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КИНЕТИЧЕСКАЯ МОДЕЛЬ РАЗЛОЖЕНИЯ ДИОКСИДА ТИОМОЧЕВИНЫ В ВОДНЫХ РАСТВОРАХ РАЗЛИЧНОЙ КИСЛОТНОСТИ

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Предложен стехиометрический механизм полного разложения диоксида тиомочевины в водном растворе при pH 4,0, основанный на зависимости концентраций диоксида тиомочевины и продуктов его разложения во времени и литературных данных. Концентрация диоксида тиомочевины определялась иодометрическим методом, а промежуточных веществ – полярографически. Для полярографии использовали стеклянную двухэлектродную электрохимическую ячейку и полярограф типа ПУ-1 в дифференциальном режиме. В качестве рабочего использовался капельный ртутный электрод, а в качестве вспомогательного - хлоридсеребряный. Константы скорости для отдельных стадий определены путем математического моделирования на основании решения системы дифференциальных уравнений. Рассчитаны абсолютные погрешности констант скорости, коэффициенты корреляции и критерии Фишера. Верификация предполагаемой кинетической модели проводилась с использованием сравнения экспериментальных и расчетных концентраций, F-критерия и расчетных значений коэффициентов корреляции отдельных стадий процесса. Предполагаемая кинетическая модель разложения диоксида тиомочевины включает в себя ряд последовательных стадий с участием различных соединений, таких как монооксид серы, тиосерная, сернистая, дитионовая, сульфоксиловая кислоты в качестве промежуточных веществ. Для проверки универсальности модели проведено моделирование кинетики реакции разложения диоксида тиомочевины при значении pH 8,85. Экспериментальные кинетические данные были взяты из литературы. Начальные приближения констант отдельных стадий брались из предыдущих расчетов. Анализ совокупности полученных при моделировании расчетных данных: значений концентраций, критерия Фишера, коэффициентов корреляции позволил сделать вывод о применимости предлагаемого механизма процесса разложения диоксида тиомочевины также и в слабощелочной среде.

Ключевые слова: диоксид тиомочевины, стехиометрический механизм, кинетическая модель, константа скорости

KINETIC MODEL OF THIOUREA DIOXIDE DECOMPOSITION IN AQUEOUS SOLUTIONS OF DIFFERENT ACIDITY

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A stoichiometric mechanism for full thiourea dioxide decomposition in aqueous solution under pH of 4.0 is proposed based on dependences of concentrations of thiourea dioxide and its decomposition products on the time and literature data. The concentration of thiourea dioxide was measured via iodometry, while the intermediates were quantified using the polarography. Polarography was carried out in glass two-electrode electrochemical cell by means of PU-1 polarograph in differential mode. Dropping mercury electrode was used as working one and silver chloride as a reference one. Rate constants for individual stages are obtained via mathematical modeling, presented a system of differential equations. Absolute errors of rate constants, correlation coefficients, and F-factors were also calculated. Verification of supposed kinetic model was conducted using the comparison between experimental and calculated concentrations, F-test and the calculated values of correlation coefficients of the individual stages of the process. Supposed kinetic model of decomposition consists of a number of consequent stages including various compounds such as sulfur monoxide, thiosulfuric, sulfuric, dithionic, hydrosulfuric acids as intermediates was used for previously obtained data for pH of 8.85. To test the universality of supposed model, we simulated kinetics of thiourea dioxide decomposition reaction at pH of 8.85. Experimental kinetic data were taken from literature. The initial approximations of the individual stages constants were taken from previous calculations. Analysis of calculated data: concentration values, F-test, correlation coefficients allowed to conclude about the applicability of proposed mechanism for the process of thiourea dioxide decomposition in a weakly alkaline medium.

Key words: thiourea dioxide, stoichiometric mechanism, kinetic model, rate constant

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INTRODUCTION

Thiourea dioxide (ThDO) is a highly potent reducing compound in aqueous solutions. C-S bond in its molecule is easily ruptured and the products of ThDO decomposition cause its reducing ability [1-9].

Several works [10-16] demonstrate the first stage of thiourea dioxide decomposition in neutral medium to form sulfoxilic acid [17] and urea:

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

H_2SO_2 is unstable and decomposes further into sulfite ion, thiosulfate ion, and other sulfuric compounds.

In the literature [12] discovered that ThDO solutions are highly unstable under pH 11 and above. The decomposition will result in the formation of urea as the main nitrogenous compound and SO_2^{2-} as the primal sulfur-containing product.

