Topics in the November 2006 Exam Paper for CHEM1902

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

2006-N-3:

- Kinetics

2006-N-4:

- Metals in Biology

2006-N-5:

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2006-N-6:

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2006-N-8:

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2006-N-9:

- Carboxylic Acids and Derivatives
- Organic Mechanisms and Molecular Orbitals

2006-N-10:

- Synthetic Strategies

Marks

- Calculate the pH of a solution that is prepared by mixing 750 mL of 1.0 M potassium dihydrogenphosphate with 250 mL of 1.0 M potassium hydrogenphosphate. **2**

  For H_3PO_4, pK_{a1} = 2.15, pK_{a2} = 7.20, pK_{a3} = 12.38

The hydrogenphosphate anion is the conjugate base of dihydrogenphosphate, corresponding to the second ionization of phosphoric acid (K_{a2}). K_{a1} is much larger than K_{a2} so the equilibrium will not be greatly affected by protonation of dihydrogenphosphate. K_{a3} is much smaller than K_{a2} so the equilibrium will also not be greatly affected by deprotonation of hydrogenphosphate. The solution is a buffer and the pH can be calculated using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}\right) = \text{p}K_{a2} + \log_{10}\left(\frac{[\text{hydrogenphosphate}]}{[\text{dihydrogenphosphate}]}\right)$$

After mixing, a 1.00 L solution is formed that contains 0.750 mol of dihydrogenphosphate and 0.250 mol of hydrogenphosphate. Thus:

$$\text{pH} = 7.20 + \log_{10}\left(\frac{0.250}{0.750}\right) = 6.72$$

Answer: **pH = 6.72**

- 2.00 g of solid calcium hydroxide is added to 1.00 L of water. What proportion of the calcium hydroxide remains undissolved when the system has reached equilibrium? $K_{sp}(Ca(OH)_2) = 6.5 \times 10^{-6}$ M^3 **4**

The formula mass of $Ca(OH)_2$ is (40.08 Ca)) + 2 × (16.00 (O) + 1.008 (H)) = 74.096. 2.00 g of $Ca(OH)_2$ therefore corresponds to:

$$\text{amount of } Ca(OH)_2 = \frac{\text{mass}}{\text{formula mass}} = \frac{2.00}{74.096} = 0.0270 \text{ mol}$$

The solubility equilibrium and constant are given by:

$$Ca(OH)_2 \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq) \quad K_{sp} = [Ca^{2+}(aq)][OH^-(aq)]^2$$

If S mol dissolves in 1.00 L then $[Ca^{2+}(aq)] = S$ and $[OH^-(aq)] = 2S$. Thus,

$$K_{sp} = (S)(2S)^2 = 4S^3 = 6.5\ 8\ 10^{-6} \quad \text{so } S = 0.0118 \text{ mol}$$

The amount that remains undissolved is (0.0270) – (0.0118) = 0.0152 mol. The proportion that is undissolved is $\frac{0.0152}{0.0270} \times 100\% = 56\%$.

Answer: **56%**

ANSWER CONTINUES ON THE NEXT PAGE

What volume (in mL) of 10.0 M nitric acid must be added to this mixture in order to just dissolve all of the calcium hydroxide? Assume the volume of the nitric acid is small and can be ignored in the calculation of the total volume.

If all of the $Ca(OH)_2$ dissolves then $[Ca^{2+}(aq)] = 0.0270$ M. The [OH(aq)] required to achieve this is given by:

$$K_{sp} = [Ca^{2+}(aq)][OH^-(aq)]^2 = (0.0270) \times [OH^-(aq)]^2 = 6.5 \times 10^{-6}$$

$$[OH^-(aq)] = 0.0155 \text{ M}$$

As dissolution of 0.0270 mol of $Ca(OH)_2$ produces (2 × 0.0270) = 0.0540 mol of OH^-, the remainder has been neutralized by the added nitric acid:

number of moles of nitric acid added = 0.0540 – 0.0155 = 0.0384 mol

The volume of 10.0 M nitric acid which contains this amount is given by:

$$\text{volume of nitric acid} = \frac{\text{number of moles}}{\text{concentration}} = \frac{0.0384}{10.0} = 3.84 \times 10^{-3} \text{ L} = 3.84 \text{ mL}$$

Answer: **3.84 mL**

Marks 7

- The major pollutants NO(g), CO(g), NO_2(g) and CO_2(g) are emitted by cars and can react according to the following equation.

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The following rate data were collected at 225 °C.

