Answer *any* **four** questions.

1 The study of organic compounds includes the collection of kinetic data and thermodynamic data of the compounds.

(a) The kinetics of the hydrolysis of the ester, $CH_3CH_2CO_2CH_3$, may be investigated by the following method.

$CH_3CH_2CO_2CH_3 + H_2O$ ® $CH_3CH_2CO_2H + CH_3OH$

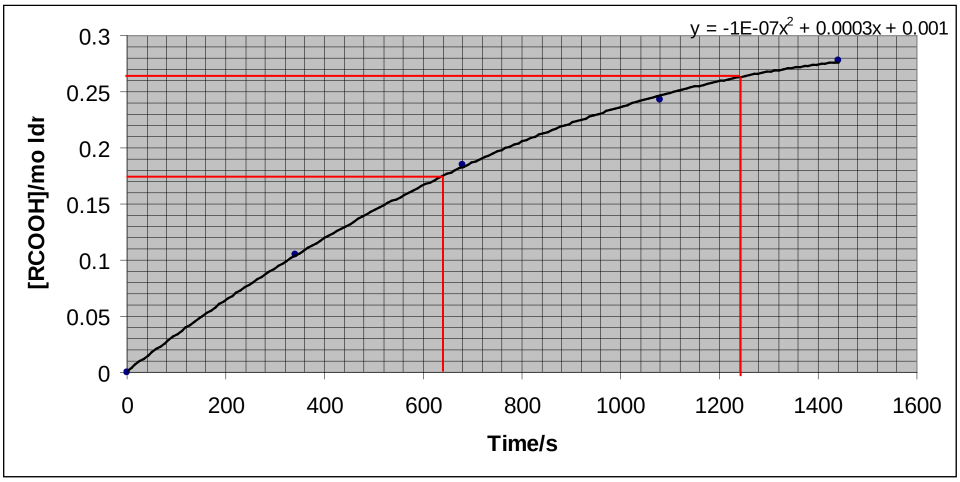
In a 1 dm^3 mixture, 0.350 mol of the ester was hydrolysed by heating with water and using hydrochloric acid as catalyst. The following results were obtained.

Time/s	Concentration of $CH_3CH_2CO_2H$/mol dm^{-3}
0	0
340	0.105
680	0.185
1080	0.243
1440	0.278

(i) Suggest how the progress of this reaction may be followed in order to obtain the results as stated.

<u>Taking samples of reaction at the stated intervals</u> (i.e. at 340 s, 680 s, 1080 s and 1440 s) and **<u>quenching</u>** it with large amount of cold water. **<u>Titrate sample</u>** with dilute NaOH and suitable indicator.

(ii) By drawing a suitable graph using the data given above, show that the reaction is first order with respect to the ester. It has been found that the hydrolysis reaction is first order with respect to the hydrochloric acid.



The half life of the ester is approximately 640 seconds based on the data. Hence, the order of reaction with respect to the ester is 1 since a constant half life is established.

(iii) Deduce the units of the rate constant.

Rate = k[ester][HC*l*]
Units for k is **$\text{mol}^{-1}\ \text{dm}^{3}\ \text{s}^{-1}$**

(iv) State and explain the effect of a catalyst on the rate constant.

The catalyst **increases the rate constant** by **decreasing the activation energy** of the reaction and offers an **alternative pathway** for reaction.

(v) Using suitable bond energy values from the *Data Booklet*, calculate the ΔH for the hydrolysis of the ester.

ΔH = [8 ´ 410 + 2 ´ 350 + 2 ´ 360 + 740 + 2 ´ 460] – [8 ´ 410 + 2 ´ 350 + 2 ´ 360 + 740 + 2 ´ 460]
= **$0\ \text{kJ mol}^{-1}$**

