## 2015 HCI Prelim H2 Chemistry Paper 3 Answers

- 1 (a) (i) Heterogeneous catalysis [1]
  - (ii) Optical isomerism [1]



(iii) The <u>addition of H<sub>2</sub> to one side (bottom face)</u> of the planar alkene molecule creates a <u>chiral alkane molecule</u>. [1]

When the <u>opposite side (top face)</u> of the alkene is now <u>adsorbed to the surface</u> of the Ni catalyst, the <u>addition of H<sub>2</sub> produces a chiral alkane molecule which is the non-superimposable mirror image</u> of the product formed at the bottom face. **[1]** 

As there is <u>50% chance for each side (face) of the alkene to bind to the surface</u> of the catalyst, <u>the two enantiomers are produced in a 1:1 ratio</u> resulting in a <u>racemic mixture</u>. Hence the product mixture does not rotate the plane of plane-polarised light. **[1]** 

If a diagram is used, it will substitute the 1<sup>st</sup> two marks: Show opposite faces adsorbed to the catalyst surface [1] Indicate which carbon forms the chiral alkane and the corresponding enantiomer. [1]



(b) (i)  $\Delta H^{\oplus}_{\text{reaction}} = \Sigma(B.E. \text{ of Bonds Broken}) - \Sigma(B.E. \text{ of Bonds Formed})$ =  $\Sigma[B.E (C = C) + B.E. (H - H)] - \Sigma[B.E (C - C) + B.E. (C - H) \times 2]$ = (610 + 436) - (350 + 410 × 2) = - 124 kJ mol<sup>-1</sup>

> Correct bond energies used [1] Correct equation and answer [1]

(ii)  $\Delta H^{\ominus}_{reaction}$  is exothermic.  $\Delta S^{\ominus}_{reaction}$  is negative as there is a decrease in the number of moles of gas in the

reaction. [1]

Given that  $\Delta G^{\ominus}_{reaction} = \Delta H^{\ominus}_{reaction} - T\Delta S^{\ominus}_{reaction}$   $\Delta G^{\ominus}_{reaction}$  is expected to be <u>negative</u> only <u>at low temperatures</u> and so the reaction would be <u>spontaneous</u> only <u>at low temperatures</u>. [1]

 (iii) Although the reaction is energetically feasible, the <u>activation energy is very high.</u> Or as the <u>low temperatures</u> are necessary for the reaction to be feasible, the <u>rate of</u> reaction may be very slow. [1]

Hence the <u>catalyst provides an alternative pathway with a lower activation energy</u> and the reaction speeds up. **[1]** 

- (d) (i) A homogeneous catalyst acts in the <u>same phase as the reactants</u>. [1]
  - (ii) Oxidation number of Rh in compound 2: +3 [1]  $x + (-1) + [(-1) \times 2] = 0$  x = +3(working is not required)
  - (iii) The coordination number indicates the <u>number of dative bonds</u> about the central atom or ion. [1]

Wilkinson's catalyst:coordination number = 4Compound 3:coordination number = 6

[1/2] for each correct coordination number

(iv) Rh is able to exhibit <u>variable oxidation states</u>. [1]
 The proposed mechanism requires the addition of H<sub>2</sub> to Rh in the form of two hydride ligands, which causes the <u>oxidation state of Rh to increase from +1 to +3</u>. [1]

Rh is able to form <u>complexes of variable coordination numbers</u>. **[1]** The proposed mechanism requires the <u>alkene and H<sub>2</sub> to bind to Rh as ligands</u> before the addition reaction occurs. Or <u>coordination number changes from 4 to 6</u> from Wilkinson's catalyst to Compound 3. **[1]** 

2 (a) Chlorine is a <u>greenish yellow gas</u>. Bromine is a <u>reddish-brown liquid</u>. Iodine is a <u>black solid</u>.
 [1]

Down the group, the <u>volatility decreases</u> as the <u>number of electrons in the halogen</u> <u>molecule increases</u>. The <u>size of the electron cloud increases</u>, making the electron cloud more polarizable and hence giving rise to <u>stronger dispersion forces</u>. Thus <u>more energy is</u> <u>required</u> to overcome the stronger dispersion forces between the molecules for them to vaporize. **[2]** 

(b) Add a few drops of aqueous  $\underline{AgNO_3}$  to the sample solution, followed by <u>dilute aqueous</u> <u>ammonia</u>.

