2023 Y6 H2 Chemistry Preliminary Exam Paper 3 Suggested Solutions

Section A

1(a)(i) Both diamond and silicon have giant covalent structures. During melting, strong Si–Si and C–C covalent bonds between atoms are broken in silicon and diamond respectively.

Si–Si covalent bonds are weaker than C–C as the valence orbitals of Si are more diffuse than that of C, thus overlapping of the orbitals of Si is less effective than that of C. Hence less energy is required to break the weaker Si–Si bonds during melting compared to C–C bonds in diamond.

1(a)(ii) Al_2O_3 is amphoteric/reacts with both acids and bases, while SiO_2 is acidic/reacts with bases only.

$Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$
$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq)$
$SiO_2(s) + 2OH^-(conc) \rightarrow SiO_3^{2-}(aq) + H_2O(l)$

or

$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$
$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na^+[Al(OH)_4]^-(aq)$
$SiO_2(s) + 2NaOH(conc) \rightarrow Na_2SiO_3(aq) + H_2O(l)$

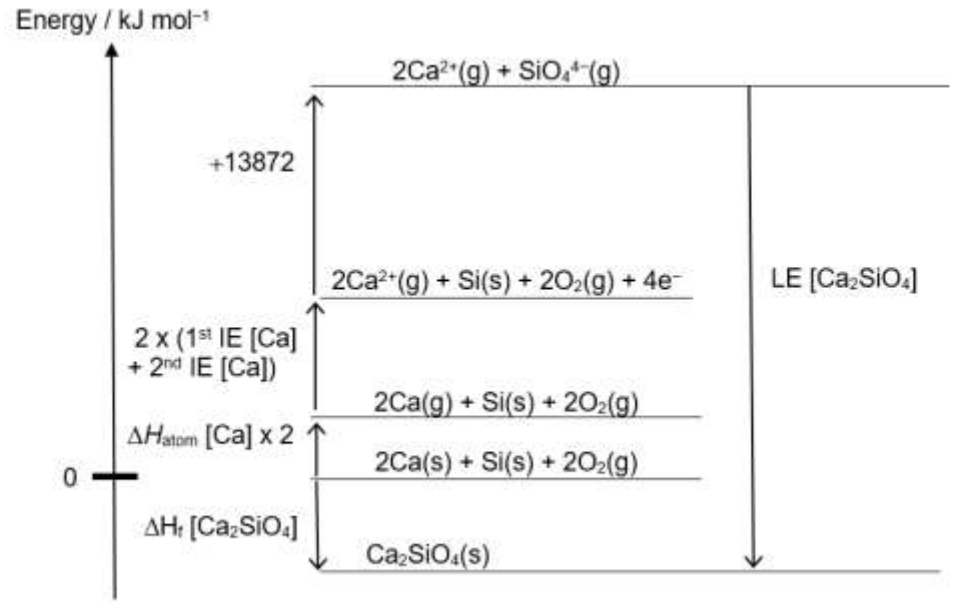
1(b)(i) For reaction 2, $\Delta H^\ominus = 2(-110.5) - (-910.9) = +689.9\ \text{kJ mol}^{-1}$

Assuming that $\Delta H^\ominus$ and $\Delta S^\ominus$ are independent of temperature,
$\Delta G^\ominus_{2500K} = +689.9 - (2500)(+361 \times 10^{-3}) = -213\ \text{kJ mol}^{-1}$ (3s.f.)

Reaction 2 has negative $\Delta G^\ominus_{2500K}$ and is spontaneous, whereas reaction 1 has positive $\Delta G^\ominus_{2500K}$ and is non–spontaneous. Hence reaction 2 is the preferred method for the extraction of Si from SiO_2.

1(b)(ii) $\Delta S^\ominus$ is positive as there is an increase in the number/moles/amount of gaseous particles (from 0 to 2) in the equation.

