

Topics in the November 2008 Exam Paper for CHEM1902

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- [Calculations Involving \$pK_a\$](#)
- [Solubility Equilibrium](#)

2008-N-3:

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2008-N-13:

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- Stereochemistry

2008-N-14:

- Alcohols
- Carboxylic Acids and Derivatives

2008-N-15:

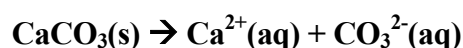
- Aromatic Compounds

Marks
4

- The ocean contains a variety of forms of CO_3^{2-} and CO_2 with a variety of acid-base and solubility equilibria determining their concentrations. There is concern that increasing levels of CO_2 will lead to increased dissolution of CaCO_3 and critically affect the survival of life forms that rely on a carbonaceous skeleton.

Calculate the concentrations of Ca^{2+} and CO_3^{2-} in a saturated solution of CaCO_3 . (The K_{sp} of CaCO_3 is 3.3×10^{-9} .)

The dissolution of CaCO_3 follows the reaction,



If the molar solubility of CaCO_3 is S then $[\text{Ca}^{2+}(\text{aq})] = [\text{CO}_3^{2-}(\text{aq})] = S$.

The solubility product is given by:

$$K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})][\text{CO}_3^{2-}(\text{aq})] = (S)(S) = S^2$$

As $K_{\text{sp}} = 3.3 \times 10^{-9}$,

$$S^2 = 3.3 \times 10^{-9} \text{ or } S = 5.7 \times 10^{-5} \text{ M}$$

$$[\text{Ca}^{2+}] = 5.7 \times 10^{-5} \text{ M}$$

$$[\text{CO}_3^{2-}] = 5.7 \times 10^{-5} \text{ M}$$

Calculate the pH of such a solution. (The $\text{p}K_{\text{a}}$ of HCO_3^- is 10.33).

CO_3^{2-} is a weak base and will react with water to produce HCO_3^- :

	CO_3^{2-}	H_2O	\rightleftharpoons	OH^-	HCO_3^-
initial	5.7×10^{-5}	large		0	0
change	$-x$	negligible		$+x$	$+x$
final	$5.7 \times 10^{-5} - x$	large		x	x

The equilibrium constant K_{b} is given by:

$$K_{\text{b}} = \frac{[\text{OH}^-(\text{aq})][\text{HCO}_3^-(\text{aq})]}{[\text{CO}_3^{2-}(\text{aq})]} = \frac{x^2}{5.7 \times 10^{-5} - x}$$

As $\text{p}K_{\text{a}} + \text{p}K_{\text{b}} = 14.00$, $\text{p}K_{\text{b}} = 14.00 - 10.33 = 3.67$. As $\text{p}K_{\text{b}} = -\log K_{\text{b}}$, so

$$K_{\text{b}} = 10^{-3.67}.$$

ANSWER CONTINUES ON THE NEXT PAGE

As the concentration of the base is so small, the 'small x ' approximation cannot be used and it is necessary to solve the quadratic equation. From above,

$$x^2 + 10^{-3.67}x - (5.7 \times 10^{-5} \times 10^{-3.67}) = 0$$

Solving this using the quadratic formula gives $x = 4.67 \times 10^{-5} = [\text{OH}^-(\text{aq})]$. Hence,

$$\text{pOH} = -\log_{10}[\text{OH}^-(\text{aq})] = 4.33$$

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

$$\text{pH} = 14.00 - 4.33 = 9.67$$

$$\text{pH} = 9.67$$

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The pH of surface ocean water is currently 8.10 (having fallen from a pre-industrial era level of 8.16), the concentration of HCO_3^- is $2.5 \times 10^{-3} \text{ M}$, and it is saturated with CaCO_3 . Calculate the concentration of Ca^{2+} in these conditions.

From 2008-N-2,

$$K_b = \frac{[\text{OH}^-(\text{aq})][\text{HCO}_3^-(\text{aq})]}{[\text{CO}_3^{2-}(\text{aq})]} = 10^{-3.67}$$

If pH = 8.10 then pOH = 14.00 – 8.10 = 5.90 and so $[\text{OH}^-(\text{aq})] = 10^{-5.90} \text{ M}$.

