

21st



**6 theoretical problems
2 practical problems**

THE TWENTY-FIRST INTERNATIONAL CHEMISTRY OLYMPIAD 2–10 JULY 1989, HALLE, GERMAN DEMOCRATIC REPUBLIC

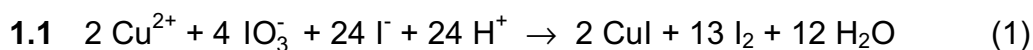
THEORETICAL PROBLEMS

PROBLEM 1

To determine the solubility product of copper(II) iodate, $\text{Cu}(\text{IO}_3)_2$, by iodometric titration in an acidic solution (25 °C) 30.00 cm³ of a 0.100 molar sodium thiosulphate solution are needed to titrate 20.00 cm³ of a saturated aqueous solution $\text{Cu}(\text{IO}_3)_2$.

- 1.1 Write the sequence of balanced equations for the above described reactions.
1.2 Calculate the initial concentration of Cu^{2+} and the solubility product of copper(II) iodate. Activity coefficients can be neglected.

SOLUTION



- 1.2 From (2):

$$n(\text{S}_2\text{O}_3^{2-}) = c V = 0,100 \text{ mol dm}^{-3} \times 0,03000 \text{ dm}^3 = 3,00 \times 10^{-3} \text{ mol}$$

From (2) and (1):

$$n(\text{I}_2) = 1,50 \times 10^{-3} \text{ mol}$$

$$n(\text{Cu}^{2+}) = \frac{1,50 \times 10^{-3} \text{ mol}}{13} \times 2 = 2,31 \times 10^{-4} \text{ mol}$$

$$c(\text{Cu}^{2+}) = \frac{2,31 \times 10^{-4} \text{ mol}}{0,02000 \text{ dm}^3} = 1,15 \times 10^{-2} \text{ mol}$$

$$[\text{Cu}^{2+}] = 1,15 \times 10^{-2}$$

$$[\text{IO}_3^-] = 2 [\text{Cu}^{2+}]$$

$$K_{sp} = [\text{Cu}^{2+}] [\text{IO}_3^-]^2 = 4 [\text{Cu}^{2+}]^3 = 4 \times (1.15 \times 10^{-2})^3 = 6.08 \times 10^{-6}$$

PROBLEM 2

A mixture of gases containing mainly carbon monoxide and hydrogen is produced by the reaction of alkanes with steam:



2.1 Using equations (1) and (2) write down an overall reaction (3) so that the net enthalpy change is zero.

2.2 The synthesis of methanol from carbon monoxide and hydrogen is carried out either
 a) in two steps, where the starting mixture corresponding to equation (3) is compressed from 0.1×10^6 Pa to 3×10^6 Pa, and the mixture of products thereof compressed again from 3×10^6 Pa to 6×10^6 Pa

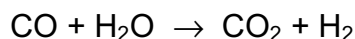
or

b) in one step, where the mixture of products corresponding to equation (3) is compressed from 0.1×10^6 Pa to 6×10^6 Pa.

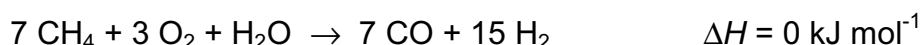
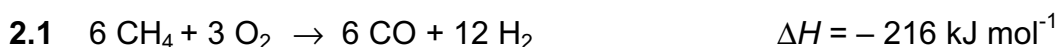
Calculate the work of compression, W_a , according to the two step reaction for 100 cm^3 of starting mixture and calculate the difference in the work of compression between the reactions 1 and 2.

Assume for calculations a complete reaction at constant pressure. Temperature remains constant at 500 K, ideal gas behaviour is assumed.

To produce hydrogen for the synthesis of ammonia, a mixture of 40.0 mol CO and 40.0 mol of hydrogen, 18.0 mol of carbon dioxide and 2.0 mol of nitrogen are in contact with 200.0 mol of steam in a reactor where the conversion equilibrium is established.



2.3 Calculate the number of moles of each gas leaving the reactor.

SOLUTION

- a) For a pressure increase in two steps under the conditions given, the work of compression is:

$$\begin{aligned}
 W_2 &= n_1 RT \ln \frac{p_1}{p_2} + n_2 RT \ln \frac{p_2}{p_1} = n_1 RT \left(\ln \frac{p_1}{p_0} + 2 \ln \frac{p_2}{p_1} \right) \\
 &= 100 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 500 \text{ K} \times \left(\ln \frac{3.0 \text{ MPa}}{0.1 \text{ MPa}} + 2 \ln \frac{6.0 \text{ MPa}}{3.0 \text{ MPa}} \right) = 1.99 \text{ MJ}
 \end{aligned}$$

- b) For a pressure increase in one step the work of compression only depends on n_2 , p_2 and p_0 :

$$W_1 = n_2 RT \ln \frac{p_2}{p_0} = 100 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 500 \text{ K} \times \ln \frac{6.0 \text{ MPa}}{0.1 \text{ MPa}} = 3.40 \text{ MJ}$$