1(c)



Or

$$\begin{tikzcd}
\mathrm{2Ca(s) + Si(s) + 2O_2(g)} \arrow[rr, "\Delta H_f\ \mathrm{[Ca_2SiO_4]}"'] \arrow[d, "H_{atom}\ \mathrm{[Ca]} \times 2"] & & \mathrm{CaSiO_4(s)} \\
\mathrm{2Ca(g) + Si(s) + 2O_2(g)} \arrow[d, "2 \times (1^{st}\ \mathrm{IE\ [Ca]} + 2^{nd}\ \mathrm{IE\ [Ca]})"] & & \\
\mathrm{2Ca^{2+}(g) + 4e^{-} + Si(s) + 2O_2(g)} \arrow[d, "+13872\ \mathrm{kJ\ mol^{-1}}"] & & \\
\mathrm{2Ca^{2+}(g) + SiO_4^{4-}(g)} \arrow[uuurr, "\mathrm{LE\ [CaSiO_4]}"'] & &
\end{tikzcd}$$

Using Hess' Law,
$-2306 = 2(+121) + 2(+590 + 1150) + 13872 + \text{LE}\ [Ca_2SiO_4]$
LE $[Ca_2SiO_4]$ = $\underline{-19900\ \text{kJ mol}^{-1}}$ (3s.f.)

1(d)(i) The standard electrode potential, $E^\ominus$, of a half–cell is the <u>electromotive force / potential difference, measured at 298 K, between the half–cell and the standard hydrogen electrode</u>, in which the concentration of any reacting species in solution is <u>1 mol dm^{-3}</u> and any gaseous species is at a pressure of <u>1 bar</u>.

1(d)(ii) Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ (x2)

Overall: $O_2 + 2H_2O + 2Fe \rightarrow 4OH^- + 2Fe^{2+}$

$E^\ominus_{cell} = +0.40 - (-0.44) = +0.84$ V

1(d)(iii) $\Delta G^\ominus = -nFE^\ominus_{cell} = -4(96500)(+0.84) = -324240\ \text{J mol}^{-1} = \underline{-324\ \text{kJ mol}^{-1}}$

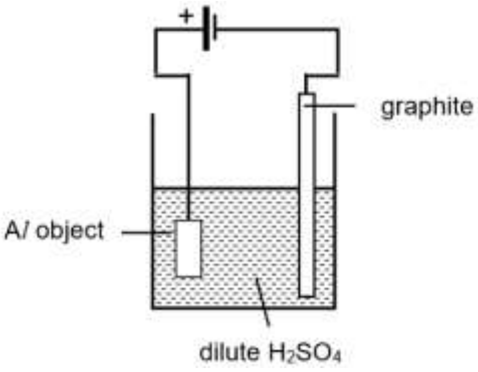
1(d)(iv) (I) Oiling the bicycle chain minimises contact between H_2O / O_2 and Fe, thus rusting stops/slows down.

(II) $Zn^{2+} + 2e^- \rightleftharpoons Zn \qquad E^{\ominus} = -0.76\ V$

$Fe^{2+} + 2e^- \rightleftharpoons Fe \qquad E^{\ominus} = -0.44\ V$

Zn is more easily oxidised than Fe, since $E^{\ominus}(Zn^{2+}/Zn)$ is more negative than $E^{\ominus}(Fe^{2+}/Fe)$. Hence Zn rusts in place of Fe.

1(e)



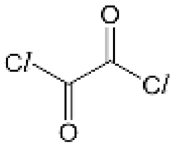
2(a)(i) High temperature and low pressure.

2(a)(ii) $V = (5.2)(8.31)(15+273)/101300 = 0.123\ m^3 = 123\ dm^3$

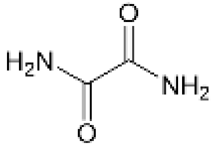
2(a)(iii) Hydrogen bonding in ammonia caused the molecules to be closer to one another, thus the gas occupies a volume smaller than expected.

2(b) Step 2: NH_3
Step 3: $LiAlH_4$, dry ether

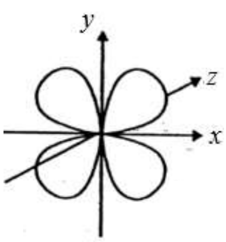
A is



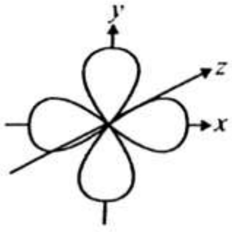
B is



2(c)(i)



d_{xy}



$d_{x^2-y^2}$

2(c)(ii) In an octahedral environment, lone pairs on the ligands approach the central metal ion along the x, y and z axes.

$3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals have their greatest electron density along the co-ordinate axes on which the ligands are situated. Hence electrons in these orbitals are pointing towards the lone pairs of ligands and will be repelled by them.