The literature on the subject shows decomposition of thiourea dioxide in an aqueous solution to cause the formation of sulfur-containing intermediates with variable oxidation degrees, such as the sulfoxilic acid (H_2SO_2) or its anions (HSO_2^-, SO_2^{2-}), as well as dithionite-, sulfite- and thiosulfate-ions. Since that, ThDO decomposition and the formation of active reducing agents, determining speed and selectivity of reduction processes in aqueous solutions, are affected by various factors needed to be accounted for specifically.

Hence, the quantitative characteristics, e.g. rate constants of individual stages, are of particular interest. Previously we determined such parameters for the processes in weak acidic medium [14]. This paper contributes fundamental ground for the decomposition process by building a kinetic model and calculating rate constants of individual stages on the base of experimental data and already existing literature.

EXPERIMENTAL

Thiourea dioxide was obtained by oxidizing thiourea (99%), with hydrogen peroxide (30%) according to the method [14]. Mass fraction of ThDO in the final product is 95.5%. The purity of the compound was determined using the iodometric method [14].

Kinetic experiments under pH 4.0 were performed by dissolving 0.15-0.2 g of thiourea dioxide in 20 ml of distilled water, thermostating for 2 min under the temperature of 354 K and then adding 0.2 ml of 0.2 M ammonia solution and hermetically sealing the solution.

Reacting solution of 2 ml was sampled at certain intervals of time during the decomposition. The concentration of ThDO were determined by the method described in the work [14].

The concentrations of SO_3^{2-} and $S_2O_3^{2-}$ were determined by using polarography. Polarography was carried out in glass two-electrode electrochemical cell by means of PU-1 polarograph in differential mode. Dropping mercury electrode was used as working and silver chloride as a reference one. The solution was bubbled with argon in order to protect the dissolved particles from oxidation. The process was undertaken with the rate of potential sweep of 4 mV/s and mercury drop period of 4 s (provided by the special forced drop separation device).

Calibration method was used to determine the components concentration in the mixture. Britton-Robinson buffer was utilized as the background electrolyte.

A cooled sample of 1 ml was placed in the polarographic cell, next, 6 ml of Britton-Robinson buffer was added and the solution was bubbled with argon. Polarogram was obtained in the potential range from +0.3 V to -1 V. The first polarographic maximum was observed at -0.04 V relative to silver chloride electrode. It corresponds to the reduction of SO_3^{2-}. The second one was observed at -0.42 V being characteristic of $S_2O_3^{2-}$ reduction.

KINETICS

The search for optimal constant values was conducted using the *wkinet* software, developed at the department of physical chemistry, MSU. Verification of supposed kinetic model was conducted using the comparison between experimental and calculated concentrations, F-test and the calculated values of correlation coefficients of the individual stages of the process.

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 of ratio constants and correlation coefficients the information matrix calculations [18] were conducted for each experiment via the following equation:

$$\mathrm{M} = \sum_{\mathrm{u}=1}^{\mathrm{N}} \mathrm{F_u} \mathrm{D}^{-1} \mathrm{F_u^T} \qquad (2)$$

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

$$\frac{\partial \mathrm{C_i}}{\partial \mathrm{k_j}} \approx \frac{\Delta \widehat{\mathrm{C_\imath}}}{\Delta \mathrm{k_j}} = \frac{\widehat{\mathrm{C_\imath}}(\mathrm{k_j}+\Delta \mathrm{k_j}) - \widehat{\mathrm{C_\imath}}(\mathrm{k_j})}{\Delta \mathrm{k_j}} \qquad (3)$$

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

$$\delta \mathrm{k_i} = \sqrt{\frac{1}{\mathrm{M_{ii}}/\mathrm{N}}} \qquad (4)$$

Where Mii – diagonal matrix elements; N – the number of experiments.

Correlation coefficients were calculated as follows:

$$\rho_{\mathrm{k_i,k_j}} = \frac{\mathrm{M_{ij}}}{\sqrt{(\mathrm{M_{ii}})(\mathrm{M_{jj}})}} \qquad (5)$$

Where M_{ij} – non-diagonal matrix elements.

