Kinetics and Catalysis, Vol. 43, No. 2, 2002, pp. 249–260. Translated from Kinetika i Kataliz, Vol. 43, No. 2, 2002, pp. 273–284.
Original Russian Text Copyright © 2002 by Ermakov, Purmal'.

Catalysis of HSO_3^-/SO_3^{2-} Oxidation by Manganese Ions

A. N. Ermakov* and A. P. Purmal'**
** Institute of Energy Problems of Chemical Physics, Russian Academy of Sciences, Moscow, 117829 Russia*
*** Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117977 Russia*

Received April 19, 2001

Abstract—Among transition metal ions, Mn(II) ions are considered to be the most active catalysts of HSO_3^-/SO_3^{2-} oxidation. All published data on the kinetics of the catalytic oxidation of HSO_3^-/SO_3^{2-} by manganese ions are analyzed in this review. In addition to primary experimental data, information on the rate constants of the reactions of $S\dot{O}_{3-5}^{-}$ and HSO_5^- with Mn(II)/Mn(III) or Fe(II)/Fe(III) ions was also engaged in this analysis. Unavoidable impurities of iron ions in aqueous solutions were found to be responsible for the observed catalytic activity of manganese ions. Manganese ions are highly efficient activators of iron ions. Manganese ions are catalytically inert in the absence of iron ions. These metal ions form a synergistic pair in which Mn(II) ions increase the catalytic properties of iron ions many times. This effect results from the catalysis of a rate-limiting step of chain propagation in sulfite oxidation and from a shift in the distribution of iron species toward Fe(III), which participates in a step of chain initiation.

INTRODUCTION

According to published data [1], Mn(II) ions head the series of the catalytic activity of transition metal ions toward liquid-phase sulfite oxidation (henceforth, an equilibrium mixture of $SO_2(aq)$–HSO_3^-–SO_3^{2-} is denoted as sulfite S(IV)): Mn > Fe > Cu > Co > Ni. Although published data [2–21] on the partial kinetic orders of reaction and on apparent rate constants (k_{obs}) are widely discrepant, the high catalytic activity of Mn(II) ions is beyond question. Many researchers have been engaged in the analysis of the mechanism of this catalytic reaction [1, 9, 11, 14, 17, 18, 22–27]; we have also worked on this problem [28–31]. The most important result of our analysis was a conclusion [29, 30] that Mn(II) ions themselves are catalytically inactive in sulfite oxidation. It was found that the previously observed [2–20] sulfite oxidation "catalysis" by manganese ions is associated with an enhanced effect of uncontrollable trace impurities of iron ions ($[Fe]_0 = (2$–$50) \times 10^{-8}$ mol/l [9, 17, 32]) present in water or other reagents at any degree of purification. This conclusion allowed us [30] to qualify the repeatedly described sulfite oxidation catalysis by Mn(II) ions as a synergistic effect of these ions and impurity iron ions on sulfite oxidation.

An undoubtedly topical problem is to interpret the mechanisms of such processes and to control them. We revealed a number of previously unknown important features of these mechanisms by a detailed analysis of both published data [2–20] and our own experimental results [28, 33] on the kinetics of sulfite oxidation catalysis by manganese ions.

REACTION DYNAMICS OF SULFITE OXIDATION CATALYSIS BY MANGANESE(II) IONS

Order of Reaction with Respect to Mn(II)

The most interesting and puzzling appearance of the catalytic activity of Mn(II) ions in sulfite oxidation consists in variations in the order of reaction with respect to manganese. The order of reaction with respect to manganese varied from 2 to 0 depending on the experimental values of pH, [S(IV)], or [Mn(II)]. In the majority of studies, the second order with respect to manganese was observed only at low concentrations of the metal ion, which were lower than a concentration of $[Mn(II)]_{max}$ [2, 3, 5–9, 12]. The $w_{Mn} \sim [Mn(II)]^{1.7–2.0}$ relation at $[Mn(II)]_{max} \le 10^{-4}$ mol/l was first found as early as 1934 [2]. This fact was subsequently supported in experiments at concentrations of $[Mn(II)]_{max} \le 8 \times 10^{-5}$ mol/l [3], $[Mn(II)]_{max} \le 10^{-4}$ mol/l [5], $[Mn(II)]_{max} \le 5 \times 10^{-6}$ mol/l [6], $[Mn(II)]_{max} \times 10^{-4}$ mol/l [7], $[Mn(II)] \le 3 \times 10^{-4}$ mol/l [9], and $[Mn(II)] \le 10^{-4}$ mol/l [12]. In addition, published data [9] indicate that $[Mn(II)]_{max}$ increases with [S(IV)]. In the cited experiments (in the absence of buffer additives), a decrease in [S(IV)] from 6×10^{-2} to 10^{-2} mol/l, which was accompanied by a change in pH from 1.65 to 2.17, resulted in a decrease in $[Mn(II)]_{max}$ from 3×10^{-4} to 10^{-4} mol/l. However, the results of an extensive and detailed study [17] fall out of this list of consistent data. In the quoted expression for w_{Mn} (pH 4 and $[S(IV)] = 2.3 \times 10^{-5}$ mol/l, i.e., under conditions noticeably different from those in the studies cited above), a term proportional to $[Mn(II)]^2$ appears as a

0023-1584/02/4302-0249$27.00 © 2002 MAIK "Nauka / Interperiodica"

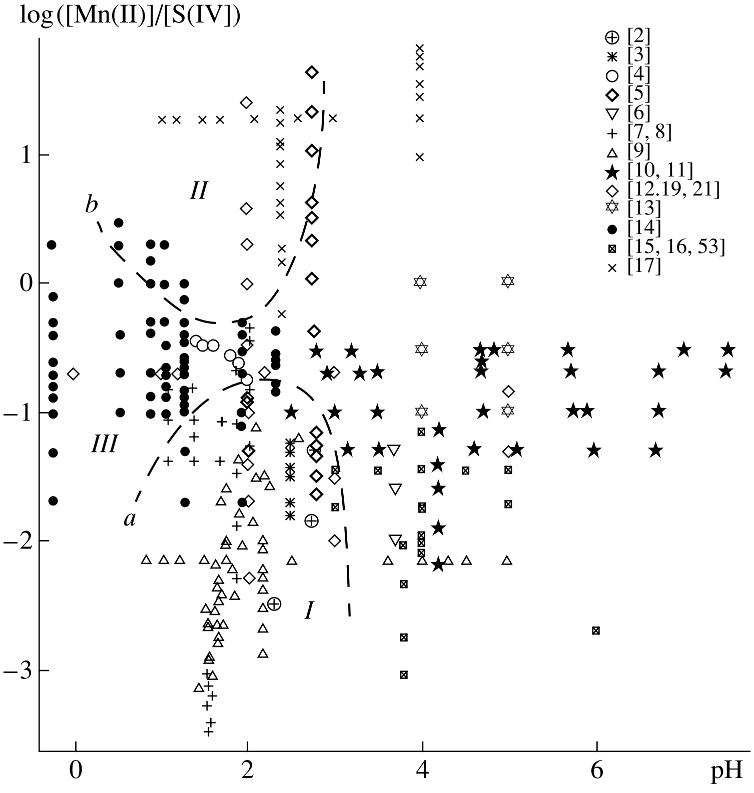

Fig. 1. Catalysis of the oxygen oxidation of sulfite by manganese ions. Differentiation of the ranges of pH and [Mn(II)]/[S(IV)] corresponding to different orders of reaction with respect to manganese (see text): (*I*) second, (*II*) zero, and (*III*) first orders with respect to manganese.

summand in the numerator. Thus, the quadratic dependence of w_{Mn} on [Mn(II)] appears only at sufficiently high [Mn(II)]; that is, the order of reaction should increase from 1 to 2 with increasing [Mn(II)]. Contrary to this, the first order of reaction with respect to manganese was found in the cited experiments at both low ($\leq 10^{-4}$ mol/l) and high ($\geq 10^{-4}$ mol/l) values of [Mn(II)]. For this reason, the term [Mn(II)] was also included as a summand in the denominator of the expression $w_{Mn} = (k[Mn(II)] + k'[Mn(II)]^2)[HSO_3^-]/(A + [Mn(II)]$. Here, k, k', and A are empirical constants, and [Mn(II)] is the total concentration of manganese ions, which includes both free and metal complex–bound Mn^{2+} ions. Collins [14] was the first to report an increase in the order of reaction with respect to manganese from 1 to 2 with an increase in the concentration of metal ions. At pH 0.89 and 1.05 ([S(IV)] = 2×10^{-4} mol/l), a change from the first to the second order was observed [14] at [Mn(II)] ≈ $(5–7) \times 10^{-5}$ mol/l. However, this change in the mode of catalytic sulfite oxidation was observed only in a very narrow range of pH. For example, at pH 0.53 and –0.25 and [S(IV)] = 2×10^{-4} mol/l, an increase in the concentration of manganese ions ($10^{-5} \leq$ [Mn(II)] $\leq 10^{-3}$ mol/l) was unaccompanied by a change in the order of reaction with respect to manganese: $w_{Mn} \sim$ [Mn(II)]. The reaction order also remained unchanged on varying [Mn(II)] within the above limits at pH 1.28 ([S(IV)] = 4×10^{-3} mol/l); however, under these conditions, $w_{Mn} \sim [Mn(II)]^2$. In the context of the above metamorphoses of the dependence of w_{Mn} on [Mn(II)], experimental data [5] are of particular interest. It was found by a combination of batch and flow-system experiments that an increase in [Mn(II)] ($3 \times 10^{-5} \leq$ [Mn(II)] ≤ 0.1 mol/l) at fixed [S(IV)] ≈ 2×10^{-3} mol/l and pH ≈2.7 resulted in a monotonic decrease in the reaction order from 2 to 0. In these experiments, high flow rates of the reactants under conditions of high [Mn(II)] and, as a consequence, high w_{Mn} ($>10^{-3}$ mol l^{-1} s^{-1}; $\tau_{1/2} \leq 1$s) eliminated the inhibiting effect of oxygen supplied to the reaction zone (one-phase bulk study) [8, 13]. A decrease in the order of reaction with respect to manganese from 1 to 0 was also firmly established in experiments [17, 20] performed under batch conditions (pH 2.4; [S(IV)] = 2.3×10^{-5} mol/l). Such a trend toward the reaction order decreasing as [Mn(II)] increased was also observed experimentally [7] (bubbling O_2/N_2 mixtures containing SO_2 (0.5–1%) through aqueous $MnSO_4$ solutions). Therefore, we can state that an increase in [Mn(II)] at constant pH and [S(IV)] only results in a decrease in the reaction order with respect to manganese.

