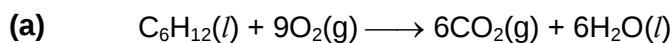


Raffles Institution
2013 H2 Chemistry Preliminary Examinations Paper 2
(Suggested Solutions)

1

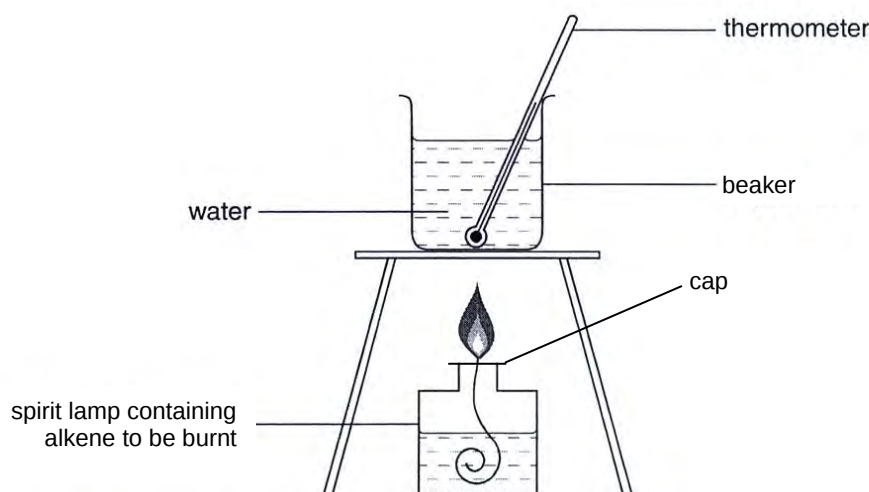


- (b)(i) Assuming no heat loss,
 heat evolved from combustion = heat gained by calorimeter set-up
 $-\Delta H_c^\ominus [\text{cis-hex-3-ene}] \times \text{amt of cis-hex-3-ene} = C \times \text{temperature rise}$
 $-(-3733)(0.20 / 84.0) = C(5.0)$
 $C = 1.7776 = 1.78 \text{ kJ K}^{-1} \text{ (3 s.f.)}$

- (b)(ii) Assuming no heat loss,
 heat evolved from combustion = heat gained by calorimeter set-up
 $-\Delta H_c^\ominus [\text{trans-hex-3-ene}] \times \text{amt of trans-hex-3-ene} = C \times \text{temperature rise}$
 $-\Delta H_c^\ominus [\text{trans-hex-3-ene}] \times (0.22 / 84.0) = (1.7776)(5.4)$
 $\Delta H_c^\ominus [\text{trans-hex-3-ene}] = -3665 = -3670 \text{ kJ mol}^{-1} \text{ (3 s.f.)}$

- (b)(iii) $\Delta H_{\text{iso}}^\ominus = \Delta H_c^\ominus [\text{cis-hex-3-ene}] - \Delta H_c^\ominus [\text{trans-hex-3-ene}]$
 $= -3733 - (-3665)$
 $= -68.0 \text{ kJ mol}^{-1}$

(c)



Experimental set-up

1. **Fill up one spirit lamp with *cis*-hex-3-ene** (to about 80% capacity), taking care to avoid getting any *cis*-hex-3-ene on the outside surface of the lamp.
2. **Set up the apparatus as shown above**, such that the beaker is about 2-3 cm from the tip of the wick.

Calibration of calorimeter set-up

3. Using a 250 cm³ beaker, **measure out 200 cm³ of water**.
4. Using an electronic weighing balance, weigh the mass of the spirit lamp filled with *cis*-hex-3-ene. **Record this mass**.
5. Using the thermometer, read the **temperature** of the water and **record it**.
6. **Use the lighter to light the lamp and place it under the beaker of water**, centering the flame under the bottom of the beaker and **ensuring the flame is at an approximately constant distance** below it.
7. Using the thermometer, carefully and gently stir the water.
8. When the temperature has risen to about **5 °C**, **blow out (extinguish)** the flame.
9. Continue to stir the water, **recording the highest temperature** reached.
10. While the lamp is cooling, clean the soot off from the bottom of the beaker.
11. **Re-weigh the spirit lamp** when it has cooled to room temperature. Record this mass.
12. Repeat **Steps 3 to 11**, using the same lamp after cleaning it. (For a more accurate estimate of the heat capacity.)

