

Topics in the November 2010 Exam Paper for CHEM1902

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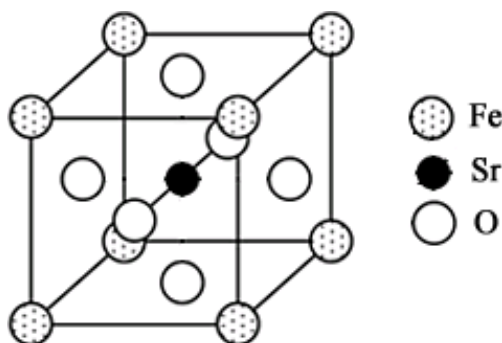
- [Aldehydes and Ketones](#)
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2010-N-12:

- [Aromatic Compounds](#)

Marks
9

- SrFeO_3 crystallises with the perovskite structure, shown below. The structure is cubic with iron atoms on each corner, oxygen atoms at the centre of each face and a strontium atom at the centre of the cube. Mixed metal oxides such as this are of current research interest because of their magnetic and possible superconducting properties.



Show the structure is consistent with the formula SrFeO_3 and give the coordination numbers of the Sr, Fe and O atoms.

There is a Fe atom on each of the 8 corners, each of which is shared between 8 cells so contribute $1/8$ to each: number of Fe atoms = $8 \times 1/8 = 1$.

There is a O atom on each of the 6 faces, each of which is shared between 2 cells so contribute $1/2$ to each: number of O atoms = $6 \times 1/2 = 3$.

There is a single Sr atom which is at the centre and is unshared: number of Sr atoms = 1.

The formula is thus FeSrO_3 .

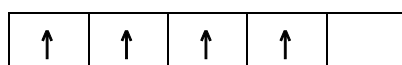
Each Fe atom is surrounded by 12 O atoms: it has a coordination number of 12.

Each Sr atom is surrounded by 6 O atoms: it has a coordination number of 6.

Each O atom is surrounded by 2 Sr atoms, at a distance of $0.5a$, and 4 Fe atoms, at a distance of $0.707a$. As coordination number is defined as the number of nearest neighbours, it is 2.

Using the box notation to represent atomic orbitals, work out how many unpaired electrons are present on the iron cation in this compound.

As Sr^{2+} and 3O^{2-} are present, iron must have an oxidation number of +4. As iron has 8 valence electrons, Fe^{4+} has $(8 - 4) = 4$ valence electrons and a d^4 configuration. These are arranged in the five d orbitals to minimise repulsion by maximising the number of unpaired spins:



There are 4 unpaired electrons

ANSWER CONTINUES ON THE NEXT PAGE

It is possible to substitute the Sr^{2+} ions at the centre of the unit cell by La^{3+} ions to make a series of compounds with the formula $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ with $0 \leq x \leq 1$. Suggest why this substitution is achieved without significant change to the unit cell dimensions and describe how charge balance is achieved in these compounds.

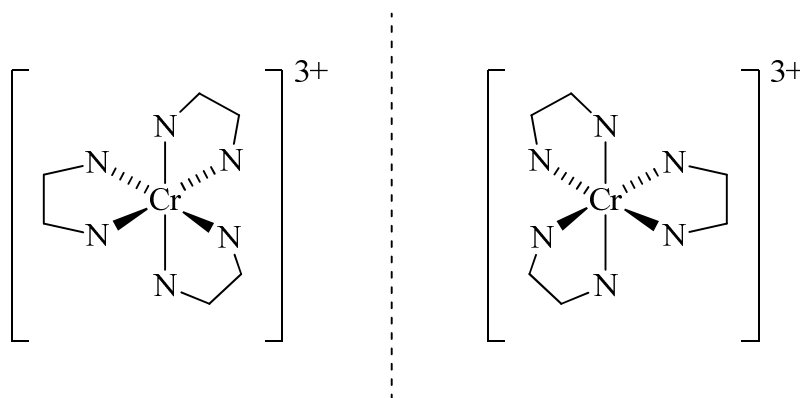
La^{3+} has a similar size to Sr^{2+} as they are diagonally related on the Periodic Table. La^{3+} has an extra shell but has a higher charge. As a result, La^{3+} is able to occupy the same position in the unit cell as Sr^{2+} without the unit cell being strained.

Each time a La^{3+} replaces a Sr^{2+} , a Fe^{4+} is reduced to Fe^{3+} to ensure charge balance is maintained.

- The species $[\text{Cr}(\text{en})_3][\text{FeCl}_4]_3$ is an example of a salt in which both the anion and cation are comprised of coordination complexes. Name the complex using standard IUPAC nomenclature (en = ethane-1,2-diamine).

tris(ethane-1,2-diamine)chromium(III) tetrachloridoferrate(III)

Draw the structure of the cation. Is this complex chiral? Briefly explain your reasoning.



