Kinetics and Mechanism of the Oxidation of HSO_3^- by O_2. 2. The Manganese(II)-Catalyzed Reaction

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The Mn^{2+}-catalyzed oxidation of HSO_3^- by O_2 has been studied in the pH region 4.5 and at bisulfite ion concentrations from 1.5×10^{-3} to 1.2×10^{-2} M. The reaction was found to obey a three-term rate law: $-d[O_2]/dt = k_\alpha[HSO_3^-]^2 + k_\beta[HSO_3^-][Mn^{2+}] + k_\gamma[Mn^{2+}]^2$ with $k_\alpha = 3.6 \times 10^{-3}$ M^{-1} s^{-1}, $k_\beta = 1.23$ M^{-1} s^{-1}, and $k_\gamma = 98.6$ M^{-1} s^{-1} at pH 4.50, 25 °C, and ionic strength 0.050 M. The kinetic behavior of the reaction resembles markedly that of the uncatalyzed reaction. The rate of the reaction is independent of oxygen concentration, $S_2O_7^{2-}$ and HSO_5^- are intermediates in the reaction, and the reaction is catalyzed by $S_2O_8^{2-}$ and strongly inhibited by methanol. The experimental results can be quantitatively explained by the addition to the uncatalyzed reaction mechanism of a chain propagation reaction involving Mn^{2+} and $SO_5^{\bullet-}$. Among several alternatives, the manganese propagation may be represented as follows: (I) $Mn^{2+} + SO_5^{\bullet-} \rightarrow Mn(III) + HSO_5^-$; (II) $Mn(III) + HSO_3^- \rightarrow Mn^{2+} + SO_3^{\bullet-}$. The resulting mechanism leads to the three-term rate law where the first term is the uncatalyzed rate and the second term can be predicted quantitatively from the uncatalyzed rate and the last term. It was inferred from the yield of $S_2O_7^{2-}$ that, unlike the reaction between $SO_5^{\bullet-}$ and HSO_3^-, there is little or no branching of the first reaction to form the $SO_4^{\bullet-}$ radical. The ratio of the rate constant of (I) to that of the reaction of $SO_5^{\bullet-}$ with HSO_3^- in the uncatalyzed reaction mechanism has been determined to be 124. The quantitative agreement between the experimental data and predictions for the effect of $S_2O_8^{2-}$ has substantiated the validity of the proposed mechanism. The pH dependence of the reaction rate can be almost entirely accounted for by the pH dependence of the reaction between HSO_5^- and HSO_3^-, indicating that reaction I is independent of the hydrogen ion concentration in the pH region studied. While methanol inhibits the reaction, the quantitative discrepancy between predictions and experiments suggests that the reactions with alcohols are more complex than previously thought. Further work in this area is needed to understand fully the reaction mechanism when alcohol is present.

Introduction

The catalysis of the oxidation of S(IV) species by oxygen in aqueous solution has received considerable attention.[1−12] At pH 4.5 where bisulfite ion is the principal species the net reaction is

$$2HSO_3^- + O_2 \rightarrow 2SO_4^{2-} + 2H^+ \qquad (1)$$

The reaction is of importance in flue gas desulfurization processes where manganese in the fly ash can catalyze the reaction. The catalysis may also at times be of significance in the formation of acid rain in water droplets in the atmosphere.

Previous investigators have reported a variety of rate laws, partly because different pH regions were investigated as well as a wide range of bisulfite and manganese(II) concentrations. Generally, there is agreement that the catalysis is independent of the oxygen concentration and that there is zero- or first-order dependence on bisulfite ion concentration. The manganous ion concentration dependence has been reported to be anywhere from square power to less than zero power, i.e. inhibition under some conditions. Many mechanisms have been proposed, including both chain and nonchain mechanisms. Chain initiation is usually assumed to be by unknown metal ion impurities. Further discussion of the literature will be given after the results of this work have been presented.

In the present study, the rate law for the manganous ion catalyzed reaction of the bisulfite ion with oxygen was determined in the pH region of approximately 4.5 at 25 °C and ionic strength 0.050 M. At the higher manganous ion concentrations, we confirmed the results of Coughanowr and Krause[2] and Huss, Lim, and Eckert[10] that the rate law assumed the unusual form of simply a square-power dependence on manganous ion concentration, with no dependence on either bisulfite ion or oxygen concentration.

Because of a marked similarity of the kinetic behavior to that observed with the uncatalyzed reaction, it seemed likely that the manganous ion catalysis took place through alteration of one part of the uncatalyzed reaction. In previous studies[13] of the uncatalyzed reaction (part 1 of this work), a chain reaction

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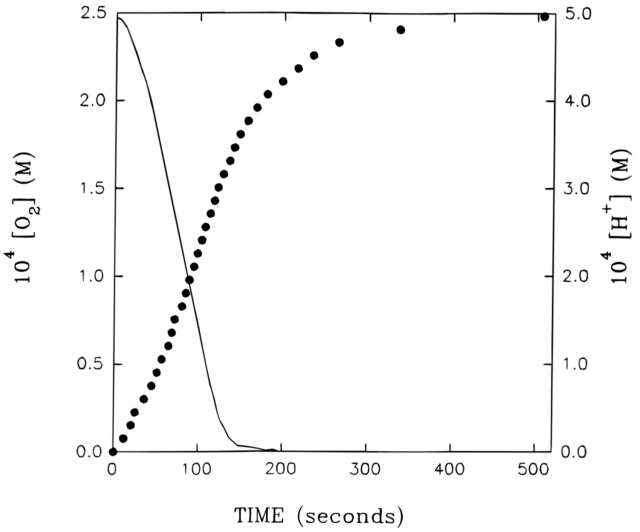

Figure 1. Typical kinetic curves of the Mn^{2+}-catalyzed HSO_3^-−O_2 reaction: solid line, oxygen concentration; filled circles, cumulative concentration of hydrogen ion produced by the reaction. Conditions: initial $[HSO_3^-] = 3.12 \times 10^{-3}$ M, $[Mn^{2+}] = 1.63 \times 10^{-4}$ M, $T = 25$ °C, pH = 4.50, $\mu = 0.050$ M.

mechanism was proposed that involved the chain carriers $SO_3^{\bullet -}$, $SO_4^{\bullet -}$, and $SO_5^{\bullet -}$, as well as the two intermediates HSO_5^- (peroxymonosulfate ion) and $S_2O_7^{2-}$ (disulfate ion). Evidence was presented for chain initiation by the reaction of HSO_5^- with HSO_3^-. It will be shown how the manganous ion catalysis can be fitted into this mechanism with little modification.

Experimental Methods

The following chemicals were used: SO_2 and NH_3 gases (Matheson), NaOH crystal (Fisher), hydrochloric acid (Fisher), potassium nitrate (Fisher), sodium thiosulfate (Mallinkrodt), methanol (Fisher), sodium bicarbonate (Baker Analyzed reagent), $MnSO_4 \cdot H_2O$ (Mallinkrodt) and EDTA disodium salt (Sigma). House deionized water was distilled, and the middle 60% of the distillate was used as solvent in all experiments. Bisulfite solutions were generated with gaseous SO_2 and NH_3. The apparatus used in this work has been described in the previous paper.[13] All experiments were carried out at 25 °C, and the ionic strength was maintained at 0.050 M by the addition of NH_4Cl or KNO_3.

The kinetics of the reaction of the bisulfite ion with oxygen was followed in two ways: by measuring the oxygen concentration change with an oxygen probe and by monitoring the amount of base that had to be added to keep the pH constant. Buffer solutions were avoided because they might enter into the reaction. To obtain the rates of both the catalyzed and uncatalyzed reactions, the reaction was usually initiated by injecting a small amount of freshly prepared bisulfite stock solution into an air-saturated NH_4Cl or KNO_3 solution, and a small volume of concentrated $MnSO_4$ solution was added only after the uncatalyzed reaction had reached the steady state rate.

Results

A. Empirical Rate Law. All reactions were carried out with HSO_3^- in excess with respect to O_2. A typical kinetic curve of the reaction is shown in Figure 1. One notices that the kinetic behavior of the system is very similar to that of the uncatalyzed reaction, i.e. build-up of rate to a steady state and then constant rate of disappearance of oxygen until the oxygen is all consumed. The bending of the oxygen concentration vs time curve near the end of the reaction is an artifact caused by the measurable rate of response of the oxygen meter.[14] The linear decrease in $[O_2]$ at the steady state of the reaction clearly indicates a zero-order dependence of the rate of the reaction on oxygen concentration. The zero-order dependence on O_2 was found in all experiments carried out in this work. The hydrogen ion concentration curve gives the concentration of hydrogen ion formed by the reaction, as measured by the base that it was necessary to add to keep the pH constant. The continued production of hydrogen ion after all of the oxygen was consumed is a clear indication that $S_2O_7^{2-}$ is formed in the reaction, as shown in previous work.[13]

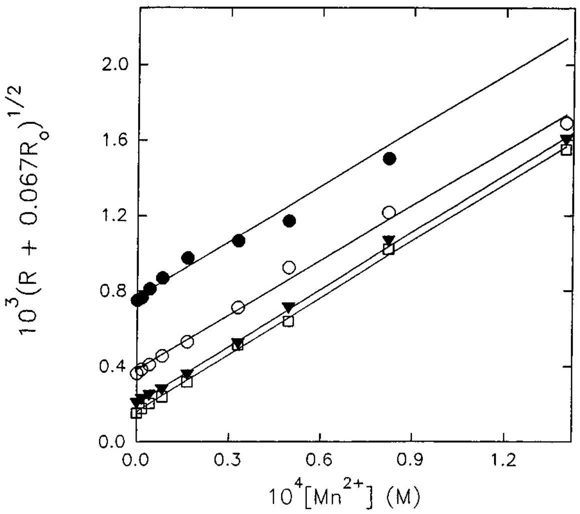

Figure 2. Effects of Mn^{2+} on the rate of the Mn^{2+}-catalyzed HSO_3^-−O_2 reaction: Data were plotted according to eq 9. Symbols are the experimental results, and the solid lines the least-squares fits. Bisulfite ion concentrations: (□) 1.55×10^{-3} M; (▼) 3.08×10^{-3} M; (○) 5.98×10^{-3} M; (●)1.19×10^{-2} M. $T = 25$ °C, pH = 4.50, and $\mu = 0.050$ M.

Experiments were performed at pH 4.50 at a series of different bisulfite concentrations but varying manganous ion concentration. The results are presented in Figure 2 where $(R + 0.067R_0)^{1/2}$ has been plotted versus the manganous ion concentration, where R is the observed rate of the disappearance of oxygen ($-d[O_2]/dt$) and R_0 is the rate in the absence of manganous ion. (The reason for the choice of ordinate and abcissa functions will be made clear later.) For a fixed bisulfite ion concentration, $(R + 0.067R_0)^{1/2}$ is of the form $a + b[Mn^{2+}]$. On squaring, it is seen that the rate of the reaction R has terms zero order, first order, and second order in manganous ion concentration. The first is simply the uncatalyzed reaction whose rate depends on the square power of the bisulfite ion concentration. It will be shown later that the data of Figure 2 give a first- and zero-order bisulfite dependence for the second and third terms respectively.

B. Reaction Mechanism. The observation that the manganous ion catalyzed reaction of oxygen with the bisulfite ion is inhibited by alcohol, catalyzed by the peroxydisulfate ion, has no dependence on the oxygen concentration, and produces the intermediate $S_2O_7^{2-}$ strongly suggests that the manganous ion is altering one part of the uncatalyzed chain reaction since the latter reaction exhibits also all of the above characteristics. The mechanism deduced[13] for the uncatalyzed reaction in the region of pH 4.50 is the following, where no attempt is made

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to represent correctly the acidity dependence. The letters identifying the reactions are the same as in ref 13.

propagation

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

$$SO_5^{\bullet -} + HSO_3^- \rightarrow HSO_5^- + SO_3^{\bullet -} \qquad (b)$$

$$SO_5^{\bullet -} + HSO_3^- \rightarrow SO_4^{\bullet -} + SO_4^{2-} + H^+ \qquad (c)$$

$$SO_4^{\bullet -} + HSO_3^- \rightarrow SO_4^{2-} + SO_3^{\bullet -} + H^+ \qquad (d)$$

$$SO_5^{\bullet -} + SO_5^{\bullet -} \rightarrow O_2 + SO_4^{\bullet -} + SO_4^{\bullet -} \qquad (e)$$

initiation

$$HSO_5^- + HSO_3^- \rightarrow SO_4^{\bullet -} + SO_3^{\bullet -} + H_2O \qquad (f)$$

termination

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

follow reactions

$$HSO_5^- + HSO_3^- \rightarrow S_2O_7^{2-} + H_2O \qquad (h)$$

$$HSO_5^- + HSO_3^- \rightarrow SO_4^{2-} + SO_4^{2-} + 2H^+ \qquad (i)$$

$$S_2O_7^{2-} + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \qquad (j)$$

The basis for the mechanism is detailed in ref 13. The peroxysulfate species HSO_5^- is an intermediate formed in the reaction and present at very low concentration. The intermediate disulfate ion, $S_2O_7^{2-}$, is also formed in the reaction but can persist even after all the oxygen is gone because reaction j has a first-order lifetime of a little more than 1 min at 25 °C.

The rate of the reaction for the uncatalyzed reaction is proportional to the second power of the bisulfite ion concentration and independent of the oxygen concentration.

$$-\frac{d[O_2]}{dt} = \frac{k_f k_b (k_b + k_c)}{k_g (k_h + k_i)} [HSO_3^-]^2 \qquad (2)$$

At high manganese concentrations the square-power dependence on bisulfite of the uncatalyzed reaction is replaced by a square-power dependence on manganese ion concentration. Bisulfite ion enters into the rate law[13] for the uncatalyzed reaction through the initiation (reaction f), propagation reactions b and c, and reactions h and i where it appears in the denominator. Since bisulfite ion enters to the square power through the product of the rate of (b) with that of (b) plus (c), it is tempting to suggest that the role of the manganous ion is to replace the bisulfite ion in these propagation steps. Were it to do so, the cross term containing bisulfite ion and manganous ion to the first power would be at least accounted for qualitatively.

