Contribution from the Department of Chemistry,
University of Missouri—Columbia, Columbia, Missouri 65211

Kinetic Study of the Formation of the Oxo Diperoxo Complexes of Molybdenum(VI) and Tungsten(VI) and Their Reduction by Iron(II), Europium(II), the Methyl Viologen Radical Cation, and the Dithionite Ion

Lisa M. Schwane and Richard C. Thompson*

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The rate law for the formation of $MoO(OH)(O_2)_2^-$ from Mo(VI) and H_2O_2 is rate = $k_f[Mo(VI)][H_2O_2]$ at $[H^+] \leq 0.0030$ M. The values of k_f at 25 °C and $I = 0.10$ M are $(6.7 \pm 0.3) \times 10^3$, $(2.0 \pm 0.1) \times 10^3$, and $8.6 \pm 0.8\ M^{-1}\ s^{-1}$ in 0.0030 M $HClO_4$, at pH 4.0 (acetic acid, acetate buffer), and at pH 7.0 (MOPS buffer), respectively. The value of k_f for $WO(OH)(O_2)_2^-$ is $3.0 \pm 0.4\ M^{-1}\ s^{-1}$ at pH 7.0. At $[H^+] \geq 0.10$ M, the rate law is second order with respect to H_2O_2 for the formation of $MoO(O_2)_2$; the transition from a first- to a second-order peroxide dependence was observed at 0.0090 and 0.014 M H^+. Formation constants were determined at pH 4.0 and 6.1–7.8 for $MoO(OH)(O_2)_2^-$ and pH 6.1–7.7 for $WO(OH)(O_2)_2^-$. The formation of an intermediate tentatively formulated as $M(VI)-(O_2^{2-})-Fe(III)$ was detected in the iron(II) systems. The formation kinetics of the intermediate and iron(III) for the Mo(VI) system were determined at an isosbestic at 255 nm and obey the following rate expression: $-d[H_2O_2]/dt = [Fe^{2+}]\{((2.8 \pm 0.1) \times 10^4\ M^{-1}\ s^{-1})[MoO(O_2)_2] + ((5.6 \pm 0.2) \times 10^4\ M^{-1}\ s^{-1})[MoO(OH)(O_2)_2^-] + (63 \pm 1\ M^{-1}\ s^{-1})[H_2O_2]\}$ at 25 °C. A partial spectrum and the first-order decay kinetics of the intermediate were determined for the Mo(VI) system. The rate law for the reaction of $WO(OH)(O_2)_2^-$ and Eu^{2+} in 0.0050 M $HClO_4$, at $I = 0.10$ M, and at 25 °C is $-d[H_2O_2]/dt = [Eu^{2+}]\{((2.8 \pm 0.4) \times 10^4\ M^{-1}\ s^{-1})[WO(OH)(O_2)_2^-] + (1.9 \pm 0.1\ M^{-1}\ s^{-1})[H_2O_2]\}$. The Mo(VI) system is complicated by competitive reduction of traces of uncomplexed Mo(VI). Second-order rate constants for the Eu^{2+} reduction of $MoO(O_2)_2$, $MoO(OH)(O_2)_2^-$, and Mo(VI) were derived from the kinetic data. The ratio $k\{O_2-Eu(II)\}/k\{H_2O_2-Eu(II)\}$ was determined to be ca. 3×10^4. The rate laws for the dithionite systems were half-order with respect to $[S_2O_4^{2-}]$, consistent with SO_2^- as the reactive reductant. Second-order rate constants ($M^{-1}\ s^{-1}$) for the reduction of $WO(OH)(O_2)_2^-$, $MoO(OH)(O_2)_2^-$, and H_2O_2 by SO_2^- were 8.0×10^5, 1.7×10^5, and 2.9×10^3, respectively, at 25 °C and pH 7.0. Second-order rate constants ($M^{-1}\ s^{-1}$) for the reduction of Mo(VI), $MoO(O_2)_2 + MoO(OH)(O_2)_2^-$, and H_2O_2 by the methyl viologen radical cation at 25 °C in 0.010 M $HClO_4$ were determined to be $(2.9 \pm 0.1) \times 10^5$, $(6 \pm 1) \times 10^4$, and 3.0 ± 0.2, respectively. The rate enhancements for the oxo diperoxo complexes of Mo(VI) and W(VI) relative to hydrogen peroxide are substantial (60–13 000) and fall within the range observed previously for several reductants that undergo oxygen atom transfer from peroxide. We propose that all the present substrates react by an inner-sphere, one-electron reduction of the peroxo ligand to produce a hydroxyl radical intermediate. The hydroxyl radical can oxidize the remaining peroxo ligand in the oxo diperoxo complex to form a superoxo Mo(VI) or W(VI) intermediate, which is rapidly reduced to peroxide by the reductant. We also conclude that Mo(VI) and W(VI) are versatile catalysts for reduction of hydrogen peroxide at least over the pH range 0–7.

Introduction

Molybdenum(VI) rapidly combines with hydrogen peroxide in acidic, aqueous solution to form an oxo diperoxo complex with a large formation constant.[1] There is substantial evidence that the structure of this complex is pentagonal bipyramidal, with an apical oxo and two η^2 equatorial peroxo ligands;[2,3] we will write the complex $MoO(O_2)_2(H_2O)_2$ as $MoO(O_2)_2$, and its hydrolyzed form ($pK_a = 1.85$) $MoO(OH)(O_2)_2(H_2O)^-$ as $MoO(OH)(O_2)_2^-$. Tungsten(VI) forms an analogous but more acidic complex ($pK_a = 0.1$); quantitative data for its rate of formation and formation constant are not available due to complexities in the chemistry of tungsten(VI) in acidic solution.[4]

We have found that these oxo diperoxo complexes are orders of magnitude more reactive as oxygen atom transfer reagents toward a variety of substrates than is hydrogen peroxide.[4,5] The source of the oxygen atom has been established as peroxidic with both (thiolato)- and (sulfenato)cobalt(III) substrates by oxygen-18 tracer experiments.[4] The reactions are strictly catalytic with respect to Mo(VI) and W(VI) provided sufficient hydrogen peroxide is present to maintain them as the oxo diperoxo complexes.

We have examined the redox reactions of the oxo diperoxo complexes from pH 0 to pH 7. Aside from hydrolysis as mentioned above, no new species have been detected over this wide range. This conclusion is drawn in part from equilibrium studies at pH 4.0 for the Mo(VI) system and from pH 6.1 to pH 7.8 for both Mo(VI) and W(VI). In addition, we have extended the earlier studies on the formation kinetics of oxodiperoxomolybdenum(VI) to weakly acidic and neutral media.

In the present study, we have employed the substrates iron(II), europium(II), dithionite ion, and the methyl viologen radical cation ($MV^{\bullet+}$). These ions usually function as one-electron reducing agents, and with the exception of europium(II), the kinetics of their reactions with hydrogen peroxide have been reported.[6-9] Masarwa et al. have proposed that one-electron reductions of hydrogen peroxide must proceed by an inner-sphere mechanism.[10] The obvious extension to the oxo diperoxo complexes is the requirement of inner-sphere pathways for both oxygen atom transfer and one-electron reductions. It is therefore of interest to see whether marked activation of peroxide is operative toward the latter substrates as well.

The "Fenton-like" chemistry of the oxo diperoxo complexes may differ from that found for hydrogen peroxide with respect to the fate of the hydroxyl radical presumably formed as an intermediate. If it escapes the complex, then the two systems are virtually identical except for differences in reaction rates. However, the hydroxyl radical may instead be "caged" in the group 6, d^0 metal ion complex. If so, oxidation of the remaining peroxo ligand to form a superoxo complex is a possibility. This speculative superoxo complex would be expected to be very reactive toward the substrate. The results of the present study, especially with iron(II) as the reductant, provide some evidence that this intricate chemistry in fact does play a role in the one-electron reductions of the oxo diperoxo complexes.

Experimental Section

Reagents. The preparation and analysis of solutions of molybdenum(VI), tungsten(VI), H_2O_2, $LiClO_4$, and $Fe(ClO_4)_2$ have been described previously.[1,11] Sodium dithionite (Fluka Chemie, ~97%), methyl

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(1) Lydon, J. D.; Schwane, L. M.; Thompson, R. C. *Inorg. Chem.* **1987**, *26*, 2606.
(2) Stomberg, R. *Acta Chem. Scand., Ser. A* **1988**, *A42*, 284.
(3) Dengel, A. C.; Griffith, W. P.; Powell, R. D.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1987**, 991.
(4) Ghiron, A. F.; Thompson, R. C. *Inorg. Chem.* **1988**, *27*, 4766.
(5) Monzyk, M.; Thompson, R. C. Unpublished observations, 1988.
(6) Po, H. N.; Sutin, N. *Inorg. Chem.* **1968**, *7*, 261.
(7) Creutz, C.; Sutin, N. *Inorg. Chem.* **1974**, *13*, 2041.
(8) Levey, G.; Rieger, A. L.; Edwards, J. O. *J. Org. Chem.* **1981**, *46*, 1255.
(9) Levey, G.; Ebbesen, T. W. *J. Phys. Chem.* **1983**, *87*, 829.
(10) Masarwa, M.; Cohen, H.; Meyerstein, D.; Hickman, D. L.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 4293.
(11) Thompson, R. C. *Inorg. Chem.* **1986**, *25*, 184.

