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Registry No. $VO_4H_2^-$, 34786-97-5; ethanol, 64-17-5; vanadium, 7440-62-2.

Kinetics and Mechanism of the Permanganate Ion Oxidation of Sulfite in Alkaline Solutions. The Nature of Short-Lived Intermediates

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Abstract: The oxidation of sulfite by permanganate ion has been studied by the stopped-flow technique combined with rapid scan spectrophotometry. The overall reaction involves manganate(VI) as an intermediate, whose fate depends on the pH. The formation and disappearance of manganate(VI) represent two distinct phases: (1) reduction of permanganate to manganate(VI) via outersphere electron transfer; (2) slower disproportionation of manganate(VI) to permanganate and a soluble manganese(IV) product. The direct oxidation of sulfite by manganate(VI) is too slow to compete with the permanganate route. Manganate(V) has been detected for the first time by rapid scan spectrophotometry as an intermediate of manganate(VI) disproportionation. The first phase obeys overall second-order kinetics, the rate constant being pH-independent between 13 and 9.5. Disproportionation is second order in manganate, and the observed rate constant increases with decreasing pH.

Mechanistic studies on permanganate oxidations of both organic and inorganic substrates are invariably encumbered by difficulties due to the multitude of possible oxidation states, which may be involved as intermediates in the reduction of manganate(VII). Thermodynamic stabilities of the individual oxidation states, though known from available redox potentials, do not always represent usable information for judging whether or not a given valence state will play the role of an intermediate. The lifetime together with the accessible techniques of detection will ultimately determine the degree of certainty with which a transient manganese species can be assigned an oxidation state.

It is relatively easy to detect and identify manganese(III) intermediates, as has been done in permanganate oxidations of unsaturated compounds in acidic solutions.[2-5] The manganese(IV) state is detectable by chemical techniques.[6-8] Manganate(V) esters have been invoked as intermediates in a variety of reactions between unsaturated compounds and permanganate ion in both acidic[4-6] and alkaline[2,9-15] media as well as in nonaqueous solvents.[11,12] The difficulties encountered in the detection of this oxidation state as a transient have led to disagreement over the identity of some short-lived intermediates, a case in point being cinnamic acid oxidation.[6,12,13] As no stable compounds of the manganate(V) ester type have been reported, it is not known what spectral characteristics should be expected for an intermediate of that structure. The evidence presented thus far for manganate(V) ester intermediates is of indirect nature. The MnO_4^{3-} ion, however, has been prepared in strongly alkaline aqueous solution,[16] and its UV–vis spectrum is known.[2,17] We have recently communicated the detection of MnO_4^{3-} as a short-lived intermediate in the oxidation of sulfite ion by alkaline permanganate.[18] This appears to be the first case in which a manganese(V) species has been positively identified by a spectroscopic technique as a transient in a permanganate oxidation. We now report a kinetic study of this reaction with special reference to the nature and sequence of short-lived intermediates.

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Experimental Section

The detection of intermediates was performed by using a stopped-flow spectrophotometer described earlier.[19] The instrument has a dead time of about 1 ms. In order to ensure that the reactant solutions did not contain dissolved oxygen, the vertically mounted reservoir vessels were purged with high-purity N_2 (Air Products). Deaerated solutions were then transferred to air-tight drive syringes without the access of air.