If one assumes that reactions b and c in the propagation are replaced by

$$Mn^{2+} + SO_5^{\bullet -} \rightarrow \qquad (3)$$

to eventually yield $SO_3^{\bullet -}$ and at least some HSO_5^- and to re-form Mn^{2+} with manganous ion always the dominant manganese species, the rate law would have the correct limiting form at high manganous ion concentrations, i.e. square-power dependence on manganous ion and no dependence on oxygen or bisulfite ion concentrations. The propagation reactions resulting from reaction 3 might generate either $SO_3^{\bullet -}$ or $SO_4^{\bullet -}$, in analogy to reactions b and c. Let f be the fraction of (3) that produces $SO_3^{\bullet -}$ and HSO_5^-. The complete rate for the combined catalyzed and uncatalyzed reactions, without regard to dependence on hydrogen ion concentration, is then

$$-\frac{d[O_2]}{dt} = \frac{k_f}{k_g (k_h + k_i)} \{(k_b + k_c)[HSO_3^-] + k_3[Mn^{2+}]\}\{k_b[HSO_3^-] + f k_3 [Mn^{2+}]\} \qquad (4)$$

Equation 4 has the correct limiting square-power dependencies for $[HSO_3^-]$ and $[Mn^{2+}]$ as well as the cross term. To simplify the expressions let R_0 be the uncatalyzed rate, i.e.

$$R_0 = \frac{k_f k_b (k_b + k_c)[HSO_3^-]^2}{(k_h + k_i) k_g} \qquad (5)$$

and define

$$R_M = \frac{k_f f k_3^2 [Mn^{2+}]^2}{k_g (k_h + k_i)} \qquad (6)$$

and let $g = k_b/(k_b + k_c)$. Substituting in (4)

$$R = -\frac{d[O_2]}{dt} = R_0 + (f^{1/2}/g^{1/2} + g^{1/2}/f^{1/2}) R_0^{1/2} R_M^{1/2} + R_M \qquad (7)$$

$$R - R_0\{1 - {}^1/_4[(f/g)^{1/2} + (g/f)^{1/2}]^2\} = \{[(f/g)^{1/2} + (g/f)^{1/2}] R_0^{1/2}/2 + R_M^{1/2}\}^2 \qquad (8)$$

From previous work[13] g equals approximately 0.60[15] while f equals approximately unity, as will be discussed later. Then

$$(R + 0.067R_0)^{1/2} = 1.033 R_0^{1/2} + R_M^{1/2} \qquad (9)$$

A plot of $(R + 0.067R_0)^{1/2}$ versus $[Mn^{2+}]$ at constant $[HSO_3^-]$ should yield a straight line whose slope is $\{k_f f k_3^2/(k_g(k_h + k_i))\}^{1/2}$. Such data are shown in Figure 2. The average value of the slopes of the four curves is 9.9 $M^{-1/2}\ s^{-1/2}$. The constancy of the slopes at different bisulfite ion concentrations establishes the lack of dependence of R_M on bisulfite ion. The agreement between the experimental results and the predictions of eq 9 is evident.

Equation 9 also predicts that a plot of the intercepts of Figure 2 versus $[HSO_3^-]$ should yield a straight line passing through the origin. The data are plotted in Figure 3. The solid line is the dependence expected from ref 13. The agreement is good except for the point at the lowest bisulfite concentration.

The data presented in Figures 2 and 3 demonstrate that within experimental accuracy rate law 4 can describe quantitatively the catalysis by manganous ion. In particular, it should be noted that the cross term in the rate law involving $[Mn^{2+}][HSO_3^-]$ and its value is correctly predicted from the uncatalyzed term and the $[Mn^{2+}]^2$ term, thus strongly supporting the validity of the mechanism.

From the data one calculates for the three terms of the rate law $-d[O_2]/dt = k_\alpha[HSO_3^-]^2 + k_\beta[HSO_3^-\ ][Mn^{2+}\ ] + k_\gamma$-

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(15) Recently a value of $k_b/(k_b + k_c) \geq 0.96$ at pH 3 was reported (Warneck, P.; Ziajka, J. *Ber. Bunsen-Ges. Phys. Chem.* **1995**, *99*, 59) compared to our value of 0.60 at pH 4−6.[13] In their rather complex experiments, the $HSO_3^- - O_2$ reaction was catalyzed by the addition of Fe(III) and inhibited by the addition of benzene.

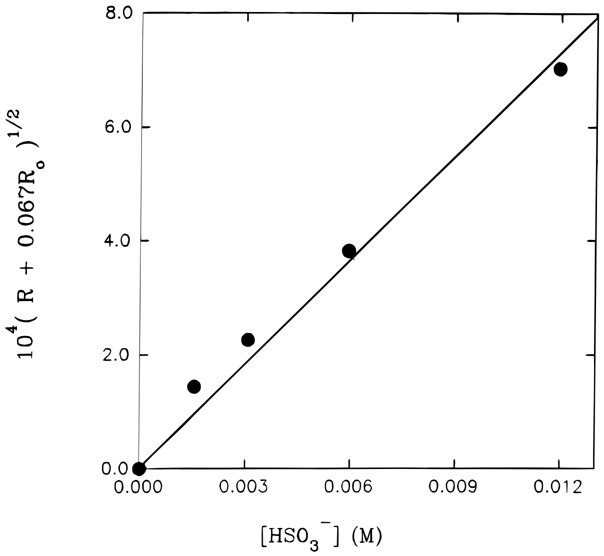

Figure 3. Bisulfite ion dependence of the intercepts of Figure 2. The filled circles are from Figure 2 at $[Mn^{2+}] = 0$, and the solid line is the dependence expected from ref 13.

Table 1. Yield of $S_2O_7^{2-}$ in the Mn^{2+}-Catalyzed Reaction[a]

			fraction yield of $S_2O_7^{2-}$	
pH	$[HSO_3^-]$ (M)	$[Mn^{2+}]$ (M)	exptl	"expected"[b]
4.50	3.12×10^{-3}	1.63×10^{-4}	0.83	0.83
4.00	1.5×10^{-2}	1.0×10^{-3}	0.85	0.85
4.00	2.76×10^{-3}	2.44×10^{-4}	0.86	0.86

[a] Temperature 25 °C, ionic strength 0.050 M. [b] Calculated assuming $f = 1$.

$[Mn^{2+}]^2$ the following values at pH 4.50 and ionic strength 0.050 M: $k_\alpha = 3.6 \times 10^{-3}$ M^{-1} s^{-1}, $k_\beta = 1.23$ M^{-1} s^{-1}, $k_\gamma = 98.6$ M^{-1} s^{-1}.

An additional useful quantity can be derived from the data of Figures 2 and 3, i.e. $k_3/(k_b + k_c)$, which equals the ratio of the slope of Figure 2 to the slope of Figure 3 divided by 1.033. It is 124.

The mechanistic details of reaction 3 and the subsequent re-formation of Mn^{2+} will be discussed later.

C. Yield of $S_2O_7^{2-}$. For the uncatalyzed reaction, it was shown[13] that $S_2O_7^{2-}$, disulfate ion, is an intermediate in the region of pH 4.5. Its presence was related to reaction h[13,16] and therefore was an indicator of the formation of HSO_5^- through reaction b. It was shown[13] that approximately 60% of the propagation step involving $SO_5^{\bullet-}$ occurs through reaction b and 40% through reaction c. It was of interest to investigate the yield of $S_2O_7^{2-}$ in the manganese ion catalyzed reaction.

The method used was essentially that described in ref 13. Under conditions where the manganese ion catalyzed reaction predominated and the reaction was rapid relative to the hydrolysis of $S_2O_7^{2-}$ by reaction j, the acid liberated after consumption of all of the oxygen was determined as a measure of the $S_2O_7^{2-}$ present at the time of oxygen disappearance. This value was then corrected for $S_2O_7^{2-}$ hydrolysis that occurred during the $O_2-HSO_3^-$ reaction.[13] The results for three such experiments are shown in Table 1.

Because the uncatalyzed propagation reactions b and c are not negligible in the experiments of Table 1, the observed yield is somewhat shifted toward that of the uncatalyzed reaction, which is 0.53 at pH 4.50 and 0.54 at pH 4.0.[13] The yields of Table 1 indicate, however, that a higher fraction of the propagation reactions must proceed through formation of HSO_5^- than the 0.53 and 0.54 fractions found for the uncatalyzed reaction. If it is assumed that all of the manganese ion catalyzed reaction goes through HSO_5^- the yields "expected" are those given in the last column of Table 1. The perfect agreement is fortuitous, since the experimental accuracy is only about 3%. It should be noted that the maximum yields of $S_2O_7^{2-}$ if all of the reaction produced HSO_5^- would only be 0.90 and 0.89 at pH 4.00 and 4.50, respectively, because of the split between reactions h and i.[16]

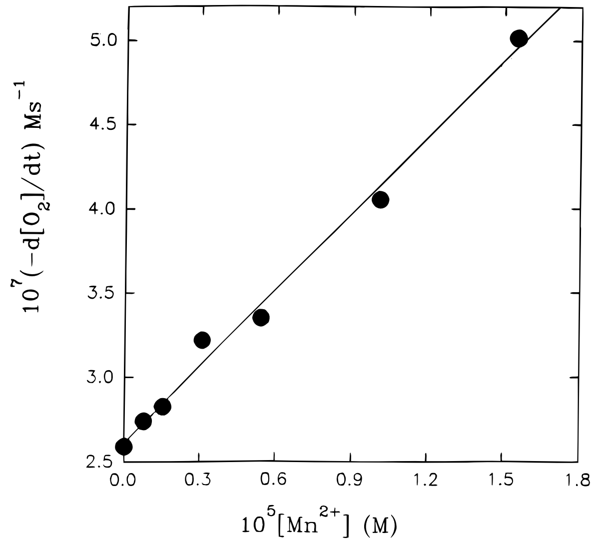

Figure 4. Mn^{2+} dependence in the presence of both Mn^{2+} and $S_2O_8^{2-}$: filled circles, experimental data; solid line, prediction from eq 11. Conditions: $[S_2O_8^{2-}] = 3.25 \times 10^{-3}$ M, $[HSO_3^-] = 2.31 \times 10^{-3}$ M, pH = 4.50, $T = 25$ °C, $\mu = 0.050$ M.

D. Catalysis by the Peroxydisulfate Ion. In the previous paper,[13] it was shown that the peroxydisulfate ion catalyzes the reaction between the bisulfite ion and oxygen. There it was shown that the effect could be interpreted as arising from the initiation reaction

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-} \qquad (10)$$

with rapid conversion of $SO_4^{\bullet-}$ to $SO_3^{\bullet-}$ by reaction d. The effect of peroxydisulfate ion on the manganese-catalyzed reaction should be predictable from the peroxydisulfate results in ref 13 and the present results on manganous ion catalysis in the absence of the peroxydisulfate ion, thus providing a further test of the mechanism.

Insertion of reaction 10 into the mechanism leads to the predicted rate law

$$-\frac{d[O_2]}{dt} = \frac{R_{0m}}{2} + \left\{\frac{R_{0m}^{\ 2}}{4} + \frac{\{(k_b + k_c)[HSO_3^-] + k_3[Mn^{2+}]\}^2[S_2O_8^{2-}]k_{10}}{k_g}\right\}^{1/2} \qquad (11)$$

where R_{0m} is the rate that would be observed in the absence of $S_2O_8^{2-}$, i.e. R of eq 7.

A series of rate measurements were made where peroxydisulfate and bisulfite ion concentrations were held constant while the manganous ion concentration was varied, as shown in Figure 4. The bisulfite concentration was low and the peroxydisulfate concentration relatively high so that nearly all of the initiation should have occurred by peroxydisulfate decomposition (reaction 10). Under these conditions, $R_{0m}/2 \ll \{(k_b + k_c)[HSO_3^-] + k_3[Mn^{2+}]\}(k_{10}[S_2O_8^{2-}]/k_g)^{1/2}$ in eq 11, so the rate becomes a

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(16) Connick, R. E.; Lee, S.; Adamic, R. *Inorg. Chem.* **1993**, *32*, 565.

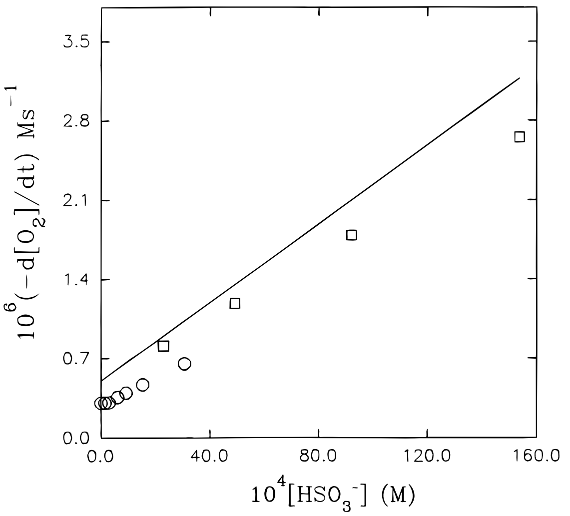

Figure 5. HSO_3^- dependence in the $HSO_3^- - O_2$ reaction with both Mn^{2+} and $S_2O_8^{2-}$ present. The solid line is the predicted behavior from eq 11. Conditions: $[S_2O_8^{2-}] = 3.25 \times 10^{-3}$ M, $[Mn^{2+}] = 1.63 \times 10^{-4}$ M. The two types of symbols indicate different runs.

linear function of the manganous ion concentration, as is found experimentally: Figure 4. From the ratio of the slope to intercept, one calculates $k_3/(k_b + k_c) = 134$. The value is to be compared with the average value of 124 obtained from the data of Figures 2 and 3. This reasonably good agreement substantiates the mechanistic hypothesis that peroxydisulfate enters into a separate part of the mechanism (initiation) than does the manganous ion (propagation).

