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Decomposition of Thiourea Dioxide under Aerobic and Anaerobic Conditions in an Aqueous Alkaline Solution

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Abstract—The kinetics and mechanism of the decomposition of thiourea dioxide in an aqueous alkaline solution under aerobic and anaerobic conditions are established. It is discovered that along with the decomposition of thiourea dioxide molecules with C–S bond cleavage and the subsequent formation of sulfoxyl acid anions, there is a reversible stage of the formation of thiourea and peroxide anions. The rate constants of the indicated stages are determined via mathematical modeling using the experimental data.

Keywords: thiourea dioxide, kinetic model, complex reaction mechanism, electronic absorption spectra **DOI:** 10.1134/S0036024420100209

INTRODUCTION

Thiourea dioxide (TDO) or formamidine sulfinic acid in aqueous solutions is used as a reducing agent for both organic [1, 2] and inorganic [3–5] compounds. In concentrated aqueous-alkaline solutions, its activity is so high that it allows the reduction of cadmium cations to a metal with a fairly high negative redox potential [6]. It is known from numerous literature sources that the high reducing activity of TDO molecules is explained by their decomposition with breaking of the weak bonds between carbon and sulfur and the formation of intermediates: sulfoxyl acid anions $(SO_2^{2^-})$, radical anions $(\dot{S}O_2^{-})$, and dithionite anions $(S_2O_4^{2^-})$ [7–12]. These particles that have strong reducing properties.

It should be noted that the stoichiometric mechanism of decomposition of aqueous-alkaline solutions of thiourea dioxide has been studied in a number of works [13–15]. However, they did not determine the rate constants of the individual stages of the process nor perform a comparative analysis of the kinetics of the decomposition of TDO in air and inert atmospheres. One of the aims of this work was to solve these problems.

EXPERIMENTAL

Thiourea dioxide was synthesized from thiourea by oxidizing it with an aqueous solution of hydrogen peroxide, according to the procedure described in [16]. The content of the main substance in the final product, determined iodometrically, was 99.1% [17]. The IR absorption spectrum corresponded to that of aminoiminomethanesulfinic acid (another name for TDO), which was listed in the NIST Chemistry WebBook database. All reagents were of chemically pure grade.

Spectrophotometry was used to study the kinetics of TDO decomposition, since (according to the data of [18]) the initial material (thiourea dioxide) displays maximum absorption at $\lambda = 270$ nm in the electronic spectrum, but the reaction products do not absorb in this region of the spectrum. A LEKISS 2110 UV spectrophotometer (Finland) was used to measure electronic absorption spectra.

In our kinetic experiment, 1 g of NaOH was dissolved in a 100 mL flask. In the second 50 mL flask, 8.6 mg of TDO was dissolved and adjusted to the mark with distilled water. A reference NaOH solution was deposited in one cell of the spectrophotometer, and an alkaline TDO solution prepared prior to the experiment by adding NaOH solution to the aqueous TDO solution was deposited in the other. It should be noted that TDO does not decompose in a neutral solution. To obtain kinetic curves, changes in the optical density of the solutions over time were recorded automatically at constant wavelengths. The absorption spectra of solutions of thiourea dioxide of various concentrations were recorded earlier at the wavelength of 270 nm corresponding to the absorption maximum, and the linear dependence of optical density on concentration was confirmed. The coefficient of extinction, calculated on the basis of the Bouguer–Lambert–Beer law, was $\varepsilon = 563.41$.

The sodium hydroxide and TDO solutions were preliminarily purged with argon under anaerobic conditions, and a kinetic experiment was performed after closing the cell tightly with a paraffin ribbon.

The presence of dithionite ions was determined qualitatively on an Ecotest-VA device (Russia) using



Fig. 1. Electronic absorption spectra of a solution of thiourea dioxide under aerobic conditions at different points in time, min: (1) 0, (2) 17, (3) 20, (4) 42; T = 301 K; $C_{\text{NaOH}} = 0.12$ mol/L.

an electrochemical cell with three electrodes: a ceramic working electrode, a silver chloride reference electrode, and a glassy carbon auxiliary electrode. To obtain the current-voltage dependence in a solution of thiourea dioxide, 1 mL of an aqueous alkaline solution of it with a NaOH concentration of 0.25 mol/L and an initial TDO concentration of 1.7×10^{-3} mol/L, was mixed in a cell with 25 mL of Robinson–Britton buffer solution (pH 9) after holding for 2 min.