Yes, it is chiral as it is not superimposable on its mirror image.

If the salt is dissolved in water and a saturated solution of KCl is added to the solution, different coloured complexes can be crystallised from the solution. Write the formulae for two of these complexes.

$[\text{Cr}(\text{en})_3][\text{FeCl}_4]_2\text{Cl}$, $[\text{Cr}(\text{en})_3][\text{FeCl}_4]\text{Cl}_2$, $[\text{Cr}(\text{en})_3]\text{Cl}_3$ and $\text{K}[\text{FeCl}_4]$ are all possible.

- Aqua ligands in coordination complexes are generally acidic. Briefly explain this phenomenon using $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ as an example.

Co^{3+} has a high charge and is relatively small: it has a high charge density. When attached to water, it polarises the O–H bond in the aqua ligand.

This weakens the O–H bond causing the complex to be acidic in aqueous solution.

Solution A consists of a 0.10 M aqueous solution of $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)](\text{NO}_3)_3$ at 25 °C. Calculate the pH of Solution A. The $\text{p}K_a$ of $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+} = 5.69$.

As $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ is a weak acid, $[\text{H}_3\text{O}^+]$ must be calculated using a reaction table (acid = $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ and base = $[\text{Co}(\text{NH}_3)_5(\text{OH})]^{2+}$

	acid	H_2O	\rightleftharpoons	H_3O^+	base
initial	0.10	large		0	0
change	-x	negligible		+x	+x
final	$0.10 - x$	large		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{base}]}{[\text{acid}]} = \frac{x^2}{0.10 - x}$$

As $\text{p}K_a = -\log_{10} K_a$, $K_a = 10^{-5.69}$ and is very small, $0.10 - x \sim 0.10$ and hence:

$$x^2 = 0.10 \times 10^{-5.69} \quad \text{or} \quad x = 4.5 \times 10^{-4} \text{ M} = [\text{H}_3\text{O}^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = -\log_{10} (4.5 \times 10^{-4}) = 3.35$$

pH = 3.35

At 25 °C, 1.00 L of Solution B consists of 28.5 g of $[\text{Co}(\text{NH}_3)_5(\text{OH})](\text{NO}_3)_2$ dissolved in water. Calculate the pH of Solution B.

The molar mass of $[\text{Co}(\text{NH}_3)_5(\text{OH})](\text{NO}_3)_2$ is:

$$\begin{aligned} \text{molar mass} &= (58.93 \text{ (Co)} + 7 \times 14.01 \text{ (N)} + 7 \times 16.00 \text{ (O)} + 16 \times 1.008 \text{ (H)}) \text{ g mol}^{-1} \\ &= 285.128 \text{ g mol}^{-1} \end{aligned}$$

The number of moles present in 28.5 g is therefore:

$$\text{number of moles} = \text{mass} / \text{molar mass} = (28.5 \text{ g}) / (285.128 \text{ g mol}^{-1}) = 0.100 \text{ mol}$$

ANSWER CONTINUES ON THE NEXT PAGE

If this is present in 1.00 L, then $[\text{base}] = 0.100 \text{ M}$.

As it is a weak base, $[\text{OH}^-]$ must be calculated by considering the equilibrium:

	base	H_2O	\rightleftharpoons	acid	OH^-
initial	0.100	large		0	0
change	-y	negligible		+y	+y
final	$0.100 - y$	large		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = \frac{y^2}{(0.100 - y)}$$

For an acid and its conjugate base:

$$\text{p}K_a + \text{p}K_b = 14.00$$

$$\text{p}K_b = 14.00 - 5.69 = 8.31$$

As $\text{p}K_b = 8.31$, $K_b = 10^{-8.31}$. K_b is very small so $0.100 - y \sim 0.100$ and hence:

$$y^2 = 0.100 \times 10^{-8.31} \text{ or } y = 2.21 \times 10^{-5} \text{ M} = [\text{OH}^-]$$

Hence, the pOH is given by:

$$\text{pOH} = -\log_{10}[\text{OH}^-] = \log_{10}[2.21 \times 10^{-5}] = 4.65$$

Finally, $\text{pH} + \text{pOH} = 14.00$ so

$$\text{pH} = 14.00 - 4.65 = 9.35$$

$$\text{pH} = 9.35$$

Using both Solutions A and B, calculate the volumes (in mL) required to prepare a 1.0 L solution with a $\text{pH} = 7.00$.