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Table I. Conditional Formation Constants for the Oxo Diperoxo Complexes of Mo(VI) and W(VI) at 25 °C in Various Buffer Systems[a]

pH	buffer	$10^{-6}K_f\{Mo(VI)\}$, M^{-2}	$10^{-6}K_f\{W(VI)\}$, M^{-2}
7.77	EPPS	0.86 ± 0.17	
7.74	MOPS	0.99 ± 0.07	1.2 ± 0.1
7.68	HEPES	1.2 ± 0.3	
7.14	phosphate	1.6 ± 0.3	1.1 ± 0.3
7.13	MOPS	4.0 ± 0.3	2.9 ± 0.6
7.13	HEPES	2.3 ± 0.5	
6.60	MES	8.6 ± 0.7	
6.12	MES	22 ± 5	16 ± 2
6.12[b]	MES		14 ± 4
6.12[c]	MES		15 ± 6
4.0[d]	acetate	600 ± 300	

[a] Conditions: $[Mo(VI)]_{tot}$ or $[W(VI)]_{tot} = 8.00 \times 10^{-5}$ M, $[H_2O_2]_0 = (0.16-3.03) \times 10^{-3}$ M, and $[buffer]_{tot} = 0.010$ M unless otherwise indicated. K_f is defined as [oxo diperoxo complex]/$\{[M(VI)][H_2O_2]^2\}$, and entries and uncertainties are average values and deviations, respectively, of four to six independent determinations. [b] $[W(VI)]_{tot} = 1.0 \times 10^{-4}$ M. [c] $[W(VI)]_{tot} = 1.2 \times 10^{-4}$ M. [d] Conditions: $[Mo(VI)]_{tot} = (1.08-4.43) \times 10^{-4}$ M, $[H_2O_2]_0 = (1.00-6.00) \times 10^{-4}$ M, $[buffer]_{tot} = 0.010$ M, $[KNO_3] = 0.10$ M. Value of K_f is an average of 24 independent determinations.

viologen dichloride hydrate (Aldrich), and the biological buffers MOPS, MES, HEPES, and EPPS (Aldrich) were used as received. Triflic acid was purified by vacuum distillation.

All other chemicals were of reagent grade and were used as supplied. Deionized water was distilled twice before use; the last distillation was from alkaline permanganate.

Analytical Procedures. Solutions of $Eu(ClO_4)_2$ and $Eu(CF_3SO_3)_2$ were prepared by reduction of Eu(III) with amalgamated zinc under nitrogen or argon and were assayed spectrophotometrically ($\epsilon = 642$ M^{-1} cm^{-1} at 320 nm).[12] Solutions of $Na_2S_2O_4$ were prepared under anaerobic conditions; concentrations were calculated by spectral measurements at 350 nm ($\epsilon = 1.0 \times 10^3$ M^{-1} cm^{-1}). This extinction coefficient is in agreement with that previously reported.[13] Reduction of MV^{2+} over amalgamated zinc, under anaerobic conditions, was allowed to proceed to about 30% completion; the MV^+ formed was assayed at 605 nm ($\epsilon = 1.7 \times 10^4$ M^{-1} cm^{-1}).[9] Solutions were prepared in water and then mixed with acidic solutions of the oxidant on the stopped-flow instrument to minimize problems with instability of MV^+ in acidic solutions. Solutions of O_2 were prepared by saturation with either pure oxygen or air, and concentrations were estimated by means of Henry's law.

Determination of the Formation Constants of $MoO(OH)(O_2)_2^-$ and $WO(OH)(O_2)_2^-$. The procedures used have been described previously.[1,4] The decomposition of hydrogen peroxide in the biological buffers around pH 7 was significant, and as a result the total peroxide concentration at the time of the spectral measurements (310 and 256 nm for the Mo(VI) and W(VI) systems, respectively) was determined by iodometric titration.

Kinetic Studies. A Durrum D-110 stopped-flow spectrophotometer was used in the kinetic studies. Each kinetic experiment was repeated until three consecutive traces were superimposable. The data were usually collected by use of a Nicolet 3091 digital oscilloscope equipped with a bubble memory that allowed collection of multiple runs. The plungers for the drive and stop syringes were fitted with O-rings to provide tight fits for the anaerobic experiments. Details of the multimixing accessory have been described previously.[14]

The kinetics of the H_2O_2-Fe^{2+} reaction under conditions appropriate to our experiments with the oxo diperoxo complexes (excess $[H_2O_2]$, 25 °C, and $I = 1.0$ M maintained by use of $LiClO_4$) were measured by following the formation of Fe(III) at 280 nm. The rate expression $-d[H_2O_2]/dt = 63 \pm 1$ M^{-1} s^{-1} $[H_2O_2][Fe^{2+}]$ was determined. The value of the acid-independent, second-order rate constant is somewhat larger than determined previously with $[Fe^{2+}]$ in large excess (53 M^{-1} s^{-1}).[11]

In agreement with other reports, we found that Fe(II) is unreactive toward Mo(VI) in acidic solutions with $[H^+] \leq 1.0$ M.[15]

Results

Conditional Formation Constants and Formation Kinetics of the Oxo Diperoxo Complexes at Low Acidities. Our previous studies were confined to Mo(VI) in strongly acidic solutions (0.10–1.00 M H^+). We have summarized in Table I the values of K_f, defined as [oxo diperoxo complex]$\{[Mo(VI)][H_2O_2]^2\}$, determined at pH 4.0 in acetate–acetic acid buffer and from pH 6.1 to pH 7.9 by use of the buffers MES, MOPS, HEPES, EPPS, and phosphate. Values for the oxodiperoxotungsten(VI) complex were measured in the near-neutral region where monomeric tungstate ion is the principal uncomplexed tungsten(VI) species.[16] Complexities in the chemistry of tungsten(VI) preclude equilibrium studies in more acidic solutions.

Table II. Kinetic Results for the Formation of the Oxodiperoxomolybdenum(VI) Complex at 25 °C in Weakly Acidic Solution[a]

$10^3[H^+]$, M	$10^3[H_2O_2]_0$, M	$10^4[Mo(VI)]_0$, M	k_{obs},[b] s^{-1}	$10^{-3}k_{obs}/[H_2O_2]_{av}$, M^{-1} s^{-1}
14.0	2.00	1.50	$27._9$	
14.0	1.00	1.50	6.9_9	
14.0	0.60	0.75	3.3_6	
9.0	4.00	0.75	$91._8$	
9.0	3.00	0.75	$62._2$	
9.0	2.00	0.75	$28._5$	
9.0	1.00	0.75	9.6_6	
9.0	0.75	0.75	5.6_0	
3.0	10.0	3.00	$62._7$	6.4_6
3.0	5.00	3.00	$33._7$	7.1_7
3.0	2.00	3.00	$11._2$	6.5_9
				6.7 ± 0.3 (av)
0.10[c]	10.0	2.00	$20._1$	2.0_5
0.10[c]	8.00	2.00	$15._9$	2.0_4
0.10[c]	6.00	2.00	$11._6$	2.0_0
0.10[c]	5.00	2.00	9.2_1	1.9_2
0.10[c]	4.00	2.00	7.3_6	1.9_4
				2.0 ± 0.1 (av)

[a] Monitored at 310 nm. Ionic strength maintained at 0.10 M with use of NaCl, unless otherwise indicated. [b] Values are slopes of plots of $-\ln(A_\infty - A)$ vs time. [c] pH adjusted to 4.0 with acetate buffer; $[buffer]_{tot} = 0.010$ M. Ionic strength maintained at 0.10 M with use of KNO_3.

Only in the case of phosphate was spectral evidence obtained for complexation of the oxo diperoxo complexes by the buffer. We note that the values of the formation constant determined in phosphate buffer were diminished from those obtained in the weakly complexing or noncomplexing buffer systems[17] at the same pH. The spectrum of oxodiperoxomolybdenum(VI) measured in acetate buffer was identical with that of $MoO(OH)(O_2)_2^-$ determined previously in the absence of buffers. We conclude that, with the exception of phosphate, the conditional formation constants listed in Table I refer to the formation of the hydrolyzed forms of the oxo diperoxo complexes of Mo(VI) and W(VI). The reason for the large uncertainties in the values stems principally from experimental difficulties in determining very large formation constants by spectrophotometry. This problem was especially manifest at pH 4 where the values of K_f is ca. 6×10^8 M^{-2} for the Mo(VI) complex.

The rate of formation of oxohydroxodiperoxomolybdenum(VI) was measured at 0.014 M H^+, 0.0090 M H^+, 0.0030 M H^+, pH 4.0, and pH 6.5–7.5; only the higher pH range was used for the W(VI) analogue. The experiments were performed with sufficient excess H_2O_2 to ensure essentially complete complexation of the Mo(VI) or W(VI) at equilibrium, based on the conditional formation constants. Plots of $-\ln(A_\infty - A)$ vs time were linear for at least 3 half-lives. The slopes of these pseudo-first-order plots, k_{obs}, and the experimental conditions are summarized in Tables II and III. At a given acidity plots of log k_{obs} vs log $[H_2O_2]_{av}$, where $[H_2O_2]_{av} = [H_2O_2]_0 - [Mo(VI)]_0$ or $[W(VI)]_0$, were linear. The slopes of these plots were (for Mo(VI)) 1.66, 1.59, 1.00, 1.08,

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(12) Muralidharan, S.; Espenson, J. H. *Inorg. Chem.* **1984**, *23*, 636.
(13) Dixon, M. *Biochim. Biophys. Acta* **1971**, *226*, 241.
(14) Bourke, G. C. M.; Thompson, R. C. *Inorg. Chem.* **1988**, *26*, 903.
(15) Millan, C.; Diebler, H. *J. Chem. Soc., Dalton Trans.* **1988**, 2397.
(16) Cruywagen, J. J.; van der Merwe, I. F. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1701.
(17) Good, N. E.; Winget, G. D.; Winter, W.; Connolly, T. N.; Izawa, S.; Singh, R. M. M. *Biochemistry* **1966**, *5*, 467.