It means

$$\Delta W = W_1 - W_2 = \underline{1.41 \text{ MJ}}$$

2.3 With $K = 3.3$, the following equilibrium is valid:

$$K = \frac{n_{\text{CO}_2} \times n_{\text{H}_2}}{n_{\text{CO}} \times n_{\text{H}_2\text{O}}} = \frac{(18 + x)(40 + x)}{(40 - x)(200 - x)}$$

$$x_{1/2} = 184 \pm 151.6; \quad x_1 = 33.2; \quad x_2 = 336.4$$

The composition of the leaving gas is:

6.8 mol CO, 51.2 mol CO₂, 2.0 mol CH₄ and N₂, 73.2 mol H₂ and 166.8 mol H₂O.

PROBLEM 3

Sulphur dioxide is removed from waste gases of coal power stations by washing with aqueous suspensions of calcium carbonate or calcium hydroxide. The residue formed is recovered.

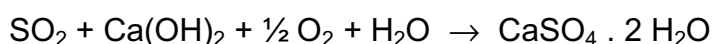
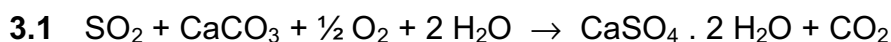
- 3.1** Write all reactions as balanced equations.
- 3.2** How many kilograms of calcium carbonate are daily consumed to remove 95 % of the sulphur dioxide if 10000 m³/h of waste gas (corrected to 0 °C and standard pressure) containing 0.15 % sulphur dioxide by volume are processed? How many kilograms of gypsum are recovered thereby?
- 3.3** Assuming that the sulphur dioxide is not being removed and equally spread in an atmospheric liquid water pool of 5000 m³ and fully returned on earth as rain, what is the expected pH of the condensed water?
- 3.4** If a sodium sulphite solution is used for absorption, sulphur dioxide and the sulphite solution can be recovered. Write down the balanced equations and point out possible pathways to increase the recovery of sulphur dioxide from an aqueous solution.

Note:

Protolysis of sulphur dioxide in aqueous solutions can be described by the first step dissociation of sulphurous acid. The dissociation constant $K_{a,1}(\text{H}_2\text{SO}_3) = 10^{-2.25}$.

Assume ideal gases and a constant temperature of 0 °C at standard pressure.

$M(\text{CaCO}_3) = 100 \text{ g mol}^{-1}$; $M(\text{CaSO}_4) = 172 \text{ g mol}^{-1}$.

SOLUTION

3.2 Under given conditions:

$$n(\text{SO}_2)/\text{h} = v(\text{SO}_2/\text{h}) / V = 669.34 \text{ mol h}^{-1}$$

$$m(\text{CaCO}_3/\text{d}) = n(\text{SO}_2/\text{h}) \times M(\text{CaCO}_3) \times 24 \text{ h} \cdot \text{d}^{-1} \times 0.95 = 1.53 \times 10^3 \text{ kg/d}$$

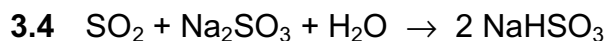
$$m(\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}) = \frac{M(\text{CaSO}_4 \cdot 2 \text{H}_2\text{O})}{M(\text{CaCO}_3)} \times m(\text{CaCO}_3) / d = 2.63 \times 10^3 \text{ kg/d}$$

$$3.3 \quad pH = -\log[\text{H}_3\text{O}^+]; \quad K_a = \frac{[\text{H}_3\text{O}^+]^2}{[\text{SO}_2] - [\text{H}_3\text{O}^+]}$$

$$[\text{H}_3\text{O}^+]_{1/2} = -\frac{K_a}{2} \pm \sqrt{\frac{K_a^2}{4} + K_a [\text{SO}_2]}$$

Solving for $[\text{H}_3\text{O}^+]$:

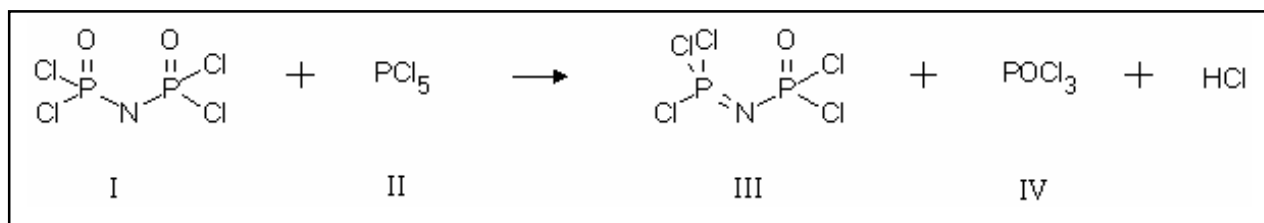
If $[\text{SO}_2] = n(\text{SO}_2) / V = 1.34 \times 10^{-4}$ and $K_a = 1 \times 10^{-2.25}$, then $[\text{H}_3\text{O}^+] = 1.32 \times 10^{-4}$ and $pH = 3.88$



Possibilities to increase the recovery of SO_2 are: temperature rise, reduced pressure, lower pH -value.

