outer-sphere reaction of $Ru_2(CH_3COO)_2(C_2O_4)_2(H_2O)_2^-$ and $TiOH^{2+}$ would be about 0.3 M^{-1} s^{-1} and that for Ti^{3+} would be expected to be 0.02 M^{-1} s^{-1}. Both of these mechanisms predict slow overall rates, and a linear dependence of redox rate on [Ti(III)]. Neither of these features are observed.

Nonlinear dependence of rate on [Ti(III)] for the reduction of $Ru_2(CH_3COO)_2(C_2O_4)_2(H_2O)_2^-$ indicates formation of a trinuclear complex in which one oxalate group binds a titanium atom to the diruthenium oxidant. The reaction rate decreases as acidity increases, even in the range of [Ti(III)] in which the rate is independent of [Ti(III)]. This base catalysis cannot be understood on the basis of deprotonation of Ti^{3+} but requires an acid–base equilibrium involving the intermediate.[2d] The following mechanism for the reaction between $Ru_2(CH_3COO)_2(C_2O_4)_2(H_2O)_2^-$ and $Ti(H_2O)_6^{3+}$ is consistent with the observed data and also is consistent with results of prior studies of related systems:

$$Ti^{3+} + Ru_2(CH_3COO)_2(C_2O_4)_2^- \xrightleftharpoons{K_f} Ru_2(CH_3COO)_2(C_2O_4)_2Ti^{2+}$$

$$Ru_2(CH_3COO)_2(C_2O_4)_2Ti^{2+} \xrightleftharpoons{K_a'} Ru_2(CH_3COO)_2(C_2O_4)_2TiOH^+ + H^+$$

$$Ru_2(CH_3COO)_2(C_2O_4)_2Ti^{III}OH^+ \xrightarrow{k_{ET}} Ru_2(CH_3COO)_2(C_2O_4)_2Ti^{IV}OH^+$$

$$Ru_2(CH_3COO)_2(C_2O_4)_2Ti^{IV}OH^+ \xrightarrow{k_d} Ru_2(CH_3COO)_2(C_2O_4)_2^{2-} + Ti^{IV}{}_n$$

The charge of the present oxidant should make the rate constant formation of the intermediate larger than the rate constant ($k = 10^5$ M^{-1} s^{-1}) measured for formation of the corresponding intermediate in the reduction of monomeric ruthenium(III) oxalato complexes. (Ti(III) substitution reactions have associative character.) If the first two steps are rapidly established equilibria, this mechanism would yield

$$k = \frac{k_{ET}K_fK_a'[Ti(III)]}{[H^+] + K_a'[Ti(III)][H^+] + K_fK_a'[Ti(III)]} \qquad (1)$$

Values of k_s(calcd) in Table I are computed by using eq 1 and the values $K_f = 300$ M^{-1}, $K_a' = 0.013$ M^{-1}, and $k_{ET} = 30$ s^{-1}. The data require $K_f > 200$ M^{-1}. The estimate of K_a used is conservative, in view of the fact that in the Ti(III) reduction[1g] of $Co(NH_3)_5F^{2+}$, a reaction that involves deprotonation of Ti(III) contained in a similar intermediate, the value of K_a is 0.07 M^{-1}. The limiting rate of 3×10 s^{-1} reached at high [Ti(III)] is a measure of k_{ET}, the rate of intramolecular ET within the conjugate base of the initial trinuclear intermediate. If the intermediate were as weak an acid as Ti^{3+}, then $k_{et} < 10^3$ s^{-1}, still 2 orders of magnitude smaller than the corresponding value for monomeric oxidants.

Although oxalate is an efficient bridging group for ET from Ti(III) when part of a monomeric Ru(III) complex, the ET reaction involving Ti(III) and the μ-oxalato dimer is relatively slow. This can be understood since spectra indicate that the LUMO of the oxalato dimer (the electron-acceptor orbital of the redox reaction) lies at higher energy than does the corresponding orbital of the monomeric oxidants. Increase of energy gap between donor and acceptor orbitals would decrease the effective overlap between these orbitals. Thermodynamic driving force is small for the reactions of interest here. Electronic factors such as orbital energy match then become of major importance. It may be possible to use systems like these to control ET in solution-phase and also, perhaps, solid-phase reactions.

