Inorg. Chem. **1998,** *37,* 4939−4944 **4939**

Iron−Manganese Redox Processes and Synergism in the Mechanism for Manganese-Catalyzed Autoxidation of Hydrogen Sulfite

Sture Fronaeus, Johan Berglund, and Lars I. Elding*,†

Inorganic Chemistry 1, Chemical Center, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

Received March 2, 1998

The mechanism for manganese-catalyzed aqueous autoxidation of hydrogen sulfite at pH 2.4 has been revised on the basis of previous comprehensive kinetic studies and thermodynamic data for iron−manganese redox processes and manganese(II) and -(III) protolysis equilibria. The catalytically active manganese species is concluded to be an oxo- (or hydroxo-) bridged mixed-valence complex of composition $\mathrm{(OH)Mn^{III}OMn^{II}(aq)}$ with a formation constant β' of $(3 \pm 1) \times 10^4\ \mathrm{M^{-1}}$ from kinetics or ca. $7 \times 10^4\ \mathrm{M^{-1}}$ from thermodynamics. It is formed via rapid reaction between $\mathrm{Mn(H_2O)_6}^{2+}$ and hydrolyzed manganese(III) aqua hydroxo complexes, and it initiates the chain reaction via formation of a precursor complex with $\mathrm{HSO_3}^-$, within which fast bridged electron transfer from S(IV) to Mn(III) takes place, resulting in formation of chain propagating sulfite radicals, $\mathrm{SO_3}^{\bullet-}$. The very high acidity of $\mathrm{Mn^{3+}(aq)}$, indicating a strong bond $\mathrm{Mn^{III}{-}OH_2}$ in hydrolyzed manganese(III), makes an attack by $\mathrm{HSO_3}^-$ on substitution labile Mn(II) in the bridged complex more favorable than one directly on manganese(III). The synergistic effect observed in systems containing iron as well as manganese and the chain initiation by trace concentrations of iron(III) of ca. 5×10^{-8} M can also be rationalized in terms of formation of this bridged mixed-valence dimanganese(II,III) complex. The presence of iron(III) in a Mn(II)/$\mathrm{HSO_3}^-$ system results in rapid establishment of an iron−manganese redox equilibrium, increasing the concentration of manganese(III) and of the catalytically active bridged complex. The bridged complex oxidizes $\mathrm{HSO_3}^-$ several orders of magnitude faster than does iron(III) itself. Comparison with some previous studies shows that the different experimental rate laws reported do not necessarily indicate different reaction mechanisms. Instead, they can be rationalized in terms of different rate-determining steps within the same complex chain reaction mechanism, depending on the experimental conditions used.

Introduction

Aqueous phase oxidation of hydrogen sulfite by molecular oxygen catalyzed by transition metal ions—in particular Mn(II/III) and Fe(II/III)—is an important process in the generation of acid rain.[1−9] Many kinetic studies on these systems have been published, but the mechanistic interpretations are contradictory.[6−9] Most reaction schemes postulated are based on the photoinduced free-radical mechanism proposed by Bäckström in 1934.[10] More recent studies on catalysis by Co(II/III),[11] Cu(II/III),[12] Mn(II/III),[8,13,14] and Fe(II/III)[15−17] indicate that the catalyzed autoxidation of sulfur(IV) may be interpreted in terms of a common mechanism, where redox cycling of the metal ion is fundamental.[6,7,18] Thus, the key reactions seem to be chain initiation by reaction between sulfite and the metal ion in its higher oxidation state to form sulfite radicals, followed by reoxidation of the reduced metal ion by strongly oxidizing chain carriers such as $\mathrm{SO_5}^{\bullet-}$, according to eqs 1 and 2.

$$\mathrm{M(III)} + \mathrm{SO_3}^{2-} \rightarrow \mathrm{M(II)} + \mathrm{SO_3}^{\bullet-} \tag{1}$$

$$\mathrm{M(II)} + \mathrm{SO_5}^{\bullet-} + \mathrm{H^+} \rightarrow \mathrm{HSO_5}^{-} + \mathrm{M(III)} \tag{2}$$

We have earlier studied the manganese-catalyzed autoxidation spectrophotometrically at 25 °C.[13] For pH 2.4, $0.13\ \mathrm{M} \le 10^4[\mathrm{Mn(II)}] \le 5.2$ M, $[\mathrm{Mn(III)}] \le 4 \times 10^{-8}$ M, initial $[\mathrm{S(IV)}] = 2.3 \times 10^{-5}$ M, and $[\mathrm{O_2}] \approx 2.5 \times 10^{-4}$ M, there is a first-order disappearance of $\mathrm{HSO_3}^-$ with an observed pseudo-first-order rate constant according to eq 3, where A and B are

$$k_{\mathrm{obsd}} = k[\mathrm{Mn(II)}](1 + B[\mathrm{Mn(III)}]_0)/(A + [\mathrm{Mn(II)}]) \tag{3}$$

constants and $[\mathrm{Mn(III)}]_0$ denotes the concentration of initially

---

[†] Fax: +46-46-2224439. E-mail: LarsI.Elding@inorg.lu.se.

(1) Graedel, T. E.; Weschler, C. J.; Mandich, M. L. *Nature* **1985**, *317*, 240.

(2) Graedel, T. E.; Mandich, M. L.; Weschler, C. J. *J. Geophys. Res.* **1986**, *91*, 5205.

(3) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Atmospheric chemistry: Fundamentals and experimental techniques*; John Wiley & Sons: New York, 1986.

(4) Warneck, P. *Chemistry of the natural atmosphere*; Academic Press: San Diego, CA, 1988.

(5) Warneck, P. *Fresenius' J. Anal. Chem.* **1991**, *340*, 585.

(6) Berglund, J.; Elding, L. I. *Atmos. Environ.* **1996**, *29*, 1379 and references therein.

(7) Brandt, C.; van Eldik, R. *Chem. Rev.* **1995**, *95*, 119 and references therein.

(8) Connick, R. E.; Zhang, Y.-X. *Inorg. Chem.* **1996**, *35*, 4613.

(9) Yermakov, A. N.; Poskrebyshev, G. A.; Purmal, A. P. *Prog. React. Kinet.* **1997**, *22*, 141.

