO_2\ (g)$

OR $2C_2H_5OH\ (l) + 4H_2O\ (l) + O_2\ (g) \rightarrow 10H_2\ (g) + 4CO_2\ (g)$

(ii) The sign of entropy change should be positive.

There is a greater number of moles of gas on the product side of the equation hence there is greater disorder and therefore a greater number of ways to distribute the energy.

(iii) Ethanol has more hydrogen atoms and hence can produce more hydrogen fuel per mole of ethanol

Methanol is toxic while ethanol is not.

(c) (i) $H_2\ (g) + ½O_2\ (g) \rightarrow H_2O\ (g)$

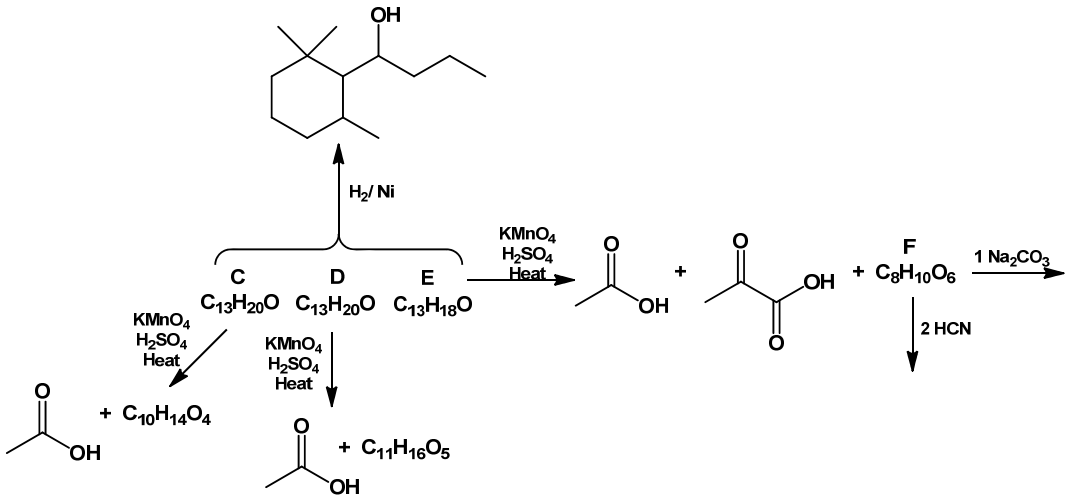
$C_2H_5OH\ (l\ or\ g) + 3O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (g)$

(ii) ΔH_c of H_2 = (436 + ½ x 496) – (2 x 460) = - 236 kJ mol^{-1}

ΔH_c of C_2H_5OH
= (410 x 5 + 350 x 1 + 360 x 1 + 460 x 1 + 496 x 3) – (2 x 2 x 740 + 3 x 2 x 460)
= - 1010 kJ mol^{-1}

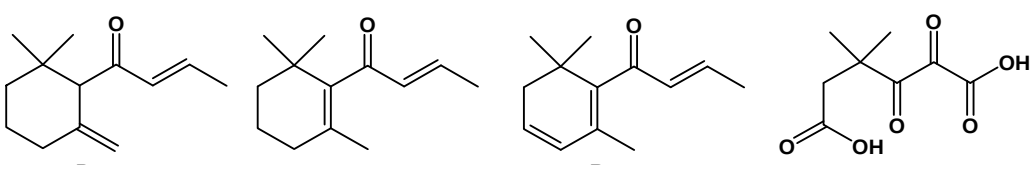
(iii) Since ethanol produces more heat and a greater number of moles of gas per mole of ethanol compared to hydrogen on combustion, ethanol is the more efficient fuel.