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$3d_{xy}$, $3d_{yz}$, $3d_{xz}$ orbitals have their greatest electron density in between the co-ordinate axes. Hence the repulsion between electrons in these orbitals and those of the approaching ligands will be less compared to electrons in $3d_{x^2-y^2}$ or $3d_{z^2}$ orbitals.

Hence, $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are at a higher energy level and $3d_{xy}$, $3d_{yz}$, $3d_{xz}$ orbitals are at a lower energy level.

2(d)(i) $Cr(OH)_3$

2(d)(ii) Oxidation

2(d)(iii) $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

This reaction involves the combination of two ions with the elimination of a small molecule, H_2O.

2(d)(iv) OH^- and H_2O are different ligands of different strength. The d orbitals of Cr^{3+} are hence split into two sets of slightly different energy levels to different extents, creating different energy gaps for different complexes, which in turn absorb energies of different wavelengths from the visible light spectrum for d-d transitions, thus displaying different colours.

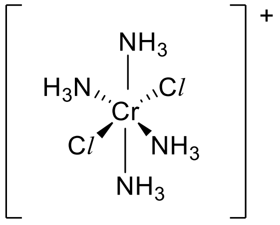
2(d)(v) The ability to display variable oxidation states in their compounds.

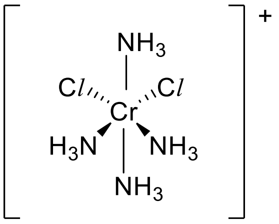
This is due to the close similarity in energy of the 3d and 4s electrons, which thus allows for different number of these electrons to participate in chemical bonding.

2(e)(i) $AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+Cl^-(aq)$

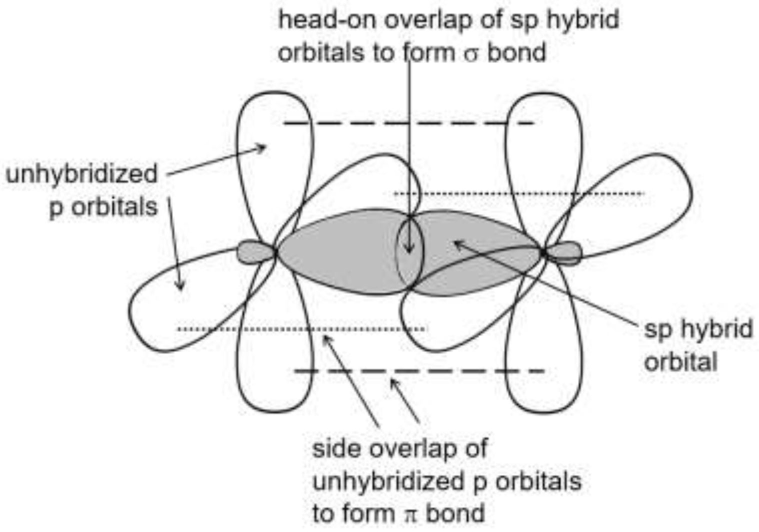
2(e)(ii) Cation: $[Cr(NH_3)_4Cl_2]^+$ Anion: Cl^-

2(e)(iii)

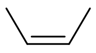




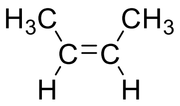
3(a)(i) The carbon atoms in C≡C are sp hybridised.
The σ bond is formed from head-on overlap of sp hybrid orbitals of each atom.
2 π bonds are formed. Each π bond is formed from the side-on overlap of one unhybridised p-orbital from each atom.



3(a)(ii)



or

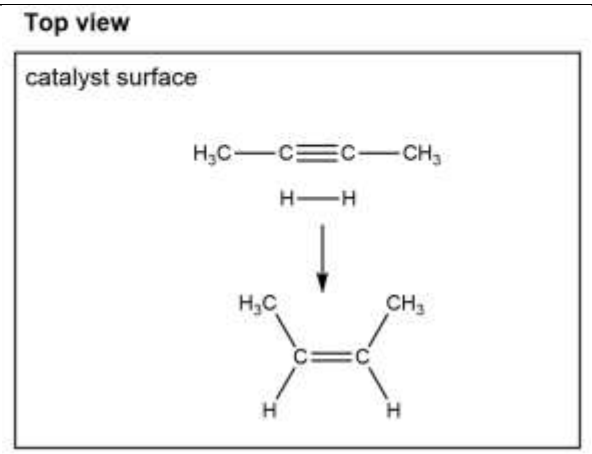


3(a)(iii) But-2-yne and hydrogen <u>adsorb</u> onto the surface of the Lindlar's catalyst through the formation of weak bonds / interactions with the surface of the catalyst.