Figures 1 and 2 (points) graphically summarize data on the concentration conditions of various publications

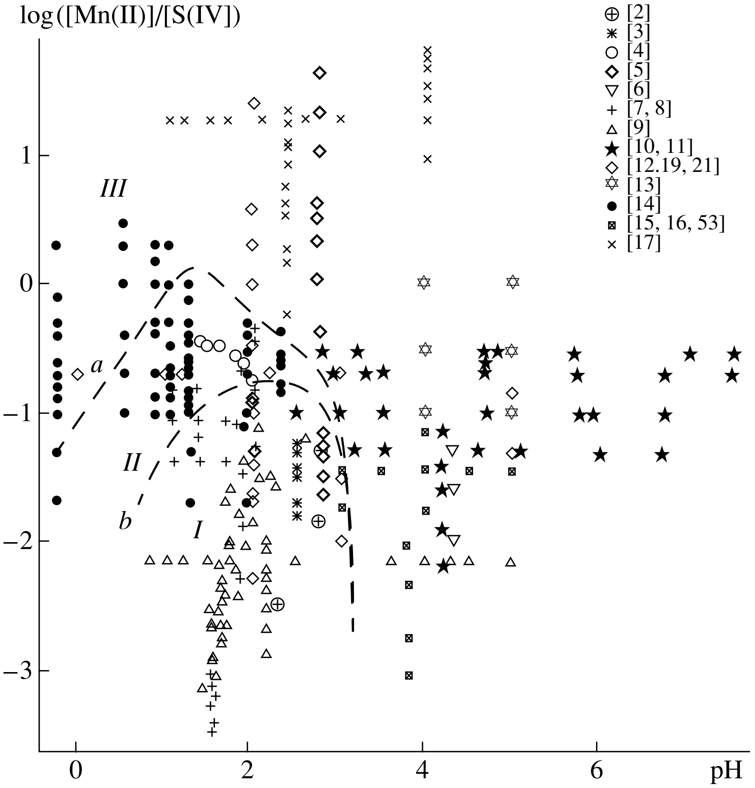

Fig. 2. Catalysis of sulfite oxidation by manganese ions. Differentiation of the ranges of pH and [Mn(II)]/[S(IV)] corresponding to different orders of reaction with respect to sulfite: (*I*) minus first, (*II*) zero, and (*III*) first orders with respect to sulfite.

concerning the kinetics of catalytic sulfite oxidation in the presence of Mn(II) ions. Each type of the points reflects the experimental values of pH and [Mn(II)]/[S(IV)] at which the orders of the catalytic sulfite oxidation reaction with respect to manganese (Fig. 1) and sulfite (Fig. 2) were determined in the cited publications. Among the entire variety of data, we marked with dashed curves *a* and *b* in Fig. 1 the ranges of pH and [Mn(II)]/[S(IV)] ratios in which catalytic sulfite oxidation is a second-order [2, 3, 5, 7, 9, 12] or zero-order reaction [5, 7, 14, 17, 19, 21] with respect to manganese (see regions *I* and *II*, respectively). However, the experimental data by Penkett *et al.* [6] do not meet this demarcation of conditions. In these experiments, the quadratic dependence of w_{Mn} on [Mn(II)] at pH 3.7 was observed up to $([Mn(II)]/[S(IV)]_{max} \approx 5 \times 10^{-2}$. However, data in Fig. 1 suggest that this mode of catalytic sulfite oxidation is impossible under the specified conditions (see below). It is likely that Penkett *et al.* [6] have drawn an erroneous conclusion, as if catalytic sulfite oxidation in their experiments were a second-order reaction with respect to manganese based on insufficient experimental data and a relatively narrow range of [Mn(II)]. This prevented them from reliably distinguishing between first and second orders with respect to manganese. The experimental conditions used by Huss *et al.* [9] also exhibit an illusory contradiction with the demarcation of catalytic sulfite oxidation modes shown in Fig. 1. In test runs oriented to determine the reaction order of catalytic sulfite oxidation with respect to sulfite, Huss *et al.* [9] observed $w_{Mn} \sim$ [Mn(II)][S(IV)] in place of the law $w_{Mn} \sim [Mn(II)]^2$ at values of pH and [Mn(II)]/[S(IV)] that correspond to region *I*. This inconsistency was explained by a considerable difference in ionic strength (μ) between these experiments ($\mu \approx 0.5$ mol/l) and the experiments performed for determining the reaction order of catalytic sulfite oxidation with respect to manganese ($\mu \approx 0$). Huss *et al.* [9] found that the effective reaction rate constant that appears in the expression for the rate of catalytic sulfite oxidation $w_{Mn} = 10^{(6.39 - 4.07\mu^{1/2})/(1 + \mu^{1/2})}[Mn(II)]^2 + 10^{(3.48 - 1.01\mu^{1/2})/(1 + \mu^{1/2})} \times$ [Mn(II)][S(IV)] with the quadratic term decreases to a lesser degree than an analogous quantity of the linear term as μ increased from ~0 to 0.5 mol/l. Thus, another boundary (shifted down) of region *I* as compared to that given in Fig. 1 corresponds to the experiments on determining the reaction order of catalytic sulfite oxidation with respect to sulfite at $\mu \approx 0.5$ mol/l.

Similar attempts to differentiate the modes of the test reaction depending on pH, [Mn(II)], and [S(IV)] were made previously [5, 7, 12, 14, etc.]. This becomes evident from an analysis of the forms of empirical expressions for w_{Mn} proposed in the above publications. For example, we used the expression for w_{Mn} taken from [9] (see above) for calculating ($\mu \approx 0$) the ratios [Mn(II)]/[S(IV)] required for the second order of reaction with respect to manganese at low pH (≤2). We found that these values are consistent with those based on experimental results [2, 3, 5, 7, 8], that is, with the position of curve *a* shown in Fig. 1. A different situation arises at higher pH values (≥2.3). It follows from the shape of the expression for w_{Mn} [9] that the law $w_{\mathrm{Mn}} \sim [\mathrm{Mn(II)}]^2$ is obeyed in the specified range of pH if the ratio $[\mathrm{Mn(II)}]/[\mathrm{S(IV)}] \le 0.1$. However, the law $w_{\mathrm{Mn}} \sim [\mathrm{Mn(II)}]$ was experimentally observed instead. As will be demonstrated below, the reason for this discrepancy is the erroneous qualification of catalytic sulfite oxidation as a zero-order reaction with respect to sulfite, which was made by a number of researchers [2, 3, 5, 8, 9, 12]. The adequacy of the pattern shown in Fig. 1 for the differentiation of the reaction conditions of catalytic sulfite oxidation follows from the consideration given below. According to Fig. 1, a decrease in the reaction order with respect to manganese (from 2 to 0) with the increasing ratio [Mn(II)]/[S(IV)] should be expected only in acid solutions and the "optimum" range of pH for such experiments is very narrow (pH ≈ 2 ± 1). In this case, as mentioned above, low ratios $[\mathrm{Mn(II)}]/[\mathrm{S(IV)}] \le 0.2$ correspond to the second order, whereas high ratios correspond to the zero order. This conclusion is consistent with published data [5, 7]; in these publications, a decrease in the reaction order with respect to Mn(II) at pH ≈ 1.5–2.7 was established. Based on the above pattern, it is reasonable to expect that the first order of reaction with respect to manganese corresponds to the region of pH and [Mn(II)]/[S(IV)] marked as *III* in Fig. 1. This is supported by the concentration conditions shown in Fig. 1 for experiments described in [10–15, 17], in which the first order of reaction with respect to Mn(II) was observed in the region indicated by *III*.

