about the intimate mechanism involved, and we suggest that the method should be of wide and profitable application. Indeed, a very recent study[27] of isomerizations of some Ru(CO)$_2$Cl$_2$L$_2$ complexes has shown that they proceed via a CO dissociative mechanism and that rates increase with increasing size of L but decrease with increasing basicity. Only four different ligands were involved, and the data are unfortunately not suitable for quantitative analysis according to the method described here.

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Registry No. etpb, 824-11-3; *ax*-Ru(CO)$_4$etpb, 121916-49-2; Ru(CO)$_4$P(OEt)$_3$, 75627-87-1; *ax*-Ru(CO)$_4$P(OPh)$_3$, 121808-89-7; Ru(CO)$_4$P-*n*-Bu$_3$, 57967-87-0; Ru(CO)$_4$PEt$_3$, 121808-90-0; Ru(CO)$_4$P(CH$_2$CH$_2$CN)$_3$, 121808-91-1; Ru(CO)$_4$PPhEt$_2$, 121808-92-2; Ru(CO)$_4$PPh$_2$Et, 121808-93-3; Ru(CO)$_4$P(*p*-MeOPh)$_3$, 121808-94-4; Ru(CO)$_4$P(*p*-MePh)$_3$, 121808-95-5; Ru(CO)$_4$P(*p*-ClPh)$_3$, 121808-96-6; Ru(CO)$_4$P(NMe$_2$)$_3$, 121808-97-7; Ru(CO)$_4$PBz$_3$, 121808-98-8; Ru(CO)$_4$PCy$_3$, 121808-99-9; Ru(CO)$_4$P-*t*-Bu$_3$, 69661-89-8; *ax*-Ru(CO)$_4$AsPh$_3$, 85848-64-2; *ax*-Ru(CO)$_4$SbPh$_3$, 85848-65-3; P(OEt)$_3$, 122-52-1; P(OPh)$_3$, 101-02-0; P-*n*-Bu$_3$, 998-40-3; PEt$_3$, 554-70-1; P(CH$_2$CH$_2$CN)$_3$, 4023-53-4; PPhEt$_2$, 1605-53-4; PPh$_2$Et, 607-01-2; P(*p*-MeOPh)$_3$, 855-38-9; P(*p*-MePh)$_3$, 1038-95-5; P(*p*-ClPh)$_3$, 1159-54-2; P(NMe$_3$)$_3$, 1608-26-0; PBz$_3$, 7650-89-7; PCy$_3$, 2622-14-2; P-*t*-Bu$_3$, 13716-12-6; AsPh$_3$, 603-32-7; SbPh$_3$, 603-36-1; *eq*-Ru(CO)$_4$etpb, 121916-47-0; *eq*-Ru(CO)$_4$P(OPh)$_3$, 121916-48-1; *eq*-Ru(CO)$_4$AsPh$_3$, 85781-13-1; *eq*-Ru(CO)$_4$SbPh$_3$, 71356-99-5.

Supplementary Material Available: A table of all the rate constants for different values of [L] or [L′] obtained from different values of ν(CO) (5 pages). Ordering information is given on any current masthead page.

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Comparative Kinetic Study of Oxygen Atom Transfer Reactions of Oxohydroxodiperoxomolybdenum(VI) and Oxo(oxalato)diperoxomolybdenum(VI) in Aqueous Solution

