2014 HCI H2 Chemistry Prelims Paper 3 Mark Scheme

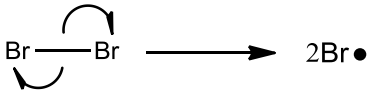
1 (a) Description:
Cl_2 reacts explosively with H_2 under direct sunlight.
Br_2 reacts slowly with H_2 upon heating.
I_2 reacts partially/reversibly with H_2 upon heating.

Explanation:
Down the group, the bond strength for H–X decreases in order of H–C*l* > H–Br > H–I.
The enthalpy of reaction to become less exothermic, thus the reaction is less vigorous down the group.

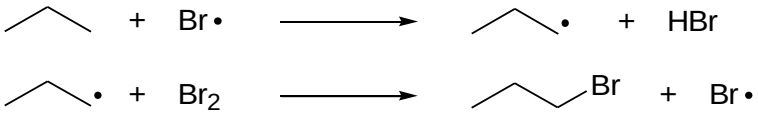
[2]

(b) (i) Name of mechanism: Free radical substitution

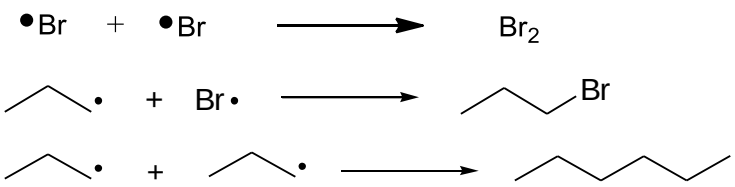
Initiation:



Propagation:



Termination:



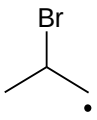
[3]

(ii) Large excess of alkane / limited amount of bromine. **[1]**

(c) (i) The bromine is added on the least substituted carbon atom. **[1]**

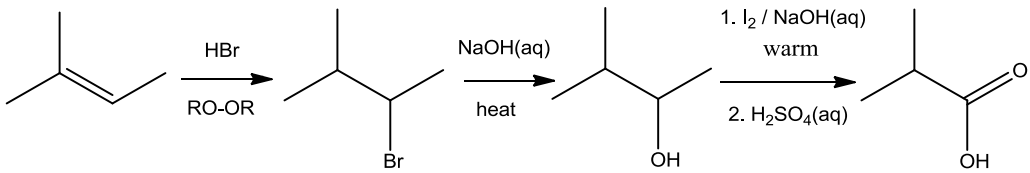
(ii) Bromine radical is electron deficient, while C=C bond is electron rich.
OR The π bond of the C=C bond is weaker than the σ bond of the C-H bond. Hence, the radical will attack the alkene preferentially. **[1]**

(iii)



The intermediate formed in the reaction has more electron donating alkyl groups attached to the carbon radical compared to that drawn above. Hence it is more stable, which will lead to the formation of the major product. **[2]**

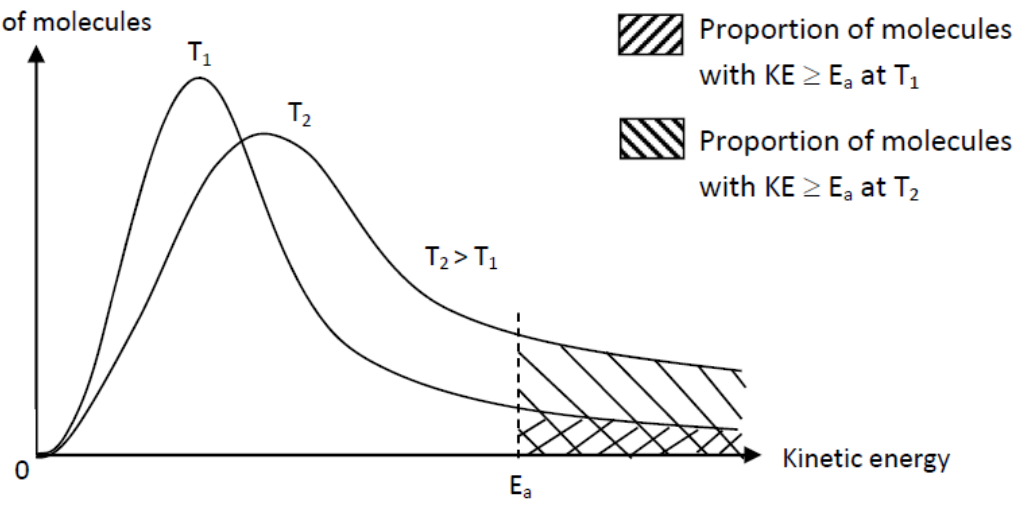
(iv)