(10) Bäckström, H. L. J. *Z. Phys. Chem.* **1934**, *25B*, 122.

(11) Coichev, N.; van Eldik, R. *Inorg. Chem.* **1991**, *30*, 2375.

(12) Anast, J. M.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 2319.

(13) Berglund, J.; Fronaeus, S.; Elding, L. I. *Inorg. Chem.* **1993**, *32*, 4527.

(14) Coichev, N.; van Eldik, R. *Inorg. Chim. Acta* **1991**, *185*, 69.

(15) Bal Reddy, K.; Coichev, N.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* **1991**, 481.

(16) Bal Reddy, K.; van Eldik, R. *Atmos. Environ.* **1992**, *26A*, 661.

(17) Brandt, C.; Fábián, I.; van Eldik, R. *Inorg. Chem.* **1994**, *33*, 687.

(18) van Eldik, R.; Coichev, N.; Bal Reddy, K.; Gerhard, A. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 478.

added Mn(III) (in the following text, [Mn(II)] and [Mn(III)] denote the total concentrations of manganese(II) and -(III), respectively). We have interpreted the kinetics in terms of a free-radical chain mechanism according to eqs 4−8.[13]

$$Mn^{2+} + HSO_3^- \rightarrow MnHSO_3^+ \qquad (4)$$

$$Mn(III) + MnHSO_3^+ \rightarrow 2Mn(II) + SO_3^{\bullet -} + H^+ \qquad (5)$$

$$SO_3^{\bullet -} + O_2 \rightarrow SO_5^{\bullet -} \qquad (6)$$

$$Mn^{2+} + SO_5^{\bullet -} + H^+ \rightarrow Mn(III) + HSO_5^{\bullet -} \qquad (7)$$

$$HSO_3^- + HSO_5^- \rightarrow 2HSO_4^- \qquad (8)$$

Rapid formation of a manganese(II) hydrogen sulfite complex according to eq 4 was assumed in order to account for the saturation kinetics observed at high concentrations of manganese(II); cf. eq 3. The reaction sequence (4)−(8) is compatible with this experimental rate law only if the assumed complex $MnHSO_3^+$ is fairly strong with a stability constant $\beta_1 = A^{-1} \approx 3 \times 10^4$ M^{-1}. Connick and Zhang[8] have recently pointed out that a hypothetical complex between manganese(II) and hydrogen sulfite must be at least 500 times weaker, a conclusion which led them to discard the above mechanism. We have confirmed spectrophotometrically that the stability constant of the complex formed according to eq 4 cannot be as large as 3×10^4 M^{-1}. This fact necessitates a modification of the reaction mechanism.

The aim of the present work is 2-fold: (i) First, we want to combine the earlier comprehensive kinetic data[13] with thermodynamic calculations on iron−manganese redox equilibria in the hydrogen sulfite solutions used and with protolysis data for Mn^{3+}(aq) and Mn^{2+}(aq). Such calculations should elucidate the nature of the oxidizing manganese species operating according to eq 1 and might also explain its high catalytic activity and the iron−manganese synergism displayed in mixed iron−manganese systems. (ii) Second, we want to rationalize the very different experimental rate laws that have been obtained, in particular by ourselves[13] and Connick and Zhang,[8] which seem to be due to differences between the experimental conditions used.

Mechanism

As pointed out before,[13] Diebler and Sutin have studied the rate of self-exchange of $Mn(H_2O)_6^{2+/3+}$ in 3 M perchloric acid.[19] They observed that the rate is much greater in solutions where manganese(III) is hydrolyzed; the most probable explanation for this fact is formation of a mixed-valence manganese(II,III) complex with an electron-mediating oxo bridge between the two metal centers. Measurements by Biedermann and Palombari[20] for pH ≤ 0.6 indicate that there will be an extensive hydrolysis of manganese(III) at pH 2.4. Manganese(II) is not hydrolyzed at this pH. pK_{a1} for $Mn(H_2O)_6^{2+}$ is about 11 at 25 °C,[21] which means that $\beta_1 \approx 10^3$ M^{-1} for formation of $MnOH^+$. Thus, hydroxo- or oxo-bridged mixed-valence complexes between $Mn(H_2O)_6^{2+}$ and hydrolysis products of manganese(III) $Mn(OH)_j^{3-j}$ (j = 2 and 3) are likely to be formed under the experimental conditions used in the determination of eq 3. As discussed in more detail below these bridged complexes can be schematically denoted as $(OH)Mn^{III}-O-Mn^{II}$.

Hydrogen sulfite is expected to attack the mixed-valence species forming precursor complexes $(OH)Mn^{III}-O-Mn^{II}O_3SH$, within which subsequent fast electron transfer from HSO_3^- to Mn(III) can occur. Thus, reactions 4 and 5 in the above reaction mechanism should be exchanged for reactions 9 and 10.

$$Mn^{2+} + Mn(III) \rightleftarrows (OH)Mn^{III}-O-Mn^{II} \qquad (9)$$

$$(OH)Mn^{III}-O-Mn^{II} + HSO_3^- \rightarrow 2Mn^{2+} + SO_3^{\bullet -} + H_2O \qquad (10)$$

The saturation kinetics observed for high manganese(II) concentrations as described by eq 3 can then be rationalized in terms of formation of the mixed-valence complex instead of $MnHSO_3$. Introducing a formation constant β' for this complex, eq 11, we arrive at eq 12, where $[Mn^{2+}] \approx [Mn(II)]$, since $[Mn(II)] \gg [Mn(III)]$.

$$\beta' = [(OH)MnIII-O-Mn^{II}]/([Mn(III)][Mn^{2+}]) \qquad (11)$$

$$[(OH)Mn^{III}-O-Mn^{II}] = [Mn(III)]\beta'[Mn^{2+}]/(1 + \beta'[Mn^{2+}]) \qquad (12)$$

According to this mechanism, eqs 6−10 with reaction 10 rate determining, the observed pseudo-first-order rate constant for disappearance of HSO_3^- will be described by eq 13.

