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КИНЕТИКА РАЗЛОЖЕНИЯ ДИОКСИДА ТИОМОЧЕВИНЫ В ВОДНО-ЭТАНОЛЬНО-АММИАЧНОМ РАСТВОРЕ

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На основе экспериментальных зависимостей концентрации диоксида тиомочевины от времени и данных литературы предложен стехиометрический механизм разложения диоксида тиомочевины в водно-этанольно-аммиачном растворе. Концентрацию диоксида тиомочевины и промежуточных продуктов его разложения определяли иодометрическим и полярографическим методами соответственно. Установлено, что при концентрации этанола менее 0,1 мольной доли разложение диоксида тиомочевины происходит по гетеролитическому механизму с образованием сульфоксиловой кислоты, а при высоких концентрациях спирта - по гомолитическому механизму с образованием анион-радикалов. Определены константы скорости отдельных стадий процесса разложения, рассчитаны абсолютные погрешности констант скорости, коэффициенты корреляции и критерии Фишера. Показано, что наблюдается линейная корреляция между логарифмом константы равновесия стадии распада диоксида тиомочевины и обратной величиной диэлектрической проницаемости водно-спиртовых растворов. С целью проверки предложенного механизма процесса разложения исследована кинетика восстановления ионов никеля (II) диоксидом тиомочевины в водно-аммиачном растворе с добавками этанола. Концентрация ионов никеля определялась методом комплексонометрического титрования. Установлено, что при концентрациях этанола не менее 0,13 мольной доли кинетика реакции описывается уравнением первого порядка по концентрации ионов никеля, а при меньших концентрациях спирта наблюдается дробный порядок по концентрации никеля. Предложен стехиометрический механизм указанной реакции, включающий стадии восстановления ионов никеля за счет молекул сульфоксиловой кислоты при концентрациях этанола менее 0,1 мольной доли и за счет ион-радикалов - при увеличении концентрации спирта, что подтверждает вывод о влиянии концентрации спирта на механизм разложения диоксида тиомочевины.

Ключевые слова: диоксид тиомочевины, стехиометрический механизм, кинетическая модель, константа скорости, восстановление никель-ионов

KINETICS OF THIOUREA DIOXIDE DECOMPOSITION IN WATER-ETHANOL-AMMONIA SOLUTION

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A stoichiometric mechanism for thiourea dioxide decomposition in water- ethanol-ammonia solution is proposed based on dependences of concentrations of thiourea dioxide over time and literature data. The concentration of thiourea dioxide was measured with iodometry, while the intermediates were qualitatively detected using the polarography. The set of the obtained data allows to consider that at low concentration of alcohol (approximately up to 0.1 molar ratio) the thiourea dioxide decomposition proceeds on the heterolytic mechanism with formation of sulfoxylic acid,

and at high concentrations of alcohol – on homolytic mechanism with the formation of anion radicals. Rate constants for individual stages of heterolytic mechanism are obtained by mathematical modeling, presented a system of differential equations. Absolute errors of rate constants, correlation coefficients, and F-factors were also calculated. The linear correlation was found between the equilibrium constant logarithm of the decay stage of thiourea dioxide and the inverse value of the dielectric constant of water-alcohol solutions. The kinetics of reduction of nickel ions with thiourea dioxide in an aqueous ammonia solution with ethanol additives was also studied. Concentration of nickel ions was determined using complexometric titration. Obtained kinetic data showed that at alcohol concentrations of 0.13 molar ratio and more, reaction kinetics is described by a first-order equation. At lower ethanol concentrations, a fractional order is observed on the concentration of nickel ions. A stoichiometric mechanism of this reaction is proposed due to sulfoxylic acid molecules with alcohol concentrations less than 0.1 molar ratio and due to radical ions with alcohol concentrations more than 0.1 molar ratio. Thus, the study of nickel ion reduction kinetics confirmed the conclusion about influence of alcohol concentration on the decomposition mechanism of thiourea dioxide.