Experiment	$[NO_2]_0$ (M)	$[CO]_0$ (M)	Initial rate ($d[NO_2]/dt$, M s^{-1})
1	0.263	0.826	1.44×10^{-5}
2	0.263	0.413	1.44×10^{-5}
3	0.526	0.413	5.76×10^{-5}

Determine the rate law for the reaction.

Between experiments (1) and (2), $[NO_2]_0$ is constant and $[CO]_0$ is halved. The rate does not change. The rate is independent of [CO]: zero order with respect to [CO].

Between experiments (2) and (3), $[CO]_0$ is kept constant and $[NO_2]_0$ is doubled. The rate increases by a factor of four: the rate is second order with respect to $[NO_2]$.

Overall,

rate α $[NO_2]^2 = k[NO_2]^2$

Calculate the value of the rate constant at 225 °C.

In experiment (1), rate= 1.44×10^{-5} M s^{-1} when $[NO_2]$ = 0.263 M. Using the rate law:

$1.44 \times 10^{-5} = k \times (0.263)^2$ so $k = 2.08 \times 10^{-4}$

The units of k can be deduced from the rate law:

rate = $k[NO_2]^2$

M s^{-1} = (units of k) × $(M)^2$ so k must have units of "M^{-1} s^{-1}"

Answer: **2.08×10^{-4} M^{-1} s^{-1}**

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the rate of appearance of CO_2 when $[NO_2] = [CO] = 0.500$ M.

When $[NO_2] = 0.500$ M, rate = $\frac{d[NO_2]}{dt} = (2.08 \times 10^{-4}) \times (0.500)^2 = 5.20 \times 10^{-5}$ M s^{-1}

From the chemical equation, one mole of CO_2 is produced for every mole of NO_2 that is removed. Thus, rate of appearance of CO_2 = rate of loss of NO_2.

Answer: **5.20×10^{-5} M s^{-1}**

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

A possible mechanism is:

$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ (slow)

$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ (fast)

The first step is slow and is rate determining. For this step, rate α $[NO_2]^2$, as observed. The second step is fast and does not contribute to the overall rate of the reaction and so the rate is independent of [CO(g)].

Marks

- Silicate based minerals and materials are all based on the SiO_4^{2-} tetrahedron which can be linked to produce ring, chain, sheet and 3-d network structures. Select two examples, list the intermolecular forces between the units, and explain how these contribute to the physical properties of minerals or materials made up of these units. **4**

Talc consists of two-dimensional silicate sheets with Mg^{2+} and OH^- counter ions lying in between. The sheets are made up of SiO_4^{2-} tetrahedra linked to three others by strong covalent bonds. The sheets are negatively charged and are held together by the counter ions. Sliding of the sheets relative to one another does not greatly affect these interactions so is relatively easy. This gliding of the sheets past one another gives talc a greasy feel.

Quartz consists of a three-dimensional structure as the SiO_4^{2-} tetrahedral are linked to four others by strong covalent bonds. It therefore has very high melting point.

Asbestos consists of one dimensional chains of SiO_4^{2-} tetrahedral which are linked to two others by strong covalent bonds. These chains give the minerals a fibrous character and can be woven. The high strength of the covalent bonds give the minerals high thermal stability so that asbestos minerals are used for thermal insulation.

- Iron, copper and zinc all play important natural roles in our biology. Select one of these elements and explain what features of its chemistry are important in allowing the element to carry out its roles. **4**

Iron is stable in two oxidation states, Fe^{2+} and Fe^{3+}, of similar stability. Both can can form octahedral complexes. In haemoglobin, the Fe^{2+} forms five bonds to the haem unit and the protein. The sixth site is available to bind molecular oxygen and this is accompanied by a change in the oxidation state to Fe^{3+}. The O_2 is carried to body tissues where it is released and the iron is returned to Fe^{2+}.

Copper is stable in two oxidation state, Cu^+ and Cu^{2+}, of similar stability. Copper is involved in electron transfer proteins where is uses its ability to change oxidation state to provide or remove electrons as required.

Zinc forms only one oxidation state, Zn^{2+}. This cation is smaller and is a good Lewis acid. Water bonded to it loses a proton to form OH^- which is used in carbonic anhydrase to capture carbon dioxide for transport.

ANSWER CONTINUES ON THE NEXT PAGE

Platinum complexes and lithium salts are active pharmaceutical agents. Select one and explain what features of its metal's chemistry are important in allowing it to be an effective pharmaceutical.

***cis*-Platin: $[Pt(NH_3)_2Cl_2]$ can bind to DNA by losing the chloride ions in the square planar complex. The corresponding *trans* compound is inactive. Lability of the Cl's and the shape of square planar complex are both crucial to the effectiveness of this platinum compound.**

Lithium salts are used to treat manic depression and other psychological disorders. Li^+ has the same charge as Na^+ and a similar size to Mg^{2+} and it is possible that its effects are due to interaction with these cations in neurons.

