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Kinetic Model of the Decomposition of Sodium Hydroxymethanesulfinate in Aqueous Solution

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Abstract—A kinetic model of the decomposition of sodium hydroxymethanesulfinate (rongalite) in aqueous solution at an initial value of pH 7.9 was considered. This multistep reaction was found to include oxidation decomposition in a solution surface layer and bulk reactions both with and without the participation of oxygen. To evaluate the parameters of this model, it was modified over three time intervals. The adequacy of this model to experimental data supported the hypothesis on the catalytic effect of “active sulfur” in the decomposition of rongalite.

INTRODUCTION

Sodium hydroxymethanesulfinate (rongalite) is used as a reducing agent in the finishing of textile fabrics, the production of synthetic rubber, and other processes [1]. The decomposition reactions of the reducing agent, which occur in parallel with the main reactions, result in the conspicuous consumption of the agent in manufacturing processes. In this connection, it is a topical problem to develop a kinetic model of rongalite decomposition and to calculate its parameters.

EXPERIMENTAL

Sodium hydroxymethanesulfinate (rongalite) $HOCH_2SO_2Na \cdot 2H_2O$ prepared by the double recrystallization of a commercial-grade product was used in this study. The main substance content was no lower than 99.4%, as determined by iodometry.

The kinetics of rongalite decomposition in an aqueous solution was studied at 343 ± 0.5 K. The concentration of rongalite was 0.60–0.65 mol/l. In the course of reaction, pH was measured with the use of an EV-74 ion meter. The test solution was sampled at regular intervals, and the samples were analyzed for sodium hydroxymethanesulfinate by iodometry and for intermediate products (sulfite sulfur compounds (SO_3^{2-} and HSO_3^-), thiosulfate ($S_2O_3^{2-}$), and dithionite ($S_2O_4^{2-}$)) by polarography.

Polarographic analysis was performed on a PU-1 polarograph in a two-electrode glass electrochemical cell. A mercury-dropping electrode served as a working electrode (drop time of 4 s), and a mercury pool was a reference electrode. To determine the concentration of dithionite, polarograms were measured under conditions of classical polarography in a supporting electrolyte with pH 9 from an initial potential of –0.3 V to a final potential of –0.9 V; the potential sweep rate was 4 mV/s. To simultaneously determine thiosulfate and sulfite, polarograms were measured in a supporting electrolyte with pH 4.7 in a differential mode from an initial potential of 0.3 V to a final potential of –1 V with a sweep amplitude of 11 mV.

RESULTS AND DISCUSSION

We studied the kinetics of rongalite decomposition and found that under anaerobic conditions this process includes the following three steps: (*a*) reactions with the participation of oxygen (t = 0–20 min), (*b*) an induction period (t = 20–240 min), and (*c*) reactions without the participation of oxygen (t > 240 min). At step *a*, the reaction occurred at a reasonably high rate and the rongalite concentration decreased by 5–15% of the initial value. During the induction period, the concentration of rongalite remained almost unchanged. At step *c*, the rongalite concentration continuously decreased with time (see the table).

Based on an analysis of published data [1, 2] and our experimental results, we can write the overall stoichiometric equation of the reaction of rongalite decomposition under anaerobic conditions as follows:

$$3HOCH_2SO_2Na + O_2 = HOCH_2SO_3Na + S + HCOOH + CH_3OH + Na_2SO_4. \quad \text{(I)}$$

However, it was found previously [2, 3] that this reaction occurs by a complex mechanism. It includes both the steps of oxidation decomposition due to atmospheric air in the bulk and at the surface of the solution and the steps of oxygen-free decomposition. It was found experimentally under anaerobic conditions [2, 3] that the oxidation decomposition of rongalite primarily occurred with the participation of oxygen dissolved in water. This is likely due to an insignificant rate of the surface absorption of O_2 molecules from atmospheric air. The rates of reactions with the participation of oxygen decreased to almost zero as dissolved oxygen was consumed.

In a general form, the reaction mechanism of rongalite decomposition in an aqueous solution can be represented by the following scheme:

$$\underset{\mathbf{X_1}}{HOCH_2SO_2^-} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \underset{\mathbf{X_2}}{HSO_2^-} + \underset{\mathbf{X_3}}{CH_2O}, \qquad \text{(II)}$$

$$HSO_2^- + \underset{\mathbf{X_6}}{O_2} + H_2O \xrightarrow{k_3} O_2^- + \underset{\mathbf{X_4}}{HSO_3^-} + 2H^+, \qquad \text{(III)}$$

$$HSO_3^- + O_2 + H_2O \xrightarrow{k_4} O_2^- + HSO_4^- + 2H^+, \qquad \text{(IV)}$$