Registry No. $HRu_2(CH_3COO)_2(C_2O_4)_2(H_2O)_2$, 88968-52-9; $Ru_2(CH_3COO)_2(C_2O_4)_2(H_2O)_2^-$, 86570-54-9; $Ti(H_2O)_6^{3+}$, 17524-20-8.

Contribution from the Chemical Kinetics Division,
National Bureau of Standards, Washington, D.C. 20234

Kinetics of the Manganese(III)–Sulfur(IV) Reaction in Aqueous Perchloric Acid Solutions

P. A. SISKOS,[†] N. C. PETERSON,[‡] and R. E. HUIE*

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The reaction of Mn(III) with S(IV) has been studied in perchloric acid solutions. The stoichiometry of the reaction is one Mn^{3+} consumed per SO_2 consumed, and the production of dithionate was confirmed. The reaction shows a strong inverse dependence on acid concentration. At 5.92 M acid concentration and over the temperature range 15.4–34.9 °C, the rate constant is $k = (1.1 \pm 0.5) \times 10^7 \exp(-1970 \pm 100/T)$ M^{-1} s^{-1}.

Introduction

Oxidation of S(IV) by oxygen (autoxidation) in aqueous solution is known to be catalyzed by manganese ions,[1,2] and a considerable amount of work has been devoted to understanding the kinetics and mechanism of the overall reaction.[3-9] The interest in the autoxidation reaction has increased because of concern about the rate of conversion of S(IV) to S(VI) in flue gas scrubbers, in atmospheric water droplets, and in biological systems. In spite of this interest, the mechanism of S(IV) oxidation by dissolved oxygen is not established. Although early work suggested that it involved the induced oxidation of a complex of Mn(II) and SO_2 with the subsequent reaction of Mn(III) with another S(IV) species,[2] recent work using EPR failed to detect any change in the concentration

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[†] Visiting Scientist. Permanent address: Laboratory of Analytical Chemistry, University of Athens, Athens, Greece.

[‡] Visiting Scientist. Permanent address: Department of Chemistry, Polytechnic Institute of New York, Brooklyn, NY 11201.

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of Mn(II) or the presence of Mn(III) in laboratory experiments simulating the operation of a flue gas scrubber.[10] This result could arise if the reaction rate of Mn(III) with S(IV) is very fast so that the steady-state concentration of Mn(III) is very low or if Mn(III) is not produced. Our interest in that problem led us to undertake a study of the rate constant for the Mn(III) + S(IV) reaction in order to help clarify any possible role of Mn(III) in the S(IV) oxidation by oxygen in aqueous solution.

Experimental Section

Reagents. All solutions were prepared with use of triply distilled, degassed water. A stock solution of perchloric acid (Fisher, ACS reagent grade[11a]) was standardized by titration with 0.1 M NaOH. Sodium perchlorate (G. Frederick Smith) stock solution was standardized by passing an aliquot through a cation-exchange column in the acid form, eluting with distilled water, and titrating the resulting $HClO_4$ with 0.1 M NaOH. Sulfur dioxide solutions were prepared daily by dissolving sodium sulfite (Fisher, Certified ACS, two separate lots of 98.78% and 98.2% Na_2SO_3) in perchloric acid in a volumetric flask filled to the top to eliminate the head space. The volume of the flask was corrected for this additional volume. Measurements of the UV absorption at 280 nm, due to SO_2, demonstrated that this procedure prevented significant loss of SO_2 from these solutions during the course of an experiment.