A second set of experiments were run keeping the manganous ion and peroxydisulfate concentrations constant while varying the bisulfite ion concentration, as shown in Figure 5. Two sets of experiments were performed as indicated by the different symbols (see caption to Figure 5). In this case, it was necessary to use the full expression given by eq 11 in interpreting the data. The line shown in the figure is the rate calculated from eq 11 using the following values:

$$k_3/(k_b + k_c) = 124$$

$$(k_b + k_c)(k_h + k_i)k_{10}/k_f k_b = 2.26 \times 10^{-3} \text{ (from ref 13)}$$

Values of R_{0m} were calculated from eq 7; the rate constants in (7) were obtained from Figures 2 and 3. The agreement between calculated and experimental results is not overwhelming but, considering the irreproducibility in the experimental measurements,[13] is not bad. A wide range of conditions is covered in Figure 5. At the lowest bisulfite ion concentration, the reaction is essentially completely initiated by $S_2O_8^{2-}$ and propagated 95% by Mn^{2+} (reaction 3), while at the highest bisulfite concentration, although nearly all initiation still comes from $S_2O_8^{2-}$, reactions b and c contribute 5 times as much as reaction 3 (Mn^{2+}) to the propagation.

E. Inhibition by Methanol. As with the uncatalyzed reaction[13] the addition of increasing amounts of methanol causes a very remarkable decrease in rate, as shown in Figure 6. The phenomenon was explained previously[13] by adding to the mechanism the reaction

$$CH_3OH + SO_4^{\bullet -} \rightarrow \text{nonchain-propagating products} \quad (12)$$

Inclusion of this step in the mechanism for the manganous ion catalyzed reaction leads to the following steady state rate law:

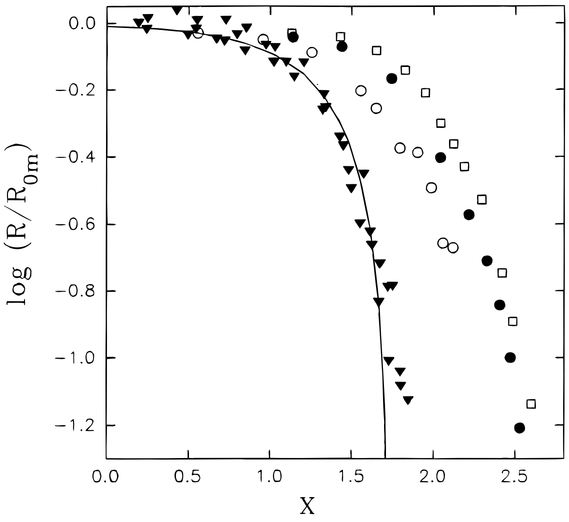

Figure 6. Inhibition by methanol of the Mn^{2+}-catalyzed oxidation of HSO_3^- by O_2. The solid line is the calculated response "expected" for all of the experiments based on the data of ref 13. See text for abcissa. Conditions: (▼) $[HSO_3^-] = 3.65 \times 10^{-3}$ M (these data are from three separate runs under the same conditions as in Figure 10 of ref 13, i.e. no manganese present); (□, ●) $[HSO_3^-] = 1.19 \times 10^{-3}$ M, $[Mn^{2+}] = 9.85 \times 10^{-5}$ M; (○) $[HSO_3^-] = 3.12 \times 10^{-3}$ M, $[Mn^{2+}] = 1.63 \times 10^{-4}$ M. In all experiments pH = 4.50, $T = 25$ °C, and $\mu = 0.050$ M.

$$R = -\frac{d[O_2]}{dt} = R_{0m} - \frac{k_{12}k_c(k_b + k_c)[M][HSO_3^-]}{2k_g k_d} \times \left\{1 + \frac{k_3[Mn^{2+}]}{(k_b + k_c)[HSO_3^-]}\right\} \quad (13)$$

where M represents methanol and R_{0m} is the rate in the absence of methanol, i.e. the rate given by eq 4. At constant bisulfite, manganous, and hydrogen ion but various methanol concentrations the rate is of the form

$$R = R_{0m} - a[M] \quad (14)$$

A plot of R versus the methanol concentration should give a curve decreasing to zero rate when $[M] = R_{0m}/a$. To facilitate comparison of experiments at differing HSO_3^- and Mn^{2+} concentrations, one can plot $\log(R/R_{0m})$ versus the quantity

$$\log\left\{\frac{[HSO_3^-][M]}{R_{0m}}\left(1 + \frac{k_3[Mn^{2+}]}{(k_b + k_c)[HSO_3^-]}\right)\right\} = X$$

The value of $k_3/(k_b + k_c) = 124$ was determined earlier. The data from all experiments should now fall on the same curve. As seen in Figure 6, where $\log(R/R_{0m})$ is plotted versus X, this is not the case. The solid curve is the theoretical prediction based on the uncatalyzed reaction of ref 13. The three sets of manganese data show that a higher alcohol concentration than predicted is necessary to reduce the rate by a given percentage. In addition, the manganese data do not show as steep a falloff in rate as predicted. Obviously the inhibition is more complex than indicated by the simple addition of eq 12, at least in the presence of manganous ion. It should be noted that in experiment ○ of Figure 6 the propagation by manganous ion (reaction 3) is approximately 10-fold greater than that by (b) plus (c) while in experiments □ and ● the competing propagation steps are roughly equal.

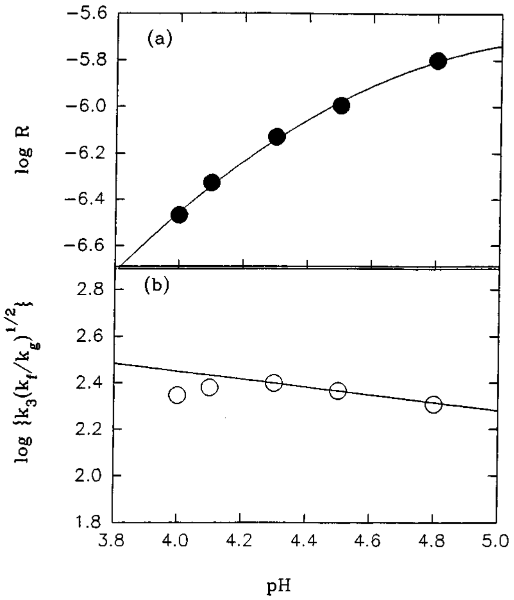

Figure 7. pH dependence of the Mn^{2+}-catalyzed oxidation of HSO_3^- by O_2. (a) The effect of pH on the rate of the reaction. Symbols are experimental results. The curve through the symbols has no theoretical meaning. (b) The effect of pH on $\log\{k_3(k_f/k_g)^{1/2}\}$. Symbols are experimental results. The solid line has a slope of −0.17. Conditions: $[HSO_3^-] = 2.02 \times 10^{-3}$ M, $[Mn^{2+}] = 7.39 \times 10^{-5}$ M, $T = 25$ °C, $\mu = 0.050$ M.

F. Hydrogen Ion Dependence. In the pH region 4.4−5.3, the uncatalyzed steady state rate increases rapidly with increasing pH with an apparent inverse square-power dependence on hydrogen ion concentration.[13] The manganous ion catalyzed reaction rate is much less dependent on pH, as shown in Figure 7a by the circles. The experimental results were obtained by adding small volumes of $NaHCO_3$ solution to a reaction solution containing HSO_3^- , Mn^{2+}, and O_2, so as to raise the pH incrementally. The curve through the points has no theoretical significance.