PROBLEM 4

³²P labelled phosphorus pentachloride (half-life $t_{1/2} = 14.3$ days) is used to study the electrophilic attack of a PCl_4^+ cation on nitrogen or on oxygen.



The reaction is carried out in CCl_4 and the solvent and product **IV** distilled off. Samples of **III** (remaining in the distillation flask), of **IV** (in the distillate) and samples of the starting material **II** are hydrolyzed by heating with a strong sodium hydroxide solution. The phosphate ions formed are precipitated as ammonium magnesium phosphate. Purified samples of the three precipitates are then dissolved by known volumes of water and the radioactivity measured.

- 4.1 Write the balanced equations for the reaction of red phosphorus forming PCl_5
- 4.2 Write the reaction equations for complete hydrolysis of the compounds **II** and **III** using sodium hydroxide.
- 4.3 How long does it take in order to lower the initial radioactivity to 10^{-3} of the initial value?
- 4.4 Write two alternative mechanisms for the reaction of labelled PCl_4^- with the anion of **I**.
- 4.5 After hydrolysis the precipitated ammonium magnesium phosphates show the following values for radioactivity:
 - II. 2380 Bq for 128 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$
 - III. 28 Bq for 153 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$
 - IV. 2627 Bq for 142 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$

Using these data, what can you say about the nucleophilic centre attacked by PCl_4^- ?

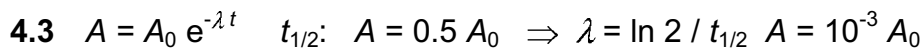
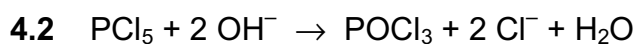
Data: For H_3PO_4 : $pK_1 = 2.2$; $pK_2 = 7.2$; $pK_3 = 12.4$

Solubility product of $\text{Mg}(\text{NH}_4)\text{PO}_4$: $pK_s = 12.6$

Equilibrium concentration of $\text{NH}_4^+ = 0.1 \text{ mol dm}^{-3}$

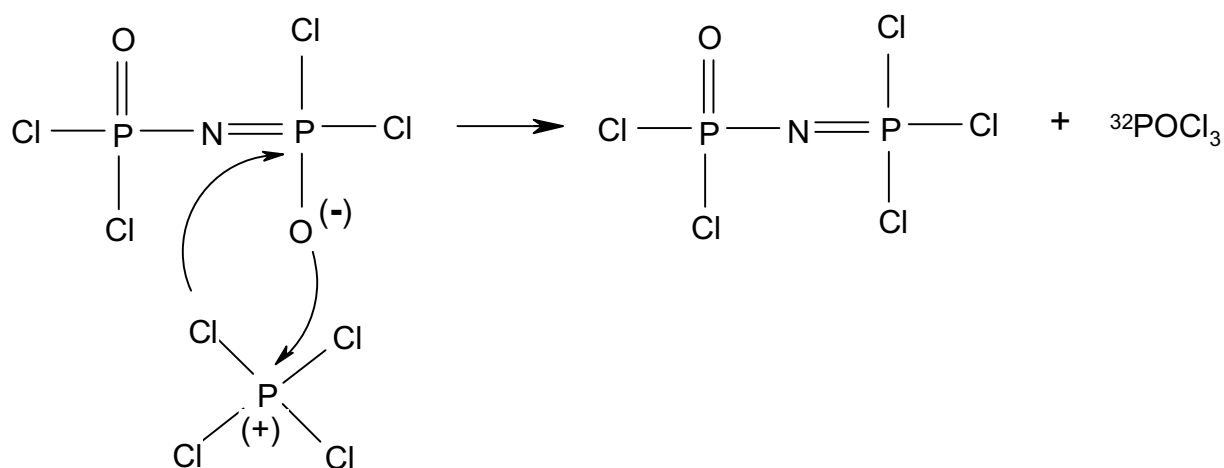
4.6 Calculate the solubility for $\text{Mg}(\text{NH}_4)\text{PO}_4$ at pH equal to 10 under idealized conditions (activity coefficients can be neglected).