Manganese(III) solutions in $HClO_4$ were prepared from a manganous perchlorate (Alfa) solution with use of electrolytic oxidation at a platinum anode at about 6 V and 2 mA cm^{-2}, while the solution was stirred with a magnetic stirrer. The solutions contained an excess of Mn(II) to suppress the disproportionation reaction

$$\mathrm{Mn(III)} + \mathrm{Mn(III)} \overset{K_d}{\rightleftharpoons} \mathrm{Mn(II)} + \mathrm{Mn(IV)} \qquad (1)$$

These solutions were prepared fresh daily, although they appeared to be stable for at least 1 week at 6 M $HClO_4$.

The concentration of Mn(III) was determined from its absorbance at 470 nm. Literature values of the absorptivity[12-14] were confirmed by measuring the absorbance at 240 and 260 nm due to ferric ion produced by reaction with excess ferrous ion.

Kinetics. Rate constants were measured with a Durrum Model D-100 stopped-flow spectrophotometer, following the decrease of the Mn(III) absorption at 470 nm. Initial experiments were performed with the electronics provided with the spectrophotometer. Most measurements, however, were carried out with an Extranuclear Model 021 fast electrometer and Model 103 preamplifier, with a $10^6\ \Omega$ input resistor. Triggering was accomplished by passing a flag attached to the stopping syringe plunger through an optical trigger. The output step was shaped by a Schmitt trigger and fed to the trigger input of the transient analyzer (Biomation Model 2805), operating in the pretrigger mode and interfaced to a dedicated microcomputer system. The data (2048 eight-bit words) were stored on flexible magnetic disks for subsequent nonlinear least-squares analysis. Typically, three replicate runs were made and the results averaged. The stated uncertainties indicate the standard deviation of the results.

Stoichiometry. Stoichiometry measurements were made with both excess Mn(III) and excess SO_2 by measuring the manganese(III) absorption at 470 nm and the SO_2 absorption at 280 nm, respectively, before and after mixing. Absorbance measurements were done with a Cary Model 219 spectrophotometer.

Results

Table I. Stoichiometry Measurements

init [Mn(III)], mM	init [SO_2], mM	final [Mn(III)], mM	final [SO_2], mM	ΔMn(III)/ΔSO_2
1.215	0.37	0.85	0	0.99
1.79	0.715	1.06	0	1.02
2.13	1.07	0.95	0	1.10
1.42	4.28	0	2.85	0.99
1.18	5.36	0	4.27	1.09
				av 1.04 ± 0.05

Table II. Dependence of First-Order Rate Constant on SO_2 Concentration[a]

[Mn(III)], mM	[SO_2], mM	k_0, s^{-1}	[Mn(III)], mM	[SO_2], mM	k_0, s^{-1}
0.73	2.78	61.3 ± 3.4	1.30	4.85	106.4 ± 5.6
0.73	4.57	102.0 ± 4.2	0.73	9.14	187.7 ± 6.2
1.05	4.70	101.1 ± 2.3	0.73	22.9	551.7 ± 11.6
1.05	4.85	128.8 ± 2.8			

[a] Conditions: [Mn(II)] = 24 mM; [$HClO_4$] = 5.77 M; T = 25 °C.

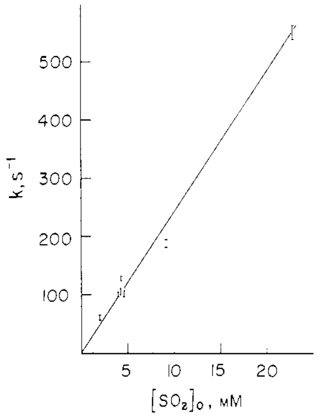

Figure 1. Plot of the first-order rate constant against concentration of SO_2 ([Mn(II) = 24 mM; [$HClO_4$] = 5.77 M; T = 25 °C).