$$2CH_2O + H_2O \xrightarrow{k_5} \underset{\mathbf{X_7}}{HCOOH} + CH_3OH, \qquad \text{(V)}$$

$$CH_2O + HSO_3^- \underset{k_7}{\overset{k_6}{\rightleftarrows}} \underset{\mathbf{X_8}}{HOCH_2SO_3^-}, \qquad \text{(VI)}$$

$$HSO_3^- + HSO_2^- \xrightarrow{k_8} \underset{\mathbf{X_9}}{S_2O_4^{2-}} + H_2O, \qquad \text{(VII)}$$

$$2S_2O_4^{2-} + H_2O \xrightarrow{k_9} 2HSO_3^- + \underset{\mathbf{X_5}}{S_2O_3^{2-}}, \qquad \text{(VIII)}$$

$$S_2O_3^{2-} \xrightarrow{k_{10}} S_a + SO_3^{2-}. \qquad \text{(IX)}$$

Taking into account the above notation, a mathematical model for the kinetics of the test reaction can be written as follows:

$$dX_1/dt = -k_1X_1 + k_2X_2X_3, \qquad (1)$$

$$dX_2/dt = k_1X_1 - k_2X_2X_3 - k_3X_2X_6 - k_8X_2X_4, \qquad (2)$$

$$\begin{aligned} dX_3/dt = {} & k_1X_1 - k_2X_2X_3 \\ & - 2k_5X_3^2 - k_6X_3X_4 + k_7X_8, \end{aligned} \qquad (3)$$

$$\begin{aligned} dX_4/dt = {} & k_3X_2X_6 - k_4X_4X_6 - k_6X_3X_4 \\ & + k_7X_8 - k_8X_2X_4 + 2k_9X_9^2 + k_{10}X_5, \end{aligned} \qquad (4)$$

$$dX_5/dt = k_9X_9^2 - k_{10}X_5, \qquad (5)$$

$$dX_6/dt = -k_3X_2X_6 - k_4X_4X_6, \qquad (6)$$

$$dX_7/dt = k_5X_3^2, \qquad (7)$$

$$dX_8/dt = k_6X_3X_4 - k_7X_8. \qquad (8)$$

At the initial stage of the development of a kinetic model, the parameters were chosen without considering reactions (III) and (IV). Moreover, we assumed that steps (II) and (V)–(IX) occur in the course of the overall decomposition process. To estimate model parameters, the following initial reactant concentrations (mol/l) were specified:

$$X_1^0 = 0.56, \quad X_2^0 = 0, \quad X_3^0 = 5.2 \times 10^{-2},$$

$$X_4^0 = 1.3 \times 10^{-2}, \quad X_5^0 = 0, \quad X_7^0 = 1.41 \times 10^{-8},$$

$$X_8^0 = 0, \quad X_9^0 = 0.$$

The initial concentration of formaldehyde (X_3^0) was determined from a decrease in the concentration of rongalite in reaction (II). We assumed that the amount of formaldehyde formed at this step was equal to a decrease in the concentration of rongalite. The initial concentration of sulfite (X_4^0) was equal to the amount of HSO_3^- formed at step *a* from decomposed sulfoxylate (HSO_2^-). The concentration of HCOOH (X_7^0) was calculated taking into account the measured pH value. The above values of X_i^0 refer to a point in time corre-

Experimental and calculated (without considering steps (II) and (IV)) concentrations (mol/l) of the reactants in the course of sodium hydroxymethanesulfinate (rongalite) decomposition in aqueous solutions

t, min	[rongalite]		$[HSO_3^-] \times 10^3$		$[H^+] \times 10^3$		$[S_2O_4^{2-}] \times 10^3$		$[S_2O_3^{2-}] \times 10^3$	
	experimental	calculated	experimental	calculated	experimental	calculated	experimental	calculated	experimental	calculated
0	0.560	0.560	13	13	1.41×10^{-5}	0	0	0	0	0
20	0.560	0.554	13	8.97	1.78×10^{-5}	0.10	3.5	3.50	0.1	0.24
60	0.560	0.550	8.7	5.82	1×10^{-3}	0.30	4.0	5.98	0.6	1.47
100	0.560	0.546	5.3	4.88	2.5×10^{-1}	0.60	4.0	6.38	2.15	3.00
140	0.560	0.543	2.9	4.52	7.94×10^{-1}	0.90	3.8	6.23	3.25	4.54
160	0.552	0.542	1.6	4.41	1.58	1.08	3.5	6.10	3.8	5.29
220	0.548	0.538	0.8	4.16	1.78	1.57	3.0	5.62	3.9	7.42
260	0.459	0.536	0.5	4.00	1.76	1.92	2.2	5.30	3.9	8.75
280	0.433	0.535	0.3	3.93	2.0	2.10	1.8	5.14	3.9	9.39

sponding to the completion of step *a* of the decomposition process (20 min after the onset of the experiment).