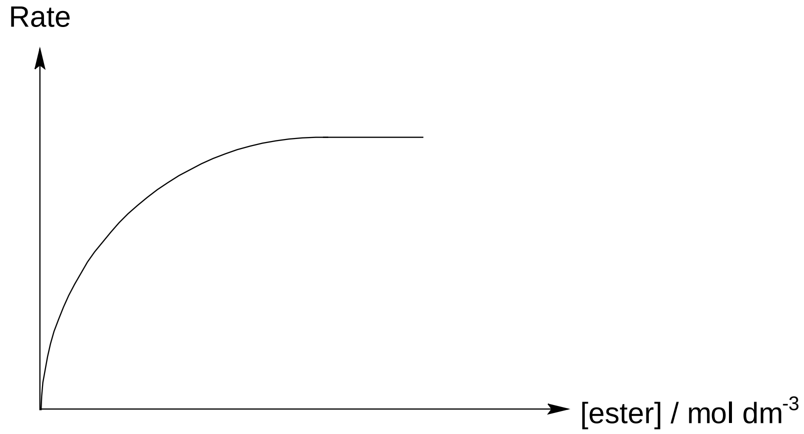
(vi) Given that the standard enthalpy change of reaction for the hydrolysis is +7.6 kJ mol^{-1}, suggest a reason for the difference between this given value and the value that you have calculated in **(a)(v)**.

The **ester is not in gaseous phase** which would make the calculation by bond energy inaccurate.

[11]

(b) Hydrolysis of ester can be achieved in the biological system by enzymes known as esterase. Enzymes are proteins that catalysed a specific chemical transformation in the biological system. Such enzymes are generally quaternary proteins.

(i) Sketch and explain the graph showing how the rate of hydrolysis changes with increasing concentration of the ester.



At **low concentration** of ester, the rate of hydrolysis is roughly proportional to the concentration of ester and therefore the **order of reaction with respect to ester is about 1**.

At **moderate concentration** of ester, the rate of hydrolysis is no longer proportional to the concentration of ester and therefore the **order of reaction with respect to ester is mixed order**.

At **high concentration** of ester, the rate of hydrolysis is independent to the concentration of ester and therefore the **order of reaction with respect to ester is about 0**.

(ii) Explain the meaning of quaternary structure of proteins.

The quaternary structure of a protein refers to the **spatial arrangement of two or more polypeptide chains**, held together into a specific geometry by bonding interactions like van der Waals' forces, hydrogen bonding, ionic bonds and disulfide bridges.

(iii) List 2 other major functions of proteins in the body.

- As enzymatic catalysts (e.g. amylase breaks down starch in the digestive system)
- As transport molecules (e.g. haemoglobin transports oxygen)
- As storage molecules (e.g. iron is stored in the liver as a complex with protein ferritin)
- In movement (e.g. proteins are the major component of muscles)
- For mechanical support (e.g. skin and bone contain collagen – a fibrous protein)
- Mediate cell responses (e.g. rhodopsin is a protein in the eye used for vision)
- For immunity / protection against diseases (antibody proteins)
- For control of growth and cell differentiation (hormones)

(iv) Suggest and explain a chemical method for distinguishing the following pair of esters. You should state the expected observations.

$HCO_2CH_2CH_3$ and $CH_3CH_2CO_2CH_3$

Method 1:
Add **aqueous NaOH** separately to the 2 compounds and **heat**. Then, add **aqueous iodine** to both compounds.

Observations:
Yellow ppt. observed for $HCO_2CH_2CH_3$.
No yellow ppt. observed for $CH_3CH_2CO_2CH_3$.

OR

Method 2:
Add **acidified $KMnO_4$** separately to the 2 compounds and **heat**.

Observations:
For $HCO_2CH_2CH_3$, **purple** colour is **decolourised**. **Effervescence** observed. **Gas** evolved gives **white precipitate with limewater**. (Gas is CO_2.)
For $CH_3CH_2CO_2CH_3$, **purple** colour is **decolourised**. **No effervescence** observed.

[9]

[Total: 20]

2 This question is about the chemistry of the transition metal, nickel and its compound.

(a) Explain why the colour of $[Ni(NH_3)_6]^{2+}(aq)$ is blue.

The **d orbitals** of Ni^{2+} are **split into two groups** of different energy levels by NH_3 ligands. When white light shines on the complex, a d electron undergoes **d–d transition** and is **promoted to a higher energy d orbital**. During the transition, the d electron **absorbs** in the **orange region** of the **visible spectrum**. The blue colour observed is the colour of **transmitted light**, which is a mixture of **remaining wavelengths** that are not absorbed.

