Topics in the June 2013 Exam Paper for CHEM1102

Click on the links for resources on each topic.

2013-J-2:

- Metals in Biology
- Coordination Chemistry

2013-J-3:

- Weak Acids and Bases
- Calculations Involving pK_a

2013-J-4:

- Periodic Trends in Aqueous Oxide

2013-J-5:

- Weak Acids and Bases
- Calculations Involving pK_a
- Solubility Equilibrium

2013-J-6:

- Crystal Structures

2013-J-7:

- Physical States and Phase Diagrams
- Intermolecular Forces and Phase Behaviour

2013-J-8:

- Kinetics

2013-J-9:

- Alcohols
- Alkenes
- Organic Halogen Compounds
- Carboxylic Acids and Derivatives

2013-J-10:

- Alkenes

2013-J-11:

- Stereochemistry

2013-J-12:

- Stereochemistry

2013-J-13:

- Synthetic Strategies

2013-J-14:

- Carboxylic Acids and Derivatives

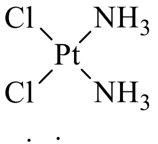
Marks 8

- Use the information already provided to complete the following table.
  (ox = oxalate = $C_2O_4^{2-}$)

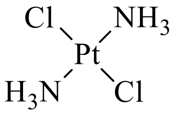
Formula	$[CrCl_2(NH_3)_4]^n$	$[Fe(ox)_3]^n$	$[ZnCl_2(NH_3)_2]^n$
Oxidation state of transition metal ion	**+III**	+III	**+II**
Number of *d*-electrons in the transition metal ion	**3**	**5**	10
Number of unpaired *d*-electrons in the transition metal ion	**3**	**5**	**0**
Charge of complex (*i.e.* n)	1+	**3-**	**0**
Is the metal atom paramagnetic?	**Yes**	**Yes**	**No**

The complex $[PtCl_2(NH_3)_2]$ has two isomers, while its zinc analogue (in the table) exists in only one form. Using diagrams where appropriate, explain why this is so.

The Pt compound has square planar geometry and hence 2 isomers, where the Cl groups are either opposite each other (*trans*) or next to each other (*cis*). The Zn compound has tetrahedral geometry and hence only one structure exists



cis-isomer



trans-isomer

Marks
4

- What is the pH of a 0.1 M solution of ammonium chloride, given the K_b for ammonia is 1.8×10^{-5}.

The ammonium ion, NH_4^+, is the conjugate acid of NH_3. The K_a of a conjugate acid and base are related by:

$$K_a \times K_b = 10^{-14.00}$$

Hence,

$$K_a = 10^{-14.00} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$$

NH_4^+ is a weak acid so $[H_3O^+]$ must be calculated using the equilibrium:

	NH_4^+	H_2O	$\rightleftharpoons$	NH_3	H_3O^+
initial	**0.1**	**large**		**0**	**0**
change	$-x$	**negligible**		$+x$	$+x$
final	$0.1 - x$	**large**		x	x

The equilibrium constant K_a is given by:

$$K_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{x^2}{(0.1 - x)} = 5.6 \times 10^{-10}$$

As K_b is *very* small, $0.1 - x \sim 0.1$ and hence:

$$x^2 = 0.1 \times 5.6 \times 10^{-10} \text{ or } x = 7.5 \times 10^{-6} \text{ M} = [H_3O^+]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H_3O^+] = \log_{10}[7.5 \times 10^{-6}] = 5.1$$

pH = **5.1**

What is the ratio of ammonia to ammonium ion in this solution?

From above, $[NH_3] = x$ M $= 7.5 \times 10^{-6}$ M and $[NH_4^+] = (0.1 - x)$ M $= 0.1$ M. Hence:

$$[NH_3] / [NH_4^+] = 7 \times 10^{-5}$$

Answer: **7×10^{-5}**

Marks

Describe the periodic trends exhibited by atomic radii. Justify these trends in terms of principal quantum number, *n*, and effective nuclear charge, Z_{eff}.

2

Atomic radius decreases across a period as the number of protons and electrons is increasing. As the electrons are all be added to the same shell, they do not shield each other from the increasing nuclear charge and consequently Z_{eff} increases and the electrons are pulled closer to the nucleus.

Atomic radii increase going down a group. As *n* increases, the size of the orbitals increases and the electrons in these orbitals are shielded from the nuclear charge by electrons with smaller *n*. They are thus less tightly held and further from the nucleus.