Key words: thiourea dioxide, stoichiometric mechanism, kinetic model, rate constant, reduction of nikel-ions

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INTRODUCTION

The rates of reduction processes with thiourea dioxide (ThDO) are largely determined by the mechanism and rate of thiourea dioxide decomposition. The composition and nature of solvent plays a large role in this. In aqueous solutions, the decomposition of ThDO molecules proceeds heterolytically with the formation of sulfoxylic acid or its anions [1, 2] and urea. The reaction proceeds according to equation 1 in neutral and weakly acidic solutions.

$$(NH_2)_2CSO_2 + H_2O \leftrightarrow (NH_2)_2CO + H_2SO_2 \quad (1)$$

In weak alkaline solution the reaction proceeds according to equation 2.

$$(NH_2)_2CSO_2 + 2OH^- \rightarrow SO_2^{2-} + \\ + (NH_2)_2CO + H_2O \quad (2)$$

The decomposition of thiourea dioxide in a strongly alkaline medium (pH > 11) in the presence of dioxygen was studied and published in literature [3]. Under these conditions thiourea dioxide exhibits the strongest reductive properties. It is assumed that in the first stage of molecular decomposition, in addition to sulfoxylate anions, a carbon compound is formed with two imine groups according to the scheme:

$$(NH_2)_2CSO_2 + OH^- \rightarrow HSO_2^- + :C(NH)_2 + H_2O \quad (3)$$

The primary decomposition of ThDO in non-aqueous solvents proceeds mainly by the homolytically with forming of radical ions [4, 5]:

$$(NH_2)_2CSO_2 \rightarrow SO_2^{\dot{-}} + (NH_2)_2\dot{C}^+ \quad (4)$$

Additions of the non-aqueous component to the ThDO solution leads to a concurention between the heterolytic and homolytic mechanisms of the decomposition [6]. This, in turn, makes possibility to regulate the reducing activity with various substrates.

It should be noted that sulfoxylic acid and its anions are unstable and undergo further transformations with the formation of sulfite, thiosulfate and other sulfur-containing compounds [7, 8]. However, as shown in a number of processes, the limiting stage in the reduction processes using thiourea dioxide is decay ThDO molecules breaking of carbon – sulfur bond [9-11].

The influence of butanol, pentanol, octanol and decanol additions on thiourea dioxide decomposition rate and processes for preparation of powdered nickel and copper are presented in [12]. It was shown that alcohols additions lead to an increase in both the decomposition of thiourea dioxide and the reduction rate of nickel and copper ions.

The main task of this work is the finding the effect of aliphatic alcohols, which is well mixed with water and investigation of the mechanism and kinetics of ThDO decomposition.

EXPERIMENTAL

Thiourea dioxide was obtained by oxidation of commertially available thiourea, with hydrogen peroxide according to published method [13]. The purity of

ThDO in the final product is 98.0% according to iodometric titration [14].

The kinetic experiments were performed by dissolving 0.15-0.2 g of thiourea dioxide in distilled water, thermostating for 2 min under the temperature of 343 K and then adding 0.2ml of 0.2M aqueous ammonia solution and ethanol with concentration of 96%. The amounts of water and alcohol in various experiments were taken such that the total volume of mixture was been 20 ml.

The 2 ml of prepared solution was sampled at certain intervals of time during the decomposition. A cooled sample of 1ml then was transferred into the flask as well as 5 ml of 1% $NaHCO_3$ and 3 ml of 0.1N iodine solution. After that, the flask was placed in the dark for the 2 min. Then 5 ml of 2N HCl was added and the solution was titrated by 0.1N $Na_2S_2O_3$. The total concentration of ThDO and its decomposition's products were obtained using this way.

To determine the radical anion $SO_2^{\dot{-}}$, 1 ml of cooled reaction sample was transferred to a polarographic cell, 6 ml of Robinson-Britton buffer solution with pH 6.80 was added, purged with argon for 5 min. and then polarograms were recordeded, using a mercury dripping electrode as a working and silver chloride – as a reference electrode. The polarograph brand PU-1 was used. The potential sweep rate was 4 mV/s. The period of mercury dripping every 4 s was provided by a special device for the forced separation of the drop from the capillar. The radical anion was recorded by the appearance of a polarographic wave with a potential of -1.14V.

Conducting kinetic experiments on nickel ion reduction, 10 ml of nickel chloride solution and 10 ml of ThDO solution were mixed and kept in a thermostat for 2 min. Ammonia solution was added and sealed with a stopper. After a certain period of time, 1 ml of the reaction mass was taken, cooled in ice water to stop the reaction. The sample was analyzed for the content of nickel ions using complexometric titration [15]. For this, 1 ml of the cooled sample was transferred for titration, 5 ml of ammonia buffer solution, 10 ml of distilled water, and murexide was added and titrated with a 0.001N EDTA solution.