Under the conditions of the experiment, the manganous ion square term contributed most importantly to the rate, but the cross term contributed the order of 25%. The uncatalyzed term was always small. To deal with all of the contributions, one can use eq 9 to deduce the pH dependence of k_3. By substitution of the experimental values for R_0 from Figure 3 of ref 13, values of R_M can be calculated. According to the proposed mechanism, R_M is given by eq 6. The acidity dependence of $k_h + k_i$ is known from direct measurements[16] and is given for ionic strength 0.050 M and 25 °C in ref 13, eq 33. Multiplying R_M by $(k_h + k_i)$, dividing by $[Mn^{2+}]^2$, and then taking the square root give $k_3(k_f/k_g)^{1/2}$. Values of this quantity are plotted in Figure 7b. It is seen that there is very little acidity dependence. In ref 13 for the pH region 4.4−5.3, small hydrogen ion dependence powers of +0.21 for k_f and −0.12 for k_g were found but with considerable uncertainty. The power dependence on hydrogen ion concentration of $(k_f/k_g)^{1/2}$ is then roughly +0.17 and thus might account for the slight downward tilt of the data at higher pH values. The line in Figure 7b is drawn with a slope of −0.17. In any event, the acidity dependence of k_3 appears to be small and may be zero.

Discussion

While the postulation of the catalytic role of the manganous ion as a replacement of propagation steps b and c by reaction 3 leads to a rate law in agreement with experiment, the products formed in (3) are not obvious. The simplest hypothesis would be that the manganous ion is complexed by the sulfite ion and the sulfite attached to the manganous ion is activated to react faster than bisulfite or sulfite ions:

$$MnSO_3 + SO_5^{\bullet -} \rightarrow SO_5^{2-} + Mn^{2+} + SO_3^{\bullet -} \quad (15)$$

If essentially all of the manganese was complexed, the observed rate law would be expected, assuming the remainder of the uncatalyzed mechanism was unchanged. That such an explanation is incorrect was shown by adding a small volume of $MnCl_2$ stock solution to an anaerobic 9.52×10^{-3} M HSO_3^- solution at pH 4.52 and ionic strength 0.050 M such that the total Mn(II) in the mixture was 5.40×10^{-3} M. The observed pH change was less than 0.01 pH unit (the accuracy limit of the pH meter used) whereas it would have been a decrease of 2.11 pH units if all of the manganous ion were complexed by the bisulfite ion to yield $MnSO_3$ and H^+. Complexation by bisulfite ion was presumed to be too weak to be of importance.

With complexation ruled out, it seems likely that oxidation of the manganous ion is occurring by a one-electron step. The $Mn^{3+}-Mn^{2+}$ standard potential is given as +1.60 V.[17] Extrapolation to pH 4.50 is difficult because the necessary hydrolysis equilibrium constants are not known. A value of 2.5 in 3 M $(H^+-Li^+)ClO_4^-$ is reported[17] for the first hydrolysis constant at 25 °C, and a very uncertain value of 0.5, for the second. It seems likely that the standard potential will be decreased by more than 0.4 V at pH 4.5. The manganous ion could then be oxidized by $SO_5^{\bullet -}$, whose estimated reduction potential to HSO_5^- is +1.24 V[13] at pH 4.50. The following propagation reactions could then take place where Mn(III) is arbitrarily written as $Mn\mathit{OH}^{2+}$ to indicate some degree of hydrolysis:

$$Mn^{2+} + SO_5^{\bullet -} + H_2O \rightarrow HSO_5^- + Mn\mathit{OH}^{2+} \quad (16)$$

$$Mn\mathit{OH}^{2+} + HSO_3^- \rightarrow Mn^{2+} + SO_3^{\bullet -} + H_2O \quad (17)$$

Reactions 16 and 17 combined with reactions a−j provide a mechanism that leads to the observed rate law as long as essentially all of the manganese is present as manganous ion.

A possible modification of reactions 16 and 17 would be for Mn^{2+} and $SO_5^{\bullet -}$ to form a complex intermediate which then reacts rapidly with the bisulfite ion:

$$Mn^{2+} + SO_5^{\bullet -} \rightarrow MnSO_5^+ \quad (18)$$

$$MnSO_5^+ + HSO_3^- \rightarrow Mn^{2+} + HSO_5^- + SO_3^{\bullet -} \quad (19)$$

One electron changes between other oxidation states are considered to be less likely than that between the +2 and +3 states.

Since the manganese-catalyzed reaction appears to go all, or nearly all, through HSO_5^-, reactions 17 and 19 have been written that way. In the case of the uncatalyzed reaction, 40% of the propagation goes to $SO_4^{\bullet -}$ through reaction c and then to $SO_3^{\bullet -}$ by reaction d. We do not find a plausible set of reactions in the case of manganese that starting with reaction 3 would lead to $SO_4^{\bullet -}$ and then to $SO_3^{\bullet -}$ by reaction d.

In the formulation of the experimental rate law, it was assumed that essentially all of the added manganese was present as manganous ion. Such would be expected if reaction 17 or 19 is much more rapid than (16) or (18), respectively. It seems

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

likely that reduction of Mn(III) by the bisulfite ion would be extremely rapid under our conditions.[18]

It is difficult to make a direct comparison between the present results and the many measurements of manganous ion catalysis of the $HSO_3^- - O_2$ reaction reported in the literature. The work that comes closest in experimental conditions is that of Huss, Lim, and Eckert,[10] who studied the reaction at 25 °C but at somewhat lower pH. If one divides the measurement at pH 4.00 of Figure 7a by $[Mn^{2+}]^2$, a rough estimate of $k_\gamma \cong 60\ M^{-1}\ s^{-1}$ is obtained. From the formula of Huss et al. one calculates at ionic strength 0.050 M $k_\gamma = 62\ M^{-1}\ s^{-1}$, although their Figure 7 indicates this value could be as much as 20% higher at pH 4.00. Agreement with the more limited data of Coughanowr and Krause[2] in their Figure 3 is also indicated, since Huss et al.[10] in their Figure 3 showed reasonably good agreement with the Coughanowr and Krause results. The work of Martin and Hill[20] agrees with that of Huss et al.

Other investigators have generally worked at quite different pH's (ca. 6−12) or with other reagents (such as Co^{+2}, Fe^{2+}, Fe^{+3}, etc.) present so that it is not possible to make meaningful comparisons.

Rate laws reported for catalysis by the manganous ion generally show no dependence on oxygen concentration and various powers for bisulfite and manganous ion concentration dependencies. Huss, Lim, and Eckert[10] found in carefully controlled experiments a two-term rate law of the form $R = k_1[Mn(II)]^2 + k_2[Mn(II)][HSO_3^-]$. This result differs from ours only in the omission of the uncatalyzed term and the recognition that k_2 is calculable from k_1 and the uncatalyzed rate. Coughanowr and Krause reported the more limited rate law corresponding to the first term of the Huss et al rate law. Rate laws reported by other investigators generally refer to conditions not applicable to the present study.

Many mechanisms have been proposed previously for manganous ion catalysis. Several investigators[21] studying the oxidation of SO_2 in water droplets in the atmosphere have favored a nonchain reaction,[22] a choice that seems unlikely considering the sensitivity to inhibitors and catalysts. Huss et al.[10] proposed a chain reaction for the first term of their rate law and nonchain path for the second term. Their initiation step involved the rather fanciful reaction of Mn_2^{4+} with the bisulfite ion.