If $[\text{HCO}_3^-] = 2.5 \times 10^{-3} \text{ M}$, then

$$[\text{CO}_3^{2-}] = \frac{[\text{OH}^-(\text{aq})][\text{HCO}_3^-(\text{aq})]}{K_b} = \frac{(10^{-5.90})(2.5 \times 10^{-3})}{(10^{-3.67})} = 1.47 \times 10^{-5}$$

From 2008-N-2, $K_{sp} = [\text{Ca}^{2+}(\text{aq})][\text{CO}_3^{2-}(\text{aq})] = 3.3 \times 10^{-9}$. Hence,

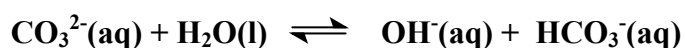
$$[\text{Ca}^{2+}(\text{aq})] = K_{sp} / [\text{CO}_3^{2-}(\text{aq})] = 3.3 \times 10^{-9} / (1.47 \times 10^{-5}) = 2.2 \times 10^{-4} \text{ M}$$

$$[\text{Ca}^{2+}] = 2.2 \times 10^{-4} \text{ M}$$

The pH is expected to drop to about 7.8 by the end of the century as CO_2 levels increase further. What effect will this have on the solubility of CaCO_3 in sea water? Use chemical equations to assist with explaining your answer.

The solubility of CaCO_3 will increase.

At a lower pH, $[\text{OH}^-(\text{aq})]$ will be lower. The equilibrium below will be shifted to the right:



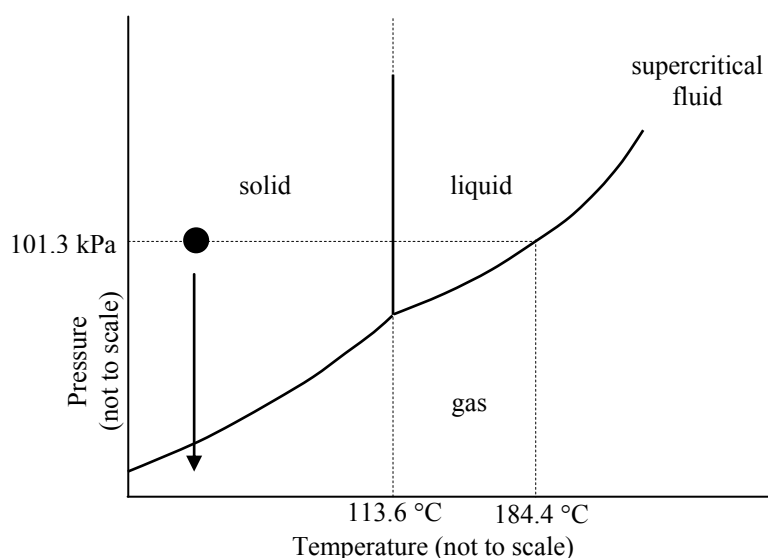
With lower $[\text{CO}_3^{2-}(\text{aq})]$, $[\text{Ca}^{2+}(\text{aq})]$ will increase as $[\text{Ca}^{2+}(\text{aq})] = K_{sp} / [\text{CO}_3^{2-}(\text{aq})]$. The solubility will be increased.

Marks
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- F_2 and Cl_2 are gases at room temperature, Br_2 is a liquid, and I_2 is a solid. Explain why the melting points and boiling points of the halogens increase going down the group.

Going down the group, the atoms get bigger - they have more electrons and these occupy orbitals of higher n values which are larger and more diffuse.

Hence, they have bigger and more polarisable electron clouds. Dispersion forces depend on the polarizability of the electron cloud and therefore increase going down the group. The melting and boiling points increase accordingly.



Shown above is the phase diagram for iodine. What are the melting and boiling points of iodine at atmospheric pressure?

Atmospheric pressure corresponds to 101.3 kPa. The dotted line corresponding to this pressure crosses the boundary between solid and liquid at 113.6 °C. This is the normal melting point. The dotted line corresponding to this pressure crosses the boundary between liquid and gas at 184.4 °C. This is the normal boiling point.

In what way would you need to change the conditions to make iodine, initially at room temperature and pressure, sublime?

Under these conditions, iodine is a solid (shown by the dot on the phase diagram). To turn it from solid to gas (sublime) requires lowering the pressure (shown by the arrow on the diagram) until it is below that on the solid – gas boundary.

Describe what will happen if pressure is applied to a sample of solid iodine.

At room temperature and pressure, iodine is a solid (shown by the dot on the phase diagram). Increasing the pressure will not do anything to the phase.

Marks
5

- Alfred Werner, one of the founders of the field of coordination chemistry, prepared a series of platinum complexes that contained ammonia and chloride ions. One of these had the empirical formula $\text{PtCl}_4 \cdot 4\text{NH}_3$ and when reacted with silver nitrate released two chloride ions per formula unit. Write the structural formula of this compound and write the name of this compound.

Ag^+ will react with uncoordinated Cl^- to form AgCl(s) . As it reacts with two Cl^- ions per formula unit, there must be 2Cl^- counter ions.

The remaining 2Cl^- ions and the 4NH_3 molecules are coordinated to the metal.