Absorptivity Measurements. The absorptivity of Mn(III) in 5.77 M $HClO_4$ was measured by allowing a solution of Mn(III) in 5.77 M $HClO_4$ with an absorbance at 470 nm of 0.117 to react with 10^{-2} M ferrous ammonium sulfate in 5.77 M $HClO_4$ and diluting 1 mL of the resulting solution to 5 mL with 5.77 M $HClO_4$. The ferric ion absorbance was 1.061 at 260 nm and 1.504 at 240 nm with use of 1.00-cm cells. When the ferric ion absorptivities[11b] $\epsilon_{260} = 2.88 \times 10^3$ cm^{-1} M^{-1} and $\epsilon_{240} = 4.16 \times 10^3$ cm-1 M^{-1} were used, an effective absorptivity of 64.1 cm^{-1} M^{-1} at 470 nm for Mn(III) was calculated.

The hydrolysis of Mn^{3+} was investigated by Wells and Davis,[12] by Diebler and Sutin,[13] and by Fackler and Chawla.[14] Reaction 2 is observed during the time of measurement, followed by a slow formation of dimers or higher polymers. The polymerization reaction(s) was observed to be slow, requiring days to reach equilibrium. We have adopted the value of K_h obtained by Wells and Davis, i.e. $K_h = 0.93 \pm 0.03$ at ionic strength 4.0 and 25 °C. Our observations of the absorption spectra are consistent with this value.

$$\mathrm{Mn}^{3+} + \mathrm{H_2O} \overset{K_h}{\rightleftharpoons} \mathrm{MnOH}^{2+} + \mathrm{H}^+ \qquad (2)$$

Several measurements of the absorptivity of SO_2 at 280 nm were also made in the course of this work. A value of ϵ_{280} = 367 ± 18 M^{-1} cm^{-1} in 5.77 M $HClO_4$ was derived, compared to a reported[15] value of ϵ_{276} = 388 M^{-1} cm^{-1} in 0.1 M H_2SO_4.

Stoichiometry. The results of stoichiometry measurements on the reaction of Mn(III) with SO_2 in 5.77 M $HClO_4$ at room temperature are given in Table I. The average value of ΔMn(III)/ΔSO_2 is 1.04 ± 0.05. The products of the reaction with excess Mn(III) were investigated by neutralizing the solution, filtering it, and adding $Pb(ClO_4)_2$. No precipitate

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Table III. Measured and Calculated Dependence of the First-Order Rate Constant on Added Mn(II)[a]

Mn(III)/Mn(II)	[Mn(II)], mM	k_0, s^{-1}	$k_0(1 + 3.2 \times [Mn(II)])$, s^{-1}
0.0385	24.1	141.1 ± 3.1	152
0.0193	48.2	126.7 ± 0.9	146
0.0125	74.1	122.8 ± 1.4	152

[a] Conditions: $[Mn(III)]_0 = 0.93$ mM; $[SO_2]_0 = 4.57$ mM; $[HClO_4] = 5.77$ M, $T = 25$ °C.

Table IV. Dependence of First-Order Rate Constant on Acidity[a]

$[Mn(III)]_0$, mM	$[HClO_4]$, M	k_0, s^{-1}	$k_0(K_h + [H^+]) \times (K_1 + [H^+])$
0.72	5.02	206.3 ± 14.0	6170
0.58	3.46	490.0 ± 10.3	7460
0.45	2.31	1026 ± 16.8	7710

[a] Conditions: $[SO_2]_0 = 4.91$ mM; $[Mn(II)] = 24$ mM, $T =$ 25 °C; ionic strength 5.02 M.

was observed until nitric acid was added and the resulting mixture boiled. This, along with the stoichiometry results, is strong evidence that the product of the reaction is the dithionate ion, $S_2O_6^{2-}$.[16]

Rate Constants. All rate measurements were carried out with SO_2 in excess, with the Mn(III) concentration monitored by following the transmission of 470-nm light through the sample. Data showing the effect of SO_2 concentration on the first-order rate constant at constant acidity are presented in Table II and Figure 1. A proportional relationship is evident, and from the slope of the plot a second-order rate constant of 2.42×10^4 M^{-1} s^{-1} is derived. The influence of various other parameters on the measured rate was also investigated. As Mn(II) was a necessary component of the mixture, the effect of additional Mn(II) was investigated. The results in Table III show an 11 and 13% decrease in k_0 upon doubling and tripling the Mn(II) concentration. The reaction was also studied in the presence of 5 mM sodium dithionate. There was no observed effect. The lack of reactivity of dithionate was confirmed by monitoring a mixture of 5 mM $Na_2S_2O_6$ and 0.9 mM Mn(III) in 3.5 M acid. No decrease in absorbance at 470 nm was observed after 2 h.

