Kinetics and Mechanism for Manganese-Catalyzed Oxidation of Sulfur(IV) by Oxygen in Aqueous Solution

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The kinetics for manganese-catalyzed autoxidation of sulfur(IV) ($SO_2{\cdot}nH_2O$, HSO_3^-, SO_3^{2-}) in aqueous solution has been studied spectrophotometrically at 25 °C, $1 < pH < 4$, $[S(IV)] \approx 2.3 \times 10^{-5}$ M, 1×10^{-6} M $\leq [Mn(II)] \leq 1.5 \times 10^{-3}$ M, $[Mn(III)] \leq 4 \times 10^{-8}$ M, $[O_2] \approx 2.5 \times 10^{-4}$ M, and low ionic strength. In the absence of added manganese(III), the kinetic traces display an induction period followed by a reaction first-order in sulfur(IV). Addition of a small amount of manganese(III) increases the rate significantly and suppresses the induction period. At pH 2.4, the first-order rate constant is $k_{obsd} = k[Mn(II)](1 + B[Mn(III)]_0)/(A + [Mn(II)])$, where A and B are constants and $[Mn(III)]_0$ is the concentration of initially added manganese(III). The experiments are interpreted in terms of a free-radical chain mechanism. The first step, with rate constant $k_8 = (1.3 \pm 0.6) \times 10^6$ M^{-1} s^{-1}, is a reaction between manganese(III) and a manganese(II) hydrogen sulfite complex with stability constant $\beta_1 = (3 \pm 1) \times 10^4$ M^{-1}: $Mn(III) + MnHSO_3^+ \xrightarrow{k_8} 2Mn(II) + SO_3^- + H^+$. The catalytic activity of Mn(III/II) may be explained by formation of an oxo- (or hydroxo-) bridged mixed-valence precursor complex $Mn^{III}{-}O{-}Mn^{II}{-}HSO_3$, in which bridged electron transfer produces the SO_3^- radical. When $[Fe(III)] < 10^{-6}$ M is added to the reacting system, the oxidation rate becomes much faster than the sum of the individual contributions from the manganese and iron catalyses; i.e., a synergistic effect is displayed. Initiation of the manganese-catalyzed oxidation in the absence of initially added manganese(III) is shown to be due to a trace impurity of ca. $(1–2) \times 10^{-8}$ M iron(III). The SO_3^- radical is generated by the oxidation of sulfur(IV) by iron(III). In subsequent steps, manganese(II) is oxidized to manganese(III) by SO_5^- formed by oxidation of SO_3^- with dissolved oxygen. Computer simulation of the overall kinetics shows that an iron(III) concentration of 2×10^{-8} M is indeed sufficient to initiate the manganese-catalyzed oxidation and explains the autocatalysis. At pH 4.0, the first-order rate constant is $k_{obsd} = (k[Mn(II)] + k'[Mn(II)]^2)/(A + [Mn(II)])$. The quadratic manganese(II) term indicates formation of a sulfito-bridged manganese(II) complex, $MnSO_3Mn^{2+}$, which can also be attacked by manganese(III), forming SO_3^- radicals. Several discrepancies in previous literature may be explained by the reaction mechanism derived.

Introduction

The oxidation of sulfur(IV), i.e. an equilibrium mixture of $SO_2{\cdot}nH_2O$, HSO_3^-, and SO_3^{2-}, by oxygen in aqueous solution catalyzed by transition metal ions has been the subject of a large number of experimental studies.[1–69] The catalysis by manganese(II)[1–34] and iron(III/II)[19,20,34,39–56] has been extensively investigated, and some studies of copper[34,43,44,61–66] and cobalt[57–60] catalysis have also been performed. Iron and manganese seem

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to be the most efficient transition metal catalysts for this oxidation. In atmospheric aqueous systems, catalyzed oxidation of dissolved sulfur dioxide by these transition metal ions is considered to contribute significantly to the formation of acid rain.[16,67,68]

The interpretation of the observed kinetics in terms of reaction mechanisms is inconsistent for many of these catalyzed reactions. In particular, this is the case for the manganese catalysis. A reaction mechanism involving formation of a manganese(II) sulfite complex followed by dioxygen binding to this complex and intramolecular electron transfer between the coordinated dioxygen molecule and the sulfite was suggested already by Basset and Parker in 1951[4] and this mechanism has been repeatedly proposed thereafter,[12,14,23,24] but a firm experimental basis has not been presented so far.

The possible role of manganese(III) in the manganese-catalyzed oxidation has been discussed,[2,17,23,30,33] but to our knowledge there is only one report so far in which it is experimentally shown that the rate is influenced by manganese(III).[33] This study was performed in azide medium to stabilize Mn(III), and it gave only a qualitative information on the rate law. Recently, studies of copper(III/II),[64] cobalt(III/II),[60] iron(III/II),[53,54] and manganese(III/II)[33] catalysis have been performed. It has been proposed that a common mechanism operates in all these systems.[69] In this mechanism, the trivalent metal ion reacts with sulfur(IV), initiating a radical chain in which sulfur(IV) is oxidized to sulfate by dissolved oxygen. The reduced metal is reoxidized to the trivalent state by strong sulfur oxidants generated in the chain.

The aim of the present study was to elucidate the kinetics of the manganese-catalyzed oxidation of sulfur(IV) in aqueous solution and to find a mechanism which can account also for previous experimental results. In particular, the role of manganese(III) in the catalysis and the proposed complex formation between manganese(II) and sulfur(IV) has been studied and the free-radical mechanism examined. Special attention has been paid to the interference of low concentrations of iron(III) and the previously observed synergism between iron(III) and manganese(II).[16,26,27,35–38]

Experimental Section

Chemicals and Solutions. Manganese(II) perchlorate, $Mn(ClO_4)_2 \cdot 6H_2O$, was either used as supplied from Johnson Matthey GmbH or synthesized according to Purcell and Marianelli.[70] Manganese metal in the form of powder (Aldrich, 50 mesh, 99.9%) was added to ca. 20 mL of water in a beaker. The slurry was stirred with a magnetic stirrer, and an equimolar amount of concentrated perchloric acid (Merck, suprapur) was added dropwise. The solution was filtered to remove traces of undissolved metal and then gently evaporated until crystallization began. $Mn(ClO_4)_2 \cdot 6H_2O$ was recrystallized twice from water to remove traces of acid and dried in a vacuum desiccator over phosphorus pentoxide. Stock solutions of manganese perchlorate were prepared by dissolving $Mn(ClO_4)_2 \cdot 6H_2O$ in water or dilute perchloric acid. The concentration of manganese(II) was determined by atomic absorption spectroscopy. No significant differences could be observed between the experiments by using the different manganese(II) salt preparations.

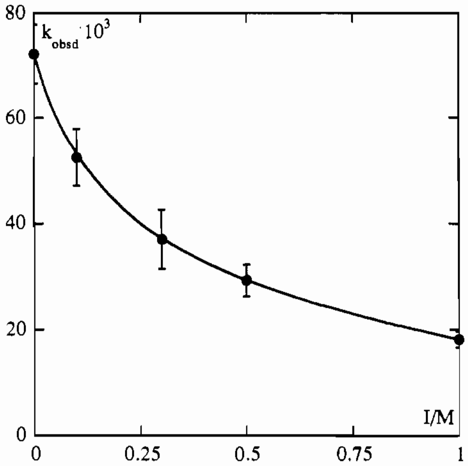

Figure 1. k_{obsd} as a function of ionic strength. Conditions: [Mn(II)] = 4.3×10^{-4} M, $[S(IV)]_0 = 2.3 \times 10^{-5}$ M, $[O_2] \approx 2.5 \times 10^{-4}$ M, pH 4, and 25 °C. The errors are given as the standard deviation from at least five measurements.

Solutions of manganese(III) were prepared by electrochemical oxidation of manganese(II) perchlorate.[23] A 1.81-g amount of $Mn(ClO_4)_2 \cdot 6H_2O$ was dissolved in 100 mL of 4.96 M perchloric acid (Merck, pa) and oxidized at a platinum anode at about 1.25 V and 2 mA cm^{-2} under stirring. In order to avoid disproportionation of manganese(III) according to reaction 1, the final solution contained manganese(II) in

$$2Mn^{3+} + 2H_2O \rightleftharpoons MnO_2 + 4H^+ + Mn^{2+} \qquad (1)$$

excess. The concentration of manganese(III) was determined spectrophotometrically at 470 nm where the molar absorptivity is 64.1 cm^{-1} M^{-1} in 5.8 M $HClO_4$.[23] The solution was stable for several days.

Oxygen-free stock solutions of sodium sulfite, Na_2SO_3 (Merck, pa), in water were prepared under nitrogen in a glovebox. Water was flushed with nitrogen for at least half an hour to remove dissolved oxygen. The stock solutions were prepared fresh daily, and the concentration of sulfite was shown to be constant by iodometric titrations[71] at different times during the experiments.

The autoxidation of sulfur(IV) in aqueous solution is known to be very sensitive to trace impurities due to the catalytic activity of transition metal ions even at very low concentrations and to chain terminating reactions due to the presence of organic impurities. Therefore, no adjustment of the ionic strength was made for most of the experiments in order to avoid contamination from the supporting electrolyte. The experiments were performed under the conditions $[S(IV)] \approx 2.3 \times 10^{-5}$ M, 1×10^{-6} M $\leq$ [Mn(II)] $\leq 1.5 \times 10^{-3}$ M, [Mn(III)] $\leq 4 \times 10^{-8}$ M, [Fe(III)] $\leq 1 \times 10^{-6}$ M, $[O_2] \approx 2.5 \times 10^{-4}$ M, and $1 \leq \text{pH} \leq 4$. The temperature was 25 °C. The ionic strength, I, was waried in the range 0.13 mM $\leq I \leq$ 5.2 mM. In this region, the ionic strength dependence of the rate constant is pronounced, cf. Figure 1, but the error in the observed rate constants due to ionic strength variation was never more than a few percent. In the experiments where the pH dependence was studied, the ionic strength had to be adjusted, and sodium perchlorate, $NaClO_4 \cdot H_2O$ (Merck, pa), was used as a supporting electrolyte. In those experiments the ionic strength was 1.0 M. All solutions were prepared with use of deionized (Millipore, Milli-Q) water.

Hydrolysis and Disproportionation Reactions of Manganese(III) and Manganese(II). Manganese(III) is stable only under conditions of excess manganese(II) and highly acidic solutions, cf. reaction 1.[72,73] In the pH range 1–4 there is little doubt that manganese(III) disproportionates even if manganese(II) is kept in a large excess.

$Mn(H_2O)_6^{3+}$ is a strong acid, and even in strongly acidic solution the hydrolysis is considerable. The stability constants for the two first mononuclear hydroxo complexes have been determined[73] as $\log \beta_1 = 0.4$ and $\log \beta_2 = 0.1$ at $I = 3$M and 25 °C. The formation of higher hydroxo complexes in the present experiments cannot be excluded, but an increase

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of pH also leads to disproportionation of manganese(III) which makes it impossible to study the hydrolysis at pH > 0.[73] Disregarding disproportionation, at pH 1–4, the solutions will contain hydrolyzed species such as $Mn(OH)(H_2O)_5^{2+}$ and $Mn(OH)_2(H_2O)_4^{+}$. It is also known that manganese(III) aqua complexes form polynuclear hydrolysis products.[73] However, at the very low manganese(III) concentrations used in the present study, it can be safely assumed that only mononuclear complexes are present.[73] Below, Mn(III) denotes hydrolyzed manganese(III) without any further specification of the predominant species.

The pK_a value of $Mn(H_2O)_6^{2+}$ is approximately 11,[74] which means that manganese(II) is present predominantly as this complex in the actual pH range used in the present study.

Equilibria in the Sulfur(IV) System. The equilibria for the sulfur(IV) system in water can be written as $SO_2{\cdot}nH_2O \rightleftharpoons HSO_3^- + H_3O^+ + (n-2)H_2O$ ($pK_1 = 1.9, I = 1$ M, 25 °C),[75] $HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$ ($pK_2 = 6.3, I = 1$ M, 25 °C),[75] and $2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$ ($pK_3 = 1.15$).[76] At the sulfur(IV) concentrations used in the present study the presence of $S_2O_5^{2-}$ is negligible, and at pH < 4 the predominant species are HSO_3^- and $SO_2{\cdot}nH_2O$.

Apparatus and Measurements. The kinetics were followed at 200 nm using a Varian Cary 2200 spectrophotometer and thermostated Quarts Suprasil cells. The temperature was held constant at 25 °C. Hydrogen sulfite starts to absorb strongly below 230 nm and has an absorbance maximum at approximately 190 nm with $\epsilon \approx 3700$ cm^{-1} M^{-1}.[77] Experiments performed in the absence of oxygen to prevent oxidation of sulfur(IV) indicated that the molar absorptivity of the manganese(II)/sulfur(IV) complex formed was the same as for the noncomplexed ligand; see discussion below. The molar absorptivity of manganese(II) is much lower and was determined to $\epsilon \approx 51$ cm^{-1} M^{-1} at 200 nm. The product of the reactions is sulfate, which does not absorb at 200 nm. The decrease in absorbance at 200 nm was therefore proportional to the change in total concentration of hydrogen sulfite, $C(HSO_3^-)$.

In the experiments without initially added manganese(III), a manganese(II) solution was prepared from the stock solution of manganese(II) and pH was adjusted with dilute air-saturated perchloric acid. A 3-mL volume of this solution was transferred to the spectrophotometer cell, and the reaction was initiated by adding 10 μL of the sulfur(IV) oxygen-free stock solution with a micropipet. In the experiments with added manganese(III), a manganese(III/II) solution was prepared from the manganese(III/II) stock solution by dilution with the manganese(II) stock solution. This solution was then diluted 300 times with air-saturated water directly in the cell, and the reaction was again initiated by adding 10 μL of the sulfur(IV) stock solution kept in the glovebox. The dilution of the solution in the cell by the addition of sulfur(IV) was never more than 1/300, and the system was pH-buffered by the presence of the perchloric acid. The pH of the final solution was measured with an Orion combination glass electrode and found to agree with calculated values. The final solution in the cell was stirred with a magnetic stirrer to assure rapid mixing. This method made it possible to study reactions with half-lives more than ca. 5 s. Under the present experimental conditions, no influence of light could be observed at 200 nm.

The kinetics were evaluated by means of an OLIS least-squares minimizing program, Model 4300, spectrophotometry version 9.08,[78] implemented on a Victor V286A PC computer. The Kaleidagraph program for Macintosh[79] was used to fit experimental data by least-squares regression analysis and nonlinear curve fitting. Simulations of kinetic traces for a given reaction mechanism were performed by use of the FACSIMILE chemical modeling package,[80] implemented on a Digital VAX station 3100 M38.

Results

Some typical kinetic traces for the manganese(III/II)-catalyzed oxidation of sulfur(IV) are shown in Figure 2. If no manganese(III) is added, the oxidation is autocatalytic with an induction period. After the induction period, the curve can be fitted to a first-order disappearance of hydrogen sulfite according to

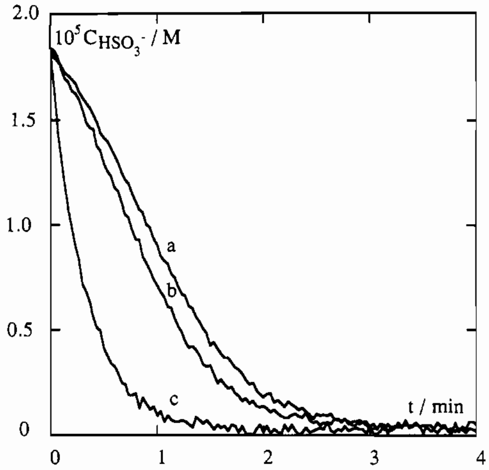

Figure 2. $C(HSO_3^-)$ as a function of time. Conditions: [Mn(II)] = 3.64 × 10^{-5} M, $[O_2] \approx 2.5 \times 10^{-4}$ M, pH 2.4, and 25 °C. Key: $[Mn(III)]_0$ = 0 (a), 0.57 × 10^{-8} M (b), and 1.13 × 10^{-8} M (c).

Table I. Observed Pseudo-First-Order Rate Constants as a Function of the Manganese(II) Concentration at Different Initially Added Concentrations of Manganese(III)[a]

$10^8[Mn(III)]_0$/M	10^4[Mn(II)]/M, $10^3 k_{obsd}$/s^{-1}
0	0.13, 10 ± 2; 0.33, 23 ± 4; 0.43, 40 ± 8; 0.48, 18 ± 2; 0.49, 25 ± 2; 0.79, 53 ± 13; 0.95, 38 ± 4; 1.3, 58 ± 8 1.6, 58 ± 9; 1.9, 49 ± 13; 2.6, 59 ± 17; 2.8, 42 ± 3; 3.3, 39 ± 6; 5.1, 54 ± 2
1.1	0.17, 11 ± 1; 0.17, 15 ± 1; 0.23, 17 ± 3; 0.23, 26 ± 2; 0.30, 25 ± 2; 0.36, 41 ± 3; 0.43, 36 ± 2; 0.56, 45 ± 3; 0.56, 48 ± 1; 0.69, 50 ± 2; 1.0, 52 ± 2; 1.3, 58 ± 3; 2.1, 47 ± 2; 2.6, 50 ± 1
1.4	0.033, 4 ± 1; 0.10, 21 ± 3; 0.17, 36 ± 6; 0.30, 59 ± 17; 0.30, 36 ± 9; 0.56, 49 ± 7; 0.83, 70 ± 10; 1.1, 56 ± 7; 2.2, 57 ± 16; 2.2, 71 ± 8; 4.3, 56 ± 6; 4.3, 92 ± 8; 5.2, 111 ± 36; 5.2, 60 ± 8
1.8	0.2, 7 ± 4; 0.36, 50 ± 2; 0.69, 66 ± 6; 1.32, 82 ± 4; 2.7, 63 ± 4; 5.2, 54 ± 3
2.5	0.058, 8 ± 2; 0.15, 50 ± 3; 0.24, 71 ± 5; 0.42, 101 ± 9; 0.79, 113 ± 8; 1.2, 114 ± 7; 1.5, 130 ± 19; 2.3, 104 ± 10; 3.0, 107 ± 13

[a] The errors are given as the standard deviation from at least five measurements. $[S(IV)]_0 = 2.3 \times 10^{-5}$ M, $[O_2] \approx 2.5 \times 10^{-4}$ M, pH 2.4, temperature 25 °C.

$$-dC(HSO_3^-)/dt = k_{obsd}C(HSO_3^-) \qquad (2)$$

Introduction of trace amounts of manganese(III) affects the kinetics significantly. The induction period disappears gradually when the manganese(III) concentration is increased, it finally vanishes completely, and the kinetics can be evaluated as a simple first-order reaction from the start. The experimental errors in the observed first-order rate constants are quite large due to interference from the induction period and, when manganese(III) is present, due to fast reactions with half-lives near the limit of the experimental method used. (Standard stopped-flow instruments are useless at 200 nm.) The evaluation of the kinetic traces showing autocatalytic behavior was done using the first-order kinetic parts of the kinetic traces as indicated by the statistic information given by the curve-fitting program. The relatively large scattering of the measured absorbance during a run and the inability to sample enough data points in the beginning of the fast reactions made it difficult to determine exactly when the induction periods were finished. Therefore, a quantitative evaluation of the influence of manganese(III) on the induction period was not feasible. Experimental results are summarized in Tables I and II.

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Table II. Observed Pseudo-First-Order Rate Constants as a Function of the Initial Concentration of Manganese(III) at Different Manganese(II) Concentrations[a]

10^4[Mn(II)]/M	10^8[Mn(III)]$_0$/M	10^3k_{obsd}/s^{-1}
0.36	0	21 ± 2
	0	30 ± 1
	0.28	24 ± 1
	0.28	25 ± 1
	0.57	29 ± 2
	0.57	31 ± 1
	1.1	47 ± 2
	1.1	51 ± 1
	2.3	69 ± 6
	2.3	70 ± 4
	3.4	93 ± 8
0.43	0	40 ± 8
	0.98	53 ± 3
	2.0	92 ± 11
	2.9	121 ± 12
	3.9	151 ± 20
0.79	0	53 ± 13
	0.98	62 ± 4
	2.0	115 ± 12
	2.4	139 ± 10
	2.9	129 ± 20
1.6	0	58 ± 9
	0.98	65 ± 2
	2.0	117 ± 6
	2.4	121 ± 16
	2.9	139 ± 14
2.8	0	42 ± 3
	0.98	60 ± 7
	2.0	104 ± 9
	2.4	126 ± 11
	2.9	136 ± 16

[a] The errors are given as the standard deviation from at least five measurements. [S(IV)]$_0$ = 2.3 × 10^{-5} M, [O$_2$] ≈ 2.5 × 10^{-4}, pH 2.4, temperature 25 °C.

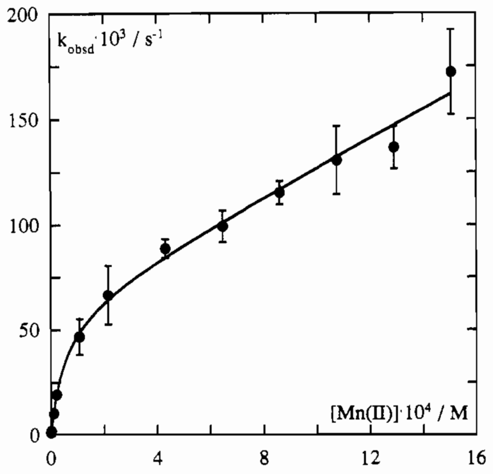

Figure 3. k_{obsd} as a function of [Mn(II)] at 25 °C and pH 4.0 with [S(IV)]$_0$ = 2.3 × 10^{-5} M and [O$_2$] ≈ 2.5 × 10^{-4} M. The errors are given as the standard deviation from at least five measurements. The solid line represents the fit of eq 3a to the experimental data.

The dependence of the observed rate constant on the manganese(II) concentration at pH 4.0 without added manganese(III) is shown in Figure 3. The experimental results can be fitted to eq 3a, where [Mn(II)] denotes the total concentration of

$$k_{obsd} = \frac{k[\mathrm{Mn(II)}] + k'[\mathrm{Mn(II)}]^2}{A + [\mathrm{Mn(II)}]} \qquad (3a)$$

manganese(II), i.e. [Mn(II)] = [Mn^{2+}] + [MnHSO$_3^+$]; see discussion below. At high and low manganese(II) concentrations, k_{obsd} is linear functions of [Mn(II)] according to eqs 3b,c. The calculated parameters of eq 3a are given in Table III. The manganese(III) stock solution had to be strongly acidic to avoid disproportionation. Dilution of this solution to pH 4 was not feasible. Therefore, the influence of manganese(III) could not be studied at pH 4.

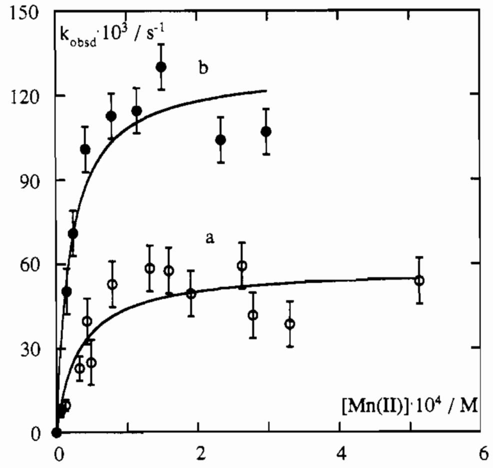

Figure 4. k_{obsd} as a function of [Mn(II)] at 25 °C and pH 2.4 with [S(IV)]$_0$ = 2.3 × 10^{-5} M and [O$_2$] ≈ 2.5 × 10^{-4} M in all experiments. Key: [Mn(III)]$_0$ = 0 (a) and 2.5 × 10^{-8} M (b). The errors are given as the mean standard deviations for k_{obsd} > 30 × 10^{-3} s^{-1} and as the standard deviations for the single points for k_{obsd} < 30 × 10^{-3} s^{-1}. The solid lines represent the fit of eq 5 to the experimental data.

$$k_{obsd} \rightarrow (k/A)[\mathrm{Mn(II)}] \qquad ([\mathrm{Mn(II)}] \rightarrow 0) \qquad (3b)$$

$$k_{obsd} \rightarrow k + k'[\mathrm{Mn(II)}] \qquad ([\mathrm{Mn(II)}] \rightarrow \infty) \qquad (3c)$$

For pH 2.4, the [Mn(II)] dependence can be described by eq 4a, where [Mn(III)]$_0$ denotes initially added manganese(III).

$$k_{obsd} = \frac{k[\mathrm{Mn(II)}](1 + B[\mathrm{Mn(III)}]_0)}{A + [\mathrm{Mn(II)}]} \qquad (4a)$$

Equation 4a agrees with eq 3a when the second term in eq 3a is excluded and [Mn(III)]$_0$ = 0. The limiting values of k_{obsd} in this case are given by eqs 4b,c. The oxidation is zero-order with

$$k_{obsd} \rightarrow k[\mathrm{Mn(II)}](1 + B[\mathrm{Mn(III)}]_0)/A \qquad ([\mathrm{Mn(II)}] \rightarrow 0) \qquad (4b)$$

$$k_{obsd} \rightarrow k(1 + B[\mathrm{Mn(III)}]_0) \qquad ([\mathrm{Mn(II)}] \rightarrow \infty) \qquad (4c)$$

respect to manganese(II) when the concentration is larger than ca. 1 × 10^{-4} M according to eq 4c. At low concentrations, the observed rate constant is still a linear function of the manganese(II) concentration; cf. Table I and Figure 4. In order to evaluate the parameters k, A, and B of eq 4a, eq 5 was fitted to

$$k_{obsd} = n_1[\mathrm{Mn(II)}]/(A + [\mathrm{Mn(II)}]) \qquad n_1 = k + kB[\mathrm{Mn(III)}]_0 \qquad (5)$$

the experimental points for five different initial manganese(III) concentrations by use of a nonlinear curve-fitting program. Values of A and n_1 were obtained and the parameters k and B were evaluated from the intercept and slope, respectively, of a plot of n_1 as a function of [Mn(III)]$_0$, Figure 5. All parameters are given in Table III.

Equation 4a can be rewritten as eq 4d, where $m = k[\mathrm{Mn(II)}]/(A + [\mathrm{Mn(II)}])$ and $k_s = kB[\mathrm{Mn(II)}]/(A + [\mathrm{Mn(II)}])$. Thus,

$$k_{obsd} = k_s[\mathrm{Mn(III)}]_0 + m \qquad (4d)$$

for constant [Mn(II)], the observed rate constant is a linear function of the concentration of initially added manganese(III); cf. Figure 6 and Table II. Note that both the slopes and intercepts

Table III. Constants Determined from the [Mn(II)] Dependence (Table I; Figures 3–5)[a]

$10^8[Mn(III)]_0$/M	pH	$10^3 n_1/s^{-1}$	$10^2 k/s^{-1}$	$10^2\langle k\rangle/s^{-1}$	$k'/M^{-1}\,s^{-1}$	$10^5 A$/M	$10^5\langle A\rangle$/M	$10^{-7}\langle B\rangle/M^{-1}$	$10^{-3}(k/A)/M^{-1}\,s^{-1}$
0	4		6.6 ± 0.9		68 ± 7	5 ± 2			1.2 ± 0.5
0	2.4	59 ± 7				4 ± 2			
1.1	2.4	64 ± 8				3 ± 1			
1.4	2.4	80 ± 11				2 ± 1			
1.8	2.4	74 ± 15				3 ± 2			
2.5	2.4	130 ± 10				2 ± 1			
0–2.5	2.4			4.6 ± 2			2.9 ± 0.9	5.6 ± 0.8	1.6 ± 0.7

[a] $[S(IV)]_0 = 2.3 \times 10^{-5}$ M, $[O_2] \approx 2.5 \times 10^{-4}$ M, temperature 25 °C. The constants are defined in the text. The errors are given as one standard deviation.

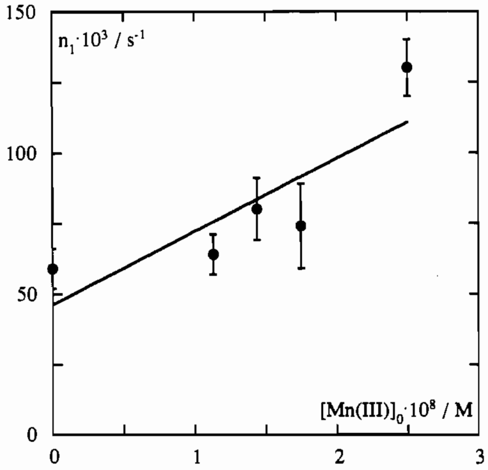

Figure 5. The parameter n_1 of eq 5 as a function of $[Mn(III)]_0$. The errors are given as one standard deviation. The solid line represents the best fit obtained with linear regression analysis.

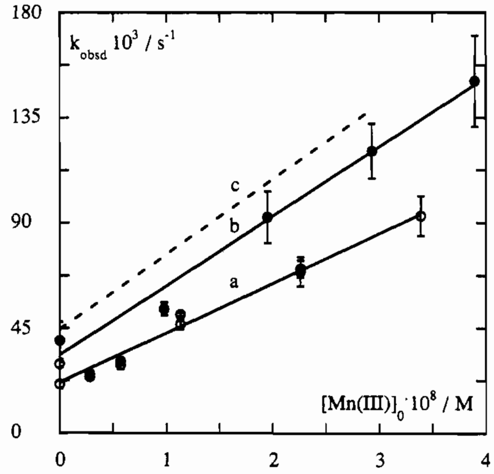

Figure 6. k_{obsd} as a function of $[Mn(III)]_0$. Conditions: $[S(IV)]_0 = 2.3 \times 10^{-5}$ M, $[O_2] \approx 2.5 \times 10^{-4}$ M, pH 2.4, and 25 °C. Key: [Mn(II)] = 3.6×10^{-5} M (a), 4.3×10^{-5} M (b), 0.79×10^{-4} M, 1.6×10^{-4} M, 2.8×10^{-4} M (c). The errors are given as the standard deviation from at least five measurements. The solid lines represent the best fit obtained from linear regression analysis. The dotted line represents the limiting values of k_{obsd} for high Mn(II) concentrations obtained from linear regression analysis using data from the three different manganese(II) concentrations given in (c).