The ratio of acid to conjugate base needed can be calculated using the Henderson-Hasselbalch equation, $\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$:

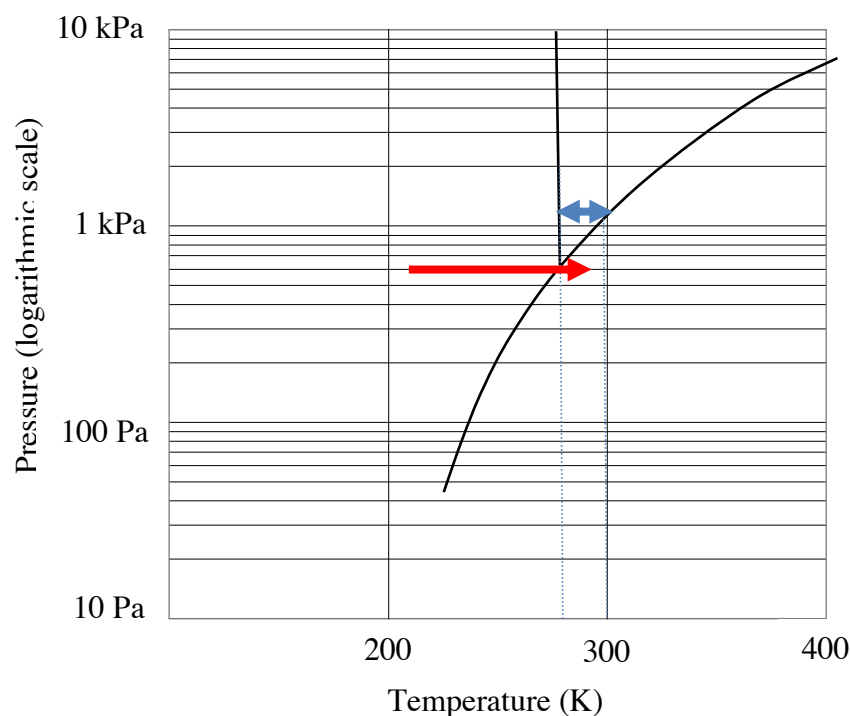
$$7.00 = 5.69 + \log \frac{[\text{base}]}{[\text{acid}]} \quad \text{so} \quad \frac{[\text{base}]}{[\text{acid}]} = 10^{1.31} = 20.4$$

As the base and acid have the same concentration, this is also the ratio of the volumes needed. As $V_{\text{acid}} + V_{\text{base}} = 1.0 \text{ L}$ and $V_{\text{base}} / V_{\text{acid}} = 20.4$:

$$V_{\text{acid}} = 0.047 \text{ L and } V_{\text{base}} = 0.953 \text{ L}$$

Marks
5

- The diagram below shows part of the phase diagram of water.



The average pressure on the surface of Mars is around 0.6 kPa. If the night time temperature is -60°C and a summer day temperature is 20°C , describe what happens to any water on the surface of Mars as the sun rises.

This process is illustrated by the red arrow in the phase diagram above. The process occurs just *below* the triple point so the phase changes from solid (at -60°C) to gas (at 20°C).

Water sublimates as the sun rises on Mars.

(Note the logarithmic scale on the graph. Each horizontal line between 100 Pa (0.1 kPa) and 1 kPa (1000 Pa) represents an increase of 100 Pa (0.1 kPa).)

The highest surface pressure on Mars is thought to occur at the Hellas Basin, a low-lying area created by the impact of a large asteroid. If the pressure in this region is 1.2 kPa, use the phase diagram to estimate the temperature range in which liquid water will occur. Show your working on the phase diagram.

At 1.2 kPa, water is a liquid in the temperature range covered by the double-headed blue arrow in the phase diagram above.

Within the accuracy possible on the diagram, this corresponds to the temperature range 272 – 305 K.

Marks
2

- The critical point of H₂O is over 250 °C higher than for H₂S, H₂Se and H₂Te. Describe, at the molecular level, what needs to happen to the interactions between the water molecules to reach the critical point and why this requires a higher temperature in water than in the other group 16 hydrides.

At the critical point, the gas and liquid phases are indistinguishable.

As a liquid is heated and undergoes a phase change in a closed container, the density of the liquid decreases and the density of the vapour increases. When these values are the same, there is no longer a phase boundary and a supercritical fluid has been produced.

Water has strong H-bonds, whereas H₂S, H₂Se, H₂Te have much weaker dispersion and dipole-dipole interactions. The stronger H-bonds require a higher temperature to overcome the intermolecular forces, so water has a higher critical temperature than the other Group 16 hydrides.

4

- A dilute solution of ammonia has a pH of 10.54. Calculate what amount of HCl(g) must be added to 1.0 L of this solution to give a final pH of 8.46. The pK_a of NH₄⁺ is 9.24.

In the initial solution, pH = 10.54 so pOH = 14.00 – 10.54 = 3.46 and:

$$[\text{OH}^-(\text{aq})] = 10^{-3.46} = 0.000347 \text{ M}$$

This is formed by the reaction below.