The second order of catalytic sulfite oxidation reaction with respect to manganese gave rise to speculations about the participation of various metal complexes, including binuclear complexes [7, 9] etc., in this process. In the last few years [27], it was suggested that metal complexes of the following two types participate in the catalytic oxidation of sulfite: a sulfite complex ($\mathrm{Mn^{2+} + HSO_3^- \Leftrightarrow MnHSO_3^+}$) and a binuclear sulfite complex ($\mathrm{Mn^{2+} + MnHSO_3^+ \Leftrightarrow MnSO_3Mn^{2+} + H^+}$). The formation of $\mathrm{MnSO_3Mn^{2+}}$ was postulated by Berglund *et al.* [17] to bring into agreement experimental data on the zero order of reaction with respect to manganese at high manganese concentrations and at pH 2.4 and the apparent first order of reaction at the same values of [Mn(II)] but at pH 4 (see above). Based on this hypothesis and their own kinetic data, Berglund *et al.* [17] evaluated the stability constant of the $\mathrm{MnHSO_3^+}$ complex: $\beta = 3 \times 10^4$ l/mol. Collins [14] also considered the participation of the binuclear complexes of manganese ions in catalytic sulfite oxidation. He noted an increase in the order of reaction with respect to manganese from 1 to 2 with increasing Mn(II) concentration in acid solutions (pH ≈ 0.9). Note that independent data on the existence of such complexes, as well as evidence for the formation of these complexes in the course of sulfite oxidation "catalysis" by manganese ions, are not available. The independence of the reaction rate from [Mn(II)], which was observed at high manganese concentrations (see, for example, [5, 7, 8]), also cannot be interpreted in terms of the hypothesis on the crucial role of binuclear complexes.

Reaction Order with Respect to Sulfite

It is believed (see, for example, [24]) that the kinetics of catalytic sulfite oxidation in the presence of manganese ions is characterized by first and zero orders with respect to sulfite. In this case, the first order was observed at low [S(IV)], whereas the zero order was detected in concentrated sulfite solutions. In contrast to convincing evidence for the first order [9–12, 14, 15–17, 20], the interpretations of experimental data on the zero order of catalytic sulfite oxidation reaction with respect to sulfite given in the majority of publications are dubious. Only published data [14] seem undoubted; in this publication, a conclusion on a change in the reaction order from 1 to 0 with increasing [S(IV)] at pH –0.22 was drawn from the experimental dependence of the initial rate of reaction on the concentration of sulfite. In other publications [2–5, 9, 12], a conclusion on the zero order of reaction with respect to sulfite was drawn because the reaction rate remained constant as [S(IV)] decreased in the course of reaction. Both first and zero orders of catalytic sulfite oxidation reaction with respect to sulfite seem reasonably explained on the assumption that the $\mathrm{MnHSO_3^+}$ metal complexes are formed [17, 20, 24] (see above). In accordance with these notions, the first order of reaction with respect to sulfite is expected at $[\mathrm{S(IV)}] \le \beta^{-1}$, whereas the zero order is expected at $[\mathrm{S(IV)}] \gg \beta^{-1}$.

Martin [12] was the first to report on an increase in the order of reaction with respect to sulfite, detected by measuring w_{Mn}, with decreasing sulfite concentration (from 10^{-4} to 10^{-6} mol/l or lower) in the course of reaction. To monitor [S(IV)], Martin [12] applied a sensitive (to 10^{-7} mol/l) electrochemical technique; more recently, Martin and Hill [19] used an optical technique. In this case, the "pure" first order with respect to sulfite was detected only at $[\mathrm{S(IV)}] \le 10^{-6}$ mol/l ($[\mathrm{S(IV)}] \ll \beta^{-1}$). A conclusion on the zero order of reaction based on the fact that w_{Mn} remained constant in the course of sulfite oxidation at high [S(IV)] was drawn in [2, 3, 5, 6, 12]. The first order of reaction with respect to sulfite in the concentration range $[\mathrm{S(IV)}] = (4\text{–}20) \times 10^{-6}$ mol/l ($\le\beta^{-1}$) was supported later on in [10, 11]. Experimental data [15] stand apart; the relationship $w_{\mathrm{Mn}} \sim [\mathrm{S(IV)}]^{0.65}$ was derived from these data at $[\mathrm{S(IV)}] > \beta^{-1}$ (pH 4; $[\mathrm{S(IV)}] = 10^{-4}$ and [Mn(II)] =

(2–15) × 10^{-6} mol/l). The inconsistency of data [15] with the expected zero order of reaction with respect to S(IV) under these conditions in [17] was explained by the fact that Grgić *et al.* [15] ignored the induction period of reaction. Huss *et al.* [9], who examined catalytic sulfite oxidation with a large excess of sulfite over Mn(II) at pH 1.67 and 2.17 when $w_{Mn} \sim [Mn(II)]^2$ (see region *I* in Fig. 1), also considered the zero order of reaction with respect to sulfite. However, the experimental data [9] are indicative of an inhibiting effect of sulfite on the rate of reaction, that is, of a negative order of reaction with respect to sulfite. Comparing w_{Mn} at $[Mn(II)] = 10^{-4}$ mol/l, $[S(IV)]_1 = 10^{-2}$ mol/l, and $[S(IV)]_2 = 6 \times 10^{-2}$ mol/l, we obtain $w_{Mn}([S(IV)]_2)/w_{Mn}([S(IV)]_1) \approx 0.3$; that is the rate of reaction decreases as [S(IV)] increases! According to these data, the negative order of reaction with respect to S(IV) is approximately equal to ~–0.7; however, they refer to different pH values because the experiments [9] were performed in the absence of buffer additives. At the same time, Huss *et al.* [9] found that $[H^+]$ has almost no effect on w_{Mn} at pH ≈ 1.3–3 at similar [Mn(II)]/[S(IV)] ratios. It also follows from published data[1] [7] that w_{Mn} is almost independent of pH at the same ratios [Mn(II)]/[S(IV)]: $w_{Mn} = [Mn(II)]^2/(a + b[H_2SO_4])$, where $a = 1.6 \times 10^{-2}$ mol l^{-1} s and $b = 0.198$ s. Using the pH-dependent concentration of HSO_3^- in place of [S(IV)], we found that the values of w_{Mn} experimentally measured by Huss *et al.* [9] at different pH are proportional to $[HSO_3^-]^{-1}$. The experimental data of Collins [14] are also indicative of a negative order of reaction with respect to sulfite under conditions of constant [Mn(II)] (4×10^{-4} mol/l) and pH (1.3). Collins [14] detected a fourfold decrease in the initial value of w_{Mn} as [S(IV)] that was increased by a factor of 4! However, these observations are inconsistent with conclusions [2, 5, 12] on the zero order of reaction at comparable concentration conditions. How to bring these seemingly inconsistent data to agreement? In our opinion, a negative order of reaction with respect to sulfite also took place in experiments described in [2, 5, 12]. The fact that w_{Mn} did not increase with decreasing [S(IV)] in the course of reaction in these experiments (as would be the case with a negative order of reaction) should be explained. In this context, note that, for example, Coughanowr and Krause [5] performed the experiments under consideration at concentrations of dissolved oxygen lower than the initial [S(IV)]. Thus, in these experiments, it was possible to measure w_{Mn} only at comparatively low conversions of sulfite, that is, under conditions when it was impossible to detect the above increase in w_{Mn} with decreasing sulfite concentration. Under these conditions, it is extremely difficult to distinguish between zero and negative orders of reaction based on the shapes of kinetic curves. The fact of an increase in w_{Mn} with decreasing sulfite concentration in the course of reaction was experimentally revealed by Martin [12] and Martin and Hill [19]. Contrary to Martin's opinion [12, 19] on the alleged zero order of reaction with respect to sulfite observed in these experiments, the reaction order was negative to a degree of sulfite conversion equal to at least 0.5. This is evidenced by the inconstancy of the slope of kinetic curves [19], which increased with the degree of sulfite conversion, and this increase corresponded to an increase in the order of reaction. As the sulfite conversion further increased, the slope of kinetic curves changed again, and this change corresponded to going from zero to first order, as mentioned by Martin and Hill [19]. Note that the cited publication is the only work in which a change in the reaction order with respect to sulfite from –1 to 1 was observed in the course of reaction.