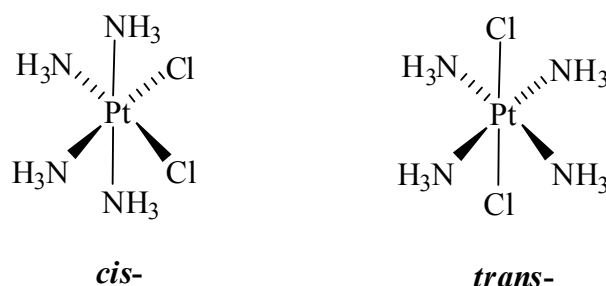
The oxidation number of the metal is +IV. The complex ion is thus $[\text{PtCl}_2(\text{NH}_3)_4]^{2+}$.

The coordination compound is $[\text{PtCl}_2(\text{NH}_3)_4]\text{Cl}_2$.

The name of this compound is tetraamminedichloridoplatinum(IV) chloride

Draw the possible structures of the metal complex.

With 2Cl^- and 4NH_3 ligands, two isomers are possible:



What types of isomers can be formed by a compound with this empirical formula?

Geometric (*cis* and *trans*) isomerism is possible (as above).

What is the *d* electron configuration of the Pt in this complex?

Platinum is in group 10 so Pt(IV) has $(10 - 4) = 6$ *d*-electrons: $5d^6$.

Marks
5

- 2-Bromo-2-methylpropane reacts with hydroxide ions to give 2-methyl-2-propanol.



The following rate data were collected at 55 °C.

Experiment	$[(\text{CH}_3)_3\text{CBr}]_0$ (M)	$[\text{OH}^-]_0$ (M)	Initial rate ($d[(\text{CH}_3)_3\text{COH}]/dt$, M s^{-1})
1	0.050	0.10	5.0×10^{-4}
2	0.20	0.10	2.0×10^{-3}
3	0.20	0.30	2.0×10^{-3}

Determine the rate law for the reaction.

Between experiments (1) and (2), $[\text{OH}^-]_0$ is constant. $[(\text{CH}_3)_3\text{CBr}]_0$ is increased by a factor of 4 and this leads to the rate increasing by a factor of 4: rate $\propto [(\text{CH}_3)_3\text{CBr}]$.

Between experiments (2) and (3), $[(\text{CH}_3)_3\text{CBr}]_0$ is constant. $[\text{OH}^-]_0$ is increased by a factor of 3 and this leads to no change in the rate. The rate is independent of $[\text{OH}^-]_0$.

Overall, rate $= k[(\text{CH}_3)_3\text{CBr}]$.

Calculate the value of the rate constant at 55 °C.

From the rate law, $k = \text{rate} / [(\text{CH}_3)_3\text{CBr}]$.

For experiment 1, rate $= 5 \times 10^{-4} \text{ M s}^{-1}$ and $[(\text{CH}_3)_3\text{CBr}] = 0.050 \text{ M}$ and so

$$k = (5 \times 10^{-4} \text{ M s}^{-1}) / (0.050 \text{ M}) = 1.0 \times 10^{-2} \text{ s}^{-1}$$

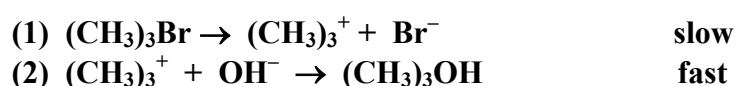
Answer: $k = 1.0 \times 10^{-2} \text{ s}^{-1}$

Suggest a possible mechanism for the reaction based on the form of the rate law.
Explain your answer.

The rate is independent of $[\text{OH}^-]$ suggesting that it is involved in a step after the rate determining step.

The rate is directly proportional to $[(\text{CH}_3)_3\text{CBr}]$ suggesting that a rate determining step which is unimolecular in $(\text{CH}_3)_3\text{CBr}$.

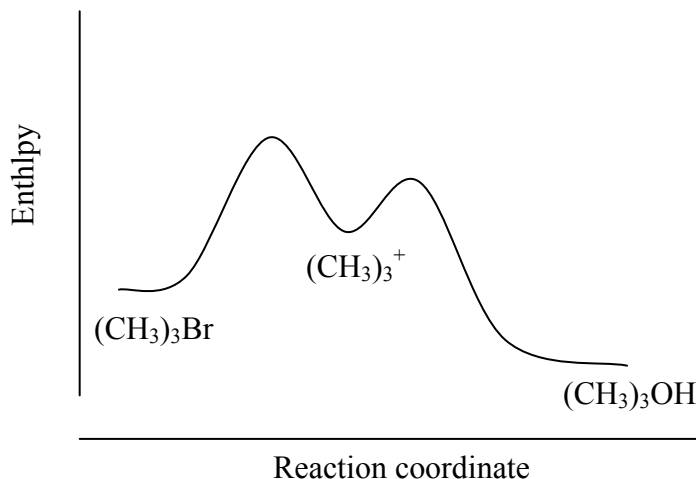
A possible mechanism is:



The reaction is exothermic. Draw the potential energy vs reaction coordinate diagram for this mechanism, labelling all species that can be isolated.