Table IV. Calculated and Experimentally Determined Intercepts (m) and Slopes (k_s) from the Initial [Mn(III)] Dependence (Table II; Figure 6)

10^4[Mn(II)]/M	$10^2 m_{calc}/s^{-1}$ [a]	$10^2 m_{exp}/s^{-1}$ [b]	$10^{-6} k_{s(calc)}/M^{-1}\,s^{-1}$ [a]	$10^{-6} k_{s(exp)}/M^{-1}\,s^{-1}$ [b]
0.36	2.6	2.2 ± 0.1	1.5	2.1 ± 0.1
0.43	2.8	3.3 ± 0.5	1.6	3.0 ± 0.2
0.79	3.4	4.6 ± 1.2	1.9	3.2 ± 0.6
1.6	3.9	5.0 ± 0.9	2.2	3.0 ± 0.5
2.8	4.2	3.6 ± 0.6	2.4	3.5 ± 0.3
4.0	4.3		2.4	
→ ∞	4.6		2.6	

[a] The calculations of k_s and m are based on the constants determined from the [Mn(II)] dependence; cf. Table III. [b] The errors are given as one standard deviation. $[S(IV)]_0 = 2.3 \times 10^{-5}$ M, $[O_2] \approx 2.5 \times 10^{-4}$ M, temperature 25 °C.

should reach limiting values when [Mn(II)] → ∞ as can be seen from eq 4d. This is also obvious from Figure 4 and Table I. In Figure 6 line c is the best fit to the results obtained for [Mn(II)] = 0.79×10^{-4}, 1.6×10^{-4}, and 2.8×10^{-4} M and it represents the limiting values of the observed rate constant when the rate of reaction is no longer dependent on the manganese(II) concentration. Values of the slopes and intercepts calculated from k, A, and B are given in Table IV together with the experimental values obtained from Figure 6. There is a fairly good agreement between the experimental and calculated values of the intercepts. The experimentally determined slopes are a factor of less than 2 larger than the calculated ones, which is still acceptable, in view of the experimental errors.

The pH dependence of the manganese(II)-catalyzed oxidation with no added manganese(III) was studied in the region $1 < \text{pH} < 4$. The rate of reaction decreases below pH 2, which is in the region where the percentage of hydrogen sulfite in the sulfur(IV) system decreases and the percentage of $SO_2 \cdot H_2O$ starts to build up.

Synergism. Oxidation of sulfur(IV) by dissolved oxygen in aqueous solution is very slow, and it has been questioned whether the oxidation takes place at all in the absence of transition metal ions.[46,81] Since it is practically impossible to exclude completely trace concentrations of metals in water and chemicals, and since introduction of ligands forming strong chelates with such impurities may also inhibit the chain reaction connected with the oxidation, it is inherently difficult to study the uncatalyzed oxidation of sulfur(IV). Trace impurities of iron are particularly important since iron(III/II) is a very efficient catalyst for the sulfur(IV) oxidation.[54] There is also a synergism when both manganese and iron are present simultaneously, even if the iron concentration is very low. Therefore, the catalyzed autoxidation of sulfur(IV) was studied in the the presence of low added iron(III) concentrations in order to compare the results with (i) the manganese(III/II) experiments performed in what was considered to be iron-free solutions and (ii) with experiments performed in the presence of both manganese and iron. The iron catalysis at pH 2.4 for iron(III) concentrations below 1 μM was followed at 200 nm under exactly the same conditions as for the manganese catalysis. Iron(III) forms complexes with sulfur(IV),[50,51] but for iron(III) concentrations below 1 μM and a sulfur(IV) concentration of 2×10^{-5} M the decrease in absorbance at 200 nm could be attributed to the oxidation of noncomplexed sulfur(IV). There is no induction period in the iron(III)-catalyzed oxidation, and the reaction follows first-order kinetics in sulfur(IV). When iron(III) was introduced at a concentration of 1 μM into a Mn(II)/S(IV) system, the reaction became much faster than the sum of

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Table V. Iron(III)–Manganese(II) Synergism[a]

$10^5[\mathrm{Mn(II)}]/\mathrm{M}$	$10^6[\mathrm{Fe(III)}]_{\mathrm{added}}/\mathrm{M}$	$10^3 k_{\mathrm{obsd}}/\mathrm{s}^{-1}$
1.0		33 ± 5
	1.0	1.09 ± 0.04
1.0	0.90	85 ± 4

[a] $[\mathrm{S(IV)}]_0 = 2.3 \times 10^{-5}$ M, $[\mathrm{O_2}] \approx 2.5 \times 10^{-4}$ M, pH 2.4, temperature 25 °C. The errors are given as the standard deviation from at least five measurements.

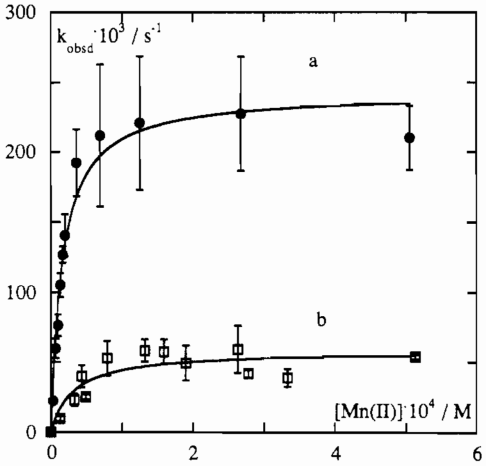

Figure 7. k_{obsd} as a function of [Mn(II)] in experiments with and without added Fe(III) at 25 °C and pH 2.4 with $[\mathrm{S(IV)}]_0 = 2.3 \times 10^{-5}$ M and $[\mathrm{O_2}] \approx 2.5 \times 10^{-4}$ M in all experiments. Key: $[\mathrm{Mn(III)}]_0 = 1.75 \times 10^{-8}$ M, $[\mathrm{Fe(III)}]_{\mathrm{added}} = 1.0 \times 10^{-6}$ M (a); $[\mathrm{Mn(III)}]_0 = [\mathrm{Fe(III)}]_{\mathrm{added}} = 0$ (b). The errors are given as the standard deviation from at least five measurements. The solid lines represent the fit of eq 5 to the experimental data with n_1 and A as parameters.

the individual contributions from the iron(III)- and manganese(II)-catalyzed paths under identical conditions, Table V. The presence of iron(III) does not seem to alter the induction period. The synergistic effect is not affected by the presence of manganese(III). The saturation kinetics with increasing concentrations of manganese(II) observed in the absence of added iron(III), cf. Figure 4, is observed also when iron(III) is added; cf. Figure 7.

Discussion

Mechanism. As mentioned above, two types of mechanism for manganese-catalyzed autoxidation of sulfur(IV) in aqueous solution have been proposed: (i) manganese-mediated electron transfer from sulfur(IV) to dioxygen within a manganese(II) complex and (ii) a radical chain reaction in which manganese(III) plays a significant role.

In the case of iron and copper catalysis, it has been shown that sulfito complexes are formed prior to electron transfer.[50–52,65,66] When sulfur(IV) is mixed with copper(II) or iron(III), changes in UV–vis spectra can be attributed to complex formation, and it has been possible to determine stability constants for these complexes directly from spectrophotometric equilibrium measurements.[50,51,65] When sulfur(IV) is mixed with manganese(II), no spectral changes are detected. However, this does not exclude complex formation, since manganese(II) is a d^5 metal ion which only gives weak, spin-forbidden, electronic transitions in the UV–vis region. Previous mechanisms suggesting formation of a manganese(II)/sulfur(IV) complex have never been supported by experimental proof of the existence of such a complex.

Evidence in favor of a mechanism including radicals has been reported in a large number of studies. Warneck[68] recently showed that phenol was produced when benzene was present in the manganese-catalyzed oxidation of hydrogen sulfite. Benzene reacts with hydroxo and sulfate radicals and is oxidized to phenol, which indicates that one or both of these radicals are generated during the oxidation of sulfur(IV) in the presence of manganese(II). The autoxidation of a divalent metal ion to the trivalent state has recently been shown to be accelerated several orders of magnitude by the presence of sulfur(IV), which is a strong reducing agent.[49,69] These observations give strong evidence for the generation of sulfur-radical oxidants in the metal-catalyzed oxidation of sulfur(IV). Moreover, the metal ion catalysis has been shown[68] to be inhibited by radical scavengers and different organic impurities, which also indicates the presence of free radicals.

The photoinduced autoxidation of sulfur(IV) in aqueous solution in the absence of metal ions has been studied during almost a century and is fairly well understood. On the basis of early work by Bäckström et al.[83,84] and Haber,[85] a radical chain mechanism involving the radicals $\mathrm{SO_3^-}$, $\mathrm{SO_4^-}$, and $\mathrm{SO_5^-}$ has been suggested for this uncatalyzed oxidation.[77,86,87] On the basis of this mechanism and the discovery of the sulfite-induced autoxidation of divalent metal ions, Margerum et al.[64] and later van Eldik et al.[69] proposed a similar free-radical mechanism for the copper-, iron-, cobalt- and manganese-catalyzed autoxidation of sulfur(IV) in aqueous solution. In this mechanism, the trivalent metal ion initiates the chain reaction by reacting with sulfur(IV) species, generating sulfite radicals. In subsequent steps, the metal ion is reoxidized by peroxomonosulfate radicals and peroxomonosulfate generated in the chain, and sulfate is formed as the final reaction product. This mechanism may be general and applicable to all catalytically active metal ions. In that case, the lack of multiple valence states for metal ions such as nickel and zinc could explain the poor catalytic activity of those ions.