The influence of acidity on the rate is pronounced over the range 2.3–5 M, as shown in Table IV. The ionic strength was kept constant at 5.02 M in these runs by the addition of $NaClO_4$. It was not possible to extend these measurements to lower hydrogen ion concentrations, for at $[H^+] = 2.3$ M the observed k_0 of 1000 s^{-1} is close to the maximum attainable with the present apparatus. Indeed, with the apparatus dead time of 1 ms, and with $k_0 = 1000$ s^{-1}, the reaction can only be observed for times after the initial concentration has fallen to e^{-1} of its initial value.

The temperature dependence of the reaction at a perchloric acid concentration of 5.92 M was investigated by measuring the rate of reaction with a 10-fold excess of SO_2 over the temperature range 15.4–34.9 °C. These results are presented in Table V. Second-order rate constants k were derived by dividing the first-order rate constants, k_0, by $[SO_2]_0 - 0.5[Mn(III)]_0$, the average SO_2 concentration during the course of the reaction. These results are plotted in Arrhenius form in Figure 2. A least-squares fit yields

$$k = (1.1 \pm 0.5) \times 10^7 \exp\left(\frac{-1970 \pm 100}{T}\right) M^{-1} s^{-1}$$

where the stated uncertainties are the standard errors from the least-squares fit.

Table V. Dependence of Second-Order Rate Constant on Temperature[a]

T, °C	k_0, s^{-1}	$10^{-4}k$, M^{-1} s^{-1}	T, °C	k_0, s^{-1}	$10^{-4}k$, M^{-1} s^{-1}
15.4	148.9 ± 8.3	1.21	28.3	197.0 ± 7.4	1.60
20.2	164.8 ± 1.7	1.34	30.4	210.7 ± 8.7	1.71
22.6	181.5 ± 6.5	1.47	34.9	231.0 ± 2.1	1.87
24.9	183.9 ± 2.9	1.49			

[a] Conditions: $[Mn(III)]_0 = 1.11$ mM; $[Mn(II)] = 97$ mM; $[SO_2]_0 = 12.3$ mM; $[HClO_4] = 5.92$ M.

Table VI. Dependence of Second-Order Rate Constant on Temperature with Added Na_2SO_4[a]

T_1, °C	$[SO_2]$, mM	[Mn(III)], mM	k_0, s^{-1}	$10^{-4}k$, M^{-1} s^{-1}
15.5	23.1	1.09	142.8 ± 3.6	1.27
15.8	40.6	1.66	261.1 ± 1.3	1.31
20.3	40.6	1.66	262.8 ± 1.7	1.29
25.0	23.1	1.09	164.8 ± 3.4	1.46
25.0	40.6	1.66	315.8 ± 5.3	1.59
34.5	23.1	1.09	202.7 ± 5.5	1.79

[a] Conditions: $[Mn(II)] = 82$ mM; $[HClO_4] = 5.86$ M; $[Na_2SO_4] = 195$ mM.

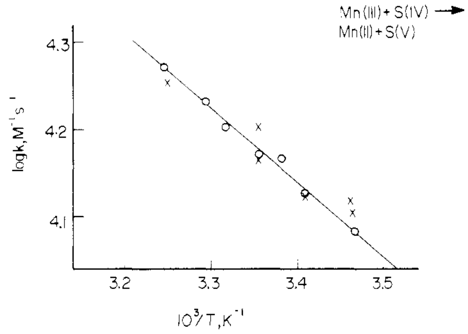

Figure 2. Plot of the logarithm of the second-order rate constant against $10^3/T$: (O) $[HClO_4] = 5.92$ M, no added $[Na_2SO_4]$; (×) $[HClO_4] = 5.86$ M, 195 mM Na_2SO_4 added.