Table III. Kinetic Results for the Formation of the Oxo Hydroxo Diperoxo Complexes of Mo(VI) and W(VI) in Neutral Solution[a]

pH	*T*, °C	$[H_2O_2]_0$, M	$k_{obs}\{Mo(VI)\}$,[b] s^{-1}	$k_{obs}\{W(VI)\}$,[b] s^{-1}
7.00	25.0	0.0100	0.069	
7.00[c]	25.0	0.0100	0.074	
7.00	25.0	0.0200	0.15_3	0.046
7.00[c]	25.0	0.0200	0.15_5	
7.00	25.0	0.0500	0.40_1	0.13_1
7.00[c]	25.0	0.0500	0.44_6	
7.00	25.0	0.100	0.88_1	0.33_3
7.00[c]	25.0	0.100	0.94_3	
7.00	25.0	0.200	1.8_4	0.64_3
7.00[c]	25.0	0.200	2.0_1	
7.00	25.0	0.280	2.6_3	0.78_9
7.00	25.0	0.400		1.4_6
6.50[d]	25.0	0.100	1.1_0	0.62_0
6.50[e]	25.0	0.100	1.2_2	0.42_6
7.50[e]	25.0	0.100	0.85_6	0.29_2
7.00	19.4	0.100	0.56_5	0.21_9
7.00	19.4	0.200	1.1_9	0.48_3
7.00	14.5	0.100	0.43_0	0.17_7
7.00	14.5	0.200	0.85_8	0.33_7
7.00	10.0	0.100	0.29_7	
7.00	10.0	0.200	0.62_0	

[a] Monitored at 310 (Mo(VI)) or 300 nm (W(VI)). Conditions: $[Mo(VI)]_0 = (1.00\text{–}3.00) \times 10^{-4}$ M, $[W(VI)]_0 = (3.00\text{–}6.00) \times 10^{-4}$ M, $[\text{buffer (MOPS)}]_{tot} = 0.010$ M, ionic strength maintained at 0.10 M by use of NaCl unless otherwise indicated. [b] Values are slopes of plots of $-\ln (A_\infty - A)$ vs time. [c] Ionic strength maintained with KNO_3. [d] $[\text{buffer (MES)}]_{tot} = 0.020$ M. [e] $[\text{Buffer (MOPS)}]_{tot} = 0.020$ M.

and 1.09 at 0.014 M H^+, 0.0090 M H^+, 0.0030 M H^+, pH 4.0, and pH 7.0, respectively, and (for W(VI)) 1.12 at pH 7.0. These results indicate that the formation rate law is principally first-order with respect to hydrogen peroxide at acidities ≤0.003 M. We do not understand why the apparent order is slightly greater than unity in all the buffered media, but exactly unity at 0.0030 M H^+. In our previous study, we reported a second-order dependence with respect to hydrogen peroxide in the acidity range 0.10–1.00 M H^+. The transition from first to second-order dependence is observed at 0.0090 and 0.014 M H^+ under our experimental conditions. Possible reasons for this unusual behavior will be proposed in the Discussion Section.

Test of Beer's Law for the Oxo Diperoxo Complexes of Mo(VI) and W(VI). A crystal structure of $K_2Mo_2O_{11}\cdot4H_2O$ showed a dimeric structure for oxodiperoxomolybdenum(VI), in which two $[(H_2O)(O_2)_2MoO]$ units were bridged by an oxo ligand in the equatorial plane.[18] We therefore tested for possible dimerization in solution by spectrophotometry, under conditions of sufficient excess $[H_2O_2]$ such that >99% of the Mo(VI) or W(VI) was complexed. Experiments were conducted at 1.0 and 9.3×10^{-4} M H^+ with Mo(VI) (where $MoO(O_2)_2$ and $MoO(OH)(O_2)_2^-$ are the predominant forms, respectively), and at 0.75 M H^+ with W(VI) (where equal amounts of $WO(O_2)_2$ and $WO(OH)(O_2)_2^-$ are present). Beer's law was obeyed at 370 nm over the concentration range 0.0020–0.040 M Mo(VI); it was impractical to extend the range any higher. In addition, spectral scans over the limited wavelength range available due to increasing absorbance by the excess H_2O_2 in the near-UV region revealed no unusual features. Beer's law was obeyed for [W(VI)] to 0.020 M at both 295 and 310 nm, but monotonic deviations were observed from 0.020 to 0.040 M W(VI). We conclude that rather high concentrations of the oxo diperoxo complexes can be used without interference from dimerization, especially in the case of Mo(VI).

Kinetic Studies of the Oxidation of Iron(II) by the Oxo Diperoxo Complexes of Mo(VI) and W(VI). Preliminary experiments revealed the formation and decay of an absorbing intermediate. A partial spectrum of the intermediate formed in the Mo(VI) system is presented in Figure 1. Corrections were applied for the absorbance due to $MoO(O_2)_2$; spectral interference from the other reagents is negligible from 320 to 360 nm under the experimental conditions. The Mo(VI) was maintained as the oxo diperoxo complex during the redox reaction due to its very rapid formation rate.

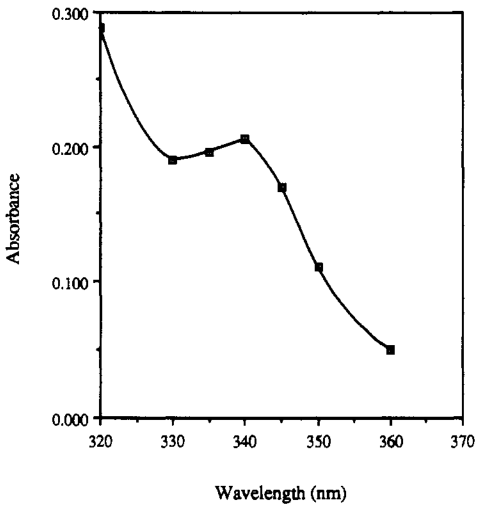

Figure 1. Partial spectrum of the intermediate formed during the oxidation of iron(II) by oxodiperoxomolybdenum(VI). Absorbance due to $MoO(O_2)_2$ has been subtracted. Conditions: $[Mo(VI)]_0 = 8.00 \times 10^{-5}$ M, $[H_2O_2]_0 = 8.00 \times 10^{-3}$ M, $[Fe(II)]_0 = 8.00 \times 10^{-4}$ M, $[HClO_4] = 1.0$ M, $T = 25$ °C.

Table IV. Kinetic Results for the Formation of the Intermediate Produced in the Oxidation of Iron(II) by Oxodiperoxomolybdenum(VI)[a]

$[H^+]$, M	$10^5[Mo(VI)]_0$, M	$10^3[H_2O_2]_0$, M	k_{obs},[b] s^{-1}	$10^{-4}k_4$,[c] $M^{-1}\ s^{-1}$
1.00	2.50	8.00	2.42	2.84
1.00	8.00	8.00	5.84	3.04
1.00[d]	8.00	8.00	5.68	2.78
1.00	8.00	16.0	6.45	2.93
1.00[d]	8.00	16.0	6.71	2.98
				2.9 ± 0.1 (av)
0.40	2.50	8.00	2.40	2.80
0.40	5.00	8.00	3.80	2.80
0.40	8.00	8.00	5.35	2.73
				2.8 ± 0.1 (av)
0.10	2.50	8.00	2.42	2.83
0.10	5.00	8.00	4.11	3.12
				3.0 ± 0.2 (av)
0.050	2.50	8.00	2.92	3.83
0.050	5.00	8.00	4.98	3.98
0.050	8.00	9.00	7.58	4.12
				4.0 ± 0.2 (av)
0.020	2.50	8.00	3.33	4.66
0.020	5.00	8.00	5.79	4.80
0.020	8.00	8.00	8.25	4.54
				4.7 ± 0.2 (av)

[a] Monitored at 255 nm. Conditions: $[Fe^{2+}]_0 = (1.00\text{–}1.50) \times 10^{-4}$ M, ionic strength maintained at 1.0 M with use of $LiClO_4$, $T = 25.0$ °C. [b] Values are slopes of plots of $-\ln (A_\infty - A)$ vs time. [c] Determined by use of eq 2. [d] Values determined on a different day and with different stock solutions.

Only a monotonic increase in absorbance was observed under comparable experimental conditions over the wavelength range 250–280 nm, where iron(III) is highly absorbing. Linear plots of $-\ln (A_\infty - A)$ vs time were obtained, but the variation of the slopes with reactant concentrations was consistent with a reasonable rate expression only at 255 nm. This behavior suggests that an isosbestic between the intermediate and the iron(III) product occurs at 255 nm, provided the formation and decay of the intermediate obey pseudo-first-order kinetics under the experimental conditions.[19] If we accept for the moment that this

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(18) Stomberg, R. *Acta Chem. Scand.* **1968**, *22*, 1076.

(19) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 65–71.

Table V. Kinetic Results for the Decomposition of the Intermediate Formed in the Oxidation of Iron(II) by the Oxodiperoxomolybdenum(VI) Complex[a]

$[H^+]$, M	$10^4[Fe(II)]_0$, M	$10^4[Mo(VI)]_0$, M	t_{max}, ms	k_d,[b] s^{-1}
1.00[c]	0.50	1.00	140 ± 20	8 ± 2
1.00[c]	0.50	2.00	110 ± 20	6 ± 2
1.00[c]	0.50	4.00	80 ± 20	5 ± 2
1.00	1.00	1.00	150 ± 20	7 ± 2
1.00	1.00	2.00	110 ± 20	6 ± 1
1.00	1.00	4.00	80 ± 20	5 ± 2
1.00	1.00	6.00	60 ± 20	6 ± 3
1.00	4.00	0.50	200 ± 20	6 ± 1
1.00	4.00	0.80	160 ± 20	7 ± 2
1.00	8.00	0.80	140 ± 20	9 ± 2
				7 ± 1 (av)
0.40	4.00	0.50	130 ± 15	14 ± 3
0.40	4.00	0.80	125 ± 15	11 ± 2
0.40	8.00	0.80	110 ± 15	14 ± 3
				13 ± 2 (av)
0.10	4.00	0.50	70 ± 10	35 ± 7
0.10	4.00	0.80	65 ± 10	32 ± 7
0.10	8.00	0.80	70 ± 10	29 ± 7
				32 ± 3 (av)
0.050	4.00	0.50	60 ± 10	40 ± 9
0.050	4.00	0.80	50 ± 10	42 ± 9
0.050	8.00	0.80	55 ± 10	36 ± 10
				39 ± 5 (av)

[a] Monitored at 340 nm unless otherwise indicted. Conditions: $[H_2O_2]_0 = 8.00 \times 10^{-3}$ M, ionic strength maintained at 1.0 M with use of $LiClO_4$, $T = 25$ °C. [b] Determined by use of eq 3. [c] Monitored at 310 nm.

interpretation is correct, then the slopes of the kinetic plots (k_{obs}) correspond to the pseudo-first-order rate constants for the formation of the intermediate and iron(III). The values of k_{obs} determined in this study and the experimental conditions are summarized in Table IV.