[3]

(d) (i) Unit of k: s^{-1} (or h^{-1} or min^{-1}) **[1]**

(ii)



At higher temperatures, the proportion of molecules with kinetic energy greater than or equal to activation energy increases. Thus, frequency of *effective* collision increases, rate constant increases. **[3]**

(iii) Chlorine radical acts as homogeneous catalyst.
It exists as same phase as reactants and is regenerated. **[2]**

(iv) C-C*l* bond in CFCs can be broken down by UV light to form chlorine radicals, which react with ozone. **[1]**

2 (a) Longifolene is a <u>non–polar</u> molecule. It is <u>does not form favourable interactions</u> with water. **[1]**

(b) In order of increasing basicity: Hydrazine, ammonia, ethylamine

Each <u>nitrogen atom</u> on hydrazine is <u>bonded to an electron withdrawing nitrogen atom,</u> which reduces the availability of the lone pair of electrons to accept a proton. Hence, it is a weaker base compared to ammonia.

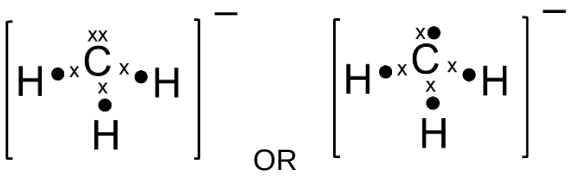
<u>Ethylamine has an electron donating alkyl group</u> bonded to the nitrogen atom, increasing the availability of the lone pair of electrons to accept a proton compared to ammonia and hydrazine. Hence it is the strongest base. **[3]**

(c) (i) **I**: Li*Al*H_4/ dry ether or H_2/Ni or $NaBH_4$/ methanol
II: $KMnO_4$ or $K_2Cr_2O_7$/ H_2SO_4(aq) / heat
IV: SOCl_2 or PCl_3 or PCl_5 or conc H*Cl*
V: Ethanolic NaOH, heat **[4]**

(ii) Add 2,4–dinitrophenylhydrazine to the sample.
Orange precipitate observed with **A**. No orange precipitate with **B**.

Accept other tests, i.e. PCl_3, PCl_5, oxidising agent tests, etc. **[2]**

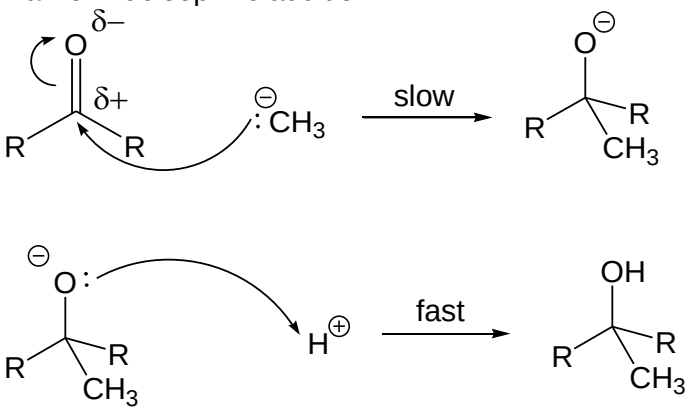
(d) (i)



Trigonal pyramidal **[2]**

(ii) H*Cl*(aq) or HNO_3(aq) or H_2SO_4(aq) or H_2O(*l*) **[1]**

(iii) **Name:** Nucleophilic addition



[3]

(e) (i) The folding of the farnesyl carbocation results in a locked ring structure which reduces the possible conformations of the molecule. There is hence less ways to distribute energy in the system, so ΔS is negative. **[2]**

(ii) 4 **[1]**

(iii) Laboratory synthesized longifolene contains one of the optical isomer which smells differently from extracted longifolene which contains the other optical isomer. OR

Laboratory synthesized longifolene could be a racemic mixture while extracted longifolene contains only one optical isomer. Each optical isomer would smell differently, hence the samples have different smells. OR

Laboratory samples may contain a mixture of the different stereoisomers but the natural sample only contains one optical isomer. Each optical isomer would interact differently with the body and smell differently, hence the 2 samples have different smell. **[1]**

3(a) (i) [2] O–H bond is polar as <u>O is more electronegative than H</u>.