RESULTS AND DISCUSSION

Based on experimental and literature data we can assume ThDO decomposition process at pH 4.0 to be as following:

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

$$H_2SO_2 \overset{k_2}{\rightarrow} SO + H_2O \qquad (6)$$

$$2SO + H_2O \overset{k_3}{\rightarrow} H_2SO_3 + S \qquad (7)$$

$$SO + H_2SO_3 \overset{k_4}{\rightarrow} H_2S_2O_4 \qquad (8)$$

$$2H_2S_2O_4 + H_2O \overset{k_5}{\rightarrow} S + 3H_2SO_3 \qquad (9)$$

$$S + H_2SO_3 \overset{k_6}{\rightarrow} H_2S_2O_3 \qquad (10)$$

$$H_2S_2O_4 + S + 2H_2O \overset{k_7}{\rightarrow} H_2S + 2H_2SO_3 \qquad (11)$$

$$H_2S_2O_3 + S \overset{k_8}{\rightarrow} H_2S_3O_3 \qquad (12)$$

$$H_2S + S \overset{k_9}{\rightarrow} H_2S_2 \qquad (13)$$

Reversibility of the stage (1) is proven by the fact of slowing effect of urea addition on thiourea's decomposition. $H_2S_2O_4$, formed in (8), quickly decomposes (9, 11) in acidic medium [15]. This leads to the absence of dithionite-ions on polarograms. Thiosulfate is supposed to be produced in (10) and sources of sulfite ion is the sulfoxylic acid anhydride and $H_2S_2O_4$. We included (12) and (13) in the scheme because the end products of ThDO and dithionit-ion's decompositions are polysulphides and polythionates [19].

Note, that such system of reactions is the result of mass quantity of processed calculations, that included different combinations of stages from the literature. There were attempts to exclude some stages, for example, (12) and (13), or summarize stages, like (9) and (11). During this calculations molecularity lower or equal to 2 was a necessary condition (water molecules were an exception).

Mathematic model of ThDO decomposition was a system of differential rate equations for reactions (1), (6)-(13).

Rate constants k_1, k_2, k_{-1} were not varied during the search for the solution of reverse kinetic task due to them being previously determined [14].

Initial approximations for finding stage rate constants for composition and decomposition of dithionite-ion, k_4 and k_5, were taken from [20]: 0.51 l/(mol·min) and 0.01 l/(mol·min) accordingly. Evaluation of initial approximations for k_3 and k_6 was conducted based on starting kinetic curve sections for sulfite- and thiosulfate-ion on Fig. 1. The concentration of SO was approximated to be 10^{-6} mol/l and concentration of sulfite-ion to be 10^{-3} mol/l. Thus, initial approximations for k_3 and k_6 equated 10^8 and 10^2 accordingly. Initial approximations for k_7 were varied from 10^{-3} to 10^6.

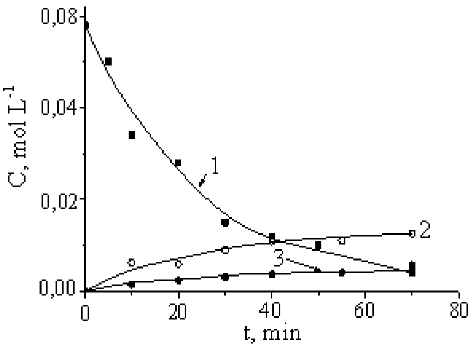


Fig. 1. Comparison between experimental (filled circle) and simulated (solid line) concentrations for the reaction of ThDO decomposition. T = 354 K, pH =4.0: (1) ThDO; (2) SO_3^{2-}; (3) $S_2O_3^{2-}$
Рис. 1. Сравнение между экспериментальными (значки) и расчетными (линии) значениями концентраций для реакции разложения ДОТМ. T = 354 K, pH =4,0: (1) ДОТМ; (2) SO_3^{2-}; (3) $S_2O_3^{2-}$

Modeling was conducted in two steps. The initial stage didn't include (12) and (13). After that, they were incorporated into the bigger picture, while initial approximations of rate constants k_3-k_7 were taken as optimized numbers from the previous stage. Initial approximations of constants k_8 and k_9 were also varied from 10^{-3} to 10^6 in order to obtain the minimal value of the sum of squares of differences of experimental and calculated concentration values for sulfite- and thiosulfate-ions.

Tab. 1 contains calculated rate constants for ThDO decomposition. Fig. 1 presents experimental and calculated kinetic curves for detected solution components.

Fig. 2 presents calculated kinetic curves for ThDO decomposition, unrelated to experimental data. At the same time the sulfoxilic acid anhydride concentration remains the same through the time and its value is approximately equal to 10^{-7} mol/l.