In addition to the normal mode of the stopped-flow instrument, providing *%T* vs. time traces, we also recorded sequential spectra of the reacting mixture. In this mode, a beam of white light (tungsten lamp) was directed on the observation cell, and the transmitted light was led by a light pipe to the entrance slit of a Tracor Northern Diode Array Rapid Scan Spectrophotometer (DARSS) combined with a TN-1710 Multichannel Analyzer. The minimum scan time was 5.15 ms, and a total of 16 spectra could be stored and displayed in the 200–800-nm nominal range. At the highest resolution, 512 diodes could be used to acquire transmission or absorbance data. The wavelength vs. channel number calibration was done with known light sources. The optical system used provided excellent agreement between DARSS spectra and those obtained on a Varian 219 spectrophotometer, as exemplified by the spectrum of an aqueous $KMnO_4$ solution, which is sufficiently rich in detail for checking the resolution. It should be noted that below 400 nm, the DARSS spectrum indicates zero absorbance for MnO_4^- which is due to the glass light pipes used. Absorbance spectra are calculated by the photometric processor module of the TN-1710, using a reference (background) spectrum, which is usually that of the solvent water. The above artifact arises from the practically zero transmission of both sample and reference below 400 nm, which is "interpreted" by the microprocessor as identical absorbances for sample and reference, i.e., zero absorbance for the sample. In view of this, the regions below 400 nm in all the spectra have been disregarded. A fortunate consequence of the cut off artifact is that the DARSS spectra of manganese(IV) exhibit a maximum at 450 nm, which although not real is of considerable help in monitoring the fate of this species (cf. later).

Potassium permanganate and sodium sulfite were reagent-grade chemicals. Sulfite stock solutions were prepared and standardized under N_2, and doubly distilled water was purged with N_2 before dissolving the solid sodium sulfite to avoid its known autoxidation reaction.[20] NBS buffer solutions were used whenever necessary; in the kinetic runs, the buffer was added to the sulfite solution of MnO_4^{2-} to avoid oxidation by MnO_4^-. Manganate(VI) was prepared by boiling an alkaline $KMnO_4$ solution.[16]

Results and Discussion

Stoichiometry. In strongly alkaline aqueous solutions (pH > 12.5), sulfite is rapidly oxidized to sulfate by permanganate ion

$$2MnO_4^- + SO_3^{2-} + 2OH^- \rightarrow 2MnO_4^{2-} + SO_4^{2-} + H_2O \quad (1)$$

as confirmed by spectrophotometric titrations of sulfite with permanganate. After the equivalence point corresponding to reaction 1, blue solutions are formed, whose spectra are superpositions of the known spectra of the MnO_4^- and MnO_4^{2-} ions, with no indication of any other manganese species.

If the titration is carried out below pH 12, then added increments of the permanganate solution produce a transient green color (manganate ion) which subsequently fades to a tobacco yellow, persisting from several minutes up to 1–2 h. The tobacco-colored solutions slowly become cloudy and then brown MnO_2 is gradually formed and precipitated. The stability of the tobacco-colored solutions depends on a variety of factors, precipitation being faster from more concentrated solutions. It is also accelerated if the pH is decreased further or a background electrolyte ($NaClO_4$) is present.

However, if the MnO_4^- concentration is (2–10) × 10^{-4} M, the tobacco-yellow solutions are stable for hours in the presence of up to a 10-fold excess of sulfite. The spectrum of the yellow species can be recorded at ease. It is shown in Figure 1 together with the spectra of permanganate and manganate ions for comparison. Spectrophotometric titrations under conditions where the yellow species is stable reveal the stoichiometry

$$2MnO_4^- + 3SO_3^{2-} + H_2O \rightarrow 2MnO_{2(sol)} + 3SO_4^{2-} + 2OH^- \quad (2)$$

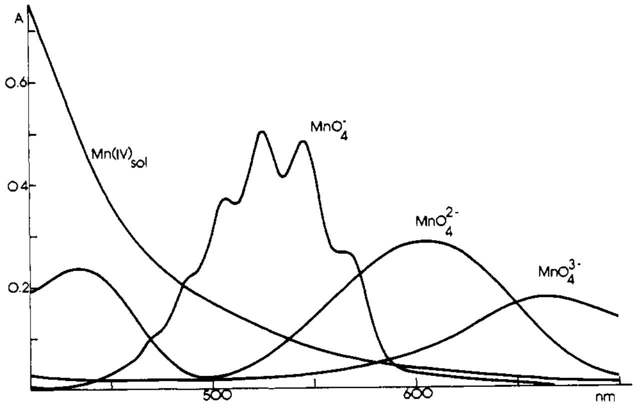

Figure 1. UV–vis. spectra of manganese species in the oxidation states VII–IV: 2 × 10^{-4} M solutions; 1-cm cells; t = 20 °C.

where $MnO_{2(sol)}$ stands for the soluble manganese(IV) species.