H_2O molecule is bent. There is a <u>net dipole</u> (or overall dipole) for the molecule.

(ii) [2] <u>H_2O forms stronger hydrogen bond</u> than NH_3 because <u>O is more electronegative than N</u>.

<u>H_2O forms more hydrogen bonds</u> than NH_3 <u>per molecule</u>.

Boiling water involves overcoming more hydrogen bonds and stronger hydrogen bonds, which need more energy.

(b) (i) A complex ion is an ion that contains a central metal cation or atom, dative bonded by surrounding anions or molecules, known as ligands. **[2]**

(ii) [1] Transition metal ions have <u>high charge density</u> and polarising power. They have a strong tendency to form dative covalent bonds with ligands.

or Transition metal ions have <u>vacant 3d orbitals</u> (as well as 4s and 4p orbitals) of low energy level (or suitable energy) that can <u>accommodate lone pair of electrons</u> donated by ligands, resulting in dative bond formation.

(iii) [2] $Cu(OH)_2 + 4NH_3 \rightarrow Cu(NH_3)_4(OH)_2$
or $Cu(OH)_2 + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2OH^-$

A dark blue (or deep blue) solution is formed.

(c) [2] $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

$K_{NH_3} = [NH_4^+][NH_2^-] = 1 \times 10^{-30}$

At equilibrium, $[NH_4^+] = [NH_2^-]$

$\therefore [NH_4^+] = \sqrt{K_{NH3}} = \underline{\mathbf{1.00 \times 10^{-15}}}$ mol dm^{-3}

(d) [2] pH = 9 $\Rightarrow$ pOH = 5 $\Rightarrow [OH^-] = 10^{-5}$ mol dm^{-3}

$[salt][OH^-] / [base] = K_b = 1.8 \times 10^{-5}$
$\Rightarrow$ [salt]/[base] = 1.8 = 18/10

$\therefore$ he has to convert 0.18 mol of NH_3 into NH_4Cl so that the resultant buffer contains 0.10 mol of NH_3 and 0.18 mol of NH_4Cl, which gives the 18/10 ratio.

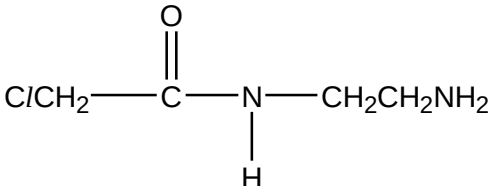
n(HCl) needed = 0.18 mol
Volume of HCl needed = 0.18 dm^3 or 180 cm^3 (no s.f. penalty $\because$ exact ans)

(e) [4] For phenylamine: $Br_2(aq)$
For benzene: Br_2, $FeBr_3$ (or $AlBr_3$)

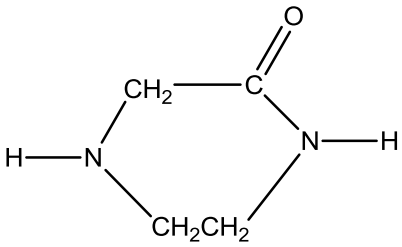
Comment on <u>two</u> differences:
For benzene to undergo electrophilic substitution, a (Lewis acid) catalyst like $FeBr_3$ is needed and only mono-substitution occurs. For phenylamine, no catalyst is needed and tri-substitution occurs.

Explain:
<u>Lone pair of N</u> of NH_2 group <u>delocalises into the benzene ring</u>. This <u>increases the electron density in the benzene ring</u>, making the benzene ring more susceptible towards electrophilic substitution (or electrophilic attack).

(f) **[3]**



C:



The COCl carbon is attached to <u>two highly electronegative</u> atoms, Cl and O, as compared to only one electronegative Cl in the case for the CH_2Cl carbon. Hence, the <u>COCl carbon has a higher partial positive charge than the CH_2Cl carbon</u>
OR
The COCl carbon has trigonal planar geometry while the CH_2Cl carbon has tetrahedral geometry. The <u>planar geometry of the COCl carbon</u> makes it <u>less hindered</u> for the nucleophile to attack.