Hence, [NH₄⁺(aq)] = [OH⁻(aq)] = 0.000347 M. This reaction corresponds to K_b for NH₃. As K_a for NH₄⁺ = 9.24, K_b = 14.00 – 9.24 = 4.76 and

$$K_b = \frac{[\text{NH}_4^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{NH}_3(\text{aq})]} = \frac{(10^{-3.46})(10^{-3.46})}{[\text{NH}_3(\text{aq})]} = 10^{-4.76}$$

Hence, [NH₃(aq)] = 10^{-2.16} = 0.00692 M

This reacts with the added HCl(g):

	H ⁺ (aq)	NH ₃ (aq)	⇌	NH ₄ ⁺ (aq)
initial	<i>x</i>	0.00692		0.000347
final	0	0.00692 – <i>x</i>		0.000347 + <i>x</i>

ANSWER CONTINUES ON THE NEXT PAGE

At the final pH of 8.46, the Henderson-Hasselbalch equation can be used:

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{NH}_3(\text{aq})]}{[\text{NH}_4^+(\text{aq})]}$$

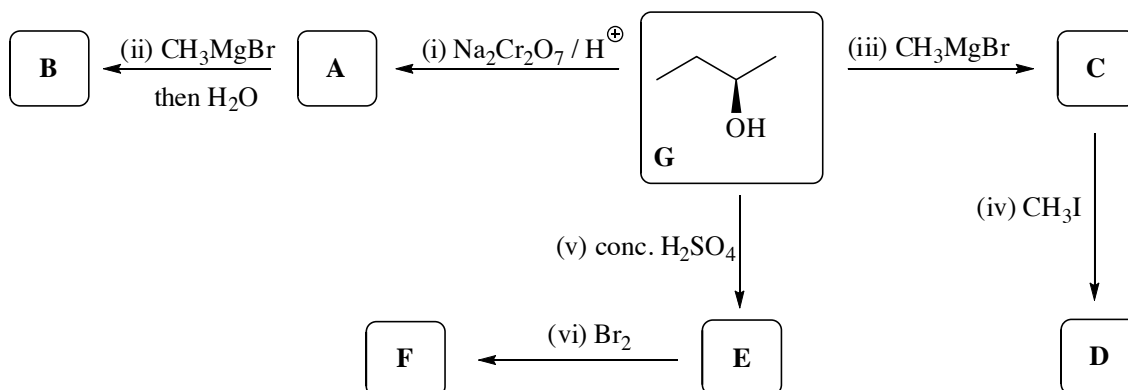
$$8.46 = 9.24 + \log \left(\frac{0.00692 - x}{0.000347 + x} \right)$$

Solving this gives $x = 0.0059$ mol.

Answer: 0.0059 mol

**Marks
10**

- Consider the following reaction sequences beginning with the alcohol **G**.



What is the systematic name for **G**?

(R)-2-butanol

Suggest structures for compounds **A** – **F** in the reaction sequences above.

A		B		C	
D		E		F	

What type of reaction is occurring at each of the following steps?

Step (iii)	acid/base
Step (iv)	S_N2 (nucleophilic substitution)
Step (v)	elimination
Step (vi)	electrophilic addition

Marks
8

- Shown on the next page are the mass (MS), infrared (IR), ^1H and ^{13}C NMR spectra for a compound of empirical formula $\text{C}_{10}\text{H}_{11}\text{ClO}$. Use this information to deduce a structure for this compound. (NMR chemical shift ranges can be found on the following page.) Show your working below.