Marks
4

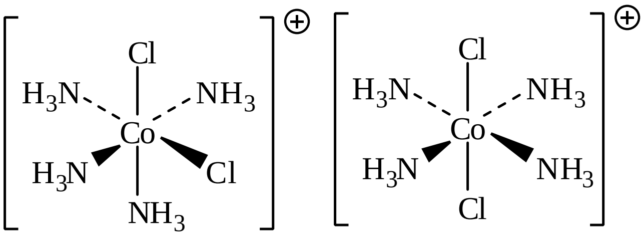
- Consider the complex $[CoCl_2(NH_3)_4]Cl{\cdot}2H_2O$.

  Write the systematic name of this complex.

tetraamminedichlorocobalt(III) chloride-2-water

What type(s) of isomerism is/are possible for this complex?

Stereoisomerism: *cis* and *trans*:



cis ***trans***

How many *d* electrons are there in the cobalt in this complex?

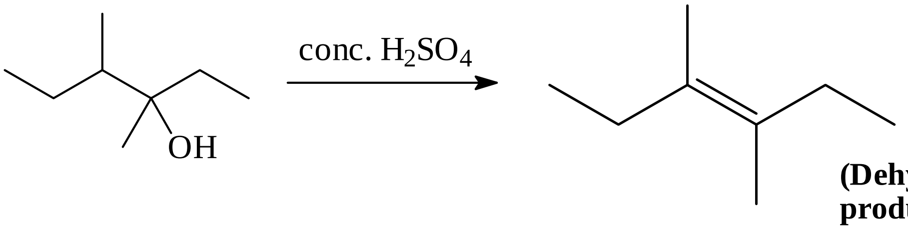
Co^{3+}: d^6

What oxidation state of platinum has the same number of valence shell *d* electrons as the cobalt in this complex?

Pt^{4+} is also d^6

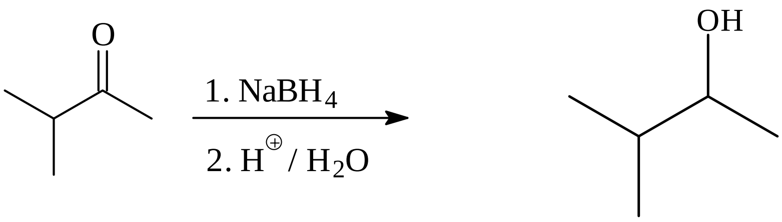
Marks
6

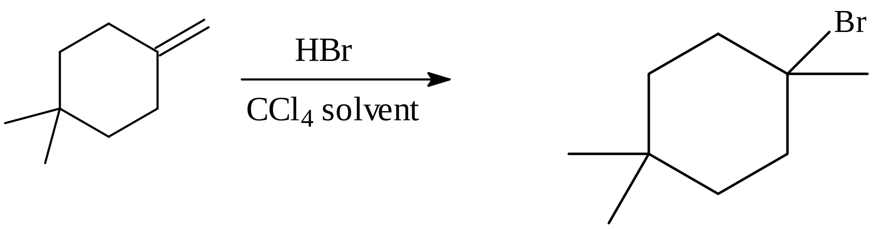
- Draw the structure(s) of the major organic product(s) formed in each of the following reactions. Give the names of the products where requested.



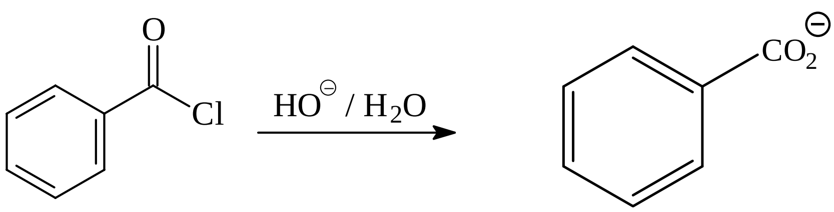
(Dehydration to produce most substituted double bond: Zeitsev's rule)

Name(s): **(*E*)-3,4-dimethyl-3-hexene**





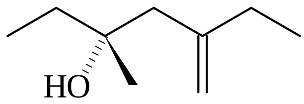
Name(s): 1-bromo-1,4,4-trimethylcyclohexane



Marks
7

- Compound **X** undergoes an addition reaction on treatment with dilute aqueous sulfuric acid to form a mixture of diol compounds.