$$k_{obsd} = 2k_{10}[Mn(II)][Mn(III)]/(\beta'^{-1} + [Mn(II)]) \qquad (13)$$

A comparison with the experimental rate law eq 3 yields $A^{-1} = \beta'$, $B^{-1} + [Mn(III)]_0 = [Mn(III)]$, and $kB = 2k_{10}$. The experimental data in ref 13 can then be used to calculate $\beta' = (3 \pm 1) \times 10^4$ M^{-1}, B^{-1} (average) $\approx 1.5 \times 10^{-8}$ M, and $k_{10} \approx 1.5 \times 10^6$ M^{-1} s^{-1}. It is also evident that when the chain reaction has attained steady state, [Mn(III)] will be larger than $[Mn(III)]_0$ by the quantity B^{-1}. Thus, for $[Mn(III)]_0 = 0$, there will still be an autoxidation of HSO_3^- after an induction period. We have proposed that the reaction in this case is initiated according to eq 1 by iron(III), present in trace concentrations as unavoidable impurities in the solutions.[13] At the same time some manganese(II) will be oxidized to manganese(III) directly and according to eq 2, starting the autocatalytic reaction.

A synergism has been observed when iron(III) is added to a $Mn(II)/HSO_3^-$ system; the reaction rate becomes much higher than the sum of the contributions from the individual systems.[13] This effect can also be explained by the above mechanism, considering the fact that manganese(III) is a much more effective oxidant than iron(III); the rate constant k_{10} is ca. 5×10^3 times larger than that for reaction between Fe(III) and HSO_3^-.[13,16] Thus, the occurrence of a synergism further supports our presumption that iron(III) impurities start the chain reaction in the absence of a deliberately added initiator. The proposed reaction mechanism is summarized in Scheme 1, and the pertinent rate constants are found in Table 1.

Calculations

Thermodynamics. After the induction period, if any, when the strictly first-order disappearance of HSO_3^- indicates that the concentrations of manganese(II) and -(III) no longer change,

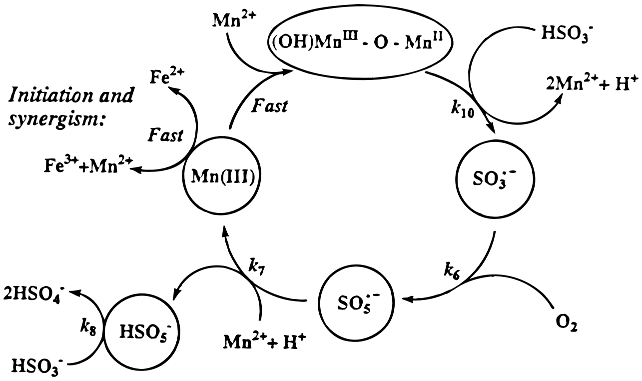
---

(19) Diebler, H.; Sutin, N. *J. Phys. Chem.* **1964**, *68*, 174.

(20) Biedermann, G.; Palombari, R. *Acta Chem. Scand.* **1978**, *A32*, 381.

(21) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1976; Vol. 4, p 5.

Scheme 1. Catalytic Cycle for the Manganese-Catalyzed Autoxidation of Hydrogen Sulfite at pH 2.4, Including Iron/Manganese Synergism and Chain Initiation by Trace Concentrations of Iron(III)[a]



[a] Notation for rate constants is according to equations in the text and values of rate constants in Table 1. Mn(III) denotes mixed hydroxo aqua complexes of manganese(III).

Table 1. Selected Values of Rate Constants in Scheme 1 (Notation According to Reaction Number)

k_n/s^{-1} M^{-1}	values	ref
k_6	2.5×10^9, 1.1×10^9	13, 38, 39
k_7	10^8	13, 30
k_8	4.3×10^4	37
k_{10}	1.5×10^6, 1.6×10^6	this work

a rapid redox equilibrium between manganese(II/III) and iron(II/III) is established according to eq 14, where K is the

$$K = [\mathrm{Fe}^{2+}][\mathrm{Mn}^{3+}]/([\mathrm{Fe}^{3+}][\mathrm{Mn}^{2+}]) \tag{14}$$

equilibrium constant. Then [Fe^{2+}] is equal to B^{-1}. The standard redox potentials are $E°(\mathrm{Mn}^{2+/3+}) \approx 1.50$ V[22] and $E°(\mathrm{Fe}^{2+/3+}) = 0.77$ V. A mean value of p$K_{a1} = 2.40$ for the hydrolysis of Fe^{3+}(aq) in dilute solutions based on several investigations[23] yields $[\mathrm{Fe}^{3+}] \approx 0.50$[Fe(III)] at pH 2.4. Hydrolysis of Fe^{2+}(aq) and Mn^{2+}(aq) will be negligible at this pH.

For $[\mathrm{Mn}^{2+}] > 2.5 \times 10^{-4}$ M the rate constant k_{obsd} is independent of [Mn(II)], and it follows from eq 12 that, for $\beta' \geq 3 \times 10^4$ M^{-1}, $[\mathrm{Mn(III)}] \approx [(\mathrm{OH})\mathrm{Mn}^{\mathrm{III}}{-}\mathrm{O}{-}\mathrm{Mn}^{\mathrm{II}}]$. If it is assumed that $\mathrm{Mn(OH)}_j^{3-j}$ forms a mixed-valence complex with Mn^{2+}(aq) with the stability constant β', eq 15 is easily derived.

$$[\mathrm{Mn(III)}] = \beta'\beta_{aj}[\mathrm{H}^+]^{-j}[\mathrm{Mn}^{3+}][\mathrm{Mn}^{2+}] \tag{15a}$$

$$\beta_{aj} = \prod_{n=1}^{j} K_{an} \qquad j = 2, 3 \tag{15b}$$

Here, K_{an} denotes the protolysis constants for Mn^{3+}(aq). Then, from eqs 14 and 15 we obtain eq 16 for the ratio K' between the total concentrations.