If a <u>white ppt</u> forms which <u>dissolves in dilute aqueous ammonia</u>, the sample contains  $C\Gamma$  ion. Ag<sup>+</sup>(aq) +  $C\Gamma$  (aq)  $\rightarrow$  AgC*l* (s) --- white ppt

AgCl (s) + 2NH<sub>3</sub> (aq)  $\rightarrow$  Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> (aq) + Cl<sup>-</sup> aq)

If a <u>cream ppt</u> forms which is <u>insoluble in dilute aqueous ammonia</u>, the sample contains Br ion.

Ag<sup>+</sup>(aq) + Br<sup>-</sup>(aq) → AgBr (s) --- cream ppt {AgBr (s) + 2NH<sub>3</sub> (aq) → Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> (aq) + Br<sup>-</sup> (aq)} – this reaction occurs as well but does not decrease the [Ag<sup>+</sup>] sufficiently to make AgBr dissolve completely since  $K_{sp}$ (AgBr) is lower than  $K_{sp}$ (AgCl).

- [1] for correct reagents
- [1] for equation for AgX precipitation and colours of ppt
- [1] for equation with ammonia and correct observation of solubility

OR

Add a few drops of  $\underline{Cl_2(aq)}$  into the sample solution.

If the <u>solution turns</u> from colorless to <u>vellow-orange</u>, the sample contains  $Br^-$  ion.  $Cl_2(aq) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$ 

If the solution does not turn yellow-orange (OR remains colourless), the sample contains  $C\Gamma$  ion.

[1] for correct reagents

[1] for correct observations for both ions

[1] for redox equation

(c) (i) Pyridinium tribromide is a solid and is less volatile, hence it is safer to use compared to bromine which is a fuming liquid and gives off toxic bromine fumes. [1]
 OR Pyridinium tribromide is a solid, hence it is easier to weigh and use compared to bromine which is a fuming liquid.

Pyridinium tribromide is given as an ionic salt, hence students can deduce it is a solid and will be less volatile compared to bromine which is furning and toxic, and relate its advantage to safety and ease of use.

- (ii)  $\begin{bmatrix} Br Br Br \end{bmatrix}^{-}$
- (iii) Step 1: condensation [1] OR nucleophilic (acyl) substitution or addition-elimination

Step 2: electrophilic substitution [1]

(iv) In Route 2, the Br<sub>2</sub> reacts with phenylamine. The <u>lone pair on NH<sub>2</sub> delocalises into</u> the benzene ring and increases electron density in the ring. The <u>ring is highly</u> activated towards electrophilic attack, hence it is able to undergo <u>further</u> brominations to give multi-brominated products. [1]

In Route 1, the anilide is not as activated as phenylamine as the <u>-NHCOR group is</u> less electron-donating due to the <u>delocalization of the nitrogen lone pair into the -</u> <u>C=O group as well</u>. [1]

- (v) The bulky –NHCOR group sterically hinders the approach of the electrophile towards the 2<sup>nd</sup> carbon. Hence substitution occurs mainly on the 4<sup>th</sup> position. [1]
- (vi) Phenylamine is the most basic of the three, followed by bromophenylamine and then bromoanilide. [1]

Bromoanilide is the least basic. In the amide group, the <u>lone pair on N is delocalized</u> into the C=O group (as well as into the benzene ring) and least (or not) available for <u>protonation</u>.

In bromophenylamine and phenylamine, the lone pair on N delocalizes into the benzene ring. However, bromophenylamine is less basic because its <u>Br substituent</u> is electron-withdrawing and decreases the electron density on the benzene ring. Hence the lone pair on N delocalizes into the benzene ring to a greater extent and is less available for protonation, compared to phenylamine. **[1]** 

(d) (i) amount of  $Br_2 = 16.0 \times 10^{-3} / (79.9 \times 2) = 1.00 \times 10^{-4} \text{ mol}$ 

 $[Br_2] = 1.00 \times 10^{-4} / (150/1000) = 6.67 \times 10^{-4} \text{ mol dm}^{-3}$  [1]