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The conditional equilibrium constants at 25 °C and pH 4.0 for the reactions $MoO_3(C_2O_4)^{2-} + 2H_2O_2 = MoO(O_2)_2(C_2O_4)^{2-} + 2H_2O$ and Mo(VI) + $2H_2O_2$ = oxohydroxodiperoxomolybdenum(VI) are $(2.6 \pm 0.8) \times 10^7$ M^{-2} and $(6 \pm 3) \times 10^8$ M^{-2}, respectively. The corresponding rate laws for the formation of these oxodiperoxo complexes are $k_7K_6[H_2O_2]^2/(1 + K_6[H_2O_2])$, where $k_7 = 160 \pm 15$ M^{-1} s^{-1} and $K_6 = 17 \pm 3$ M^{-1}, and $(1.9 \pm 0.1) \times 10^3$ M^{-1} s^{-1} [Mo(VI)][H_2O_2]. A reaction scheme is proposed to account for the unusual formation rate expression for $MoO(O_2)_2(C_2O_4)^{2-}$. The oxygen atom transfer reactions from peroxo ligands in $MoO(O_2)_2(C_2O_4)^{2-}$ and $MoO(OH)(O_2)_2^-$ to the sulfur atom in (en)$_2$Co(SCH$_2$CH$_2$NH$_2$)$^{2+}$, (en)$_2$Co(S{O}CH$_2$CH$_2$NH$_2$)$^{2+}$, and (CH$_3$)$_2$SO obey the rate expression rate = *k*[oxodiperoxo complex][substrate] under our experimental conditions. At 25 °C and pH 4.0 the values of the rate constants (M^{-1} s^{-1}) are $(3.9 \pm 0.1) \times 10^4$, 103 ± 5, and $(2.3 \pm 0.1) \times 10^{-2}$, respectively, for $MoO(O_2)_2(C_2O_4)^{2-}$ and $(4.4 \pm 0.5) \times 10^3$, 13 ± 1, and $(2.7 \pm 0.1) \times 10^{-3}$, respectively, for $MoO(OH)(O_2)_2^-$. These values are 3–4 orders of magnitude larger than those observed for hydrogen peroxide and demonstrate the remarkable activation of peroxide in these oxodiperoxo complexes. There are no coordination sites at the metal center available in $MoO(O_2)_2(C_2O_4)^{2-}$ for the sulfur acceptor in the substrates, and no rate retardation is observed for this complex compared to $MoO(OH)(O_2)_2^-$. We therefore conclude that direct attack of the sulfur atom in the substrates at an η^2-bound peroxo ligand in the oxodiperoxo complexes is the dominant pathway in these reactions.

Introduction

The oxo diperoxo complexes of molybdenum(VI) and tungsten(VI) are remarkable oxygen atom transfer reagents. There is substantial evidence that the structure of these complexes both in the solid state and in solution is pentagonal bipyramidal, with an apical oxo ligand and two η^2-equatorial peroxo ligands.[1,2] Most of the reported work has dealt with organic substrates in weakly coordinating solvent systems. Two principal mechanisms have been proposed—either direct attack by the substrate at the peroxo ligand or coordination of the substrate to the metal center prior to oxygen atom transfer from an adjacent peroxo ligand.[3-7] A distinction between the two pathways can usually be made by comparing the reaction rates of a heteroligand oxo diperoxo complex with no available coordination sites on the metal center with that of the "bare" oxo diperoxo complex or one containing labile ligands.

We have examined some oxygen atom transfer reactions of the oxo diperoxo complexes of Mo(VI) and W(VI) in aqueous solution.[8,9] We have found that these complexes are orders of magnitude more reactive toward a variety of substrates than is hydrogen peroxide. We have established that the source of the oxygen atom gained by both a (thiolato)- and a (sulfenato)cobalt(III) complex is peroxidic by means of oxygen-18 tracer experiments.[8] These studies did not, however, establish if a direct attack by the substrate at the peroxo ligand occurred without prior coordination to the molybdenum(VI) center. We have now examined this mechanistic feature by use of a heteroligand oxodiperoxomolybdenum(VI) complex in which no coordination site on the metal is available for the substrate. In aqueous solution, it is more difficult to establish that the heteroligand complex is intact throughout the reaction due to the coordinating ability of water molecules and hydroxide ions.

We have used the $MoO(O_2)_2(C_2O_4)^{2-}$ complex ion in solutions buffered at pH 4.0 by use of $HC_2O_4^-$ and $C_2O_4^{2-}$ for our studies. We will show that this species is robust under our experimental

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conditions and will endeavor to demonstrate that its integrity is preserved during the oxygen atom transfer reactions with the substrates $(en)_2Co(SCH_2CH_2NH_2)^{2+}$, $(en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+}$, and $(CH_3)_2SO$. We will compare these kinetic results with those determined with $MoO(OH)(O_2)_2^-$,[10] the predominant form in an acetic acid, acetate ion buffer at pH 4.0. The basic idea is that if substitution at molybdenum(VI) by the sulfur atom in the substrate is a prerequisite with $MoO(OH)(O_2)_2^-$, then the corresponding rates with the oxalato complex should be considerably slower.