Now, let us demonstrate that a negative order of reaction with respect to sulfite also results in a nearly constant value of w_{Mn} under conditions specified in [2, 5, 9, 12]. For this purpose, we write an expression for the reaction rate in the form $w_{Mn} = -d[S(IV)]/dt = k_{obs}[Mn(II)]^2/[HSO_3^-] = k_{obs}[Mn(II)]^2\gamma/[S(IV)]$, where $\gamma \approx (1 + [H^+]/K_1)$, and $K_1 \approx 1.4 \times 10^{-2}$ mol/l is the equilibrium constant of the dissociation $SO_{2(aq)} \Leftrightarrow HSO_3^- + H^+$ [1]. The value of γ is almost equal to unity at pH ≈ 3. For example, this was the case in the study [5], where a kinetic curve of S(IV) consumption in the batch system of interest was given as an illustration. The integration of the above equation gives the expression $[S(IV)] = ([S(IV)]_0^2 - 2k_{obs}[Mn(II)]^2 t)^{1/2}$, and the series expansion with consideration for the first two terms results in $[S(IV)] = [S(IV)]_0(1 - k_{obs}[Mn(II)]^2 t/[S(IV)]_0^2)$, where $[S(IV)]_0$ is the initial concentration of sulfite. This suggests the constancy of the reaction rate $w_{Mn} \approx k_{obs}[Mn(II)^2/[S(IV)]_0$, which was observed experimentally [2, 5, 12, 14, 19], when the real order of reaction with respect to sulfite was negative. Analyzing the kinetic curve from [5] (pH ≈ 2.7, $[S(IV)]_0 \approx 2 \times 10^{-3}$ and $[Mn(II)] \le 10^{-4}$ mol/l) and using $w_{Mn} = 3 \times 10^{-6}$ mol l^{-1} s^{-1}, which was measured in these experiments, we can calculate $k_{obs} \approx 0.5$ s^{-1}. A similar result of $k_{obs} \approx 0.6$ s^{-1} was obtained with the use of experimental data [2] on the kinetics of sulfite consumption (pH 2.5; $[S(IV)] \approx 6 \times 10^{-3}$ and $[Mn(II)] \le 10^{-4}$ mol/l). Finally, based on experimental data [12] (pH 2; $[S(IV)]_0 = 2.5 \times 10^{-4}$ and $[Mn(II)] = 2.5 \times 10^{-5}$ mol/l), we obtain $k_{obs} \approx 0.02$ s^{-1}. What is the reason for differences between the values of k_{obs} estimated here? This is, probably, due to different concentrations of impurity iron ions ($[Fe]_0$) in these experiments. Taking the rate of reaction to be proportional to $[Fe]_0$ for the reaction of sulfite autoxidation as

---

[1] This equation, which describes the dependence of the rate of catalytic sulfite oxidation and follows from data [7], was derived by Collins [14].

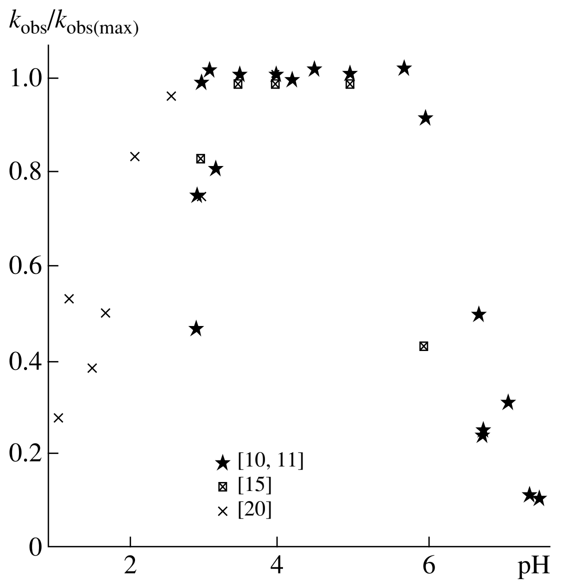

Fig. 3. Catalysis of the oxygen oxidation of sulfite by manganese ions. The pH dependence of the ratio $k_{obs}/k_{obs(max)}$.

before [30], finally, for the rate of catalytic sulfite oxidation under the given conditions (region *I* in Fig. 1), we have $w_{Mn} = k'_{obs}[Mn(II)]^2[Fe]_0/[HSO_3^-]$, where $k'_{obs} = k_{obs}/[Fe]_0$.

Figure 2 demonstrates the results of our analysis of the variable order of reaction with respect to sulfite at different pH and [Mn(II)]/[S(IV)]. Regions *I*, *II*, and *III* marked with dashed curves *a* and *b* in Fig. 2 refer to the modes of catalytic sulfite oxidation with the orders of reaction with respect to sulfite different by unity: –1, 0, and 1, respectively. They were distinguished based on original published data that are indicative of an increase, constancy, or a decrease of w_{Mn} on varying [S(IV)]. It can be seen that the region in which catalytic sulfite oxidation occurs with the negative first order of reaction with respect to sulfite corresponds to the values of pH and [Mn(II)]/[S(IV)] at which the order of this reaction with respect to manganese was found to be second in the experiments under consideration. As can be seen, the lowest values of the ratio $[Mn(II)]/[S(IV)] < 0.2$ and pH 2 ± 1 correspond to this region. However, as follows from Fig. 2, the same range of pH is also typical of the mode of catalytic sulfide oxidation with the zero order of reaction with respect to sulfite. However, as can be seen, the zero order with respect to sulfite at the specified pH values requires higher [Mn(II)]/[S(IV)] ratios. Both the modes of catalytic sulfite oxidation under discussion are difficult to distinguish with the use of the independence of w_{Mn} from [S(IV)] in the course of reaction as a differentiating criterion [2, 3, 5, 12] because of the coincidence of pH ranges and similar shapes of the kinetic curves. Outside regions *I* and *II*, catalytic sulfite oxidation is a first-order reaction with respect to sulfite. This is supported by concentration conditions shown in Fig. 2 for a number of studies [10–17] in which the first order of reaction with respect to sulfite was observed experimentally. To finish an analysis of data on the relationship $w_{Mn} \sim [S(IV)]^n$ $(-1 \le n \le +1)$ with the use of Fig. 2, note that the full spectrum of the allowed values of *n* can be observed only in acid sulfite solutions ($1 \le pH \le 3$).

Reaction Order with Respect to H^+

The character of the pH dependence of w_{Mn}, which was reported in the publications cited above and elsewhere, did not allow us to reliably distinguish between the modes of catalytic sulfite oxidation on variations in pH and [Mn(II)]/[S(IV)], as was done in an analysis of the dependence of the rate of this reaction on the concentrations of manganese and sulfite ions. Information on the pH dependence of w_{Mn} can be briefly reduced to the following:

(1) At the ratios $[Mn(II)]/[S(IV)] \ge 0.2$ and low pH (0–3), $w_{Mn} \sim 1[H^+]$ [12]. This dependence can be interpreted as the reflection of the acid–base equilibrium $SO_{2(aq)} \Leftrightarrow HSO_3^- + H^+$ ($pK_1 = 1.86$ [1]).

(2) In the range $-0.22 \le pH \le 2$ and at the concentration ratio $[Mn(II)]/[S(IV)] = 4 \times 10^{-2}$, Collins [14] found a minimum in the reaction rate at pH ≈ 0.3. This observation remains unexplained.

(3) At $[Mn(II)]/[S(IV)] \ge 0.2$, a bell-shaped plot of w_{Mn} against Ph with a maximum at pH 3–5 was observed in a number of studies [10, 11, 15] (see points in Fig. 3), whereas the reaction rate at $[Mn(II)]/[S(IV)] \ll 1$ was almost independent of pH in a range of pH 1–3 [7, 9]. Data relating to the conditions of $[Mn(II)]/[S(IV)] \ge 0.2$ are given in Fig. 3 as the pH dependence of the observed reaction rate constant k_{obs} normalized to the maximum value of $k_{obs(max)}$. The right branch of a bell-shaped curve (Fig. 3) cannot be explained by the dissociation equilibrium $HSO_3^- \Leftrightarrow SO_3^{2-} + H^+$ ($pK_2 = 7.2$ [1]) or the hydrolysis equilibrium of Mn(II) ions ($pK_{Mn^{2+}} \approx 11$ [34]). As mentioned above, the catalysis of sulfite oxidation by manganese ions does not take place without the participation of iron ions. In the case of sulfite oxidation catalysis by iron ions at $[Fe(III)] \approx [Fe]_0$, an analogous bell-shaped plot of w_{Fe} against pH was observed [11, 15, 35]. In terms of this interpretation, the practical independence of w_{Mn} from pH at high [S(IV)], when Fe(II) is the predominant ionic species of iron in solution, can also be explained [30]. In summary, based on the above analysis of the reaction kinetics of catalytic sulfite oxidation, the reaction rate can be expressed in the form