Marks
2

From 2008-N-6, the mechanism involves two steps: a slow first step and a fast second step. As the first step is rate determining, it has a higher activation energy. As the reaction is exothermic overall, the products have lower enthalpy than the reactants.



- A 300.0 mL solution of HCl has a pH of 1.22. Given that the pK_a of iodic acid, HIO_3 , is 0.79, how many moles of sodium iodate, NaIO_3 , would need to be added to this solution to raise its pH to 2.00?

3

Using $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$,

$$[\text{H}^+(\text{aq})]_{\text{initial}} = 10^{-1.22} = 0.060 \text{ M}$$

$$[\text{H}^+(\text{aq})]_{\text{final}} = 10^{-2.00} = 0.010 \text{ M}$$

Using $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$,

$$[\text{H}^+(\text{aq})]_{\text{initial}} = 10^{-1.22} = 0.060 \text{ M}$$

$$[\text{H}^+(\text{aq})]_{\text{final}} = 10^{-2.00} = 0.010 \text{ M}$$

The change of $(0.060 - 0.010 \text{ M}) = 0.050 \text{ M}$ occurs due to the reaction with IO_3^- (aq) to produce $\text{HIO}_3(\text{aq})$. If $[\text{IO}_3^-(\text{aq})] = x$, the reaction table is:

	$\text{H}^+(\text{aq}) +$	$\text{IO}_3^-(\text{aq})$	\rightleftharpoons	$\text{HIO}_3(\text{aq})$
initial	0.060	x		0
change	-0.050	-0.050		+0.050
final	0.010	$x - 0.050$		0.050

ANSWER CONTINUES ON THE NEXT PAGE

As $\text{p}K_{\text{a}} = 0.79 = -\log_{10}K_{\text{a}}$:

$$K_{\text{a}} = \frac{[\text{H}^{+}(\text{aq})][\text{IO}_3^{-}(\text{aq})]}{[\text{HIO}_3(\text{aq})]} = \frac{(0.010) \times (x - 0.050)}{0.050} = 10^{-0.79}$$

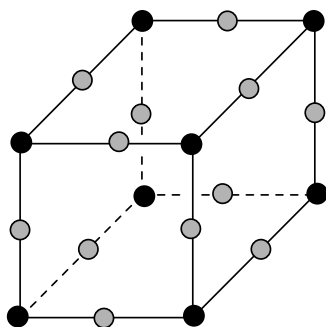
Thus, $x = 0.86 \text{ M} = [\text{IO}_3^{-}(\text{aq})]_{\text{initial}}$. This concentration corresponds to a 300.0 mL solution so the number of moles that have been added is:

$$\begin{aligned}\text{number of moles} &= \text{concentration} \times \text{volume} \\ &= (0.86 \text{ M}) \times (0.3000 \text{ L}) = 0.26 \text{ mol}\end{aligned}$$

Answer: 0.26 mol

Marks
5

- The diagram below shows the structure of an oxide of rhenium. The unit cell is cubic with rhenium at each of the corners and oxygen in the centre of each of the edges.



What is the chemical formula of this oxide?

There are 8 Re atoms on the corners, each contributing 1/8 to the unit cell: total number of Re atoms = $8 \times 1/8 = 1$.

There are 12 O atoms on the edges, each contributing 1/4 to the unit cell: total number of O atoms = $12 \times 1/4 = 3$.

The formula is thus ReO_3 .

Answer: **ReO_3**

What are the coordination numbers of rhenium and oxygen in this compound?

Re: **6 (octahedral)**

O: **2 (linear)**

There is a large hole at the centre of the cell that in some compounds is occupied by a cation. What is the coordination number of a cation occupying this site?

12 coordinate.

Given that the density of this oxide is 7.1 g cm^{-3} , calculate the length of the cell edge. (The structure is cubic.)

The unit cell contains one formula unit of ReO_3 .

The formula mass of ReO_3 is $(186.2 (\text{Re}) + 3 \times 16.00 (\text{O})) = 234.2 \text{ g mol}^{-1}$.