The <u>value of  $K_c > 1$ </u> shows that the equilibrium is product favoured. The concentration of Br<sup>-</sup> is 0.5/6.67 x 10<sup>-4</sup> = 750 times more than that of Br<sub>2</sub>. The <u>large excess of Br<sup>-</sup></u> will push the equilibrium position very much to the right, such that the reaction is almost complete. **[1]** 

- (ii) Assuming the reaction is complete,  $[Br_3^-]$  at eqm = 6.67 x 10<sup>-4</sup> mol dm<sup>-3</sup>  $[Br^-]$  at eqm = 0.5 - 6.67 x 10<sup>-4</sup> = 0.499 mol dm<sup>-3</sup> [1]
- (iii)  $K_{\rm C} = [{\rm Br_3}^-] / [{\rm Br_2}][{\rm Br}^-]$   $100 = 6.67 \times 10^{-4} / [{\rm Br_2}] (0.499)$  $[{\rm Br_2}] = 1.34 \times 10^{-5} \text{ mol dm}^{-3}$  [1]

3 (a) (i) No. of moles of sulfoxide recovered = 91.3% of theoretical no. of moles  $\therefore$  no of moles of thioanisole used = theoretical no of moles of sulfoxide = (9.82/(124.1 + 16.0))/(91.3/100) = (9.82/140.1)/(91.3/100) = 0.07677 mol [1] correct substitution of  $M_r$  and % yield  $\therefore$  mass of thioanisole used = 0.07677 x 124.1 = 9.53 g (must be 3 s.f.) [1]

(ii) Since  $IO_4^-$  and thioanisole react in a 1:1 ratio,  $\Rightarrow$  no of moles of  $IO_4^-$  required = 0.07677 mol (from (i))  $\therefore$  volume of sodium iodate solution required = 0.07677/0.500 x 1000 = 154 cm<sup>3</sup> [1] (allow ecf from no of moles of thioanisole in (i)) (iii) Oxidation state of iodine in  $IO_4^- = +7$  $\therefore$  change in oxidation state of iodine = (+5) - (+7) = -2

By observing the structure of thioether and sulfoxide product, the sulfur atom changes its oxidation state by +2 (due to new double-bond formation with the more electronegative oxygen atom) [1]

As such,  $IO_4^-$  and thioanisole should react in a 1:1 ratio.

(b) (i) Electrophilic addition [1]



Note: not necessary to show all 3 lone pairs on S atom in 2nd step (only 1 is necessary)

(iii) Isopropyl methyl sulfide



 $NO_2$ 

(accept other unambiguous ways of drawing the structure)





3-nitrobenzenesulfonic acid

3-nitrobenzenesulfonic acid

G

NH3<sup>+</sup>Cl<sup>-</sup>

[2] (1 mark for each correct structure)

Step 1: conc.  $HNO_3$ , conc.  $H_2SO_4$ , >55 °C [1] (since  $-SO_3H$  is deactivating) Step 2: Sn, excess conc. HCl, heat [1] (no need to follow with NaOH since we add it in the next step anyway) Step 3: heat with NaOH(aq) [1] OR Inverse Steps 2 and 3, then **G** will be as follows (all others remain unchanged):

HO<sub>3</sub>S



Formula of each chloride must be correctly written [1]

Trend must be correct: [1]

- pH 7 must be clearly indicated on axis (if not, this mark is lost)

- trend in pH must be correct (neutral for NaCl, slightly below neutral for MgCl<sub>2</sub> (accept 6-6.5), lower for AlCl<sub>3</sub>, and lowest for SiCl<sub>4</sub> and PCl<sub>5</sub> (accept if PCl<sub>5</sub> is at lower pH than SiCl<sub>4</sub>)

- (e) (i) J contains  $NaAl(OH)_4$  or  $Al(OH)_4^-$  [1]
  - (ii)  $Al_2O_3$  is amphoteric, and so it is dissolves in NaOH(aq) [1/2]

 $Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$  [1] with correct state symbols Accept: ionic equation (without Na+ spectator ion)

 $TiO_2$  is basic in nature, and does not dissolve in NaOH, hence it remains as a solid and can be separated from the solution (filtered out) [1/2]