The simplest rate expression for the formation kinetics is given in eq 1. The second term takes into account the formation of

$$-d[H_2O_2]/dt = \tfrac{1}{2}d[Fe(III)]/dt = k_4[\text{oxodiperoxomolybdenum(VI)}][Fe(II)] + k_5[H_2O_2][Fe(II)] \qquad (1)$$

iron(III) by the known reaction of Fe^{2+} and H_2O_2. Values of k_4 can be calculated from our experimental data by means of eq 2,

$$k_4 = \{k_{obs} - 2k_5[H_2O_2]_{av}\}/\{2[Mo(VI)]_{tot}\} \qquad (2)$$

with $[H_2O_2]_{av} = [H_2O_2]_0 - 2[Mo(VI)]_{tot} - [Fe(II)]_0/4$. We have determined independently the value of k_5 (63 M^{-1} s^{-1}) appropriate to our experimental conditions, as summarized in the Experimental Section, since the contribution of the H_2O_2 pathway is 12–42%.

The resulting values of k_4 are listed in the last column of Table IV. The consistent values at a given acidity over a modest range of [Mo(VI)] and $[H_2O_2]$ provide significant support for our kinetic interpretation. A small increase in the rate parameter is observed at acidities below 0.10 M.

We were unable to find experimental conditions where the decay of the intermediate was free of kinetic interference from its formation rate. A further complication in determining the decay kinetics is uncertainty in the yield of the intermediate. As a result, we settled for the technique of estimating the time at which a maximum in the absorbance of the intermediate as measured at 340 nm occurred (t_{max}) over a range of experimental conditions. The values obtained are summarized in Table V. It can be shown that eq 3 holds if both the formation and decay kinetics obey

$$t_{max} = \ln (k_d/k_f)/(k_d - k_f) \qquad (3)$$

pseudo-first-order kinetics.[19] In this expression k_f takes into account all pathways for the oxidation of iron(II), which we have calculated for each experiment by the relationship $k_f = 2k_4[Mo(VI)]_{tot} + 2k_5[H_2O_2]_{av}$, and k_d is the first-order decay constant for the intermediate. The values of k_d thus obtained are listed in the last column of Table V. In spite of the substantial uncertainties, the consistent values obtained at a given acidity over a wide range of reactant concentrations provide strong support for the kinetic interpretation and establish that the decay of the intermediate follows first-order kinetics. It is important to note also that values obtained at 310 nm are indistinguishable from those measured at 340 nm. The decay constant increases with decreasing acidity, a feature that will become important in the speculation about the identity of the intermediate (vide infra).

Table VI. Kinetic Results for the Oxidation of Europium(II) by Dioxygen and Hydrogen Peroxide at 25 °C in Acidic Solution[a]

$10^4[O_2]_0$, M	$10^2[H_2O_2]_0$, M	$[HClO_4]$, M	$10^4[Eu(II)]_0$, M	k_6,[b] M^{-1} s^{-1}	$10^{-4}k_7$,[c] M^{-1} s^{-1}
	2.00	0.10	3.66	2.2_7	
	6.00	0.10	2.50	2.2_6	
	2.00	0.0050	4.21	2.0_5	
	6.00	0.0050	4.17	1.9_0	
	6.00	0.0050	4.30	1.9_0	
1.2_8		0.10	5.74		5.7
1.2_8		0.10	6.56		6.2
6.2_8		0.10	2.58		6.2
6.3_1		0.10	1.53		5.7
1.2_8		0.0050	0.630		6.1
6.2_1		0.0050	0.462		6.2
6.2_1		0.0050	0.913		5.9

[a] Monitored at 320 nm. Ionic strength maintained at 0.10 M by use of $LiClO_4$. [b] Defined in eq 4. Values are obtained from the slopes of plots of $-\ln (A - A_\infty)$, where $k_6 = \text{slope}/\{2([H_2O_2]_0 - [Eu(II)]_0/4)\}$. [c] Defined in eq 5. Values are obtained from the slopes of plots of $\ln \{[O_2]/[Eu(II)]\}$, where $k_7 = (\text{slope})/\{2[O_2]_0 - [Eu(II)]_0\}$.

We attempted to isolate the decay kinetics by means of quite different experimental conditions, in which $[Fe^{2+}]_0 = 0.020$ M, $[H_2O_2]_0 = 5.0 \times 10^{-4}$ M, $[Mo(VI)]_0 = 1.5 \times 10^{-3}$ M, $[HClO_4] = 0.10$ M, and $I = 1.0$ M. However, little if any intermediate was observed at 310 nm. While this line of investigation was not pursued, one possible explanation is that the decay rate of the intermediate is enhanced by the excess iron(II) under these conditions.

Studies of the iron(II)–oxodiperoxotungsten(VI) system were less successful. An intermediate is definitely formed with an absorption maximum at lower wavelength than that for the oxodiperoxomolybdenum(VI) system; we were unable to determine the exact position due to spectral interference from the iron(III) product(s). We were also unable to locate an isosbestic between the intermediate and iron(III), although qualitatively the rate of formation of the intermediate in the W(VI) system is somewhat more rapid than that determined for Mo(VI).

Kinetic Studies of the Oxidation of Europium(II) by the Oxo Diperoxo Complexes of Mo(VI) and W(VI). Europium(II) in acidic solution reacts rapidly with dissolved dioxygen but rather slowly with hydrogen peroxide. The rates of these reactions were examined briefly by monitoring the disappearance of europium(II) at its 320 nm absorption maximum. Plots of $-\ln (A - A_\infty)$ vs time were linear for at least 80% of the total reaction when the $[H_2O_2]$ was present in large excess. The data are consistent with the rate expression given in eq 4 values of the second-order rate constants k_6 and the experimental conditions are summarized in Table VI.

$$-d[H_2O_2]/dt = -\tfrac{1}{2}d[Eu(II)]/dt = k_6[H_2O_2][Eu(II)] \qquad (4)$$

The dioxygen system was studied with either oxygen or europium(II) in excess. Second-order rate plots, under the assumption of the stoichiometry $\Delta[Eu^{2+}]/\Delta[O_2] = 2.00$, were linear for greater than 90% of total reaction. This behavior is in agreement with the rate expression given in eq 5, and values of the rate parameter k_7 are given in Table VI.

$$-d[O_2]/dt = -\tfrac{1}{2}d[Eu(II)]/dt = k_7[O_2][Eu(II)] \qquad (5)$$

The oxidation of europium(II) by the oxo diperoxo complexes of Mo(VI) and W(VI) was also monitored at 320 nm. Sufficient excess $[H_2O_2]$ was used to ensure greater than 99% complexation

Table VII. Kinetic Results for the Oxidation of Europium(II) by the Oxodiperoxomolybdenum(VI) Complex[a]

$[H^+]$, M	$10^4[Mo(VI)]_0$, M	$10^3[H_2O_2]_0$, M	$10^4[Eu(II)]_0$, M	k_{obs},[b] s^{-1}	$10^{-3}k_{2nd}$,[c] $M^{-1}\ s^{-1}$
0.10	0.500	1.40	1.46	0.566	5.6_0
0.10[d]	0.500	1.40	2.09	0.491	4.8_6
0.10	0.500	1.50	1.35	0.487	4.8_1
0.10	0.500	1.50	2.53	0.453	4.4_6
0.10	0.500	1.60	0.87	0.438	4.3_2
0.10	0.500	2.00	3.63	0.366	3.5_8
0.10	0.500	2.50	2.65	0.300	2.9_0
0.10	0.500	3.00	3.10	0.268	2.5_5
0.10[d]	0.500	3.00	1.93	0.290	2.7_7
0.10	1.00	3.00	3.40	0.519	2.5_4
0.10	2.50	3.00	2.63	1.46	2.9_0
0.10	1.00	6.00	2.03	0.496	2.3_5
0.10	2.50	6.00	3.42	1.04	2.0_2
0.10	2.50	12.0	2.53	0.912	1.7_2
0.10	2.50	50.0	3.60	0.908	1.3_7
0.0050	0.500	0.500	0.80	0.521	5.2_0
0.0050	0.500	0.700	1.00	0.485	4.8_3
0.0050	0.500	0.800	0.80	0.469	4.6_6
0.0050	0.500	1.38	4.10	0.337	3.3_2
0.0050	0.500	1.50	4.35	0.331	3.2_6
0.0050	1.00	1.50	4.14	0.659	3.2_7
0.0050	0.500	1.57	4.10	0.335	3.3_0
0.0050	0.500	1.75	3.72	0.324	3.1_9
0.0050	0.500	2.00	3.90	0.317	3.1_2
0.0050	0.500	3.00	4.51	0.314	3.0_4
0.0050	1.00	3.00	4.04	0.596	2.9_3

[a] Monitored at 320 nm. Conditions: ionic strength maintained at 0.10 M with use of $LiClO_4$ and $T = 25.0$ °C. [b] Values are slopes of plots of $-\ln (A - A_\infty)$ vs time. [c] Determined by use of eq 6. [d] Triflic acid used instead of perchloric acid.