Experimental Section

Reagents. The preparation and analysis of solutions of molybdenum(VI) and hydrogen peroxide have been described previously.[11] The perchlorate salt of (2-aminoethanethiolato-*N*,*S*)bis(1,2-ethanediamine)cobalt(III) was prepared by the method of Nosco and Deutsch.[12] Dimethyl sulfoxide was distilled under vacuum before use. 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.

Kinetic Studies. The reactions of the thiolato and the sulfenato complexes were monitored at 365 nm, an absorption maximum for the sulfenato complex, $(en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+}$. Stopped-flow procedures were used for the rapid reactions, and a Zeiss PMQII spectrophotometer equipped with a thermostated, rapid-mixing (ca. 1 s) sample compartment was used for the slower reactions of the cobalt(III) complexes. The formation kinetics of $MoO(OH)(O_2)_2^-$ and $MoO(O_2)_2(C_2O_4)^{2-}$ were monitored at 310 nm and from 290 to 340 nm, respectively. The reactions of $(CH_3)_2SO$ were monitored by iodometric titrations of the total $[H_2O_2]$ in aliquots removed from the reaction mixture at suitable times.

A Cary 14 spectrophotometer was used to collect spectra.

A large excess $[H_2O_2]$ relative to [Mo(VI)] was employed in all the catalyzed reactions. Small corrections to the observed rates for contributions of oxidation of the substrate by the free hydrogen peroxide were applied to reactions of the thiolato complex. This correction was unnecessary for the reactions of the sulfenato complex and dimethyl sulfoxide.

We have demonstrated previously that quantitative conversion of the thiolato complex to the sulfenato complex and of the sulfenato complex to the sulfinato complex occurs under our experimental conditions.[8] The conversion of dimethyl sulfoxide to dimethyl sulfone was demonstrated by determining the ratio $\Delta[H_2O_2]/[DMSO]_0 = 1.0$ for spent reaction mixtures originally containing excess $[H_2O_2]$.

Results

Equilibrium and Spectral Studies. Cruywagen has determined a formation constant of 4.2×10^{13} M^{-3} at 25 °C for $MoO_3(C_2O_4)^{2-}$, as shown in eq 1.[13] We calculate a conditional formation

$$MoO_4^{2-} + C_2O_4^{2-} + 2H^+ = MoO_3(C_2O_4)^{2-} + H_2O \quad (1)$$

constant of 2.2×10^3 at pH 4.0 in a buffered solution in which $[HC_2O_4^-] + [C_2O_4^{2-}]$ is 0.010 M. Under these conditions $MoO_3(C_2O_4)^{2-}$ will be the predominant form of molybdenum(VI) at low concentrations of the metal ion. We have determined a value of $K_f = (2.6 \pm 0.8) \times 10^7$ M^{-2} for eq 2. This value is the

$$MoO_3(C_2O_4)^{2-} + 2H_2O_2 = MoO(O_2)_2(C_2O_4)^{2-} + 2H_2O \quad (2)$$

average of 15 independent measurements monitored at 328 nm, where oxo(oxalato)diperoxomolybdenum(VI) is the principal absorbing species, under the following conditions: $[Mo(VI)]_0 = 3.00 \times 10^{-4}$ M, $[H_2O_2]_0 = (0.200\text{–}1.41) \times 10^{-3}$ M, $[HC_2O_4^-] + [C_2O_4^{2-}] = 0.010$ M, $I = 0.1$ M (KNO_3), pH 4.0, and $T = 25.0$ °C.