[3]

(b) $Ni(CO)_4$ is a compound formed by the reaction between nickel and carbon monoxide. The Mond process was developed by Ludwig Mond to extract and purify nickel from its ores. One of the stages of this process involves the decomposition of $Ni(CO)_4$ at 227 °C to give nickel as shown in this equation below:

$$Ni(CO)_4(g) \rightleftharpoons Ni(s) + 4CO(g)$$

The equilibrium constant, K_p, for the equilibrium at 227 °C is 1.01 atm^3. A sample of gaseous $Ni(CO)_4$ was placed in a 2 dm^3 evacuated container at 227 °C. At equilibrium, the partial pressure of CO was 2.00 atm.
$[1\ atm = 1.01 \times 10^5\ Pa]$

(i) Sketch the shapes of the hybrid orbitals around the C atom in carbon monoxide.

Show 2 sp hybrid orbitals

(ii) Write an expression for K_p.

K_p =

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(iii) Calculate the total pressure of the system at equilibrium.

$(2.00)^4 / p_{Ni(CO)4} = 1.01$
$p_{Ni(CO)4}$ = 15.842 = **15.8 atm**
total pressure of system = 15.842 + 2.00 = **17.8 atm**

(iv) Calculate the mass of $Ni(CO)_4$ placed in the container initially.

	$Ni(CO)_4(g)$	$\rightleftharpoons$ $Ni(s)$	+ $4CO(g)$
Initial p/atm	15.8 + (2.00/4) = **16.3**	–	0
Eqm p/atm	15.8	–	2.00

Let mass of $Ni(CO)_4$ be m.
pV = nRT = (m/M)RT
$16.3 \times 1.01 \times 10^5 \times 2 \times 10^{-3}$
= {m / [58.7 + 4 x (12.0 + 16.0)]} x 8.31 x (227 + 273)
m = 135.27 = **135 g**

[8]

(c) Ni is commonly used in catalytic hydrogenation reactions. One such example is given below.

Compound **A**, $C_{10}H_{12}NOCl$, has a chiral centre and dissolves in dilute sulfuric acid. It reacts with 2,4–dinitrophenylhydrazine to form an orange precipitate, but does not react with Tollens' reagent. **A** reacts with H_2 in the presence of Ni catalyst followed by addition of aqueous bromine to form **B**, $C_{10}H_{11}NOClBr_3$. When 1 mol of compound **B** is heated under reflux with aqueous iodine and excess alkali, followed by careful acidification, compound **C**, $C_8H_4NO_4Br_3$ is formed together with *2 mol* of yellow solid CHI_3.

Deduce the structures of compounds **A**, **B** and **C**, giving reasons for your answer.

- **A** has comparable number of carbon and hydrogen atoms and more than 6 carbon atoms
  Þ **A** contains a **benzene ring**

- **A** dissolves in dilute acid
  Þ **A** undergoes **neutralisation** and is likely to contain an **amine** group

- **A** undergoes **condensation** with 2,4–DNPH to form a orange precipitate, but does not undergo oxidation with Tollens' reagent
  Þ **A** contains a **ketone**

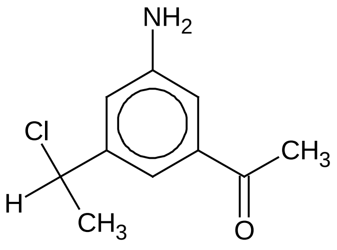
- **A** undergoes **reduction** with H_2/Ni to give **B**
  Þ Ketone in **A** is reduced to a **secondary alcohol**

- **A** undergoes **electrophilic substitution** with aqueous Br_2 to give **B**, which contains 3 bromine atoms.
  Þ **A** contains **phenylamine** group

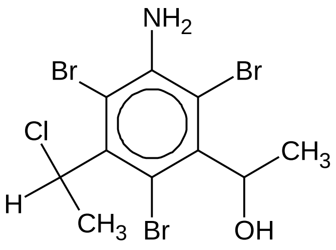
- **B** undergoes **oxidation** with aq alkaline I_2
  Þ **B** likely to contain **$CH_3CH(OH)$–**
  Þ **C** contains **carboxylic acid** groups

- **B** also undergoes **nucleophilic substitution** with excess alkali due to loss of Cl in the molecular formula of compound **C**
  Þ **B** is a **chloroalkane**