KINETICS

The rate constants of reaction stages were calculated using experimental data. The mathematical model of the process was presented as the system of differential rate equations in accordance with kinetic. The first step in determining numerical values of rate constants was the choice of their initial approximations. The search for optimal constant values was conducted using the *wkinet* software, developed at the department of physical chemistry, MSU.

Verification of proposed kinetic model was conducted using the comparison between experimental and calculated concentrations, F-test (Fisher criterion) and the calculated values of correlation coefficients for the individual stages of the process.

F-test's values (F_p) were calculated as the ratio of the combined variance of reproducibility $\sigma^2(c)$ to the excess variance σ_{res}^2 for each experiment [16]. The combined variance of reproducibility was calculated based on data of five parallel experiments using the following equation:

$$\sigma^2(c) = \frac{\sum_{i=1}^{k}\sum_{m=1}^{n}(C_{im}-\overline{C_{\imath m}})^2}{k(n-1)}. \qquad (5)$$

Where the i stands for the number of experimental concentration values in each m-experiment; n – the number of experiments; k – the number of the concentration measuring in each experiment; c_{im} – experimental concentration value; $\overline{c_{\imath m}}$– average concentration.

Variances were calculated for each experiment as the ratio of squares sums differences between calculated and observed concentration values to the difference between the number of measurements and the number of changed parameters.

F-test's value was calculated as the ratio of excess variances to the combined variance of reproducibility. It was compared at all times with literature data for significance level 0.05 and tied freedom degrees.

In order to find out the absolute error values in ratio constants and correlation coefficients the information matrix calculations [16] were conducted for each experiment via the following equation:

$$M = \sum_{u=1}^{N} F_u D^{-1} F_u^T, \qquad (6)$$

F_u – matrix of derivatives of reagents concentrations with respect to rate constants for time moments u. Each element is calculated using the equation:

$$\frac{\partial C_i}{\partial k_j} \approx \frac{\Delta\widehat{C_\imath}}{\Delta k_j} = \frac{\widehat{C_\imath}(k_j+\Delta k_j)-\widehat{C_\imath}(k_j)}{\Delta k_j}, \qquad (7)$$

$\hat{c}(k_j)$ – calculated concentration value of i-component in case of optimal rate constant value k_j; $\hat{c}_\imath\left(k_j + \Delta k_j\right)$ – calculated concentrationvalue of i-component in case of rate constant скорости $k_j + \Delta k_j$ (Δk_j=0.1k_j); D – dispersional-covariational matrix of concentrations. Experimental component concentrations were calculated using a system of differential rate equations. The following equation was used to calculate absolute errors for rate constants:

$$\delta k_i = \sqrt{\frac{1}{M_{ii}/_N}}, \qquad (8)$$

M_{ii} – diagonal matrix elements; N – the number of experiments.

Correlation coefficients were calculated as follows:

$$\rho_{k_i,k_j} = \frac{M_{ij}}{\sqrt{(M_{ii})(M_{jj})}}, \qquad (9)$$

M_{ij} – non-diagonal matrix elements.

RESULTS AND DISCUSSION

Fig. 1 and 2 show dependences of thiourea dioxide concentrations from the time during its decomposition in water – ammonia solution with ethanol additives. At low concentrations of ethanol (0.008-0.041 molar ratio) reaction order for thiourea dioxide is fractional, and at ethanol concentrations from 0.1 molar ratio and above it was the first. Reaction rate constants, calculated by first order kinetic equation, does not depend on the concentration of ethanol and their numerical value is 0.016 ± 0.004 min^{-1} at 70 °C.

Polarography of ThDO solutions with the addition of ethanol at concentrations above 0.1 molecular ratio showed presence of wave typical for anion-radical.

Analysis of experimental results and literature data suggests that at low concentrations of alcohol thiourea dioxide decomposition proceeds by heterolytic mechanism with the formation of sulfoxylic acid according to equation (1). The high concentrations of alcohol changed the mechanism of decomposition into homolytic to form of radical anions according to equation (4).