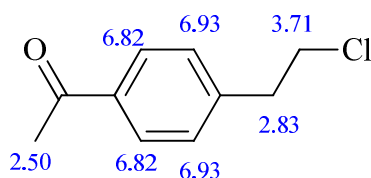
Working

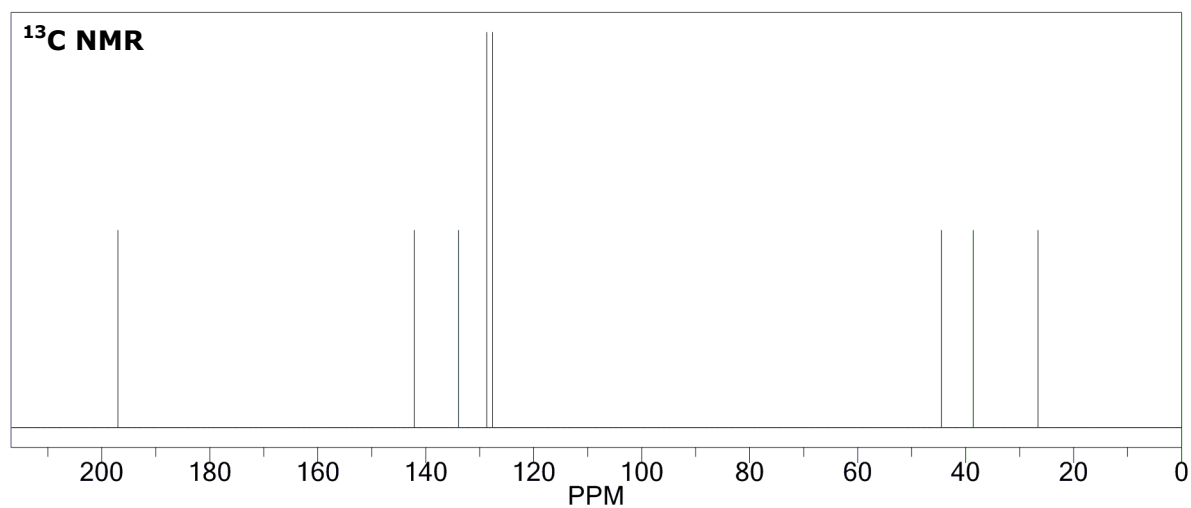
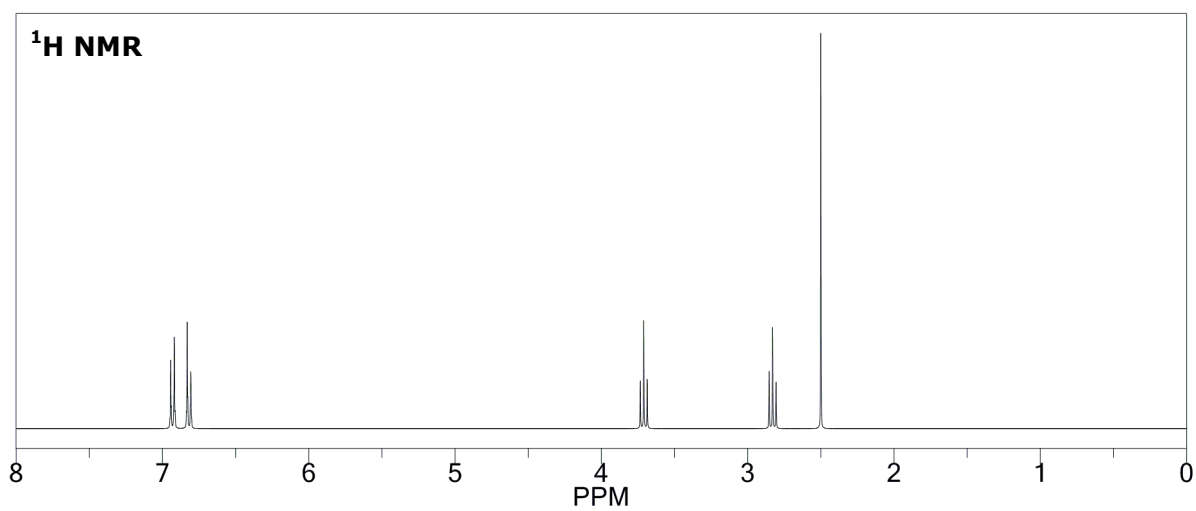
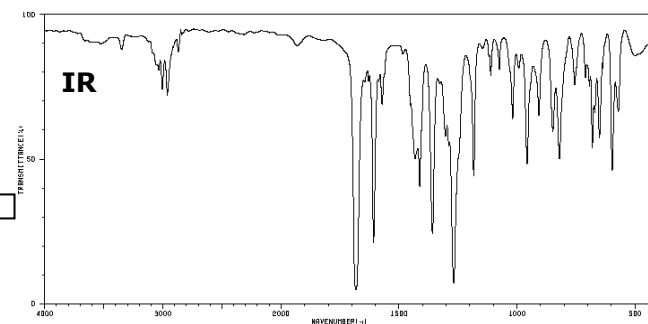
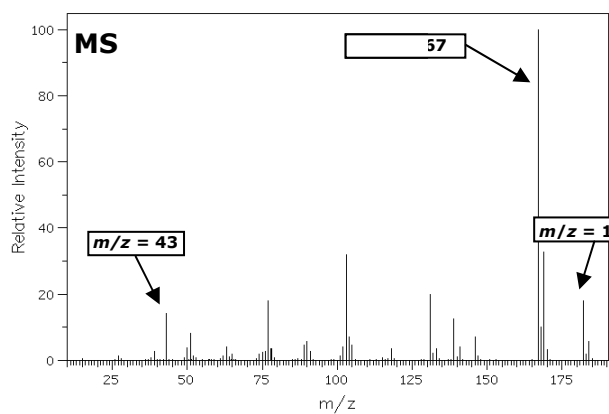
Peak at $m/z = 43$ in MS typical of COCH_3 , confirmed by peak at 1700 cm^{-1} in IR and singlet at 2.5 in ^1H NMR.