Table VIII. Kinetic Results for the Oxidation of Europium(II) by the Oxodiperoxotungsten(VI) Complex[a]

$10^5[W(VI)]_0$, M	$[H_2O_2]_0$, M	$10^4[Eu(II)]_0$, M	k_{obs},[b] s^{-1}	$10^{-4}k_{2nd}$,[c] $M^{-1}\ s^{-1}$
1.00	0.0100	2.00	0.452	2.0_7
1.00	0.0300	2.00	0.645	2.6_4
1.00	0.0300	1.50	0.635	2.5_9
10.0	0.0300	2.00	4.89	2.3_9
1.00	0.0600	1.50	0.774	2.7_0
1.00	0.100	2.00	1.01	3.0_8
1.00	0.250	2.00	1.66	3.4_3

[a] Monitored at 320 nm. Conditions: 0.0050 M $HClO_4$, ionic strength maintained at 0.10 M with the use of $LiClO_4$, and $T = 25.0$ °C. [b] Values are slopes of plots of $-\ln (A - A_\infty)$ vs time. [c] Determined by the use of eq 6.

of the metal ion under equilibrium conditions. Plots of $-\ln (A - A_\infty)$ vs time were linear for at least 85% of total reaction. The slopes of these plots, k_{obs}, and the experimental conditions for the Mo(VI) and W(VI) systems are presented in Table VII and Table VIII, respectively. The values of the second-order rate constant k_{2nd}, as defined by eq 6, are presented in the last column of these

$$k_{2nd} = \{k_{obs} - 2k_6[H_2O_2]_{av}\}/\{2[\mathrm{Mo(VI)\ or\ W(VI)}]_0\} \quad (6)$$

tables. A clear trend toward decreasing values of k_{2nd} with increasing excess $[H_2O_2]_0$ is seen for the Mo(VI) system in 0.10 M H^+; the effect is barely discernible for the low acid runs except at the lowest concentrations of hydrogen peroxide. A possible reason is that traces of uncomplexed Mo(VI) react rapidly with Eu(II), and the reduced molybdenum species is rapidly oxidized by hydrogen peroxide back to Mo(VI). We therefore briefly examined the Mo(VI)–Eu(II) system independently under similar experimental conditions by monitoring formation of Mo(V) and disappearance of Eu(II) at 295 nm, an absorption maximum for the known stable form of Mo(V), $Mo_2O_4^{2+}$.[20] We observed a very rapid decrease in absorbance followed by a slower increase. Qualitatively, this is consistent with a rapid loss of Eu(II) to form a weakly absorbing monomeric Mo(V) species, which then dimerizes to the known, highly absorbing $Mo_2O_4^{2+}$.[21] We also monitored the system at 410 nm where a monomeric Mo(V) species stable only in concentrated HCl has an absorption maximum, but the absorptivity of $Mo_2O_4^{2+}$ is weak.[22-24] Here a rapid increase in absorbance followed by a slower decrease was observed, but the apparent rates of the two processes did not match those observed at 295 nm. The Mo(VI)–Eu(II) system is obviously quite complex, and it would require considerable effort to sort out the mechanistic details. Nevertheless, it is safe to conclude that Eu(II) reduces Mo(VI) very rapidly and that the rate of this reaction appears to be somewhat faster in 0.0050 M H^+ than in 0.10 M H^+.

We were able to demonstrate directly that any reduced forms of molybdenum formed by the Mo(VI)–Eu(II) reaction are reoxidized to the hexavalent state extremely rapidly by hydrogen peroxide. Multimixing, stopped-flow techniques were used in which the first mixing yielded initial concentrations of Mo(VI) and Eu(II) of 0.30 mM in 0.10 M triflic acid at 25 °C. This reaction mixture was "aged" for 60 ms, a time period sufficient for nearly complete reaction, and then mixed with an equal volume of 2.0 mM H_2O_2 in 0.10 M triflic acid. The kinetic traces then observed at 295 and 400 nm were consistent with the formation of oxodiperoxomolybdenum(VI) from Mo(VI) and H_2O_2. This demonstrates that under the experimental conditions the reduced form or forms of molybdenum react with hydrogen peroxide at rates too fast to be measured by stopped-flow methods.

The values of k_{2nd} for the oxidation of europium(II) by oxodiperoxotungsten(VI) show considerable scatter and if anything slightly increase with increasing $[H_2O_2]_0$. We do not know the rate of formation of the W(VI) complex under these acidic conditions, but the linearity of the pseudo-first-order rate plots suggest that the W(VI) is maintained as the reactive oxo diperoxo complex as does the result where the $[W(VI)]_0/[Eu(II)]_0$ ratio was 0.50 rather than 0.050. Other studies suggest that W(VI) is generally more difficult to reduce than is Mo(VI).[25] We conclude that the rate expression given in eq 7 adequately correlates our limited data under the experimental conditions specified in Table VIII.

$$-d[H_2O_2]/dt = ((2.8 \pm 0.4) \times 10^4\ M^{-1}\ s^{-1}) \times [WO(OH)(O_2)_2^-][Eu^{2+}] + k_6[H_2O_2][Eu^{2+}] \quad (7)$$

Kinetic Studies of the Oxidation of Dithionite Ion by the Oxo Diperoxo Complexes of Mo(VI) and W(VI). The rate law for the $S_2O_4^{2-}$–H_2O_2 reaction in phosphate buffer at pH 6.5 has been reported to be first-order in hydrogen peroxide and half-order with respect to dithionite.[7] We have repeated some of the experiments, and obtained linear plots of $(A - A_\infty)^{1/2}$ vs time under the conditions summarized in Table IX. The values of the three-halves-order rate constants, k_8, are in excellent agreement with the literature value of 0.096 $M^{-1/2}\ s^{-1}$. The kinetics plots obtained with substitution of MES and MOPS buffers for phosphate showed some curvature, but the values of k_8 were similar. We decided to investigate the corresponding reactions of the oxo diperoxo complexes of Mo(VI) and W(VI) in the presence of the noncomplexing buffers. We determined independently that dithionite is unreactive toward MoO_4^{2-} and WO_4^{2-} in a near-neutral solution, at least on the stopped-flow time scale. The experimental conditions and values of k_9, as defined in eq 8, are also listed in

$$k_9 = \{2k_{obs}/(2\epsilon_{350})^{1/2} - k_8[H_2O_2]_{av}\}/[\mathrm{Mo(VI)\ or\ W(VI)}]_0 \quad (8)$$

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(20) Sasaki, Y.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1974**, 1468.

(21) Paffett, M. T.; Anson, F. C. *Inorg. Chem.* **1981**, *20*, 3967.

(22) Haight, G. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 663.

(23) Kim, C.; Murmann, R. K. *Inorg. Chem.* **1984**, *23*, 263.

(24) Kim, C.; Murmann, R. K.; Schlemper, E. O. *Transition Met. Chem.* (*Weinheim, Ger.*) **1984**, *9*, 260.

(25) See, for example, Ooi et al. (Ooi, B.; Petrou, A. L.; Sykes, A. G. *Inorg. Chem.* **1988**, *27*, 3626), in which the conclusion that W(IV) and W(V) are much stronger reducing agents than their molybdenum analogues is presented.

Table IX. Kinetic Results for the Oxidation of Dithionite Ion by Hydrogen Peroxide and the Oxo Diperoxo Complexes of Mo(VI) and W(VI) at 25 °C[a]

pH	buffer	$10^2[H_2O_2]_0$, M	10^4Mo(VI)$]_0$, M	$10^4[W(VI)]_0$, M	k_{obs},[b] s^{-1}	k_8,[c] $M^{-0.5}$ s^{-1}	k_9,[d] $M^{-0.5}$ s^{-1}
6.5	phosphate	9.00			0.196	0.096	
6.5	phosphate	18.0			0.369	0.091	
6.5	MES	9.00			0.240	0.12	
6.5	MES	18.0			0.539	0.12	
7.0	MOPS	12.5			0.326	0.12	
7.0	MOPS	25.0			0.572	0.10	
7.5	MOPS	9.00			0.228	0.11	
7.5	MOPS	18.0			0.408	0.10	
6.5	MES	1.00	1.50		0.0409		4.1
6.5	MES	1.00	3.00		0.0628		5.4
6.5	MES	2.00	3.00		0.074		2.9
							4 ± 1 (av)
7.0	MOPS	1.00	1.00		0.0402		7.0
7.0	MOPS	1.00	3.00		0.0678		6.5
7.0	MOPS	2.00	3.00		0.0835		5.1
							6 ± 1 (av)
7.0	MOPS	1.00		3.00	0.226		30
7.0	MOPS	2.50		3.00	0.280		32
7.0	MOPS	2.50		6.00	0.438		28
							30 ± 2 (av)
7.5	MOPS	1.00	1.00		0.0408		7.7
7.5	MOPS	1.00	3.00		0.0551		4.9
7.5	MOPS	2.00	3.00		0.0800		5.4
							6 ± 1 (av)

[a] Monitored at 350 nm. Conditions: $[Na_2S_2O_4]_0 = (4.0\text{–}6.0) \times 10^{-4}$ M, $[\text{buffer}]_{tot} = 0.010$ M, ionic strength maintained at 0.10 M with use of KNO_3. [b] Values are slopes of plots of $-(A - A_\infty)^{1/2}$ vs time. [c] $k_8 = 2k_{obs}/\{[H_2O_2]_{av}\,(2\epsilon_{350})^{1/2}\}$. [d] Determined by use of eq 8.