We have also determined the conditional formation constant for $MoO(OH)(O_2)_2^-$ at 25 °C and pH 4.0 in acetic acid, acetate buffer. The value of K_f is $(6 \pm 3) \times 10^8$ M^{-2} if the reaction is written as in eq 3. This value is the average of 24 independent

$$Mo(VI) + 2H_2O_2 = \text{oxohydroxodiperoxomolybdenum(VI)} \quad (3)$$

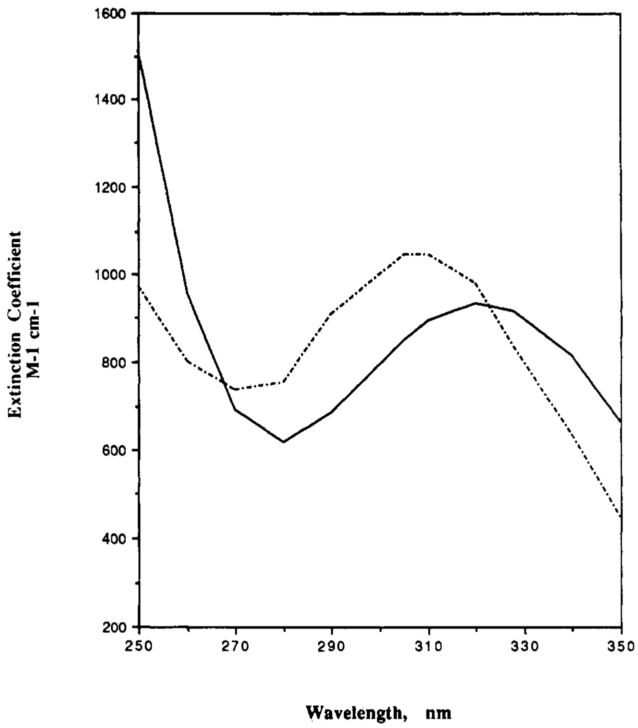

Figure 1. Absorption spectra of $MoO(O_2)_2(C_2O_4)^{2-}$ (solid curve) and $MoO(OH)(O_2)_2^-$ (dashed curve) in oxalate and acetate buffer, respectively, at pH 4.0. Conditions: $[Mo(VI)]_t = 3.00 \times 10^{-4}$ M, [buffer] = 0.010 M, and $[H_2O_2]_t = 1.00 \times 10^{-3}$ (acetate buffer) and 8.00×10^{-3} M (oxalate buffer).

measurements monitored at 310 nm under the following conditions: $[Mo(VI)]_0 = (1.08\text{–}4.43) \times 10^{-4}$ M, $[H_2O_2]_0 = (1.00\text{–}6.00) \times 10^{-4}$ M, $[HC_2H_3O_2] + [C_2H_3O_2^-] = 0.010$ M, and $I = 0.1$ M (KNO_3). We have previously shown that $MoO(OH)(O_2)_2^-$ is the predominant complex ion under these conditions.[8,11] Equation 3 may be rewritten in terms of the major species as shown in eq 4, for which the conditional formation constant is 4×10^4 M^{-2} at pH 4.0.[14-16]

$$MoO_4^{2-} + 2H_2O_2 + H^+ = MoO(OH)(O_2)_2^- + 2H_2O \quad (4)$$

The spectra of $MoO(O_2)_2(C_2O_4)^{2-}$ and $MoO(OH)(O_2)_2^-$ are shown in Figure 1.[17] The maxima and corresponding extinction coefficients (M^{-1} cm^{-1}) are 322 (967 ± 15) and 310 nm (1023 ± 28), respectively. The results of an additional experiment are pertinent. An oxalate solution buffered at pH 4.0 was gradually added to a solution intially containing 5.89×10^{-4} M Mo(VI) and 0.065 M H_2O_2 in acetate buffer at pH 4.0. The spectrum was initially that of $MoO(OH)(O_2)_2^-$, but gradually shifted to that of $MoO(O_2)_2(C_2O_4)^{2-}$. The conversion was virtually complete when the [oxalate buffer] was ca. 1.5×10^{-3} M, in agreement with predictions based on the above formation constants.

Kinetic Studies of the Formation of $MoO(OH)(O_2)_2^-$ and $MoO(O_2)_2(C_2O_4)^{2-}$. The equilibrium data allow us to prepare solutions in which the molybdenum(VI) is present principally as the desired oxo diperoxo complex. However, if these complexes are to be used as oxygen atom transfer catalysts, we must also know their rates of formation to ensure that their structure is preserved throughout the reaction. We have therefore examined the formation kinetics for $MoO(OH)(O_2)_2^-$ in acetate buffer and $MoO(O_2)_2(C_2O_4)^{2-}$ in oxalate buffer at pH 4.0 and 25 °C by stopped-flow procedures. Simple pseudo-first-order kinetics were observed in acetate buffer, with no detectable effect of buffer concentration or wavelength. The results summarized in Table

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(10) We will omit the water ligand in our formula for this oxodiperoxo complex.