The difference in decomposition mechanisms is apparently possible due to a change in the structure of the solvent. Thus, in work [17], where Raman spectra of water – ethanol solutions were studied, it was found that energy of hydrogen bonding between molecules – components of solution changes at different alcohol concentrations. In the concentration range of 0.09-0.11 molar ratio alcohol the structure of an aqueous solution is stabilized by ethanol molecules and hydrogen bonds between hydroxyl groups. This conclusion also confirmed by data from other authors [18]. In experiments on Rayleigh light scattering by water - ethanol solutions the scattering maximum was observed at an alcohol concentration of 0.11 molar ratio. It is assumed that with a further increase in the concentration of alcohol there is a weakening of hydrogen bonds between molecules - components in binary solution.

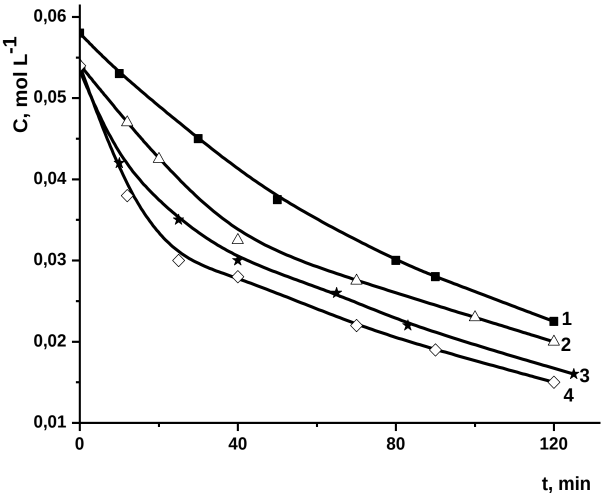

Fig. 1. Dependence of thiourea dioxide concentrations on the time. $X_{ethanol}$, molar ratio: 1 – 0.007; 2 – 0.016; 3 – 0.032; 4 – 0.041; C_{NH3} = 2.24·10^{-3} mol l^{-1}; T = 343 K

Рис. 1. Зависимость концентрации диоксида тиомочевины от времени. $X_{этанол}$, мольная доля: 1 – 0,007; 2 – 0,016; 3 – 0,032; 4 – 0,041; C_{NH3} = 2,24·10^{-3} моль/л; T = 343 K

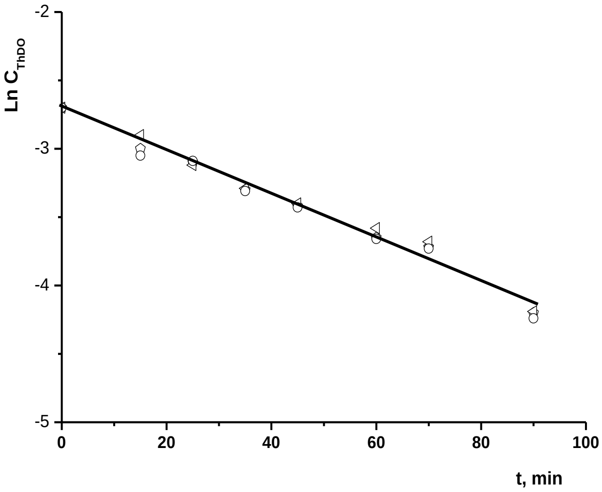

Fig. 2. Dependence of thiourea dioxide concentrations on the time. $X_{ethanol}$, molar ratio: o – 0.100; Δ- 0.240; ⌂ – 0.540; C_{NH3} = 2.24·10^{-3} mol l^{-1}; T = 343 K

Рис. 2. Зависимость натурального логарифма концентрации диоксида тиомочевины от времени. $X_{этанол}$, мольная доля: о – 0,100; Δ- 0,240; ⌂ – 0,540; C_{NH3} = 2,24·10^{-3} моль/л; T = 343 K

For small concentrations of alcohol, we calculated the rate constants of individual stages of ThDO decomposition, taking into account that the reversal stage (1) is followed by the decomposition stage of sulfoxylic acid molecules, as shown in [8].

$$(NH_2)_2CSO_2 + H_2O \xleftrightarrow[k_{-1}]{k_1} (NH_2)_2CO + H_2SO_2 \qquad (1)$$

$$H_2SO_2 \overset{k_2}{\rightarrow} SO + H_2O \qquad (10)$$

Reversibility of the stage (1) confirmed by the fact of slowing effect of urea additions on ThDO decomposition rate. Although the composition of SO from H_2SO_2 in (10) seems unlikely, it was mentioned previously [7].