Table X Kinetic Results for the Oxidation of Viologen Radical Cation by Hydrogen Peroxide, Molybdenum(VI), and the Oxodiperoxomolybdenum(VI) Complex at 25 °C[a]

$10^5[MV^+]_0$, M	$10^3[H_2O_2]_0$, M	$10^4[Mo(VI)]_0$, M	k_{obs},[b] s^{-1}	k_{10},[c] M^{-1} s^{-1}	$10^{-5}k_{11}$,[d] M^{-1} s^{-1}	$10^{-4}k_{12}$,[e] M^{-1} s^{-1}
0.66	50.0		0.162	3.2		
0.92	50.0		0.150	3.0		
1.2	50.0		0.145	2.9		
0.92		1.00	30.0		3.0	
2.3		1.00	26.8		2.7	
2.3		1.20	35.4		2.9	
1.9	0.250	0.500	3.53			7.1
3.3	0.500	0.500	4.17			8.3
0.62	3.50	3.50	18.8			5.4
0.77	3.50	3.50	23.8			6.8
0.97	3.50	3.50	18.5			5.3
1.3	3.50	3.50	18.9			5.4
1.9	3.50	3.50	20.0			5.7
2.9	3.50	3.50	24.8			7.1
3.0	3.50	3.50	25.2			7.2
0.59	5.00	3.50	14.1			4.0
2.1	5.00	3.40	18.2			5.2
3.4	5.00	3.50	16.3			4.7
						6.0 ± 1.1 (av)

[a] Monitored at 605 nm. $[HClO_4] = 0.010$ M. [b] Values are slopes of plots of $-\ln(A - A_\infty)$ vs time. [c] $k_{10} = k_{obs}/[H_2O_2]_{av}$. [d] $k_{11} = k_{obs}/[Mo(VI)]_{av}$, where $[Mo(VI)]_{av} = [Mo(VI)]_0 - [MV^{\bullet+}]_0/2$. [e] Determined by use of eq 11.

Table IX, where k_{obs} is the slope of the $-(A - A_\infty)^{1/2}$ vs time plots and $\epsilon = 1.0 \times 10^3$ M^{-1} cm^{-1} for dithionite at 350 nm.

The half-order rate plots were linear for at least 80% of the total reaction for the W(VI) system at pH 7.0 (MOPS) and for the Mo(VI) system at pH 7.5 (MOPS). Curvature in the plots was observed with Mo(VI) at pH 6.5 (MES) and pH 7.0 (MOPS). Significant scatter was observed for the values of k_9 in all cases. Nevertheless, the data are in approximate agreement with the general rate expression given in eq 9.

$$-d[H_2O_2]/dt = -d[S_2O_4^{2-}]/dt = [S_2O_4^{2-}]^{1/2}\{k_9[\text{oxo diperoxo complex}] + k_8[H_2O_2]\} \quad (9)$$

Kinetic Studies of the Oxidation of the Methyl Viologen Radical Cation with the Oxo Diperoxo Complex of Mo(VI). The oxidation of the methyl viologen radical cation, $MV^{\bullet+}$, by hydrogen peroxide has been studied previously.[8,9] We briefly reinvestigated this reaction. Plots of $-\ln(A - A_\infty)$ vs time were linear to 80% of total reaction; the slopes of these plots, k_{obs}, and the experimental conditions are summarized in Table X. The second-order rate constants k_{10} are in good agreement with the literature values. We have assumed, based on the previous study, that the stoichiometry of the reaction is 1:1.

We found that Mo(VI) in 0.010 M $HClO_4$ rapidly oxidizes $MV^{\bullet+}$. The results of this brief investigation are also given in Table X, and are consistent with the rate expression given in eq 10, with the value of $(2.9 \pm 0.2) \times 10^5$ M^{-1} s^{-1} for k_{11} at 25 °C.

$$-d[MV^{\bullet+}]/dt = k_{11}[MV^{\bullet+}][Mo(VI)] \quad (10)$$

The experimental conditions and kinetic results for the oxidation of $MV^{\bullet+}$ by the oxo diperoxo complex of Mo(VI) are presented in Table X. While plots of $-\ln(A - A_\infty)$ vs time were linear to approximately 80% of total reaction, there was a severe curvature in the direction of increasing reaction rate past this point. The values of the second-order rate constant k_{12} were obtained from the slopes of the kinetic plots, k_{obs}, by use of eq 11. The values

$$k_{12} = \{k_{obs} - k_{10}[H_2O_2]_{av}\}/[Mo(VI)]_0 \qquad (11)$$

of k_{12} listed in the last column of Table X show considerable scatter. We have assumed that the contribution of the reaction of traces of uncomplexed Mo(VI) with $MV^{\bullet+}$ is negligible under the experimental conditions employed due to the small values of the ratio $k_{11}[Mo(VI)]/k_{12}$[oxodiperoxomolybdenum(VI)].

Discussion

Our previous study of the formation constants for oxodiperoxomolybdenum(VI) was limited to the acidity range 0.10–1.0 M H^+; the results were consistent with eq 12.[1] We can use eq

$$HMoO_3^+ + 2H_2O_2 \rightleftharpoons MoO(O_2)_2 + H^+ + 2H_2O \quad K_{2:1} \qquad (12)$$

12 to estimate the values of the conditional formation constants at pH 4 and 7 by taking into account the speciation of monomeric molybdenum(VI) among $HMoO_3^+$, MoO_3, $HMoO_4^-$, and MoO_4^{2-} and the hydrolysis of $MoO(O_2)_2$.[26-28] While this is a gross extrapolation, it is interesting that the calculated values agree with the experimental values listed in Table I to within a factor of 2. We consider this result as strong evidence that $MoO(O_2)_2$ and $MoO(OH)(O_2)_2^-$ are the principal oxodiperoxomolybdenum(VI) species over the entire acidic to neutral region. In addition, the linear Beer's law behavior indicates that dimerization is unimportant up to at least 0.040 M Mo(VI). In basic media other forms must become important since it is well established that the tetraperoxo species $Mo(O_2)_4^{2-}$ predominates in strongly basic solution.[29,30]

We were also able to measure the conditional formation constants for $WO(OH)(O_2)_2^-$ from pH 6.1 to pH 7.7. This was possible because the oligomerization of W(VI) that occurs in more acidic media is negligible.[16] The values of K_f listed in Table I are virtually identical with those for Mo(VI) within the substantial experimental uncertainty.

The rate law for the formation of oxodiperoxomolybdenum(VI) is unusual in that the dependence on hydrogen peroxide is second-order at $[H^+] \geq 0.1$ M but first-order at $[H^+] \leq 0.003$ M. The simplest interpretation is that entry of the second peroxide is rate determining in the former case, but entry of the first peroxide is limiting in the latter case. Presumably, in all cases, a monoperoxomolybdenum(VI) intermediate present at low concentration is involved. It is very difficult and probably not worthwhile to devise a "mechanism" that would cover the entire pH region examined due to considerable complexities in the acid–base chemistry of molybdenum(VI). However, in the transition acidity region where the order with respect to hydrogen peroxide is between 1 and 2, the principal molybdenum(VI) species is MoO_3. We therefore suggest that in this transition region the rate of *dissociation* of peroxide from the monoperoxomolybdenum(VI) intermediate drops sharply with decreasing acidity. This could arise if the intermediate is weakly acidic, with a pK_a comparable to that of $MoO(O_2)_2$. Mild support for this suggesting comes from the fact that MoO_3 is weakly basic ($pK_{protonation} = -0.85$) whereas $MoO(O_2)_2$ is weakly acidic ($pK_a = 1.9$). It is also possible that the rate of gain of the second peroxide ligand by the monoperoxo intermediate is strongly pH dependent in the transition acidity region, but it seems unlikely to use that this is the principal reason for the change in order with respect to hydrogen peroxide.

The second-order rate constants for the formation of the oxo hydroxo diperoxo complexes of Mo(VI) and W(VI) in neutral solution, calculated from the data in Table III (8.6 ± 0.8 and 3.0 ± 0.4 $M^{-1}\,s^{-1}$ at pH 7.0 and 25 °C, respectively), show that the Mo(VI) complex forms slightly faster than its W(VI) counterpart. We also note that these formation rates where tetrahedral Mo(VI) and W(VI) species predominate are very much slower than those in acidic solution where octahedral forms are dominant. This would be anticipated since the geometry of the oxo diperoxo complexes is more nearly octahedral.

Our kinetic study of the reduction of oxodiperoxomolybdenum(VI) by iron(II) revealed the formation of an intermediate. The kinetic data summarized in Table IV demonstrate that oxodiperoxomolybdenum(VI) is much more reactive than is hydrogen peroxide toward iron(II). The small dependence on acidity is consistent with eq 13, where at 25 °C the rate constants

$$-d[H_2O_2]/dt = [Fe^{2+}]\{k_{4n}[MoO(O_2)_2] + k_{4h}[MoO(OH)(O_2)_2^-] + k_5[H_2O_2]\} \qquad (13)$$

k_{4n}, k_{4h}, and k_5 have the values (2.8 ± 0.1) × 10^4, (5.6 ± 0.2) × 10^4, and 63 ± 1 $M^{-1}\,s^{-1}$, respectively.