SOLUTION

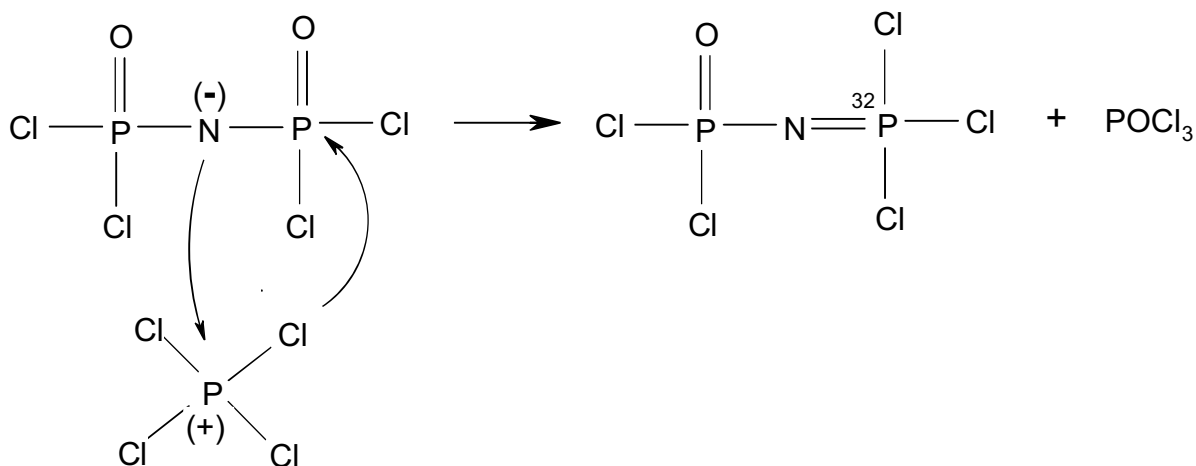


$$t = \frac{\ln A \ln A_0}{\lambda} = \frac{\ln 10^3}{\frac{\ln 2}{14.3}} \text{ d} = 142.5 \text{ d}$$

4.4



1st mechanism



2nd mechanism

- 4.5 Specific activities $A_{\text{sp}}(\text{II}) = 18.6 \text{ Bq/mg}$,
 $A_{\text{sp}}(\text{III}) = 0.18 \text{ Bq/mg}$,
 $A_{\text{sp}}(\text{IV}) = 18.5 \text{ Bq/mg}$.

Because of $A_{\text{sp}}(\text{II}) \approx A_{\text{sp}}(\text{IV})$ the first mechanism, proposed in d), is probable and therefore it is PCl_4^+ that attacks the O-atom.

- 4.6 Given data: $K_{\text{sp}} = [\text{Mg}^{2+}][\text{NH}_4^+][\text{PO}_4^{3-}] = 10^{-12.6}$; $[\text{NH}_4^+] = 0.1$; $\text{pH} = 10$; $\text{p}K_1 = 2.2$;
 $\text{p}K_2 = 7.2$; $\text{p}K_3 = 12.4$.

Exact solution:

$$2 [\text{Mg}^{2+}] + [\text{NH}_4^+] + [\text{H}_3\text{O}^+] = [\text{H}_2\text{PO}_4^-] + 2 [\text{HPO}_4^{2-}] + 3 [\text{PO}_4^{3-}] + [\text{OH}^-]$$

$$[\text{HPO}_4^{2-}] = \frac{[\text{PO}_4^{3-}][\text{H}^+]}{K_3}$$

$$[\text{H}_2\text{PO}_4^-] = \frac{[\text{HPO}_4^{2-}][\text{H}^+]}{K_2} = \frac{[\text{PO}_4^{3-}][\text{H}^+]^2}{K_2 K_3}$$

$$[\text{PO}_4^{3-}] = \frac{K_{\text{sp}}}{[\text{NH}_4^+][\text{Mg}^{2+}]}$$

$$\Rightarrow 2 [\text{Mg}^{2+}] = \left(\frac{[\text{H}^+]^2}{K_1 K_3} + \frac{2 [\text{H}^+]}{K_3} + 3 \right) \frac{K_{\text{sp}}}{[\text{NH}_4^+]} - [\text{Mg}^{2+}] ([\text{NH}_4^+] + [\text{H}^+] - [\text{OH}^-])$$

etc.

A simpler solution:

At pH = 10 the main component is HPO_4^{2-} :

$$[\text{HPO}_4^{2-}] = \frac{[\text{PO}_4^{3-}][\text{H}^+]}{K_3} = 10^{2.4} [\text{PO}_4^{3-}]$$

$$[\text{H}_2\text{PO}_4^-] = \frac{[\text{HPO}_4^{2-}][\text{H}^+]}{K_2} = 10^{-2.8} [\text{HPO}_4^{2-}]$$

$$S = [\text{Mg}^{2+}] [\text{HPO}_4^{2-}] \text{ and } K_{sp} = [\text{NH}_4^+] \times S \times K_3 \times \frac{S}{[\text{H}^+]}$$

$$pS = 0.5 (pK_{sp} + pH - pK_3 - p[\text{NH}_4^+]) = 0.5 (12.6 + 10.0 - 12.4 - 1.0) = 4.6;$$

$$S = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$$

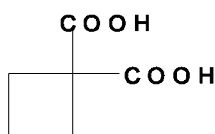
PROBLEM 5

Carboxylic acids are a chemically and biologically important class of organic compounds.

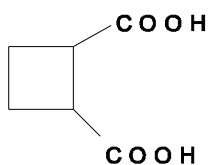
- 5.1 Draw the constitutional (structural) formulae of all isomeric cyclobutanedicarboxylic acids and give the systematic names for these compounds.
- 5.2 There are three stereoisomers, I, II and III, of cyclobutane-1,2-dicarboxylic acid. Draw perspective or stereo formulas of I, II and III indicating the relative configuration of each molecule.
- 5.3 Which pairs of stereoisomers I, II and III are diastereoisomers and which are enantiomers of each other?
- 5.4 Which reaction can be used to determine the relative configuration of diastereoisomers?
- 5.5 How may the enantiomers of cyclobutane-1,2-dicarboxylic acid be separated?
- 5.6 Indicate the absolute configurations of each asymmetric centre on the structures of the stereoisomers I, II and III using the Cahn-Ingold-Prelog rules (*R,S* system).

SOLUTION

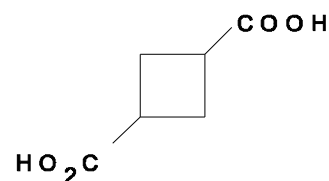
- 5.1 Constitutional isomers:



1,1 - cyclobutane -
dicarboxylic acid

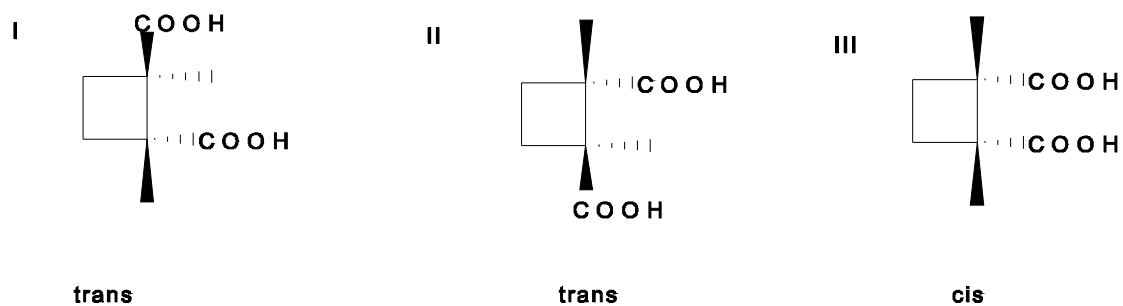


1,2 - cyclobutane -
dicarboxylic acid



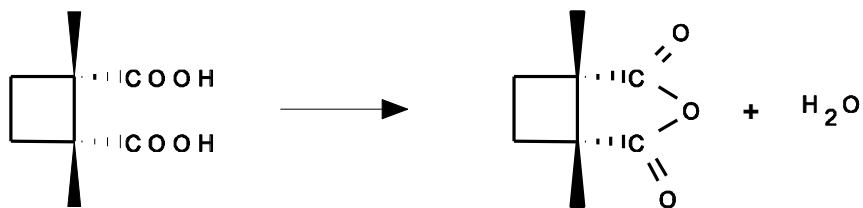
1,3 - cyclobutane -
dicarboxylic acid

- 5.2 Stereoisomers:



5.3 Diastereomers are I, III and II, III. Enantiomeric pairs are I and II.

5.4 On losing water the *cis*-diastereomer forms the corresponding anhydride according to:



5.5 The trans-diastereomer can be precipitated with an optically active base.

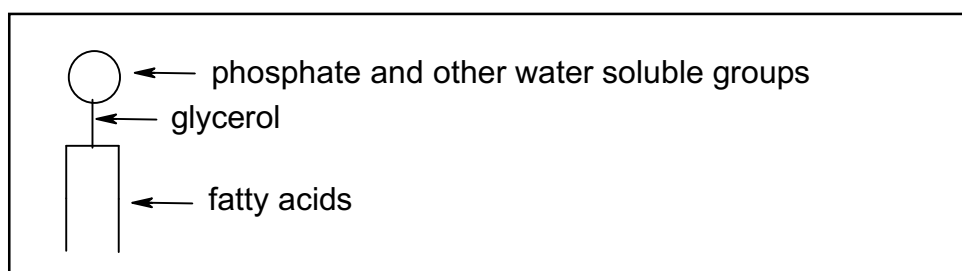
5.6 Stereoisomers absolute configuration:

I: *R,R*; II: *S,S*; III: *R,S*

PROBLEM 6

Fats (lipids) contain a non-polar (hydrophobic) and a polar (hydrophilic) group. The lipids insoluble in water, have important biological functions.

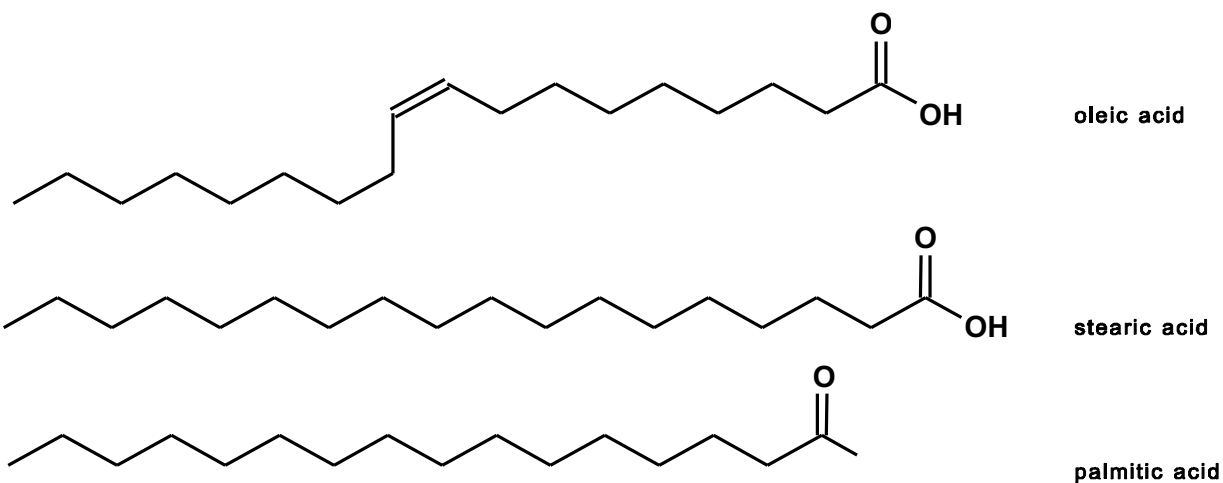
- 6.1 Draw the structures of Z-octadec-9-enoic acid (oleic acid), octadecanoic acid (stearic acid), and hexadecanoic acid (palmitic acid).
- 6.2 Using these three fatty acids in part 6.1 draw one possible structure of a triacyl glyceride.
- 6.3 Write the equation for the hydrolysis reaction of your triacyl glyceride in part 6.2 in aqueous NaOH solution. Give the mechanism of the hydrolysis of one of the fatty acids from your glyceride.
- 6.4 Which of the following fatty acids, $C_{21}H_{43}COOH$, $C_{17}H_{35}COOH$ or $C_5H_{11}COOH$, is the least soluble in water?
- 6.5 Phospholipids are an important class of bioorganic compounds. Draw the structure of the phosphatidic acid derived from your triacyl glyceride in part 6.2.
- 6.6 Phospholipids are frequently characterized by the diagram:



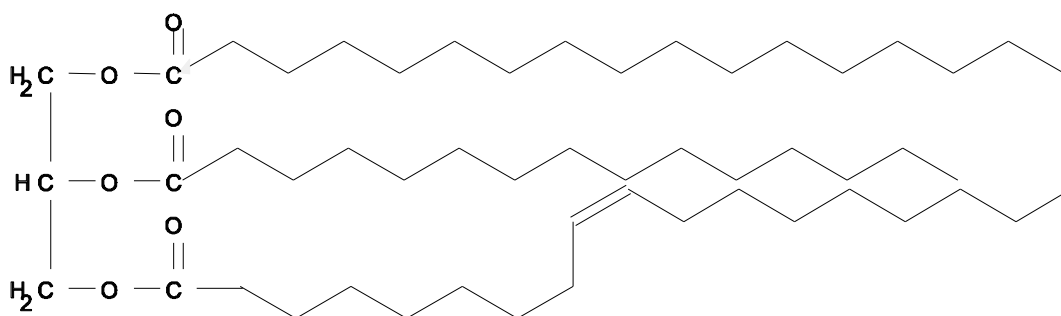
- Mark the hydrophilic and hydrophobic groups on a copy of the above diagram.
- Draw two possibilities for the association of six identical molecules of a phospholipid in water using the above diagram.
- Biomembranes consist of a phospholipid bi-layer. Draw such a model for a membrane using the above diagram.
- Such a model (iii) is incomplete. What other bio-macromolecules are contained in such biomembranes?

SOLUTION

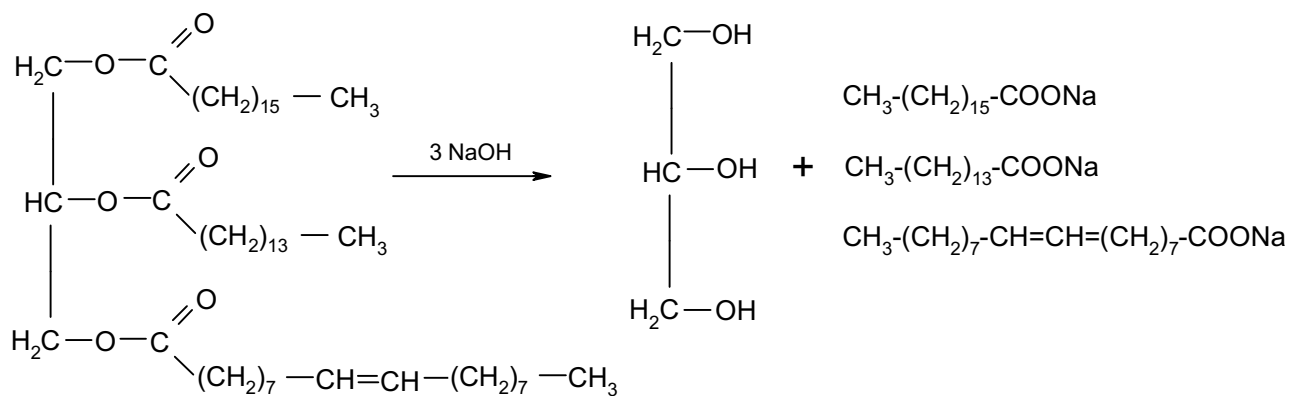
6.1

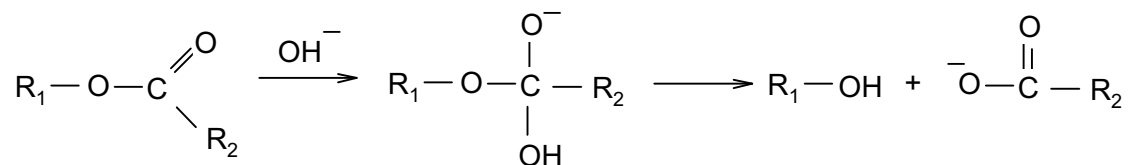


6.2 A possible structure of a triacyl glyceride with the fatty acids mentioned is:



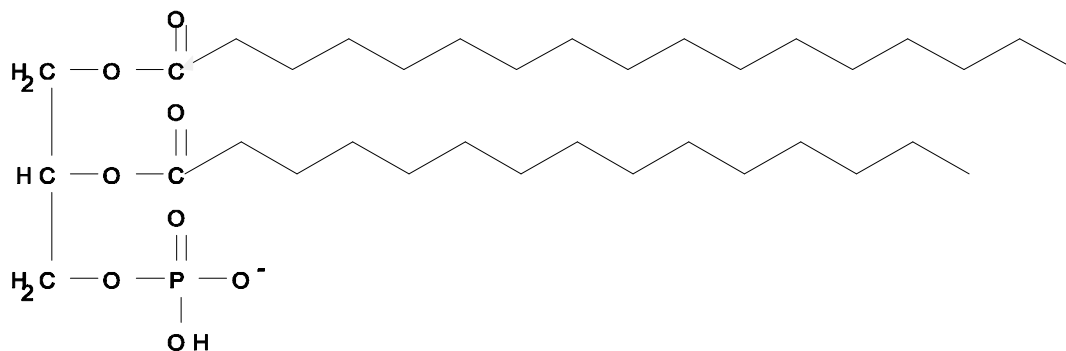
6.3



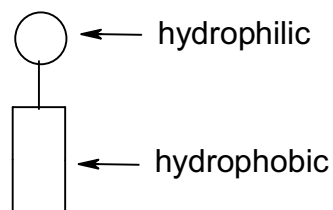


6.4 It is C₂₁H₄₃COOH.

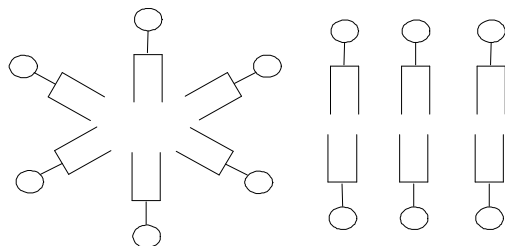
6.5 An example for a phospholipid is:



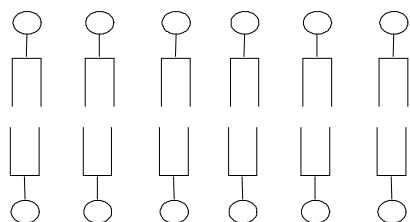
6.6 i)



ii)



iii)



phospholipid bilayer

iv) For example, proteins (enzymes)

PRACTICAL PROBLEMS**PROBLEM 1 (Practical)****Synthesis**

Preparation of 2-Ethanoxybenzoic Acid (Acetylsalicylic Acid, also known as Aspirin) by Ethanoylation (Acetylation) of 2-Hydroxybenzoic Acid (Salicylic Acid) with Ethanoic Anhydride (acetic anhydride).