Determining mass and temperature changes using *trans*-hex-3-ene

13. Repeat **Step 1** by filling the other spirit lamp with *trans*-hex-3-ene.
14. Repeat **Steps 3 to 11**, using this new spirit lamp, recording the relevant masses and temperatures.
15. For a more accurate estimate of the data, **Step 14** can be repeated.

The value for the standard enthalpy change of combustion of *trans*-hex-3-ene can then be found by similar calculations as shown in **(b)**.

(d) Hexenes are inflammable liquids and are hence a **fire hazard**.

Any of the following:

Containers of the hexenes should be covered and stored away, when not in use;
proper disposal of hexenes;
the wick should be lit away from any nearby hexenes.

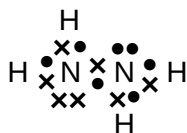
Or

Hexenes are volatile and hence a **health hazard**, causing respiratory problems.

Experiment to be carried out in fume cupboard to avoid inhaling toxic vapour of hexene.

2

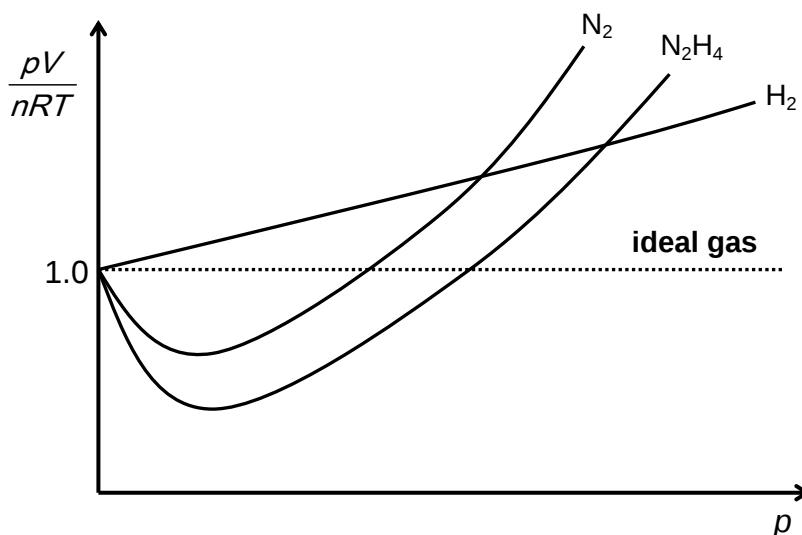
(a)



(b)

 sp^3 ; 107°

(c)



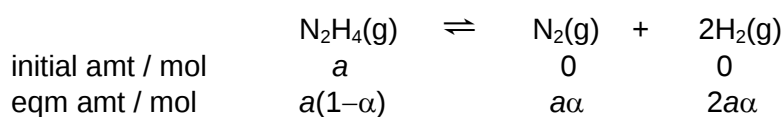
(d)

$$pV = nRT = (m/M)RT$$

$$(101 \times 10^3)(10 \times 10^{-3}) = (m / 20)(8.31)(150 + 273)$$

$$m = 5.75 \text{ g}$$

(e)(i)

Let the initial amt of N_2H_4 be a .

Total amt of gases present at eqm
 $= a(1-\alpha) + a\alpha + 2a\alpha = a(1+2\alpha) \text{ mol}$

$$\text{average } M_r = \frac{1-\alpha}{1+2\alpha} M_r(N_2H_4) + \frac{\alpha}{1+2\alpha} M_r(N_2) + \frac{2\alpha}{1+2\alpha} M_r(H_2)$$

$$20 = \frac{1-\alpha}{1+2\alpha} (32.0) + \frac{\alpha}{1+2\alpha} (28.0) + \frac{2\alpha}{1+2\alpha} (2.0)$$

$$\alpha = 0.30$$

(e)(ii)

$$p_{N_2H_4} = \chi_{N_2H_4} p_T = \frac{1-\alpha}{(1+2\alpha)} p_T = \frac{1-0.3}{(1+0.6)} (1) = 0.4375 \text{ atm} = 0.438 \text{ atm}$$

$$p_{N_2} = \chi_{N_2} p_T = \frac{\alpha}{(1+2\alpha)} p_T = \frac{0.3}{(1+0.6)} (1) = 0.1875 \text{ atm} = 0.188 \text{ atm}$$

$$p_{H_2} = \chi_{H_2} p_T = \frac{2\alpha}{(1+2\alpha)} p_T = \frac{2(0.3)}{(1+0.6)} (1) = 0.375 \text{ atm}$$

$$K_p = \frac{p_{N_2} p_{H_2}^2}{p_{N_2H_4}} = \frac{(0.1875)(0.375)^2}{0.4375} = 6.03 \times 10^{-2} \text{ atm}^2$$

(e)(iii) α will decrease.

3

- (a) When pH increases, the **concentration of H^+ decreases**.
By Le Chatelier's Principle, the **position of equilibrium shifts to the right** to increase the concentration of H^+ , causing the fraction of HF to decrease.

- (b) Since $\frac{[HF]}{[F^-]} = 0.5$,
 $\Rightarrow [HF]_{eqm} = [F^-]_{eqm}$
 $\Rightarrow$ buffer solution at maximum buffering capacity.

$$pH = pK_a + \lg \frac{[F^-]}{[HF]}$$

$$\Rightarrow 3.2 = pK_a + \lg 1$$

$$\Rightarrow K_a = 10^{-3.2} = 6.31 \times 10^{-4} \text{ mol dm}^{-3}$$

- (c)(i) $a = \frac{1}{2}$

- (c)(ii) The addition of H^+ causes the position of the equilibrium (2) to shift right, reducing $[F^-]$ in solution.

This, in turn, causes the position of equilibrium (1) to shift right, increasing $[Ca^{2+}]$ in solution.

- (c)(iii) From the graph, at pH 3.0,
 fraction of HF = 0.61 and fraction of F^- = 0.39

$$\frac{[F^-(aq)]}{[HF(aq)]} = \frac{0.39}{0.61} = 0.639$$

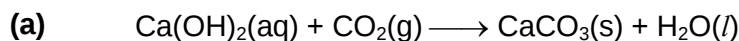
$$\text{At pH 3.0, } [F^-] = (0.639)(4.63 \times 10^{-4}) = 2.96 \times 10^{-4} \text{ mol dm}^{-3}$$

- (c)(iv) $[Ca^{2+}] = \frac{1}{2} ([HF] + [F^-])$

- (c)(v) From (iii) and (iv),
 $[Ca^{2+}] = 0.5 \times (4.63 + 2.96) \times 10^{-4} = 3.795 \times 10^{-4} \text{ mol dm}^{-3}$

$$K_{sp} = [Ca^{2+}][F^-]^2 = (3.795 \times 10^{-4})(2.96 \times 10^{-4})^2 = 3.33 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$$

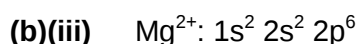
4



(b)(ii) As shown by plot (II), **MgCO₃ decomposes more readily** than BaCO₃.

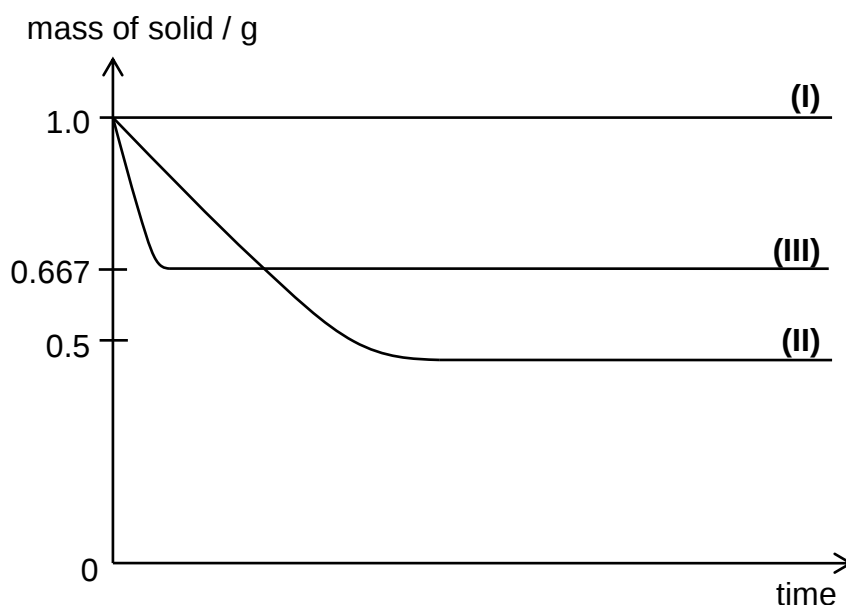
Mg²⁺ is **smaller** than Ba²⁺ and has a **higher charge density** and **polarising power**.