In the present study, the occurrence of an induction period and the strong influence of manganese(III) on both the rate of reaction and and on the autocatalytic behavior indicate participation of free radicals. The saturation of the rate of oxidation at pH 2.4 when the concentration of manganese(II) is increased, cf. Figure 4, can only be interpreted in terms of a complex formation between manganese(II) and hydrogen sulfite, eq 6, with a stability constant,

$$\mathrm{Mn^{2+} + HSO_3^- \rightleftharpoons MnHSO_3^+} \qquad (6)$$

$$\beta_1 = \frac{[\mathrm{MnHSO_3^+}]}{[\mathrm{Mn^{2+}}][\mathrm{HSO_3^-}]} \qquad (7)$$

β_1, of eq 7. $\mathrm{MnHSO_3^+}$ is the active species in the catalytic process described below. Unfortunately, there is so far no independent experimental evidence for this complex formation. (Spectrophotometric measurements only indicate that the molar absorptivity of an assumed complex, $\mathrm{MnHSO_3^+}$, does not vary significantly from that of free hydrogen sulfite.) When a manganese(II) hydrogen sulfite complex is introduced into the previously proposed radical mechanism suggested by Margerum et al.[64] and van Eldik et al.,[69] the following reaction scheme is obtained for the manganese-catalyzed autoxidation of sulfur(IV) in aqueous solution:

$$\mathrm{Mn^{2+} + HSO_3^- \rightleftharpoons MnHSO_3^+} \qquad (6)$$

$$\mathrm{Mn(III) + MnHSO_3^+ \rightarrow 2\,Mn(II) + SO_3^- + H^+} \qquad (8)$$

$$\mathrm{SO_3^- + O_2 \rightarrow SO_5^-} \qquad (9)$$

$$\mathrm{Mn(II) + SO_5^- + H^+ \rightarrow Mn(III) + HSO_5^-} \qquad (10)$$

$$\mathrm{MnHSO_3^+ + SO_5^- \rightarrow Mn(II) + SO_3^- + HSO_5^-} \qquad (11a)$$

$$\mathrm{\rightarrow Mn(II) + SO_4^- + HSO_4^-} \qquad (11b)$$

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Table VI. Rate Constants for Reactions 8–21 and 32[a] Used for Deduction of the Mechanism (Eqs 6, 8–10, 13)

reacn	no.	rate const/$M^{-1}\,s^{-1}$	ref	comments
$Mn(III) + HSO_3^- \rightarrow Mn^{2+} + SO_3^- + H^+$	8	$>2.4 \times 10^4$	23	
$SO_3^- + O_2 \rightarrow SO_5^-$	9	2.5×10^9, 1.1×10^9	82, 89	
$SO_5^- + HSO_3^- \rightarrow$ (a) $HSO_5^- + SO_3^-$	11a	$k_a + k_b = 1.2 \times 10^4$	82, 90	no branching ratio known
$\rightarrow$ (b) $HSO_4^- + SO_4^-$	11b	$k_a + k_b < 3 \times 10^5$		
$HSO_5^- + HSO_3^- \rightarrow 2HSO_4^-$	13	4.3×10^4	91	at pH 2.4 ($k = 1.07 \times 10^7[H^+]$ at pH <4)
$Mn^{2+} + SO_4^- \rightarrow Mn(III) + SO_4^{2-}$	14	3×10^7	82, 92	
$SO_4^- + HSO_3^- \rightarrow SO_3^- + HSO_4^-$	15	8×10^8	90	
$Mn^{2+} + OH + H^+ \rightarrow Mn(III) + H_2O$	16	2.6×10^7	99	
$HSO_3^- + OH \rightarrow SO_3^- + H_2O$	17	4.5×10^9	90	
$SO_5^- + SO_5^- \rightarrow S_2O_8^{2-} + O_2$	19	1.4×10^8, 1.5×10^8	90, 100	
$\rightarrow 2SO_4^{2-} + O_2$	19	6×10^8	90	
$SO_3^- + SO_3^- \rightarrow S_2O_6^{2-}$	20	1.8×10^8, 2.5×10^8	93, 100	
$\rightarrow SO_3 + SO_3^{2-}$	20	2.3×10^8	93	
$SO_4^- + SO_4^- \rightarrow S_2O_8^{2-}$	21	4.4×10^8, 4.05×10^8	94, 100	
$Fe(III) + HSO_3^- \rightarrow Fe(II) + SO_3^- + H^+$	32	318	54	

[a] The numbers given after the reactions refer to the reactions in the mechanism. Note that some of the rate constants given in this table are determined in the absence of manganese; cf. text.

$$Mn(II) + HSO_5^- \rightarrow Mn(III) + SO_4^{2-} + OH \quad (12a)$$

$$\rightarrow Mn(III) + SO_4^- + OH^- \quad (12b)$$

$$MnHSO_3^+ + HSO_5^- \rightarrow Mn(II) + 2HSO_4^- \quad (13)$$

$$Mn(II) + SO_4^- \rightarrow Mn(III) + SO_4^{2-} \quad (14)$$

$$MnHSO_3^+ + SO_4^- \rightarrow Mn(II) + SO_3^- + HSO_4^- \quad (15)$$

$$Mn(II) + OH + H^+ \rightarrow Mn(III) + H_2O \quad (16)$$

$$MnHSO_3^+ + OH \rightarrow Mn(II) + SO_3^- + H_2O \quad (17)$$

$$SO_3^- + OH \rightarrow HSO_4^- \quad (18)$$

$$SO_5^- + SO_5^- \rightarrow P \quad (19)$$

$$SO_3^- + SO_3^- \rightarrow P \quad (20)$$

$$SO_4^- + SO_4^- \rightarrow P \quad (21)$$

In this reaction sequence, the products, P, formed in the very rapid reactions 19–21 can be left unspecified. As commented above, Mn(II) denotes the hexaaquamanganese(II) ion and the manganese(II) hydrogen sulfite complex. Mn(III) denotes any hydrolyzed manganese(III) species.

Many of the rate constants for the individual steps, reactions 6 and 8–21, have been determined. A summary is given in Table VI. In some cases, reactions 11a, 11b, 13, 15, and 17, the reactions have been studied in the absence of manganese. The rate constants in Table VI are given for the reactions of the noncomplexed sulfur(IV) ligand, e.g.

$$HSO_3^- + SO_5^- \rightarrow SO_3^- + HSO_5^- \quad (11c)$$

If those rate constants are considered as rough estimates for the reactions where hydrogen sulfite is coordinated to manganese(II), it is possible to simplify the reaction scheme since some of the reactions listed can be neglected in comparison with competitive, faster ones. The manganese(II) hydrogen sulfite complex is formed in the rapid preequilibrium 6. In the second step, reaction 8, manganese(III) oxidizes the complex bound hydrogen sulfite ligand and generates the SO_3^- radical. This radical rapidly reacts with oxygen, forming peroxomonosulfate radicals, SO_5^-, reaction 9. The peroxomonosulfate radical reacts predominantly with manganese(II), and manganese(III) is regenerated, reaction 10. This reaction has recently been studied by pulse radiolysis[88] indicating that it is very fast, $k_{10} \approx 10^8\ M^{-1}\,s^{-1}$, compared with reaction 11 with $k_{11a} + k_{11b} \approx 10^4\ M^{-1}\,s^{-1}$.[82,90] Therefore, reaction 11 can be neglected in comparison with reaction 10 since the concentrations of the reactants in reactions 10 and 11 are about equal in the present study. The oxidation of manganese(II) to manganese(III) by hydrogen peroxomonosulfate, reaction 12, has not been studied quantitatively, as far as we know. However, qualitative studies by Warneck[68] and in our laboratory indicate that this reaction is very slow. In spite of this, reaction 12a may be considered in the simplified scheme below as a possible pathway for autocatalysis, generating hydroxo radicals as well as regenerating manganese(III). Thus, since reactions 11 and 12b are slow compared to other competitive processes, practically no sulfate radicals are generated and reactions 14, 15, and 21 can be neglected as well in a simplified mechanism. If reaction 12a is included, hydroxo radicals are produced and therefore reactions 16 and 17 must be considered. For the same reasons that excluded reaction 11, however, reaction 16 can be neglected in favor of reaction 17 by comparison of the rate constants given in Table VI. A simplified reaction mechanism can thus be written as follows:

$$Mn^{2+} + HSO_3^- \rightleftharpoons MnHSO_3^+ \quad (6)$$

$$Mn(III) + MnHSO_3^+ \rightarrow 2Mn(II) + SO_3^- + H^+ \quad (8)$$

$$SO_3^- + O_2 \rightarrow SO_5^- \quad (9)$$

$$Mn(II) + SO_5^- + H^+ \rightarrow Mn(III) + HSO_5^- \quad (10)$$

$$Mn(II) + HSO_5^- \rightarrow Mn(III) + SO_4^{2-} + OH \quad (12a)$$

$$MnHSO_3^+ + HSO_5^- \rightarrow Mn(II) + 2HSO_4^- \quad (13)$$

$$MnHSO_3^+ + OH \rightarrow Mn(II) + SO_3^- + H_2O \quad (17)$$

The chain-terminating steps 18–20 can be excluded since they play no role in the evaluation of the rate law.

In the simplified mechanism above, three parallel main reactions i–iii can be identified. By adding the reaction steps 8–10, we arrive at reaction 22, which is a chain reaction catalyzed by manganese(II). The second reaction ii is the simple elementary process 13 with reaction rate r_{13}. The third reaction iii is the sum

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$$\text{(i)}\quad MnHSO_3^+ + O_2 \rightarrow HSO_5^- + Mn(II) \qquad (22)$$

$$\text{(ii)}\quad MnHSO_3^+ + HSO_5^- \rightarrow 2HSO_4^- + Mn(II) \qquad (13)$$

$$\text{(iii)}\quad 2Mn(II) + HSO_3^- + O_2 + 2H^+ \rightarrow 2Mn(III) + HSO_4^- + H_2O \qquad (23)$$

of reactions 6, 9, 10, 12a, and 17 and describes the sulfite induced oxidation of manganese(II) (eq 23).