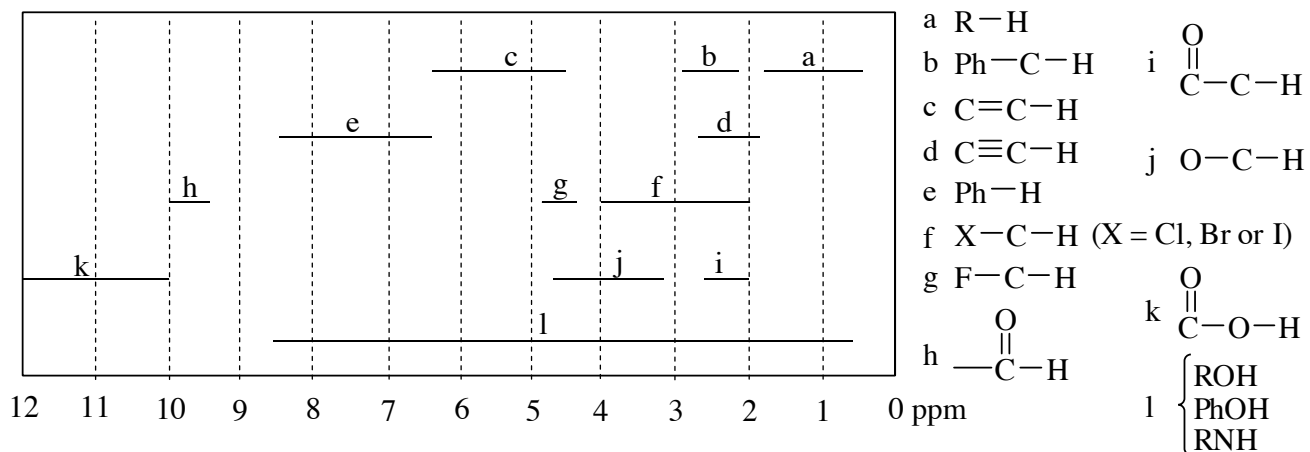
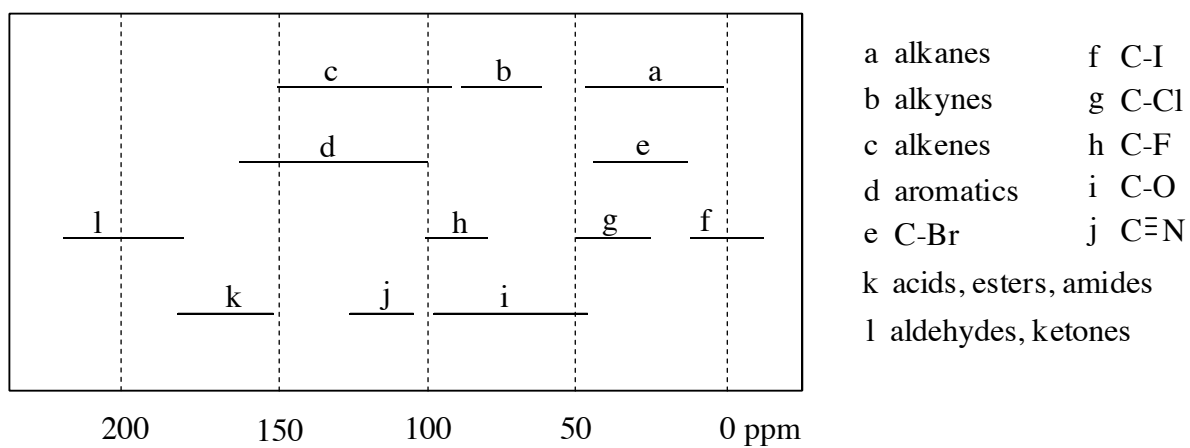
Doublets in ^1H NMR just below 7 are characteristic of a 1,4-disubstituted benzene ring.

Triplets at 2.8 and 3.7 in ^1H NMR suggest 2 adjacent CH_2 groups.