Table 1

Optimized kinetic parameters*) for proposed model of ThDO decomposition at pH 4.0

***Таблица 1.* Оптимальные значения кинетических параметров*) для предлагаемой модели разложения ДОТМ при pH 4,0**

Item	Value
k_1	$(7.1 \pm 0.1)\times10^{-2}$
k_{-1}	510 ± 50
k_2	22 ± 1
k_3	$(4.2 \pm 0.1)\times10^{9}$
k_4	$(5.9 \pm 0.1)\times10^{4}$
k_5	49 ± 4
k_6	574 ± 2
k_7	1027 ± 16
k_8	992 ± 5
k_9	584 ± 62
F_p	0.85
$(F_p)_{tab}$	4.07

*) unit for k1 and k2 is min^{-1}; for others rate constants is L mol^{-1} min^{-1}

*) значения для k1 и k2 имеют размерность $мин^{-1}$; для остальных констант размерность в л $моль^{-1}$ $мин^{-1}$

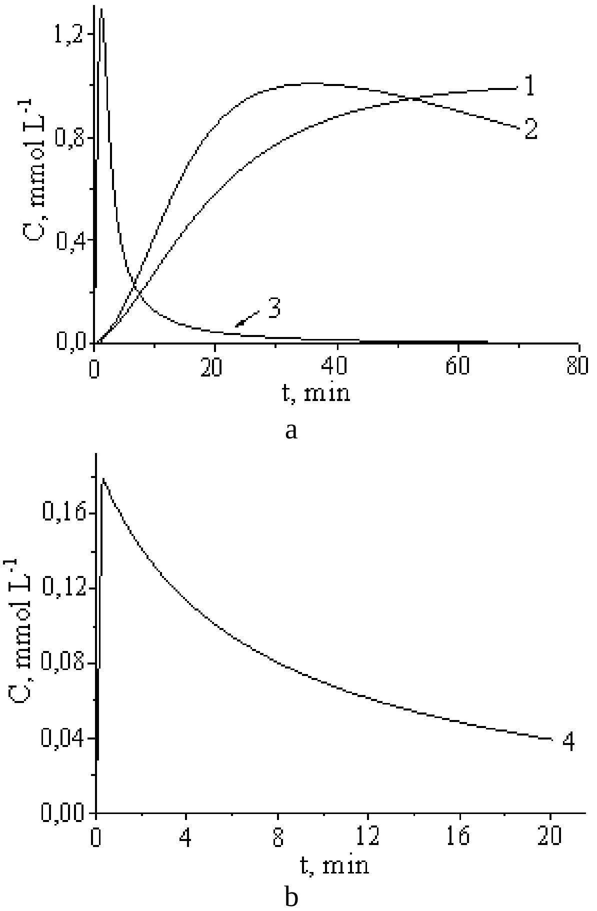
Table 2

Correlation coefficients ($\rho_{ki,\,kj}$) of rate constants for proposed model ThDO decomposition at pH 4.0

***Таблица 2.* Коэффициенты корреляции ($\rho_{ki,\,kj}$) для констант скорости предлагаемой модели разложения ДОТМ при pH 4,0**

i	$\rho_{ki,\,kj}$					
	J					
	3	4	5	6	7	8
4	0.997	-	-	-	-	-
5	0.857	0.814	-	-	-	-
6	0.805	0.757	0.996	-	-	-
7	0.999	0.998	0.872	0.799	-	-
8	0.517	0.450	0.877	0.927	0.496	-
9	0.990	0.988	0.776	0.715	0.994	0.393

Errors of calculated rate constants values and correlation coefficients (Tab. 2) were calculated according to procedure presented in “Kinetics” section.



a

b

Fig. 2. Simulated concentrations for the reaction of ThDO decomposition. T = 354 K, pH =4.0: (1) H_2S; (2) $H_2S_2O_4$; (3) S; H_2SO_2 (4)

Рис. 2. Расчетные значения концентраций для реакции разложения ДОТМ. T = 354 K, pH =4,0: (1) H_2S; (2) $H_2S_2O_4$; (3) S; H_2SO_2 (4)

Analysis of the results of modeling of full ThDO decomposition in aqueous ammonia solution under pH 4.0 indicates that supposed kinetic model describes changes in concentrations, present in the experimental data. However, many coefficients are close to 1. This fact indicates the ambiguousness of the obtained solutions for differential equations systems. In order to improve kinetic model, additional data is needed, for example, concentrations of other intermediate and final substances.

To verify supposed mechanism and kinetic model of full ThDO decomposition in aqueous solution experimental data, obtained in [19], were used. That data was obtained under pH 8.85.

Concentrations of ThDO, sulfite- and dithionite-ions were used in calculations. ThDO concentration was determined via iodometric titration. Dithionite- and sulfite-ions concentrations were determined using the polarographic method.