This is the mass of 1 mol. The mass of 1 formula unit is therefore:

$$\text{mass} = 234.2 \text{ g mol}^{-1} / 6.022 \times 10^{23} \text{ mol}^{-1} = 3.889 \times 10^{-22} \text{ g}$$

ANSWER CONTINUES ON THE NEXT PAGE

As density = mass / volume,

$$\text{volume} = \text{mass} / \text{density} = (3.889 \times 10^{-32} \text{ g}) / (7.1 \text{ g cm}^{-3}) = 5.48 \times 10^{-23} \text{ cm}^3$$

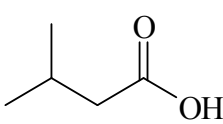
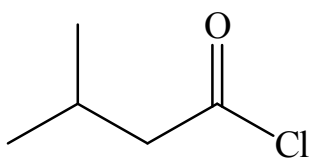
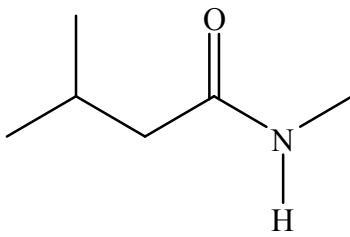
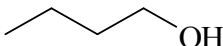
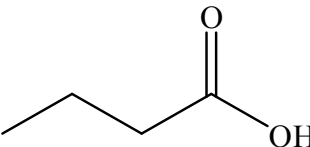
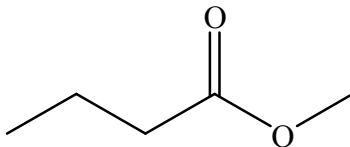
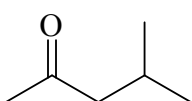
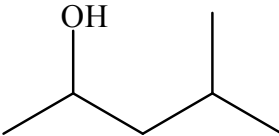
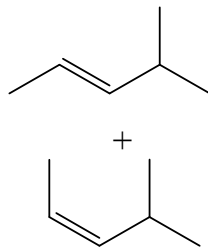
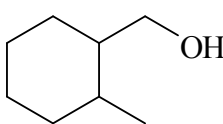
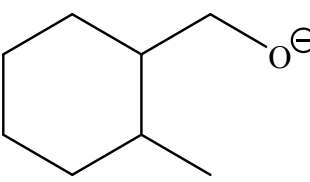
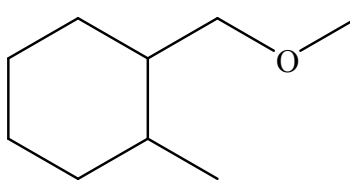
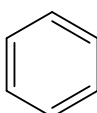
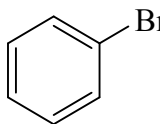
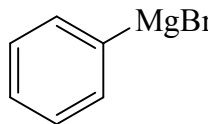
As the cell is cubic, if the side length is a , the volume is a^3 and,

$$a = (5.48 \times 10^{-23} \text{ cm}^3)^{1/3} = 3.8 \times 10^{-8} \text{ cm} = 3.8 \times 10^{-10} \text{ m or } 380 \text{ pm}.$$

Answer: **380 pm**

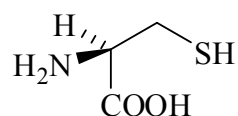
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- Complete the following table by drawing the structures of the intermediate and final organic product(s) as required. The intermediate product is formed when the starting material is treated with Reagent 1. The final product is formed when the intermediate product is treated with Reagent 2.

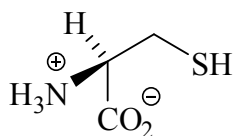
Starting material	Intermediate product	Final product
	Reagent 1: SOCl_2 	Reagent 2: CH_3NH_2  $+ \text{CH}_3\text{NH}_2^+ \text{Cl}^-$
	Reagent 1: $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+$ 	Reagent 2: $\text{CH}_3\text{OH} / \text{H}^+$ 
	Reagent 1: NaBH_4 then H_2O 	Reagent 2: conc. H_2SO_4 
	Reagent 1: CH_3MgBr 	Reagent 2: CH_3I 
	Reagent 1: $\text{Br}_2 / \text{FeBr}_3$ (cat.) 	Reagent 2: $\text{Mg} / \text{dry ether}$ 

Marks
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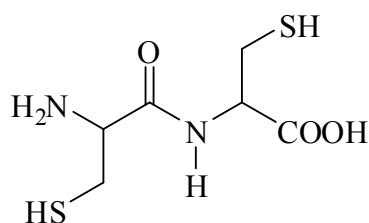
- Consider the amino acid L-cysteine shown below.



Draw the zwitterionic form of L-cysteine.



Draw the dipeptide L-cysteinyl-L-cysteine.