**- [1]** 

- (iii) Fe(OH)<sub>3</sub> OR Fe<sub>2</sub>O<sub>3</sub> [1] Accept: iron(III) hydroxide OR iron(III) oxide (oxidation state of iron must be stated)
- (iv) Step A requires heating to decompose the hydroxide.  $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

4 (a) (i)

$$2SO_{2}(g) + O_{2}(g) \rightleftharpoons 2SO_{3}(g)$$
Initial P / atm  $\frac{1}{2} \times 4$   $\frac{1}{2} \times 2$  0 (from doubling of volume) [1]  
Change  $-1.8$   $-0.9$   $+1.8$  (from 90% conversion of SO<sub>2</sub>)  
At eqm / atm  $0.2$   $0.1$   $1.8$   
I. Total P =  $0.2 + 0.1 + 1.8 = 2.1$  atm [1]  
II.  $x(O_{2}) = \frac{0.1}{2.1} = 0.0476$  [1]  
III.  $n = \frac{(2.1 \times 1.01 \times 10^{5}) \times (60 \times 10^{-3})}{8.31 \times (450 + 273)} = 2.12$  mol [1]

- (ii) The actual total pressure will be <u>smaller</u> than in (a)(i) because the gases (are not ideal, and) have <u>non-negligible intermolecular forces</u> which reduce the pressure on the container. [1]
- (b) (i) The F atom in H₂F<sup>+</sup> has two lone pairs and two bond pairs, hence, bent / V-shaped [1] Accept a diagram leading to a statement of 'bent / V-shaped'.



- (ii) Brønsted acid: HF [1/2] and Brønsted base: HF [1/2]
- (iii) Lewis acid:  $SbF_5$  [½] and Lewis base: F<sup>-</sup> [½]



(ii) It is <u>harder to remove a positively charged H<sup>+</sup> from the negatively charged thioglycolate</u> <u>anion HA<sup>-</sup></u> due to the attraction of opposite charges compared to the loss of H<sup>+</sup> from an uncharged thioglycolic acid molecule H<sub>2</sub>A. [1] This results in HA<sup>-</sup> being a <u>weaker acid compared to H<sub>2</sub>A</u> and hence larger pK<sub>a</sub>. [1]

Accept: The  $-CO_2H$  group in  $H_2A$  is a stronger acid than -SH group because the  $-CO_2^-$  is stabilized by resonance (the negative charge on the carboxylate ion is delocalized over two highly electronegative oxygen atoms), while the  $-S^-$  ion is not similarly stabilized.

(iii) 
$$K_{a} = \frac{[H^{+}][A^{2-}]}{[HA^{-}]}$$
  
 $\frac{[A^{2-}]}{[HA^{-}]} = \frac{K_{a}}{[H^{+}]}$   
 $\frac{[A^{2-}]}{[HA^{-}]} = \frac{10^{-10.31}}{10^{-9.3}} = 0.098$  [1]

OR  

$$pK_a = pH - lg \frac{[A^{2-}]}{[HA^{-}]}$$
  
 $10.31 = 9.3 - lg \frac{[A^{2-}]}{[HA^{-}]}$   
 $lg \frac{[A^{2-}]}{[HA^{-}]} = -1.01$   
 $\frac{[A^{2-}]}{[HA^{-}]} = 0.098$ 

- (iv) Not an effective buffer because <u>ratio of concentrations of HA<sup>-</sup> and A<sup>2-</sup> is too small</u> / <u>not close to 1</u> / <u>the reservoir of A<sup>2-</sup> is too low compared to HA<sup>-</sup></u>, (and therefore HA<sup>-</sup> will be used up very quickly when H<sup>+</sup> is added). [1]
- (v) Not suitable because the working range of phenolphthalein is 9.3 ± 1, but at pH 9.3, thioglycolic acid has not reached its second equivalence point, [½] which occurs only after 10.31 [½].



X, Y, B [3] (1 mark for each compound) Step 1: electrophilic addition [1] Step 2: nucleophilic substitution [1]

In Step 1,  $H_2S$  adds across the C=C double bond; the absence of chiral carbon in X rules out the Markovnikov product.

In Step 2, the –SH group acts as a nucleophile for substituting I in  $CH_3I$ , and loses its H as a proton.