This <u>increases the surface concentration</u> of the reactants and brings the reactants in <u>closer proximity</u> and proper orientation for reaction to take place. This also <u>weakens</u> the covalent <u>bonds</u> <u>within</u> reactant <u>molecules</u>, <u>lowering the activation energy</u> for reaction.

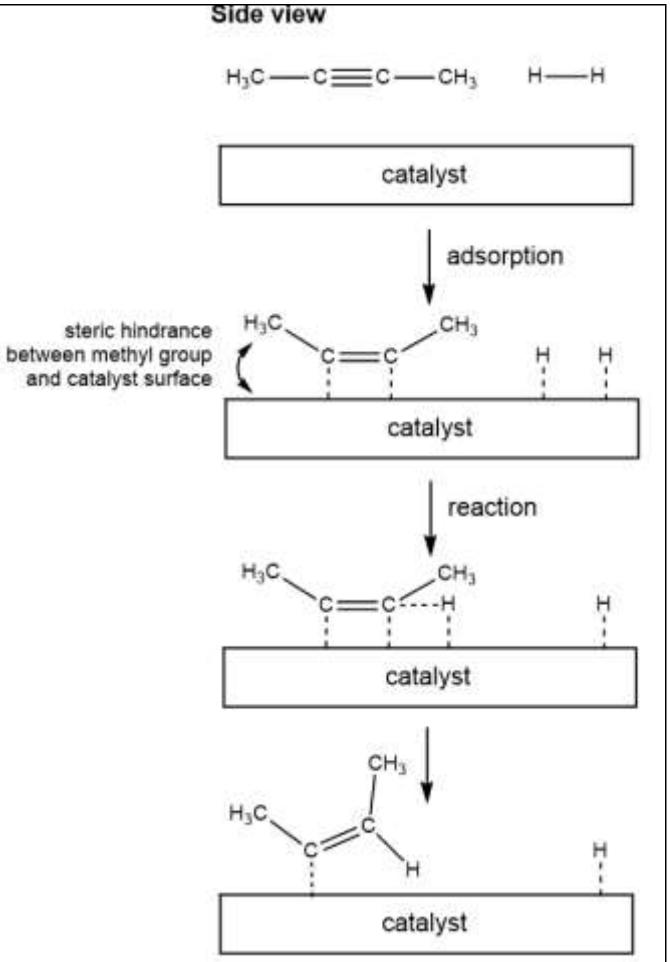
Once formed, the product molecules can easily <u>desorb</u> from the surface of the catalyst.

3(a)(iv) Upon adsorption of but-2-yne and H_2 on the catalyst surface, <u>H_2 collides and forms bonds with one side of the alkyne molecule</u> at the same time, adding two H atoms to the same side.

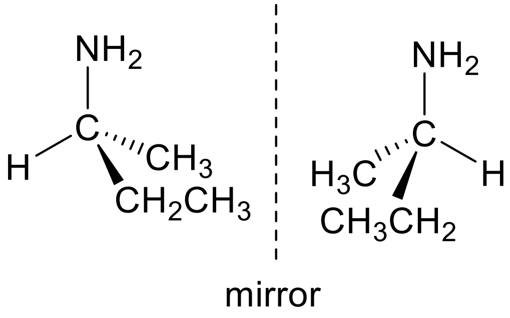


OR

Upon adsorption of but-2-yne and H_2 on the catalyst surface, the bulky methyl groups on but-2-yne experience electronic repulsion from the catalyst surface and point away from the catalyst surface. The H atoms then add to the side of the alkyne that was previously temporily bonded to the catalyst surface.

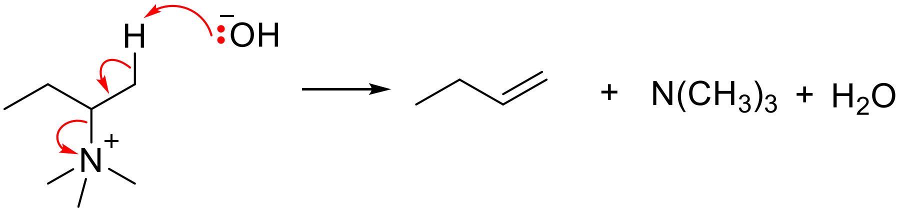


3(b)(i)