Giving reasons, order either the set of oxyacids or the binary acids in terms of increasing acidity.

2

$HClO$, $HClO_2$, $HClO_3$, $HClO_4$ or H_2O, H_2S, H_2Se, H_2Te

All $HClO_n$ acids have the structure $HOClO_{n-1}$. As the number of oxygens increases, more electron density is drawn away from the O–H bond and weakens it. The weaker the O–H bond, the stronger the acid, so the order is $HClO < HClO_2 < HClO_3 < HClO_4$.

In binary acids such as H_2S and H_2Se, the H–Se bonds is longer than the H–S bonds as Se is larger than S. The H–Se bond is therefore weaker than the H–S bond and H_2Se is thus a stronger acid than H_2S. The order is therefore $H_2O < H_2S < H_2Se < H_2Te$.

Marks 4

- What is the pH of a solution which is 0.10 M in both acetic acid and sodium acetate? The K_a for acetic acid is 1.8×10^{-5}.

By definition, $pK_a = -\log_{10}K_a$. Hence:

$$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$$

Using the Henderson-Hasselbalch equation, $pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$

With [base] = [acetate] = 0.10 M and [acid] = [acetic acid] = 0.10 M, therefore:

$$pH = 4.74 + \log \frac{0.10}{0.10} = 4.74$$

Answer: **4.74**

What is the final pH if 0.010 mol of HCl is added to 1.0 L of the above solution?

Using number of moles = concentration × volume, the number of moles of acetate and acetic acid originally present in 1.0 L of a 0.10 M solutions are:

$$n_{\text{acetate}} = 0.10 \text{ mol L}^{-1} \times 1.0 \text{ L} = 0.10 \text{ mol}$$
$$n_{\text{acetic acid}} = 0.10 \text{ mol L}^{-1} \times 1.0 \text{ L} = 0.10 \text{ mol}$$

The added H_3O^+ from HCl will react with the acetate to produce more acetic acid:

$$\text{acetate} + H_3O^+ \rightarrow \text{acetic acid} + H_2O$$

Hence, after addition of HCl, the amount of acetate will decrease and the amount of acetic acid will increase:

$$n_{\text{acetate}} = (0.10 - 0.010) \text{ mol} = 0.09 \text{ mol}$$
$$n_{\text{acetic acid}} = (0.10 + 0.010) \text{ mol} = 0.11 \text{ mol}$$

Using concentration = number of moles / volume, their concentrations will become:

$$[\text{acetate}] = 0.09 \text{ mol} / 1.0 \text{ L} = 0.09 \text{ M}$$
$$[\text{acetic acid}] = 0.11 \text{ mol} / 1.0 \text{ L} = 0.11 \text{ M}$$

Using the Henderson-Hasselbalch equation,

$$pH = 4.74 + \log \frac{0.09}{0.11} = 4.65$$

Answer: **4.65**

ANSWER CONTINUES ON THE NEXT PAGE

- The K_{sp} for $Fe(OH)_3$ is 2.64×10^{-39}. What is its molar solubility in water? 2

The dissolution reaction and is equilibrium constant expression are:

$$\mathbf{Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^{-}(aq) \qquad K_{sp} = [Fe^{3+}(aq)][OH^{-}(aq)]^3}$$

The molar solubility is the number of moles that dissolve in a litre. If *s* mol dissolves in a litre:

$$\mathbf{[Fe^{3+}(aq)] = s\ M \quad \text{and} \quad [OH^{-}(aq)] = 3s\ M}$$

Hence:

$$\mathbf{K_{sp} = (s)(3s)^3 = 27s^4 = 2.64 \times 10^{-39}}$$

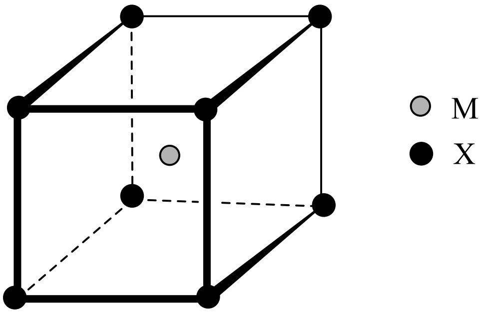
so

$$\mathbf{s = 9.94 \times 10^{-11}\ M}$$

Answer: **9.94×10^{-11} M**

Marks
2

- The unit cell below has a cation (M) at the centre of the cell and anions (X) at the corners.