For comparison, the polarogram was taken of sodium dithionite while preliminarily mixing a solution of it in 0.04 mL of distilled water with a concentration of 5.74×10^{-4} mol/L and 25 mL of Robinson–Britton buffer solution (pH 9) inside an electrochemical cell. In all cases, the potential sweep rate was 50 mV/s, the initial potential was +200 mV, and the final potential was -1700 mV. All polarograms were recorded at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the electronic absorption spectra at different points in time during the decomposition of TDO under aerobic conditions. We can see there was a drop in the height of the maximum at $\lambda = 270$ nm, which corresponds to the absorption of TDO. A maximum that, according to the literature [13], is associated with the formation of dithionite anions, emerges and grows at $\lambda = 315$ nm.

Since no isobestic point is observed in the spectrum, ions $S_2O_4^{2-}$ formed not from thiourea dioxide molecules but from sulfoxyl acid anions SO_2^{2-} upon interacting with the oxygen in the air as a result of a sequence of stages:

$$(NH_2)_2CSO_2 + 2OH^-$$

 $\rightarrow SO_2^{2-} + (NH_2)_2CO + H_2O,$
(1)



Fig. 2. Semilogarithmic transformation of the kinetic curve $A = f(\tau)$. Aerobic conditions; $\lambda = 270$ nm; $C_{\text{NaOH}} = 0.13 \text{ mol/L}$; T = 301 K.

$$\mathrm{SO}_2^{2-} + \mathrm{O}_2 \to \dot{\mathrm{SO}}_2^{-} + \mathrm{O}_2^{\bullet}, \qquad (2)$$

$$2\mathbf{\dot{S}O}_2^- \rightleftharpoons \mathbf{S}_2\mathbf{O}_4^{2-}.$$
 (3)

As is shown below, the formation of dithionite is not observed under anaerobic conditions.

In order to qualitatively confirm the formation of dithionite anions, we obtained the current voltage dependence for both the TDO solution and the sodium dithionite solution. In both cases, the presence of a maximum in the current–voltage dependence at the potential of -0.7 V corresponding to the oxidation of dithionite ions, is also confirmed by the data in [8].

Figure 2 shows the dependence of optical density on time in semilogarithmic coordinates, which shows that decomposition under aerobic conditions is described by a first-order kinetic equation in terms of TDO. The observed rate constant is $7.14 \times 10^{-4} \text{ s}^{-1}$, which is comparable to an order of magnitude with the value of the rate constant indicated in the literature [14].

Figure 3 shows the time dependence of the optical density obtained at the two wavelengths corresponding to the absorption maxima of TDO and dithionite. The kinetic curve with the extremum point for dithionite confirms that it was an intermediate product of TDO decomposition.

It forms in stages (1)-(3), while the required amount of oxygen participates in the reaction due to diffusion from the environment. Its consumption is possible, due to the shift of the equilibrium of stage (3) to the right and the interaction between anion radicals

 $\dot{S}O_2^-$ and superoxide according to the reaction

$$\dot{S}O_2^- + O_2^\bullet + OH^- \to SO_3^{2-} + HO_2^-.$$
 (4)

We may assume that in the absence of atmospheric oxygen (under anaerobic conditions), decomposition proceeds according to reaction (1) and obeys the first-

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Fig. 3. Dependence of optical density on time for TDO $((1) \lambda = 270 \text{ nm})$ and dithionite $((2) \lambda = 315 \text{ nm})$ under anaerobic conditions: $C_{\text{NaOH}} = 0.13 \text{ mol/L}$; T = 301 K.

order kinetic equation for the concentration of thiourea dioxide. However, this assumption is incorrect, as is shown by the experimental data in Fig. 4.

First of all, the decomposition of TDO does not proceed to the end as it does under aerobic conditions. Second, the first order of TDO concentration is not observed. Third, dithionite ions still form in the process, but their concentration reaches a certain constant value and then remains the same.

The latter can be explained by purging with argon failing to completely remove all of the dissolved oxygen, and it reacts according to (2) in the initial stage of the process. In the future, oxygen does not enter from the external environment, and the concentration of dithionite ions remains constant. On the kinetic curve for TDO, a kink is observed at the time of oxygen depletion.

With a high degree of probability, we may assume that the drop in the rate of decomposition is associated with the reversibility of primary stage (1) of the decomposition of TDO molecules with C-S bond cleavage, as is observed in neutral and acidic media [10]. However, adding urea does not inhibit the decomposition process.