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(17) This spectrum of $MoO(OH)(O_2)_2^-$ is virtually identical with that measured in unbuffered solution at pH ca. 4.

Table I. Kinetic Results for the Formation of Oxohydroxodiperoxomolybdenum(VI) and Oxo(oxalato)diperoxomolybdenum(VI) at pH 4.0 and 25 °C[a]

buffer	$10^2[H_2O_2]_0$, M	k_{obs},[b] s^{-1}	$10^{-3}\ k_{obs}/[H_2O_2]_{av}$,[c] $M^{-1}\ s^{-1}$
acetate	0.400	7.3_6	1.8
acetate	0.500	9.2_1	1.8
acetate	0.600	$11._6$	1.9
acetate	0.800	$15._9$	2.0
acetate	1.00	$20._1$	2.0
acetate	1.00		1.7 ± 0.1[d]
oxalate	1.00	0.18_6 (0.22)	
oxalate	2.00	0.72_1 (0.72)	
oxalate	4.00	2.5_8 (2.53)	
oxalate	4.00	2.6_6 (2.53)	
oxalate	6.00	4.8_8 (4.76)	
oxalate	8.00	8.0_1 (7.27)	
oxalate[e]	8.00	8.2_6 (7.27)	
oxalate	10.0	9.6_0 (9.95)	
oxalate	15.0	$16._1$ (17.1)	

[a] Ionic strength maintained at 0.10 M with use of KNO_3. Total buffer concentration $\{([HC_2H_3O_2] + [C_2H_3O_2^-])$ or $([HC_2O_4^-] + [C_2O_4^{2-}])\} = 0.010$ M and $[Mo(VI)]_0 = 2.00 \times 10^{-4}$ M unless otherwise indicated. Reactions were monitored at 310 (acetate buffer) and 295 nm (oxalate buffer) unless otherwise indicated. [b] Values are slopes of plots of $-\ln (A_\infty - A)$ vs time. Values in parentheses for the oxalate system were calculated by the use of eq 8 with least-squares-determined values for k_7 and K_6. [c] $[H_2O_2]_{av} = [H_2O_2]_0 - 0.80[Mo(VI)]_0$. [d] Average value of four earlier experiments monitored at 295 and 328 nm with $[\text{buffer}]_t = 0.010$ and 0.020 M. [e] Total buffer concentration = 0.020 M.