$$K' = [\mathrm{Fe(II)}][\mathrm{Mn(III)}]/([\mathrm{Fe(III)}][\mathrm{Mn(II)}]) \tag{16a}$$

$$K' = 0.5\,K\beta'\beta_{aj}[\mathrm{Mn(II)}][\mathrm{H}^+]^{-j} \tag{16b}$$

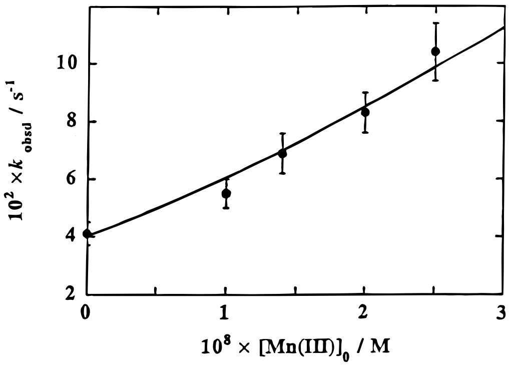


Figure 1. k_{obsd} as a function of [Mn(III)]$_0$. Conditions: $[\mathrm{Mn(II)}] = 2.8 \times 10^{-4}$ M, $[\mathrm{S(IV)}]_0 = 2.3 \times 10^{-5}$ M, $[\mathrm{O_2}] \approx 2.5 \times 10^{-4}$ M, pH 2.4, and temperature 25 °C. The curve has been calculated from thermodynamic data using eq 17c with the parameter values $K' = 9.7 \times 10^{-6}$, $C = 2.8 \times 10^{-4}$ M, $[\mathrm{Fe(III)}]_0 = 7 \times 10^{-8}$ M, and $2k_{10} = 3.2 \times 10^6$ M^{-1} s^{-1}. For comparison, kinetics data (mean values from at least 10 measurements with standard deviations) from Table 1, ref 13, are included.

Kinetics. Experimental data for k_{obsd} vs [Mn(III)]$_0$ for a constant concentration of $[\mathrm{Mn(II)}] = 2.8 \times 10^{-4}$ M taken from ref 13 have been plotted in Figure 1. For this condition, it follows from eq 13 that

$$k_{\mathrm{obsd}} = 2k_{10}[\mathrm{Mn(III)}] \tag{17a}$$

where

$$[\mathrm{Mn(III)}] = [\mathrm{Mn(III)}]_0 + [\mathrm{Fe(II)}] \tag{17b}$$

For $[\mathrm{Mn(III)}]_0 > 1 \times 10^{-8}$ M, the plot of the experimental k_{obsd} in Figure 1 can be approximated by a straight line with slope 3.0×10^6 M^{-1} s^{-1}. As [Fe(II)] decreases for increasing [Mn(III)]$_0$, the true constant $2k_{10}$ in eq 17 a should have a somewhat higher value. Using tentatively $2k_{10} = 3.2 \times 10^6$ M^{-1} s^{-1} and the k_{obsd} value $2k_{10}[\mathrm{Fe(II)}] = (4.2 \pm 0.3) \times 10^{-2}$ s^{-1} at $[\mathrm{Mn(III)}]_0 = 0$ gives the equilibrium value $(1.3 \pm 0.2) \times 10^{-8}$ M for [Fe(II)] and [Mn(III)] of solution a in Table 2. For solution b, where Fe(III) has been added, k_{obsd} yields [Mn(III)] according to eq 17. Then, from [Mn(III)] − [Mn(III)]$_0$ and [Fe(III)]$_{\mathrm{added}}$ − [Fe(II)] we obtain [Fe(II)] and [Fe(III)]. The equilibrium concentrations of solution b, inserted into eq 16, yield the value of 9.7×10^{-6} for K' of eq 16. By use of eq 16, we get [Fe(III)] of solution a, and then by adding [Fe(II)], the total concentration of the iron impurities, we obtain $[\mathrm{Fe(III)}]_0 \approx 7 \times 10^{-8}$ M. This value seems very reasonable.[24]

Finally, from eqs 16 and 17 and with the known parameters K', [Mn(II)], and [Fe(III)]$_0$, k_{obsd} as a function of [Mn(III)]$_0$ can be calculated. Equation 16a is written $K'C = [\mathrm{Fe(II)}]([\mathrm{Mn(III)}]_0 + [\mathrm{Fe(II)}])/([\mathrm{Fe(III)}]_0 - [\mathrm{Fe(II)}])$ with $C = [\mathrm{Mn(II)}]$ and is solved with respect to [Fe(II)]. Then, combination with eqs 17a,b yields eq 17c.

$$k_{\mathrm{obsd}} = 2k_{10}\{0.5([\mathrm{Mn(III)}]_0 - K'C) + (0.25([\mathrm{Mn(III)}]_0 + K'C)^2 + K'C[\mathrm{Fe(III)}]_0)^{1/2}\} \tag{17c}$$

The curve in Figure 1, derived by use of thermodynamic data, agrees well with the kinetic measurements. A least-squares fit with k_{10} as parameter gives $k_{10} = (1.6 \pm 0.1) \times 10^6$ M^{-1} s^{-1} in good agreement with the tentative value given above and with the value derived from the kinetics, 1.5×10^6 M^{-1} s^{-1}.

Composition of the Mixed-Valence Complex. By use of eq 16, it is possible to test which mixed-valence complex with

---

(22) Latimer, W. M. *Oxidation Potentials*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952; p 237.

(23) Sillén, L. G.; Martell, A. E. *Stability Constants, Special Publication No. 17*; The Chemical Society: London, 1964, p 53.

(24) Brimblecombe, P.; Spedding, D. J. *Atmos. Environ.* **1974**, *8*, 937.