The following reaction constants were used as invariable parameters of the kinetic model: k_1 = 0.418 min^{-1} [4], $k_2 = 3.02 \times 10^5$ l mol^{-1} min^{-1} [4], and $k_5 = 7.67 \times 10^5$ l mol^{-1} min^{-1} (calculated from the time dependence of pH at an initial portion of the kinetic curve). The initial approximations of all the other parameters were varied.

The parameters of the model were chosen by minimizing the criterion of efficiency of the form

$$\mathbf{R}(\mathbf{k}) = \sum_{\mathbf{i}=\mathbf{1}}^{\mathbf{n}} (\mathbf{X_i} - \bar{\bar{\mathbf{X}}}_\mathbf{i})^\mathbf{T} \mathbf{D}_\mathbf{i}^{-1} (\mathbf{X_i} - \bar{\bar{\mathbf{X}}}_\mathbf{i}), \qquad (9)$$

where $\mathbf{X_i}$ and $\bar{\bar{\mathbf{X}}}_\mathbf{i}$ are the experimental and calculated concentration vectors, respectively, and $\mathbf{D_i}$ is the dispersion–covariance matrix of measurements. The functional $\mathbf{R}(\mathbf{k})$ was minimized by the Gauss–Newton method [5] using the equations

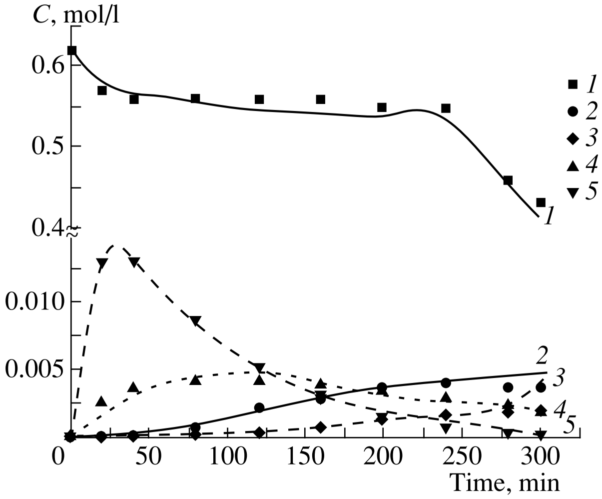
$$\mathbf{k}_{\mathbf{n}+\mathbf{1}} = \mathbf{k_n} + \boldsymbol{\rho}\mathbf{g_n}; \quad \mathbf{g_n} = -\mathbf{H}_\mathbf{n}^{-1}\nabla\mathbf{R_n}, \qquad (10)$$

where $\mathbf{k}$ is the vector of parameters, $\mathbf{n}$ is the iteration number, $\boldsymbol{\rho}$ is the descent step, $\mathbf{g_n}$ is the descent direction vector, and $\mathbf{H_n}$, $\nabla\mathbf{R_n}$ is the second-derivative matrix and the $\mathbf{R}\{\mathbf{k}\}$ function gradient vectors for parameters. The table summarizes the experimental and calculated kinetic data. An analysis of these data shows that the proposed kinetic model, which does not take into account steps (III) and (IV) ($k_3 = k_4 = 0$), is inadequate to the experimental data. Only a weak change in the calculated concentrations of sodium hydroxymethanesulfinate corresponding to the induction period of the reaction was observed. This model does not describe step *c*—the period of rapid decomposition.

It follows from the table (experimental data) that a dramatic increase in the concentration of H^+ ions (up to pH ≈ 2.8) and an increase in the concentration of $S_2O_3^{2-}$ finished at approximately the same point in time (180 min). It is well known that thiosulfate is unstable in an acidic medium, and it undergoes decomposition to form sulfite and elemental sulfur [6]. Moreover, it was found [7] that “active sulfur” formed from thiosulfate in an acidic medium can serve as a catalyst of rongalite decomposition. Thus, the constancy of the concentration of $S_2O_3^{2-}$ can be explained by the fact that the rates of its formation in reaction (VIII) and consumption in reaction (IX) are commensurable.

In this context, the kinetic model was modified for different time intervals.

The first interval (to 200 min) lasted up to the time of attaining a constant value of pH ≈ 2.8. Step (II) was assumed reversible, and step (IX) was eliminated (k_{10} = 0). Steps (III) and (IV) were also taken into account in the simulation. The initial reactant concentrations (mol/l) had the following values:



Simulation of sodium hydroxymethanesulfinate decomposition with the use of a modified kinetic model for different time intervals (solid lines show calculation; points indicate experimental data; *C* is concentration): (*1*) sodium hydroxymethanesulfinate, (*2*) $S_2O_3^{2-}$, (*3*) H^+, (*4*) $S_2O_4^{2-}$, and (*5*) HSO_3^-.