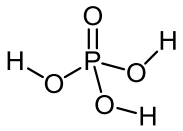
4 **(a)** **(i)** $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$ **[1]**

(ii) Step 2: $PCl_4OH + H_2O \rightarrow PCl_3(OH)_2 + HCl$
Step 3: $PCl_3(OH)_2 \rightarrow POCl_3 + H_2O$ **[2]**

(b) **(i)** $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$
Hydrolysis
pH = 1 (accept any value from 0 – 3) **[3]**

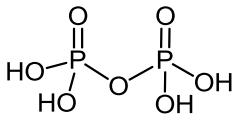
(ii) +5 **[1]**

(iii)



[1]

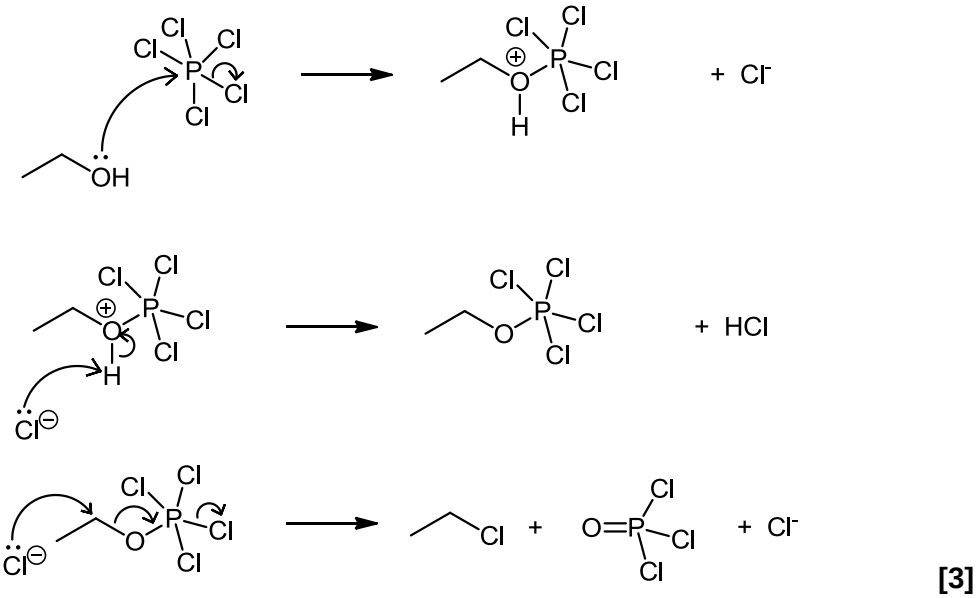
(iv)



[1]

(v) $H_6P_4O_{13}$ **[1]** (or $H_4P_4O_{12}$ if cyclic)

(c) **(i)**



[3]

(ii) The high bond energy / strength of P=O bond that is formed drives this reaction to completion. **[1]**

(iii) To ethanal: $K_2Cr_2O_7$, dilute H_2SO_4, heat with immediate distillation
To ethanoic acid: $K_2Cr_2O_7$ OR $KMnO_4$, dilute H_2SO_4, heat (with reflux) **[2]**

(d) <u>Test 1</u>: To all three unknowns, add dilute NaOH and heat. (hydrolyse the ester and amide bonds)

The sample which gives off a gas that turned moist red litmus paper blue is **Y**, whilte the samples which did not give off any gas is **X** or **Z**.

<u>Test 2</u>: To the hydrolysed products of the other two unknowns, add I_2(aq), NaOH(aq) and heat. (test for presence of $CH_3CH(OH)-$ group)

The sample which gives the yellow ppt of CHI_3 is **X**, while the sample which does not give the yellow ppt is **Z**.

Alternative answer:
Test 1: To all three unknowns, add dilute H_2SO_4 and heat. Then add I_2(aq), NaOH(aq) and heat.

The sample which gives the yellow ppt of CHI_3 is **X**, while the sample which does not give the yellow ppt is **Y** or **Z**.

Test 2: To the other two unknowns, add dilute H_2SO_4 and heat. Then add $KMnO_4$, dilute H_2SO_4 and heat.