Table 2. Iron−Manganese Equilibrium in Two Different Solutions without (a) and with (b) Added Fe(III)[a]

solution	10^8[Mn(III)]$_0$/M	10^6[Fe(III)]$_{add}$/M	10^8[Mn(III)]/M	10^8[Fe(III)]/M	10^8[Fe(II)]/M	$10^3 k_{obsd}$/s^{-1}
a	0	0	1.3 ± 0.2	6.2 ± 0.3	1.3 ± 0.2	42 ± 3
b	1.75	1.00	6.1 ± 0.9	96 ± 1	4.3 ± 0.9	190 ± 10

[a] Conditions: $[\mathrm{Mn(II)}] = 2.8 \times 10^{-4}$ M, $[\mathrm{S(IV)}]_0 = 2.3 \times 10^{-5}$ M, $[\mathrm{O_2}] = 2.5 \times 10^{-4}$ M, pH 2.4, and temperature 25 °C. The errors are given as the standard deviation from at least five measurements.

a tentative composition $\mathrm{Mn^{III}(OH)}_j\mathrm{Mn^{II}}$ ($j = 2$ or 3) that yields a value of β' in agreement with that determined from kinetics. The crucial parameter is $E°(\mathrm{Mn^{2+/3+}})$. From measurements in a 3 M $\mathrm{LiClO_4}$ ionic medium giving $K_{a1} \approx 2.5$ M and $K_{a2} \approx 0.5$ M for protolysis of $\mathrm{Mn^{3+}}$(aq), the high value of $E°(\mathrm{Mn^{2+/3+}}) = 1.60$ V has been calculated on questionable premises.[20] The value of K_{a3} is not known. A reasonable estimate is to assume that $K_{a3}/K_{a2} \approx K_{a2}/K_{a1}$ (cf. the K_{aj} values of $\mathrm{H_3PO_4}$), which gives $K_{a3} \approx 0.1$ M. It has been reported that K_{a1} has approximately the same value in dilute solutions as in the salt medium,[20] but this need not be the case for K_{a2} and K_{a3}.

If we first assume that there is no mixed-valence complex (which implies that we exchange β'[Mn(II)] for 1; cf. eq 15) and put $j = 3$, we find $K = 9.3 \times 10^{-12}$ from eq 16. This corresponds to $E°(\mathrm{Mn^{2+/3+}}) = 1.42$ V. On the other hand, if we select $\beta' = 3 \times 10^5$ M^{-1} as an upper limit for the complex $\mathrm{Mn^{III}(OH)_3Mn^{II}}$, the result is $K = 1.1 \times 10^{-13}$ corresponding to $E°(\mathrm{Mn^{2+/3+}}) = 1.53$ V. The correct value should lie somewhere between these two limits. We have selected the literature value of 1.50 V,[22] corresponding to $K = 4.6 \times 10^{-13}$.

For $j = 2$ we obtain $\beta' = 2 \times 10^6$ M^{-1}. This is much higher than the value of 3×10^4 M^{-1} derived from kinetics. This means that such a high β' value is required to satisfy the condition $[\mathrm{Mn(III)}] = [\mathrm{Mn^{III}(OH)_2Mn^{II}}]$ according to eq 15. The β' value based on kinetics is about 65 times lower, indicating that this complex amounts only to ca. 1.5% of [Mn(III)]. Therefore it will be less important for the catalysis.

For $j = 3$ eq 16 yields $\beta' \approx 7 \times 10^4$ M^{-1}. This value is in reasonable agreement with that calculated from the kinetics by use of eq 13 and indicates that a mixed-valence complex of the composition $\mathrm{Mn^{III}(OH)_3Mn^{II}}$ or—equivalent and more likely, since hydroxo bridges between these highly charged metal centers are not probable—an oxo-bridged complex $\mathrm{(OH)Mn^{III}\text{-}OMn^{II}}$ is formed. The large value of β' means that the concentration of this species will be approximately equal to the total concentration [Mn(III)].

To further test the value of the constant β_{a3} used in eq 16 we can use another estimate of K_{a3} as well as try to calculate the change in β_{a3} when using dilute solutions instead of a 3 M perchlorate medium.

The kinetic measurements can be rationalized well by formation of a single mixed-valence complex that is predominant for $[\mathrm{Mn(II)}] > 2.5 \times 10^{-4}$ M. This means that $\mathrm{Mn(OH)_3}$ will be the predominant hydrolysis product that forms the complex at pH 2.4. Hence it follows that $[\mathrm{Mn(OH)_3}]/[\mathrm{Mn(OH)_2^+}] \geq 10$ which yields $K_{a3} \geq 0.04$ M. On the other hand, at the upper limit for studies of the hydrolysis (pH 0), the formation of $\mathrm{Mn(OH)_3}$ is not observable in the measurements,[20] which means that the ratio is ≤ 0.1 and $K_{a3} \leq 0.1$ M. Thus, the value selected above seems reasonable.

To arrive at β_{a3} for dilute solutions, $\beta_{a3}°$, the activity coefficients f of different species $\mathrm{Mn(OH)}_j^{3-j}$ in the 3 M salt medium have to be taken into account. As expressions for these activity coefficients are not available, we postulate that $f(\mathrm{MnOH^{2+}})/f(\mathrm{Mn^{3+}}) \approx f(\mathrm{FeOH^{2+}})/f(\mathrm{Fe^{3+}})$ and that the linear concentration term in the extended Debye−Hückel formula[25] of log f is approximately the same for different $\mathrm{Mn(OH)}_j^{3-j}$. Thus, ratios between the activity coefficients can be easily calculated from the ordinary charge term.

From $\mathrm{p}K_{a1}° \approx 2.40$ and $\mathrm{p}K_{a1} \approx 3.00$ in 3 M $\mathrm{NaClO_4}$[23] for $\mathrm{Fe^{3+}}$(aq) we get $K_{a1}°/K_{a1} \approx 4.0$, and the same relation should hold for $\mathrm{Mn^{3+}}$(aq). Then, $f(\mathrm{H^+})$ is obtained from eq 18, giving

$$f(\mathrm{H^+})f(\mathrm{MnOH^{2+}})/f(\mathrm{Mn^{3+}}) = K_{a1}°/K_{a1} \qquad (18)$$

$K_{a2}°/K_{a2} \approx 0.95$ and $K_{a3}°/K_{a3} \approx 0.22$. The value of $\beta_{a3}° \approx 0.85\beta_{a3}$ inserted in eq 16, only entails an insignificant change in the β' value.

Discussion

The thermodynamic calculations confirm the conclusions from the kinetic measurements that a mixed-valence complex is formed with a stability constant β' of ca. $(5 \pm 2) \times 10^4$ M^{-1}. It should be emphasized that the two methods are independent, since eq 17, which is applicable at the [Mn(II)] value used and forms the basis for the thermodynamic calculations, does not contain the quantity β'.