The mathematic model of ThDO decomposition can be described as follows:

$$-\frac{dC_{(NH_2)_2CSO_2}}{d\tau} = k_1 C_{(NH_2)_2CSO_2} - $$
$$- k_{-1} C_{(NH_2)_2CO} C_{H_2SO_2} \qquad (11)$$

$$\frac{dC_{H_2SO_2}}{d\tau} = k_1 C_{(NH_2)_2CSO_2} - k_{-1} C_{(NH_2)_2CO} C_{H_2SO_2} - k_2 C_{H_2SO_2} \qquad (12)$$

The calculation of rate constants was carried out using the procedure described in the previous section. The initial approximations of the constants k_1, k_{-1}, k_2 are given in [8]. The values of rate constants calculated for different concentrations of ethanol and the F-test's values are shown in Table 1. Table 2 presents correlation coefficients between kinetic parameters.

Table 1

The optimal values of rate constants, the equilibrium constant of stage (1), F-test's values (F_p) and dielectric constants (ε) for different ethanol concentrations

Таблица 1. **Оптимальные значения констант скорости, константы равновесия стадии (1), значения критериев Фишера и относительная диэлектрическая проницаемость для различных концентраций водного раствора этанола**

$X_{ethanol}$, molar ratio	$k_1 \cdot 10^2$, min^{-1}	$k_{-1} \cdot 10^{-2}$, $L \cdot mol^{-1} \cdot min^{-1}$	$K_c \cdot 10^5$, $mol \cdot L^{-1}$	k_2, min^{-1}	F_p	$(F_p)_{tabl}$	ε
0.007	0.900±0.005	1.79±0.02	5.02	22±5	4.5	19.3	79
0.016	1.68±0.03	11.1±0.1	1.51	22±5	3.7	19.3	66
0.032	5.37±0.04	51.3±0.1	1.05	23±5	11	19	62
0.044	56.9±0.1	619.10±0.22	0.92	28±5	5.9	19.25	60

Table 2

Correlation coefficients ($\rho_{ki,kj}$) of rate constants for proposed model of ThDO decomposition

Таблица 2. **Коэффициенты корреляции констант скорости ($\rho_{ki,kj}$) для предлагаемой модели разложения диоксида тиомочевины**

$X_{ethanol}$, molar ratio	$\rho_{k_1,k_{-1}}$	ρ_{k_1,k_2}	$\rho_{k_2,k_{-1}}$
0.007	0.35	0.93	0.39
0.016	0.42	0.22	0.32
0.032	0.35	0.34	0.43
0.044	0.38	0.15	0.26

It can be assumed, that the proposed stoichiometric mechanism, including of stages (1) and (10), does not contradict to the experimental data, obtained for small concentrations of ethanol, and the calculated values of rate constants can be used in various processes using thiourea dioxide under reaction conditions.

It is of interest to establish a correlation between the calculated values of rate constants with some physicochemical properties of the solvent.

As well known, the radical reactions rate does not depends on solvent nature [19]. This is confirmed by the fact that homolytic decomposition of ThDO molecules rate in a water – ammonia solution in the presence of ethanol remains unchanged at various concentrations of alcohol (Fig. 2). At the same time, the rate of heterolytic decomposition of thiourea dioxide molecules should depend on the value characterizing electrical properties of medium, for example, polarity.

Table 1 shows dielectric constants for binary solvents water - ethanol (assuming that ammonia does not change dielectric constants of solvent and does not affect the qualitative nature of this dependence), calculated using Odelevsky equation [20]:

$$\varepsilon = A + \sqrt{A^2 + 0{,}5\varepsilon_1\varepsilon_2} \qquad (13)$$

$$A = 0{,}25[(3\theta_1\text{-}1)\ \varepsilon_1 + (3\theta_2\text{-}1)\ \varepsilon_2] \qquad (14)$$

In equations (13) and (14) θ_1 and θ_2 are molecular ratios of water and alcohol respectively; $\varepsilon_1 = 81$ is relative dielectric constant of water; $\varepsilon_2 = 24$ is relative dielectric constant of ethanol [21].