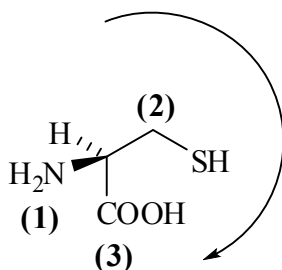


Assign the absolute configuration (*R* or *S*) of L-cysteine. Show your working.

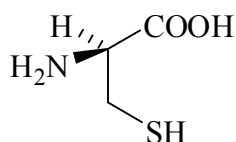
Absolute configuration is (*R*)-

Priorities: $-\text{NH}_2 > -\text{CH}_2\text{SH} > -\text{COOH} > -\text{H}$

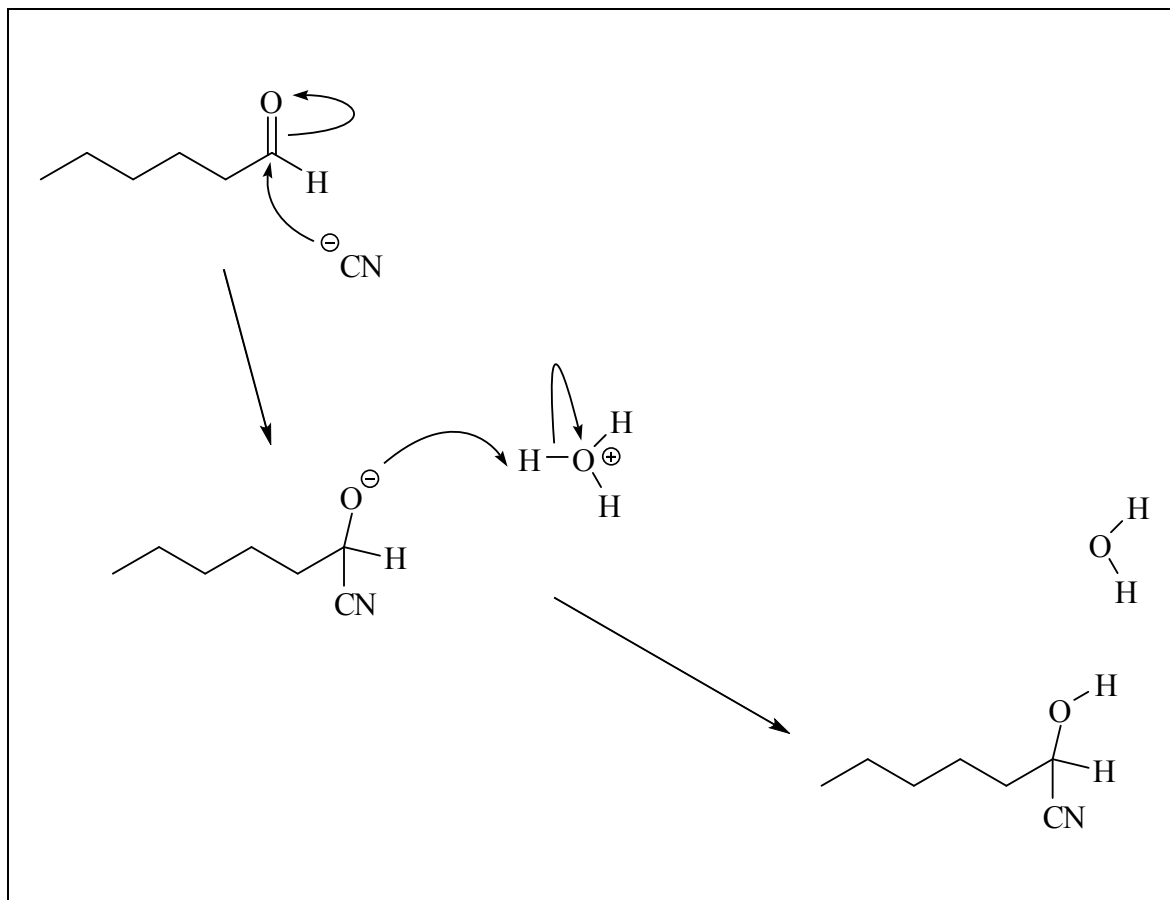
With H at back, the order of $-\text{NH}_2 \rightarrow -\text{CH}_2\text{SH} \rightarrow -\text{COOH}$ goes clockwise



Draw the enantiomer of L-cysteine.