During the condensation in Step 3,  $H_2O$  is lost between the  $-CO_2H$  group and  $CH_3SH$  to

form 
$$-C-S-CH_3$$

5 (a) (i) The melting point of Ru is higher than that of Sr. In Sr, only the 5s electrons are involved in metallic bonding. In Ru, <u>both 5s and 4d electrons are involved in metallic bonding due</u> to their proximities in energies [1]. <u>More energy</u> is required to overcome the <u>stronger</u> metallic bonding in Ru compared to Sr [1].



The IE increases as more electrons are removed. As more electrons are removed, the <u>number of protons is more than the number of electrons and there are stronger</u> <u>electrostatic forces of attraction on the remaining electrons</u> [1]. More energy is needed to remove another electron from the increasingly positively charged ion. There is a <u>big increase in IE</u> between the 2<sup>nd</sup> to the 3<sup>rd</sup> electrons removed. The 3<sup>rd</sup>

There is a <u>big increase in IE</u> between the 2<sup>nd</sup> to the 3<sup>nd</sup> electrons removed. The 3<sup>nd</sup> electron is removed from an <u>inner quantum shell</u> [½].

There is a <u>small increase in IE</u> between the  $8^{th}$  and  $9^{th}$  electrons removed. The  $9^{th}$  electron removed is from <u>4s subshell which is closer to the nucleus compared to 4p</u> <u>subshell</u> [½].

- (b) (i) The standard electrode potential of a half-cell is the potential associated with a given half-reaction when all components are in their standard states (temperature of 298 K, pressure of any gas at 1 atm, and concentration of any ion at 1 mol dm<sup>-3</sup>), measured relative to the standard hydrogen electrode. [1]
  - (ii)  $E_{\text{cell}}^{\ominus} = +0.23 (-0.76) = +0.99 \text{ V} > 0 \text{ [1]}$  $2\text{Ru}^{3+}(\text{aq}) + 2\text{n(s)} \rightarrow 2\text{Ru}^{2+}(\text{aq}) + 2\text{n}^{2+}(\text{aq}) \text{ [1]}$

(ii)

(iii)  $A_r$  of Ru = 101,  $M_r$  of orange crystal = 101/0.369 = 273.7 To balance the charges, Ru<sup>2+</sup> : C*l*<sup>-</sup> is 1:2 [1]  $M_r$  of NH<sub>3</sub> ligands = 273.7 - 101 - 2(35.5) = 101.7 Number of NH<sub>3</sub> ligands = 101.7/(14.0 + 3.0)  $\approx$  6 Formula for orange crystals: [Ru(NH<sub>3</sub>)<sub>6</sub>]C*l*<sub>2</sub> [1]

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## [1] for each of the 3 steps

Accept protonation using just  $H^+$  in first step and deprotonation without using  $A^-$  in last step

(ii)	Test/Observation	Deduction
	P reacts with acidified ethanol to	P undergoes nucleophilic addition with acidified
		$\Phi$ <b>P</b> contains aldehyde/ketone functional group.
	Both <b>P</b> and <b>R</b> yield a colourless gas which forms a white precipitate with limewater when warmed with aqueous sodium	<b>P</b> and <b>R</b> undergoes <u>acid-base</u> reaction with $Na_2CO_3$ to give <u>CO<sub>2</sub></u> gas. $\Phi$ <b>P</b> and <b>R</b> contain <u>carboxylic acid</u> functional group [1]
	carbonate.	
	With alkaline aqueous iodine, <b>P</b> gives a yellow precipitate	<b>P</b> reacts with alkaline aqueous iodine to give <u>CHI<sub>3</sub></u> ppt. $\Phi$ <b>P</b> contains <u>CH<sub>3</sub>CH(OH)- or CH<sub>3</sub>CO-</u> group [1]
	Treating <b>P</b> with methanolic sodium borohydride yields compound <b>Q</b> , $C_9H_{10}O_3$ .	Carboxylic acid in <b>P</b> cannot be reduced by methanolic NaBH <sub>4</sub> . <b>P</b> contains <u>ketone</u> group which undergoes <u>reduction</u> [1]
		P [1]



[1] for each correct structure (accept 1,2 or 1,3 or 1,4 di-substituted structures)[1] for each correct deduction, max 3 out of 4 available