Derived Constants. If reactions 12a and 17 are neglected and the steady-state approximation is applied to the intermediates SO_3^-, SO_5^-, and HSO_5^-, the following relationships are obtained: $-r_8 + r_9 = 0$, $-r_9 + r_{10} = 0$, and $-r_{10} + r_{13} = 0$, where r denotes the rates of reaction. Thus, $r_8 = r_9 = r_{10} = r_{13}$ and

$$-dC(HSO_3^-)/dt = r_8 + r_{13} = 2r_8 = 2k_8[Mn(III)][MnHSO_3^+] \qquad (24)$$

By introduction of β_1 of eq 7, eqs 25 and 26 are easily derived.

$$[MnHSO_3^+] = C(HSO_3^-)\beta_1[Mn^{2+}]/(1 + \beta_1[Mn^{2+}]) \qquad (25)$$

$$[Mn(II)] = [Mn^{2+}](1 + \beta_1[HSO_3^-]) \qquad (26)$$

Eliminating $[Mn^{2+}]$, the rate expression 24 can be rewritten as

$$-dC(HSO_3^-)/dt = \frac{[Mn(II)]}{\beta_1^{-1} + [HSO_3^-] + [Mn(II)]} 2k_8[Mn(III)]C(HSO_3^-) \qquad (27)$$

In eq 27, $[Mn(III)] = [Mn(III)]_0 + [Fe(III)]_0$ as will be discussed below. $[Mn(III)]_0$ is the concentration of the initially added manganese(III), and $[Fe(III)]_0$ is the trace concentration of iron(III) impurities. Equation 27 is identical with the experimental rate equation 4a if $A = \beta_1^{-1} + [HSO_3^-]$, $B = 2k_8/k$, and $k = 2k_8[Fe(III)]_0$. A value of $k_8 = (1.3 \pm 0.6) \times 10^6$ M^{-1} s^{-1} can be calculated from the data in Table III. If the complex formation between manganese(II) and hydrogen sulfite is strong, the concentration of free hydrogen sulfite is very small and $A \approx \beta_1^{-1}$. The parameter A is $(2.9 \pm 0.9) \times 10^{-5}$ M^{-1}, cf. Table III, which means that $\beta_1 \approx (3 \pm 1) \times 10^4$ M^{-1} under this condition. Since $[Fe(III)]_0 = B^{-1}$ and $B = (5.6 \pm 0.8) \times 10^7$ M^{-1}, the concentration of trace impurities of iron(III) in the solutions is approximately 2×10^{-8} M. If the line in Figure 5 is extrapolated to the intersection with the x-axis, a value of $[Fe(III)]_0 \approx 1.9 \times 10^{-8}$ M is obtained. Similarly, extrapolations of the lines in Figure 6 give values in the range $(1-1.5) \times 10^{-8}$ M. This is what should be expected if there is an additional contribution to the Mn(III) concentration which originates from iron(III) impurities, giving $[Mn(III)] = [Mn(III)]_0 + [Fe(III)]_0$ as introduced above. The value of $[Fe(III)]_0 \approx (1-2) \times 10^{-8}$ M obtained from the extrapolations corresponds very well with the one from the calculations above.

Siskos et al.[23] determined the rate constant for the oxidation of sulfur dioxide by manganese(III) as 2.4×10^4 M^{-1} s^{-1} at 25 °C in a 5 M perchloric acid medium. They also noted that decreasing the concentration of perchloric acid resulted in a reaction too fast to be monitored by the stopped-flow method. Accordingly, our value for this rate constant at pH 2.4 is 2 orders of magnitude larger than that reported by Siskos et al. This may be explained by an increased reactivity of hydrogen sulfite compared with sulfur dioxide. In the present study, hydrogen sulfite is coordinated to manganese(II), which also increases the rate of oxidation, as discussed below. The pH dependence for the manganese-catalyzed autoxidation of sulfur(IV) observed in the present study shows that the oxidation rate increases up to approximately pH 2 where it starts to level out. This is in the region where hydrogen sulfite becomes the predominant S(IV) species, which indicates that hydrogen sulfite is more easily oxidized than sulfur dioxide. The increased reactivity of hydrogen sulfite compared with sulfur dioxide may be due to the fact that hydrogen sulfite forms stronger complexes with manganese(II) than sulfur dioxide. The pH dependence observed in the present study is also in good agreement with results reported by Ibusuki and Barnes,[24] who performed measurements under similar conditions.

On the basis of their kinetic data, Siskos et al.[23] proposed that a complex formation between manganese(II) and sulfur dioxide was a possibility. A small value of 3.2 M^{-1} was estimated for the stability constant at 5 M ionic strength. This constant probably is larger at lower ionic strength, and as noted above, a complex with hydrogen sulfite is likely to have a considerably larger stability than a complex between manganese(II) and sulfur dioxide. Roy et al.[95] calculated the equilibrium constant for the formation of $MnSO_3$ using an ion-pairing model to be 1000 M^{-1}. They also reported that there is a good correlation between the stability constants for the formation of the divalent metal complexes with sulfite and sulfate and that sulfito complexes of these metal ions in general have larger stability constants than the sulfate complexes. The stability constant for manganese(II) sulfate has been determined[74] to 182 M^{-1} when extrapolated to zero ionic strength. Recently, stability constants for the sulfito complexes of copper(II)[65] and iron(III)[51] were determined as 1.8×10^4 M^{-1} at 0.4 M ionic strength and 600 M^{-1} at 0.1 M ionic strength, respectively. Näsänen[96] determined the stability constant for manganese(II) carbonate potentiometrically to 3.4×10^3 M^{-1} for a 0.1 M ionic medium. The value of 3×10^4 M^{-1} for the stability constant for the manganese(II) hydrogen sulfite complex calculated from the present experiments is very reasonable in view of all those observations.

The experimental rate law eq 3a at pH 4 includes a quadratic manganese(II) term which is not present at pH 2.4. For pH 4, the observed rate constant increases linearily for manganese(II) concentrations larger than approximately 2×10^{-4} M; cf. Figure 3. There is no saturation as observed for pH 2.4. The quadratic manganese(II) term indicates that a bridged manganese(II) complex is formed. A bridged sulfito complex seems most likely:

$$MnHSO_3^+ + Mn^{2+} \rightleftharpoons MnSO_3Mn^{2+} + H^+ \qquad (28)$$

Equilibrium 28 is pH-dependent, and decreasing the pH suppresses the formation of the bridged complex. When it is present, Mn(III) can attack it (eq 29),

$$MnSO_3Mn^{2+} + Mn(III) \rightarrow 3Mn^{2+} + SO_3^- \qquad (29)$$

generating sulfite radicals by a reaction parallel to reaction 8 in the proposed mechanism. Diebler and Sutin[97] studied the exchange reaction between manganese(II) and manganese(III) in 3 M perchloric acid at 25 °C. The rate constant was estimated to be 3×10^{-4} M^{-1} s^{-1}. They also found that the rate of exchange between manganese(II) and the hydrolysis products of manganese(III) was much faster. This probably indicates formation of an oxo- (or hydroxo-) bridged precursor complex, Mn^{III}–O–Mn^{II}, in which subsequent electron transfer might take place. At pH 2.4 manganese(III) is hydrolyzed and the predominant species for the very low total concentration of manganese(III) used here is $Mn(OH)_2(H_2O)_4^+$, based on the stability constants given above. However, as mentioned above, it has not been possible to study the hydrolysis of manganese(III) at pH > 0, but further mononuclear hydrolysis products of manganese(III) are likely to

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be present at pH 2.4. Therefore, the formation of complexes between manganese(III) and hydrogen sulfite should be difficult due to the presence of hydroxo ligands already strongly bound to the metal center which makes the net ionic charge decrease considerably. Manganese(II), on the other hand, is not hydrolyzed but exists partly as a complex with hydrogen sulfite. Hydrolyzed manganese(III) may attack this complex, reaction 8, forming an oxo- (or hydroxo-) bridged precursor complex, Mn^{III}–O–Mn^{II}–HSO_3. Within this complex, bridged electron transfer from the manganese(II) hydrogen sulfite moiety to manganese(III) probably is fast according to the results obtained by Diebler and Sutin. The successor complex formed decomposes rapidly, giving two Mn(II) and one SO_3^- radical. Similarly, hydrolyzed manganese(III) may attack the bridged sulfito complex formed in equilibrium 28 and generate SO_3^- by a similar bridged electron transfer. The experimental parameter k' of eq 3a includes the unknown equilibrium constant of reaction 28, which means that it is not possible to calculate the rate constant for reaction 29 from the present experiments. However, the equilibrium constant of reaction 28 is probably very small, indicating a large value of the rate constant for reaction 29.

Chain Initiation. In the proposed mechanism, the chain reaction is initiated by a reaction between manganese(III) and a manganese(II) hydrogen sulfite complex which generates sulfite radicals, reaction 8. In the absence of added manganese(III), sulfur(IV) is still oxidized, however, and the reaction displays an induction period. The initiation of the process under those conditions has to be accounted for. van Eldik et al.[60] argued that initiation of the oxidation of sulfur(IV) in the absence of trivalent metal ions might be due to the oxidation of the divalent metal ion by molecular oxygen, reaction 30. However, this reaction is

$$M(II) + O_2 \rightarrow M(III) + O_2^- \qquad (30)$$

probably thermodynamically very unfavorable in the case of manganese under the conditions used in the present study. Margerum et al.,[64] in their copper(III/II) study, suggested that the initiation in absence of copper(III) may be due to disproportionation of copper(II) to copper(I) and copper(III) or formation of peroxomonosulfate by reaction 31. The peroxomonosulfate can then oxidize copper(II) to copper(III). Manganese(II) does not disproportionate, but the latter possibility cannot be excluded in the present system.

$$SO_3^{2-} + O_2 \rightarrow SO_5^{2-} \qquad (31)$$

We propose, however, that the initiation of the reaction in absence of added manganese(III) is due to low concentrations of iron(III), present as unavoidable impurities in chemicals and solvents. As noted above, it is difficult to exclude trace concentrations of iron(III) even in highly purified water. Previous analyses[81] show that iron may be present at concentrations of 8×10^{-9} to 5×10^{-7} M in purified water. Another study[46] indicated that the concentration of iron(III) in the "pure" water used in that study was 5×10^{-8} M. The present experiments indicate that the concentration of trace impurities of iron(III) is approximately $(1\text{–}2) \times 10^{-8}$ M, which is of the same order of magnitude. If iron(III) is present, it reacts with sulfur(IV) and generates sulfite radicals, which rapidly form peroxomonosulfate radicals by reaction with oxygen. The peroxomonosulfate radical can then oxidize manganese(II) to manganese(III), reaction 10. In this way the iron(III) initially present can generate manganese(III). Note that the oxidation of produced iron(II) by peroxomonosulfate radicals cannot compete with the oxidation of manganese(II). The rate constant for the reaction between manganese(II) and peroxomonosulfite radical is approximately 10^8 M^{-1} s^{-1},[88] and the concentration of manganese in the present system is several orders of magnitude larger than the iron(II) concentration generated from ca. 2×10^{-8} M iron(III). Thus, the total manganese(III) concentration should increase by a quantity that is equal to the initial concentration of iron(III), as pointed out above. The rate constant for the reaction 32 between

$$Fe(III) + HSO_3^- \rightarrow Fe(II) + SO_3^- + H^+ \qquad (32)$$

iron(III) and hydrogen sulfite at pH 3.1 and 0.1 M ionic strength is 318 M^{-1} s^{-1}.[54] The rate constant for the oxidation of hydrogen sulfite by manganese(III) determined in the present study is approximately 3 orders of magnitude larger. The induction period observed in the absence of added manganese(III) may be explained by the buildup of manganese(III) concentration in the reactions following the rather slow oxidation of sulfur(IV) by iron(III) present at very low concentrations.