(d) Summary of the reaction scheme:



Observations	Deductions
C can exist as a pair of enantiomers but **D** and **E** does not show any optical activity.	**C** contains a chiral carbon whereas **D** and **E** does not contain chiral carbon (or are symmetrical).
1 mol of **C** and **D** reacts with 2 mol of liquid bromine. 1 mol of **E** reacts with 3 mol of liquid bromine.	Electrophilic addition. **C** and **D** have 2 C=C, R has 3 C=C.
C, **D** and **E** react with hydrogen in the presence of nickel to give the same compound.	(Catalytic) reduction/hydrogenation occurs.
C undergoes oxidative cleavage with acidified $KMnO_4$ to give ethanoic acid and a compound containing 10C.	**C** contains a terminal alkene as there is loss of CO_2. **D** does not contain terminal alkene. **C** and **D** contains the CH_3CH=C structure.
D undergoes oxidative cleavage with acidified $KMnO_4$ to give ethanoic acid and a compound containing 11C.	
F reacts with 1 mole of Na_2CO_3 to produce CO_2.	Acid-base reaction occurs and **F** is dibasic (dicarboxylic acid).
F reacts with 2 moles of HCN under cold condition with base as the catalyst.	Nucleophilic addition occurs and **F** contains 2 carbonyl groups.

Structures of unknown:



C **D** **E** **F**

3 **(a)** Enzymes are highly specific in the type of reactions which they catalyze, without any side-reactions.

Enzymes can be denatured by high temperature / have an optimum temperature at which they function most efficiently.

Enzymes have an optimum set of pH at which they function most efficiently.

Any **two** properties

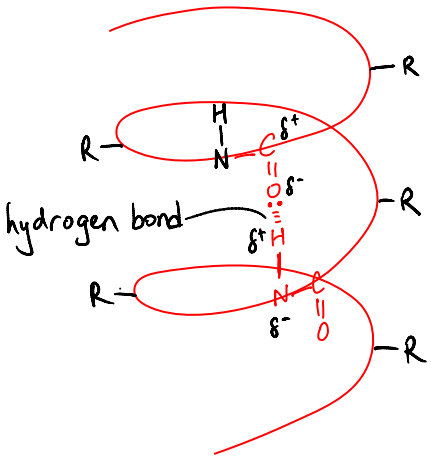
(bi) Step 1: $SOD–Cu^{2+} + O_2^- \rightarrow O_2 + SOD–Cu^+$

$E^{\ominus}_{cell}$ = +0.42 – (–0.33) = +0.75V (> 0, hence feasible)

Step 2: $SOD–Cu^+ + O_2^- + 2H^+ \rightarrow H_2O_2 + SOD–Cu^{2+}$

$E^{\ominus}_{cell}$ = +0.89 – (+0.42) = +0.47V (> 0, hence feasible)

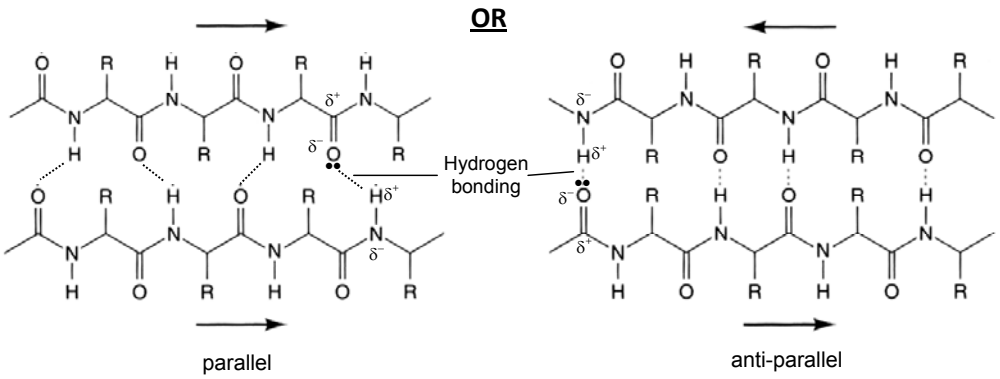
(bii) α-helix



Correctly drawn diagram (helical structure and illustration of hydrogen bond)

- Backbone of the polypeptide chain coiled to form a helical arrangement with 3.6 amino acids per turn of helix
- Stabilized by hydrogen bonds formed between the peptide C=O and the peptide N-H group four amino acid residues away
- Side-chain of each amino acid residue points outwards from the helix (described or shown in diagram)