As much of the work on the manganese-catalyzed oxidation of sulfite was carried out with use of solutions containing significant amounts of sulfate, rate constants were also measured as a function of temperature in 5.86 M perchloric acid with 0.195 M sodium sulfite added. These results are given in Table VI and also plotted in Figure 2. There is little difference between the two sets of data apparent, suggesting that any possible formation of a Mn(III)–sulfate complex does not affect the reaction rate.

Discussion

Both of the reactants Mn(III) and SO_2 undergo acid hydrolysis:

$$Mn^{3+} + H_2O \overset{K_h}{\rightleftharpoons} MnOH^{2+} + H^+ \tag{2a}$$

$$SO_2 + H_2O \overset{K_1}{\rightleftharpoons} HSO_3^- + H^+ \tag{2b}$$

We have used a first hydrolysis constant of $K_h = 0.93$, as discussed earlier. The electrochemical studies of Biedermann and Palombari[17] also indicated a significant amount of $Mn(OH)_2^+$. For the purposes of this discussion, however, only the first hydrolysis constant will be used. The first hydrolysis constant for SO_2 is $K_1 = 0.014$.[18] At the acid concentrations

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

used, the concentration of sulfite ion from the second hydrolysis is far too low to be important.

The effect of increasing the hydrogen ion concentration is to decrease the rate. The large magnitude of this effect, shown in Table IV, precludes measurements over a range of hydrogen ion concentrations sufficient for complete analysis of the hydrogen ion dependence of the rate. It is possible, however, to exclude some possible rate-determining steps. If one considers the four reactions (3)–(6) involving only one of the two

$$Mn^{3+} + SO_2 + H_2O \xrightarrow{k_3} Mn^{2+} + HSO_3 + H^+ \quad (3)$$

$$MnOH^{2+} + SO_2 \xrightarrow{k_4} Mn^{2+} + HSO_3 \quad (4)$$

$$Mn^{3+} + HSO_3^- \xrightarrow{k_5} Mn^{2+} + HSO_3 \quad (5)$$

$$MnOH^{2+} + HSO_3^- \xrightarrow{k_6} Mn^{2+} + HSO_3 + OH^- \quad (6)$$

principal manganese species of eq 2a and one of the two principal S(IV) species of reaction 2b, it is possible to exclude major contributions to the rate from reactions 3–5. The hydrogen ion dependence predicted from the rate-determining step of reaction 3 would require k to increase with increasing acidity. Reactions 4 and 5 both lead to hydrogen ion dependence considerably smaller than that observed experimentally.

If the hydrolysis equilibria are established rapidly relative to the electron-transfer process and if the rate-determining step is assumed to be reaction 6, the following expression for the dependence of k_0 on hydrogen ion results

$$T_s^{-1}k_0 = k_6K_1K_h/([H^+] + K_h)([H^+] + K_1) \quad (7)$$

where T_s is the analytical concentration of S(IV).

From eq 7 it is evident that at constant S(IV) that

$$k_0(K_h + [H^+])(K_1 + [H^+])$$

would be independent of hydrogen ion concentration. This quantity is shown in Table IV. The variation is only 15% from the average value, which suggests that reaction 6 may represent a major part of the observed rate, with smaller contributions possible from other hydrolyzed species. The systematic increase in this calculated value, however, suggests a measurable contribution to the rate from more highly hydrolyzed species, for example $Mn(OH)_2^+$ or SO_3^{2-}.

