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Mechanism of Decomposition of Sodium Hydroxymethanesulfinate in Aqueous Solution

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Abstract—Sodium hydroxymethanesulfinate decomposes in air in three stages. The first stage involves oxygen, the second is the induction period, and the third occurs without oxygen. Reactions occurring in these stages are suggested. Additions of surfactants hinder diffusion of oxygen through the surface film formed on the solution–air phase boundary and thus inhibit the first stage of the process.

Sodium hydroxymethanesulfinate (rongalite) is a commercially produced reductant. It is used in diverse fields, such as printing and dyeing of textiles, synthetic rubber production, synthesis of stabilizers for polymeric materials, etc. [1]. One of the problems arising when using rongalite is its poor stability. Decomposition reactions occurring concurrently with the target reactions result in overexpenditure of rongalite in industrial processes. Fore example, in the rongalite–potash procedure for fabric printing, rongalite is added to the dyeing formulation in a sixfold amount relative to that required for reduction of the vat dye [2].

Decomposition of rongalite was studied in numerous works [3, 4]. However, experimental data were mainly obtained for the inert atmosphere, and these data are apparently insufficient for quantitative description of the process. This study was aimed at elucidating in more detail the reaction mechanism and obtaining kinetic data on rongalite decomposition in air, i.e., under conditions of rongalite use in practice.

Figure 1 shows the kinetic curves of decomposition of sodium hydroxymethanesulfinate in aqueous solution in air (in the absence and in the presence of surfactants) and under an inert gas. Three characteristic sections (process stages) can be distinguished in the kinetic curves. In the first, initial stage the reaction is relatively fast, and from 5 to 15% of the initial amount of rongalite is consumed. The second stage is the induction period in which the reductant concentration remains practically constant. In the third stage, the rongalite concentration gradually decreases.

The kinetic parameters of the reaction under various conditions are listed in the table. K_1 is the rate constant in the initial stage, calculated by the first-order kinetic equation. The first order with respect to rongalite and the zero order with respect to oxygen were found in [5]. The rate constants obtained from the experiments with no additives coincide within experimental error with those reported in [5]. The rate constants K_2 were calculated by the zero-order kinetic equation for the sections of the kinetic curves corresponding to gradual decrease of the rongalite concentration with time (correlation factor r = 0.97–0.998). The degree of rongalite decomposition α was determined before the onset of the final stage.

Data in the table (decrease in the degree of rongalite decomposition before induction period in an inert gas atmosphere and in the decomposition rate in the initial period in the presence of surfactants) suggest that in the initial stage rongalite decomposes by oxidation with atmospheric oxygen. Insignificant decomposition of rongalite in an inert atmosphere is due to

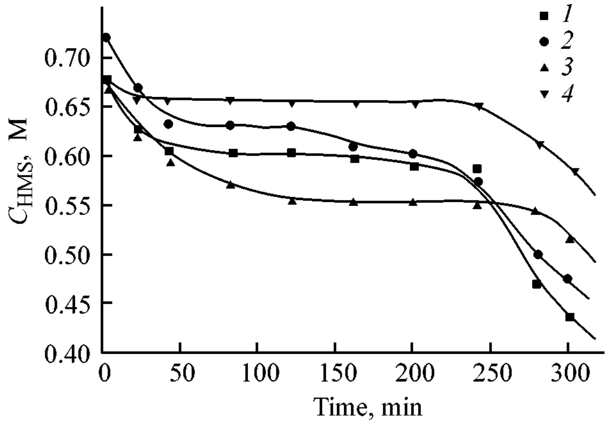

Fig. 1. Variation with time of the sodium hydroxymethanesulfinate concentration C_{HMS}: (*1*) without adding surfactants, (*2*) with addition of Fenoksol, (*3*) with addition of Meteks, and (*4*) under argon without adding surfactants; the same for Figs. 2–5.

Kinetic parameters of decomposition of sodium hydroxymethanesulfinate in aqueous solution at 343 K

Reaction conditions	$K_1 \times 10^3$, min^{-1}	$K_2 \times 10^3$, $\text{mol l}^{-1}\ \text{min}^{-1}$	α, %[a]	Reaction conditions	$K_1 \times 10^3$, min^{-1}	$K_2 \times 10^3$, $\text{mol l}^{-1}\ \text{min}^{-1}$	α, %[a]
In air, no additions	6.8 ± 0.5	1.2 ± 0.6	11	Meteks added	1.3 ± 0.6	0.8 ± 0.1	14
Under inert gas, no additions	7.0 ± 0.5	0.8 ± 0.2	3	Fenoksol added	0.9 ± 0.4	0.8 ± 0.3	11

[a] (α) Degree of decomposition in the initial section of the kinetic curve.

a minor amount of oxygen dissolved in water or introduced with rongalite powder. This conclusion agrees with the results obtained by Koksharov *et al.* [6] who found that the limiting stage of oxidative decomposition of rongalite is phase transfer of oxygen; the reaction occurs in a 7.3–8.5-μm surface layer.

Inhibition of rongalite decomposition in the presence of added surfactants may be due to formation on the solution surface of a film consisting of surfactant molecules, decelerating (by a factor of 1.65 according to [6]) the oxygen uptake by the surface.