Unfortunately, authors did not search for the concentration of thiosulfate-ions. It could have increased the fidelity of kinetic parameters calculation.

It was expected that kinetic model of full ThDO decomposition under 8.85 pH can be described by the previously listed system of differential equations.

Rate constants k_1, k_2, k_3 were calculated by using Arrhenius equation on activation energies values [14] and were not varied during the following steps.

Table 3

Optimized kinetic parameters*) for proposed model of ThDO decomposition at pH 8.85

Таблица 3. **Оптимальные значения кинетических параметров для предлагаемой модели разложения ДОТМ при рН 8,85**

Item	Value
k_1	$(1.4 \pm 0.1)\times10^{-2}$
k_{-1}	3.6 ± 0.1
k_2	19.9 ± 0.1
k_3	$(8.1 \pm 0.5)\times10^{5}$
k_4	$(1.90 \pm 0.02)\times10^{3}$
k_5	1.60 ± 0.02
k_6	19.3 ± 0.1
k_7	37.20 ± 0.04
k_8	1.0 ± 0.2
k_9	120 ± 3
F_p	2.19
$(F_p)_{tab}$	3.84

*) unit for k1 and k2 is min^{-1}; for others rate constants is L mol^{-1} min^{-1}

*) значения для k1 и k2 имеют размерность мин$^{-1}$; для остальных констант размерность в л моль$^{-1}$ мин$^{-1}$

Table 4

Correlation coefficients ($\rho_{ki,\,kj}$) of rate constants for proposed model ThDO decomposition at pH 8.85

Таблица 4. **Коэффициенты корреляции ($\rho_{ki,\,kj}$) для констант скорости предлагаемой модели разложения ДОТМ при рН 8,85**

i	($\rho_{ki,\,kj}$)					
	J					
	3	4	5	6	7	8
4	0.89	-	-	-	-	-
5	0.93	0.98	-	-	-	-
6	0.47	0.83	0.75	-	-	-
7	0.42	0.79	0.71	0.98	-	-
8	0.76	0.96	0.94	0.91	0.99	-
9	0.82	0.98	0.99	0.99	0.99	0.99

Initial approximations for other constants were taken from calculations for pH 4.0. The search for their values was also conducted in two steps.

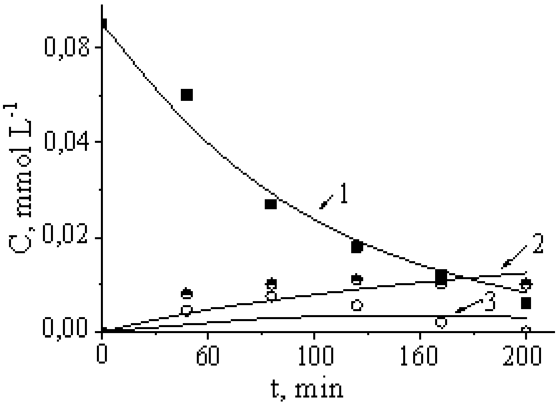


Fig. 3. Comparison between experimental (filled circle) and simulated (solid line) concentrations for the reaction of ThDO decomposition. T = 308 K, pH =8.85: (1) ThDO; (2) SO_3^{2-}; (3) $S_2O_4^{2-}$

Рис. 3. Сравнение между экспериментальными (значки) и расчетными (линии) значениями концентраций для реакции разложения ДОТМ. T = 308 K, pH =8,85: (1) ДОТМ; (2) SO_3^{2-}; (3) $S_2O_4^{2-}$

Tab. 3, 4 represents the calculated values of ThDO decomposition rate constants and correlation coefficients ($\rho_{ki,\ kj}$) of rate constants, while Fig. 3 – results of the concentrations calculations. Comparison of rate constants numerical values (Tab. 1 and 3) indicates the drastic decrease (in four orders of magnitude) of k_3 with the increase of pH. It is probably related to this stage being accelerated by H^+ via acidic catalysis.

The decrease in other constants values is more related to the decrease in temperature rather than changes in pH. It should be noted that concentration of sulfoxilic acid anhydride increased with the doubling of pH while average concentration value of sulfoxilate-ion decreased.

SUMMARY

Supposed stoichiometric mechanism of ThDO decomposition can be applied universally for pH from 4.0 to 8.85. However, in strong alkaline medium (pH>11) the process will differ as shown in introduction due to the stability of sulfoxilic acid.

The work is performed at the research Institute of Thermodynamics and kinetics of chemical processes.

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