In this context it may be noted that a study of nickel(II)-catalyzed autoxidation of sulfur(IV) has been performed in our laboratory. It was clearly shown that the rate of oxidation was dependent on which of two different nickel(II) nitrate preparations were used. ICP analysis showed that the salt giving the faster reactions also contained significantly more trace impurities, including iron. It was concluded that the so called "nickel catalysis" most probably is due to a catalysis by trace metal impurities and that nickel(II) itself is an inactive or very poor catalyst. Those observations clearly demonstrate the importance of minimizing the presence of impurities in studying metal ion autoxidation of sulfur(IV).

Simulations. In order to check the validity of the proposed mechanism for the manganese-catalyzed oxidation, the FACSIMILE kinetic modeling program[80] was used to fit the simplified mechanism, reactions 6, 8–10, 13, and 32, to the experiments. Reasonably good fits were obtained for individual runs. Figure 8 gives an example of a parameter fit to the experimental curve displayed in Figure 2a. The initial conditions were $\beta_1 = 3 \times 10^4$ M^{-1}, $k_8 = 1.3 \times 10^6$ M^{-1} s^{-1}, $k_9 = 2.5 \times 10^9$ M^{-1} s^{-1}, $k_{10} = 10^8$ M^{-1} s^{-1}, $k_{13} = 4.3 \times 10^4$ M^{-1} s^{-1}, $k_{32} = 318$ M^{-1} s^{-1}, and $[Fe(III)]_0 = 2 \times 10^{-8}$ M. Other conditions are given in Figure 2a. The parameters k_8, k_{10}, k_{13}, k_{32}, and $[Fe(III)]_0$ were varied. The fits were most strongly influenced by k_{32} and $[Fe(III)]_0$. Only minor changes were observed when k_8 and k_{13} were varied. The value of k_{10} does not influence the kinetics significantly in the range $10^6 < k_{10} < 10^{10}$ M^{-1} s^{-1}. In order to fit the experimental curve, either k_{32} or $[Fe(III)]_0$ had to be adjusted upward. In the parameter fit obtained in Figure 8 only k_{32} was varied and the fitted value was $(1.5 \pm 0.1) \times 10^3$ M^{-1} s^{-1}, significantly different from the starting value. Computer fittings to other kinetic runs also gave relatively large scatter. A direct determination of all the parameters in this complicated system by computer fitting was therefore not feasible. This is probably due to the large experimental scatter, caused for instance by different trace iron(III) concentrations in different runs.

However, simulations were useful to demonstrate that the proposed mechanism describes the kinetics qualitatively. The conditions for those simulations are given in Table VII and Figure 8. The results in Figure 8 show clearly that the presence of 2×10^{-8} M iron(III) is sufficient to initiate the oxidation and to give rise to the autocatalytic behavior observed in the experiments; cf. Figure 2a. It is also shown qualitatively that the mechanism accounts for the other major experimental observations; viz., (i) the rate of reaction reaches a saturation value when the concentration of manganese(II) is increased and (ii) addition of manganese(III) increases the rate of reaction and suppresses the induction period. When the complete reaction scheme, reactions 6, 8–21, and 32, was used as the kinetic model, only reactions 12a,b significantly changed the results of the simulations displayed in Figure 8, using the simplified mechanism. In the simulations with the complete reaction scheme, the rate constants for the additional reactions were taken from Table VI with the assumption that the rate constants for the complexed hydrogen sulfite are roughly the same as for the noncomplexed ligand. There are no

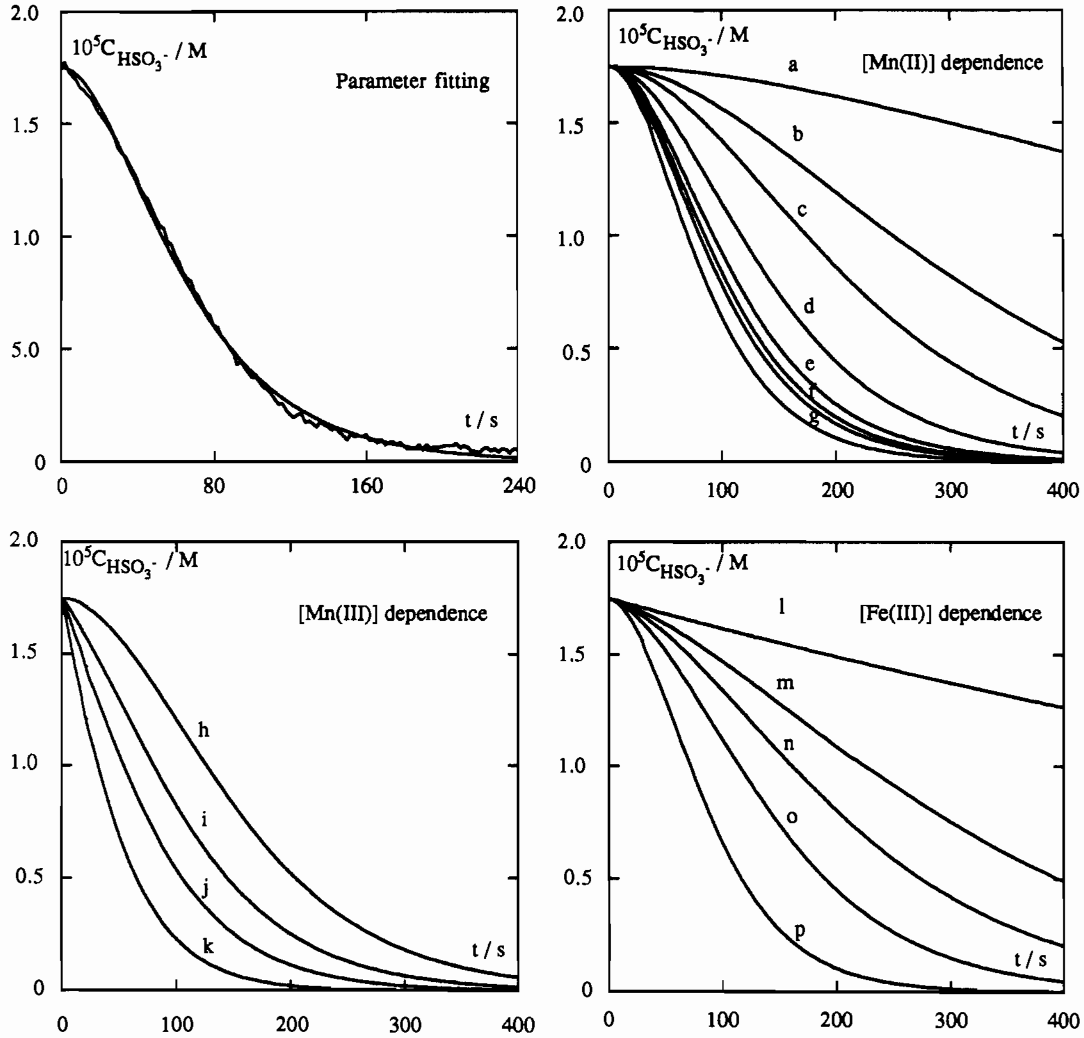

Figure 8. FACSIMILE fit and simulations of the proposed reaction mechanism. Reactions 6, 8–10, 13, and 32 have been used as a kinetic model. For conditions used in the fit, see text. The simulations were performed under the following conditions: $[S(IV)]_0 = 2.3 \times 10^{-5}$ M, $[O_2] = 2.5 \times 10^{-4}$ M, pH 2.4, $\beta_1 = 3 \times 10^4$ M^{-1}, $k_8 = 1.3 \times 10^6$ M^{-1} s^{-1}, $k_9 = 2.5 \times 10^9$ M^{-1} s^{-1}, $k_{10} = 10^8$ M^{-1} s^{-1}, $k_{13} = 4.3 \times 10^4$ M^{-1} s^{-1}, and $k_{32} = 318$ M^{-1} s^{-1}. The concentrations of Mn(III), Mn(II), and Fe(III) are given in Table VII.

Table VII. Concentrations of Mn(II), Mn(III), and Fe(III) Used in the FACSIMILE Simulations Shown in Figure 8

notation	10^5[Mn(II)]/M	10^8[Mn(III)]/M	10^8[Fe(III)]/M
a	0.10		2.0
b	0.50		2.0
c	1.0		2.0
d	2.5		2.0
e	5.0		2.0
f	7.5		2.0
g	10		2.0
g	50		2.0
h	2.0		2.0
i	2.0	0.50	2.0
j	2.0	1.0	2.0
k	2.0	2.0	2.0
l	2.0	0.10	
m	2.0	0.10	0.50
n	2.0	0.10	1.0
o	2.0	0.10	2.0
p	2.0	0.10	5.0

reported rate constants for reactions 12a,b as far as we know. It was shown that these reactions only influenced the simulations when k_{12a} or k_{12b} were larger than approximately 1 M^{-1} s^{-1}. Preliminary studies of these reactions, as mentioned above, have shown that they are very slow, if they exist at all. However, if reaction 12a is incorporated into the mechanism it results in a sulfite-induced oxidation of manganese(II), reaction 23. For catalyzed autoxidation of sulfur(IV) by iron, cobalt, and copper it has been shown[54,60,64] that a reaction equivalent to reaction 23, where manganese is replaced by the actual metal ion, is very important in the regeneration of the trivalent state of these metal ions in the catalytic cycle. In the case of manganese, the very low rate of reaction 12a under the present experimental conditions makes the contribution from this pathway less likely, as shown in the simulations. Therefore, initial buildup of manganese(III) due to the presence of iron(III) impurities is probably a more efficient mechanism for the autocatalysis in the absence of initially added manganese(III). However, it should be noted that reaction 23 may be important for the manganese catalysis in systems where manganese(III) is stabilized by the presence of some complexing agent. This might be the case in the recent study of sulfite-induced autoxidation of manganese(II) to manganese(III) performed in azide medium.[33]

Synergism. The synergism observed when both iron(III) and manganese(II) are present in comparable concentrations can be explained qualitatively by the same sort of arguments as above. Iron(III) promotes the oxidation of manganese(II) to manganese(III) by generating strong radical sulfur oxidants. Manganese(III) is a much more efficient oxidant than iron(III), which makes the generation of manganese(III) very favorable in the production of sulfite radicals. Under steady-state conditions, the two redox couples, iron(III/II) and manganese(III/II), may both be active in a mixed system which increases the rate of sulfur(IV) oxidation significantly.