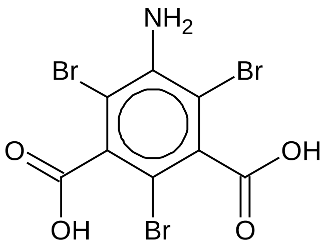
- 2 moles of CHI_3 is formed per mole of compound **B**
  Þ **3rd and 5th position** of the benzene ring must be substituted



A



B



C

[9]
[Total: 20]

3 This question is about the varied chemical uses of HC*l*.

(a) **(i)** In the electrolysis of a solution of hydrochloric acid with inert platinum electrodes, an ammeter showed a reading of 0.450 A in the external circuit of the cell. 110 cm^3 of gas was evolved at the cathode after 30 minutes under room temperature and pressure. Determine the actual current used in the electrolysis process. Hence, determine the percentage error (if any) of the ammeter reading.

At the cathode, $2H^+ + 2e$ à H_2
Amount of hydrogen gas evolved = 110 / 24000 = 0.004583 mol
Amount of hydrogen gas evolved =
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Q = 0.004583 x 2 x 96500 = 884.583 C

$$I = \frac{Q}{t} = \frac{884.583}{30\text{´}\ 60} = 0.4914\text{ A}$$

$$\%\text{ error} = \left|\frac{0.450 - 0.4914}{0.4914}\right|\text{´}\ 100\% = 8.42\%$$

(ii) A student carried out a reaction involving acidified potassium dichromate(VI), together with an unknown half–cell which consists of transition metal ions. The Gibbs Free Energy of the reaction was known to be –324 kJ mol^{-1} and the procedure involved transferring 6 mol of electrons from the unknown solution to potassium dichromate(VI).

Using the expression of D*G*^{q} = –nFE$^q_{cell}$, where n is the number of moles of electrons transferred, F is the Faraday constant and E$^q_{cell}$ is the overall cell potential, determine the E$^q_{cell}$ value and hence deduce the identity of the unknown half cell.

Using $\Delta G = -\,nFE^q_{cell}$
$-324 \times 10^3 = -\,6\,(96500)\,E^q_{cell}$
$E^q_{cell} = +\,0.560$ V

Since procedure involved transfer of 6 mol of electrons from potassium dichromate (VI) to the unknown solution,

Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e$ à $2Cr^{3+} + 7H_2O$ (+1.33)
$E_{red} = +1.33$ V

Using $E^q_{cell} = E^q_{red} - E^q_{oxd}$
$0.560 = +1.33 - E^q_{oxd}$

$E^q_{oxd} = -(0.560 - 1.33) = +0.77$ V
The E^q_{oxd} tally with the **Fe^{3+}/Fe^{2+} half cell**

[4]

(b) A sample of sodium hypochlorite, NaOC*l*, was dissolved in 100 cm^3 of 0.123 mol dm^{-3} HOC*l* ($pK_a = 7.50$) solution forming a buffer of pH 6.20. The buffer is then used to absorb HC*l* gas. Calculate the concentration of gaseous HC*l* (in mol dm^{-3}) that is required to be added to the buffer solution until it reaches pH 6. [5]

pH = pKa + lg **Error! Objects cannot be created from editing field codes.**
6.20= 7.50 + lg **Error! Objects cannot be created from editing field codes.**
lg**Error! Objects cannot be created from editing field codes.** = –1.30
Error! Objects cannot be created from editing field codes. = 0.0501
Error! Objects cannot be created from editing field codes.= 0.0501 x 0.123

= 0.006162 mol dm^{-3}

On addition of HCl, let x be the concentration of H^+
[HOCl]new = 0.123 + x
$[OCl^-]$new = 0.006162 – x
6.00 = 7.50 + lg **Error! Objects cannot be created from editing field codes.**
6.00 = 7.50 + lg **Error! Objects cannot be created from editing field codes.**
–1.50 = lg **Error! Objects cannot be created from editing field codes.**
0.03162 = **Error! Objects cannot be created from editing field codes.**
0.03162(0.123) + 0.03162x = 0.006162 – x
1.03162x = 0.00227
x = 0.00220 mol dm^{-3}

(c) The decomposition temperature of hydrogen chloride is close to 3000 K. Predict, with reasoning, if the decomposition temperature of hydrogen astatide would be higher or lower than 3000 K.