Oxidative decomposition of rongalite can be described by the following scheme [5]:

$$HOCH_2SO_2^- \rightleftarrows HSO_2^- + CH_2O, \qquad (1)$$

$$HSO_2^- + 2O_2 \rightarrow 2O_2^{\cdot-} + SO_2 + H^+, \qquad (2)$$

$$2O_2^{\cdot-} + 2H^+ \rightarrow O_2 + H_2O_2, \qquad (3)$$

$$SO_2 + 2OH^- \rightarrow SO_3^{2-} + H_2O, \qquad (4)$$

$$SO_3^{2-} + H_2O_2 \rightarrow SO_4^{2-} + H_2O. \qquad (5)$$

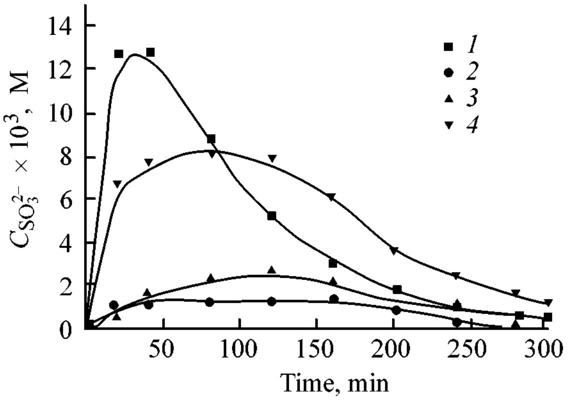

Fig. 2. Variation of the SO_3^{2-} concentration with time.

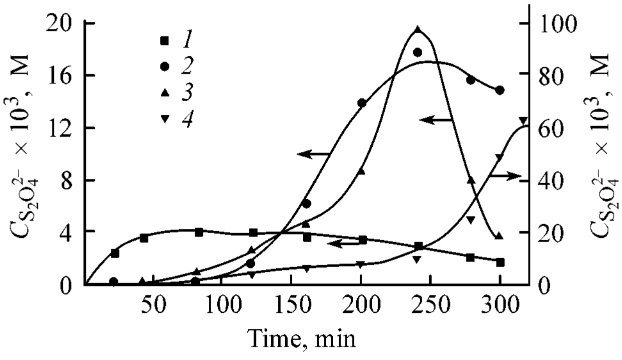

Fig. 3. Variation of the $S_2O_4^{2-}$ concentration with time.

These reactions proceed at a noticeable rate until the amount of the accumulated CH_2O becomes sufficient to shift the equilibrium of reaction (1) to the left and attain the quasiequilibrium. The inhibiting effect of formaldehyde was observed in [1, 4].

The major decomposition products in the initial period, according to reactions (1)–(5), are CH_2O, SO_3^{2-}, and SO_4^{2-}. However, the kinetic curves (Figs. 2, 3) show that, firstly, sulfite is not the final reaction product: Its concentration reaches a maximum in the first stage and then starts to decrease. Secondly, decrease in the sulfite concentration is accompanied by accumulation of dithionite which can form by reversible reaction (6) [7]:

$$HSO_3^- + HSO_2^- \rightleftarrows S_2O_4^{2-} + H_2O. \qquad (6)$$

Simultaneously with this reaction, formaldehyde in the induction period disproportionates by the Cannizzaro reaction:

$$2CH_2O + H_2O \rightarrow HCOOH + CH_3OH. \qquad (7)$$

This is suggested by a decrease in the solution pH (Fig. 4). The induction period ends when the solution pH decreases to 4–5, and in acidic solution dithionite starts to rapidly decompose (Fig. 3).

According to published data [7], decomposition of dithionite involves noncatalytic reaction (8) yielding active (noncolloidal) sulfur and autocatalytic reaction (9):

$$2H_2S_2O_4 \rightarrow S_a + 3SO_2 + 2H_2O, \tag{8}$$

$$3H_2S_2O_4 \rightarrow H_2S + 5SO_2 + 2H_2O. \tag{9}$$

The latter reaction is catalyzed by H_2S, SO_2, and active polymeric sulfur species. Formation of H_2S and active sulfur species (S_a) was detected by us previously in polarographic studies of deaerated acidic solutions of rongalite [4].

Despite formation in reactions (8) and (9) of sulfite sulfur (SO_2), its concentration does not increase in the final stage (Fig. 2). This is due to a reversible reaction of sulfite (SO_2, HSO_3^-, SO_3^{2-}) with formaldehyde; in acidic solutions the equilibrium is shifted toward formation of the formaldehyde bisulfite adduct.

$$HSO_3^- + CH_2O \rightleftarrows HOCH_2SO_3^-. \tag{10}$$

Acidification of the solution due to reaction (7) is accompanied by decomposition of the dithionite [reactions (8) and (9)], binding of formaldehyde by reaction (10), and shift of the equilibria of reactions (6) and (7) to the right, which causes decomposition of rongalite in the final stage of the process (Fig. 1).