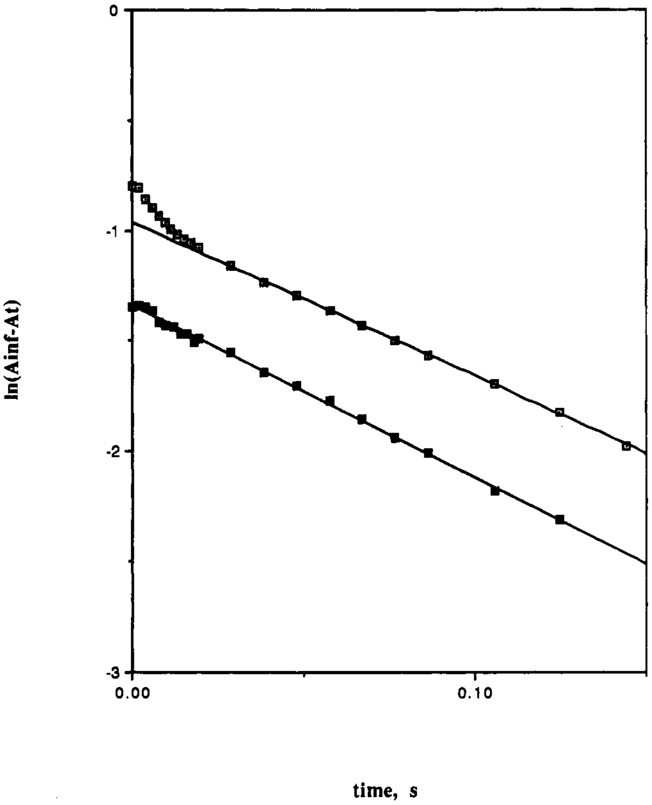

Figure 2. Kinetic traces for the formation of $MoO(O_2)_2(C_2O_4)^{2-}$ obtained at 320 (open squares) and 295 nm (solid squares). Conditions: $[Mo(VI)]_t = 3.00 \times 10^{-4}$ M, $[H_2O_2]_0 = 0.080$ M, [oxalate buffer] = 0.010 M, pH 4.0, $T = 25.0$ °C, and $I = 0.10$ M (KNO_3).

I are consistent with the rate expression given in eq 5, with $k_5 = 1.9 \times 10^3\ M^{-1}\ s^{-1}$.

$$d[MoO(OH)(O_2)_2^-]/dt = k_5[Mo(VI)][H_2O_2] \qquad (5)$$

Table II. Kinetic Results for the Oxidation of the (Thiolato)cobalt(III) Complex, the (Sulfenato)cobalt(III) Complex, and Dimethyl Sulfoxide by Hydrogen Peroxide, Oxohydroxodiperoxomolybdenum(VI), and Oxo(oxalato)diperoxomolybdenum(VI)[a]

substrate	oxidant	buffer	k, $M^{-1}\ s^{-1}$	ref
thiolato	H_2O_2	none	1.2	26–28
thiolato	$MoO(OH)(O_2)_2^-$	acetate	$(4.4 \pm 0.5) \times 10^3$	this work
thiolato	$MoO(O_2)_2(C_2O_4)^{2-}$	oxalate	$(3.9 \pm 0.1) \times 10^4$	this work
sulfenato	H_2O_2	none	3.4×10^{-4}	26–28
sulfenato	$MoO(OH)(O_2)_2^-$	acetate	13 ± 1	this work
sulfenato	$MoO(O_2)_2(C_2O_4)^{2-}$	oxalate	103 ± 5	this work
DMSO	H_2O_2	none	$<5 \times 10^{-6}$[b]	9
DMSO	$MoO(OH)(O_2)_2^-$	none	$(2.4 \pm 0.3) \times 10^{-3}$	9
DMSO	$MoO(OH)(O_2)_2^-$	acetate	$(2.7 \pm 0.1) \times 10^{-3}$	this work
DMSO	$MoO(O_2)_2(C_2O_4)^{2-}$	oxalate	$(2.3 \pm 0.1) \times 10^{-2}$	this work

[a] pH 4.0 (maintained by use of 0.010 M acetate or oxalate buffer), $I = 0.1$ M (KNO_3), and $T = 25.0$ °C. Rate constants are for the general rate law: $R = k[\text{substrate}][\text{Mo(VI) complex or } H_2O_2]$. [b] This value was determined in 1.0 M $HClO_4$, and would be expected to be considerably less at pH 4.

The kinetic traces in oxoalate-buffered solutions showed biphasic behavior at wavelengths between 300 and 340 nm, with a more rapid initial rate. This behavior was more pronounced at longer wavelengths and with higher initial concentrations of hydrogen peroxide, but disappeared at 295 nm as illustrated in Figure 2. The linear portions of the kinetic plots at $\lambda \geq 300$ nm were very similar to those obtained throughout the entire reaction at 295 nm. The results of a kinetic series monitored at 295 nm are summarized in Table I. The apparent order with respect to hydrogen peroxide is 1.66. A plot of $[H_2O_2]_{av}^2/k_{obs}$ vs $[H_2O_2]_{av}$ was linear with a slope of $(6.24 \pm 0.57) \times 10^{-3}$ M s and an intercept of $(3.78 \pm 0.44) \times 10^{-4}\ M^2$ s. The calculated values of k_{obs} for the oxalate system from these least-squares parameters are shown in parentheses in Table I. A scheme that is in the main consistent with these observations will be presented in the Discussion.