The decomposition temperature of hydrogen astatide would be lower than 3000 K because down the group,
covalent bond length of H–X **increases.**
covalent bond strength **decreases.**
bond dissociation energy **decreases.**
\ thermal stability **decreases**.

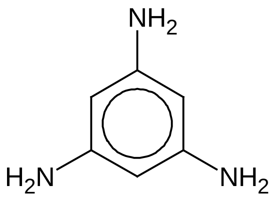
[3]

(d) Concentrated hydrochloric acid is commonly used in the reduction of trinitrobenzene (2,4,6–trinitrobenzene).

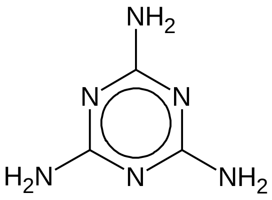
(i) Suggest the complete set of reagents, together with concentrated HC*l*, to be used in this reduction process.

Tin with (excess) concentrated HC*l*, followed by aqueous NaOH

(ii) Suggest the structural formula of the product formed.



(iii) Explain the relative basicity between the product formed in **(d)(ii)** and the melamine molecule as shown below in terms of their structures. The melamine molecule contains a triazine ring with 3 nitrogen atoms present in the ring.

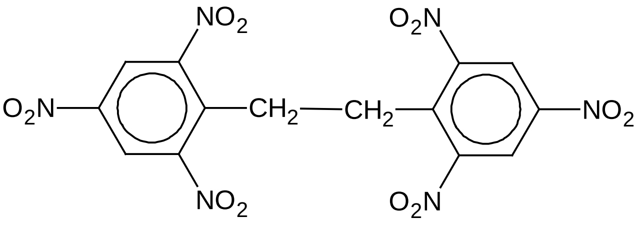


Melamine

Melamine is **less basic**. The **lone pair of electrons** on the N atom from the amine group in melamine is **more delocalised** into the **p electron cloud in triazine ring** because of the **electronegative N atoms** present in the ring. The **availability** of the lone pair of electrons to accept a proton for dative bonding is **reduced**.

[5]

(e) 2,4,6–trinitrobenzene can also undergo Friedel–Crafts alkylation with CH_3Cl to form 2,4,6–trinitromethylbezene. The alkyl side chain can then be further reacted to form useful halogen derivatives. However, some side products like hydrogen chloride gas and compound **D** can also be formed in the process.



Compound **D**

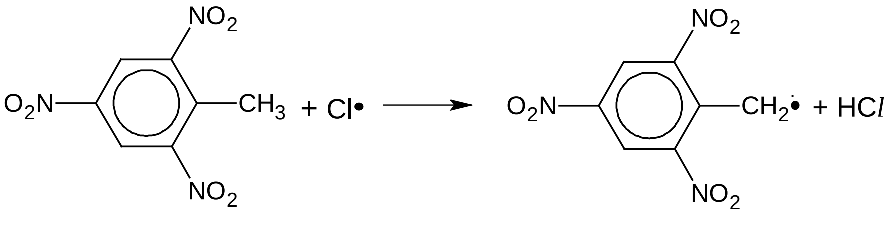
Using 2,4,6–trinitromethylbezene as the starting material, describe an appropriate mechanism that would result in the production of compound **D**. [3]

Initiation

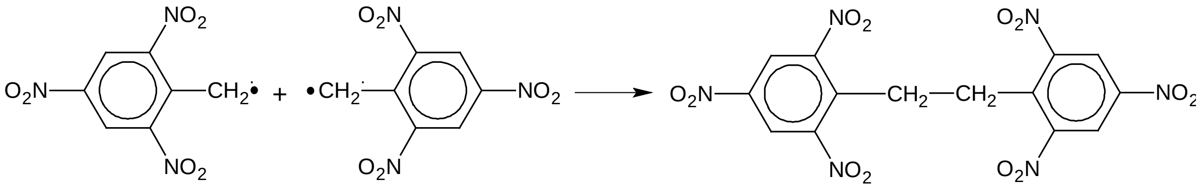
$$Cl-Cl \xrightarrow{uv} 2\,Cl\bullet$$

(Note: must use chlorine radicals so that hydrogen chloride will be produced as the side product in the propagation step)

Propagation



Termination



[Total: 20]

4 Chlorine and its compounds are used to manufacture many products such as pesticides, medicines, plastics, bleaches and solvents.

(a) 1 mol of the following compounds is added to 1 dm^3 of water.

CH_3COCl, $ClCH_2COOH$ and $SiCl_4$

Arrange the compounds in order of increasing pH of the resultant mixture formed. Briefly explain your answers, giving equations where appropriate. [4]

Resultant mixture formed when 1 mole of $ClCH_2COOH$ is added to 1 dm^3 of water is the least acidic as $ClCH_2COOH$ ionises only partially in water:

$$ClCH_2COOH + H_2O \rightleftharpoons ClCH_2COO^- + H_3O^+$$

Resultant mixture formed when 1 mole of CH_3COCl is added to 1 dm^3 of water is fairly acidic as CH_3COCl hydrolyses, forming HC*l* which is a strong acid:

CH_3COCl (l) + H_2O (l) ® CH_3COOH (aq) + H^+ (aq) + Cl^- (aq)

Resultant mixture formed when 1 mole of $SiCl_4$ is added to 1 dm^3 of water is the most acidic as 1 mole of $SiCl_4$ hydrolyses to form 4 mole of HC*l*:

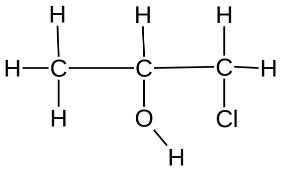
$SiCl_4$ (aq) + $2H_2O$ (l) ® SiO_2 (s) + $4H^+$ (aq) + $4Cl^-$ (aq)

Hence, in order of increasing pH of the resultant mixture formed on reaction with water:

$SiCl_4$, CH_3COCl, $ClCH_2COOH$

(b) Both chloric(I) acid, HOCl and hydrogen chloride react with propene. In the reaction between chloric(I) acid and propene, chlorine is added to carbon- 1 of propene in the major product. However, in the reaction between hydrogen chloride and propene, chlorine is added to carbon- 2 of propene in the major product.

(i) Draw the displayed formula of the major product formed between propene and chloric(I) acid.



(ii) Explain briefly why chlorine from chloric(I) acid and from hydrogen chloride add to different carbon atoms in their reactions with propene.

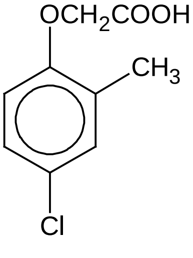
[4]

In HOC*l*, C*l* is **partially positive** so that **Cl^+ is the electrophile** and Cl^+ adds to carbon- 1 to form the more stable carbocation.

Subsequent addition of OH^- results in the formation of the major product with chlorine added to carbon- 1.

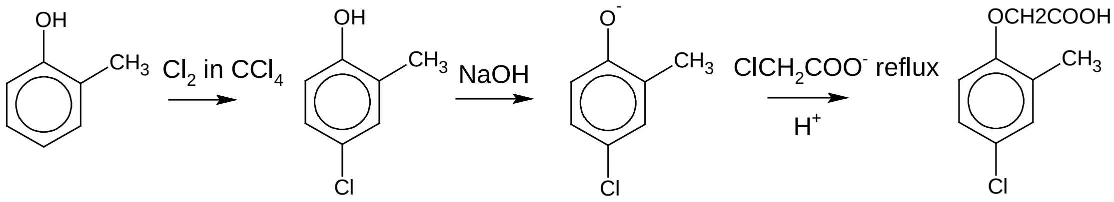
In HC*l*, chlorine is partially negative so that the **electrophile is H^+** rather than Cl^+. Hence H^+ adds to carbon- 1 to form the more stable carbocation.

(c) Despite health and environmental concerns, the chlorinated compound **MCPA**, is widely used as a weed killer.