On the other hand, introducing a thiourea additive slows the reaction and lowers the final degree of decomposition of the initial material, as was discovered for the first time. The decomposition of thiourea dioxide molecules proceeds in two parallel reactions: one with heterolytic cleavage of the C–S bond in the TDO molecule and the formation of sulfoxylate anions (reaction (1)), and one with no breaking of C–S bonds and the formation of thiourea in the reversible reaction

$$(\mathrm{NH}_2)_2\mathrm{CSO}_2 + 2\mathrm{OH}^- \xleftarrow{k_1}{\langle k_{-1} \rangle} (\mathrm{NH}_2)_2\mathrm{CS} + 2\mathrm{HO}_2^-.$$
 (5)



Fig. 4. Dependence of optical density on time for TDO ((*1*, 2) $\lambda = 270$ nm) and dithionite ((*3*) $\lambda = 315$ nm) under anaerobic conditions; curve 2, in the presence of a thiourea additive ($C_{\text{TM}} = 5.7 \times 10^{-4} \text{ mol/L}$) $C_{\text{NaOH}} = 0.12 \text{ mol/L}$; T = 301 K.

Decomposition does not slow under aerobic conditions, since thiourea can react with the superoxide formed in stage (2) and turn into urea.

Using the above results, the considered process was modeled mathematically under anaerobic conditions without considering the initial stage of interaction between sulfoxylate ions and the dissolved oxygen.

Our mathematical model with allowance for the course of reversible stage (5) and irreversible stage (1) is presented in the form of a system of differential equations:

$$-\frac{dC_{(\mathrm{NH}_{2})_{2}\mathrm{CSO}_{2}}}{d\tau} = (k_{1} + k_{2})C_{(\mathrm{NH}_{2})_{2}\mathrm{CSO}_{2}}$$
$$-k_{-1}C_{(\mathrm{NH}_{2})_{2}\mathrm{CS}}C_{\mathrm{HO}_{2}^{-}},$$
$$\frac{dC_{(\mathrm{NH}_{2})_{2}\mathrm{CS}}}{d\tau} = k_{1}C_{(\mathrm{NH}_{2})_{2}\mathrm{CSO}_{2}} - k_{-1}C_{(\mathrm{NH}_{2})_{2}\mathrm{CS}}C_{\mathrm{HO}_{2}^{-}},$$
$$\frac{dC_{\mathrm{HO}_{2}^{-}}}{d\tau} = 2k_{1}C_{(\mathrm{NH}_{2})_{2}\mathrm{CSO}_{2}} - 2k_{-1}C_{(\mathrm{NH}_{2})_{2}\mathrm{CS}}C_{\mathrm{HO}_{2}^{-}},$$

where k_1 is the rate constant of the forward stage (5); k_{-1} is the rate constant of reverse stage (5); and k_2 is the rate constant of stage (1).

The concentration of NaOH was not included in the system of equations, since it was in excess compared to that of the remaining reagents. The inverse kinetic problem was solved using the *wkinet* program developed at Moscow State University, Department of Chemistry, chair of Physical Chemistry. The concentrations of thiourea dioxide were calculated from the values of optical density measured at a wavelength of 270 nm according to the methodology described above. The initial approximation of rate constant k_1 was estimated from kinetic curve $C_{\text{TDO}} = f(\tau)$. The initial approximations varied for the other constants.



Fig. 5. Results from modeling the kinetics of the decomposition of thiourea dioxide under anaerobic conditions. Points are experimental values; lines, calculations according to the kinetic model.

The optimum values of the rate constants were sought using the gradient approach by finding the minimum of the sum of the squares of the differences between the experimental and calculated values of the TDO concentrations.

The numerical values of the optimized rate constants were equal: $k_1 = 3.73 \times 10^{-4} \text{ s}^{-1}$, $k_{-1} = 125.6 \text{ mol/(L s)}$, $k_2 = 4.39 \times 10^{-5} \text{ s}^{-1}$. The minimum value of the optimized function was 6.8885×10^{-9} . A comparison of the experimental and calculated values of the concentrations of thiourea dioxide (Fig. 5) testifies to the adequacy of the proposed kinetic model for experimental data.

CONCLUSIONS

In decomposing thiourea dioxide in an aqueous alkaline solution, a slowing of the reaction with the addition of thiourea was observed for the first time. It was shown that the decay of TDO molecules proceeds in two parallel directions: with and without carbon– sulfur bonds. There were substantial differences between the amounts of decomposition products formed under aerobic and anaerobic conditions: in the first case, the reaction proceeds to the end and the main intermediate product is dithionite anions; in the second, complete decomposition of TDO is not observed, and dithionite is formed in negligible amounts. The kinetics of the decomposition of TDO under anaerobic conditions was modeled mathematically on the basis of the experimental kinetic curves, and the numerical values of the rate constants of individual stages were calculated.

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