We conclude that the turnover of $MoO(OH)(O_2)_2^-$ will be very rapid in its oxygen atom transfer reactions in solutions containing excess hydrogen peroxide, since entry of the *first* peroxo ligand is rate determining. Replacement of a reacted peroxo ligand in the oxalato complex will be slower, however, and could become a problem if the rate of the oxygen atom transfer reaction is rapid.

Kinetic Studies of Oxygen Transfer Reactions of $MoO(OH)(O_2)_2^-$ and $MoO(O_2)_2(C_2O_4)^{2-}$. A sufficient excess $[H_2O_2]$ was used in either 0.010 M acetate or oxalate buffer solution to maintain the metal ion as $MoO(OH)(O_2)_2^-$ or $MoO(O_2)_2(C_2O_4)^{2-}$, respectively, throughout most of the oxygen atom transfer reactions. However, for the $(en)_2Co(SCH_2CH_2NH_2)^{2+}$–$MoO(O_2)_2(C_2O_4)^{2-}$ system, an excess of the oxidant was usually used due to the rapid reaction rate and the slower reformation rate of the Mo(VI) complex following bound-peroxide loss. Here biphasic kinetic traces were obtained if instead excess [substrate] was used, with initial rates comparable to those obtained under the former conditions followed by a markedly slower rate at times corresponding to consumption of the initial oxo(oxalato)diperoxomolybdenum(VI) complex. The experimental conditions and rate data obtained at pH 4.0 and 25 °C are summarized in Tables S1 and S2. The second-order rate constants determined for the oxidation of the thiolato complex $(en)_2Co(SCH_2CH_2NH_2)^{2+}$, the sulfenato complex $(en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+}$, and $(CH_3)_2SO$ by H_2O_2, $MoO(OH)(O_2)_2^-$, and $MoO(O_2)_2(C_2O_4)^{2-}$ are summarized in Table II. The products were the sulfenato complex, the sulfinato complex, and dimethyl sulfone, respectively. For each substrate, the rate constants stand in the order $MoO(O_2)_2(C_2O_4)^{2-} > MoO(OH)(O_2)_2^- \gg H_2O_2$.

Discussion

The most significant result obtained in this study is the high reactivity of oxo(oxalato)diperoxomolybdenum(VI) even though coordination of the sulfur atom of the substrate at the metal center is exceedingly unlikely. We conclude that direct attack at the peroxo ligand occurs, and we infer that the same pathway obtains for oxohydroxodiperoxomolybdenum(VI) as well. However, we still do not understand why the peroxo ligand in oxo diperoxo complexes of Mo(VI) and W(VI) is so strongly activated toward not only oxygen atom transfer reactions but also inner-sphere, one-electron oxidations as well.[18] The identity of the metal center is certainly a crucial factor—the peroxo ligand in titanium(IV) and zirconium(IV) peroxo complexes is strongly deactivated relative to hydrogen peroxide.[19-21]

We were somewhat surprised that the oxalato complex was more reactive than its analogue with no heteroligand. The rate constants obtained match more closely those of the neutral complex $MoO(O_2)_2$ determined previously in more acidic solutions.[8,9] It is interesting to note that the spectrum of the oxalato complex is very similar to that of $MoO(O_2)_2$, although this feature may be irrelevant with respect to their relative reactivities. We are inclined to discount any appreciable electrostatic effects, since the same relative rates are seen with the neutral substrate dimethyl sulfoxide. It seems more likely that the nature of the heteroligand has a specific effect on the reactivity of the oxodiperoxo complex, though not a large one. In practical applications the greater reactivity of $MoO(O_2)_2(C_2O_4)^{2-}$ would be mitigated by turnover problems if used as a catalyst and the requirement of oxalate buffers as well.