Hence it **distorts the electron cloud of the CO₃²⁻ anion**, and **weakens** the carbon-oxygen **bond within the anion to a greater extent**, resulting in MgCO₃ requiring less energy for thermal decomposition and thus it decomposes more readily.



Mg²⁺ has **one less** occupied **principal quantum shell** than that of its parent atom Mg.

(c)



(d) Let the A_r of Z be a.

$3\text{ZCO}_3 \equiv \text{Z}_3\text{O}_4$ (i.e. 3 moles of ZCO_3 decomposes to give 1 mole of Z_3O_4)

amt of $\text{ZCO}_3 = 3 \times \text{amt of } \text{Z}_3\text{O}_4$

$$1.0 / (a + 12.0 + 3 \times 16.0) = 3 \times 0.667 / (3a + 4 \times 16.0)$$

$$1 / (a + 60) = 2.001 / (3a + 64)$$

$$3a + 64 = 2.001a + 120.06$$

$$a = 56.1 \text{ (value is closest to 55.8)}$$

Z is Fe.

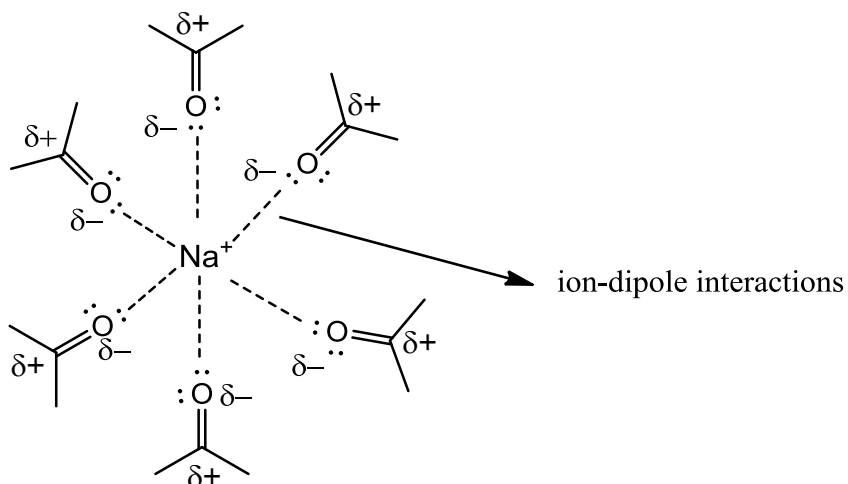
5

- (a) $\text{BE}(\text{C}-\text{Cl}) = +340 \text{ kJ mol}^{-1}$
 $\text{BE}(\text{C}-\text{I}) = +240 \text{ kJ mol}^{-1}$

The energy given out by the $\text{C}-\text{I}$ bond formed is insufficient to compensate for the energy needed to break the $\text{C}-\text{Cl}$ bond / the $\text{C}-\text{I}$ bond formed is weaker than the $\text{C}-\text{Cl}$ bond broken, hence ΔH is **endothermic**.

Since $\Delta G \approx \Delta H > 0$, the reaction is not feasible / does not go to completion.

(b)(i)



Note:

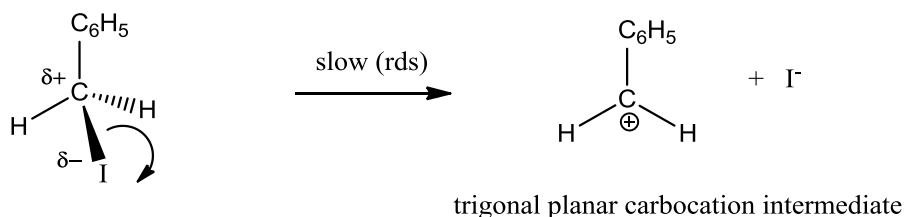
The above diagram shows what it actually looks like in 3-dimensional space i.e. Na^+ is surrounded by six propanone molecules.

Only one Na^+ with one propanone molecule is needed for this answer.