During the titrations, the transient green color of manganate(VI) appears before the color turns yellow.

The manganate ion, MnO_4^{2-}, reacts with sulfite in strongly basic solution much more slowly than does MnO_4^-. As demonstrated in experiments with alkaline MnO_4^{2-} solutions, this slow process first produces the yellow solutions, which then deposit MnO_2

$$MnO_4^{2-} + SO_3^{2-} + H_2O \rightarrow MnO_2 + SO_4^{2-} + 2OH^- \quad (3)$$

If alkaline MnO_4^{2-} is gradually neutralized with added increments of sulfuric acid solution, the known disproportionation process takes place

$$3MnO_4^{2-} + 2H_2O \rightarrow 2MnO_4^- + MnO_2 + 4OH^- \quad (4)$$

The UV–vis spectra recorded at various extents of reaction 4 are superpositions of the components shown in Figure 1. Visual observation reveals only the purple color of MnO_4^- and an incipient opalescence followed by MnO_2 precipitation.

From the above experiments, the important conclusion emerges that, prior to precipitation as brown MnO_2, manganese(IV) can exist as a soluble species. This situation arises if the manganese(IV) concentration is of the order of (2–10) × 10^{-4} M, which is very often the case in kinetic experiments on permanganate oxidations.

Intermediates. Both overall reactions 1 and 2 may in principle involve manganese(V) as a short-lived intermediate. As established visually, reaction 2 occurs via manganate(VI) as intermediate, but both the origin and fate of this species have to be elucidated, with special reference to the possible presence of manganese(V). Time evolution spectra of the reactions have been recorded by using the Diode Array Rapid Scan Spectrophotometer in the pH interval of 9.3–12.5. The spectra acquired by the DARSS were interpreted in terms of the individual spectra shown in Figure 1. The spectrum of a permanganate solution, as recorded on the DARSS, is given in Figure 1 for comparison purposes. The sequence of oxidation states was also checked by recording single wavelength stopped-flow traces, especially when the reaction was too fast for the minimum scan time of 5.15 ms of the DARSS.

A typical series of sequential spectra recorded at pH 11.9 is shown in Figure 2, for an overall period of 52.2 ms. The first spectrum (triggered 8.2 ms after the flow stopped) reveals most of the features of the MnO_4^- spectrum, with some contribution from manganate(VI). The concentration of manganate(VI) increases subsequently at the expense of permanganate: the central band decreases and two bands appear on both of its sides, at 435 and 606 nm. The latter are characteristic of manganate(VI): their intensity ratio is in good agreement with that determined from Figure 1. In the fourth spectrum, no contribution from permanganate is observable; i.e., reaction 1 has reached completion. Quantitative evaluation of these and similar spectra, based on the known molar absorptivities of permanganate and manganate(VI), reveal that these two species account for the overall manganese added within the estimated experimental error of ±2%.

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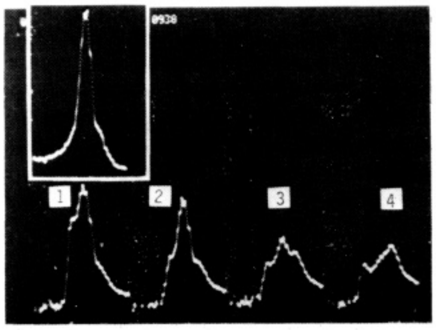

Figure 2. Four successive spectra (200–800 nm) in the first, faster phase of reaction 1. Duration of one scan: 5.15 ms. Time of triggering scan n is $t_n = 8.2 + 15.7\ (n - 1)$ ms after the flow stopped. Initial concentrations: 2×10^{-4} M MnO_4^-, 5×10^{-4} M SO_3^{2-}, pH 9.10. Solutions prepared and stored under N_2. Glass light pipes create an apparent zero absorbance below 400 nm. Insert: spectrum of MnO_4^- ion as recorded by the DARSS.