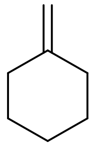


3(b)(ii) <u>excess CH_3I in ethanol</u>, <u>heat</u> in a sealed tube

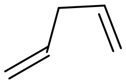
3(b)(iii)



3(b)(iv)

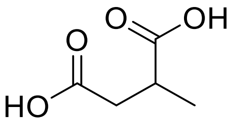
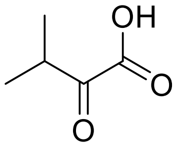


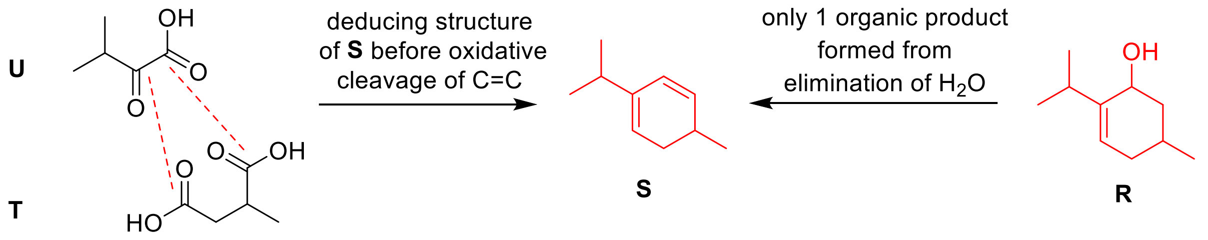
compound **D**

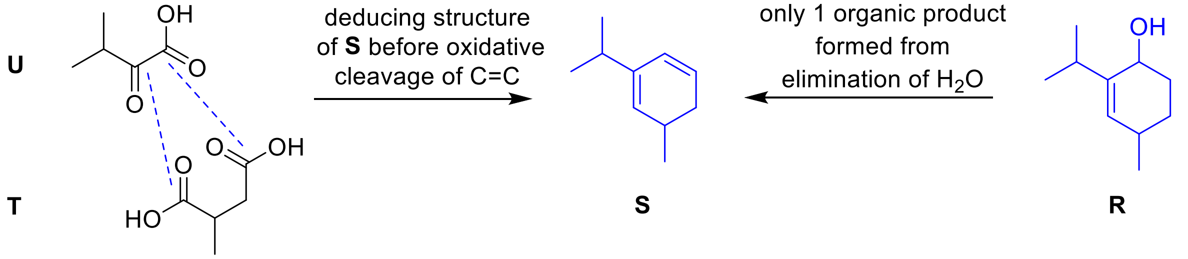


compound **E**

3(c)

Evidence	Deduction
R ($C_{10}H_{18}O$) $\xrightarrow{PCl_5}$ product	Nucleophilic substitution - **R** contains an alcohol.
1 **R** + 1 Br_2 $\longrightarrow$ product	Electrophilic addition - **R** contains 1 C=C.
R ($C_{10}H_{18}O$) $\xrightarrow[\text{heat}]{\text{conc. } H_2SO_4}$ **S** ($C_{10}H_{16}$) only product	Elimination of 1 H_2O / dehydration - Formed a C=C in **S** **or** **R** contains an alcohol
S $\xrightarrow[\text{heat}]{\text{acidified } KMnO_4}$ **T** + **U** ($C_5H_8O_4$) ($C_5H_8O_3$).	Strong oxidation / oxidative cleavage - **S** contains C=C - **T** and **U** do not contain any primary/secondary alcohol or aldehydes
1 **T** + 2NaOH $\longrightarrow$ product 1 **U** + 1NaOH $\longrightarrow$ product	Acid-base reaction - **T** contains 2 –COOH groups - **U** contains 1 –COOH group - **T** has 5 carbons, 2 –COOH and 1 chiral centre. 
U $\xrightarrow{\text{2,4-DNPH}}$ orange ppt	Condensation reaction - **U** contains carbonyl / ketone group
U $\xrightarrow{\text{alkaline } I_2}$ no yellow ppt	No oxidation reaction - does not contain $COCH_3$
U $\xrightarrow[\text{uv}]{Cl_2}$ 2 products.	Free radical substitution - **U** contains two types of hydrogen.  **U**





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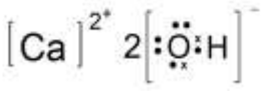
Section B

4(a)



4(b)

Mass of hydroxyapatite lost = 0.75 × 2.5 = 1.875 g
Amount of hydroxyapatite lost = 1.875 / 502.5 = 3.731×10^{-3} mol

Amount of $Ca(OH)_2$ required = 5 × 3.731×10^{-3} = 0.01866 mol
Mass of $Ca(OH)_2$ required = 0.01866 × 74.1 = 1.38 g

4(c)(i) $K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-]$

4(c)(ii) Let the solubility be y mol dm^{-3}.