What is the formula of the compound?

Number of M atoms = 1 (at the centre).
Number of X atoms = 8 × 1/8 (corners) = 1.

Hence, formula = M_1X_1 = MX

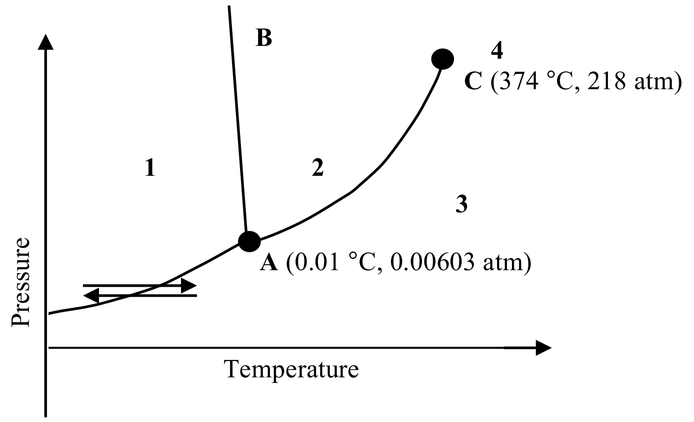
What is the coordination number of each type of ion?

Each M is surrounded by the 8 X atoms on the corners: the coordination number of M is 8.
Each X is on the corner of 8 unit cells, each with an M at its centre: the coordination number of X is also 8.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
7

- A phase diagram of water is shown below.



Identify the four phases shown as 1-4 in the phase diagram.

1: **solid**	2: **liquid**
3: **gas**	4: **supercritical fluid**

What are the phase changes highlighted by the forward and reverse arrows called?

Forward: **sublimation**	Reverse: **deposition**

What names are given to the points A and C?

A: **triple point**	C: **critical point**

The boundary line A-B is slightly tilted to the left. What are the physical and biological significances of this?

Solid water (ice) is less dense than liquid water. Ice therefore floats and rivers, lakes and oceans freeze from the top town.

As just the surface of a body of water freezes, the liquid environment for the life-forms below the surface is preserved. If the water in a cell freezes, the ice crystals take up more space than the liquid and this can cause cell walls to break.

What are the physical characteristics of water in phase 4?

It can be considered as either a very dense gas or as a rarefied liquid with physical properties (e.g. density, viscosity, diffusion coefficients) between those of liquids and gases. It is a good solvent.

Marks
3

- Given the following experimental data, find the rate law and the rate constant for the following reaction:

$$NO(g) + NO_2(g) + O_2(g) \rightarrow N_2O_5(g)$$

Run	$[NO(g)]$ / M	$[NO_2(g)]$ / M	$[O_2(g)]$ / M	Rate / M s^{-1}
1	0.10	0.10	0.10	2.1×10^{-2}
2	0.20	0.10	0.10	4.2×10^{-2}
3	0.20	0.30	0.20	1.26×10^{-1}
4	0.10	0.10	0.20	2.1×10^{-2}

Between run (1) and (2), $[NO(g)]$ is doubled but $[NO_2(g)]$ and $[O_2(g)]$ are kept constant. The doubling in $[NO(g)]$ causes a doubling in the rate: the rate is proportional to $[NO(g)]^1$.

Between run (1) and (4), $[O_2(g)]$ is doubled but $[NO(g)]$ and $[NO_2(g)]$ are kept constant. The doubling in $[O_2(g)]$ causes no change in the rate: the rate is independent of $[O_2(g)]$.

Between run (2) and (3), $[NO_2(g)]$ is trebled but $[NO(g)]$ is kept constant. Although $[O_2(g)]$ is doubled, this has no effect on the rate (see directly above). The trebling in $[NO_2(g)]$ causes the rate to treble: the rate is proportional to $[NO_2(g)]^1$

Overall:

$$\text{rate} = k[NO(g)][NO_2(g)]$$

Using run (1), rate = 2.1×10^{-2} M and $[NO(g)] = [NO_2(g)] = 0.10$ M. Hence:

$$k = \text{rate} / [NO(g)][NO_2(g)]$$
$$= 2.1 \times 10^{-2} \text{ M s}^{-1} / (0.10 \text{ M})^2$$
$$= 2.1 \text{ M}^{-1} \text{ s}^{-1}$$

Rate = $k[NO(g)][NO_2(g)]$	$k = 2.1$ M^{-1} s^{-1}

ANSWER CONTINUES ON THE NEXT PAGE

3

- The rate constant for a reaction is 5.0×10^{-3} s^{-1} at 215 °C and 1.2×10^{-1} s^{-1} at 452 °C. What is the activation energy of the reaction in kJ mol^{-1}?