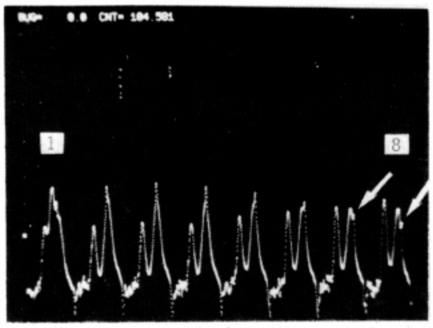

Figure 3. Eight successive spectra (200–800 nm) in the second, slower phase of reaction 1. Duration of one scan: 5.15 ms. Time of triggering scan n is $t_n = 49 + 123\ (n - 1)$ ms after the flow stopped. Conditions as in Figure 1. Arrows indicate the 660-nm band of MnO_4^{3-}.

The above behavior is consistent also with single wavelength stopped-flow traces recorded above pH 11.9. The absorbance decreases monotonically around 520–550 nm and increases likewise at 420–450 and 590–620 nm. Horizontal traces (no change in absorbance) are observed at 470 and 573 nm, where the spectra of manganate(VI) and permanganate ions intersect (Figure 1). Significantly, no intermediate can be detected around 670 nm, which is the region where the hypomanganate(V) ion is known to have a strong band.[17]

The obvious conclusion from these data is that reaction 1 does not involve manganese(V) as a detectable intermediate; therefore, the permanganate to manganate(VI) transformation occurs via transfer of a single electron in one step.

A different behavior emerges from similar DARSS experiments at pH 9–11, as exemplified by the successive spectra shown in Figure 3 (pH 9.10). Spectrum 1 triggered 49 ms after mixing the reactants (scan time 5.15 ms) reveals a situation similar to that corresponding to spectrum 2 of Figure 2, viz. a mixture of permanganate and manganate(VI) is present. In spectrum 2 triggered 172 ms after mixing, the permanganate band has disappeared from between the 435- and 606-nm manganate(VI) bands. At this stage, $A_{435} < A_{606}$. However, this situation changes gradually in the successive spectra (triggered at 123-ms intervals), and in spectrum 8 already $A_{435} > A_{606}$. This indicates that a predominantly manganate(VI) spectrum has been replaced by one revealing at least one additional species. Increasing amounts of the tobacco-yellow manganese(IV) and decreasing amounts of manganate(VI) would bring about changes like in spectra 2–8, which, therefore, are consistent with what would be expected from reaction 2, involving these two major absorbing species.

There is another characteristic feature in the spectral changes in Figure 3. Upon going from spectrum 2 to spectrum 8, the apparent tip of the 606-nm band moves toward longer wavelengths and in spectra 7 and 8 shows up as a separate maximum at 660 nm. This pattern is consistent with the presence of the long-sought manganate(V) intermediate, which, although known in very strongly alkaline solutions, has never been detected with certainty as a transient in an oxidation process. The manganate(V) spectra reported[17a,c] (Figure 1) exhibited a wide band at 670 nm with no other significant absorption in the visible range. Single wavelength stopped-flow traces show a transient absorbance maximum at 590–660 nm and a transient absorbance minimum at 520–550 nm.

Table I. Second-Order Rate Constant k_1 for the Permanganate Oxidation of Sulfite Ion from the Fast, First Phase (Aqueous Solution, T = 25 °C)[a]