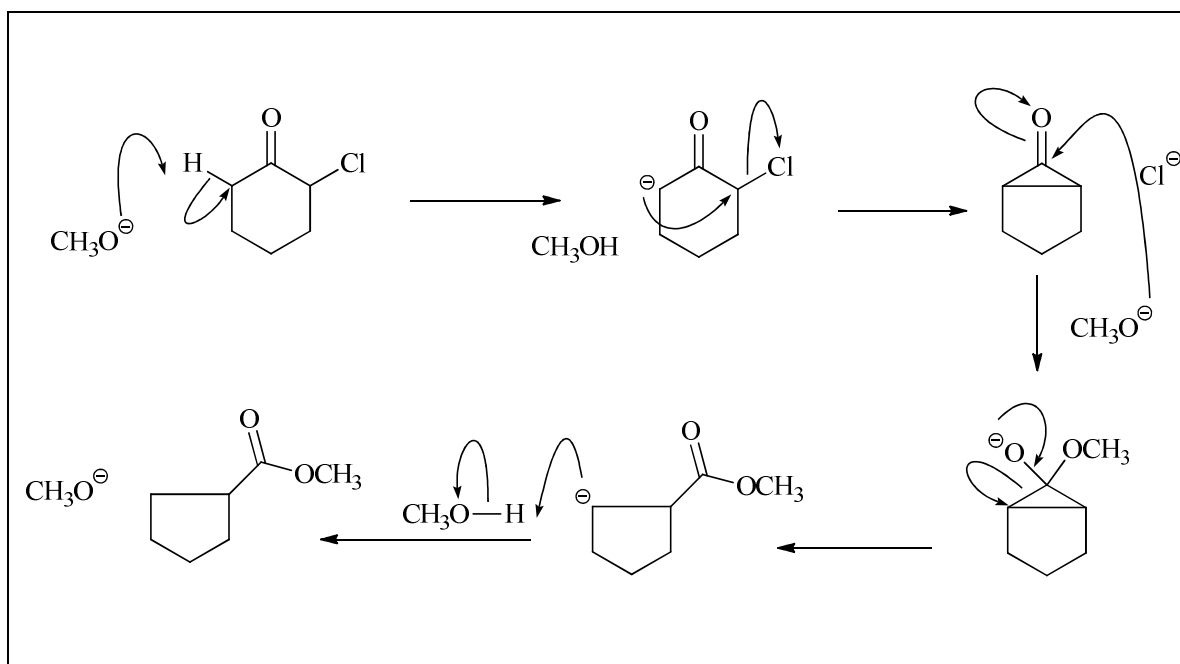
Hence structure below, supported by chemical data shift.

Structure

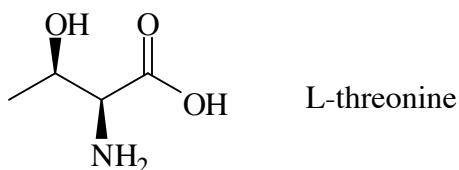


¹H NMR Chemical Shifts¹³C NMR Chemical Shifts

- Apply your understanding of 'curly arrows' to draw in the arrows required to complete a mechanism for the following reaction.



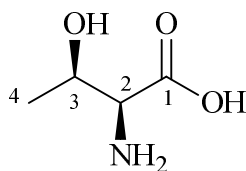
- The systematic name of threonine is 2-amino-3-hydroxybutanoic acid. Assign the absolute configuration of L-threonine. Show your working.



About C2: $\text{NH}_2 > \text{COOH} > \text{CH}(\text{OH})\text{CH}_3 > \text{H}$ - anticlockwise

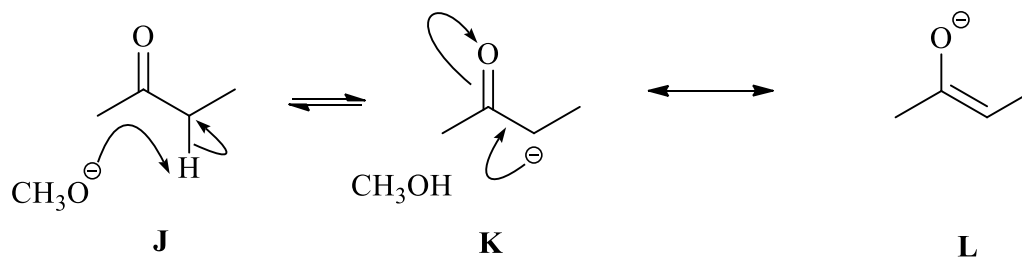
About C3: $\text{OH} > \text{CH}(\text{NH}_2)\text{COOH} > \text{CH}_3 > \text{H}$ - clockwise

Therefore (2*S*, 3*R*)-2-amino-3-hydroxybutanoic acid



Marks
6

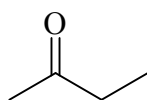
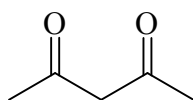
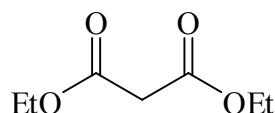
- Protons next to a carbonyl group can be removed by alkoxide bases as shown below.



Apply your understanding of resonance to propose a structure **L** that explains how the carbonyl group increases the acidity of these hydrogens.

Add curly arrows to the reaction scheme above to complete a mechanism for the deprotonation of **J** to give **K**, and the stabilisation of **K** by resonance.

The pK_a values of compounds **J**, **M** and **N** are 9, 13 and 19, but not in that order. Match each compound with the correct pK_a , and explain your answer.

**J****M****N**

pK_a values:

J = 19**M = 9****N = 13**

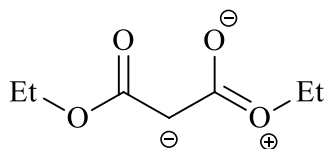
Reasoning for above assignments

M and **N** are stronger acids than **J** as the charge on the carbanion can be delocalised onto 2 carbonyl groups rather than 1 (*i.e.* there are more resonance structures).