Comparison with Previous Studies. Much effort has been devoted to understand the mechanisms for the generation of acid rain, where autoxidation of sulfur dioxide in the aqueous phase plays a significant role. The goal of many of the previous studies has been to model the experiments on the atmospheric situation, where gaseous sulfur dioxide is dissolved in aerosols or drops of water containing different solid and dissolved species. Therefore, many studies of the manganese-catalyzed oxidation have been performed in two-phase systems.[6,8,10–12,14,18,21,22,28,32] Typically, gaseous sulfur dioxide has been absorbed in aerosols, supported drops, or vigorously stirred bulk solutions containing manganese salts. This introduces additional physical complications such as mass transfer from the gaseous to the aqueous phase. The kinetic behavior in these two-phase systems and the proposed mechanisms based on such experiments may not be applicable to the oxidation in homogeneous solution and will not be further considered here. On the other hand, previous studies of the manganese-catalyzed oxidation in homogeneous aqueous solution have to be discussed with regard to the present results and conclusions.

The presence of induction periods in the manganese-catalyzed oxidation has been reported before,[2,9,16,19] whereas other previous studies do not mention this phenomenon. The neglect of induction periods may lead to completely wrong assignments of reaction order and rate laws, in particular if an initial-rate method is used in evaluation of the kinetics. For example, Grgic et al.[34] recently derived a reaction order with respect to sulfur(IV) of 0.65 from initial-rate measurements. However their kinetic traces[34,37] clearly demonstrate the presence of induction periods which make their conclusions doubtful. The possible neglect of induction periods may explain some discrepancies in other previous literature, also.

A large number of studies[2,9,16,17,19,26] on the manganese-catalyzed oxidation have been performed at considerably higher sulfur(IV) concentrations than those used in the present study. Many of these investigators claim that the reaction is zero-order with respect to sulfur(IV).[2,9,16,17] Others, who have studied the reaction in a wider range of sulfur(IV) concentration, report that the zero-order dependence at high sulfur(IV) concentrations changes to a first-order dependence with respect to sulfur(IV) at low sulfur(IV) concentrations.[26,29] By introduction of the manganese(II) hydrogen sulfite complex, reaction 6, this behavior can be easily explained. The concentration of the complex expressed as a function of the concentration of free hydrogen sulfite is given by eq 33. Increasing the concentration of sulfur(IV) leads to a saturation of the complex formation, and the rate of reaction becomes independent of the concentration of sulfur(IV). For manganese(II) concentrations considerably lower than the sulfur(IV) concentration, the concentration of free hydrogen sulfite equals the total sulfur(IV) concentration. With $\beta_1 \approx 10^4$ M^{-1}, the reaction order with respect to sulfur(IV) is then expected to start deviate from 1.0 at approximately 10^{-4} M, and it should definitely be zero above 10^{-3} M, which agrees very well with the previous experimental observations.

$$[\mathrm{MnHSO_3}^+] = \beta_1[\mathrm{Mn(II)}][\mathrm{HSO_3}^-]/(1 + \beta_1[\mathrm{HSO_3}^-]) \qquad (33)$$

A quadratic manganese(II) term in the rate law has been reported in a number of studies.[2,9,16,17,19,20,26] For instance, Huss et al.[19,20] reported the rate law 34 for the manganese(II)-catalyzed oxidation of sulfur(IV) under the experimental conditions 1×10^{-5} M < [Mn(II)] < 1 mM, 1 mM < [S(IV)] < 0.15 M, and 1 < pH < 5. In order to account for the quadratic term they introduced equilibrium 35 followed by the slow reaction 36. According to those authors, this rate-determining step would explain the observed strongly negative ionic strength dependence with $Z_AZ_B \approx -3.9$. The authors do not discuss further the structure of their proposed $\mathrm{Mn_2}^{4+}$ species. However, formation of a hydroxo- or aqua-bridged dinuclear manganese(II) complex seems very unlikely for the conditions used. On the other hand, the complex $\mathrm{Mn_2HSO_3}^{3+}$, proposed as the product of reaction 36, is basically the same species as that proposed in the present mechanism, reaction 28. It occurs to us that the formation of a sulfite-bridged complex by the mechanism of reactions 6 and 28 is much more probable to explain the second-order rate dependence on manganese(II).

$$\mathrm{d[S(IV)]}/\mathrm{d}t = K_1[\mathrm{Mn(II)}]_0{}^2 + K_2[\mathrm{Mn(II)}]_0[\mathrm{HSO_3}^-] \qquad (34)$$

$$2\mathrm{Mn}^{2+} \rightleftharpoons \mathrm{Mn_2}^{4+} \qquad (35)$$

$$\mathrm{Mn_2}^{4+} + \mathrm{HSO_3}^- \rightarrow \mathrm{Mn_2HSO_3}^{3+} \qquad (36)$$

Pasiuk-Bronikowska et al.[17,22,28,32] have studied the manganese-catalyzed oxidation of sulfur(IV) by oxygen in aqueous solution, postulating a mechanism which involves participation of manganese(III) and free sulfur radicals. They reported a reaction second-order with respect to manganese(II) at low manganese(II) concentrations, shifting to a zero-order dependence at higher concentrations.[17] Referring to Wells and Salam,[98] who claimed that manganese(II) is hydrolyzed at pH 3.5 (which is wrong), Pasiuk-Bronikowska et al.[28,32] postulated the formation of a manganese(II) oxo-bridged complex at pH 1.3–1.6 according to reaction 37. Since pK_a for $\mathrm{Mn(H_2O)_6}^{2+}$ [74] is approximately 11, hydrolysis in acidic solutions is negligible. The incorporation of the oxo-bridged MnOMn^{2+} complex in the mechanism of Pasiuk-Bronikowska et al. is therefore highly unlikely in acidic or neutral solutions with low manganese concentrations and cannot explain the second-order dependence on manganese(II) found in their studies.

$$2\mathrm{MnOH}^+ \rightleftharpoons \mathrm{MnOMn}^{2+} + \mathrm{H_2O} \qquad (37)$$

At manganese(II) concentrations < 2×10^{-5} M the present study shows that the reaction is first-order in manganese(II), eqs 3b and 4b. At pH 4 and with no added manganese(III), the second-order rate constant k/A is $(1.2 \pm 0.5) \times 10^3$ M^{-1} s^{-1}. The rate law at these low manganese(II) concentrations is in good agreement with the results reported by Ibusuki and Barnes,[24] who derived eq 38 with $k_{\mathrm{I/B}} = 5.1 \times 10^3$ M^{-1} s^{-1} for the manganese-catalyzed autoxidation at 3 < pH < 6, [S(IV)] = $(0.4–1.5) \times 10^{-5}$, [Mn(II)] = $(1–4) \times 10^{-6}$ M, and 23.7 °C. In a subsequent paper[36] dealing with the synergism of iron(III) and manganese(II), Ibusuki and Takeuchi redetermined $k_{\mathrm{I/B}}$ to 1.7×10^3 M^{-1} s^{-1}. They argued that the discrepancy could be due to different quality of the water used in the experiments and therefore different concentrations of trace impurities. The present determination of $k/A = (1.2 \pm 0.5) \times 10^3$ M^{-1} s^{-1} corresponds very well with the value of 1.7×10^3 M^{-1} s^{-1} determined by Ibusuki and Takeuchi[36] at low manganese(II) and sulfur(IV) concentrations.

$$-\mathrm{d[S(IV)]}/\mathrm{d}t = k_{\mathrm{I/B}}[\mathrm{Mn(II)}][\mathrm{S(IV)}] \qquad (38)$$

Conclusions. Manganese(III) is a necessary intermediate in the manganese-catalyzed autoxidation of sulfur(IV) in aqueous solution, taking place by a free-radical chain mechanism. The catalytically active manganese(II) species is—at pH 2.4—the manganese(II) hydrogen sulfite complex $\mathrm{MnHSO_3}^+$ with a stability constant of $(3 \pm 1) \times 10^4$ M^{-1}. In addition, at pH 4.0, most likely a sulfito-bridged manganese(II) complex, $\mathrm{MnSO_3Mn}^{2+}$, is formed. Those two sulfito complexes are suggested to react with Mn(III) aqua hydroxo species, reactions 8 and 29,

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forming oxo- (or hydroxo-) bridged mixed-valence precursor complexes which undergo bridged electron transfer, forming Mn(II) and SO_3^- radicals, thereby initiating the chain reaction. In the absence of initially added manganese(III), it is postulated that iron(III) in natural trace concentrations of the order of (1–2) × 10^{-8} M triggers the manganese catalysis. The Fe(III) reacts with hydrogen sulfite, reaction 32, producing SO_3^- radicals, which rapidly react with dissolved oxygen forming SO_5^- radicals. Those radicals oxidize Mn(II) to Mn(III). This process provides an alternative to the autocatalysis by for instance copper, cobalt, and iron, which may be explained by oxidation of the divalent metal to trivalent state by peroxomonosulfate. This latter process is extremely slow for manganese.

This mechanism, including the initiation by trace iron(III), is supported by computer simulations. Finally, the mechanism proposed can explain several discrepancies in previous literature.

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