The question of how the chain reaction starts in the absence of deliberately added initiators has been raised many times before, most recently by Connick et al.[26] They suggest initiation by reaction between $\mathrm{HSO_5^-}$ and $\mathrm{HSO_3^-}$ to form $\mathrm{SO_3^{\bullet-}}$, without further specifying how $\mathrm{HSO_5^-}$ is generated. However, application of eqs 16 and 17 to a solution with known manganese(II) concentration but without deliberately added manganese(III) and iron(III), using the established values of the constants involved, shows the presence of an initial concentration of iron(III) within the range of what is usually found in purified water. Thus, such small concentrations of iron(III) will be sufficient to initiate the manganese-catalyzed oxidation of $\mathrm{HSO_3^-}$ via the manganese(III) formed, and there will be no need for any other initiator.

One effect of the formation of the mixed-valence complex is that for constant values of [Mn(II)] and $[\mathrm{Fe(III)}]_0$ the quantity β'[Mn(II)] in eq 16b makes the equilibrium concentration [Mn(III)] higher. Consequently the autocatalytic effect will also increase.

The thermodynamic calculations give the important information that the oxo-bridged mixed-valence complex most probably has the composition $\mathrm{(OH)Mn^{III}OMn^{II}}$. For high [Mn(II)] all manganese(III) can be kept in solution as this complex, reacting fast with $\mathrm{HSO_3^-}$. According to this mechanism, it can be concluded from the experiments that $\mathrm{HSO_3^-}$ reacts considerably slower with hydrolyzed manganese(III) than with the mixed-valence complex. Simply on the basis of electrostatics, it seems likely that a mixed-valence dimanganese(II,III) complex would be more reactive toward $\mathrm{HSO_3^-}$ than hydrolyzed manganese(III), since the manganese(II) moiety of $\mathrm{(OH)Mn^{III}{-}O{-}Mn^{II}}$ provides extra positive charges. There is no obvious way to test that this conclusion is valid by direct, independent measure-

---

(25) Falkenhagen, H. *Theory of Electrolytes*; S. Hirzel: Leipzig, Germany, 1971, p 296.

(26) Connick, R. E.; Zhang, Y.-X.; Lee, S.; Adamic, R.; Chieng, P. *Inorg. Chem.* **1995**, *34*, 4543.

ments. Due to the extensive hydrolysis of $Mn(H_2O)_6^{3+}$ it is not feasible to monitor the kinetics in the pH range between 2 and 7, which is relevant for reactions in the atmospheric aqueous phase. In fact, there seems to have been no studies reported on reactions between any reductant and manganese(III) in this pH range.

However, Siskos et al. have studied the oxidation of S(IV) by $Mn(H_2O)_6^{3+}$ in perchloric acid medium under conditions of excess manganese(II). They report that the rate increases with decreasing acid concentration in the range 2.3 M $<$ [$HClO_4$] $<$ 5.92 M.[27] One possible explanation for this result would be that $MnOH^{2+}$ formed in the less acidic solutions is more reactive toward S(IV) than $Mn(H_2O)_6^{3+}$. This has been shown to be true for other reactants reducing manganese(III) by an inner-sphere mechanism.[28,29] For outer-sphere reactions with various reductants, on the other hand, $Mn(H_2O)_6^{3+}$ is more reactive than $MnOH^{2+}$, since the redox potential of the hydroxo complex is much lower than that of $Mn(H_2O)_6^{3+}$.[29] An alternative explanation to the observation by Siskos et al. would be that a bridged manganese(II,III) complex forming when hydrolyzed manganese(III) is present reacts faster than $Mn(H_2O)_6^{3+}$ with S(IV).

The extraordinary acidity of $Mn(H_2O)_6^{3+}$ as indicated by the values of K_{a1} and K_{a2} has been ascribed to a change from octahedral to a square pyramidal five-coordination at formation of $MnOH^{2+}$, involving an increase in ligand field stabilization energy.[20] This should indicate a strong bond $Mn^{III}-OH_2$ in the hydroxo aqua complex, yielding a higher value of the activation energy of a substitution of HSO_3^- for H_2O to form a precursor complex than that of the corresponding process with substitution labile $Mn(H_2O)_6^{2+}$ that is not hydrolyzed. Thus, an attack by HSO_3^- on the manganese(II) moiety of the mixed-valence complex, followed by a fast bridged electron transfer to manganese(III), is expected to be faster than a direct attack on manganese(III). Even if there is no independent indication, it is possible that the formation of the mixed-valence complex leads to a certain substitution labilization of Mn(III). In that case, an attack by HSO_3^- on the manganese(III) moiety could also contribute to the catalysis. In addition, at low [Mn(II)] with incomplete complex formation, the uncharged $Mn(OH)_3$ certainly tends to form polynuclear hydrolysis products[19] that should react more slowly with HSO_3^-.

Connick and Zhang have questioned the influence of low concentrations of added manganese(III); they argue that if Mn(III) reacts rapidly by formation of the other chain carriers, an addition of ca. 10^{-8} M Mn(III) should have no effect on the final rate.[8] The observed increase in rate with increasing additions of manganese(III) would therefore indicate that steady state is not attained. However, after the induction period, at the lowest manganese(III) concentration, the kinetic traces indicate a strictly first-order disappearance of HSO_3^-. This is evidence that the steady-state approximation in fact can be applied to the chain carriers $SO_3^{\bullet-}$ and $SO_5^{\bullet-}$; the following relationships are obtained: $2k_6[SO_3^{\bullet-}][O_2] = k_{obsd}[HSO_3^-]$ and $2k_7[SO_5^{\bullet-}][Mn(II)] = k_{obsd}[HSO_3^-]$. If values for the concentrations of O_2, HSO_3^-, Mn(II), Mn(III), and the corresponding k_{obsd} from Table 2 in ref 13 are used together with the known values of $k_6 = 2.5 \times 10^9$ M^{-1} s^{-1} and $k_7 \approx 10^8$ M^{-1} s^{-1},[13,30] it is found that $0.4 < 10^{12}[SO_3^{\bullet-}]/M < 2.5$ and $2.5 < 10^{11}[SO_5^{\bullet-}]/M < 30$. Thus, as these concentrations are much smaller than $[Mn(III)]_0$, eq 17b holds as long as steady-state is maintained.