Thiosulfate is apparently the final product of rongalite decomposition, as suggested by the shape of the kinetic curves (Fig. 5). It is formed by the reaction between the decomposition products, sulfite and active sulfur:

$$xHSO_3^- + S_a \rightarrow HS_2O_3^-. \tag{11}$$

All the reactions occurring in the final period of decomposition take place both in the presence and in the absence of atmospheric oxygen.

Additions of surfactants decrease the rate of oxidative decomposition but have practically no effect on the degree of decomposition (see table). Therefore, their use with the aim to reduce the loss of the reductant is appropriate in fast processes occurring in a thin layer of the solution, e.g., in finishing of textiles. When reduction with rongalite occurs in the bulk of solution, the use of such additives is not appropriate.

Our results suggest a complex mechanism of rongalite decomposition in the presence of atmospheric oxygen, involving both oxidative decomposition in the surface layer and reactions occurring in the bulk of solution without participation of oxygen.

EXPERIMENTAL

In our study we used sodium hydroxymethanesulfinate (rongalite) $HOCH_2SO_2Na \cdot 2H_2O$ prepared by double recrystallization of the technical-grade product.

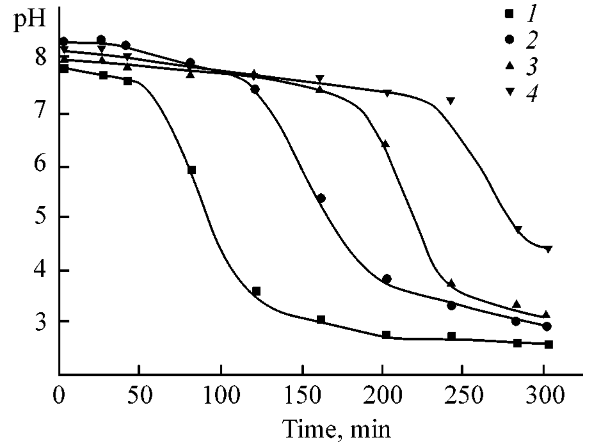

Fig. 4. Variation of the pH of the reaction medium with time.

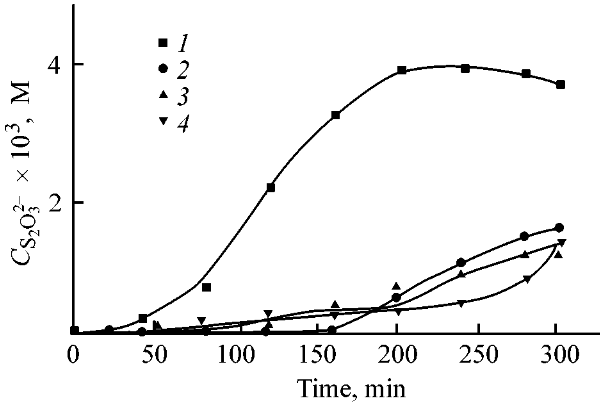

Fig. 5. Variation of the $S_2O_3^{2-}$ concentration with time.

The main substance content, determined by iodometric titration [8], was no less than 99.4%. As supporting electrolytes for polarographic studies we used the Robinson–Britton universal buffer mixture prepared from H_3BO_3, CH_3COOH, H_3PO_4, and NaOH (chemically pure grade). To construct the calibration curves (polarographic weight height vs. concentration), we used chemically pure grade $Na_2S_2O_3 \cdot 5H_2O$, Na_2SO_3, and $Na_2S_2O_4$. The concentrations of their solutions were determined by iodometric titration [8]. As surfactants we used Fenoksol BV-9/10 and Meteks (Khimprom Joint-Stock Company, Ivanovo).

The kinetics of sodium hydroxymethanesulfinate decomposition was studied at 343 ± 0.5 K. Rongalite solutions (0.60–0.65 M) were prepared in distilled water preheated to the required temperature. In the course of decomposition of the aqueous solution, pH was monitored with an EV-74 pH meter, and solution samples were taken at regular intervals and analyzed for sodium hydroxymethanesulfinate (iodometric titration) and the $S_2O_4^{2-}$, SO_3^{2-}, and $S_2O_3^{2-}$ ions (polarographically). In some experiments, a surfactant was added in an amount of 0.5 wt % relative to rongalite. The solutions were not stirred, except the experiments in an inert atmosphere in which a continuous flow of argon was passed through the solution before heating and in the course of decomposition.

Polarographic analyses were performed with a PU-1 polarograph in a two-electrode glass electrochemical cell. A mercury dropping electrode (dropping period 4 s) was the working electrode, and the bottom mercury, the reference electrode. To prevent oxidation of the compounds with atmospheric oxygen, the supporting electrolytes were purged in the cell with argon. To determine the content of dithionite, the polarograms were taken in the classical polarographic mode in the supporting electrolyte (pH 9) from the initial potential of -0.3 V to the final potential of -0.9 V; the rate of potential sweeping was 4 mV s^{-1}. To determine the content of thiosulfate and sulfite present simultaneously, the polarograms were taken in supporting electrolytes of pH 4.7 in the differential mode, with a sweeping amplitude of +11 mV, from the initial potential of $+0.3$ V to the final potential of -1 V.

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