no.	$[SO_3^{2-}]_0 \times 10^4$, M	$[MnO_4^-]_0 \times 10^4$, M	pH	μ, M	λ, nm	$k_{obsd} \times 10^{-4}$, $M^{-1}\ s^{-1}$
1	1.0	2.0	12.74	0.100	540	12.7
2	1.0	2.0	12.74	0.055	540	11.5
3	30.0	2.0	12.44	0.100	540	12.8
4	30.0	2.0	12.44	0.127	540	13.6
5	30.0	2.0	12.30	0.100	540	12.6
6	30.0	2.0	12.30	0.020	540	8.3
7	6.0	1.0	11.86	0.100	540	12.9
8	6.0	1.0	11.86	0.008	540	6.1
9	6.0	1.0	11.86	0.008	600	6.0
10	6.0	1.0	11.86	0.008	518	5.4
11	30.0	2.0	9.55	0.100	540	12.7
12	3.0	2.0	9.53	0.100	600	12.9
13	30.0	2.0	9.32	0.0	540	3.9
14	3.0	2.0	7.80	0.100	510	41.2
15	3.0	2.0	7.90	0.0	510	12.6
16	3.0	2.0	7.90	0.0	540	12.7
17	3.0	2.0	7.55	0.100	510	48.1

[a] Rate constants are average values from at least three parallel runs reproducible to within ±6%.

In conclusion, the DARSS experiments in moderately alkaline solutions have shown that the permanganate oxidation of sulfite consists of two phases. In the faster phase, MnO_4^- is reduced to MnO_4^{2-}, as in reaction 1. In the slower phase, manganate(VI) undergoes disproportionation according to eq 4, with manganate(V) as intermediate; the permanganate ions formed react rapidly with sulfite and cannot be detected in this phase.

Kinetic Measurements. Faster Phase. The faster reaction has been studied by stopped-flow spectrophotometry under a variety of conditions. The kinetic results are consistent with the rate law

$$-\frac{\mathrm{d}[MnO_4^-]}{\mathrm{d}t} = 2k_{obsd}[MnO_4^-][SO_3^{2-}] \qquad (5)$$

At a sulfite to permanganate mole ratio of 1:2, the stopped-flow traces give excellent linear plots of $1/(A_\infty - A)$ vs. time (Table I, no. 1 and 2). Under pseudo-first-order conditions, viz. at $[SO_3^{2-}]_0/[MnO_4^-]_0 = 15$, very good linear plots of log $(A - A_\infty)$ vs. time were observed. At intermediate sulfite to permanganate mole ratios of 1.5 and 6.0 (no. 12, 14–17, and 7–10), the traces were plotted according to the integrated rate equation

$$\log \frac{([SO_3^{2-}]_0 - X)[MnO_4^-]_0}{([MnO_4^-]_0 - 2X)[SO_3^{2-}]_0} = -\frac{[MnO_4^-]_0 - 2[SO_3^{2-}]_0}{2.3} k_{obsd} t$$

where

$$X = [SO_3^{2-}]_0 - [SO_3^{2-}] = \tfrac{1}{2}([MnO_4^-]_0 - [MnO_4^-])$$

The kinetic results for the fast phase are collected in Table I.

The kinetic behavior observed in the first, faster phase is consistent with the following mechanism:

$$MnO_4^- + SO_3^{2-} \xrightarrow{k_1} MnO_4^{2-} + SO_3^- \qquad (6)$$

$$MnO_4^- + HSO_3^- \xrightarrow{k_2} MnO_4^{2-} + HSO_3 \qquad (7)$$

$$MnO_4^- + SO_3^- \xrightarrow{\text{fast}} MnO_4^{2-} + SO_3 \qquad (8)$$

$$MnO_4^- + HSO_3 + OH^- \xrightarrow{\text{fast}} MnO_4^{2-} + SO_3 + H_2O \qquad (9)$$

$$SO_3 + 2OH^- \xrightarrow{\text{fast}} H_2O + SO_4^{2-} \qquad (10)$$

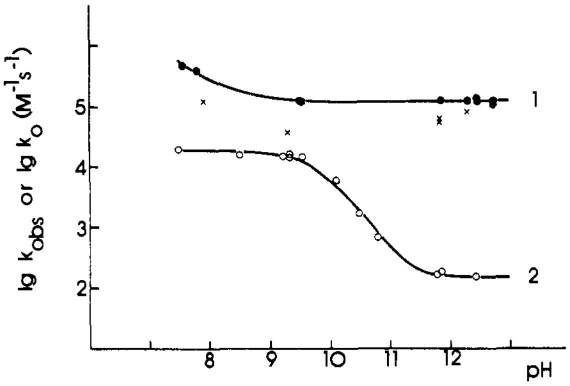

Figure 4. Second-order rate constant for the faster (k_{obsd}, curve 1) and the slower (k_0, curve 2) phase of sulfite oxidation at 20 °C, as a function of pH. The ×'s are k_{obsd} values obtained with ionic strengths far below 0.1 M (see Table I).