In the chain reaction mechanism reaction 8 has been used as the chain-terminating step. Of course there are other possibilities, for instance reactions 19 and 20, with rate constants $k_{19} \approx$

$$SO_3^{\bullet-} + SO_3^{\bullet-} \rightarrow S_2O_6^{2-} \qquad (19)$$

$$SO_5^{\bullet-} + SO_5^{\bullet-} \rightarrow S_2O_8^{2-} + O_2 \qquad (20)$$

2×10^8 M^{-1} s^{-1} and $k_{20} \approx 1.5 \times 10^8$ M^{-1} s^{-1} (cf. Table 6 in ref 13). From the rate constants k_6 and k_7 and the upper limits for $[SO_3^{\bullet-}]$ and $[SO_5^{\bullet-}]$, the ratios r_{19}/r_6 and r_{20}/r_7 (r_j denotes the rate of reaction j) can be estimated to $r_{19}/r_6 < 8 \times 10^{-10}$ and $r_{20}/r_7 < 1.4 \times 10^{-4}$. Thus, in the application of the steady-state approximation to the intermediates $SO_3^{\bullet-}$, $SO_5^{\bullet-}$, and HSO_5^-, the rates r_{19} and r_{20} are unimportant and will have no influence on the rate law.[13]

At pH 4.0 and [Mn(II)] $\leq 1.6 \times 10^{-3}$ M, measurements have been carried out only without added manganese(III) because of its disproportionation.[13] The expression obtained for the rate constant is similar to that in eq 3 for $[Mn(III)]_0 = 0$ with approximately the same values of A and k, but the rate law includes a term $k'[Mn(II)]^2$ in the numerator. Thus, despite the difference in pH, the mechanism should be the same for decreasing [Mn(II)]. At higher pH manganese(III) will be further protolyzed, and it seems likely that the mixed-valence complex will take part in the equilibrium, eq 21.

$$(OH)Mn^{III}OMn^{II} + Mn^{2+} \rightleftarrows Mn^{III}(OMn^{II})_2 + H^+ \qquad (21)$$

The product complex may form a precursor complex with HSO_3^-, resulting in a fast bridged electron transfer in a reaction parallel to reaction 10, giving rise to the $k'[Mn(II)]^2$ term in rate law.

Comparison with Previous Studies. A large number of investigations of the manganese-catalyzed oxidation of sulfur(IV) in aqueous solution have resulted in various rate laws, due to differences in the experimental conditions used (see e.g. Table 2 in ref 6). The importance of manganese(III) for the catalysis has been discussed in several investigations, but as far as we know, it has been shown experimentally by deliberate addition of manganese(III) only twice.[13,14]

As far as the manganese(II) dependence is concerned, reported rate laws vary largely. A simple one-term law, first order in both Mn(II) and HSO_3^-, is often found for very low [Mn(II)]. This is in agreement with eqs 3 and 13 for $[Mn(III)]_0 = 0$ and [Mn(II)] $\leq 1 \times 10^{-5}$ M. Such a simplified experimental law will of course give little information about the mechanism. However, it is noteworthy that the rate constant derived by Ibusuki and Takeuchi[31] by use of such a rate law is in good agreement with the value of k/A calculated from eq 3.

Several experimental rate laws include $[Mn(II)]^2$ terms. Less likely presumtions have been presented in some cases to rationalize such results. For instance, Pasiuk–Bronikowska and Bronikowski[32] and Collins[33] postulate formation of an oxo-bridged complex $Mn^{II}-O-Mn^{II}$ in acidic solutions. However, as pointed out above, Mn^{2+}(aq) is not hydrolyzed in acidic solutions and formation of the complex presumed is not

---

(27) Siskos, P. A.; Peterson, N. C.; Huie, R. E. *Inorg. Chem.* **1984**, *23*, 1134.
(28) Davies, G. *Inorg. Chim. Acta* **1975**, *14*, L13.
(29) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1985**, *24*, 3403.
(30) Berglund, J.; Buxton, G. V.; Elding, L. I.; McGowan, S.; Salmon, G. A. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3309.
(31) Ibusuki, T.; Takeuchi, K. *Atmos. Environ.* **1987**, *21*, 1555.
(32) Pasiuk-Bronikowska, W.; Bronikowski, T. *Chem. Eng. Sci.* **1989**, *44*, 1361.
(33) Collins, K. R. Ph.D. Thesis, Georgia Institute of Technology, Atlanta, GA, 1987.

thermodynamically feasible. Similarly, a suggestion by Huss et al.[34] that a species Mn_2^{4+} can be formed and take part in the initiation step is inconceivable. The only species in the solutions at pH 4 that certainly are capable of forming a bridge between two Mn^{2+} moieties are hydrolysis products of Mn^{3+}(aq), for instance according to eq 21.

In the rate laws discussed above all terms are first-order with respect to S(IV). However, some authors reporting laws containing a term second-order in Mn(II) find that it is zero-order in S(IV) (see ref 6). Others have reported that the zero-order dependence on S(IV) at high sulfur concentrations increases to a first-order dependence at low [S(IV)].[31,35,36] To illustrate such a phenomenon we will extend the mechanism above with reactions 22 and 23, which together with reactions

$$\mathrm{Mn(II)} + \mathrm{HSO_5}^- \rightarrow \mathrm{Mn(III)} + \mathrm{SO_4}^{2-} + \mathrm{OH}^\bullet \quad (22)$$

$$\mathrm{HSO_3}^- + \mathrm{OH}^\bullet \rightarrow \mathrm{SO_3}^{\bullet -} + \mathrm{H_2O} \quad (23)$$

6, 7, and 9 represent a possible sulfite-induced chain mechanism for autoxidation of manganese(II). Qualitative measurements indicate that reaction 22 is very slow.[13] If the steady-state approximation is applied to the intermediates $SO_3^{\bullet -}$, $SO_5^{\bullet -}$, $OH^\bullet$, and HSO_5^-, the following relationships are valid: $r_6 = r_7$, $r_8 = r_{10}$, $r_{22} = r_{23}$, and $r_7 = r_8 + r_{22}$. We can then use eq 24.

$$r_{22} = r_{10}r_{22}/r_8 \quad (24)$$

By inserting the expressions for the rates in the right member of eq 24, we get the rate law of eq 25.

$$r_{22} = 0.5k_{\mathrm{obsd}}k_{22}k_8^{-1}[\mathrm{Mn(II)}] \quad (25)$$

At pH 2.4, $[\mathrm{Mn(III)}]_0 = 0$, and low [Mn(II)], the expression for k_{obsd} approximates to $kA^{-1}[\mathrm{Mn(II)}]$ according to eq 3, yielding $r_{22} = 0.5kk_{22}k_8^{-1}A^{-1}[\mathrm{Mn(II)}]^2$. This expression should be valid for the values of $[\mathrm{HSO_3}^-]$ and [Mn(II)] used in the present study.