The formulation of the intermediate is difficult, in that no known species will account for the experimental data. For example, it is not $Fe(OH)_2Fe^{4+}$, which dissociates with a rate and a $[H^+]$ dependence that are different from those observed.[31,32] Nor is the intermediate a peroxoiron(III) complex, which has a different spectrum and dissociates much more rapidly.[33,34] These observations coupled with the fact that a different species is formed in the Mo(VI) and W(VI) systems lead us to tentatively formulate the intermediate as a peroxo-bridged iron(III)–molybdenum(VI) or –tungsten(VI) species. We account for its formation and decay as shown in eq 14–20 for the Mo(VI) system, where Mo-2:1 is

$$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + {}^{\bullet}OH \quad k_5 \qquad (14a)$$

$$FeOH^{2+} + H^+ \rightarrow Fe^{3+} + H_2O \quad \text{fast} \qquad (14b)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad \text{fast} \qquad (15)$$

$$Fe^{2+} + \text{Mo-2:1} \rightarrow FeOH^{2+} + {}^{\bullet}OH + \text{Mo-1:1} \quad k_{11} \qquad (16)$$

$$\text{Mo-1:1} + H_2O_2 \rightarrow \text{Mo-2:1} + H_2O \quad \text{fast} \qquad (17)$$

$$Fe^{2+} + \text{Mo-2:1} \rightarrow Fe^{3+} + I_{Mo} \quad k_{12} \qquad (18)$$

$$I_{Mo} + Fe^{2+} \rightarrow I_{Mo,Fe} \quad \text{fast} \qquad (19)$$

$$I_{Mo,Fe} \rightarrow Fe^{3+} + \text{Mo-2:1} \quad k_d \qquad (20)$$

either $MoO(O_2)_2$ or $MoO(OH)(O_2)_2^-$, Mo-1:1 is a monoperoxomolybdenum(VI) species, I_{Mo} is a superoxomolybdenum(VI) species, and $I_{Mo,Fe}$ is the observed intermediate.

Reaction 14a occurs due to the excess $[H_2O_2]$ present in the experiments, and is proposed to produce free hydroxyl radicals.[34] Reaction 15 is known to be very rapid ($k_{19} > 10^8$ $M^{-1}\,s^{-1}$).[35] Reaction 16 is included since the yield of the intermediate is not known. However, we know that the yield is not quantitative since the concentration of the oxodiperoxomolybdenum(VI) complex cannot change appreciably during the experiments according to the observed rate expression. The experimental conditions were designed such that the formation rate of oxodiperoxomolybdenumVI) is rapid relative to the redox rate; therefore, reaction 17 would be rapid. The intermediate I_{Mo} formed in reaction 18 is proposed to be a superoxomolybdenum(VI) complex that is formed by the rapid reaction of a caged ${}^{\bullet}OH$ radical (formed via the inner-sphere, Fe^{2+}–$MoO(O_2)_2$ redox reaction) with the remaining peroxo ligand. It is known that the reaction of H_2O_2 and ${}^{\bullet}OH$ to form $HO_2{}^{\bullet}$ is rapid[36] and that strong oxidants can

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(26) Cruywagen, J. J.; Heyns, J. B. B.; Rohwer, E. F. C. H. *J. Inorg. Nucl. Chem.* **1976**, *38*, 2033.

(27) Cruywagen, J. J.; Heyns, J. B. B.; Rohwer, E. F. C. H. *J. Inorg. Nucl. Chem.* **1978**, *40*, 53.

(28) Brown, P. L.; Shying, M. E.; Sylva, R. N. *J. Chem. Soc., Dalton Trans.* **1987**, 2149.

(29) Connor, J. A.; Ebsworth, E. A. V. *Adv. Inorg. Chem. Radiochem.* **1964**, *6*, 279.

(30) Roch, M.; Weber, J.; Williams, A. F. *Inorg. Chem.* **1984**, *23*, 4571.

(31) Sommer, B. A.; Margerum, D. W. *Inorg. Chem.* **1970**, *11*, 2517.

(32) Po, H. N.; Sutin, N. *Inorg. Chem.* **1971**, *10*, 428.

(33) Jayson, G. G.; Parsons, B. J.; Swallow, A. J. *J. Chem. Soc., Faraday Trans.* **1973**, *69*, 236.

(34) Rush, J. D.; Bielski, B. H. J. *J. Phys. Chem.* **1985**, *89*, 5062.

(35) Jayson, G. G.; Parsons, B. J.; Swallow, A. J. *J. Chem. Soc., Faraday Trans.* **1972**, *68*, 2053.

oxidize coordinated peroxo ligands to coordinated superoxide.[14] The formation of the observed intermediate occurs in reaction 19 via a rapid, inner-sphere reduction of the superoxo ligand by iron(II). The reaction of $HO_2^{\bullet}$ and Fe^{2+} is known to be rapid ($k = 1.2 \times 10^6$ M^{-1} s^{-1}), to be inner sphere, and to produce a peroxoiron(III) complex that loses the peroxo ligand rapidly ($k = 1.8 \times 10^3$ s^{-1}).[33,34] Iron(II) is also known to react rapidly with "superoxotitanium(IV)" (TiO_2^{3+} or $TiO(HO_2^{\bullet})^{2+}$),[37] with a second-order rate constant of 1.8×10^5 M^{-1} s^{-1},[14] and with superoxochromium(III) (CrO_2^{2+}) with a rate constant of 2.5×10^4 M^{-1} s^{-1}.[38] The latter rate constants are comparable to those observed for the Fe^{2+}–$MoO(O_2)_2$ reaction, and we have to assume that reaction 19 is more rapid. In neither of the previous studies was an intermediate containing Fe(III) detected, but instead the formation of peroxotitanium(IV) and peroxochromium(III) was found. The titanium(IV) system was monitored by observing the formation of peroxotitanium(IV) at 410 nm, where an intermediate analogous to $I_{Mo,Fe}$ may have a similar extinction coefficient; alternatively, the intermediate may simply dissociate rapidly. The chromium(III) system was monitored in the UV region; we suggest that an iron(III)-peroxo-chromium(III) species may not have been detected due to the large excess of iron(II) present in the reaction mixtures. We also do not observe appreciable formation of an intermediate in the Mo(VI) system if large excesses of iron(II) are present. In any case, the dissociation of our proposed intermediate $I_{Mo,Fe}$ is shown in reaction 20. It is not clear how to predict the acid dependence of this reaction—simple, monomeric Fe(III) complexes often show an inverse acid independence,[39] but oxo- and hydroxo-bridged Fe(III) dimers have an acid-dependent term.[32] The values of k_d are somewhat greater than that for $FeCl^{2+}$ or $Fe(OH)_2Fe^{4+}$ but substantially less than that for peroxoiron(III).[31-35,39]

The experimentally determined rate constant k_4 for the oxodiperoxomolybdenum(VI) system is equal to $k_{11} + k_{12}$ in this scheme.

An analogous scheme could be formulated for oxodiperoxotungsten(VI). It would be anticipated that the intermediate would have a different spectrum, as is observed, and that its absorption maximum would lie at a lower wavelength based on the spectra of the oxo diperoxo complexes (the maxima for $WO(O_2)_2$ and $MoO(O_2)_2$ occur at 256 and 310 nm, respectively).[1]

The reaction scheme is admittedly speculative, but we are unable to suggest an alternative one that correlates the considerable experimental observations as well.

Hydrogen peroxide is frequently invoked as an intermediate in low concentration in reductions of dioxygen. In many cases, the reduction of hydrogen peroxide is much slower than that of dioxygen, and H_2O_2 can accumulate depending on the experimental conditions. An important example is the commercial production of hydrogen peroxide by the autoxidation of 2-ethylanthrahydroquinol.[40] Similar examples with simple metal ions are scarce,[41] but our data (summarized in Table VI) demonstrate that europium(II) reacts much more rapidly with dioxygen than with hydrogen peroxide ($k_7/k_6 \cong 3 \times 10^4$).

The kinetic results for the europium(II)-oxodiperoxomolybdenum(VI) system, summarized in Table VII, demonstrate more complicated behavior than just parallel paths involving hydrogen peroxide and the complex as oxidants. We can account for the variation of the rate constant k_{2nd} by including the reaction of Mo(VI) with Eu(II), which we have shown to be very rapid. A plausible reaction scheme is outlined in eq 21–28, where Mo-2:1, I_{Mo}, and Mo-1:1 are as defined for the iron(II) system and Mo_{red} is the reduced form of molybdenum, presumably monomeric Mo(V).

$$Eu^{2+} + H_2O_2 \rightarrow EuOH^{2+} + {}^{\bullet}OH \quad k_6 \tag{21a}$$

$$EuOH^{2+} + H^+ \rightarrow Eu^{3+} + H_2O \quad \text{fast} \tag{21b}$$

$$Eu^{2+} + {}^{\bullet}OH \rightarrow Eu^{3+} + OH^- \quad \text{fast} \tag{22}$$

$$Eu^{2+} + \text{Mo-2:1} \rightarrow Eu^{3+} + I_{Mo} \quad k_{13} \tag{23}$$

$$Eu^{2+} + I_{Mo} \rightarrow Eu^{3+} + \text{Mo-1:1} \quad \text{fast} \tag{24}$$

$$\text{Mo-1:1} + H_2O_2 \rightleftharpoons \text{Mo-2:1} + H_2O \quad k_{15}, k_{-15} \tag{25}$$

$$\text{Mo-1:1} \rightleftharpoons \text{Mo(VI)} + H_2O_2 \quad k_{16}, k_{-16} \tag{26}$$

$$Eu^{2+} + \text{Mo(VI)} \rightarrow Eu^{3+} + Mo_{red} \quad k_{14} \tag{27}$$

$$Mo_{red} + H_2O_2 \rightarrow \text{Mo(VI)} + {}^{\bullet}OH \quad \text{fast} \tag{28}$$

This scheme is consistent with the observation that values of k_{2nd} (see Table VII) in 0.0050 M H^+ are reasonably constant except at very low $[H_2O_2]$. First, the Mo-1:1 formed in eq 24 would be rapidly converted to Mo-2:1 since entry of the *first* peroxide ligand is rate determining at this acidity. Second, the equilibrium [Mo(VI)] is very low due to the large value of K_f (ca. 2.4×10^8 M^{-2}). As a result, contributions from eq 27 are quite small except at very low $[H_2O_2]$, and we can safely assign a value for k_{13} of 3.0×10^3 M^{-1} s^{-1}.