β-pleated sheet

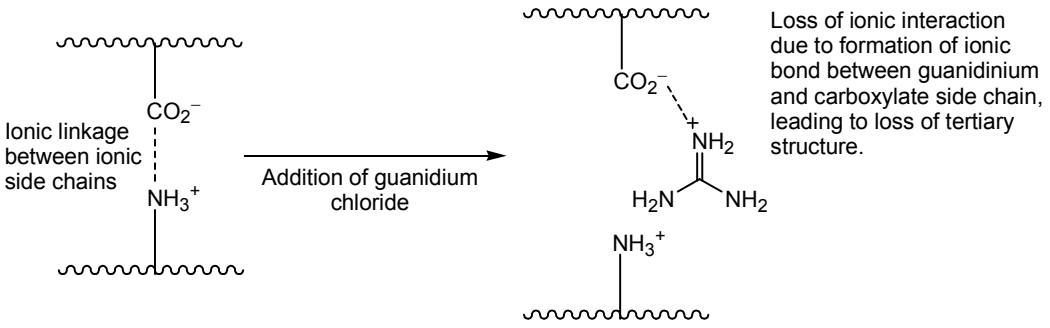


Correctly drawn diagram (parallel or anti-parallel arrangement and illustration of hydrogen bond)

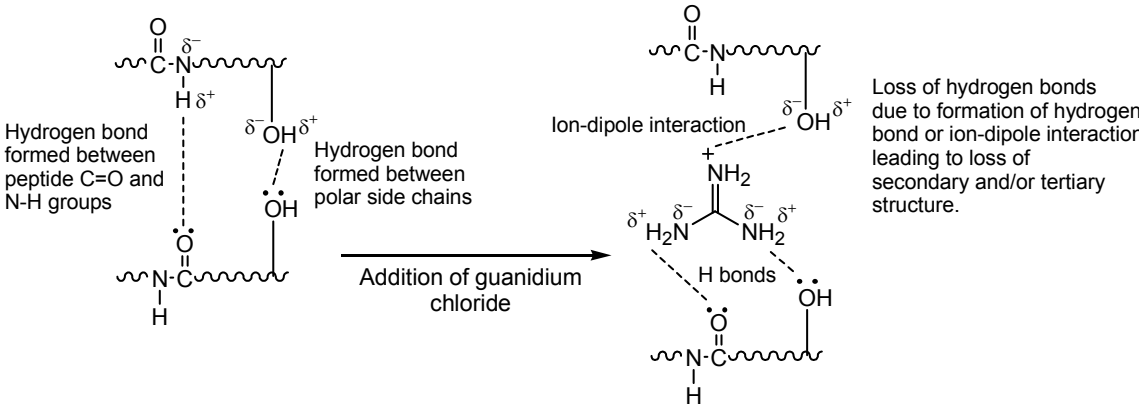
- Segments of polypeptide backbone fold back on itself with adjacent strands running in opposite directions (anti-parallel) or in same direction (parallel)
- Stabilized by hydrogen bonds formed between the peptide N-H and C=O groups from adjacent rows (described or shown in diagram)
- R-groups perpendicular to plane of sheet / point up and down from plane of sheet

(iii)

- The guanidinium cation can interfere with the ionic linkages formed between the side chains of the amino acid residues by forming ionic bonds with negatively charged side chains, hence disrupting the tertiary structure.



- It can also form hydrogen bonds/ ion-dipole interactions with the peptide C=O or N-H groups (secondary structure), and/or polar side chains (tertiary structure) of the amino acid residues, hence disrupting the hydrogen bonding interactions in the secondary and/or tertiary structures of the protein.



[1] each for describing effect on secondary and tertiary structure in words or diagram

- The primary structure of the protein will not be destroyed.
- Overall, the protein loses its 3-D configuration, and hence its function.