Van Eldik et al.[23,24] have studied the oxygen oxidation of Mn(II) to Mn(III) induced by the bisulfite−oxygen reaction. They showed that, at pH 6.8 and in the presence of N_3^- and HN_3, manganese(II) is oxidized to the azide complex of Mn(III) as the $O_2 - HSO_3^-$ reaction occurs. While their conditions are far from those used here, the formation of the 3+ oxidation state of manganese is consistent with the redox mechanism suggested in the present work.

To explain qualitatively the induced oxidation of the manganous ion, Coichev and van Eldik[23] proposed a series of reactions which include all of the reactions of our mechanism (ignoring azide complexing and protonation of SO_3^{2-}) except for our initiation reaction. In addition, many other reactions were postulated. They did not formulate a rate law from their mechanism.

Rate Law at Small Bisulfite Ion Concentration. Because of interest in the $HSO_3^- - O_2$ reaction in rain drops to yield acid rain, kinetic studies have been done on the manganese-catalyzed reaction at much lower bisulfite ion concentrations than studied here.[20,25−28] Below ca. 10^{-5} M HSO_3^- the rate becomes dependent on the bisulfite concentration and the rate law is reported to be

$$-\frac{d[O_2]}{dt} = k[HSO_3^-][Mn^{2+}] \tag{20}$$

The change in rate law was investigated first by Ibusuki and co-workers[25,26] and then by Martin[27,28] and Martin and Hill.[20] In the pH region 0−6, they found the rate of the reaction to be zero order in oxygen and first order in both manganous ion and S(IV) and to have little dependence on hydrogen ion concentration.

The change in order from a lower to a higher value with decreasing concentration of the species (HSO_3^- in this case) comes about when there are two-terms in the denominator of the rate law having different powers of the concentration of the species in question. Since the chain-terminating step appears in the denominator of chain reaction rate laws, it is likely that a new chain-terminating step is responsible. The most obvious possibility in the manganese-catalyzed reaction, relative to the uncatalyzed reaction, is the addition of the reaction

$$MnOH^{2+} + SO_5^{\bullet -} \rightarrow \text{nonchain-carrier products} \tag{21}$$

(The products might be $O_2 + SO_4^{2-} + H^+ + Mn^{2+}$.) Introduction of this additional reaction under conditions where the $[Mn^{2+}]^2$ term is otherwise dominant leads to the rate law

$$-\frac{d[O_2]}{dt} = \frac{k_f k_3^2 [Mn^{2+}]^2}{k_g(k_h + k_i)} \left\{ 1 + \frac{k_{21} k_3 [Mn^{2+}]}{k_g k_{17} [HSO_3^-]} \right\}^{-1} \tag{22}$$

As the ratio $[Mn^{2+}]/[HSO_3^-]$ increases, the rate will switch from a square-power dependence on $[Mn^{2+}]$ to first-power dependence on the manganous and bisulfite concentrations, as found experimentally.

A two-term denominator may also arise from the onset of appreciable back-reaction in the propagation or initiation steps. Such might occur in reaction f of initiation or in reaction 3 of propagation. Neither leads to the experimentally determined rate law although the latter comes close with the rate propotional to $[Mn^{2+}]^{2/3}[HSO_3^-]^{4/3}$.

Finally, a two-term denominator arises when the total concentration of two species in an equilibrium is entered into a rate law, rather than the true concentration of the species involved, as for example the total metal ion concentration of a partially complexed metal ion. This latter case has been favored by devisers of mechanisms for the manganese-catalyzed reaction, and often with no evidence for such complexing.

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(18) Reaction 17 has been shown by Siskos et al.[19] to proceed very rapidly with a bimolecular rate constant $k = (1.1 \pm 0.5) \times 10^7 \exp(-1970 \pm 100)/T\ M^{-1}\ s^{-1}$ in 5.92 M $HClO_4$ acid for the temperature range 15.4−34.5 °C. The rate of the reaction depends strongly on acidity, increasing with increasing pH. Apparently the rate has not been determined at lower acidity.

(19) Siskos, P. A.; Peterson, N. C.; Huie, R. E. *Inorg. Chem.* **1984**, *23*, 1134.

(20) Martin, L. R.; Hill, M. W. *Atmos. Environ.* **1987**, *21*, 2267.

(21) Hoffmann, M. R.; Boyce, S. D. In *Trace Atmospheric Constituents*; Schwartz, S. E., Ed.; Advances in Environmental Science and Technology, Vol. 12; Wiley-Interscience: New York, 1983.

(22) Bassett, H.; Parker, W. G. *J. Chem. Soc.* **1951**, 1540.

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

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

(25) Ibusuki, T.; Barnes, H. M. *Atmos. Environ.* **1984**, *18*, 145.

(26) Ibusuki, T.; Takeuchi, K. *Atmos. Environ.* **1987**, *21*, 1555.

(27) Martin, L. R. In *SO_2, NO and NO_2 Oxidation Mechanisms: Atmosperic Considerations;* Calvert, J. G., Ed.; Acid Precipitation Series, Vol. 3; Butterworth Publishers: Boston, MA, 1984; pp 63−100.

(28) Martin, L. R. In *Environmental Oxidants*; Nriaga, J. O., Simmons, M. S., Eds.; Wiley Series in Environmental Science and Technology, Vol. 28; John Wiley and Sons: New York, 1994; Chapter 8.

It should be possible to determine the value of $k_{21}k_3/\ k_gk_{17}$ from the experimental data in the literature. Martin and Hill[20] have concluded empirically that the two limiting forms of the rate law have about the same ionic strength dependence. Then from their formulas for the limiting rate laws at high and low values of $[Mn^{2+}]/[HSO_3^-]$ one calculates that the two terms in the denominator will contribute equally when $[Mn^{2+}]/[HSO_3^-] = 1.5 = \{k_{21}k_3/k_gk_{17}\}^{-1}$ at ionic strength from 0 to 1 M.

The above analysis has some problems. There is no way to check this ratio from the authors'[20] experiments at intermediate concentrations of bisulfite because they do not report the manganous ion concentrations. Martin and Hill's[20] rate constant for the $[Mn^{2+}][S(IV)]$ rate law is more than a factor of 5 lower than that found by Ibusuki and Barnes[25] under almost the same concentration conditions. If the Ibusuki and Barnes value is used, the above ratio becomes 8.0. The latter work was done using a stirred reactor; therefore steady state conditions were achieved, whereas they may not have been in the Martin and Hill experiments. In the uncatalyzed reaction, the approach to a steady state takes a finite time.[13]

Ibusuki and Barnes[25] found the $[Mn^{2+}][HSO_3^-]$ rate law to be independenct of pH from pH ∼3.0 to ∼5.5 but giving a decreasing rate at higher and lower pH values. The fall-off they observed at low pH may be an ionic strength effect. Martin and Hill reported that replacing salt, such as KCl, by acid, such as HCl, had no effect on the rate from ionic strength of 10^{-2} to 1.0 M and concluded the rate law did not depend on hydrogen ion concentration from pH 4.0 to 0.0. They expressed the rate law in terms of total S(IV), i.e. $[Mn^{2+}]\mathbf{[}S(IV)]$. The rather remarkable implication is that SO_2 and HSO_3^- react at the same rate in the mechanism.