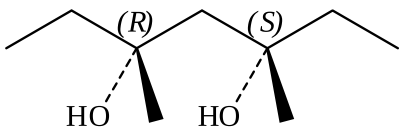
X



Draw all possible products (major and minor) that can form from this reaction. Take care to represent clearly the stereochemistry of all the products.

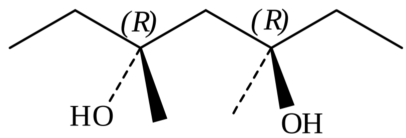
Major (from Markovnikov's rule)

achiral



(3*R*,5*S*)-3,5-dimethylheptane-3,5-diol

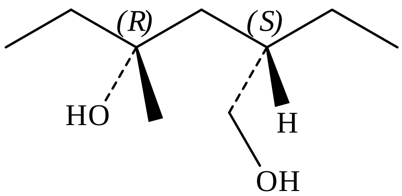
chiral



(3*R*,5*R*)-3,5-dimethylheptane-3,5-diol

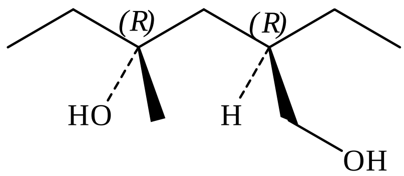
Minor (anti-Markovnikov)

chiral



(2*S*,4*R*)-2-ethyl-4-methylhexane-1,4-diol

chiral



(2*R*,4*R*)-2-ethyl-4-methylhexane-1,4-diol

Clearly label each isomer drawn above as either chiral or achiral (not chiral).

Circle one of the isomers that you expect to be a major product of the reaction and provide a full systematic name for this compound below. Make sure you include all relevant stereochemical descriptors.

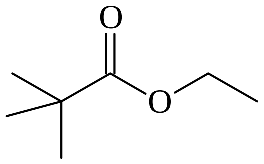
See above

Marks
5

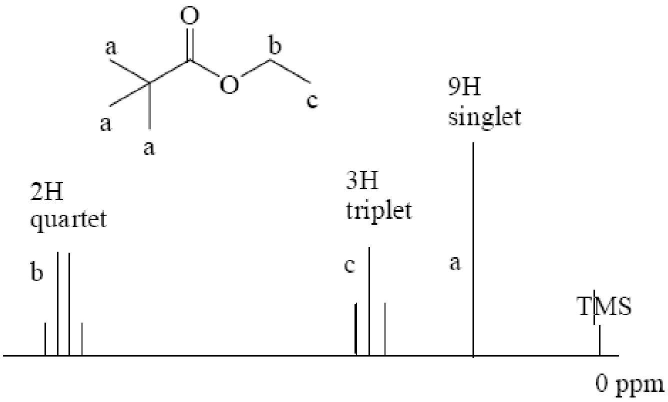
- Compound **Y** can readily be identified by ^{1}H NMR spectroscopy.

  On the diagram of **Y**, write the letters **a**, **b**, **c**, *etc*. as necessary to identify each unique hydrogen environment giving rise to a signal in the ^{1}H NMR spectrum.

Y

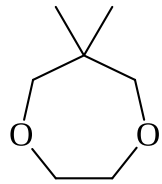


Sketch the ^{1}H NMR spectrum of compound **Y**. Label each signal in the spectrum with **a**, **b**, **c**, *etc.* to correspond with your assignments on the diagram of **Y**. Make sure you show the splitting pattern (number of fine lines) you expect to see for each signal. Also write the relative number of hydrogens you expect above each signal.



Compound **Z** is an isomer of **Y**.