$(5y)^5(3y)^3(y) = 6.80 \times 10^{-37}$
$84375\ y^9 = 6.80 \times 10^{-37}$
$y = 2.717 \times 10^{-3} = 2.72 \times 10^{-5}$

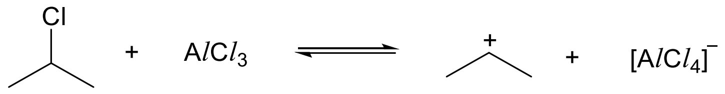
Solubility of hydroxyapatite = 2.72×10^{-5} mol dm^{-3}

4(c)(iii) Solubility of hydroxyapatite increases in an acidic environment.
$[OH^-]$ is low / H^+ reacts with OH^- and PO_4^{3-} anions shifting position of equilibrium to the right.

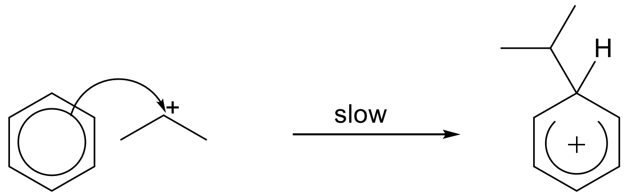
4(c)(iv) In fluoride-treated water, hydroxyapatite is converted to the less soluble fluorapatite with a lower K_{sp} value, making teeth less susceptible to tooth decay.

4(d)(i) **Electrophilic Substitution**

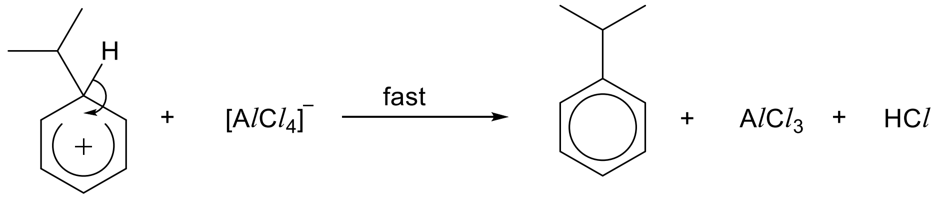
Generation of electrophile:



Step 1:



Step 2:

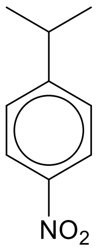


4(d)(ii) Lewis acid is an <u>electron pair acceptor</u>.

4(d)(iii)

- <u>Alkyl</u> groups are <u>activating / electron donating</u> so the <u>electron density in benzene ring increases / benzene ring becomes more electron rich / more susceptible to electrophilic attack</u>.
- The alkyl group in cumene is <u>2,4-directing</u>, hence the 1,3-disubstituted product is not favoured / benzene ring is further substituted at the 2,4-positions.
- The bulky $–CH(CH_3)_2$ <u>sterically hinders</u> the electrophilic <u>attack</u> at the 2-position; thus the 4-position product is favoured. / <u>Steric hindrance</u> between two bulky $–CH(CH_3)_2$ groups causes the 1,2-disubstituted product to be <u>unstable</u>, hence produced in less amounts.

4(e)(i)(ii)



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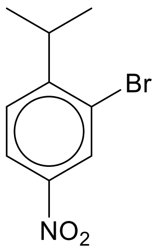
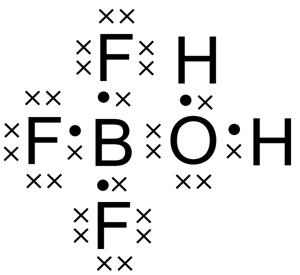


G

Step 1: conc. HNO_3, conc. H_2SO_4, 30°C
Step 2: Br_2, $FeBr_3$
Step 3: Sn, conc. HC*l*, heat under reflux, followed by NaOH(aq)

5(a)(i) Lewis acid is an <u>electron pair acceptor</u>.

5(a)(ii)



5(a)(iii) Tetrahedral, 109°

5(b)(i) $K_{sp} = [Co^{2+}][C_2O_4^{2-}]$ units: $mol^2\ dm^{-6}$

5(b)(ii) $[Co^{2+}] = \frac{5.84}{58.9} = 0.0991\ mol\ dm^{-3}$

When 94% of Co^{2+} has precipitated,
$[Co^{2+}]$ remaining = $\frac{6}{100} \times 0.0991 = 5.95 \times 10^{-3}$ mol dm^{-3}

Since the remaining leach solution is saturated,
$(5.95 \times 10^{-3})\,[C_2O_4^{2-}] = 2.7 \times 10^{-9}$

Therefore, $[C_2O_4^{2-}] = \frac{2.7 \times 10^{-9}}{5.95 \times 10^{-3}} = 4.54 \times 10^{-7}$ mol dm^{-3}

5(b)(iii) $[Ni^{2+}] = \frac{4.93}{58.7} = 0.0840$ mol dm^{-3}

When $[C_2O_4^{2-}] = 4.54 \times 10^{-7}$ mol dm^{-3},
$[Ni^{2+}][C_2O_4^{2-}] = (0.0840)(4.54 \times 10^{-7}) = 3.81 \times 10^{-8}$ mol^2 dm^{-6}

Since the ionic product $[Ni^{2+}][C_2O_4^{2-}] < K_{sp}$ of NiC_2O_4, the precipitate will not form.

5(b)(iv) As pH decreases, $[H^+]$ increases. The equilibrium positions of the acid dissociation reactions shift to the left, thus $[C_2O_4^{2-}]$ decreases.

$$CoC_2O_4(s) \rightleftharpoons Co^{2+}(aq) + C_2O_4^{2-}(aq)$$

This causes the equilibrium position of the dissolution of CoC_2O_4 to shift right, increasing the solubility of CoC_2O_4.

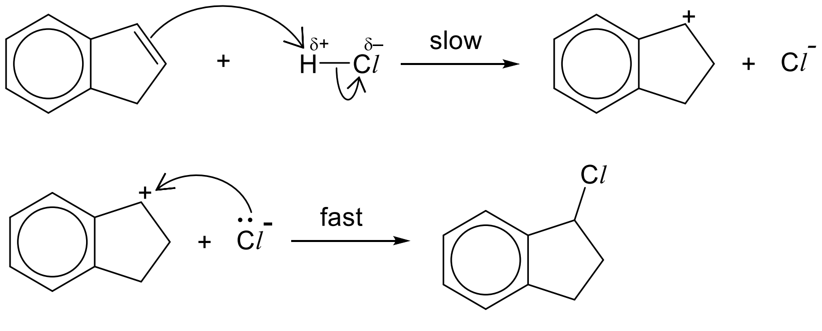
5(b)(v) A complex ion / soluble complex was formed between Co^{2+} and $C_2O_4^{2-}$.

The formation of the soluble complex decreases the uncomplexed $[Co^{2+}]$ in the solution.

To counteract the decrease in $[Co^{2+}]$, the equilibrium position of $CoC_2O_4(s) \rightleftharpoons Co^{2+}(aq) + C_2O_4^{2-}(aq)$ shifts to the right, resulting in more CoC_2O_4 dissolving and the solubility of CoC_2O_4 is increased.

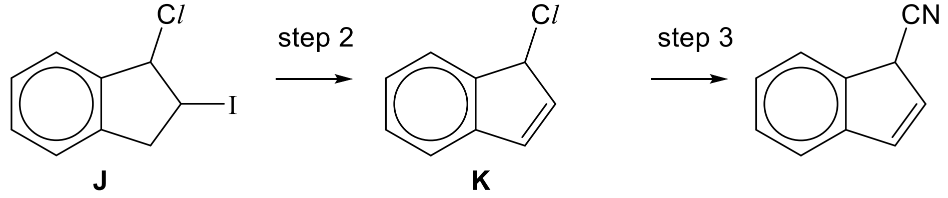
5(c) Trans isomer is not stable due to angle/ring strain.

5(d)(i) Electrophilic addition



5(d)(ii) The major product is formed because the benzylic carbocation is resonance-stabilised. In this carbocation, the empty p orbital of the positively charged carbon overlaps with the π electron cloud of the benzene ring. The π electrons of the benzene ring delocalise over the positively charged carbon and disperse the positive charge.

5(e)(i)(ii)



Step 2: ethanolic KOH, heat

Step 3: ethanolic KCN, heat

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