Enolate anions are stabilised by electron withdrawing groups which help reduce the negative charge on the carbon atom.

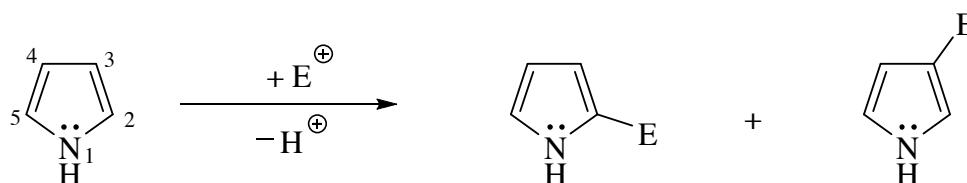
N is a weaker acid than **M** because the OEt group of the ester donates electron density towards the enolate anion, thus destabilising it.

Also the following resonance form of the ester would mean that the carbonyl group is less available to share the negative charge of the enolate anion.



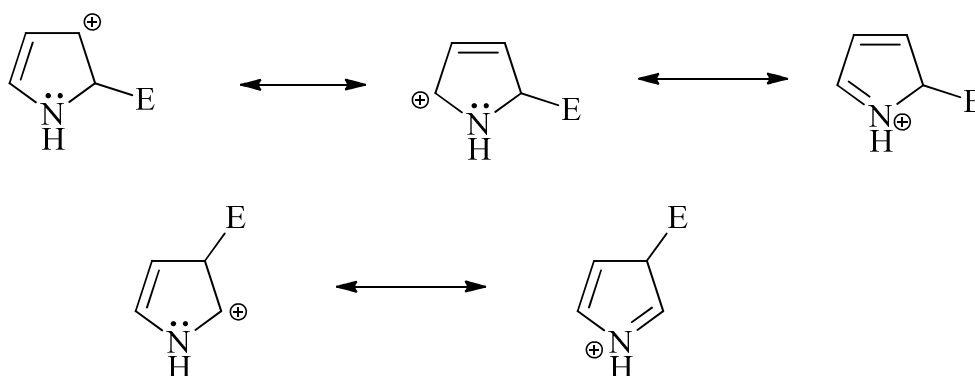
Marks
5

- In the electrophilic aromatic substitution (S_EAr) of pyrrole, the 2-substituted derivative is the major product.



Draw the cationic (Wheland-type) intermediate formed during reaction at the 2-position, and the equivalent intermediate formed during reaction at the 3-position. Using these structures, explain why reaction at the 2-position is faster, and leads to the major product.

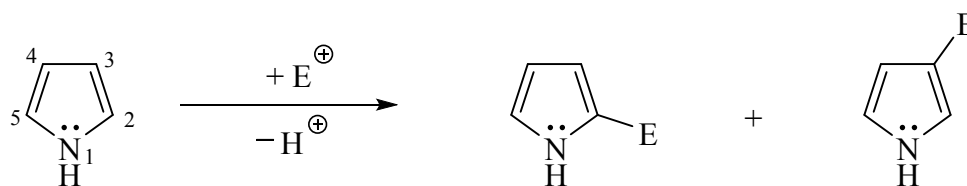
Substitution at position 2 gives 3 canonical forms for the Wheland intermediate, versus only 2 for the substitution at position 3.



The intermediate with the greater number of resonance structures is the more stable and leads to the major product.

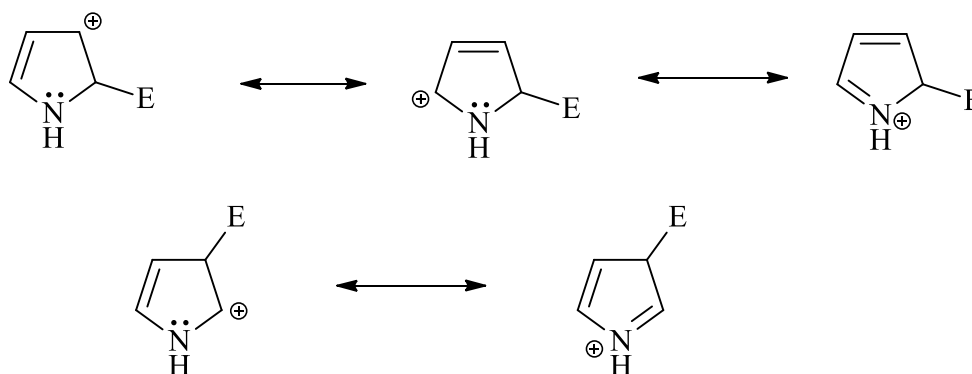
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