However, at low values of $[\mathrm{HSO_3}^-]/[\mathrm{Mn(II)}]$ reaction 23 must be exchanged for reaction 26,

$$\mathrm{Mn(II)} + \mathrm{OH}^\bullet + \mathrm{H}^+ \rightarrow \mathrm{Mn(III)} + \mathrm{H_2O} \quad (26)$$

which is more rapid under such conditions; cf. the rate constants $k_{23} = 4.5 \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$ and $k_{26} = 2.6 \times 10^7$ $\mathrm{M^{-1}\ s^{-1}}$ given in Table 6 of ref 13. This exchange implies that $r_7 = r_{10}$, and from the equality of eq 27,

$$r_{22} = r_{10}r_{22}/(r_8 + r_{22}) \quad (27)$$

we arrive at the rate law, eq 28.

$$r_{22} = 0.5k_{\mathrm{obsd}}k_{22}[\mathrm{HSO_3}^-][\mathrm{Mn(II)}]/(k_8[\mathrm{HSO_3}^-] + k_{22}[\mathrm{Mn(II)}]) \quad (28)$$

This expression takes the simple form $r_{22} = 0.5k_{\mathrm{obsd}}[\mathrm{HSO_3}^-]$; i.e., $r_{22} = r_{10}$ for $[\mathrm{HSO_3}^-]/[\mathrm{Mn(II)}] \ll k_{22}/k_8$.

Connick and Zhang[8] deduced a rate law with three terms for the manganese(II)-catalyzed HSO_3^- oxidation at pH 4.5, two of which referring to the catalysis and one to the uncatalyzed reaction. The two-term rate law for the catalyzed reaction contains one term second-order in Mn(II) and another first-order in both Mn(II) and HSO_3^-. The propagation steps are reactions 7 and 10 above with Mn(III) instead of $(OH)Mn^{III}{-}O{-}Mn^{II}$. In their case, however, with the concentration of HSO_3^- ranging from 1.5×10^{-3} to 1.2×10^{-2} M, reaction 10 will be more rapid than reaction 7, and consequently reaction 7 will be the rate-determining step. In our study, on the other hand, reaction 10 will be rate determining due to the much lower concentrations of hydrogen sulfite used.[13] Thus, both rate laws, although apparently different due to different rate-determining steps, seem to be correct and compatible with the same catalytic cycle.

Conclusion

Manganese-catalyzed autoxidation of HSO_3^- in the aqueous phase can be interpreted by a free-radical chain mechanism involving redox cycling of manganese. Manganese(III) is of fundamental importance in this process. Saturation kinetics is observed at pH 2.4 for high [Mn(II)]. This finding most probably indicates formation of a mixed-valence complex with composition $(OH)Mn^{III}{-}O{-}Mn^{II}$ as the catalytically active species. This species can form a precursor complex with HSO_3^-, within which a fast bridged electron transfer from S(IV) to Mn(III) takes place, forming chain-propagating $SO_3^{\bullet -}$ radicals. If iron(III) is added to a $Mn(II)/HSO_3^-$ system, a rapid redox equilibrium between Mn(II/III) and Fe(II/III) is established when the oxidation of HSO_3^- indicates steady state. Thermodynamic data for this equilibrium confirm formation of the mixed-valence complex, and its stability constant derived from thermodynamics agrees fairly well with that obtained experimentally from the kinetics. Measurements also show that, in the absence of initially added manganese(III) and iron(III), a reaction between iron(III), present in the solutions at concentrations of about 5×10^{-8} M, and manganese(II) can cause autocatalysis. The synergism observed when both manganese and iron are present simultaneously can also be explained by rapid manganese−iron redox equilibria, since the bridged dimanganese(II,III) complex oxidizes HSO_3^- much more rapidly than does iron(III).

The stoichiometric composition of the mixed-valence complex can be calculated from the thermodynamic data as $Mn^{III}(OH)_3Mn^{II}$ or $(OH)Mn^{III}OMn^{II}$. The positive charges provided by manganese(II) help to solubilize the hydrolyzed Mn(III), preventing it from forming polynuclear hydrolysis products. In addition the very high acidity constants of Mn^{3+}(aq), indicating a strong bond $Mn^{III}{-}OH_2$, should make an attack by HSO_3^- on the substitution labile Mn(II) moiety of the complex more favorable than one directly on manganese(III).

Comparison with previous studies shows that a variety of rate laws have been found for the manganese catalysis due to different experimental conditions used. By taking as an example the possible sulfite-induced autoxidation of Mn(II) with a chain-mechanism, we have shown how very different rate laws can be deduced at high and low values of $[\mathrm{HSO_3}^-]/[\mathrm{Mn(II)}]$.

Acknowledgment. Financial support from the Swedish Natural Science Research Council and from the European Union within the ENVIRONMENT program (Contract EV5V-CT93-0317, RINOXA) is gratefully acknowledged.

IC980225Z

---

(34) Huss, A., Jr.; Lim, P. K.; Eckert, C. A. *J. Phys. Chem.* **1982**, *86*, 4229.
(35) Ibusuki, R.; Barnes, H. M. *Atmos. Environ.* **1984**, *18*, 145.
(36) Martin, L. R.; Hill, M. W. *Atmos. Environ.* **1987**, *21*, 2267.
(37) McElroy, W. J.; Deister, U. *National Power Res. Report ESTB/L/0173/R90*; Leatherhead, U.K., 1990.
(38) Final Report, Contract No. STEP-005-C (MB), contract coordinator P. Warneck, 1992.
(39) Huie, R. E.; Clifton, A. *Radiat. Phys. Chem.* **1989**, *33*, 361.