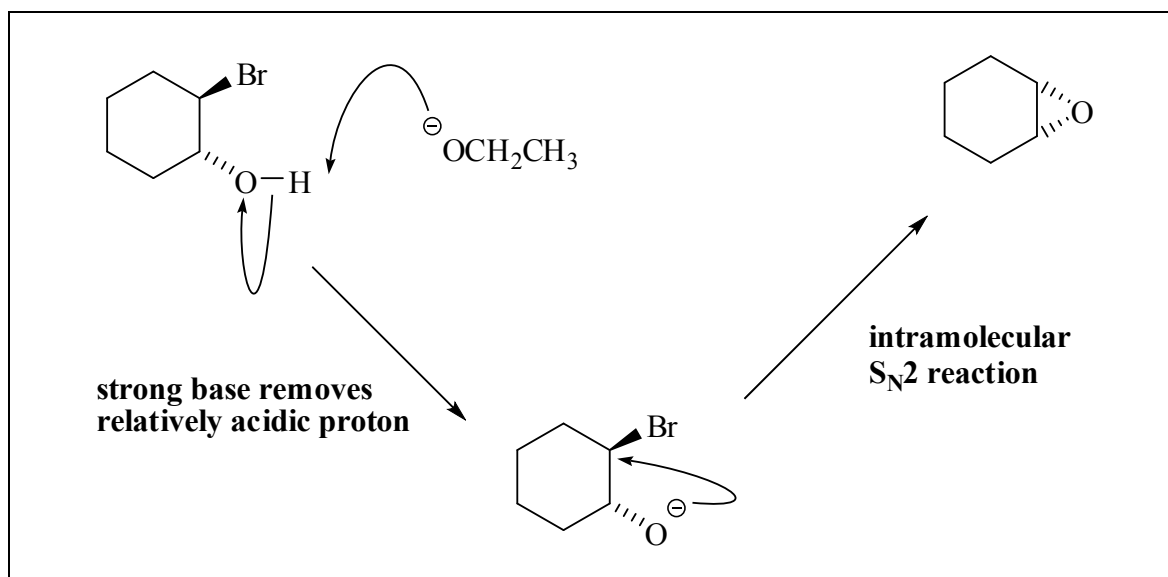


- Apply your understanding of curly arrows to propose a mechanism for the following reaction.

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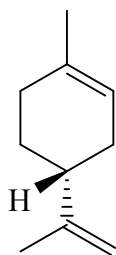
Marks
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- Propose a structure for the product of the following reaction. Outline a mechanism for its formation, showing all curly arrows and intermediates.

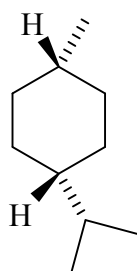


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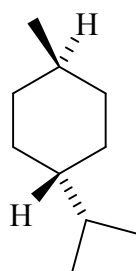
- Consider the isomer of limonene shown below.



Show the major organic products formed when limonene is treated with excess H_2 in the presence of a Pd/C catalyst. Pay particular attention to any relevant stereochemistry. Identify which would be the major product and explain why it forms preferentially.



A



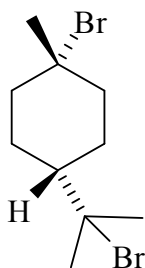
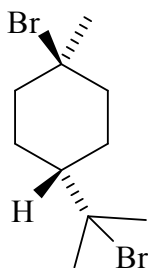
B

Isomer A would be the major product.

The reaction takes place on the surface of the catalyst. The isopropyl group provides steric hindrance to the side of the ring that is *cis* to this group.

Both H's therefore are delivered to the other side of the molecule.

Use Markovnikov's rule to predict the two major products of the reaction between limonene and excess HBr. Draw these isomers and identify the isomeric relationship between them. Specify the optical activity (active or inactive) of each isomer.



They are diastereoisomers. Both isomers are optically inactive.

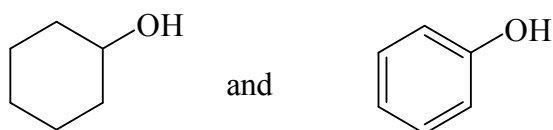
At what m/z would the molecular ion of one of these isomers appear in its mass spectrum? Explain your answer.

Br exists as two isotopes ^{79}Br and ^{81}Br , which occur in approximately equal amounts.

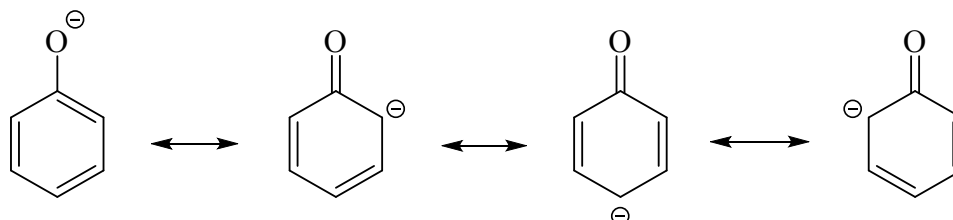
There would be 3 molecular ion peaks at m/z 296, 298 and 300 due to the ions containing 2 ^{79}Br atoms, 1 ^{79}Br and 1 ^{81}Br atom and 2 ^{81}Br atoms, respectively.