The sample which decolorizes the purple solution is **Z**, while the sample which purple solution remains is **Y**.

[4]

5 **(a)** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ **[1]**

(b) **(i)** **A**: $[Cr(H_2O)_6]^{2+}$
B: $[Cr(H_2O)_6]^{3+}$
C: $Cr(OH)_3$
D: CrO_4^{2-} **[4]**

(ii) $[Cr(OH)_6]^{3-}$ undergoes oxidation to form **D** **[1]**

(c) **(i)** <u>High ionisation energy</u> needed to remove 6 valence electrons **OR**

Cr^{6+} has <u>high charge density</u> and thus undergoes <u>hydrolysis</u> in water to form a polyatomic oxoanion. **[1]**

(ii) $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$

When the concentration of H^+ increases, position of equilibrium will <u>shift to the right</u> to offset the increase. **[2]**

(d) **(i)**

	Cr	H_2O	Br
% by mass	13.0	27.0	60
No. of moles	0.25	1.5	0.75
Mole ratio	1	6	3 **[1]**
Formula	$Cr(H_2O)_6(Br)_3$		

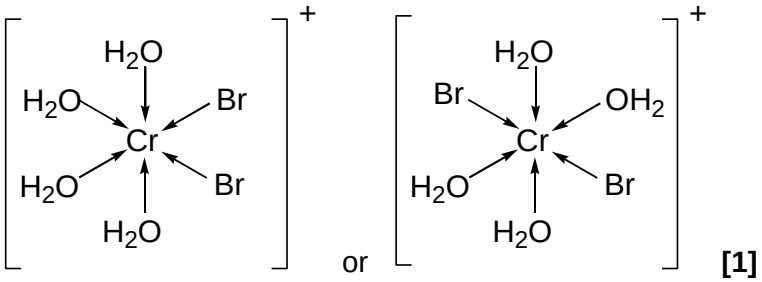
(ii) Cream precipitate: AgBr

No. of moles of AgBr = 0.188 / (108 + 79.9) = 0.00100 mol
No. of moles of **E** = 0.400 / (52.0 + 6(18.0) + 3(79.9)) = 0.00100 mol

No. of moles of Br^- anion : No of moles of **E**
1 : 1

Formula of complex cation in **E**: $[Cr(H_2O)_4(Br)_2]^+$ **[2]**

(iii)



[1]

(e) **(i)**

	$E^\ominus$ / V
$Fe^{2+} + 2e \rightleftharpoons Fe$	−0.44
$Pb^{2+} + 2e \rightleftharpoons Pb$	−0.13
$SO_4^{2-} + 4H^+ + 2e \rightleftharpoons SO_2 + 2H_2O$	+0.17 ***OR***
$2H^+ + 2e \rightleftharpoons H_2$	0.00

<u>$E^\ominus_{Fe2+/Fe}$ is more negative than $E^\ominus_{Pb2+/Pb}$</u>, Fe is <u>more easily oxidized by concentrated sulfuric acid</u> than Pb. Hence, Fe rapidly dissolves in concentrated sulfuric acid while Pb is only superficially attacked. **[2]**

OR Calculate $E^\ominus_{cell}$ and showing which reaction is more feasible.

(ii) $E^{\ominus}_{cell}$ = (+1.33) – (+0.17) = +1.16 V

Since $E^{\ominus}_{cell}$ is positive, the reaction is <u>feasible</u>. Solution changes colour from <u>orange to green</u>/ $Cr_2O_7^{2-}$ is reduced to Cr^{3+} **[2]**

(f) **(i)** PV = nRT
$(2.00 \times 1.01 \times 10^5)(0.740 \times 10^{-3}) = n\ (8.31)(300)$

n = 0.0600 mol **[1]**

(ii)

	N_2O_4 (g)	⇌	2 NO_2 (g)
Initial / mol	4.60/92.0 = 0.0500		0
Change / mol	-x		+2x
Eqm / mol	0.05 – x		+2x

0.05 – x + 2x = 0.06
x = 0.0100 mol

$$K_p = \frac{(P_{NO2})^2}{(P_{N2O4})} = \frac{\left(\frac{0.02}{0.06} \times 2\right)^2}{\left(\frac{0.04}{0.06} \times 2\right)} = 0.333 \text{ atm}$$ **[2]**