Recently, Berglund, Fronaeus, and Elding[29] ventured into a HSO_3^- and manganous ion concentration region not studied by others and reported yet new rate laws. At pH 2.4, Mn^{2+} concentrations from 0.13×10^{-4} to 5.1×10^{-4} M, and initial bisulfite ion concentration of 2.3×10^{-5} M, they found

$$-\frac{d[HSO_3^-]}{dt} = k[Mn(II)][HSO_3^-]/(A + [Mn(II)]) \qquad (23)$$

while, at pH 4.0 for Mn^{2+} concentrations up to 1.6×10^{-3} M, they found

$$-\frac{d[HSO_3^-]}{dt} = [HSO_3^-]\frac{k[Mn(II)] + k'[Mn(II)]^2}{A + [Mn(II)]} \qquad (24)$$

The two-term denominator might arise from a termination reaction of two Mn(III) species but would then appear as $[Mn^{2+}]/[HSO_3^-]$ and result in a limiting $[HSO_3^-]^2$ dependence. We will not speculate further until the rate laws have received further study.

In hypothesizing a mechanism, the authors,[29] following the lead of others,[10] proposed the unlikely complex $MnHSO_3^+$ in spite of finding no change in the absorption sepctrum of HSO_3^- on addition of the manganese ion. Assuming the spectra to be the same, they proceeded to deduce from their kinetic data a formation constant of 2×10^4. From some rather rough experiments at pH 3.00, we find the the formation constant to be at least 500-fold less, and probably much smaller. The absorbance at 275 nm of SO_2 in equilibrium with HSO_3^- was observed before and after the addition of $MnCl_2$ solution, at constant pH.

Under very low bisulfite concentrations, Berglund et al.[29] have shown that the addition of $\sim 10^{-8}$ M Mn(III) accelerates the Mn(II)-catalyzed reaction with a rate law of the form

$$-\frac{d[HSO_3^-]}{dt} = [HSO_3^-]\frac{k[Mn(II)](1 + B[Mn(III)]_0)}{A + [Mn(II)]} \qquad (25)$$

The rate becomes proportional to the concentration of Mn(III) added although it is presumed that Mn(III) may react rapidly to form other chain carriers. If a true steady state rate is achieved, the addition of $\sim 10^{-8}$ M Mn(III) should have no final effect on the rate. The sustained increase in rate would therefore indicate that a steady state rate has not been reached and that the enhanced rate caused by the increase in chain carriers persists during the lifetime of the reaction.

Very recently Berglund et al.[30] reported a pulse radiolysis study of the rate of reaction 3 to form Mn(III) at pH 3.0 and ionic strength 10^{-3} at 25 °C. They observed bimolecular rate constants in the range 2×10^8 to 2×10^{10} $M^{-1}\ s^{-1}$. Their interpretation of the results is flawed by the use of the nonexistent $Mn(HSO_3)^+$ complex (see above.) The results, however, do give support to the presence of reaction 3 in the chain mechanism.

Conclusion

A rate law which does not depend on the concentration of either of the reactants but has a square-power dependence on the catalyst concentration presents a mechanistic challenge. The proposed mechanism for the manganese-catalyzed reaction accounts for the experimental results with only a simple addition to the mechanism of the uncatalyzed reaction.[13] The three-term rate law is accounted for, and it is shown that one of the terms is quantitatively predictable from the other two. The square-power dependence on manganous ion concentration arises naturally as a consequence of involvement in the initiation reaction of the intermediate HSO_5^-, which in turn is formed by the propagation reaction.

The experiments on the peroxydisulfate ion catalysis in combination with the manganese ion catalysis support the idea that $S_2O_8^{2-}$ is an initiator[13] while manganous ion is a propagator. That a synergistic effect on the rate is produced can be seen by combining the data of Figure 4 with those of Figure 2. Such synergism arises naturally with two catalysts in a chain reaction where one affects initiation and the other affects propagation, as is evident in the derivation of the rate law from the mechanism, where propagation and initiation are combined multiplicatively rather than additively. The present situation is a little more complex because the manganous ion, through its formation of HSO_5^-, can affect the rate of initiation as well as the rate of propagation. Synergism will still result, however. Actually, in the experiments of both Figures 4 and 5, the effect of the manganous ion on the initiation was drowned out by the presence of high peroxydisulfate concentrations.

The interpretation of the methanol inhibition of the manganous-catalyzed reaction using the simple assumption of reaction 12 was not quantitatively successful. More work in this area is indicated.

In their research, Coughanowr and Krause[2] reported a change from square-power dependence on manganous ion concentration to a zero-power dependence at quite high concentration of manganese (>0.01 M). The mechanism proposed here could not lead to this result. As propagation reaction 3 becomes more rapid with increasing manganous ion concentrations, the steady state ratio $[SO_3^{\bullet -}]/[\ SO_5^{\bullet -}]$ increases and would eventually lead to termination by $SO_3^{\bullet -} + SO_5^{\bullet -} \rightarrow S_2O_8^{2-}$ or $SO_3^{\bullet -} + SO_3^{\bullet -}$

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[29] Berglund, J.; Fronaeus, S.; Elding, L. I. *Inorg. Chem.* **1993**, *32*, 4257.

[30] Berglund, J.; Elding, L. I.; Buxton, G. V.; McGowan, S.; Salmon, G. A. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3309.

$\rightarrow S_2O_6^{2-}$. In the first case, the rate law would depend on $[O_2][Mn^{2+}]$, while, in the second case, it would depend on $[O_2]^2$. But the authors reported that the rate did not depend on oxygen concentration.

The experiments of Huss et al.[10] show almost no dependence of the rate on the hydrogen ion concentration from pH 1.0 to 3.0. The experimental results of the present work in Figure 7a show a marked pH dependence of the rate between pH 4.0 and 4.8. The analysis of the data of Figure 7 shows that almost all of this dependence arises from the pH dependence of reaction h plus reaction i. The latter has been determined over the pH region 3.8−7.9[16]and shows no sign of deviating from a first-power dependence on hydrogen ion concentration at lower pH. Therefore, extrapolation of our mechanism at high $[Mn^{2+}]$ would lead to the prediction of an inverse first-power hydrogen ion dependence in the pH region studied by Huss et al.

The most satisfying solution to this dilemma would be to have some other term of our rate law develop a hydrogen ion dependence that would cancel that from reaction h plus reaction i as the pH is lowered below 4.0. The only promising candidate would appear to be the initiation reaction, which might then have a second term corresponding to the reaction

$$HSO_5^- + SO_2 \rightarrow SO_4^{\bullet -} + SO_3^{\bullet -} + H^+ \qquad (26)$$

The hydrogen ion concentration power dependence of 0.21 determined earlier[13] for k_f of the initiation reaction had considerable uncertainty. It may, however, be an indication of the developing presence of reaction 26 as the pH is lowered, although the point in Figure 7b at pH 4.00 does not support this hypothesis. Further study of the pH dependence of the rates of both the uncatalyzed and manganous ion catalyzed reactions is indicated.

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