Marks
4

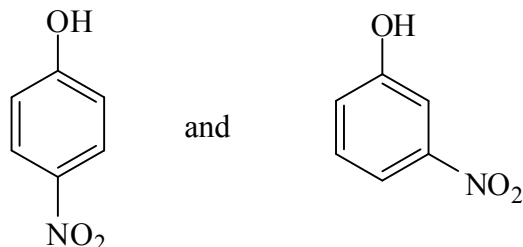
- For each of the following pairs of compounds, identify which is the stronger acid and give reasons for your choice.



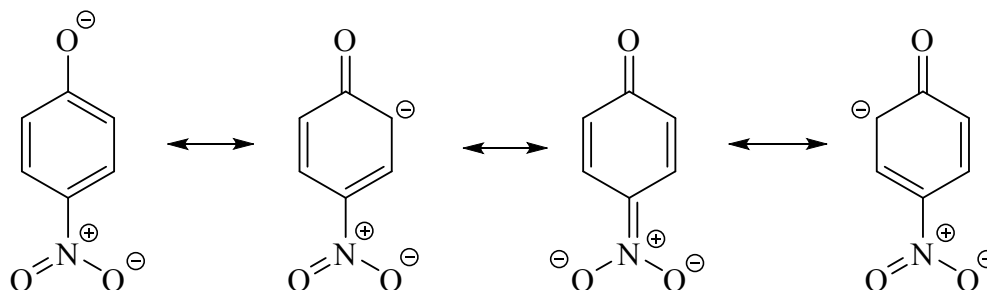
Phenol is more acidic as the phenoxide ion is resonance stabilised:



Chloroacetic acid is more acidic. The Cl atom is electronegative and pulls electrons from the carboxylic acid, thus weakening the O–H bond.

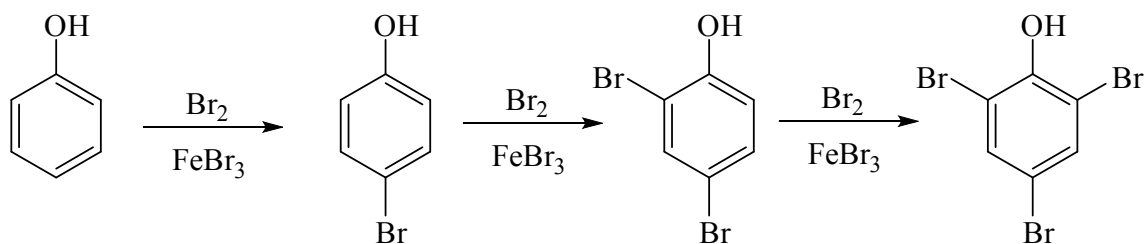


The *para* isomer is more acidic as the charge on the phenoxide ion can be delocalised into the nitro group. This is not possible with the *meta* isomer.



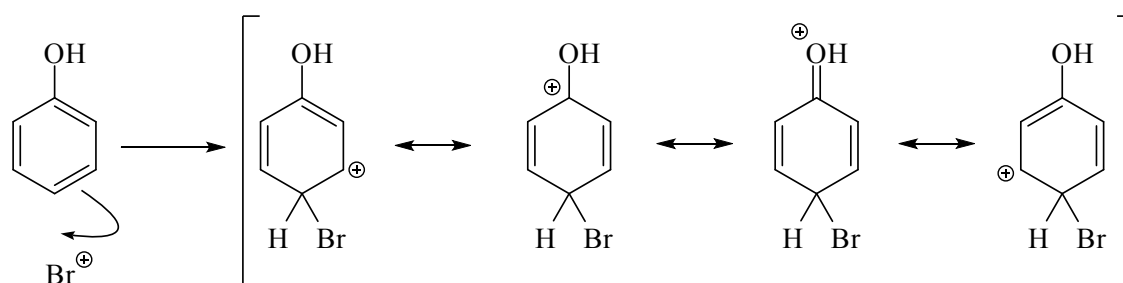
Marks
3

- The bromination of phenol proceeds as follows.



Show the Wheland intermediate for one of these steps and explain why bromination occurs at positions 2, 4 and 6, but not at positions 3 and 5.

Bromination at the 4 (or 2 or 6) position gives a Wheland intermediate that has four resonance contributors as the lone pair on the oxygen can be donated into the ring to help stabilise the charge.



Bromination at the 3 or 5 position gives a Wheland intermediate that has only three resonance contributors - the lone pair on the oxygen cannot participate in the resonance stabilisation.