The rate constant varies with temperature according to the Arrhenius equation:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

At T_1 = (215 + 273) K = 488 K and $k_1 = 5.0 \times 10^{-3}$ s^{-1}. At T_2 = (452 + 273) K = 725 K and $k_2 = 1.2 \times 10^{-1}$ s^{-1}. Hence:

$$\ln\left(\frac{1.2 \times 10^{-1}}{5.0 \times 10^{-3}}\right) = \frac{E_a}{8.314}\left(\frac{1}{488} - \frac{1}{725}\right)$$

E_a **= 39 kJ mol^{-1}**

Answer: **39 kJ mol^{-1}**

What is the rate constant for this reaction at 100 °C?

Using T_1 = 488 K and $k_1 = 5.0 \times 10^{-3}$ s^{-1}, when T_2 = (100 + 273) K = 373 K:

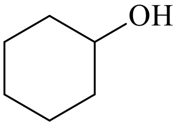
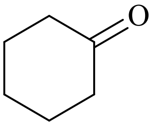
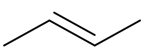
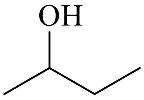
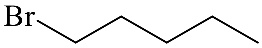
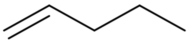
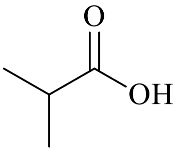
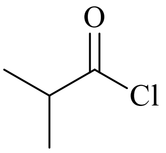
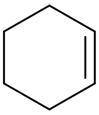
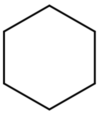
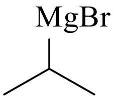
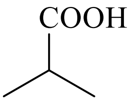
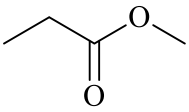
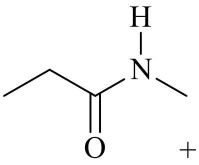
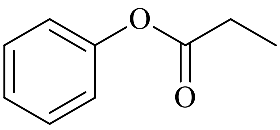
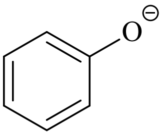
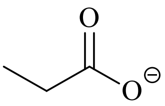
$$\ln\left(\frac{k_2}{5.0 \times 10^{-3}}\right) = \frac{39 \times 10^3}{8.314}\left(\frac{1}{488} - \frac{1}{373}\right)$$

k_2 **= 2.5×10^{-4} s^{-1}**

Answer: **2.5×10^{-4} s^{-1}**

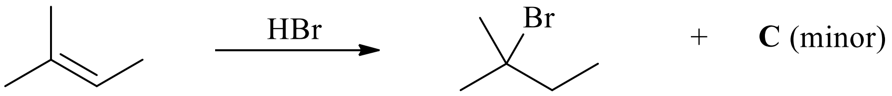
Marks
9

- Complete the following table.

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	$Cr_2O_7^{2\ominus}$/ $H^{\oplus}$	
	dilute H_2SO_4	
	hot conc. KOH in ethanol solvent	
	**$SOCl_2$**	
	H_2, Pd/C	
	1. CO_2 2. $H^{\oplus}$ / H_2O	
	**CH_3NH_2**	 + CH_3OH
	$OH^{\ominus}$ / H_2O / heat	 + 

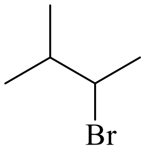
Marks
3

- When alkene **A** is reacted with HBr, the major reaction product is **B**. However, a minor product, **C**, is also formed that is isomeric with **B**.



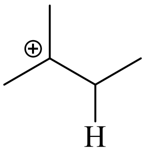
A **B** (major)

What is the structure of product **C**?

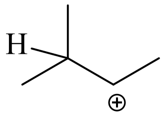


By describing an intermediate formed in this reaction, explain why less of **C** is formed than **B**.