(ci) The relative rate of reaction is lower for substrate II due to the presence of the electron-withdrawing fluorine which causes

(i) benzene ring to be less susceptible towards electrophilic attack as it is less electron rich

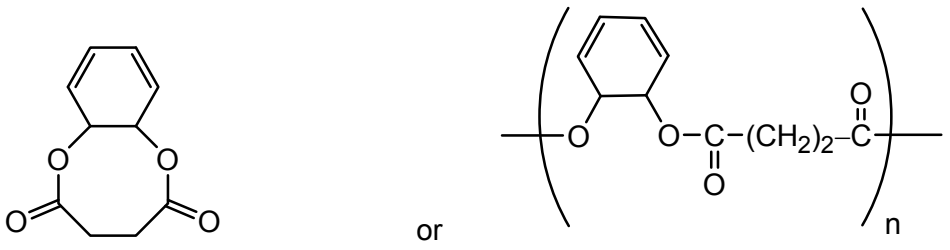
OR

(ii) phenoxide ion to bind less strongly to Cu^{2+} centre in **G** as the electron density on oxygen is decreased.

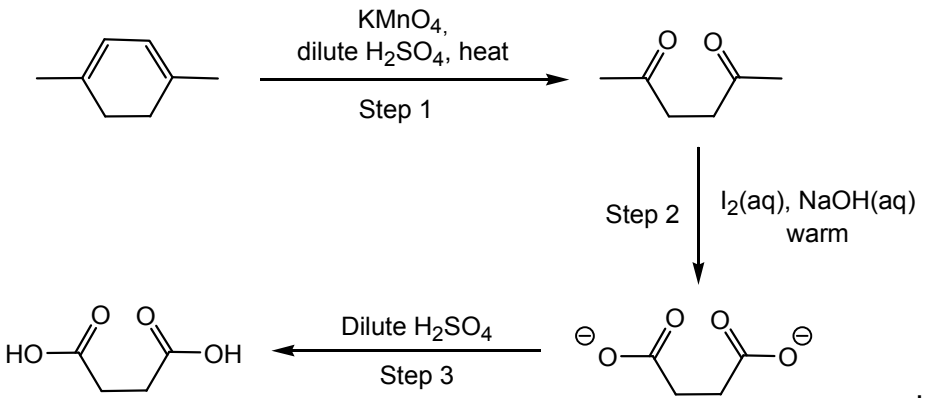
(cii) The relative rate of reaction for substrate III will be similar to that for substrate I. The breakage of the C–H (or C–D) bond adjacent to the OH group is in the fast step of the mechanism. Hence, the strength of this bond does not affect the rate of reaction.

(di) $LiAlH_4$ in dry ether, room temperature OR $NaBH_4$ in (alkaline) methanol, room temperature

(dii)



(diii)



4 **(a)** Formation of acid rain / cause respiratory problems / carcinogen / toxicity

(b) $NO + O_3 \rightarrow NO_2 + 2O$ slow
$2O \rightarrow O_2$ fast

(c) **(i)** $[NO] = [O_3]$ at each timing **or**
Concentration of both reactants fall at the same rate

(ii) Since the reaction is overall second order, the following rate equations may be possible:

Rate = $k\,[NO]^2$ or Rate = $k\,[NO][O_3]$

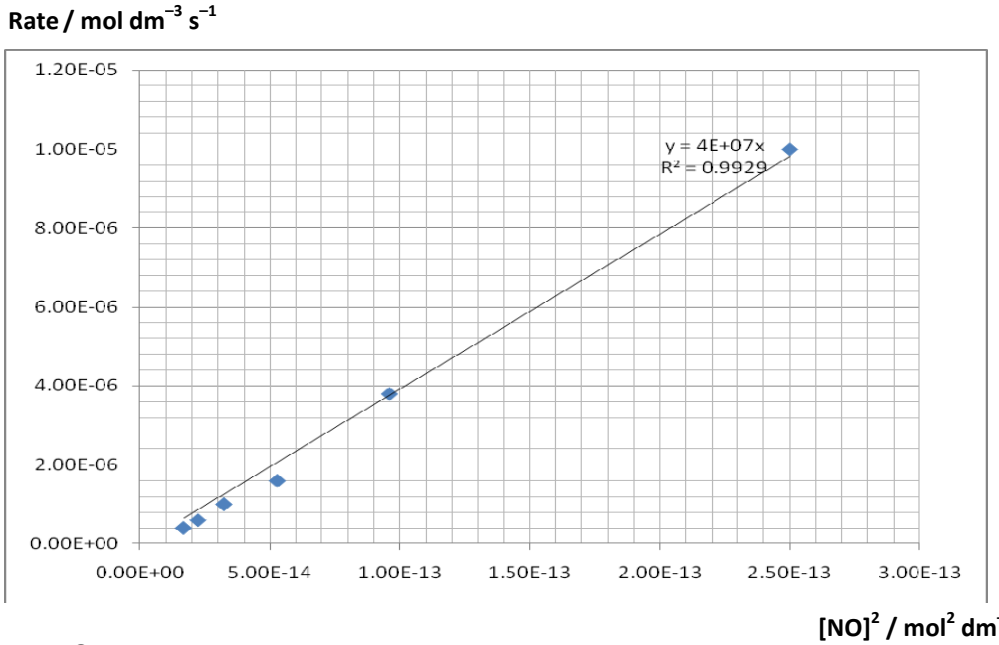
As such, a graph of ***rate against*** $[NO]^2$ or a graph of ***rate against*** $[NO][O_3]$ would give a straight line. Values for $[NO]^2$ and $[NO][O_3]$ should be identical since $[NO] = [O_3]$ at every timing.

Time / s	$[NO_2]$ / mol dm^{-3}	$\frac{\Delta[NO_2]}{\Delta t}$ / mol dm^{-3} s^{-1}	$[NO]$ / mol dm^{-3}	$[NO]^2$ / mol^2 dm^{-6}
0.05	0.50×10^{-6}	1.00×10^{-5}	5.00×10^{-7}	2.50×10^{-13}
0.10	0.69×10^{-6}	3.80×10^{-6}	3.10×10^{-7}	9.61×10^{-14}
0.15	0.77×10^{-6}	1.60×10^{-6}	2.30×10^{-7}	5.29×10^{-14}
0.20	0.82×10^{-6}	1.00×10^{-6}	1.80×10^{-7}	3.24×10^{-14}
0.25	0.85×10^{-6}	6.00×10^{-7}	1.50×10^{-7}	2.25×10^{-14}
0.30	0.87×10^{-6}	4.00×10^{-7}	1.30×10^{-7}	1.69×10^{-14}

Calculate values for:

- Reaction rate, using $\frac{\Delta[NO_2]}{\Delta t}$
- Concentration of NO at each timing, since $[NO] = 1.0 \times 10^{-6} - [NO_2]$
- $[NO]^2$ or $[NO][O_3]$

(iii)



- Correct axes
- Correct shape

Rate constant k = gradient of graph = 4×10^{7} mol^{-1} dm^{3} s^{-1}

(d) **(i)** Initial no of moles of N_2O_4 = 4.60 / (14.0 × 2 + 16.0 × 4) = 0.0500 mol

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

Initial / mol	0.0500	0
Eqm / mol	0.0500 – x	+2x

PV = nRT

$$(1.01 \times 10^{5})(1.48 \times 10^{-3}) = \left(\frac{4.60}{M_r}\right)(8.31)(300)$$

M_r = 76.7

No of moles of gas = 4.60 / 76.7 = 0.0600 mol
0.0500 – x + 2x = 0.0600
x = 0.0100 mol

Percentage conversion = (0.0100/0.0500) × 100% = 20.0%

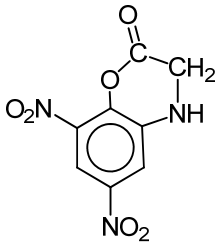
(ii) Since the forward reaction is endothermic, the increase in temperature causes the position of equilibrium N_2O_4 (g) $\rightleftharpoons$ $2NO_2$ (g) to <u>shift to the right to absorb the excess heat</u>**.** A <u>darker brown</u> is observed for the gas mixture since more NO_2 is formed.