$$w_{Mn} \sim [Mn(II)]^{(2\to 0)}[S(IV)]^{(+1\to -1)}[H^+]^{(-1\to >0)}.$$

MECHANISM OF SULFITE OXIDATION IN THE PRESENCE OF IRON AND MANGANESE IONS

Radical-Chain Mechanism of the Process

This nature of sulfite oxidation "catalysis" by manganese ions follows from experiments in which an inhibiting effect of radical scavengers on the rate of reaction was found. However, substances that not only react with radicals but also form stable complexes with iron and manganese ions are among these additives. Evidently, a kinetic analysis of the effects of these substances is difficult to perform. It is well known that benzene does not form complexes with these transition metal ions [36]; that is, its inhibiting action is indicative of a radical mechanism of the process. Thus, an additive of $[C_6H_6] = 10^{-3}$ mol/l (pH 3; $[\mathrm{Mn(II)}] = 1.5 \times 10^{-4}$ and $[\mathrm{S(IV)}] \approx 2 \times 10^{-3}$ mol/l) resulted in a decrease in the steady-state rate of catalytic sulfite oxidation by a factor of 20 [36]. The participation of radicals in catalytic sulfite oxidation in the presence of manganese ions was also supported by our experimental data on the acceleration of this reaction under exposure to ionizing radiation [28, 33]. This acceleration was $w_{\mathrm{Mn(rad)}}/w_{\mathrm{Mn}} \approx 20$ at the dose rate $I_{\mathrm{aq}} \approx 1.6 \times 10^{-2}$ Gy/s (1 Gy = 1 J/kg). At high values of I_{aq} (≥ 1 Gy/s), the experimentally observed rate of sulfite oxidation is $w_{\mathrm{Mn(rad)}} \sim I_{\mathrm{aq}}$ and it is the same as in the absence of Mn^{2+} [37]. The dependence of $w_{\mathrm{Mn(rad)}}$ on I_{aq} clearly indicates that chain propagation does not take place at high I_{aq}. The reason is a high concentration of chain-transfer agents and their rapid quadratic decay [37]. Of course, the rate of sulfite oxidation decreases with decreasing I_{aq}. However, the radiation-chemical yield (1/100 eV) of sulfite consumption $G(\mathrm{S(IV)})$, that is, a quantity proportional to the chain length, increases, as well as in the absence of Mn^{2+}; in this case, $w_{\mathrm{Mn(rad)}} \sim I_{\mathrm{aq}}^{1/2}$. However, an increase in the chain length with decreasing I_{aq} in the presence of Mn(II) ions is much greater than that in the "pure" system: $G_{\mathrm{Mn}}(-\mathrm{S(IV)}) \geq 300$, whereas $G(-\mathrm{S(IV)}) \leq 60$ ($I_{\mathrm{aq}} \approx 2 \times 10^{-3}$ Gy/s) [28].

The formation of radicals in the transition metal ion–reactants system is associated with a change in the valence state of the metal ion. On the addition of a salt of Mn(II) to an aerated sulfite solution, the reaction rate gradually and slowly increased to a steady-state value [17]. The addition of Mn(III) in a thousandth to ten-thousandth fraction of [Mn(II)] resulted in the disappearance of the acceleration period of the reaction. Berglund *et al.* [38] detected the formation of Mn(III) in the pulsed generation of $SO_5^{\cdot-}$ in S(IV) solutions in the presence of Mn(II) (pH 3) by the short-lived (≤ 100 μs) optical absorption with two peaks (the main peak at $\lambda_{\max} \approx 260$ nm and a weaker peak at $\lambda_{\max} \approx 450$ nm), which are characteristic of the optical absorption of Mn(III). According to Berglund *et al.* [38], the rate constant of the reaction of $SO_5^{\cdot-}$ with Mn(II) is 10^8 l mol^{-1} s^{-1}, which is consistent with the data of Waygood [39], who spectroscopically examined the kinetics of $SO_5^{\cdot-}$ consumption ($\lambda_{\max} \approx 260$ nm) in the laser photolysis of an aerated solution of dithionate $S_2O_6^{2-} \xrightarrow{h\nu} 2SO_3^{\cdot-} \xrightarrow{O_2} SO_5^{\cdot-}$ in the presence of Mn(II). However, a considerable difference between the rate constants of the reactions

$$SO_5^{\cdot-} + \mathrm{Fe(II)} \xrightarrow{H^+}, \quad k_7 = 3.2 \times 10^6 \ \mathrm{l\ mol^{-1}\ s^{-1}};$$

$$SO_5^{\cdot-} + \mathrm{Mn(II)} \xrightarrow{H^+}, \quad k_9 \approx 10^8 \ \mathrm{l\ mol^{-1}\ s^{-1}}$$

has attracted considerable interest, taking into account that $\Delta G^\circ_{298}(\mathrm{Fe}) < \Delta G^\circ_{298}(\mathrm{Mn})$, where $\Delta G^\circ_{298}(\mathrm{i})$ is the change in the Gibbs potential for the reactions of $SO_5^{\cdot-}$ with manganese and iron ions, respectively [40, 41]. In the case of an outer-sphere mechanism, the reaction of $SO_5^{\cdot-}$ with Fe(II) ions would be characterized by a high rate constant in accordance with the linear function $\ln k = 1.25 - 0.25\Delta G^\circ_{298}(\mathrm{i})$ [42], where k has a dimension of l mol^{-1} s^{-1}. If the reactions occur via an inner-sphere mechanism, that is, as the sequence

$$SO_5^{\cdot-} + Fe^{2+} \longrightarrow Fe^{2+}SO_5^- \longrightarrow FeOH^{2+} + HSO_5^-,$$

$$SO_5^{\cdot-} + Mn^{2+} \longrightarrow Mn^{2+}SO_5^- \longrightarrow MnOH^{2+} + HSO_5^-,$$

and the formation of complexes with $SO_5^{\cdot-}$ is the rate-limiting step, the above difference between the rate constants of these reactions can be explained. For the substitution of an uncharged particle for H_2O in a coordination sphere, $k_{\mathrm{Mn}} \approx 4 \times 10^5$ [43] and $k_{\mathrm{Fe}} \approx 5.8 \times 10^4$ l mol^{-1} s^{-1} [44]. The value of k increased by 2–4 orders of magnitude for the substitution of a charged particle for $SO_5^{\cdot-}$; that is, it is likely that a higher lability of substitution in the case of Mn^{2+} ions is responsible for the high value of the rate constant of reaction with $SO_5^{\cdot-}$. Note that Berglund *et al.* [38] did not detect the $(MnSO_5)^+$ complex. However, it is not improbable that the spectral characteristics of Mn^{3+} and $(MnSO_5)^+$ as the complex $(Mn^{3+}SO_5^{2-})$ in a partial charge transfer state are similar. The formation of such a complex was spectroscopically detected [45] in the reaction of Mn^{2+} with $O_2^{\cdot-}$ generated in the pulse radiolysis of aqueous $Mn(ClO_4)_2$ solutions. The reaction rate constant of MnO_2^+ formation is 1.5×10^8 l mol^{-1} s^{-1}, that is, close to the rate constant of Mn(III) formation in the reaction with $SO_5^{\cdot-}$ (see above). Data [38] on the reactivity of $SO_5^{\bullet -}$ radicals toward Mn(II) were supplemented by the rate constant HSO_3^-, $k_{10} = 1.3 \times 10^6$ l mol^{-1} s^{-1} of the reaction Mn(III) + HSO_3^-, which was measured by Berglund *et al.* [17]. Thus, in a cycle of chain-propagation reactions with the participation of manganese ions, chain propagation occurs in the reaction sequence $SO_5^{\bullet -} + Mn^{2+} \xrightarrow{H^+} \mathrm{Mn(III)} + HSO_5^-$, $\mathrm{Mn(III)} + HSO_3^- \Rightarrow Mn^{2+} + SO_3^{\bullet -} + H^+$ or $\mathrm{Mn(III)} + SO_3^{2-} \Rightarrow Mn^{2+} + SO_3^{\bullet -}$.

The catalysis of the rate-limiting step of chain propagation $SO_5^{\bullet -} + HSO_3^-/SO_3^{2-} \Rightarrow SO_3^{\bullet -} + HSO_5^-/SO_5^{2-}$ by manganese ions is important; however, it is not the only reason for the nonadditive cocatalytic effect of the Fe–Mn pair. If the role of manganese ions were reduced to only this catalysis, the reaction rate equation would include the product of the concentrations of iron and manganese ions. However, it was mentioned above that the relation $w_{\mathrm{Mn}} \sim [\mathrm{Mn(II)}]^2$ (see region *I* in Fig. 1) is observed under certain concentration conditions. Considering catalytic sulfite oxidation as a free-radical process, this relation can occur if manganese ions exert an accelerating effect on the reaction of chain initiation in addition to the catalysis of the rate-limiting step.

Effect of Mn Ions on the Initiation of Sulfite Oxidation

The electrochemical characteristics of the Mn(II)/Mn(I) pair (–4.46 V [14]) indicate that the generation of $SO_3^{\bullet -}$ does not occur by the interaction of Mn(II) with HSO_3^- (the redox potential of the $HSO_3^-/SO_3^{\bullet -}$ pair is –0.84 V [40]). The conversion of Mn(II) into Mn(I) is observed only in the reaction with the strongest reducing agents such as e_{aq} and $H^{\bullet}$. The generation of Mn(III) by the reaction of Mn(II) with O_2 is also impossible for the same energy reason (the redox potential of the Mn^{2+}/Mn^{3+} pair is (–1.54 V) [14]. The reaction of Mn(II) with HSO_5^- [36], which could additionally generate Mn(III), was found to be very slow ($k \le 1$ l mol^{-1} s^{-1}). One further possibility persists, namely, the effect of manganese ions on the distribution of iron ions between Fe(II) and Fe(III) species to result in an increase in [Fe(III)] and, hence, in an increase in the rate of initiation (w_i).