This scheme implies outersphere one-electron transfer as the rate-determining step. It is consistent with the tracer results of Halperin and Taube[21] and with the lack of a detectable manganate(V) intermediate. A similar mechanism has been proposed for the oxidation of sulfite by copper(III) tetraglycine by Anast and Margerum in basic media,[22] with the difference that in their scheme the electron-transfer step is reversible as required by the observed product inhibition.

There is no variation in k_{obsd} with the pH from about 9 to 13, in accordance with the lack of protonation equilibria involving either of the reactants. The mean value of $k_1 = k_{obsd}$ at $\mu = 0.1$ M is $(1.28 \pm 0.08) \times 10^5$ M^{-1} s^{-1}. An ionic strength effect on k_1 is clearly discernible. A plot of log k_1 vs. $\mu^{1/2}$ yields a slope of 1.8 in the interval between $\mu = 0.0$–0.055 M, which is consistent with the value of ca. 2.0 expected from electrostatic considerations. The linearity of this plot breaks down above $\mu = 0.055$ M, and a saturation effect is observed; i.e., k_1 increases more slowly than required by linearity. Apparently, ion-pair formation with sulfite to produce $NaSO_3^-$, which is a preferred reactant, can explain this leveling-off.

Beginning at about pH 8.0, the observed rate constant starts to increase, owing to the presence of the HSO_3^- ion (pK = 6.79),[22] which is expected to be more reactive than SO_3^{2-} on electrostatic grounds (Figure 4). From runs 14 and 17, the rate constant for the HSO_3^- path (eq 7) was estimated to be $k_2 = (3.0 \pm 0.2) \times 10^6$ M^{-1} s^{-1}.

The oxidation of sulfite ion by MnO_4^- is the fastest among the kinetically characterized outersphere oxidations of this ion: 2×10^4 M^{-1} s^{-1} (by $IrCl_6^{2-}$)[23] and 3.7×10^4 M^{-1} s^{-1} (by copper(III) tetraglycine),[22] which are comparable with k_1 of this work. Previously reported bimolecular rate constants for the oxidation of HSO_3^- are 9×10^6 M^{-1} s^{-1} (by FeL_3^{3+}, where L is 1,10-phenanthroline)[24] and 1.2×10^3 M^{-1} s^{-1} (by copper(III) tetraglycine).[22] The oxidation of SO_2 in perchloric acid by manganese(III),[25] chromium(VI),[26] aquairon(III), chloroiron(III), and chlorocopper(II)[27] involve inner-sphere mechanisms with prior complexation of the reactants. The rate-determining steps in the permanganate oxidation of nitrite ion in acidic media are the formation of reactive N(III) species.[28] An inner-sphere mechanism has been proposed for the permanganate–iron(II) reaction in acidic solution.[29]

Table II. Rate Constants for the Slower, Second Phase of the Permanganate Oxidation of Sulfite Ion (Aqueous Solution, T = 25 °C, Ionic Strength 0.1 M, with $NaClO_4$)[a]

no.	$[SO_3^{2-}]_0 \times 10^4$, M	$[MnO_4^-]_0 \times 10^4$, M	pH	λ, nm	$k_0 \times 10^{-2}$, M^{-1} s^{-1}
1	30.0	2.0	12.44	400	1.51
2	6.0	1.0	11.86	483	1.90
3	30.0	2.0	11.80	400	1.77
4	6.0	1.0	10.86	425	7.08
5	6.0	1.0	10.51	400	17.8
6	30.0	2.0	10.12	400	63.1
7	30.0	2.0	9.55	400	154
8	30.0	2.0	9.23	400	158
9	30.0	2.0	8.53	400	165
10	0.0	1.7[b]	9.34	540	168[c]
11	0.0	1.7[b]	9.34	600	152[c]

[a] Rate constants are average values from at least three parallel runs reproducible to within ±7%. [b] Concentration of manganate(VI) ion; disproportionation experiments. [c] k_d measured in disproportionation experiments.