In 0.10 M H^+, entry of the second peroxide is rate determining in the formation of $MoO(O_2)_2$, and as a result, the steady-state [Mo(VI)] should be greater than dictated by equilibrium considerations alone. Equation 29 can be derived, where values of

$$k_{2nd} = k_{13} + k_{14}\{(k_r + k_{13}[Eu^{2+}]_{av})/(k_f[H_2O_2]^2)\} \tag{29}$$

$k_r = k_{-15}$ and $k_f = k_{-16}k_{15}/k_{16}$ are available from our previous study.[1] The values of k_{2nd} determined in 0.10 M H^+ were analyzed according to this equation by a nonlinear least-squares adjustment. The resulting values of k_{13} and k_{14} are $(1.8 \pm 0.2) \times 10^3$ M^{-1} s^{-1} and $(9.2 \pm 1.9) \times 10^4$ M^{-1} s^{-1}. However, the data were correlated at least as well by the simpler expression given in eq 30, with k_{13}

$$k_{2nd} = k_{13} + k_{14}/\{K_f[H_2O_2]^2\} \tag{30}$$

$= (1.9 \pm 0.1) \times 10^3$ M^{-1} s^{-1} and $k_{14} = (2.6 \pm 0.2) \times 10^5$ M^{-1} s^{-1}. This expression would be anticipated if the [Mo(VI)] were determined solely by the equilibrium parameters. Possibly a peroxide ligand has been gained by the superoxo intermediate I_{Mo}. In any case, the value $k_{13} = 1.9 \times 10^3$ M^{-1} s^{-1} appears to be reliable.

These results indicate that $MoO(OH)(O_2)_2^-$ is slightly more reactive toward Eu^{2+} than is $MoO(O_2)_2$; the same ordering was seen with Fe^{2+}.

The tungsten(VI) system was much more straightforward, presumably due to the lack of reaction between W(VI) and Eu(II). Oxohydroxodiperoxotungsten(VI) is ~9× more reactive than its Mo(VI) analogue.

Dithionite reactions exhibit a variety of rate laws depending on whether $S_2O_4^{2-}$, SO_2^-, or both are the active reductants. Sutin and Creutz[7] report a half-order dependence on $[S_2O_4^{2-}]$ with the oxidant H_2O_2, as we find with $MoO(OH)(O_2)_2^-$ and $WO(OH)(O_2)_2^-$ in neutral solution. The reaction scheme shown in eq 31–34 is consistent with the rate law summarized in eq 9.

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^- \quad K_D, \text{fast} \tag{31}$$

$$SO_2^- + H_2O_2 \rightarrow \text{products} \quad k_{H_2O_2} \tag{32}$$

$$SO_2^- + MoO(OH)(O_2)_2^- \rightarrow \text{products} \quad k_{Mo} \tag{33}$$

$$SO_2^- + WO(OH)(O_2)_2^- \rightarrow \text{products} \quad k_W \tag{34}$$

Values of $k_{H_2O_2}$, k_{Mo}, and k_W can be calculated from the rate constants summarized in Table IX by use of the expression $k = (k_8 \text{ or } k_9)/K_D^{1/2}$. With a value for K_D of 1.4×10^{-9} M,[42] the rate

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[36] Cabelli, D. E.; Arudi, R. L.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1985**, *14*, 1041.

[37] Rotzinger, F. P.; Gratzel, M. *Inorg. Chem.* **1987**, *26*, 3704.

[38] Brynildson, M. E.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1988**, *27*, 2592.

[39] Campion, R. J.; Conocchioli, T. J.; Sutin, N. *J. Am. Chem. Soc.* **1964**, *86*, 4591.

[40] Lowenhern, F. A.; Moran, M. K. In *Faith, Keyes, and Clark, Industrial Chemicals*, 4th ed.; Wiley-Interscience: New York, 1975; p 490.

[41] One example is Cr^{2+}; see: Sellers, R. M.; Simic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6145. Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 779.

[42] Lambeth, D. O.; Palmer, G. *J. Biol. Chem.* **1973**, *248*, 6095.

Table XI. Summary of Kinetic Results for the Reduction of Hydrogen Peroxide, Oxodiperoxomolybdenum(VI), Oxodiperoxotungsten(VI), and Dioxygen at 25 °C[a]

	second-order rate constants, $M^{-1}\ s^{-1}$			
oxidant	Fe^{2+}	Eu^{2+}	SO_2^-	MV^+
H_2O_2	63	2.1	2.9×10^3	3.0
$MoO(O_2)_2$	2.8×10^4	1.9×10^3		(6×10^4)[b]
$MoO(OH)(O_2)_2^-$	5.6×10^4	3.0×10^3	1.7×10^5	
$WO(OH)(O_2)_2^-$		2.8×10^4	8.0×10^5	
O_2	*c*	6.0×10^4	$>10^8$[d]	7.7×10^8[e]

[a] Rate constants are in terms of the rate law $-d[H_2O_2]/dt = k$[reductant][oxidant], and the values are from this study unless otherwise indicated. [b] Measured only at 0.010 M H^+, where $[MoO(OH)(O_2)_2^-] = 1.4[MoO(O_2)_2]$. [c] The rate law is $-d[Fe(II)]/dt = (1.8 \times 10^3\ M^{-2}\ s^{-1})[Fe(II)]^2[O_2]$; see ref 45. [d] Reference 7. [e] Reference 46.

constants are ($M^{-1}\ s^{-1}$) 2.9×10^3, 1.7×10^5, and 8.0×10^5, respectively. The order of reactivities of the peroxo oxidants is the same as we have seen for a number of substrates.

The products of reactions 32–34 have not been identified, although sulfite and/or bisulfite are likely candidates, depending on the pH. It is also not clear whether the reactions are outer sphere, as is often proposed to be the case with SO_2^-, or inner sphere.[43] We favor the latter given the large rate constants and the probable requirement of inner-sphere reductions of peroxide if they proceed by one-electron steps. If this is correct, there are two reasonable fates for the $^{\bullet}OH$ radical produced. It can either react with the newly formed sulfur(IV) species, a reaction known to be very rapid,[44] or it can form a superoxo complex as we have proposed in the iron(II) and europium(II) systems.

Oxodiperoxomolybdenum(VI) was also found to be much more reactive toward the methyl viologen radical cation than is hydrogen peroxide. In the latter system it has been proposed that hydrogen peroxide is hydrogen bonded to the $MV^{\bullet+}$ ion, and the $^{\bullet}OH$ radical formed from the one-electron redox reaction does not escape the solvent cage of the newly formed MV^{2+} ion. Rather, it reacts in the solvent cage to form an intermediate that decays to products that have not been characterized.[8,9] With oxodiperoxomolybdenum(VI) similar chemistry may occur, although the peroxo ligand would not be bonded to $MV^{\bullet+}$ except in the transition state. Alternatively, a superoxo complex may again be produced as a reactive intermediate.

We have assembled in Table XI the available second-order rate constants for the reduction of H_2O_2, $MoO(O_2)_2$, $MoO(OH)(O_2)_2^-$, $WO(OH)(O_2)_2^-$, and O_2 by Fe^{2+}, Eu^{2+}, SO_2^-, and $MV^{\bullet+}$. The reactivity of the peroxo complexes is much greater than that of hydrogen peroxide. Values of the ratio k(oxo diperoxo complex)/$k(H_2O_2)$ range from 59 to 1.3×10^4, and lie within the range observed for several reductants that undergo oxygen atom transfer from peroxide. The principal rate difference between the two types of substrates is that the hydrolyzed oxo diperoxo complexes are slightly more reactive than the neutral species for the one-electron metal ion reductants, whereas the opposite was found with all the oxygen atom acceptors examined. We have proposed inner-sphere reduction of coordinated peroxide in the present systems. It is possible in the case of Eu^{2+} that reduction of the Mo(VI) in the complex occurs instead, followed by rapid oxidation by peroxide. We do not favor this interpretation because the reactivity pattern of the various oxo diperoxo complexes is the same as that with other reductants.

It is clear that the reducing strength of the substrate is not a major determinant in the reactivity of the oxo diperoxo complexes, a feature well substantiated by the results with Fe^{2+} and Eu^{2+}. What continues to puzzle us is why the coordinated peroxide is strongly activated in oxo diperoxo complexes of Mo(VI) and W(VI), but is deactivated in peroxotitanium(IV), for example. The O–O bond distances and stretching frequencies in the η^2-bonded peroxo complexes are very similar to those in hydrogen peroxide.[2,3] We believe that the oxo diperoxo configuration is the principal factor, although at the present time this is simply an empirical correlation. We are examining this feature with vanadium(V), which forms both oxo peroxo and oxo diperoxo complexes in solution. We anticipate that the latter will be much more reactive as an oxidant.

Our results demonstrate that Mo(VI) and W(VI) are versatile catalysts for activating peroxide toward reduction from pH 0 to pH 7 in aqueous solution. Aside from hydrolysis, we have not detected any structural changes in the oxo diperoxo complexes over this pH range. However, the formation constants and formation rates vary significantly with pH, and these features must be taken into consideration in devising experimental conditions in which the metal ions are strictly catalytic.

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Registry No. H_2O_2, 7722-84-1; Mo^{6+}, 16065-87-5; W^{6+}, 22541-27-1; $MoO(O_2)_2$, 53474-95-6; $MoO(OH)(O_2)_2^-$, 75297-10-8; $WO(OH)(O_2)_2^-$, 74273-21-5; Fe^{2+}, 15438-31-0; Eu^{2+}, 16910-54-6; SO_2^-, 12143-17-8; MV^+, 4685-14-7.

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(43) Balahura, R. J.; Johnson, M. D. *Inorg. Chem.* **1987**, *26*, 3860.
(44) Huie, R. E.; Neta, P. *Atmos. Environ.* **1987**, *21*, 1743.
(45) George, P. *J. Chem. Soc.* **1954**, 4349.
(46) Farrington, J. A.; Ebert, M.; Land, E. J.; Fletcher, K. *Biochim. Biophys. Acta* **1973**, *314*, 372.