It is well known [27, 29, 35, 46] that in the HSO_3^-/O_2/Fe(III/II) system, $FeOH^{2+}$ is the catalytically active species, which participates in the generation of $SO_3^{\bullet -}$ at the initiation step of catalytic sulfite oxidation (see Tables 1 and 2):

$$FeOH^{2+} + HSO_3^- \overset{K_4}{\rightleftarrows} FeOHSO_3H^+$$

$$\xrightarrow{k_1} Fe^{2+} + SO_3^{\bullet -} + H_2O.$$

Table 1. Radical-chain mechanism of sulfite oxidation in the presence of manganese(II) and iron ions

Reaction no.	Reaction	Rate constant, l mol^{-1} s^{-1}	References
I	$FeOHSO_3H^+ \longrightarrow Fe^{2+} + SO_3^{\bullet -} + H_2O$	0.2*	[55, 56]
II	$SO_3^{\bullet -} + O_2 \longrightarrow SO_5^{\bullet -}$	2.5×10^9	[57]
III	$SO_5^{\bullet -} + HSO_3^- \longrightarrow HSO_5^- + SO_3^{\bullet -}$	$\approx 3.4 \times 10^3$	[37]
IV	$SO_5^{\bullet -} + SO_5^{\bullet -} \longrightarrow SO_4^{\bullet -} + SO_4^{\bullet -} + O_2$	8.7×10^7	[58, 59]
V	$SO_4^{\bullet -} + HSO_3^- \longrightarrow SO_4^{2-} + SO_3^{\bullet -} + H^+$	6.8×10^8	[57]
VI	$HSO_5^- + HSO_3^- + H^+ \longrightarrow 2SO_4^{2-} + 3H^+$	$\approx 10^7\ [H^+]$	[60–62]
VII	$Fe^{2+} + SO_5^{\bullet -} \xrightarrow{H^+} Fe^{3+} + HSO_5^-$	3.2×10^6	[63]
VIII	$Fe^{2+} + HSO_5^- \longrightarrow Fe^{3+} + SO_4^{\bullet -} + OH^-$	$(3.0–3.5) \times 10^4$	[63–65]
IX	$Mn^{2+} + SO_5^{\bullet -} \xrightarrow{H^+} \mathrm{Mn(III)} + HSO_5^-$	$(1.0–2.0) \times 10^8$	[38, 39]
X	$\mathrm{Mn(III)} + HSO_3^- \longrightarrow Mn^{2+} + SO_3^{\bullet -} + H^+$	1.3×10^6	[17]
XI	$SO_5^{\bullet -} + SO_5^{\bullet -} \longrightarrow S_2O_8^{2-} + O_2$	1.3×10^7	[58, 59]

* The first-order reaction rate constant is given in s^{-1}.

Iron salts added to solutions or uncontrollable traces of iron ions in water and reagents at any degree of purification serve as a source of $FeOH^{2+}$ in sulfite solutions.

The effect of Mn(II) on the rate of initiation by iron ions can be judged from data on the concentration of impurity iron ions in solution and on the distribution of iron between the valence forms. Evidently, this effect is most pronounced under conditions of an experimentally observed second order of reaction with respect to manganese (see region *I* in Fig. 1). However, such data are absent from original publications, except for the value of $[Fe]_0$, which was analytically determined in [9]. Our own estimates of the values of impurity $[Fe]_0$ and the distribution of iron ions between the Fe(III) and Fe(II) species under conditions specified in the cited publications are given below. With the use of experimental data [9] on w_{Mn} at $[Fe]_0 = 5 \times 10^{-7}$ mol/l (pH 2.17; $[Mn(II)] = 10^{-4}$ and $[S(IV)] = 10^{-2}$ mol/l) and the above empirical equation for w_{Mn}, we found the numerical value of the observed rate constant $k'_{obs} = w_{Mn}[HSO_3^-]/[Mn(II)]^2[Fe]_0 \approx 5 \times 10^6$ l mol^{-1} s^{-1}. Previously [5, 9, 12], the expression for w_{Mn} under the specified conditions was usually given in the form $w_{Mn} = k''_{obs}[Mn(II)]^2$. Multiplying k'_{obs} by the ratio $[Fe]_0/[HSO_3^-] \approx 7 \times 10^{-5}$ for the experiments described by Huss *et al.* [9], we obtain $k''_{obs} \approx 370$ l mol^{-1} s^{-1}. This value is only 20% higher than the value of $k''_{obs} = 300$ l mol^{-1} s^{-1} found by Martin and Hill [19] in independent experiments. Thus, the assumption on the proportionality of w_{Mn} and the $[Fe]_0/[HSO_3^-]$ ratio was substantiated. Using $k''_{obs} \approx 5 \times 10^6$ l mol^{-1} s^{-1} and taking into account published data [12] on w_{Mn} measured at pH 2 and $[S(IV)] = 5 \times 10^{-4}$ mol/l, we found that, in these experiments, the concentration of impurity iron was $\approx 3 \times 10^{-8}$ mol/l. We found in a similar manner that $[Fe]_0 \approx 10^{-6}$ or 3×10^{-7} mol/l in the experiments described in [3] or [5], respectively. Hoffman and Jacob [23] estimated $k''_{obs} \approx (5–8) \times 10^2$ l mol^{-1} s^{-1} for the experiments described in [2], and we found $[Fe]_0 \approx 9 \times 10^{-7}$ mol/l for these experiments. An analogous estimation gave $[Fe]_0 \approx 6 \times 10^{-7}$ mol/l for the experimental data [7]. The above estimates of impurity $[Fe]_0$ can be considered mutually consistent. Moreover, these values of $[Fe]_0$ are close to the impurity $[Fe]_0$ evaluated previously [30] for the experiments on uncatalyzed sulfite oxidation [32, 47–50]. To judge the effect of manganese ions on the distribution of iron ions between the valence forms at given pH and [S(IV)], let us initially evaluate this distribution in the absence of Mn(II). For this purpose, we consider our experimental data on the effect of $S_2O_8^{2-}$ additives on w_i (pH ≥ 3; $[Fe]_0 \approx 5 \times 10^{-7}$ and $[S(IV)] \approx 10^{-2}$ mol/l) [50]. The addition of $S_2O_8^{2-}$ caused a dramatic increase in w_i, and a saturation effect, that is, a weak increase in w_i with $[S_2O_8^{2-}]$, was

Table 2. Dissociation and complexation equilibrium constants, $T = 298$ K [1]

Reaction no.	Reaction	Equilibrium constant K_i
I	$SO_{2(aq)} \rightleftarrows HSO_3^- + H^+$	1.4×10^{-2} mol/l
II	$HSO_3^- \rightleftarrows SO_3^{2-} + H^+$	6.2×10^{-8} mol/l
III	$[Fe(H_2O)_6]^{3+} \rightleftarrows [Fe(H_2O)_5(OH)]^{2+} + H^+$	6.0×10^{-3} mol/l
IV	$[Fe(H_2O)_5(OH)]^{2+} + HSO_3^- \rightleftarrows [Fe(H_2O)_4(HSO_3)(OH)]^+$	600 l/mol
V	$[Fe(H_2O)_5(OH)]^{2+} \rightleftarrows [Fe(H_2O)_4(OH)_2]^+ + H^+$	7.0×10^{-5}* mol/l
VI	$[Fe(H_2O)_6]^{3+} + HSO_3^- \rightleftarrows [Fe(H_2O)_5(HSO_3)]^{2+} + H_2O$	72.0 l/mol
VII	$[Fe(H_2O)_6]^{3+} + SO_3^{2-} \rightleftarrows [Fe(H_2O)_5(SO_3)]^+ + H_2O$	7.3×10^6 l/mol
VIII	$[Fe(H_2O)_5(OH)]^{2+} + SO_3^{2-} \rightleftarrows [Fe(H_2O)_4(SO_3)] + H_2O$	2.0×10^7 l/mol
IX	$[Mn(H_2O)_6]^{2+} \rightleftarrows [Mn(H_2O)_5(OH)]^+ + H^+$	$\approx 1 \times 10^{-11}$** mol/l
X	$[Mn(H_2O)_6]^{3+} \rightleftarrows [Mn(H_2O)_5(OH)]^{2+} + H^+$	2.5*** mol/l
XI	$[Fe(H_2O)_6]^{3+} + SO_4^{2-} \rightleftarrows [Fe(H_2O)_5(SO_4)]^+ + H_2O$	$\approx 2.6 \times 10^2$**** l/mol

* Taken from [66].
** Taken from [34].
*** Taken from [67].
**** Taken from [27].

observed at $[\mathrm{S_2O_8^{2-}}] \geq 10^{-2}$ mol/l. The reason for this was an acceleration of Fe(III) regeneration in the reaction $\mathrm{Fe^{2+} + S_2O_8^{2-} \xrightarrow{k} Fe^{3+} + SO_4^{\dot{-}} + SO_4^{2-}}$, $k \approx 10$ l mol^{-1} s^{-1} [36]. A comparison between w_i measured in the presence and in the absence of $\mathrm{S_2O_8^{2-}}$ resulted in $\zeta = [\mathrm{Fe(III)}]/[\mathrm{Fe(II)}] \approx 10^{-2}$. A similar analysis of the experimental data [51] gave a similar result: $\zeta \leq 10^{-2}$ (in these experiments, $\mathrm{HSO_5^-}$ additives were used as a redox initiator of sulfite autoxidation (pH 3; $[\mathrm{S(IV)}] \approx 10^{-3}$ mol/l). In summary, we have $[\mathrm{Fe(II)}] \approx [\mathrm{Fe}]_0$ at the given pH and [S(IV)] in the absence of manganese ions added.