From the presented data (table 1), it follows that rate constants in both forward and backward stages increase with increasing alcohol concentration. In this case, a linear dependence in coordinates of Kirkwood equation between lnk and (ε-1)/(2 ε+1) is not observed. However, there is a linear correlation between of equilibrium constants for stage (1) and dielectric constant of solvents. It is expressed by the equation: $\ln K_c = -4.54 - 429\ (1/\varepsilon)$ with a correlation coefficient of 0.988. This is consistent with theoretical data on the effect of solvent dielectric constant on acid – base equilibrium, taking into account only electrostatic interactions [21]. Obviously, the influence of specific and nonspecific interactions of ThDO and its decomposition products with a solvent in the studied concentration range of a binary solvents are insignificant.

It can be assumed that a change in thiourea dioxide decomposition mechanism with an increase in alcohol concentration in binary solvent should change the reducing properties. From this point of view, experiments were carried out on the reduction of nickel cations by thiourea dioxide in solutions with different concentration of alcohol. The obtained kinetic dependences are shown in Fig. 3.

These data allow us to draw an analogy with kinetic dependences for thiourea dioxide decomposition with ethanol concentrations. At low concentrations of alcohol the reduction rate of nickel ions is smaller than at concentrations higher than 0.1 molar ratio. There is also a change of nickel ions concentration order. Curves 3 and 4 (Fig. 3), constructed in coordinates ln $[Ni^{2+}]$ = f (time), linearized as first order reaction on Ni^{2+}. On the other hand, for curves 1 and 2, there is no linear dependence in these coordinates.

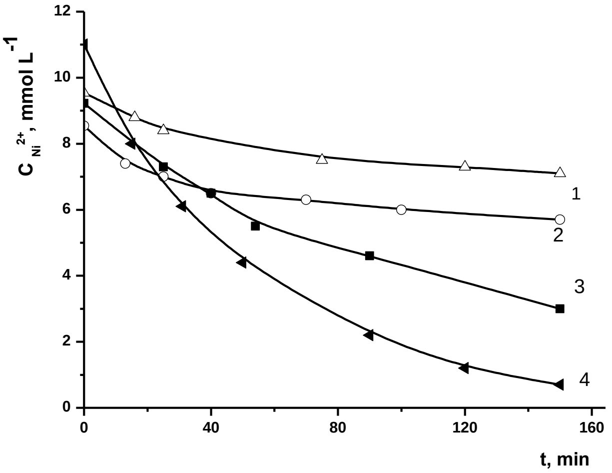

Fig. 3. The nickel cations concentrations dependence on the time. $X_{ethanol}$, molar ratio: 1 – 0.012; 2 – 0.033; 3 – 0.14; 4 – 0.24; C_{NH3} = 2.24·10^{-3} mol l^{-1}; T = 343 K; $C_{ThDO}{}^0$ = 0.059 mol l^{-1}

Рис. 3. Зависимости концентрации катионов никеля от времени. $X_{этанол}$, мольная доля: 1 – 0,012; 2 – 0,033; 3 – 0,14; 4 – 0,24; C_{NH3} = 2,24·10^{-3} моль/л; T = 343 K; $C_{ДОТМ}{}^0$ = 0,059 моль/л

Previously noted that at concentrations of ethanol less than 0.1 molecular ratio ThDO molecules break up by a heterolytic mechanism, at concentrations more than 0.1 molar ratio – homolytic. The results on study of nickel ions reduction confirm this conclusion.

At alcohol concentrations less than 0.1 molar ratio reduction of nickel ions proceeds, as shown in the literature [9], due to sulfoxylic acid according to equation (15).

$$Ni^{2+} + H_2SO_2 \rightarrow Ni + SO_2 + 2H^+ \qquad (15)$$

At concentrations more than 0.1 molar ratio the most likely reduction is due to radical ions by stoichiometric equations:

$$Ni^{2+} + 2\,SO_2^{\dot{-}} \rightarrow Ni + 2SO_2 \qquad (16)$$

Thus, when studying kinetics of reduction by thiourea dioxide in solution with ethanol additives, it is possible to take into account the fact that concentration of alcohol changed on the nature of reducing intermediates.

SUMMARY

When using thiourea dioxide in ethanol-water solutions, it is necessary to take into account that when alcohol concentrations exceed 0.1 molar ratio, the mechanism of decomposition of initial molecules and the nature of reducing intermediates are changed.

The work is presented of the research Institute of Thermodynamics and kinetics of chemical processes Ivanovo State University of Chemistry and Technology.

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