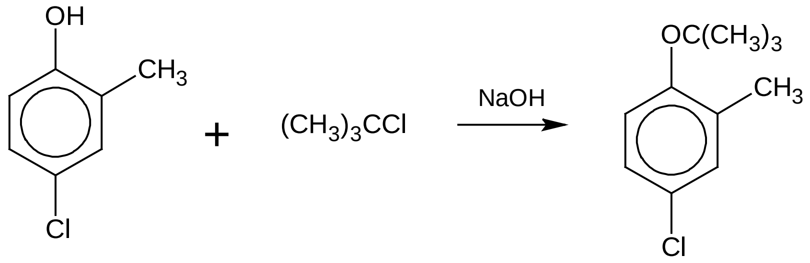


MCPA

Using **not** more than 3 steps, draw a reaction scheme to show how **MCPA** can be synthesised from 2–methylphenol. [3]

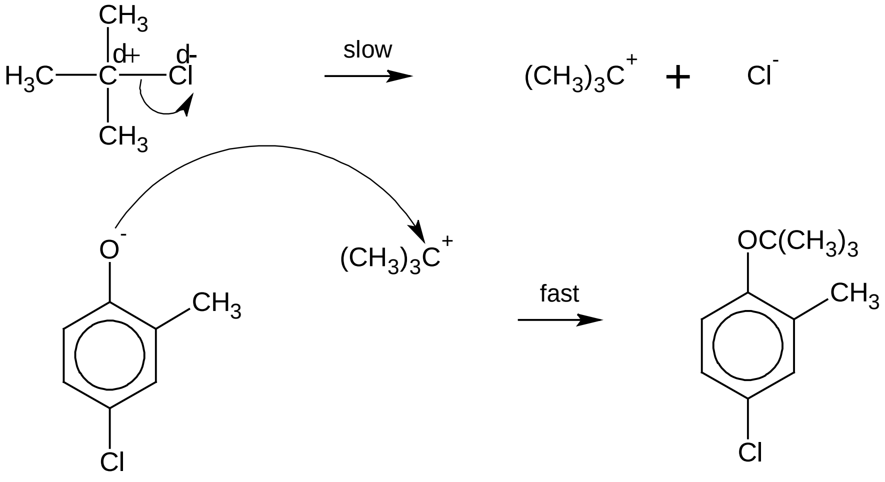


(d) Compound **E** is a derivative of **MCPA** which may be a potential insecticide. The synthesis of Compound **E** is given below.



Compound E

Describe the mechanism for the synthesis of Compound **E**.



(e) Describe the variation in melting points of the chlorides of the elements from sodium to phosphorus and explain the variation in terms of structure and bonding. [4]

Melting points of sodium chloride and magnesium chloride are **<u>higher</u>** than that of aluminium chloride, silicon tetrachloride and phospohorus pentachloride.

This is because Na*Cl* and MgCl_2 have **giant ionic lattice structures** and a **large amount of energy is required to overcome strong electrostatic forces of attrations between the ions** so that their melting points are high.

Al_2Cl_6, $SiCl_4$ and PCl_5 have **simple molecular structure with weak van der Waals forces between the molecules** so their melting points are lower than the ionic Na*Cl* and $MgCl_2$.

The order of increasing melting point is $SiCl_4$, PCl_5 and Al_2Cl_6 since van der Waals forces increases also in that order due to greater ease of distortion of electron cloud as the **number of electrons increases** from $SiCl_4$ to PCl_5 to Al_2Cl_6.

(f) Describe a reaction, **without the use of bromide solution**, which shows that chlorine is a stronger oxidising agent than iodine. [2]

React aqueous sodium thiosulfate separately with chlorine and iodine.
Chlorine is strong enough an oxidising agent to oxidise $S_2O_3^{2-}$ to SO_4^{2-} but iodine is too weak an oxidising agent to oxidise $S_2O_3^{2-}$ to SO_4^{2-}. Instead, iodine oxidises $S_2O_3^{2-}$ only to $S_4O_6^{2-}$.

OR

React aqueous iron(II) sulphate separately with chlorine and iodine.
Chlorine is strong enough an oxidising agent to oxidise Fe^{2+} to Fe^{3+} but iodine is too weak an oxidising agent to oxidise Fe^{2+} to Fe^{3+}.

[Total: 20]

5 Phosphorus is an element in Period 3 of the Periodic Table with wide ranging application in inorganic and organic synthesis.

(a) Explain why the first ionisation energy of phosphorus is higher than that of sulfur, S, and arsenic, As, respectively**.** [2]

Inter–electronic repulsion between paired 3p electrons in S makes it easier to remove one of the paired 3p electron compared to the unpaired 3p electron of P. Therefore the first ionisation energy of P is higher than that of S.
As has a larger atomic radius and outermost electron of As experiences **larger shielding effect** by inner shell of electrons. Therefore the first ionisation energy of P is higher than that of As.