Two possible intermediate carbocations can be formed. The tertiary carbocation is more stable and leads to the major product B, whilst the secondary carbocation is less stable and leads to the minor product C.



tertiary carbocation
(more stable)



secondary carbocation
(less stable)

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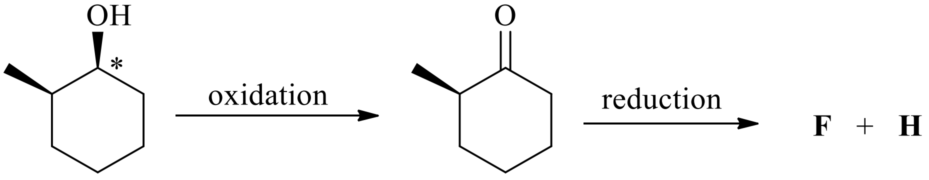
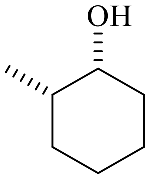
Marks
7

- Shown below is a reaction sequence beginning with the chiral alcohol, **F**.

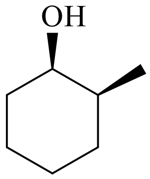


F **G**

Draw the enantiomer of **F**.



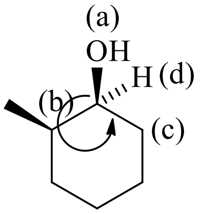
or



The specific optical rotation of **F** is +24°. What is the optical rotation of a mixture consisting of equal amounts of **F** and its enantiomer?

0°

Assign the stereochemistry of the atom in alcohol **F** indicated by the asterisk (*), showing how you arrived at your answer.



The order of priority is:

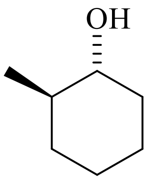
O > C(C,C,H) > C(C,H,H) > H

With lowest priority (d) at back, the order of the groups goes anticlockwise as shown. Therefore the stereochemistry is (*S*).

Alcohol **F** is oxidised to give the corresponding ketone, **G**. Is this molecule still chiral? Why/why not? Explain your answer.

The molecule is still chiral as the molecule still contains a stereogenic centre.

Ketone **G** is reduced with sodium borohydride, to give a mixture of two alcohols, **F** and **H. H** is a diastereomer of **F**. Draw the diastereomer **H**. What is the expected ratio of alcohols **F** and **H** in this mixture? Why?

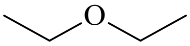


The approximate ratio will be 1:1 as attack by hydride ion is equally likely from above or below the ring.

(There may be a slight excess of F as the methyl group may slightly inhibit attack from above by steric interference.)

Marks
5

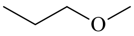
- Below is the structure of an ether, **J**.

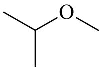


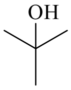
J

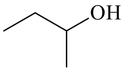
Draw a constitutional isomer of **J**.

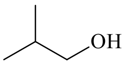
Any of the following:

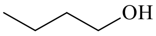






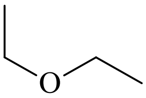






Draw a conformational isomer of **J**.

There is an infinite number of conformational isomers. Only one is given



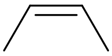
There are no configurational isomers of **J**. Why not?

As there are no rings, double bonds or stereogenic centres, the molecule does not have any diastereomers or enantiomers.

Below is the structure of an alkene, **K**, which *does* have a configurational isomer.

K

Draw this configurational isomer.

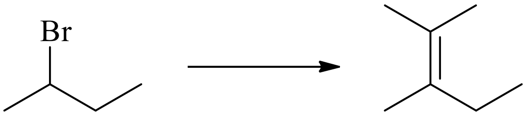


Name **K**, making sure your name distinguishes **K** from its isomer.

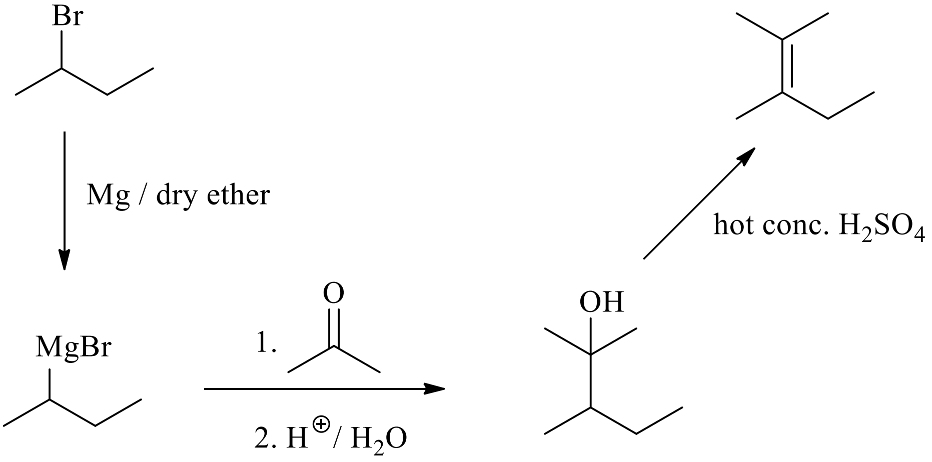
(*E*)-2-butene

Marks
5

- Devise a synthesis of the alkene **M** using 2-bromobutane (**L**) and acetone (propanone) as starting materials. Show all relevant intermediates and reagents.