Slower Phase. Manganate ion formed as the product in the first, fast reaction is rather unreactive toward SO_3^{2-}. The rate constant for this reaction was estimated from initial rate measurements, reacting alkaline solutions of MnO_4^{2-} and SO_3^{2-} at pH 12.54. First-order behavior was observed in both reactants, yielding a rate constant of 1.2 ± 0.1 M^{-1} s^{-1}. Consequently, this cannot be the route responsible for the disappearance of the manganate(VI) intermediate, occurring with half-lives of the order of a few seconds.

A reasonable assumption is that the fast formation of MnO_4^{2-} is followed by its known disproportionation, eq 4, as concluded from the DARSS experiments. This implies that the rate of disproportionation is governing sulfite oxidation at pH less than about 11.5, when manganese(IV) is the reduction product.

The rate of disproportionation was investigated by mixing an alkaline manganate(VI) solution with dilute sulfuric acid to reach a final pH of 9.34 in the stopped-flow mixing chamber. The ensuing disproportionation was monitored spectrophotometrically at 540 and 600 nm. The stopped-flow traces gave very good linear plots of $1/(A - A_\infty)$ vs. time at 540 nm (formation of MnO_4^-) or $1/(A_\infty - A)$ vs. time at 600 nm (disappearance of MnO_4^{2-}). The second-order rate constants k_d are listed in Table II (runs 10 and 11).

The slower phase of sulfite ion oxidation was found to follow the same kinetics as disproportionation measured separately. The second-order rate constant k_0 obtained from the slopes of $1(A - A_\infty)$ or $1/(A_\infty - A)$ plots are listed in Table II. Good agreement is observed between k_d and the rate constant referring to pH 9.23 and 9.55. The increase of k_0 with decreasing pH parallels the expected acceleration of disproportionation (Figure 4). The only known pH-dependent equilibrium operative in this range is the protonation of MnO_4^{2-}, with a pK of 10.15.[30] Assuming that the second-order kinetics arise from a bimolecular rate-determining step, involving manganate(VI) species, protonated or unprotonated, eq 11, the observed second-order rate constant k_0 can be expressed as

$$2MnO_4^{2-} \xrightarrow{k_{1d}} MnO_4^{3-} + MnO_4^-$$

$$MnO_4^{2-} + HMnO_4^- \xrightarrow{k_{2d}} MnO_4^{3-} + MnO_4^- + H^+$$

$$2HMnO_4^- \xrightarrow{k_{3d}} MnO_4^{3-} + MnO_4^- + 2H^+ \qquad (11)$$

$$H^+ + OH^- \xrightarrow{\text{fast}} H_2O$$

$$k_0 = \frac{k_{1d} + k_{2d}K[H^+] + k_{3d}K^2[H^+]^2}{(1 + K[H^+])^2} \qquad (12)$$

The fitting of eq 12 to the experimental k_0 values yields the

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following rate constants (using $K = 1.43 \times 10^{10}$ from ref 30)

$$k_{1d} = 150 \pm 12\ \mathrm{M^{-1}\ s^{-1}}$$

$$k_{2d} = 300 \pm 20\ \mathrm{M^{-1}\ s^{-1}}$$

$$k_{3d} = (3.4 \pm 0.2) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$$

These values cannot be directly compared with the results of Sutter et al.,[31] which refer to strongly acidic solutions.