(b) Define the second ionisation energy of phosphorus with an appropriate equation. [2]

The **second** I.E is the energy required to remove **one mole of electron** from **one mole of *singly* positively charged gaseous phosphorus ions** to form **one mole of *doubly* positively charged gaseous phosphorus ions.**

$P^+ (g)$ ® $P^{2+} (g) + e^-$

(c) When heated in air, phosphorus and sodium forms oxides which can react with acids, bases or water.

(i) Write balanced equations for the reaction between oxides for the two elements and an appropriate acid or base.

$Na_2O (s) + 2HCl (aq)$ ® $2NaCl (aq) + H_2O (l)$

P_4O_6 (s) + 12NaOH (aq) ® $4Na_3PO_3$(aq) +$6H_2O$ (l)

P_4O_{10} (s) + 12NaOH(aq) ® $4Na_3PO_4$(aq) +$6H_2O$ (l)

(ii) Describe the reactions, if any, of the two oxides with water containing universal indicator. Chemical equations are not required.

[5]

Na_2O reacts **vigorously** with water to form **basic** solution
UI colour in solution: **blue/purple**

P_4O_6 or P_4O_{10} reacts **readily** with water to form **acidic** solution.
UI colour in solution: **red**

(d) Phosphoric acid is used as a catalyst in the industrial preparation of $CH_3CH_2CH(OH)CH_3$ from compound **F**, $CH_3CH_2CH=CH_2$.

(i) State the reagent and any other conditions required in this industrial preparation.

Steam, 65 atm, 300°C

(ii) Compound **G**, which is an isomer of **F**, exists as a pair of geometric isomers. Deduce the structure of **G**.

$CH_3CH=CHCH_3$

(iii) Predict the carbon–containing products obtained when **F** and **G** are separately heated with acidified potassium manganate(VII).

[3]

F: CH_3CH_2COOH and CO_2
G: CH_3COOH

(e) PCl_5 is used for substitution reactions in organic chemistry.

An optically active compound **P**, with molecular formula $C_3H_7O_2N$, reacts with PCl_5 to give white fumes. When a solution containing **P** is warmed with aqueous sodium hydroxide, a pungent gas is evolved. Upon acidification of the resulting mixture, compound **Q**, $C_3H_6O_3$, can be isolated. When **Q** is warmed with concentrated sulphuric acid, a cyclic compound **R**, $C_6H_8O_4$, is formed. Compound **S** is a structural isomer of **Q** and is not optically active. When **S** is warmed with concentrated sulphuric acid, a non–cyclic compound **T**, $C_3H_4O_2$, is produced.

Deduce the structures of compounds **P**, **Q**, **R**, **S** and **T**. Explain the chemistry of the reactions described. [8]

· **P** is optically active
Þ **P** is **chiral**

· **P** undergoes **substitution** reaction with PCl_5

Þ **alcohol** present in **P**

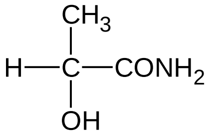
· **P** undergoes **alkaline hydrolysis** to form NH_3 when heated with NaOH
Þ **primary amide** is present in **P**

· **Q** undergoes **esterification/condensation/nucleophilic acyl substitution**
Þ **R** contains **ester group**

· **S** is not optically active
Þ **S** is **not chiral**

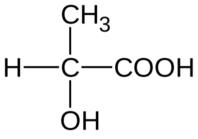
· **S** undergoes **elimination** with conc. H_2SO_4 to from **T**
Þ **alkene** present in **T**

Structure of **P**:



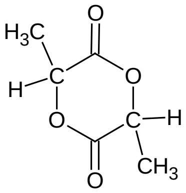
$\mathrm{H{-}C(CH_3)(OH){-}CONH_2}$

Structure of **Q**:

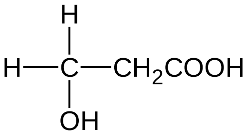


$\mathrm{H{-}C(CH_3)(OH){-}COOH}$

Structure of **R**:

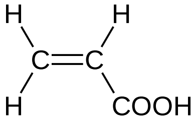


Structure of **S**:



$\mathrm{H{-}CH(OH){-}CH_2COOH}$

Structure of **T**:



[Total: 20]