Z



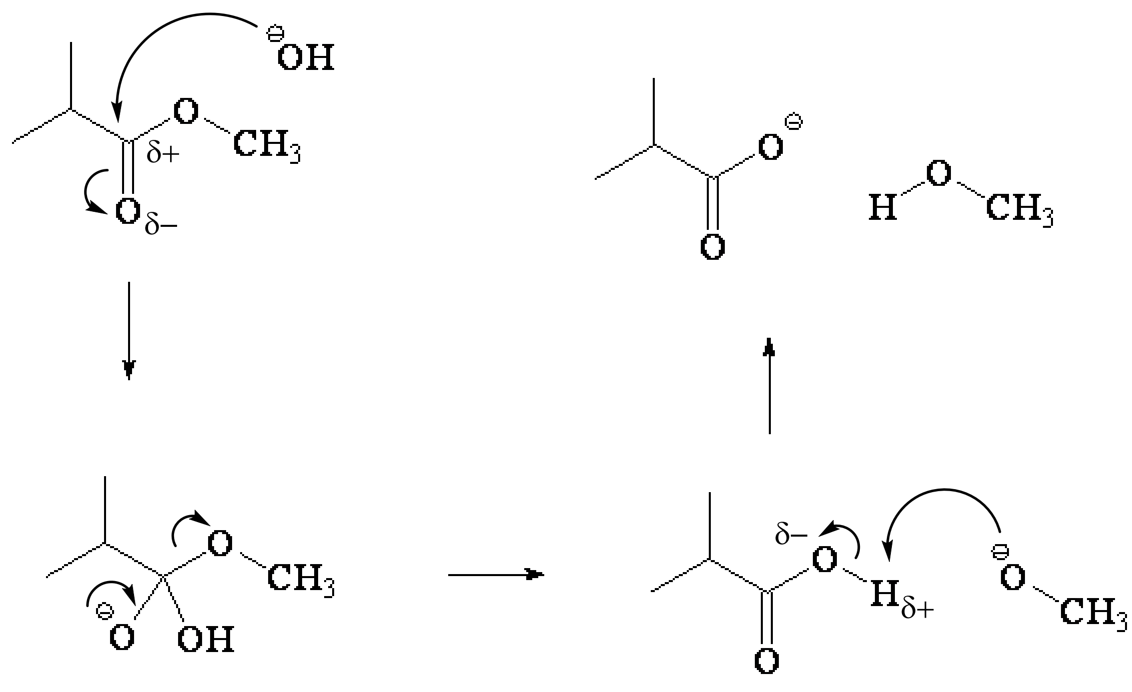
What kind of isomers are they? **Constitutional isomers**

Compounds **Y** and **Z** can be readily distinguished based on the analysis of spectroscopic data. Suggest three differences that would distinguish between the two structures.

(1) IR spectroscopy: Y has strong carbonyl absorption at about 1700 cm^{-1}. Z does not.
(2) Z has 3 signals (all singlets) with relative intensities of 3:2:2. in its ^{1}H NMR spectrum; Y has 3 signals (singlet, triplet and quartet) with relative intensities of 9:2:3 in its ^{1}H NMR spectrum.
(3) Z has 4 signals in its ^{13}C NMR spectrum, Y has 5 signals in its ^{13}C NMR spectrum.
(4) The fragmentation patterns in the mass spectrum will differ: for example. Y will give a peak due to the CH_3CH_2 group on the ester.

- Complete the mechanism for the reaction given below. Draw partial charges and curly arrows as appropriate to illustrate the bonding changes that take place.

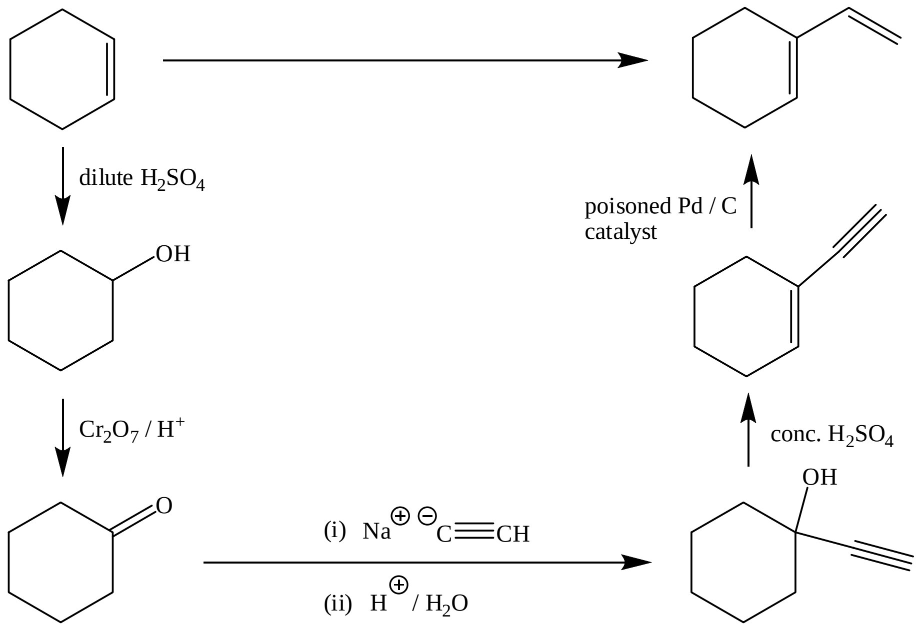
Marks
3



Marks
4

- Show clearly the reagents you would use to carry out the following chemical conversion. Draw constitutional formulas for any intermediate compounds.
  NOTE: More than one step is necessary.

Route 1:



Route 2: