

5th



International Chemistry Olympiad

**6 theoretical problems
3 practical problems**

THE FIFTH INTERNATIONAL CHEMISTRY OLYMPIAD 1–10 JULY 1973, SOFIA, BULGARIA

THEORETICAL PROBLEMS

PROBLEM 1

In nitrating a hydroxy derivative of benzene a compound is formed which contains 49.0 % by mass of oxygen. A charge of 4350 C is required for a total electroreduction of 0.458 g of the compound, efficiency being 80 %.

Problem:

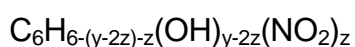
1.1 Determine the stoichiometric as well as structural formulas of the compound if the product of the electrochemical reduction is an aromatic hydroxy amino derivative.

$$F \text{ (Faraday's charge)} = 96\,500 \text{ C mol}^{-1}$$

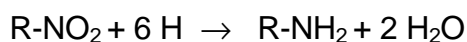
SOLUTION

1.1 a) Formula of the compound: $C_6H_xO_yN_z$

The compound is a hydroxy nitroderivative of benzene:



b) Equation of the reduction:



Combining mass of the compound:

$$E = \frac{M_r(\text{compound})}{6 z} \quad (1)$$

An amount of charge which is required for the electrochemical reduction:

$$Q = 4350 \text{ C} \times 0.8 = 3480 \text{ C}$$

Combining mass of the compound:

$$E = \frac{m}{\frac{3480 \text{ C}}{F}} = 0.458 \times \frac{96500 \text{ C}}{3480 \text{ C}} = 12.7$$

$$\text{In relation to (1): } M_r(\text{compound}) = 76.2 \times z \quad (2)$$

$$\text{c) } \% \text{ O} = \frac{y \times M_r(\text{O}) \times 100}{M_r(\text{compound})}$$

$$49 = \frac{y \times 16 \times 100}{M_r(\text{compound})}$$

$$M_r(\text{compound}) = 32.7 y$$

$$\text{d) } M_r(\text{compound}) = 6 M_r(\text{C}) + x M_r(\text{H}) + y M_r(\text{O}) + z M_r(\text{N})$$

$$M_r(\text{compound}) = 6 \times 12 + x + 16 y + 14 z$$

Taking into consideration the general formula of the unknown hydroxy derivative of benzene:

$$x = 6 - (y - 2 z) - z + y - 2 z$$

$$x = 6 - z \quad (4)$$

$$\text{Then: } M_r(\text{compound}) = 72 + 6 - z + 16 y + 14 z$$

$$M_r(\text{compound}) = 78 + 16 y + 13 z \quad (5)$$

By solving equations (2), (3), (4), and (5) we obtain:

$$\underline{M_r(\text{compound}) = 229}$$

$$x = 3$$

$$y = 7$$

$$z = 3$$

The molecular formula of the compound is: $\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ or $\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_3$.

The compound is 2, 4, 6-trinitrophenol

PROBLEM 2

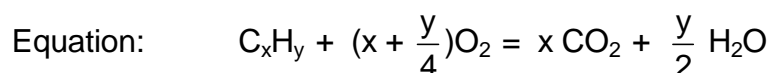
A mixture of a gaseous hydrocarbon and oxygen is in a vessel of a volume of 1 dm³ at a temperature of 406.5 K and a pressure of 101 325 Pa. There is twice as much oxygen in the mixture as is needed for the reaction with the hydrocarbon. After combustion of the hydrocarbon the pressure in the vessel (at the same temperature) is increased by 5 %.

Problem:

2.1 What hydrocarbon was in the mixture when the mass of water formed by the combustion was 0.162 g.

SOLUTION

2.1 Amounts of substances of reactants and reaction products:



$$n(\text{H}_2\text{O}) = \frac{m(\text{H}_2\text{O})}{M(\text{H}_2\text{O})} = \frac{0.162 \text{ g}}{18 \text{ g mol}^{-1}} = 0.009 \text{ mol}$$

$$n(\text{C}_x\text{H}_y) = \frac{0.009 \text{ mol}}{\frac{y}{2}} = \frac{0.018}{y} \text{ mol} \quad (1)$$

$$n(\text{O}_2) = \left(x + \frac{y}{4}\right) \times \frac{0.009 \text{ mol}}{\frac{y}{2}} = \frac{x + \frac{y}{4}}{y} \times 0.018 \text{ mol} \quad (2)$$

$$n(\text{CO}_2) = x \frac{0.009 \text{ mol}}{\frac{y}{2}} = \frac{x}{y} \times 0.018 \text{ mol} \quad (3)$$

Before reaction:

$$n(\text{mixture}) = \frac{pV}{RT} = \frac{101.325 \text{ kPa} \times 1 \text{ dm}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 406.5 \text{ K}} = 0.03 \text{ mol}$$

$$n(\text{C}_x\text{H}_y) + 2 n(\text{O}_2) = 0.03 \text{ mol} \quad (4)$$

After reaction: $p = 101.325 \text{ kPa} \times 1.05 = 106.4 \text{ kPa}$

$$n(\text{mixture}) = \frac{pV}{RT} = \frac{106.4 \text{ kPa} \times 1 \text{ dm}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 406.5 \text{ K}} = 0.0315 \text{ mol}$$

$$n(\text{CO}_2) + n(\text{O}_2) + n(\text{H}_2\text{O}) = 0.0315 \text{ mol}$$

$$n(\text{CO}_2) + n(\text{O}_2) = 0.0225 \text{ mol} \quad (5)$$

When (1), (2), and (3) are substituted in (4) and (5), an equation of two unknowns is obtained which when solved yields

$$x = 3; \quad y = 6$$

The stoichiometric formula of the unknown hydrocarbon is: C_3H_6 .

PROBLEM 3

Equal volumes (10 cm³) of 0.01-molar solutions of CH₃COOH and HClO were mixed and then diluted to a total volume of 100 cm³. Ionisation constant of CH₃COOH is equal to 1.8×10^{-5} and that for HClO is $3,7 \times 10^{-8}$.

Problems:

Calculate:

- 3.1 degree of ionisation for each of the acids in the solution,
- 3.2 degree of ionisation of HClO if the diluted solution would not contain CH₃COOH,
- 3.3 pH value for the solution containing at the same time CH₃COOH and HClO.

SOLUTION

CH₃COOH: K_1, α_1, c_1

HClO: K_2, α_2, c_2

$c_1 = c_2 = 1 \times 10^{-3} \text{ mol dm}^{-3} = c$

$$3.1 \quad K_1 = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(\alpha_1 + \alpha_2)c \times \alpha_1 c}{(1 - \alpha_1)c} = \frac{(\alpha_1 + \alpha_2)\alpha_1 c}{1 - \alpha_1} \quad (1)$$

$$K_2 = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]} = \frac{(\alpha_1 + \alpha_2)\alpha_2 c}{1 - \alpha_2} \quad (2)$$

$K_1 \gg K_2$, therefore also $\alpha_1 \gg \alpha_2$ and $\alpha_1 + \alpha_2 \approx \alpha_1$

$$K_1(1 - \alpha_1) = \alpha_1^2 c$$

$$c \alpha_1^2 + K_1 \alpha_1 - K_1 = 0$$

$$\alpha_1 = 0,125$$

When (2) is divided by (1):

$$\frac{K_2}{K_1} = \frac{(1 - \alpha_1)\alpha_2}{(1 - \alpha_2)\alpha_1}$$

After substitution of α_1 : $\alpha_2 = 2.94 \cdot 10^{-4}$

$$3.2 \quad K_2 = \frac{\alpha_2^2 c}{1 - \alpha_2}$$

$$\alpha_2 \ll 1$$

$$K_2 = \alpha_2^2 c$$

$$\alpha_2 = 6,08 \cdot 10^{-3}$$

$$3.3 \quad [\text{H}_3\text{O}^+] = \alpha_1 c + \alpha_2 c = (\alpha_1 + \alpha_2) c = (0,125 + 2,94 \times 10^{-4}) \times 10^{-3} \approx 1,25 \times 10^{-4} \text{ mol dm}^{-3}$$

pH = 3,9

PROBLEM 4

When solutions of two unknown substances are mixed together in stoichiometric ratio, 1.25 g of a precipitate are formed which contain a salt of a bivalent metal M. The precipitate when heated to 1100 °C is decomposed to 0.70 g of a solid metal oxide MO and another gaseous oxide. After evaporation of the filtrate, a dry residue with a mass of 2.0 g remains which yields two products by thermal decomposition at 215 °C: a gaseous oxide and 0.90 g of water vapour. The total volume of the gaseous mixture is 1.68 dm³ (at STP).

Problem:

- 4.1 Determine the unknown compounds and write chemical equations for the above mentioned reactions.

SOLUTION

- 4.1 a) Dry residue: 2.0 g

H₂O: 0.90 g, i. e. 0.05 mol

Gaseous oxide A_xO_y: 1.1 g

$$n(\text{mixture}) = \frac{1.68 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.075 \text{ mol}$$

$$n(\text{A}_x\text{O}_y) = n(\text{mixture}) - n(\text{H}_2\text{O}) = 0.025 \text{ mol}$$

$$M(\text{A}_x\text{O}_y) = \frac{1.1 \text{ g}}{0.025 \text{ mol}} = 44 \text{ g mol}^{-1}$$

$$x M(\text{A}) = M(\text{A}_x\text{O}_y) - y M(\text{O})$$

Solution 1:

$$\text{If } x = 1 \text{ and } y = 1, \text{ then } M(\text{A}) = M(\text{A}_x\text{O}_y) - M(\text{O}) = (44 - 16) \text{ g mol}^{-1} = 28 \text{ g mol}^{-1}$$

A = Si. It does not satisfy the requirements of the task.

Solution 2:

$$\text{If } x = 2 \text{ and } y = 1 \text{ then } M(\text{A}) = 14 \text{ g mol}^{-1}$$

A = N and the gaseous oxide is N₂O.

Solution 3:

$$\text{If } x = 1 \text{ and } y = 2 \text{ then } M(\text{A}) = 12 \text{ g mol}^{-1}$$

A = C and the gaseous oxide is CO₂.

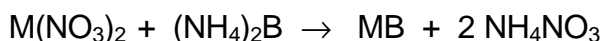
Solution 2 is correct, since it is known that gaseous N_2O is formed by thermal decomposition of NH_4NO_3 . This conclusion is supported by the following calculation:

$$M(\text{dry residue}) = \frac{2.0 \text{ g}}{0.025 \text{ mol}} = 80 \text{ g mol}^{-1} = M(\text{NH}_4\text{NO}_3)$$

Reaction of the thermal decomposition:



b) The precipitation reaction can be described by the following equation:



$$M(\text{MB}) = \frac{1.25 \text{ g}}{0.0125 \text{ mol}} = 100 \text{ g mol}^{-1}$$

$$M(\text{MO}) = \frac{0.70 \text{ g}}{0.0125 \text{ mol}} = 56 \text{ g mol}^{-1}$$

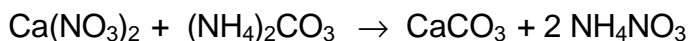
$$M(\text{M}) = M(\text{MO}) - M(\text{O}) = 56 - 16 = 40 \text{ g mol}^{-1}$$

M = Ca

Since

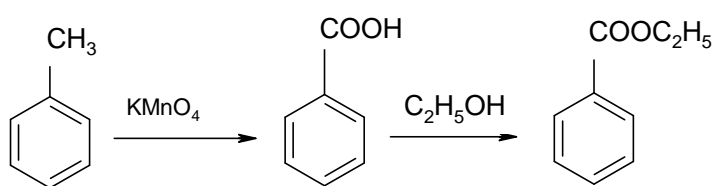
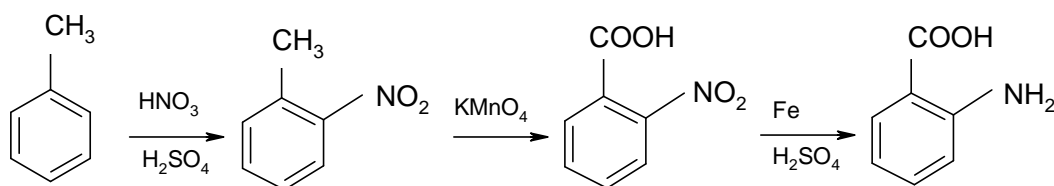
- the decomposition temperature of the precipitate is 1100 °C,
- the product of thermal decomposition is CaO,
- the molar mass of the precipitate is 100 g mol⁻¹,
- the precipitate is CaCO₃.

Reaction:

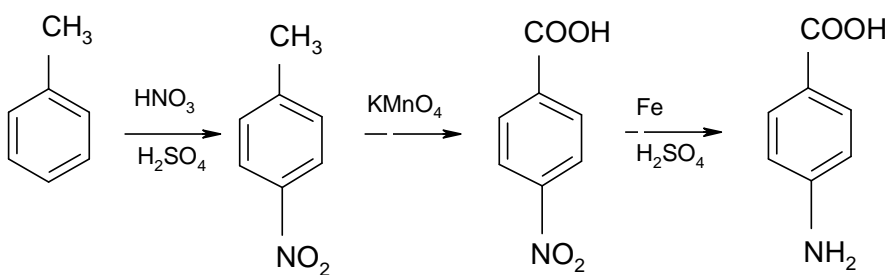
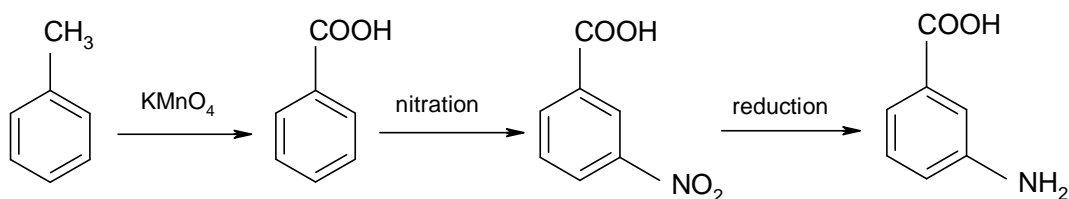


PROBLEM 5

Using your knowledge about the properties of benzene and its derivatives, write chemical equations for reactions by which ethyl ester of benzoic acid as well as o-, m-, and p-amino benzoic acids are prepared in the shortest way.

SOLUTION**a) Synthesis of ethyl ester of benzoic acid****b) Synthesis of o- and p-amino benzoic acid**

and simultaneously

**c) Synthesis of m-aminobenzoic acid**

PROBLEM 6

A gaseous mixture containing two neighbour hydrocarbons of the same homologous series was 14.4 times as dense as hydrogen. This mixture with a volume of 16.8 dm³ was hydrated and 350 g of the solution were obtained when the products of hydration were absorbed in water. Ten grams of this solution were taken and heated in the presence of silver(I) oxide which was prepared from 70 cm³ of a 1 N silver(I) nitrate solution. Unreacted Ag₂O was dissolved in an aqueous ammonia solution and a residual precipitate was filtered off. The filtrate was acidified with nitric acid and addition of an excess of sodium bromide to it resulted in 9.4 g of a precipitate.

When the mixture of the hydrocarbons that remained unreacted, was mixed with a 50 % excess of hydrogen and transmitted above a heated Pt-catalyst, its resulting volume decreased to 11.2 dm³. Volumes of gases were measured in STP conditions.

Problems:

- 6.1 What hydrocarbons were in the starting mixture?
- 6.2 Write chemical equations for the above mentioned reactions.
- 6.3 Calculate the composition of the starting mixture in % by volume.
- 6.4 How much (in %) of each hydrocarbon was hydrated?

SOLUTION

6.1 $M_r = 2 \times 14.4 = 28.8$

When reactivity of the hydrocarbons and the value of M_r are taken into consideration then the mixture can only be formed from CH₂=CH₂ ($M_r = 28$) and CH₃-CH=CH₂ ($M_r = 40$)

- 6.2 (1) $\text{CH} \equiv \text{CH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO}$
- (2) $\text{CH}_3\text{C} \equiv \text{CH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COCH}_3$
- (3) $2 \text{AgNO}_3 + 2 \text{NH}_3 + 2 \text{H}_2\text{O} \rightarrow \text{Ag}_2\text{O} + 2 \text{NH}_4\text{NO}_3$
- (4) $\text{CH}_3\text{CHO} + \text{Ag}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2 \text{Ag}$
- (5) $\text{Ag}_2\text{O} + 4 \text{NH}_3 + \text{H}_2\text{O} \rightarrow 2 [\text{Ag}(\text{NH}_3)_2]\text{OH}$

- (6) $\text{CH}_3\text{COOH} + \text{NH}_3 \rightarrow \text{CH}_3\text{COONH}_4$
 (7) $[\text{Ag}(\text{NH}_3)_2]\text{OH} + 3 \text{HNO}_3 \rightarrow \text{AgNO}_3 + 2 \text{NH}_4\text{NO}_3 + \text{H}_2\text{O}$
 (8) $\text{CH}_3\text{COONH}_4 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3 + \text{CH}_3\text{COOH}$
 (9) $\text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3$
 (10) $\text{AgNO}_3 + \text{NaBr} \rightarrow \text{AgBr} + \text{NaNO}_3$
 (11) $\text{CH} \equiv \text{CH} + 2 \text{H}_2 \rightarrow \text{CH}_3 - \text{CH}_3$
 (12) $\text{CH}_3\text{C} \equiv \text{CH} + 2 \text{H}_2 \rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_3$

6.3 According to (11) and (12) and regarding the excess of hydrogen, amounts of substances before catalytic hydrogenation are as follows:

$$n(\text{mixture}) = \frac{11.2 \text{ dm}^3}{2} = 5.6 \text{ dm}^3, \text{ i. e. } 0.25 \text{ mol}$$

$$26x + 40(0.25 - x) = 28.8 \times 0.25$$

$$x = 0.2$$

$$n(\text{C}_2\text{H}_2) = 0.2 \text{ mol}$$

$$n(\text{C}_3\text{H}_4) = 0.05 \text{ mol}$$

Before hydration:

$$n(\text{mixture}) = \frac{16.8 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.75 \text{ mol}$$

$$n(\text{AgNO}_3) = cV = 1 \text{ mol dm}^{-3} \times 0.07 \text{ dm}^3 = 0.070 \text{ mol}$$

According to (3):

$$n(\text{Ag}_2\text{O}) = 0.035 \text{ mol}$$

$$n(\text{AgBr}) = \frac{9.4 \text{ g}}{188 \text{ g mol}^{-1}} = 0.05 \text{ mol}$$

According to (10), (7) and (5):

$$\text{unreacted: } n(\text{Ag}_2\text{O}) = 0.025 \text{ mol}$$

$$\text{reacted: } n(\text{Ag}_2\text{O}) = 0.035 - 0.025 = 0.010 \text{ mol}$$

Due to dilution, reacted amounts of substances are as follows:

$$n(\text{CH}_3\text{CHO}) = n(\text{C}_2\text{H}_2) = 0.35 \text{ mol}$$

	hydration	hydrogenation	total
C ₂ H ₂	0.35 mol	0.20 mol	0.55 mol
C ₃ H ₄	0.15 mol	0.05 mol	0.20 mol
			Σ = 0.75 mol

$$\text{vol. \% C}_2\text{H}_2 = \frac{0.55 \text{ mol}}{0.75 \text{ mol}} \times 100 = 73.3$$

$$\text{vol. \% C}_3\text{H}_4 = \frac{0.20 \text{ mol}}{0.75 \text{ mol}} \times 100 = 26.7$$

6.4

$$\text{vol. \% C}_2\text{H}_2 = \frac{0.35 \text{ mol}}{0.55 \text{ mol}} \times 100 = 63.64$$

$$\text{vol. \% C}_3\text{H}_4 = \frac{0.15 \text{ mol}}{0.20 \text{ mol}} \times 100 = 75.0$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

The following solutions of salts are available in twelve numbered test-tubes: AgNO_3 , BaCl_2 , $(\text{NH}_4)_2\text{CO}_3$, NaCl , KI , ZnCl_2 , NH_4Cl , $\text{Pb}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, CrCl_3 , $\text{Cr}(\text{NO}_3)_3$, $\text{Hg}(\text{NO}_3)_2$.

The numbering of the test tubes does not correspond to the order of the salts given above. Prove the content of the test tubes by means of the least number of operations. In your answer align the proper salt with each number of the test tube. Write chemical equations for the reactions.

PROBLEM 2 (Practical)

Six test tubes contain the following compounds:

Na_2CO_3	or	NaHCO_3	NiCl_2	or	CuCl_2
AgNO_3	or	$\text{Pb}(\text{NO}_3)_2$	ZnCl_2	or	$\text{Al}(\text{NO}_3)_3$
ZnSO_4	or	KI	NH_4NO_3	or	$\text{Ba}(\text{NO}_3)_2$

The numbers of the test tubes do not correspond to the order of the compounds. Prove the content of each test tube by available reagents. Describe the reactions by chemical equations.

PROBLEM 3 (Practical)

There are three test tubes marked by numbers 1, 2, and 3. Prove the content of each test-tube by means of available reagents and write the proper formula of the compound to each number. Write chemical equations for the reactions.