The hypomanganate ion, MnO_4^{3-}, detected by DARSS as an intermediate is not stable enough in moderately alkaline solutions. Its likely fate is disproportionation yielding manganate(VI) and the product manganese(IV), eq 13. The yellow product solutions contain an unknown, soluble form of manganese(IV), observed previously in various oxidations by permanganate ion.[6-8] It can also be prepared by dissolving freshly precipitated MnO_2 in phosphoric acid and reveals oxidizing properties distinct from those of manganese(III).[32] Although the yellow species may be colloidal MnO_2 in some instances, evidence is accumulating in support of bridged dinuclear phosphatomanganese(IV)[32-34] or sulfatomanganese(IV)[35] species, at least in strongly acidic solutions. The existence of manganese(IV) complexes with polyhydroxy compounds in alkaline media is well established.[36]

$$2MnO_4^{3-} \xrightarrow{\text{fast}} MnO_4^{2-} + Mn(IV)_{(sol)} \qquad (13)$$

$$Mn(IV)_{(sol)} \xrightarrow{\text{slow}} MnO_2 \qquad (14)$$

The yellow species in this work is gradually converted to insoluble MnO_2, the rate of precipitation depending on the pH, electrolyte concentration, etc. The MnO_4^{2-} formed in eq 13 disproportionates according to eq 11. The permanganate ion produced in eq 11 is consumed for sulfite oxidation as depicted by eq 6-10.

The mechanistic conclusions emerging from the present study are also relevant to the nature and behavior of intermediates in the permanganate oxidation of olefinic and acetylenic substrates. In these cases, manganese(V) esters are routinely invoked as short-lived intermediates, but the unambiguous detection of these species remains the subject of further work. The lifetimes of the hypothetic manganate(V) esters may be too short for detection especially in less alkaline or acidic media. The occurrence of soluble manganese(IV) intermediates is, however, a distinct possibility in acidic solutions.

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Registry No. MnO_4^-, 14333-13-2; SO_3^{2-}, 14265-45-3.

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Mechanism of Hydrolysis of 2-*tert*-Butyl-2-methoxy-1,3-dithiolane. Rate-Determining Deprotonation in the Breakdown of Tetrahedral Intermediate

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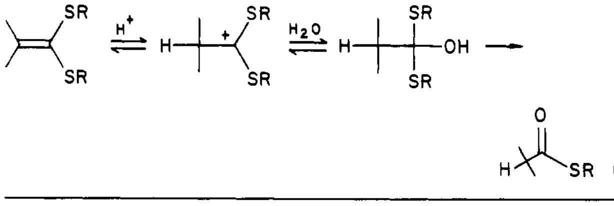
Abstract: Hydrolysis of 2-*tert*-butyl-2-methoxy-1,3-dithiolane (**1b**), as well as 2-methoxy-1,3-dithiolane (**1a**), proceeds through a three-stage process to lead to an (*S*)-2-mercaptoethyl thiocarboxylate (**4**), which involves 1,3-dithiolan-2-ylium ion (**2**) and 2-hydroxy-1,3-dithiolane (**3**) as intermediates. The initial expulsion of methanol catalyzed by acid (**1** → **2**) is rate determining at higher pHs, but the decay of **3**, which is catalyzed both by acid and base, becomes the slow step at low pHs. When the isolated salt of 2-*tert*-butyl-1,3-dithiolan-2-ylium ion (**2b**) was used, kinetic behavior of the base-catalyzed decay of **3b** was examined in detail. This reaction involves deprotonation of the neutral **3b** as a rate-determining step at high pHs but the breakdown of the anionic **3b**⁻ becomes rate determining with increasing hydronium ion or buffer concentration.

Our recent investigations showed that ketene dithioacetals undergo acid-catalyzed hydrolysis through partially reversible protonation of the carbon–carbon double bond (eq 1).[1-5] Deprotonation of the β-hydrogen is competitive with hydration of the intermediate dithio carbocation. This was ascribed to the very slow rate of hydration of the dithio carbocation.[6] For the same reason, the dithio cations are stable and can be isolated as salts. In some cases, the equilibrium constants for the hydration could



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