(d) **(i)** Cl_2 (g), $AlCl_3$ catalyst, heat

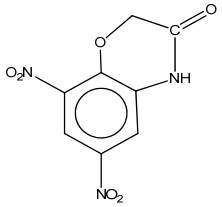
(ii) Nucleophilic substitution

(iv) **Limited** Sn, conc HCl, heat, followed by NaOH (aq)

(v)



OR



5 (a) (i) Cr^{3+} $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^3$

As chromium is able to form one or more stable ions or compounds with **incompletely filled d subshell (**e.g. Cr^{2+}, Cr^{3+}), it is a transition element.

(ii) In Zn atom the **3d level is complete and stable** and none of these 3d electrons are used in bonding. Therefore zinc atoms loses the two 4s electrons and has only one oxidation state of +2.

(Note: the argument that 3d and 4s electrons have similar energy and hence resulting in variable oxidation state will not be relevant in answering this question.)

(iii) $[Cr(H_2O)_6]^{3+} + H_2O \rightarrow [Cr(H_2O)_5(OH)]^{2+} + H_3O^+$

$Zn + 2\ H_3O^+ \rightarrow Zn^{2+} + H_2 + 2H_2O$

(iv)

		$E^{\ominus}$ / V
$Cr^{3+} + e$	$\rightleftharpoons$	Cr^{2+} –0.41
$2H^+ + e$	$\rightleftharpoons$	H_2 0.00

$Cr^{2+}(aq) + 2\ H^+(aq) \rightarrow Cr^{3+}(aq) + H_2(g)$ $\quad E^{\ominus}_{cell} = +0.41\ V > 0$, feasible

Calculation of $E^{\ominus}_{cell}$, and deduction that the redox reaction is feasible.

The H^+ acts as oxidizing agent, oxidizing the blue Cr^{2+} to the green Cr^{3+} (or eqn).

Reaction is slow because of 2 positively-charged ions reacting.

(v) White ppt is AgC*l*.

No of moles of AgC*l* = no of moles of C*l*$^-$ = 0.925/143.5 = 6.45 x 10^{-3}
Mass of C*l* in 1.00 g = 6.45 x 10^{-3} x 2 x 35.5 = 0.458 g

Orange solution that reacted with iodide is $Cr_2O_7^{2-}$.
No of moles of $Cr_2O_7^{2-}$ = 1/6 x 19.5/1000 x 0.100 = 3.25 x 10^{-4}
Mass of Cr in 1.00 g = 3.25 x 10^{-4} x 2 x 10 x 52 = 0.338 g

Mass of O in 1.00 g = 1.00 – 0.458 – 0.338 = 0.204 g

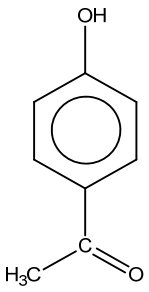
Cr : O : C*l* = 0.338/52 : 0.204/16 : 0.458/35,5 = 1 : 2 : 2

Therefore, formula of dark red liquid is CrO_2Cl_2

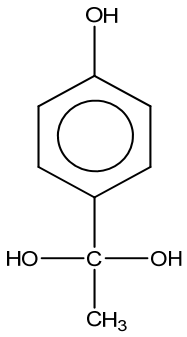
(b) **(i)** **Q** undergoes **<u>hydrolysis</u>** (S_N) reaction with aq NaOH to give **R** (which is an alcohol).

T (non-polar, hydrophobic benzene ring hence insoluble in water) has **<u>phenol group which is acidic</u>** enough to react with aq NaOH to give soluble ionic salt. **[or:** acid-base reaction, phenol group present]

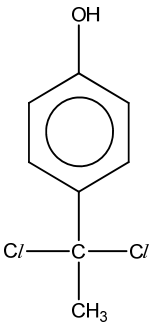
T undergoes **<u>condensation</u>** with 2,4-DNPH and gives positive triiodomethane tests, hence is a **<u>methyl ketone</u>**.



T



R



Q

(ii) Neutral $FeCl_3$, only **P** will give violet coloration.

PCl_5, only **V** will give copious white fumes of HCl.

Acidified $K_2Cr_2O_7$ and heat, only **V** will change the orange solution to green.

Aq bromine, only **P** will decolourise the orange aq bromine and give a white ppt.

DO NOT accept acidified $KMnO_4$, heat.