It is evident that, at low pH and $[\mathrm{Mn(II)}]/[\mathrm{S(IV)}] \ll k_{10}/k_9$, reaction (IX) between $\mathrm{SO_5^{\dot{-}}}$ and $\mathrm{Mn^{2+}}$ is a rate-limiting step in chain propagation with the participation of manganese ions because $[\mathrm{SO_5^{\dot{-}}}]/[\mathrm{Mn(III)}] = k_{10}[\mathrm{HSO_3^-}]/k_9[\mathrm{Mn(II)}] \gg 1$. Writing an expression for the rate of chain sulfite oxidation in the form $w_\mathrm{Mn} \approx 2k_9[\mathrm{SO_5^{\dot{-}}}][\mathrm{Mn(II)}]$, we obtain $[\mathrm{SO_5^{\dot{-}}}] \approx w_\mathrm{Mn}/2k_9\,[\mathrm{Mn(II)}]$. Substituting this expression into the equation for ζ and taking into account that $[\mathrm{Fe(II)}] \approx [\mathrm{Fe}]_0$, we find $\zeta \approx [\mathrm{Fe(III)}]/[\mathrm{Fe}]_0 \approx k_9[\mathrm{SO_5^{\dot{-}}}]/k_1\chi \approx w_\mathrm{Mn}/2k_1\chi[\mathrm{Mn(II)}]$. Here, $\chi = [\mathrm{FeOHSO_3H^+}]_\mathrm{eq}/[\mathrm{Fe(III)}]_\Sigma$, where $[\mathrm{FeOHSO_3H^+}]_\mathrm{eq}$ is the equilibrium concentration of the complex precursor of sulfite radicals (see Table 1) and $[\mathrm{Fe(III)}]_\Sigma$ is the sum of the equilibrium concentrations of all forms of Fe(III) ions in solution (see Table 2). The derived expression for ζ does not take into account the contribution from the intermediate product $\mathrm{HSO_5^-}$ (VIII) to the oxidation of bivalent iron because $w_7/w_8 \approx k_6k_7[\mathrm{HSO_3^-}]/k_8k_9[\mathrm{Mn(II)}] \gg 1$. Substituting $k''_\mathrm{obs} \times [\mathrm{Mn(II)}]^2[\mathrm{Fe}]_0/[\mathrm{HSO_3^-}]$ for w_Mn in the expression for ζ, we obtain $\zeta \approx k''_\mathrm{obs}[\mathrm{Mn(II)}]\,[\mathrm{Fe}]_0/2k_1\chi[\mathrm{HSO_3^-}]$. For the minimum $[\mathrm{Mn(II)}] = 1.3 \times 10^{-5}$ mol/l used in the experiments [9] ($[\mathrm{S(IV)}] = 10^{-2}$ mol/l; pH 2.17; $\chi \approx 0.6$), we have $\zeta \approx 2 \times 10^{-2}$. For the maximum $[\mathrm{Mn(II)}] = 10^{-4}$ mol/l at the specified pH and [S(IV)], we obtain $\zeta \approx 0.15$; that is, ~13% impurity iron occurs in the form of Fe(III) under these conditions. This value is higher than ζ in the absence of Mn(II) by a factor of ~10 (!). Evidently, this effect of manganese ions on ζ and w_i will be retained for as long as $[\mathrm{Fe(III)}]/[\mathrm{Fe}]_0 \ll 1$. With the use of the expression for ζ and the balance equation for iron ions in solution $[\mathrm{Fe}]_0 = [\mathrm{Fe(III)}] + [\mathrm{Fe(II)}]$, we obtain $[\mathrm{Mn(II)}]_\mathrm{max} \approx 2k_1\chi[\mathrm{HSO_3^-}]/k''_\mathrm{obs}[\mathrm{Fe}]_0$. For the experiments [5] (pH 2.7; $[\mathrm{S(IV)}] \approx 2 \times 10^{-3}$ mol/l), calculations by this equation give $[\mathrm{Mn(II)}]_\mathrm{max} \approx 1.4 \times 10^{-4}$ mol/l, which is almost equal to the experimental value. It also follows that an increase in the concentration of sulfite results in an increase in $[\mathrm{Mn(II)}]_\mathrm{max}$; this is in complete agreement with the results [10]. The derived expression for $[\mathrm{Mn(II)}]_\mathrm{max}$ explains the occurrence of a narrow range of pH (2 ± 1) in which the rate law $w_\mathrm{Mn} \sim [\mathrm{Mn(II)}]^2$ is obeyed (see Fig. 1). At pH > 3 (Fig. 1), the value of $[\mathrm{Mn(II)}]_\mathrm{max}$ and, as a consequence, the $[\mathrm{Mn(II)}]_\mathrm{max}/[\mathrm{S(IV)}]$ ratio decrease because of a dramatic decrease in χ. At pH < pK_1, both χ and $[\mathrm{HSO_3^-}]$ decrease to result in a decrease in $[\mathrm{Mn(II)}]_\mathrm{max}/[\mathrm{S(IV)}]$ in the region of low pH values.

What is responsible for the effect of manganese ions on ζ? It would seem that this effect could be associated with the reaction of Mn(III) with Fe(II), which accelerates the regeneration of a catalytically active Fe(III) species. This replacement of a highly active Mn(III) species by an inactive long-lived Fe(III) center ($\tau_1 \approx (k_1\chi\zeta)^{-1}$) is identical to that occurring in reaction (VII) (Table 1), and this is chain termination. However, in this case, $\tau_7 \ll (k_{\mathrm{Mn(III)\,+\,Fe(II)}}[\mathrm{Fe}]_0)^{-1}$.

It is more likely that the effect of manganese additives on ζ should be associated with a change in the concentration of the strong oxidizing agent $\mathrm{HSO_5^-}$; the rate of formation of this species increases in the presence of manganese ions. For example, Penkett *et al.* [52] reported that at higher pH values, the conversion of S(IV) into $\mathrm{HSO_5^-}$ in the course of an uncatalyzed reaction was as high as tens of percent. Under these conditions, the rate of Fe(III) regeneration by the reaction of Fe(II) with $\mathrm{HSO_5^-}$ is much higher than the rate of reaction (VII) (Table 1); that is, $w_8/w_7 \gg 1$. However, the above evaluations of the effect of Mn(II) on ζ are also indicative of an increase in ζ at low pH and high [S(IV)], when the steady-state concentration of $\mathrm{HSO_5^-}$ is low because of reaction (VI) (Table 1). This was also supported by preliminary data [53] on an increase in ζ on the addition of manganese ions to sulfite solutions. A conceivable reason for the increased efficiency of the effect of $\mathrm{HSO_5^-}$ on ζ even under the above conditions is that the interaction of Fe(II) with $\mathrm{HSO_5^-}$ is accompanied by not only the regeneration of Fe(III) but also the formation of the reactive chain-transfer agent $\mathrm{SO_4^{\dot{-}}}$ (reaction VIII from Table 1):

$$\mathrm{HSO_5^- + Fe(II) \Rightarrow Fe^{3+} + SO_4^{\dot{-}} + OH^-}$$

This interaction of Fe(II) with $\mathrm{HSO_5^-}$ can in essence be considered as a chain-branching reaction [54].

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 00-05-64029 and

01-02-16172), the Ministry of Atomic Energy of the Russian Federation, and the Ministry of Education of the Russian Federation (project no. 6-26).