The kinetic results for the formation of $MoO(O_2)_2(C_2O_4)^{2-}$ from $MoO_3(C_2O_4)^{2-}$ and H_2O_2 are unusual. We can account for most of the observations by means of the simple scheme shown in eq 6 and 7. The rate expression given in eq 8 can be derived from

$$MoO_3(C_2O_4)^{2-} + H_2O_2 \rightleftharpoons MoO_2(O_2)(C_2O_4)(H_2O)^{2-} \quad \text{rapid, } K_6 \quad (6)$$

$$MoO_2(O_2)(C_2O_4)(H_2O)^{2-} + H_2O_2 \rightarrow MoO(O_2)_2(C_2O_4)^{2-} + 2H_2O \quad \text{slow, } k_7 \quad (7)$$

$$d[2{:}1]/dt = k_7K_6([Mo(VI)]_t - [2{:}1])[H_2O_2]^2/(1 + K_6[H_2O_2]) \quad (8)$$

this scheme, where 2:1 is $MoO(O_2)_2(C_2O_4)^{2-}$ and $[Mo(VI)]_t = [MoO_3(C_2O_4)^{2-}] + [MoO_2(O_2)(C_2O_4)(H_2O)^{2-}] + [2{:}1]$. Integration of eq 8 and substitution lead to the result that plots of $-\ln(A_\infty - A)$ vs time should be linear with a slope of $k_7K_6[H_2O_2]^2/(1 + K_6[H_2O_2])$. We find experimentally that such plots are linear if the reaction is monitored at 295 nm but biphasic if monitored at longer wavelengths. We suggest that absorbance due to the monoperoxomolybdenum(VI) intermediate is appreciable at the longer wavelengths, but negligible at 295 nm. It can be shown that values of $A_\infty - A_0$ should be independent of $[H_2O_2]$ only if the extinction coefficient of the monoperoxo intermediate is negligible, as we observe for the kinetic runs monitored at 295 nm. However, these considerations do not account for the biphasic behavior observed at longer wavelengths. We suggest that the rates of the reactions shown in eq 6 and 7 are not quite as cleanly separated as implied in the simplified scheme and that the biphasic feature arises early in the reaction as the equilibrium for the monoperoxo intermediate is established. This is a plausible explanation, and our data are insufficient to merit attempts to include both the forward and reverse rate constants for eq 6 in the kinetic analysis.

The simplified reaction scheme accounts for the linear plots of $[H_2O_2]_{av}^2/k_{obs}$ vs $[H_2O_2]_{av}$ for the 295-nm data, with the resulting values of $K_6 = 17 \pm 3\ M^{-1}$ and $k_7 = 160 \pm 15\ M^{-1}\ s^{-1}$. The value of K_6 is sufficiently large to allow appreciable concentrations of the monoperoxo intermediate to be formed under our experimental conditions, although we did not achieve limiting first-order conditions with respect to $[H_2O_2]$ (the observed order was 1.66).

The analysis is somewhat speculative, but fortunately other considerations fortify the proposed scheme. First, Griffith and co-workers[2] have obtained crystals of $K_2[MoO_2(O_2)(C_2O_4)(H_2O)]\cdot H_2O$, in which the anion is exactly the monoperoxo intermediate we have proposed. Importantly, they find that if the crystals are dissolved in water the complex ion is unstable with respect to formation of $MoO(O_2)_2(C_2O_4)^{2-}$ and $MoO_3(C_2O_4)^{2-}$. Second, it is very likely that the bidentate oxalato ligand in Griffith's compound is bound exclusively in the equatorial plane.[22-24] However, in the $MoO(O_2)_2(C_2O_4)^{2-}$ ion, the oxalato ligand is bonded both in the equatorial plane and in the apical position trans to the oxo ligand.[25] These structural features provide a rationale for the observation that entry of the second peroxide is rapid for the formation of $MoO(OH)(O_2)_2^-$ but much slower for forming $MoO(O_2)_2(C_2O_4)^{2-}$ from $MoO_2(O_2)(C_2O_4)(H_2O)^{2-}$. In the latter case substantial rearrangement is required before the incoming peroxo group can bond in an η^2 fashion in the equatorial plane.

A final noteworthy feature is the observation that the reaction rate for *excess* $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ with $MoO(O_2)_2(C_2O_4)^{2-}$ dramatically slowed at times corresponding roughly to consumption of the original oxalato complex. This implies that the reactivity of the monoperoxo complex is much less than that of the diperoxo complex. This feature is in harmony with our suggestion that the oxo diperoxo configuration may be a principal requirement for activation of η^2-peroxo ligands by d^0 transition-metal ions.[18]

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Supplementary Material Available: Tables of kinetic results (Tables S1 and S2) (2 pages). Ordering information is given on any current masthead page.

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