$X_1^0 = 0.61$, $X_2^0 = 0$, $X_3^0 = 0$, $X_4^0 = 0$, $X_5^0 = 0$, $X_6^0 = 5.8 \times 10^{-2}$ (water solubility of oxygen at 70°C [8]), $X_7^0 = 1.26 \times 10^{-8}$, $X_8^0 = 0$, and $X_9^0 = 0$.

An analysis of the eigenvectors of the matrix of second derivatives obtained at the early stage of the simulation demonstrated that the estimations of k_1, k_2, k_6, and k_7 parameters have coefficients of correlation close to unity. This circumstance is responsible for the impossibility of simultaneously determining them, and only k_1 and k_6 constants were found in the subsequent calculations, whereas k_2 and k_7 were calculated using the equilibrium constants of steps (II) and (VI) taken from the literature [4, 9].

The second interval (200–240 min)—step (IX) was taken into account in the overall reaction mechanism.

The third interval (after 240 min)—step (II) was assumed irreversible, and the parameter k_1 was determined from a kinetic curve using a first-order equation ($k_1 = 4.3 \times 10^{-3}$ min^{-1}).

The figure illustrates the results of calculations performed by this model. The rate constants of the particular steps of sodium hydroxymethanesulfinate decomposition are given below:

$$k_1 = 1.50 \times 10^{-2} \pm 7.30 \times 10^{-3} \text{ min}^{-1},$$

$$k_2 = k_1/10^{-6} \text{ l mol}^{-1} \text{ min}^{-1},$$

$$k_3 = 1.27 \pm 0.12 \text{ l mol}^{-1} \text{ min}^{-1},$$

$$k_4 = 0.23 \pm 0.14 \text{ l mol}^{-1} \text{ min}^{-1},$$

$$k_5 = (4.84 \pm 0.49) \times 10^{-3} \text{ l mol}^{-1} \text{ min}^{-1},$$

$$k_6 = 0.81 \pm 0.15 \text{ l mol}^{-1} \text{ min}^{-1},$$

$$k_7 = k_6/10^7 \text{ min}^{-1},$$

$$k_8 = 0.51 \pm 0.31 \text{ l mol}^{-1} \text{ min}^{-1},$$

$$k_9 = 1.04 \times 10^{-2} \pm 1.81 \times 10^{-4} \text{ l mol}^{-1} \text{ min}^{-1}, \text{ and}$$

$$k_{10} = (4.6 \pm 6.7) \times 10^{-4} \text{ min}^{-1}.$$

The consistence between the experimental and calculated kinetic curves for all of the considered substances of the system indicates that the time modification of the mechanism is best suited to describe the kinetics of the test process. It follows from the above data that the formation of “active sulfur” from thiosulfate in reaction (IX) is the rate-limiting step of sodium hydroxymethanesulfinate decomposition. This fact provides support for the previous hypothesis that “active sulfur” formed from thiosulfate in an acidic medium catalyzes the decomposition of sodium hydroxymethanesulfinate.

REFERENCES

1. Budanov, V.V. and Makarov, S.V., in *Khimiya serosoderzhashchikh vosstanovitelei* (The Chemistry of Sulfur-Containing Reducing Agents), Moscow: Khimiya, 1994, p. 9.
2. Polenov, Yu.V., Egorova, E.V., and Pushkina, V.A., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 5, p. 722.
3. Koksharov, S.A., Chistyakova, T.V., Murav’ev, O.N., and Makarov, S.V., *Zh. Prikl. Khim.*, 1999, vol. 72, no. 7, p. 1161.
4. Polenov, Yu.V. *et al.*, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1999, vol. 42, no. 2, p. 84.
5. Bard, J., *Nonlinear Parameter Estimation*,. New York: Academic, 1974.
6. Cermak, V. and Smutek, M., *Coll. Czech. Commun.*, 1975, vol. 40, no. 11, p. 3241.
7. Makarov, S.V., Polenov, Yu.V., and Budanov, V.V., *Zh. Neorg. Khim.*, 1984, vol. 29, no. 10, p. 2456.
8. *Spravochnik khimika: Osnovnye svoistva neorganicheskikh i organicheskikh soedinenii* (Handbook on Chemistry: Main Properties of Inorganic and Organic Compounds), Nikol’skii, B.P. *et al.*, Eds., Leningrad: Khimiya, 1964, vol. 3, p. 316.
9. Deister, U., Neeb, R., Helas, G., and Warneck, P., *J. Phys. Chem.*, 1986, vol. 90, no. 14, p. 3213.