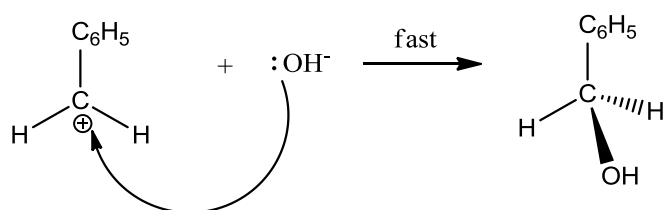
- (b)(ii) NaCl is **precipitated out** as a solid.
 By Le Chatelier's Principle, $[\text{NaCl}]$ is low and position of equilibrium shifts to the right towards completion.

- (c)(i) Mechanism: Nucleophilic Substitution ($\text{S}_{\text{N}}1$)

Step 1: Formation of carbocation



Step 2: Attack of OH^- nucleophile



(c)(ii) The $\text{C}_6\text{H}_5\text{CH}_2^+$ carbocation is **resonance stabilised** as the π electron cloud of the **benzene ring can overlap with the empty p orbital of the carbocation**.

For $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{I}$, the carbocation is not resonance-stabilised. Hence, the reaction proceeds by $\text{S}_\text{N}2$ mechanism instead.

(d)(i) Secondary alcohol; alkene

(d)(ii) As a **base / proton acceptor** to react with $\text{R}-\text{OH}$ group.

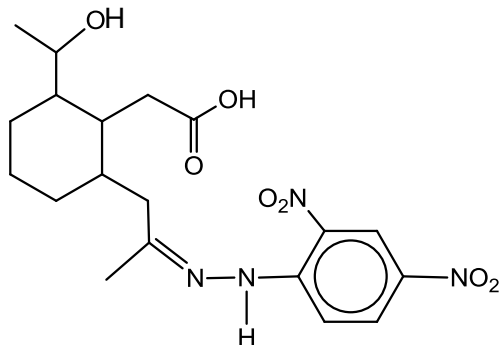
(d)(iii) Step **III**: $\text{KMnO}_4(\text{aq})$, $\text{NaOH}(\text{aq})$, heat
Step **IV**: I_2 , $\text{NaOH}(\text{aq})$, heat

(d)(iv) Secondary **alcohol**

The secondary alcohol will **undergo oxidation in reaction III** to form a methyl ketone, which **subsequently loses 1 carbon in the iodoform reaction in reaction IV**.

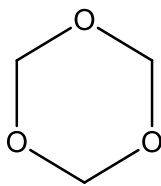
(d)(v) Test: Use 2,4-dinitrophenylhydrazine

Observations: orange ppt formed for **U** and no orange ppt for **T**

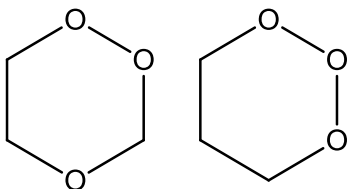


6

(a)(i)



(a)(ii)

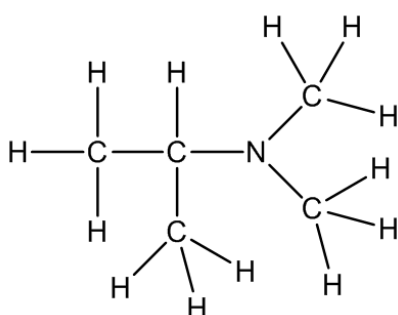


(a)(iii) Weak O–O bond due to **repulsion of lone pairs of electrons on adjacent O atoms** OR **repulsion of two δ^- charges on adjacent O atoms.**

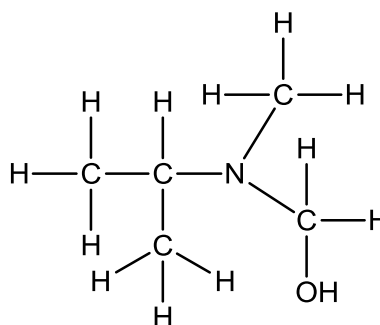
(b)(i) $2 < \text{any value} < 3.3$

The additional **methyl group** is **electron-donating**. Hence it **increases** the **electron density on N atom** which allows it to coordinate to H^+ more easily.

(b)(ii)



or



(b)(iii) For phenylamine, **lone pair on N is delocalised into the π electron cloud of the benzene ring**. Hence, the lone pair is less available for donation, and phenylamine acts as a **weak nucleophile**.