L **M**



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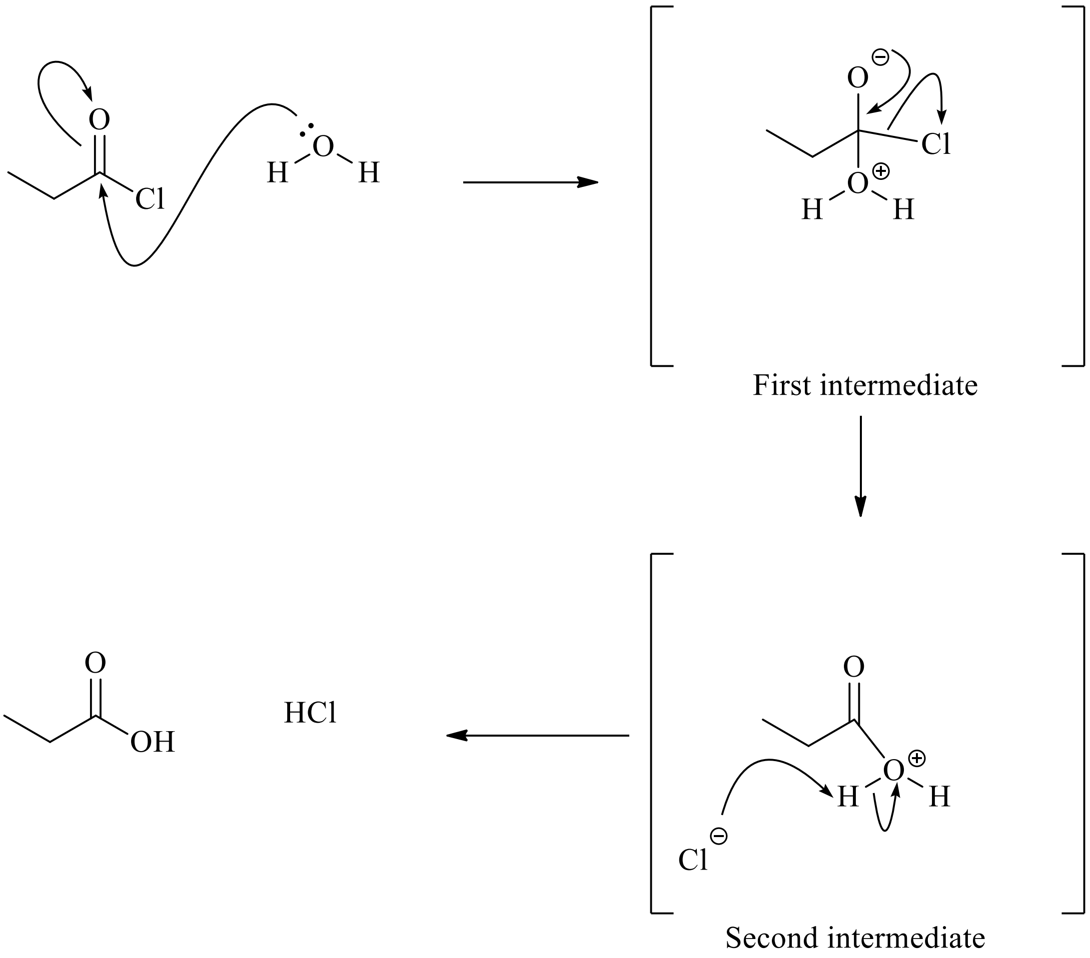
Marks
6

- Below is the reaction between an acid chloride and water to give a carboxylic acid. Provide curly arrows for this mechanism and draw the structures of the two intermediates on the pathway.



Indicate the hybridisation of the two oxygen atoms in the starting materials.

acid chloride: ***sp***^{2}	water: ***sp***^{3}

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