REFERENCES

1. Brandt, C. and van Eldik, R., *Chem. Rev.*, 1995, vol. 95, no. 1, p. 119.
2. Hoather, R.C. and Goodeve, C.F., *Trans. Faraday Soc.*, 1934, vol. 30, p. 1151.
3. Johnstone, H.F. and Coughanowr, D.R., *Ind. Eng. Chem.*, 1958, vol. 50, p. 1169.
4. Neytzell-de-Wilde, F.G. and Traverner, L., *Proc. 2nd United Nations Int. Conf. on Peaceful Uses of Atomic Energy*, Geneva: United Nations, 1958, vol. 3, p. 303.
5. Coughanowr, D.R. and Krause, F.E., *Ind. Eng. Chem. Fund.*, 1965, vol. 4, no. 1, p. 61.
6. Penkett, S.A., Jones, B.M.R., and Eggleton, A.E.J., *Atmos. Envir.*, 1979, vol. 13, p. 139.
7. Pasiuk-Bronikowska, W. and Bronikowskii, T., *Chem. Eng. Sci.*, 1981, vol. 36, p. 215.
8. Pasiuk-Bronikowska, W. and Ziajkai, J., *Chem. Eng. Sci.*, 1985, vol. 40, p. 1567.
9. Huss, A., Jr., Lim, P.K., and Eckert, C.A., *J. Phys. Chem.*, 1982, vol. 86, no. 21, p. 4224.
10. Ibusuki, T. and Barnes, H.M., *Atmos. Envir.*, 1984, vol. 18, p. 145.
11. Ibusuki, T. and Takeuchi, K., *Atmos. Envir.*, 1987, vol. 21, p. 1555.
12. Martin, L.R., *Acid Precipitation Series*, Calvert, J.G., Ed., Boston: Butterworth, 1984, vol. 3, p. 63.
13. Ulrich, R.K., Rochelle, G.T., and Prado, R.E., *Chem. Eng. Sci.*, 1986, vol. 41, no. 8, p. 2183.
14. Collins, R., *Ph.D. Thesis*, Atlanta: Georgia Institute of Technology, 1987.
15. Grgić, I., Hudnick, V., Bizjak, M., and Levec, J., *Atmos. Envir.*, 1991, vol. 25, no. 8, p. 1591.
16. Grgić, I., Hudnick, V., Bizjak, M., and Levec, J., *Atmos. Envir.*, 1992, vol. 26A, no. 4, p. 571.
17. Berglund, J., Fronaeous, S., and Elding, L.I., *Inorg. Chem.*, 1993, vol. 32, p. 4527.
18. Basset, H. and Parker, W.G., *J. Chem. Soc.*, 1951, p. 1541.
19. Martin, L.R. and Hill, M.W., *J. Phys. E: Sci. Instrum.*, 1987, vol. 20, p. 1383.
20. Berglund, J. and Elding, L.I., *Final Report Contract no. STEP-0005-C(MB), Report B*, 1992, p. 27.
21. Martin, L.R. and Good, T.W., *Atmos. Envir.*, 1991, vol. 25A, no. 10, p. 2395.
22. Huie, R.E. and Peterson, N.C., in *Trace Atmospheric Constituents, Properties, Transformations and Fates*, Schwartz, S.E., Ed., New York: Wiley, 1983, p. 117.
23. Hoffman, M.R. and Jacob, D., *Acid Precipitation Series. SO_2, NO, and NO_2 Oxidation Mechanisms: Atmospheric Consideration*, Calvert, J.G., Ed., Boston: Butterworth, 1984, vol. 3, p. 101.
24. Berglund, J., Fronaeous, S., and Elding, L.I., *Atmos. Envir.*, 1995, vol. 29, no. 12, p. 1379.
25. Golodov, V.A. and Kashnikova, L.V., *Usp. Khim.*, 1988, vol. 57, no. 11, p. 1796.
26. Gupta, K.R., Madnawat, P.V.S., Rani, A., *et al.*, *Topics in Chemistry, Series 1: Chemical Kinetics and Reaction Mechanisms*, Gupta, K.S., Ed., Jaipur: RBSA, 1991, p. 117.
27. Warneck, P., Mirabel, V., Salmon, G.A., *et al.*, *Review of the Activities and Achievements of the EUROTRAC Subproject HALIPP*, Warneck, P., Ed., Berlin: Springer, 1996, vol. 2, p. 7.
28. Yermakov, A.N., Poskrebyshev, G.A., and Purmal’, A.P., *Prog. React. Kinet.*, 1997, vol. 22, no. 2, p. 141.
29. Ermakov, A.N., Kozlov, Yu.N., and Purmal’, A.P., *Kinet. Katal.*, 1999, vol. 40, no. 5, p. 663.
30. Ermakov, A.N. and Purmal’, A.P., *Kinet. Katal.*, 2001, vol. 42, no. 4, p. 531.
31. Ermakov, A.N. and Purmal’, A.P., *Khim. Fiz.*, 2002, vol. 21, no. 1, p. 31.
32. Brimblecomb, P. and Spedding, D.J., *Atmos. Envir.*, 1974, vol. 8, p. 937.
33. Yermakov, A.N., Poskrebyshev, G.A., and Purmal’, A.P., *Atmos. Envir.*, 1997, vol. 31, no. 4, p. 621.
34. Smith, R.M. and Martell, A.E., *Critical Stability Constants*, New York: Plenum, 1976, vol. 4.
35. Bal Reddy, K. and van Eldik, R., *Atmos. Envir.*, 1992, vol. 26A, no. 4, p. 661.
36. Fischer, M., Paydar, M., Warneck, P., *et al.*, *Final Report Contract no. STEP-0005-C(MB), Report F*, 1992, p. 75.
37. Yermakov, A.N., Zhitomirsky, B.M., Poskrebyshev, G.A., *et al.*, *J. Phys. Chem.*, 1995, vol. 99, no. 10, p. 3120.
38. Berglund, J., Elding, L.I., Buxton, G.V., *et al.*, *J. Chem. Soc., Faraday Trans.*, 1994, vol. 90, no. 21, p. 3309.
39. Waygood, S., *Final Report Contract no. STEP-0005-C(MB), Report D*, 1992, p. 53.
40. Stanbury, D.M., *Adv. Inorg. Chem.*, 1989, vol. 34, p. 69.
41. Latimer, W., *Oxidation Potentials*, Engelwood Cliffs: Prentice-Hall, 1952.
42. Uskov, A., *Cand. Sci. Phys.-Math. Sci. Dissertation*, Moscow: Inst. of Chem. Phys., 1985.
43. Documman, Y., Newman, K.E., and Merbach, A.E., *Helv. Chim. Acta*, 1979, vol. 63, p. 2511.
44. Purmal’, A.P., *Doctoral (Chem.) Dissertation*, Moscow: Inst. of Chem. Phys., 1971.
45. Jacobsen, F., Holcman, J., and Sehested, K., *J. Phys. Chem.*, 1997, vol. 101, no. 7, p. 1324.
46. Ziajka, J., Beer, F., and Warneck, P., *Atmos. Envir.*, 1994, vol. 28, no. 15, p. 2549.
47. Fuller, E.C. and Crist, R.H., *J. Am. Chem. Soc.*, 1941, vol. 63, no. 6, p. 1644.
48. Miller, J.M. and de Pena, R.G., *J. Geophys. Res.*, 1972, vol. 77, p. 5905.
49. Larson, T.J., Horike, N.R., and Harrison, H., *Atmos. Envir.*, 1978, vol. 12, no. 8, p. 1597.
50. Travina, O.I., Kozlov, Yu.N., Purmal’, A.P., *et al.*, *Zh. Fiz. Khim.*, 1999, vol. 73, no. 8, p. 1361.
51. Ziajka, J., Pasiuk-Bronikowska, W., and Warneck, P., *Proc. Joint EC/EUROTRAC Workshop’95, Lactoz-Halipp, Rep. EUR 16766 EN*, Mirabel Ph., Ed., Brussels-Luxemburg, 1996, p. 114.
52. Penkett, S.A., Jones, D.M.R., Brice, K.A., *et al.*, *Atmos. Envir.*, 1979, vol. 13, p. 123.

53. Poznic, M., Grgić I., Bercić G., *Proc. EUROTRAC Symposium’98*, Borelli, P.M. and Borelli, P., Eds., Southampton: WitPRESS, 1999, vol. 1, p. 734.

54. Yermakov, A.N. and Purmal’, A.P., *Program and Abstracts, 4th Int. Conf. on Chemical Kinetics*, Gaithersburg: NIST, 1997, p. 283.

55. Brandt, C., Fabian, I., and van Eldik, R., *Inorg. Chem.*, 1994, vol. 33, no. 4, p. 687.

56. Brandt, C. and van Eldik, R., *Transition Met. Chem.*, 1998, vol. 23, p. 667.

57. Buxton, G.V., Croft, S., McGowan, S., *et al.*, *Atmos. Envir.*, 1996, vol. 30, no. 14, p. 2483.

58. Yermakov, A.N., Zhitomirsky, B.M., Poskrebyshev, G.A., *et al.*, *J. Phys. Chem.*, 1993, vol. 97, p. 10712.

59. Huie, R.E., Clifton, C.L., and Altstein, N., *Radiat. Phys. Chem.*, 1989, vol. 33, p. 361.

60. Betterton, E.A. and Hoffman, M.R., *J. Phys. Chem.*, 1988, vol. 92, p. 5962.

61. McElroy, J.W. and Deister, U., *Kinetics of the Oxidation of Sulphur(IV) by Peroxomonosulphate*, National Power Research Report ESTB/L/0173/R90, 1990.

62. Drexler, C., Elias, H., Fechner, B., Gotz, U., and Wannowius, K.J., *EUROTRAC Ann. Rep.*, 1992, part 6, p. 23.

63. Barlow, S., Buxton, G.V., Salmon, G.A., *et al.*, *EUROTRAC Ann. Rep.*, 1993, part 6, p. 48.

64. Gilbert, B.C. and Stell, J., *J. Chem. Soc., Perkin Trans.*, 1990, vol. 2, no. 2, p. 1281.

65. Warneck, P. and Ziajka, J., *Ber. Bunsenges. Phys. Chem.*, 1995, vol. 9, no. 1, p. 59.

66. Benkelberg, H.-J. and Warneck P., *J. Phys. Chem.*, 1995, vol. 99, p. 5214.

67. Biedermann, G. and Palombary, R., *Acta Chem. Scand.*, 1978, vol. 32A, p. 381.