The observation that the stoichiometry of the reaction is one to one and that dithionate appears to be a product leads to the conclusion either that Mn(III) is unreactive toward S(V) radicals in concentrated acid solution and that their only fate in this system is to dimerize or that the mechanism of the reaction does not involve S(V) radical production. Outer-sphere one-electron oxidizing agents are known to produce mixtures of dithionate and sulfate from sulfur(IV). The ratio of sulfate to dithionate increases with the formal potential of the oxidizing agent as the oxidant becomes a more efficient scavenger for sulfur(V) species. The report of Anast and Margerum[19] suggests that a formal potential of 0.63 for copper(III) is sufficient to lead to almost complete conversion of sulfur(IV) to sulfate. By contrast the oxidation of sulfur(IV) to dithionate quantitatively by Mn(III) having a formal potential of 1.5 V must be rationalized as an inner-sphere oxidation in which free sulfur(V) radicals are not scavenged.

The reaction could involve a rate-determining combination of Mn(III) with bisulfite ion

$$MnOH^{2+} + HSO_3^- \rightarrow MnSO_3^+ + H_2O \quad (8)$$

followed by the fast step

$$2MnSO_3^+ \rightarrow 2Mn^{2+} + S_2O_6^{2-} \quad (9)$$

Kinetic measurements alone are not sufficient to distinguish reaction 8 from reaction 6.

The small inhibition by manganous ion cannot readily be explained by reaction with S(V) radicals. Formation of a complex of Mn(II) with sulfur(IV) can account for the effect of manganous ion on the rate. If we assume

$$Mn^{2+} + SO_2 \overset{K_{10}}{\rightleftharpoons} MnSO_2^{2+} \quad (10)$$

then the rate law would have the form (with the protonation equilibria omitted)

$$d[Mn(III)]/dt = -k[Mn(III)][S(IV)] = -k[Mn(III)]T_s/(1 + k_{10}[Mn(II)]) \quad (11)$$

where T_s is the total S(IV) concentration, including that complexed to Mn(II). Thus, the product $k(1 + K_{10}[Mn(II)])$ will be constant. A small value of $K_{10} = 3.2\ M^{-1}$ can be estimated from the data in Table III. Although the complex is written as involving SO_2, the predominant S(IV) species, it is also possible that it involves sulfite or bisulfite ion (see reaction 12 below). If so, the equilibrium constant would be much larger.

An alternate interpretation is that a small equilibrium concentration of Mn(IV) contributes to the rate. Diebler and Sutin[13] have reported an upper limit for the disproporportion equilibrium, eq 1, of $K_d \leq 0.01$ in 6 M $HClO_4$ at 23 °C. We have calculated the equilibrium concentrations of Mn(IV) and found a linear dependence of the observed rate constant k_0 vs. [Mn(IV)] with an intercept of 113 s^{-1}. There is no experimental evidence allowing us to prefer one of these explanations of the small Mn(II) retardation of the rate.

This study was prompted by a desire to understand the Mn(II)-catalyzed oxidation of S(IV) in aqueous solution. The rate constant for the reaction is certainly fast enough to allow Mn(III) to participate without building up a detectable steady-state concentration. The effect of Mn(II) on the oxidation of S(IV) solution, however, is not only to increase the rate of oxidation greatly but also to suppress dithionate formation almost completely. The observation in the present work that dithionate is the major product of the S(IV) + Mn(III) reaction suggests that this is not an important pathway in S(IV) oxidation. Rather, the mechanism is likely closer to that proposed by Bassett and Parker,[20] where sulfite (or bisulfite) complexes the Mn(II), oxygen adds to this complex ion, and a rearrangement to a sulfato complex takes place:

$$Mn^{2+} + 2SO_3^{2-} \rightleftharpoons Mn(SO_3)_2^{2-} \quad (12)$$

$$Mn(SO_3)_2^{2-} + O_2 \rightleftharpoons Mn(SO_3)_2O_2^{2-} \quad (13)$$

$$Mn(SO_3)_2O_2^{2-} \rightarrow Mn(SO_4)_2^{2-} \quad (14)$$

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Registry No. Mn, 7439-96-5; SO_2, 7446-09-5.

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