Relative atomic masses: C: 12.011; O: 15.999; H: 1.008

Reagents

2-hydroxybenzoic acid (melting point 158 °C)

Ethanoic anhydride (boiling point 140 °C)

Phosphoric acid (85 % H₃PO₄)

Ethanol

Deionised/distilled water

Procedure

In a 100 cm³ Erlenmeyer flask mix 2.760 g of 2-hydroxybenzoic acid (from weighing bottle A) with 5.100 g of ethanoic anhydride (from flask B), and with cautious swirling add 5 – 7 drops of 85 % phosphoric acid. Heat the flask to 70 – 80 °C in a beaker of near boiling water and maintain the mixture at this temperature for 15 minutes. Remove the flask from the water bath and, with gentle swirling, add dropwise 1 cm³ of deionised water to the still hot flask; then immediately add 20 cm³ of the cold deionised water all at once to the reaction flask. Place the flask in an ice bath. If no crystals are deposited, or if oil appears, gently scratch the inner surface of the flask with a glass rod while the flask remains in the ice bath.

Using a Büchner funnel, filter the product under suction. Rinse the flask twice with a small amount of cold deionised water. Recrystallize the crude product in the 100 cm³ Erlenmeyer flask using suitable amounts of water and ethanol. If no crystals form or if oil appears, scratch gently the inner surface of the flask with a glass rod. Filter the crystals under suction and wash with a small amount of cold deionised water. Place the

crystals on the porous plate to draw water from them. When the crystals have been air dried, transfer the product to the small glass dish labeled C. This dish has previously been weighed. The dish containing the product should be given to a technician who will dry it in an oven for 30 minutes at 80 °C.

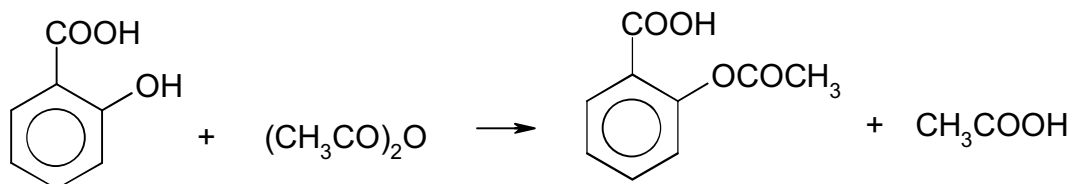
A technician should then weigh the cooled dish containing your product in your presence. Record the mass. The melting point will subsequently be taken by a technician to check the purity of your product.

Questions:

1. Write the balanced chemical equation for the reaction using structural formulae.
2. What is the percentage yield?

SOLUTION

1.



PROBLEM 2 (Practical)**Analysis**

Determination of Mass of a given Sample of 2-Ethanoyl-oxybenzoic Acid (Acetylsalicylic Acid, or Aspirin) by Volumetric Back Titration after Hydrolysis with Excess of Sodium Hydroxide.

Reagents

Aqueous solution of sodium hydroxide (about 0.5 mol dm^{-3})

Standard aqueous solution of hydrochloric acid ($0.4975 \text{ mol dm}^{-3}$)

Ethanolic phenolphthalein solution (indicator dropping bottle II)

Deionised/distilled water

Part 1:

Determine accurately the concentration of the about 0.5 mol dm^{-3} sodium hydroxide solution using the standard hydrochloric acid solution. (Record the answer as mol dm^{-3} with four places after decimal point.)

Procedure:

Pipette 20.00 cm^3 of the sodium hydroxide solution into a 300 cm^3 Erlenmeyer flask and dilute it to about 100 cm^3 with deionized water. Titrate the obtained solution with the standard $0.4975 \text{ mol dm}^{-3}$ hydrochloric acid solution using the phenolphthalein indicator. Repeat the procedure to produce three acceptable values and calculate the mean volume.

Part 2:

Determine accurately the mass of aspirin in Erlenmeyer flask I. Record your answer in g with three places after the decimal point.

Procedure:

Pipette 50.00 cm^3 of your standardized sodium hydroxide solution into the Erlenmeyer flask I (with a ground glass joint) which contains your unknown mass of aspirin. Add 3 – 5 boiling stones to the flask and boil the reaction mixture for 15 minutes using a reflux condenser and the electrical hot plate. After cooling, remove the reflux

condenser and rinse it with a small quantity of deionised water into Erlenmeyer flask I. Pour the whole solution into a 100.0 cm³ volumetric flask and fill it exactly to the mark with deionised water. Pipette 20.00 cm³ of this solution into a 300 cm³ Erlenmeyer flask and dilute to about 100 cm³ with deionised water. Back titrate the residual sodium hydroxide with the standard hydrochloric acid solution (0.4975 mol dm⁻³) using a 10 cm³ burette and phenolphthalein indicator. Repeat the volumetric procedure to produce three acceptable values and calculate the mean volume.

Questions:

- 1) Write the balanced chemical equation for the ester hydrolysis of aspirin by sodium hydroxide using structural formulae. Note that 1000 cm³ aqueous solution of 0.5000 mol dm⁻³ sodium hydroxide is equivalent to 0.0450 g of aspirin.
- 2) Calculate the mass of aspirin that you were given.

SOLUTION

1.

