s, br, 662 m, 620 s, 544 m, 490 w, 464 w cm^{-1}. The ^1H NMR spectrum was a singlet at δ 4.11. The ^{19}F NMR spectrum showed a multiplet at ϕ 43.26 (SF), a multiplet at ϕ −86.18 (OCF_2), and overlapping triplets at ϕ −111.84 (CF_2S); $J_{CF_2S-OCF_2}$ = 5.96 Hz, J_{CF_2S-SF} = 5.86 Hz. MS (EI^+) (*m/e*, species, %): 664, $CHC(CH_2OCF_2CF_2SO_2F)_3{}^+$, 0.8; 464, $[C_3H_2(CH_2OCF_2CF_2SO_2F)_2]^+$, 22.2; 451, $[CHC(CH_2OCF_2CF_2SO_2F)_2]^+$, 11.6; 285, $[C_3H_4O_2(CH_2OCF_2CF_2SO_2F)]^+$, 8.7; 265, $[C_4H_4(CH_2OCF_2CF_2SO_2F)]^+$, 27.4; 213, $FSO_2CF_2CF_2OCH_2{}^+$, 30.3; 199, $FSO_2CF_2CF_2O^+$, 3.9; 183, $FSO_2CF_2CF_2{}^+$, 2.8; 133, $FSO_2CF_2{}^+$, 4.1; 85, $C_4H_5O_2{}^+$, 88.9; 83, SO_2F^+, 2.6; 67, SOF^+, 100. Anal. Calcd for $C_{13}H_8F_{20}O_{12}S_4$: C, 18.06; H, 0.93; F, 43.98. Found: C, 18.31; H, 1.02; F, 43.0.

Preparation of $F^GSO_2CF_2{}^ECF_2{}^DOCH_2{}^CCF_2{}^BCF_2{}^ACF_2{}^BCH_2{}^COCF_2{}^DCF_2{}^ESO_2F^G$. This compound was prepared in a similar manner from $FSO_2CF_2C(O)OCH_2CF_2CF_2CF_2CH_2OC(O)CF_2SO_2F$ and SF_4/HF. Tye yield was 59.5%. It is a colorless liquid. IR: 2978 w, 1455 s, 1410 w, 1327 s, 1240 s, 1198 s, 1170–1125 s, br, 1067 w, 1032 m, 1017 w, 970 m, 891 w, 800 s, 747 w, 723 w, 658 w, 610 s, 532 w cm^{-1}. ^1H NMR: δ 4.51 (CH_2, tr). ^{19}F NMR: ϕ 44.59 (G, tr of tr), −85.02 (D, mult), −111.49 (E, d of tr), −120.33 (B, mult), −125.16 (A, mult); J_{B-C} = 12.94 Hz, J_{E-G} = 5.74 Hz, J_{D-G} = 5.49 Hz, J_{D-E} = 5.01 Hz. MS (CI^+): 557, $M - F^+$, 6.3; 473, $CF_2CF_2OCHCFCF_2CF_2CH_2OCF_2CF_2SO_2F^+$, 13.3; 377, $CH_2CF_2CF_2CF_2CH_2OCF_2CF_2SO_2F^+$, 16.4; 357, $CHCFCF_2CF_2CH_2OCF_2CF_2SO_2F^+$, 15.3; 213, $CH_2OCF_2CF_2SO_2F^+$, 8.4; 183, $CF_2CF_2SO_2F^+$, 5.7; 167, $CF_2CF_2SOF^+$, 13.9; 133, $CF_2SO_2F^+$, 13.3; 83, SO_2F^+, 20.7; 67, SOF^+, 100. Anal. Calcd for $C_9H_4F_{16}O_6S_2$: C, 18.75; H, 0.69; F, 52.78. Found: C, 18.99; H, 0.80; F, 52.4.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to NSF Grant CHE-8404974, to AFOSR Grant 82-0247, and to GRI for support of this work.

Registry No. $CF_3CH_2O(CF_2)_2SO_2F$, 109012-55-7; $CF_3CF_2CH_2O(CF_2)_2SO_2F$, 109012-56-8; $CF_3(CF_2)_2CH_2O(CF_2)_2SO_2F$, 109012-57-9; $CF_3CH(CH_3)O(CF_2)_2SO_2F$, 109012-58-0; $(CF_3)_2CHO(CF_2)_2SO_2F$, 109012-59-1; $CH_3C(CF_2)_2O(CF_2)_2SO_2F$, 109012-60-4; $EtO(CF_2)_2SO_2F$, 84506-53-6; $CF_3CH_2O(CF_2)_2SO_2OCH_2CF_3$, 109012-61-5; $CF_3CH_2O(CF_2)_2SO_2NMe_2$, 109012-62-6; $C(CH_2O(CF_2)_2SO_2F)_4$, 109012-63-7; $FSO_2(CF_2)_2OCH_2(CF_2)_3O(CF_2)_2SO_2F$, 109012-64-8; SF_4, 7783-60-0; HF, 7664-39-3; $CF_3CH_2O_2CCF_2SO_2F$, 108344-43-0; $CF_3CF_2CH_2O_2CCF_2SO_2F$, 108795-92-2; $CF_3(CF_2)_2CH_2O_2CCF_2SO_2F$, 108795-93-3; $EtO_2CCF_2SO_2F$, 756-21-8; $(CF_3)_2CHO_2CCF_2SO_2F$, 108795-89-7; $CF_3CH(CH_3)O_2CCF_2SO_2F$, 108795-90-0; $MeC(CF_3)_2O_2CCF_2SO_2F$, 108795-91-1; $CF_2(CF_2CH_2O_2CCF_2SO_2F)_2$, 108815-93-6; $C(CH_2O_2CCF_2SO_2F)_4$, 108795-95-5; $LiOCH_2CF_3$, 69163-14-0.

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

Equilibrium and Kinetic Studies of the Peroxo Complex of Molybdenum(VI) in Acidic Perchlorate Solution

John D. Lydon, Lisa M. Schwane, and Richard C. Thompson*

Received December 30, 1986

The principal equilibrium between molybdenum(VI) and hydrogen peroxide in acidic perchlorate solution is $HMoO_3{}^+ + 2H_2O_2 = MoO(O_2)_2 + H^+ + 2H_2O$. The value of the formation constant is $(9.4 \pm 0.6) \times 10^6\ M^{-1}$ at 25 °C over the range $[HClO_4] = 0.10–1.00$ M at $I = 1.00$ M ($LiClO_4$); $\Delta H_f{}^\circ = -12 \pm 1$ kcal/mol and $\Delta S_f{}^\circ = -9 \pm 3$ cal/(K mol). Oxodiperoxomolybdenum(VI) shows an absorption maximum at 328 nm with an extinction coefficient of 1040 $M^{-1}\ cm^{-1}$. On the basis of spectral variations at $[HClO_4] \leq 0.10$ M, oxodiperoxomolybdenum(VI) is proposed to hydrolyze according to $MoO(O_2)_2 + H_2O = MoO(OH)(O_2)_2{}^- + H^+$, with $K_a = 0.014$ M at 25 °C. The rapid formation of $MoO(O_2)_2$ was studied by stopped-flow procedures. The rate expression was determined to be $d[MoO(O_2)_2]/dt = k_{forward}[HMoO_3{}^+][H_2O_2]^2 - k_{reverse}[MoO(O_2)_2][H^+]$. At 25 °C and $I = 1.0$ M, $k_{forward} = (2.3 \pm 0.4) \times 10^6\ M^{-2}\ s^{-1} + ((1.0 \pm 0.1) \times 10^6\ M^{-1}\ s^{-1})/[H^+]$. The dissociation rates for $MoO(O_2)_2$ were measured in the presence of sulfur(IV), a very rapid reductant toward H_2O_2. The rate expression is proposed to be $-d[MoO(O_2)_2]/dt = k_{reverse}[MoO(O_2)_2][H^+] + k_{S(IV)}[MoO(O_2)_2][S(IV)]$; at 25 °C and $I = 1.00$ M, $k_{reverse} = 0.31 \pm 0.02\ M^{-1}\ s^{-1} + (0.15 \pm 0.01\ s^{-1})/[H^+]$. A reaction scheme is proposed in which entry and loss of the second peroxide ligand is rate-determining. The results of concentration-jump experiments are in accord with the reaction scheme. The results are compared with those obtained by other investigators for oxodiperoxochromium(VI). Diperoxo complexes of d^0 transition-metal ions appear to be much more reactive toward substrates than the monoperoxo complexes. Results of preliminary studies of the peroxo complex(es) of tungsten(VI) are presented.

Introduction

Molybdate is commonly used as a catalyst in the iodometric determination of hydrogen peroxide. A detailed kinetic study of this system in acidic solution has been reported.[1] It was proposed that a diperoxo complex of molybdenum(VI) was the reactive species toward iodide. Peroxo complexes of molybdenum(VI) have been used as oxidants for organic substrates[2] and are implicated as intermediates in the catalyzed epoxidation of olefins by alkyl hydroperoxides.[3-8] A number of crystal structures of peroxomolybdenum(VI) complexes have been reported,[9] and solution studies of the complexes have been reviewed.[10]

We have studied the redox chemistry of peroxo complexes of several d^0 transition-metal ions and compared the results to the corresponding reactions of hydrogen peroxide.[11-16] An important objective of this work is to increase our understanding of how metal ions modify the reactivity of peroxide. The advantage in using d^0 transition-metal ions is their ability to rapidly form peroxo complexes with large formation constants. We have recently turned our attention to molybdenum(VI) and are finding that its peroxo complex is markedly more reactive than hydrogen peroxide

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Table I. Experimental Results for the Conditional Ultraviolet Spectra and Dimerization Constants of Molybdenum(VI)[a]

			$10^{-3}\epsilon$,[c] M^{-1} cm^{-1}				
T, °C	$[H^+]$, M	K_D,[b] M^{-1}	240 nm	246 nm	250 nm	260 nm	270 nm
25.0	1.00	64 ± 2	1.96, 15.0	1.54, 15.4	1.37, 15.0	1.10, 11.4	0.876, 8.01
25.0	0.50	48 ± 2	2.16, 17.8	1.66, 18.7	1.42, 18.2	1.12, 14.1	0.893, 9.71
25.0	0.10	25 ± 4	2.94, 26.5	2.02, 26.7	1.57, 26.1	1.09, 25.6	
17.0	0.50	65 ± 2	2.15, 17.1		1.40, 17.3	1.11, 13.3	
10.0	0.50	77 ± 2	2.17, 17.0		1.41, 17.3	1.09, 13.2	

[a] The absorbance of at least 10 different molybdenum(VI) solutions was measured at each wavelength, temperature, and $[HClO_4]$ at an ionic strength of 1.0 M (maintained by use of $LiClO_4$). [b] Values were determined at each wavelength by a nonlinear least-squares adjustment of the individual data sets to eq 1. Values listed are the average of those determined at the wavelengths shown; K_D is a conditional dimerization constant defined in eq 1. [c] Entries are ϵ_M, ϵ_D as determined by use of eq 1.

toward a number of simple substrates.[17] A prerequisite to these studies is a detailed knowledge of the equilibrium parameters associated with the interaction of molybdenum(VI) and hydrogen peroxide in the acidic aqueous solutions used for the redox studies. Molybdenum(VI) exhibits complex chemistry in this medium. Neutral and protonated monomeric forms formulated as MoO_3 and $HMoO_3^+$ (with coordinated water molecules omitted) predominate at low concentrations of Mo(VI). Several dimeric forms are of importance at Mo(VI) concentrations greater than approximately 5×10^{-4} M over the acidity range 0.10–1.0 M.[18-20]

In this paper we report the results of spectrophotometric studies of the equilibrium between hydrogen peroxide and molybdenum(VI) in acidic perchlorate solution. In addition, we have measured the kinetics of formation and dissociation of the peroxo complex by use of the stopped-flow procedure.

Experimental Section

Reagents. The source of the molybdenum(VI) was either Fisher Certified $Na_2MoO_4 \cdot 2H_2O$ or Johnson Matthey "Puratronic" $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. Both reagents yielded identical experimental results. Fisher Certified $Na_2WO_4 \cdot 2H_2O$ was used in the tungsten(VI) studies. Solutions of H_2O_2, VO_2ClO_4, and $LiClO_4$ were prepared by methods described previously.[11,13]

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. The molybdenum(VI) salts were assayed gravimetrically as $PbMoO_4$ or $MoO_2(C_9H_6ON)_2$ by use of standard procedures.[21,22] The results of the two methods were in good agreement and showed $Na_2MoO_4 \cdot 2H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ to be 99.5 and 103.1% pure, respectively. Our batch of the latter salt apparently contains less than the stated waters of hydration. In our hands the titrimetric method described by Stark[23] was unsatisfactory. $Na_2WO_4 \cdot 2H_2O$ was assumed to be pure.

Sulfur(IV) solutions for the kinetic experiments were prepared by dissolving weighed amounts of Na_2SO_3 in the desired acid solution at 2 °C. The resulting solution was promptly drawn into a glass syringe to minimize volatilization of SO_2.

The analyses of the H_2O_2, VO_2ClO_4, and $LiClO_4$ solutions have been described previously.[11]

Determination of the Conditional Dimerization Constants of Molybdenum(VI). Cruywagen and co-workers have determined dimerization constants of molybdenum(VI) by a spectrophotometric procedure that is based on different spectra for the monomeric and dimeric forms in the ultraviolet region.[19] We have extended their studies into our range of experimental conditions by use of the same methodology. Equilibrated solutions of molybdenum(VI) in the desired acid at an ionic strength of 1.0 M, maintained with use of $LiClO_4$, were assayed spectrophotometrically from 240 to 270 nm. The observed extinction coefficients, based on the total [Mo(VI)], were analyzed by means of eq 1.

$$\epsilon_{obsd} = (\epsilon_M + \epsilon_D K_D c_M)/(1 + 2K_D c_M) \qquad (1)$$

ϵ_M = apparent extinction coefficient of all monomeric forms

ϵ_D = apparent extinction coefficient of all dimeric forms

c_M = concentration of all monomeric species

$$c_M = \{-1 + (1 + 8K_D[\mathrm{Mo(VI)}]_T)^{1/2}\}/4K_D$$

$$2\mathrm{Mo(VI)}_{monomer} = \mathrm{Mo(VI)}_{dimer} \quad K_D$$

This method is valid at a given acidity and temperature. The absorbances of at least 10 molybdenum(VI) solutions ($[\mathrm{Mo(VI)}]_T$ = $(0.0291\text{–}7.39) \times 10^{-3}$ M) were measured in each determination. The individual data sets were fit to eq 1 by a nonlinear least-squares analysis with ϵ_M, ϵ_D, and K_D as adjustable parameters. The method worked very well; the results are summarized in Table I.

Equilibrium Studies. In most of the experiments molybdenum(VI) solutions were titrated with hydrogen peroxide at a constant temperature (±0.1 °C). Both solutions contained identical concentrations of $HClO_4$ at an ionic strength of 1.0 M maintained by use of $LiClO_4$. The titrations were monitored at 328 nm, an absorption maximum for peroxo complex(es) of molybdenum(VI) with an extinction coefficient of 1040 M^{-1} cm^{-1} at $[H^+] \geq 0.20$ M and 25 °C (vide infra). The data were successfully analyzed by assuming that only a diperoxomolybdenum(VI) complex (2:1) was formed. The concentrations of 2:1, H_2O_2, $\mathrm{Mo(VI)}_{monomer}$, and $\mathrm{Mo(VI)}_{dimer}$ at each point in the titrations were calculated by use of eq 2–4, where K_D is defined in eq 1.

$$[2{:}1] = \{A_{obsd} - \epsilon_1 l[\mathrm{Mo(VI)}]_T\}/l(\epsilon_2 - \epsilon_1) \qquad (2)$$

A_{obsd} = observed absorbance

ϵ_1 = extinction coefficient of all forms of uncomplexed Mo(VI)

l = path length

ϵ_2 = extinction coefficient of 2:1

$$[H_2O_2] = [H_2O_2]_T - 2[2{:}1] \qquad (3)$$

$$[\mathrm{Mo(VI)}]_{monomer} = \{-1 + (1 + 8K_D\mathrm{Mo_T})^{1/2}\}/4K_D \qquad (4)$$

$$\mathrm{Mo_T} = [\mathrm{Mo(VI)}]_T - [2{:}1] = [\mathrm{Mo(VI)}]_{monomer} + 2[\mathrm{Mo(VI)}]_{dimer}$$

The extinction coefficients for monomeric and dimeric forms of molybdenum(VI) are nearly equal (on a per Mo(VI) basis) at 328 nm, and a value of 42 M^{-1} cm^{-1} was determined for ϵ_1.

In some experiments equilibrated solutions of Mo(VI) and H_2O_2 in 1.00 M $HClO_4$ were titrated with a solution of VO_2ClO_4 at the same acidity. The titrations were monitored at 455 nm, an absorption maximum for $VO(O_2)^+$. Molybdenum(VI) and peroxomolybdenum(VI) complex(es) are essentially transparent at this wavelength. The concentrations of $VO(O_2)^+$, H_2O_2, 2:1, and $\mathrm{Mo(VI)}_{monomer}$ at each point in the titrations were calculated by use of eq 4–7, where K_V is the formation constant for $VO(O_2)^+$.

$$[VO(O_2)^+] = \{A_{obsd} - l\epsilon_{VO_2^+}[V(V)]_T\}/l(\epsilon_{VO(O_2)^+} - \epsilon_{VO_2^+}) \qquad (5)$$

$$[H_2O_2] = [VO(O_2)^+]/\{K_V([V(V)]_T - [VO(O_2)^+])\} \qquad (6)$$

$$[2{:}1] = \{[H_2O_2]_T - [VO(O_2)^+] - [H_2O_2]\}/2 \qquad (7)$$

Values of $K_V = 3.3 \times 10^4$ M^{-1}, $\epsilon_{VO(O_2)^+} = 282$ M^{-1} cm^{-1}, and $\epsilon_{VO_2^+} = 3.2$ M^{-1} cm^{-1} were determined in 1.00 M $HClO_4$ at 25 °C and are in excellent agreement with published values.[12,24,25]

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Table II. Variation of the Extinction Coefficient of Diperoxomolybdenum(VI) with Acidity at 25 °C[a]

	ϵ,[b] M^{-1} cm^{-1}		
$[H^+]$, M	310 nm	328 nm	370 nm
1.00	917 (914)	1040 (1039)	600 (599)
0.502	909 (915)	1035 (1036)	594 (593)
0.103	932 (927)	1025 (1019)	558 (555)
0.103	930 (927)	1020 (1019)	555 (555)
0.0932	933 (928)	1015 (1017)	551 (550)
0.0833	925 (930)	1010 (1014)	542 (545)
0.0733	931 (932)	1010 (1011)	536 (538)
0.0634	938 (934)	1010 (1007)	530 (529)
0.0534	931 (938)	998 (1002)	514 (518)
0.0434	936 (942)	992 (995)	501 (503)
0.0335	947 (948)	983 (986)	480 (482)
0.0235	962 (958)	975 (971)	453 (448)
0.0136	977 (975)	948 (946)	393 (391)
0.0036	1010 (1013)	897 (894)	265 (267)
0.0036	1015 (1013)	897 (894)	268 (267)

[a] The experimental conditions were $[Mo(VI)]_T = 2.69 \times 10^{-4}$ M, $[H_2O_2]_T = 0.30$ M, and $I = 1.0$ M, maintained by use of $LiClO_4$. [b] The observed extinction coefficient at each wavelength and acidity is listed first. The calculated values, from the least-squares-determined parameters for eq 8, are listed in parentheses.

Table III. Results of a Typical Spectrophotometric Titration of an Acidic Molybdenum(VI) Solution with Hydrogen Peroxide[a]

$10^4 \times$ $[Mo(VI)]_T$, M	$10^4 \times$ $[H_2O_2]_T$, M	$10^4 \times$ $[2:1]_{eq}$,[b] M	$10^4 \times$ $[H_2O_2]_{eq}$,[c] M	$10^4 \times$ $[Mo(VI)]_{m,eq}$,[d] M	$10^{-6} \times$ $K_{2:1}$,[e] M^{-2}
3.26	0.487	0.048	0.391	3.09	10.2
3.25	0.969	0.134	0.701	3.00	9.07
3.23	1.45	0.240	0.967	2.88	8.89
3.22	1.92	0.351	1.22	2.77	8.54
3.20	2.39	0.472	1.44	2.64	8.56
3.19	2.85	0.590	1.67	2.51	8.40
3.17	3.31	0.713	1.88	2.38	8.43
3.16	3.77	0.829	2.11	2.26	8.27
3.14	4.22	0.955	2.31	2.13	8.44
3.13	4.66	1.07	2.52	2.00	8.42
3.10	5.54	1.29	2.96	1.77	8.33
3.07	6.41	1.49	3.43	1.55	8.19
3.05	6.83	1.59	3.65	1.44	8.30
3.04	7.25	1.68	3.89	1.33	8.30
3.03	7.67	1.77	4.14	1.24	8.32
3.01	8.09	1.85	4.39	1.15	8.34
3.00	8.50	1.92	4.65	1.06	8.39
2.98	8.90	1.99	4.92	0.98	8.43
2.96	9.71	2.12	5.48	0.83	8.45
2.93	10.5	2.22	6.06	0.71	8.51
2.91	11.3	2.30	6.67	0.60	8.66
2.88	12.0	2.37	7.29	0.51	8.76
2.86	12.8	2.43	7.93	0.43	9.01

[a] A solution containing 3.28×10^{-4} M Mo(VI) in 1.00 M $HClO_4$ was titrated with 9.88×10^{-3} M H_2O_2 in 1.00 M $HClO_4$ at 25.0 °C. The titration was monitored spectrophotometrically at 328 nm. [b] Values were calculated by use of eq 2. [c] Values were calculated by use of eq 3. [d] Entries are the equilibrium concentrations of monomeric forms of uncomplexed Mo(VI) and were calculated by use of eq 4. [e] The formation constant $K_{2:1}$ is defined in eq 13.

The observed extinction coefficient of diperoxomolybdenum(VI), based on the total [Mo(VI)], varied with $[H^+]$ at low acidities. A 1000-fold excess of H_2O_2 was used in these experiments to ensure >99% complexation of Mo(VI); corrections for the absorbance due to H_2O_2 were applied. The experimental data are summarized in Table II and were analyzed by use of eq 8. Calculated values of ϵ_{obsd} from the

$$\epsilon_{obsd} = \{\epsilon_{MoO(O_2)_2}[H^+] + \epsilon_{MoO(OH)(O_2)_2^-}K_a\}/(K_a + [H^+]) \qquad (8)$$

least-squares-determined values of K_a and the two extinction coefficients (vide infra) are listed in parenthese in Table II.

While sodium tungstate dihydrate is soluble in water, it is only sparingly so in molar perchloric acid. The acidic solutions ($[W(VI)] \leq 10^{-4}$ M) are metastable with respect to precipitation of hydrous tungsten trioxide. Tungsten(VI) is soluble in perchloric acid that contains a substantial excess of hydrogen peroxide, and these solutions were reasonable stable. We were able to determine an absorption maximum at 256 nm for the peroxo complex(es) of tungsten(VI). The absorbances of 1.01×10^{-4} and 5.04×10^{-4} M W(VI) solutions in 1.00 M $HClO_4$ reached constant values (after correction for absorbance due to H_2O_2) over a range of $[H_2O_2]/[W(VI)]$ ratios from 150 to 400. The extinction coefficient, based on total [W(VI)], was 1160 ± 20 M^{-1} cm^{-1} at 25 °C and was independent of acidity from 0.15 to 1.00 M. The plateau region occurred at only slightly greater $[H_2O_2]$/[metal ion] ratios than for the molybdenum(VI) system. This result suggests that the formation constant for presumably diperoxotungsten(VI) is similar to that for diperoxomolybdenum(VI). However, attempts to determine the formation constant under conditions where a measurable uncomplexed [W(VI)] was present were frustrated by slow absorbance changes that persisted for many hours. Similar difficulties were encountered in attempts to determine the extinction coefficient of W(VI) at 256 nm by use of $(0.30-1.01) \times 10^{-4}$ M W(VI) in 1.00 M $HClO_4$.

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. Twelve to twenty absorbance-time data points were analyzed for each trace. The temperature control was ±0.1 °C.

Results

Molybdenum(VI) Speciation in Acidic Solution. Several molybdenum(VI) species are present in significant concentrations under our experimental conditions. Careful work by Cruywagen and co-workers[18,20] has shown that the protonation and dimerization equilibria given in eq 9–12 are relevant. Coordinated water molecules are omitted in the formulations. We have used Cruywagen's value of 7.08 M^{-1}, determined at 25 °C and $I = 1.0$ M, for K_1. Corresponding values of 6.37 and 5.77 M^{-1} at 17 and 10 °C, respectively, and I = 1.0 M were estimated from his temperature-dependent studies measured at an ionic strength of 3.0 M. The dimerization of molybdenum(VI) is slight under our experimental conditions, but unfortunately the literature values for K_2, K_3, and K_4 were determined under the conditions 25 °C, $I = 3.0$ M, and $[H^+] \geq 0.50$ M. We therefore determined values of K_D as defined in eq 1 at several acidities and temperatures at $I = 1.0$ M (see Experimental Section and Table I).

$$MoO_3 + H^+ = HMoO_3^+ \quad K_1 \qquad (9)$$

$$2HMoO_3^+ = H_2Mo_2O_6^{2+} \quad K_2 \qquad (10)$$

$$HMo_2O_6^+ + H^+ = H_2Mo_2O_6^{2+} \quad K_3 \qquad (11)$$

$$H_2Mo_2O_6^{2+} + H^+ = H_3Mo_2O_6^{3+} \quad K_4 \qquad (12)$$

Equilibrium Studies of the Peroxo Complex(es) of Molybdenum(VI) in Acidic Solution. Acidic solutions containing molybdenum(VI) and excess hydrogen peroxide show an absorption maximum at 328 nm. The absorbance at this wavelength reaches a constant value with a sufficient excess of hydrogen peroxide for a given concentration of molybdenum(VI), typically (1.00–4.00) × 10^{-4} M. The extinction coefficient determined in the plateau region is independent of acidity over the ranges 0.20–1.00 M $HClO_4$ at $I = 1.00$ M ($LiClO_4$) and 1.00–3.00 M $HClO_4$ at $I = 3.00$ M. The value of ϵ based on the total [Mo(VI)] is 1040 M^{-1} cm^{-1} at 25 °C. This value has been determined numerous times over the course of this study and is reproducible to ±1%.

The majority of the equilibrium data was obtained from careful spectrophotometric titrations of molybdenum(VI) solutions with hydrogen peroxide monitored at 328 nm. Individual data sets were in excellent agreement with the assumption that only a diperoxomolybdenum(VI) complex was formed with an extinction coefficient of 1040 M^{-1} cm^{-1}. The results from a representative data set are summarized in Table III. The formation constant $K_{2:1}$ is defined by eq 13. Minor corrections for the absorbance

$$Mo(VI)_{monomer} + 2H_2O_2 = Mo(VI)\cdot 2H_2O_2 \quad K_{2:1} \qquad (13)$$

due to the uncomplexed molybdenum(VI) were applied (see Experimental Section).

Values of $K_{2:1}$ were accepted over the conditions $0.10[Mo(VI)]_T \leq [2:1]_{eq} \leq 0.90[Mo(VI)]_T$ and $[MoO_3]_{eq} \geq 0.03[Mo(VI)]_T$. These criteria cause the first three and last three data points in

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Table IV. Results of Spectrophotometric Titrations of Acidic Molybdenum(VI) Solutions with Hydrogen Peroxide[a]

T, °C	$[HClO_4]$, M	$10^4[Mo(VI)]_{T,0}$	$10^{-7}K_{2:1}$,[b] M^{-2}	$10^{-7}\boldsymbol{K}_{2:1}$,[c] M^{-1}	$10^{-7}K_{MoO(O_2)_2}$,[d] M^{-1}
25.0	1.00	5.16	0.753 ± 0.009	0.859 ± 0.010	
25.0	1.00	3.28	0.839 ± 0.007	0.958 ± 0.008	
25.0	1.00	2.05	0.833 ± 0.012	0.951 ± 0.014	
			0.80 ± 0.04 (av)	0.91 ± 0.05 (av)	0.90 ± 0.05 (av)
25.0	0.75	5.15	0.899 ± 0.016	0.801 ± 0.014	
25.0	0.75	3.32	0.979 ± 0.011	0.873 ± 0.010	
25.0	0.75	1.44	1.10 ± 0.04	0.980 ± 0.004	
			0.97 ± 0.06 (av)	0.86 ± 0.05 (av)	0.84 ± 0.05 (av)
25.0	0.50	5.15	1.41 ± 0.02	0.904 ± 0.013	
25.0	0.50	3.32	1.48 ± 0.04	0.949 ± 0.026	
25.0	0.50	1.45	1.61 ± 0.05	1.03 ± 0.03	
			1.5 ± 0.1 (av)	0.96 ± 0.06 (av)	0.93 ± 0.06 (av)
25.0	0.25	5.16	2.47 ± 0.04	0.966 ± 0.016	
25.0	0.25	3.32	2.63 ± 0.04	1.03 ± 0.02	
25.0	0.25	1.45	2.87 ± 0.05	1.12 ± 0.02	
			2.6 ± 0.2 (av)	1.0 ± 0.1 (av)	0.95 ± 0.07 (av)
25.0	0.10	5.16	4.72 ± 0.12	1.14 ± 0.03	
25.0	0.10	3.32	4.88 ± 0.08	1.18 ± 0.02	
25.0	0.10	1.45	5.04 ± 0.13	1.22 ± 0.03	
			4.9 ± 0.1 (av)	1.2 ± 0.1 (av)	1.1 ± 0.1 (av)
17.0	1.00	3.30	1.41 ± 0.01	1.63 ± 0.01	
17.0	0.50	3.32	2.37 ± 0.04	1.56 ± 0.03	
17.0	0.10	3.32	6.60 ± 0.31	1.70 ± 0.08	
10.0	1.00	3.30	2.48 ± 0.03	2.91 ± 0.04	
10.0	0.50	3.32	4.43 ± 0.10	2.98 ± 0.07	
10.0	0.10	3.32	10.8 ± 0.1	2.95 ± 0.03	

[a] The titrations were monitored at 328 nm. The useful range of equilibrium concentrations were [2:1] = (0.17–3.92) × 10^{-4} M, $[H_2O_2]$ = (0.41–6.67) × 10^{-4} M, $[Mo(VI)]_{monomer}$ = (0.14–4.30) × 10^{-4} M, and $[MoO_3]$ = (0.09–2.52) × 10^{-4} M. [b] Defined by eq 13. [c] Defined by eq 14; $\boldsymbol{K}_{2:1} = (1 + K_1[H^+])K_{2:1}/K_1$. [d] Defined by eq 16; $K_{MoO(O_2)_2} = \boldsymbol{K}_{2:1}\{[H^+]/([H^+] + K_a)\}$.

Table III to be rejected, with the resulting value of $K_{2:1} = (8.39 \pm 0.07) \times 10^6$ M^{-2}. We have assumed in eq 13 that dimeric forms of molybdenum(VI) are not involved in the formation of diperoxomolybdenum(VI). The total equilibrium concentrations of these dimeric species are always less, and usually much less, than 2.3% of the total [Mo(VI)] over the experimental conditions where values of $K_{2:1}$ were determined.

The results of the spectrophotometric titrations are summarized in Table IV. The values of $K_{2:1}$ listed in the fourth column are seen to increase with decreasing acidity. This variation is largely eliminated if we assume that diperoxomolybdenum(VI) is a neutral species, which we may formulate as $MoO(O_2)_2$. Values of $\boldsymbol{K}_{2:1}$, as defined in eq 14 in terms of the predominant molybdenum(VI) monomer, $HMoO_3^+$, are listed in the fifth column of Table IV.

$$HMoO_3^+ + 2H_2O_2 = MoO(O_2)_2 + H^+ + 2H_2O \quad \boldsymbol{K}_{2:1} \qquad (14)$$

The extinction coefficients of oxodiperoxomolybdenum(VI) from 260 to 360 nm were invariant with the concentration of the complex over the range 5.47 × 10^{-5} to 1.00 × 10^{-2} M in 1.00 M $HClO_4$ at 25 °C. The ratio $[H_2O_2]_T/[Mo(VI)]_T$ was ≥150 in these experiments to ensure >99% complexation of the molybdenum(VI); corrections for absorbance due to hydrogen peroxide were applied.

A significant variation in the absorption spectra of oxodiperoxymolybdenum(VI) with acidity was observed over the range of 0.0036–0.10 M H^+ at I = 1.00 M ($LiClO_4$) and 25 °C. The concentrations of molybdenum(VI) and hydrogen peroxide were 2.69 × 10^{-4} and 0.300 M, respectively. The raw experimental data are summarized in Table II in the Experimental Section and were analyzed in accordance with eq 15. The resulting values

$$MoO(O_2)_2 + H_2O = MoO(OH)(O_2)_2^- + H^+ \quad K_a \qquad (15)$$

of K_a (M), $\epsilon_{MoO(O_2)_2}$ (M^{-1} cm^{-1}), and $\epsilon_{MoO(OH)(O_2)_2^-}$ (M^{-1} cm^{-1}) were respectively 0.013 ± 0.003, 912 ± 3, and 1040 ± 8 at 310 nm, 0.015 ± 0.001, 1041 ± 2, and 858 ± 5 at 328 nm, and $0.013_5 \pm 0.000_4$, 604 ± 2, and 177 ± 4 at 370 nm. The most reliable value of K_a was determined at 370 nm, where the spectral difference between $MoO(O_2)_2$ and $MoO(OH)(O_2)_2^-$ is the greatest.

The values of $\boldsymbol{K}_{2:1}$ may be corrected for hydrolysis of oxodiperoxomolybdenum(VI) by use of eq 16, although the effect is small over the acidity range used in the equilibrium studies. The

$$K_{MoO(O_2)_2} = \boldsymbol{K}_{2:1}[H^+]/([H^+] + K_a) \qquad (16)$$

corresponding values of $K_{MoO(O_2)_2}$ at 25 °C are listed in the last column of Table IV. There is little if any variation of this formation constant with acidity, at least within the experimental uncertainty.

A competition method was utilized to further test the conclusion that only a diperoxomolybdenum(VI) complex need be considered under our experimental conditions. Appropriate solutions containing molybdenum(VI) and hydrogen peroxide in 1.00 M $HClO_4$ at 25 °C were titrated with vanadium(V), VO_2^+. The titrations were monitored spectrophotometrically at 455 nm, an absorption maximum for $VO(O_2)^+$. Small corrections were applied for absorbance due to VO_2^+; H_2O_2, Mo(VI), and peroxo complex(es) of molybdenum(VI) are transparent at this wavelength. The equilibrium concentration of H_2O_2 at each point in the titration was determined by use of the well-established equilibrium given in eq 17.[12,24,25] The data were first analyzed under the assumption

$$VO_2^+ + H_2O_2 = VO(O_2)^+ + H_2O \quad K_V \qquad (17)$$

that only a diperoxomolybdenum(VI) complex was formed. It proved difficult to identify experimental conditions where the criteria $0.10[Mo(VI)]_T \le [2:1]_{eq} \le 0.90[Mo(VI)]_T$ and $0.10[V(V)]_T \le [VO(O_2)^+]_{eq} \le 0.90[V(V)]_T$ were fulfilled. However, three titration conditions were found that yielded a total of 28 usable data points. The concentration ranges were $[Mo(VI)]_T$ = (3.84–5.81) × 10^{-4} M, $[H_2O_2]_T$ = (7.24–10.6) × 10^{-4} M, and $[V(V)]_T$ = (3.27–10.4) × 10^{-4} M. The average value of $K_{2:1}$ was (8.25 ± 0.52) × 10^6 M^{-2}, in excellent agreement with the values listed in Table IV at the same acidity and temperature.

We tested a slightly expanded model, summarized in eq 18 and 19, using the same experimental data. This model has been

$$Mo(VI)_{monomer} + H_2O_2 = Mo(VI)\cdot H_2O_2 \quad K_{1:1} \qquad (18)$$

$$Mo(VI)_{monomer} + 2H_2O_2 = Mo(VI)\cdot 2H_2O_2 \quad K_{2:1} \qquad (19)$$

Table V. Kinetic Results for the Formation of Diperoxomolybdenum(VI)[a]

T, °C	$[HClO_4]$, M	no. of expts	$10^{-6}k_f$,[b] $M^{-2}\ s^{-1}$
25.0	1.00	10	2.9 ± 0.1
25.0	0.60	6	2.8 ± 0.1
25.0	0.40	6	3.9 ± 0.1
25.0	0.20	7	5.2 ± 0.1
25.0	0.10	8	5.8 ± 0.1
17.0	0.40	8	2.6 ± 0.1
10.0	0.40	8	1.9 ± 0.1

[a] Monitored at 328 nm. Initial concentrations were [Mo(VI)] = (0.30–1.03) × 10^{-4} M and $[H_2O_2]$ = (0.30–3.00) × 10^{-3} M. The ionic strength was maintained at 1.0 M with use of lithium perchlorate. [b] Values were determined by a least-squares adjustment of the pseudo-first-order rate constants to eq 21.

proposed by Smith and Kilford and is based on kinetic results for the molybdate-catalyzed oxidation of iodide ion by hydrogen peroxide.[1] The calculated values of $K_{1:1}$ and $K_{2:1}$ are −132 ± 208 M^{-1} and (7.9 ± 0.4) × $10^6\ M^{-2}$, respectively. The limited dimerization of molybdenum(VI) was neglected in the analysis, since the already cumbersome calculations would become virtually unmanageable. We justify this approximation by the observation that if the same simplification is applied to the diperoxomolybdenum(VI)-only model discussed above, the calculated value of $K_{2:1}$ is (7.87 ± 0.48) × $10^6\ M^{-2}$. This result is sensibly the same as determined in the more complete treatment.

We conclude that while there may be trace amounts of peroxomolybdenum(VI) complexes other than the diperoxo complex, there is no justification for invoking them that can be derived from our equilibrium data alone.

Kinetic Results for the Formation of Diperoxomolybdenum(VI). The rapid rate of formation of diperoxomolybdenum(VI) was monitored at its 328-nm absorption maximum by stopped-flow procedures. Plots of $-\ln [A_\infty - A]$ vs. time were linear over 3 half-lives under the initial conditions $[H_2O_2]/[Mo(VI)] \geq 10$ in 0.10–1.00 M $HClO_4$ at $I = 1.0$ M ($LiClO_4$). The final, equilibrium [diperoxomolybdenum(VI)] ranged from 38 to 97% of the initial [Mo(VI)]. Plots of the pseudo-first-order rate constants vs. $[H_2O_2]_{av}^2$, where $[H_2O_2]_{av} = [H_2O_2]_0 -$ [diperoxomolybdenum(VI)]$_\infty$, were linear with small positive intercepts at a given acidity and temperature. These results are consistent with eq 20 and 21, where [2:1] = [diperoxomolybdenum(VI)]. The

$$d[2:1]/dt = k(\text{first order})([2:1]_\infty - [2:1]) \qquad (20)$$

$$k(\text{first order}) = k_f[H_2O_2]_{av}^2 + k_r \qquad (21)$$

values of k_f summarized in Table V gradually increase with decreasing acidity at 25 °C. Corresponding values of k_r could not be reliably determined from these data.

Kinetic Studies of the Dissociation of Diperoxomolybdenum(VI). Sulfur(IV) is rapidly oxidized to sulfur(VI) by hydrogen peroxide in acidic solution.[26] However, peroxotitanium(IV) is unreactive toward sulfur(IV); loss of $Ti(O_2)^{2+}$ in the presence of sulfur(IV) is strictly limited by the dissociation rate of the peroxo complex.[15] We therefore undertook a study of the rate of disappearance of diperoxomolybdenum(VI) in the presence of at least an 18-fold excess of sulfur(IV). The stopped-flow technique was used to mix an equilibrated solution of diperoxomolybdenum(VI) with one containing S(IV); the disappearance of the 2:1 complex was monitored at 328 nm. Plots of $-\ln [A - A_\infty]$ vs. time were strictly linear for at least 90% of total reaction. The slopes of these plots varied linearly with the average excess sulfur(IV) concentration (taken to be $[S(IV)]_0 - [H_2O_2]_0$] − [diperoxomolybdenum(VI)]$_0$) at a given acidity and temperature. The experimental results, as analyzed by use of eq 22, are summarized in Table VI.

$$\text{slope} = k_r + k_{S(IV)}[S(IV)]_{av} \qquad (22)$$

The values of k_r increase with increasing acidity. We shall defer an interpretation of this observation until the Discussion.

Table VI. Kinetic Results for the Disappearance of Diperoxomolybdenum(VI) in the Presence of Excess Sulfur(IV)[a]

T, °C	$[HClO_4]$, M	k_r,[b] s^{-1}	$k_{S(IV)}$,[b] $M^{-1}\ s^{-1}$
25.0	1.00	0.47 ± 0.01	0.5 ± 0.9 (0.6)
25.0	0.60	0.33 ± 0.01	3 ± 1 (2)
25.0	0.40	0.28 ± 0.01	3 ± 1 (4)
25.0	0.20	0.23 ± 0.01	15 ± 2 (14)
25.0	0.10	0.20 ± 0.02	48 ± 3 (48)
25.0	0.070	0.15 ± 0.01	90 ± 1 (88)
25.0	0.040	0.17 ± 0.03	198 ± 4 (213)
17.0	1.00	0.22 ± 0.01	4 ± 1
17.0	0.40	0.14 ± 0.01	3 ± 1
17.0	0.10	0.088 ± 0.002	34 ± 1
10.0	1.00	0.13_4 ± 0.001	1.1 ± 0.2
10.0	0.40	0.069 ± 0.001	2.0 ± 0.2
10.0	0.10	0.037 ± 0.005	26 ± 1

[a] Monitored at 328 nm. Initial concentrations were [S(IV)] = (0.197–1.25) × 10^{-2} M, [diperoxomolybdenum(VI)] = (1.08–1.59) × 10^{-4} M, $[H_2O_2]$ = (0.82–1.84) × 10^{-4} M, and [Mo(VI)] = (4.70–9.80) × 10^{-5} M. The ionic strength was maintained at 1.0 M with use of lithium perchlorate. [b] Values of k_r and $k_{S(IV)}$ were determined by use of eq 22. Calculated values of $k_{S(IV)}$ are given in parentheses and were estimated by use of eq 23.

We were initially disturbed by the large increase in the rate constant $k_{S(IV)}$ at low acidities. However, under the assumption that HSO_3^- and $MoO(OH)(O_2)_2^-$ are the reactive forms of sulfur(IV) and diperoxomolybdenum(VI), respectively, the associated rate constant defined as $k_{HSO_3^-}$ is related to the observed rate constant as shown in eq 23. Calculated values of the rate constant

$$k_{HSO_3^-} = k_{S(IV)}\{(K_{SO_2} + [H^+])/K_{SO_2}\}\{(K_a + [H^+])/K_a\} \qquad (23)$$

$$SO_2(aq) + H_2O = HSO_3^- + H^+ \quad K_{SO_2}$$

$k_{S(IV)}$ at 25 °C, from an estimated value of $3._1 \times 10^3\ M^{-1}\ s^{-1}$ for $k_{HSO_3^-}$, are listed in parentheses in the last column of Table VI. Values of $K_{SO_2} = 0.0144$ M[27,28] and $K_a = 0.014$ M were used. The agreement between the calculated and observed values is remarkable.

Results of Concentration-Jump Experiments. A limited series of concentration-jump experiments were performed to test further for consistency between the equilibrium and kinetic studies. An equilibrated solution of molybdenum(VI) and hydrogen peroxide was diluted in half on the stopped-flow instrument by mixing with an equal volume of a solution containing the same $[HClO_4]$ at $I = 1.0$ M. The approach to the new equilibrium was monitored at 328 nm. Plots of $-\ln [A - A_\infty]$ vs. time were linear for at least 80% of the total reaction. The slopes of these plots (k_{obsd}) and the experimental conditions are summarized in Table VII. Theoretical values of k_{obsd} were calculated by means of eq 24 and

$$k_{obsd} = k_f[H_2O_2]_{eq}^2[Mo(VI)]_{eq}(1/[Mo(VI)]_{eq} + 4/[H_2O_2]_{eq}) + k_r + f(\Delta) \qquad (24)$$

are listed in the last column. The equilibrium concentrations were calculated by use of the $K_{2:1}$ values from Table IV. Values of k_f and k_r were taken from Tables V and VI, respectively. The $f(\Delta)$ term, defined in eq 25, is a correction term that is included because the higher order terms in Δ are not completely negligible under our experimental conditions.[29]

$$f(\Delta) = -4k_f\Delta_{av}([Mo(VI)]_{eq} + [H_2O_2]_{eq} - \Delta_{av}) \qquad (25)$$

$$\Delta_{av} = ([2:1]_0 - [2:1]_{eq})/2$$

The calculated values of k_{obsd} are systematically ca. 80% of the experimental results. We conclude that the agreement is satisfactory for this type of study. The results also establish that there is only one detectable relaxation process associated with the formation and dissociation of diperoxomolybdenum(VI).

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Table VII. Results of Concentration-Jump Experiments with Equilibrated Diperoxomolybdenum(VI) Solutions[a]

T, °C	$[\mathrm{HClO_4}]$, M	$10^4[\mathrm{Mo(VI)}]_T$,[b] M	$10^4[\mathrm{H_2O_2}]_T$,[b] M	$10^4[2{:}1]_0$,[b] M	$10^4[2{:}1]_{eq}$,[b] M	k_{obsd},[c] s^{-1}	k_{calcd},[d] s^{-1}
25.0	1.00	4.12	8.00	2.75	2.15	1.7	1.5
25.0	0.60	4.12	8.00	2.92	2.39	1.4	1.1
25.0	0.40	4.12	8.00	3.04	2.52	1.4	1.2
25.0	0.20	4.12	8.00	3.20	2.77	1.3	1.1
25.0	0.10	4.12	8.00	3.29	2.90	1.4	0.95
17.0	0.40	2.00	3.99	1.37	1.07	0.51	0.37
17.0	0.40	2.50	4.99	1.81	1.47	0.55	0.42
10.0	0.40	1.51	2.99	1.02	0.81	0.24	0.16

[a] The approach to equilibrium was monitored at 328 nm. The ionic strength was maintained at 1.0 M with use of lithium perchlorate. [b] Concentrations are those present *after* mixing. $[\mathrm{Mo(VI)}]_T = [\mathrm{Mo(VI)}] + [2{:}1]$ and $[\mathrm{H_2O_2}]_T = [\mathrm{H_2O_2}] + 2[2{:}1]$. [c] Values are the slopes of plots of $-\ln [A - A_\infty]$ vs. time. [d] Determined by use of eq 24.

Peroxo Complexes(es) of Tungsten(VI) in Acidic Solution. Spectral scans of solutions containing tungsten(VI) and excess hydrogen peroxide in 1.00 M perchloric acid at 25 °C show an absorption maximum at 256 nm. The absorbance at this wavelength reaches a constant value (after correction for absorbance due to the excess hydrogen peroxide) with a sufficient excess of hydrogen peroxide. The extinction coefficient determined in the plateau region is 1160 ± 20 M^{-1} cm^{-1} at 25 °C and is independent of acidity over the range 0.15–1.0 M. Presumably a diperoxotungsten(VI) complex is formed, but we were unable to determine the formulation and equilibrium parameters due to complexities in the chemistry of free tungsten(VI) in acidic solution. Tungsten(VI) is only sparingly soluble in acidic solution (and is metastable), but it is dramatically solubilized and stabilized by the presence of excess hydrogen peroxide.

Discussion

The analysis of our equilibrium data provides strong evidence that the principal peroxo complex of molybdenum(VI) is oxodiperoxomolybdenum(VI) at acidities greater than 0.1 M. It is useful to compare our results with those reported for oxodiperoxochromium(VI) under similar experimental conditions.[24,30] It is very likely that both complexes have a pentagonal-bipyramidal geometry, with the two peroxo groups bound in an η^2 fashion in the equatorial plane and the oxo group in an apical position.[9,31]

The principal equilibrium reported for the formation of oxodiperoxochromium(VI) is given in eq 26. The value of the

$$\mathrm{HCrO_4^- + H^+ + 2H_2O_2 = CrO(O_2)_2 + 3H_2O} \qquad (26)$$

formation constant at 25 °C and $I = 3.0$ M ($\mathrm{NaClO_4}$) is $(2.0 \pm 0.2) \times 10^7\ M^{-3}$; $\Delta H_f{}^\circ = -14 \pm 2$ kcal/mol, and $\Delta S_f{}^\circ = -13 \pm 7$ cal/(K mol).[30] The formation equilibrium may be recast as shown in eq 27 by use of the protonation constant for $\mathrm{HCrO_4^-}$.

$$\begin{gathered}\mathrm{CrO_3 + 2H_2O_2 = CrO(O_2)_2 + 2H_2O} \\ K_{27} = 1.3 \times 10^8\ M^{-2}\ (25\ ^\circ C)\end{gathered} \qquad (27)$$

The formally analogous reaction for oxodiperoxomolybdenum(VI) is given in eq 28. However, whereas the coordination number

$$\begin{gathered}\mathrm{MoO_3 + 2H_2O_2 = MoO(O_2)_2 + 2H_2O} \\ K_{28} = 6.6 \times 10^7\ M^{-2}\ (25\ ^\circ C)\end{gathered} \qquad (28)$$

of $\mathrm{CrO_3}$ is undoubtedly 4, some authors have reasonably proposed that $\mathrm{MoO_3}$ and its protonated form are six-coordinate.[32] Nevertheless, the formation constants for the two oxo diperoxo complexes are very similar. The thermodynamic parameters for the formation of $\mathrm{MoO(O_2)_2}$, based on eq 14, are $\Delta H_f{}^\circ = -12 \pm 1$ kcal/mol and $\Delta S_f{}^\circ = -9 \pm 3$ cal/(K mol).

We have proposed that the spectral variations observed for oxodiperoxomolybdenum(VI) at low acidities are due to the equilibrium given again in eq 29. Crystals identified as $K_2[(H_2O)(O_2)_2OMoOMoO(O_2)_2(H_2O)]\cdot 2H_2O$ by X-ray diffraction studies are formed from concentrated solutions of molybdenum(VI) and excess hydrogen peroxide under neutral or weakly acidic conditions.[33] This result suggests that $\mathrm{MoO(OH)(O_2)_2^-}$ and possibly $\mathrm{MoO(O_2)_2}$ are susceptible to dimerization to form $\mathrm{Mo_2O_{11}^{2-}}$.[10,34] However, we obtained no spectral evidence for any dimeric peroxo species under our acidic conditions.

$$\begin{gathered}\mathrm{MoO(O_2)_2 + H_2O = MoO(OH)(O_2)_2^- = H^+} \\ K_a = 0.014\ (25\ ^\circ C)\end{gathered} \qquad (29)$$

A problem arises when we compare our results and interpretation with those reported for the oxodiperoxochromium(VI) system. Tanaka and co-workers obtained spectral evidence for two forms of oxodiperoxochromium(VI) at acidities greater than 0.1 M.[30] They quite reasonably interpreted their data as shown in eq 30. This formulation is in agreement with their equilibrium

$$\begin{gathered}\mathrm{CrO(O_2)_2 + H^+ = HCrO(O_2)_2^+} \\ K_b = 0.15\ M^{-1}\ (25\ ^\circ C)\end{gathered} \qquad (30)$$

data in that $[\mathrm{CrO(O_2)_2}]$ would not change appreciably over the acidity range ($[\mathrm{H^+}] < 0.10$ M) of their equilibrium studies. The problem is that eq 29 and 30 indicate that $\mathrm{CrO(O_2)_2}$ is more basic than $\mathrm{MoO(O_2)_2}$. If true, this feature goes against the usual periodic trends of acid–base properties.

Another interesting point is whether the oxo or a peroxo ligand is more basic in the class of oxo diperoxo complexes of d^0 transition-metal ions. Tanaka and co-workers[30] have reasonably formulated $\mathrm{HCrO(O_2)_2^+}$ as $\mathrm{Cr(OH)(O_2)_2^+}$. On the other hand, Quilitzsch and Wieghardt have proposed that a series of $\mathrm{VO(O_2)_2L^{n-}}$ complexes, where L is a bidentate ligand, are completely protonated as $\mathrm{VO(O_2)(OOH)L^{(n-1)-}}$ above 0.01 M $[\mathrm{H^+}]$.[35] Clearly more data are needed, but the latter proposal of protonation at peroxide rather than at the oxo ligand appears to have compelling experimental justification.

It is generally very difficult to determine the solution structure of transition-metal ions that contain peroxo, oxo, aquo, and possibly hydroxo or hydroperoxo ligands. However, it does appear that a major reason d^0 transition-metal ions readily form peroxo complexes even in strongly acidic solution is that they usually contain oxo ligands. The replacement of one oxo ligand by peroxide on $\mathrm{TiO^{2+}}$ and $\mathrm{VO_2^+}$ is an acid-independent process, as is the replacement of two oxo ligands by two peroxides on $\mathrm{CrO_3}$ and $\mathrm{MoO_3}$.[36] In instead water ligands are replaced by peroxide, as shown in eq 31 and 32, the formation equilibria show a strong inverse dependence on acidity.[14,24,25]

$$\mathrm{VO(O_2)^+ + H_2O_2 = VO(O_2)_2^- + 2H^+} \qquad (31)$$

$$\mathrm{4Zr^{4+} + 2H_2O_2 = Zr_4(OH)_4(O_2)_2^{8+} + 8H^+} \qquad (32)$$

The entry of the first peroxide ligand is rate-determining in the formation of oxodiperoxochromium(VI), as shown in eq 33 and 34. The formation of the proposed intermediate $\mathrm{CrO_2(O_2)}$ is

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(34) See also: (a) Chauveau, F.; Souchay, P.; Trudit, G. *Bull. Soc. Chim. Fr.* **1955**, 1519. (b) Mimoun, H.; deRoch, I. S.; Sajus, L. *Bull. Soc. Chim. Fr.* **1969**, 1481.

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(36) There is compelling evidence that oxo–peroxo oxygen exchange *does not occur* in these complexes. See: Postel, M.; Brevard, C.; Arzoumanian, H.; Reiss, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 4922.

$$H_2CrO_4 + H_2O_2 = CrO_2(O_2) + 2H_2O \quad \text{rate determining} \qquad (33)$$

$$CrO_2(O_2) + H_2O_2 = CrO(O_2)_2 + H_2O \quad \text{fast} \qquad (34)$$

thought to involve a rate-determining substitution of the coordinated water on H_2CrO_4.[30] It is surprising to us that incorporation and loss of the second peroxide (eq 34) are such rapid processes. It may be that an increase in the coordination number of chromium(VI) accompanies formation of $CrO_2(O_2)$.

Our kinetic results strongly suggest that entry of the *second* peroxide ligand is rate-determining in the formation of oxodiperoxomolybdenum(VI). It is clear that the mechanism is more complicated than for the chromium(VI) system, where reactions 33 and 34 are independent of $[H^+]$.[30] The reaction scheme shown in eq 35-39 is consistent with the kinetic data.

$$MoO_3 + H_2O_2 = MoO_2(O_2) + H_2O \quad \text{rapid, } K_{1:1} \qquad (35)$$

$$MoO_2(O_2) + H_2O_2 = MoO(O_2)_2 + H_2O \quad k_1, k_{-1} \qquad (36)$$

$$MoO_2(O_2) + H_2O_2 + H^+ = MoO(O_2)_2 + H_3O^+ \quad k_2, k_{-2} \qquad (37)$$

$$MoO(O_2)_2 + H_2O = MoO(OH)(O_2)_2^- + H^+ \quad \text{rapid, } K_a \qquad (38)$$

$$d[2{:}1]/dt = k_f[Mo(VI)][H_2O_2]^2 - k_r[2{:}1] \qquad (39)$$

$$k_f = (k_1K_{1:1}/[H^+] + k_2K_{1:1})/\{([H^+] + K_a)/(1 + K_1[H^+])\}$$

$$k_r = k_{-1} + k_{-2}[H^+]$$

At 25 °C, $k_1K_{1:1} = (7.4 \pm 0.6) \times 10^6$ M^{-2} s^{-1}, $k_2K_{1:1} = (1.6 \pm 0.3) \times 10^7$ M^{-3} s^{-1}, $k_{-1} = 0.15 \pm 0.01$ s^{-1}, and $k_{-2} = (0.31 \pm 0.02$ M^{-1} s$^{-1})[H^+]$. The dioxoperoxomolybdenum(VI) species is postulated as an intermediate in low concentration. The hydrogen ion assisted pathway for the formation and dissociation of $MoO(O_2)_2$ shown in eq 37 has precedent in the $VO(O_2)^+$ and $Ti(O_2)^{2+}$ systems.[24,25] The value of the formation constant $K_{MoO(O_2)2}$ derived from the kinetic results is $7._1 \times 10^6$ M^{-1} at 25 °C, in reasonable agreement with that determined in the equlibrium study ($9._4 \times 10^6$ M^{-1}).

We detected a direct reaction between oxodiperoxomolybdenum(VI) and sulfur(IV), although it was not our original intent to do so. Very specific pathways appear to be operative in the important peroxide–sulfur(IV) systems—reaction of H_2O_2 and HSO_3^- ($k = 2.4 \times 10^6$ M^{-1} s^{-1} at 15 °C)[26] and $MoO(OH)(O_2)_2^-$ and HSO_3^- (k ca. 3×10^3 M^{-1} s^{-1} at 25 °C).

The group VIB (6[40]) elements readily form an isostructural set of oxo diperoxo complexes under comparable experimental conditions. The formation constants appear to be very similar, although the data for the tungsten(VI) system are very limited. The interpretation of our results was greatly assisted by the extensive studies of molybdenum(VI) in acidic solution; similar studies with tungsten(VI) have not been reported. It is known that molybdenum(VI) and tungsten(VI) effectively catalyze at least some reactions of hydrogen peroxide in acidic solution.[1,17,37-39] Corresponding data for chromium(VI) are not available and would be more difficult to obtain due to the instability of $CrO(O_2)_2$ toward internal redox decomposition. Vanadium(V) promotes peroxide oxidation of iodide ion when complexed as $VO(O_2)_2^-$ (or $VO(O_2)(OOH)$) but not as the $VO(O_2)^+$ form.[25] We have found that titanium(IV) and zirconium(IV) markedly *stabilize* coordinated peroxide in acidic solution.[14-16] In our opinion the crucial factors that determine these enormously variable reactivity patterns have not been elucidated. However, comparative kinetic studies of the peroxo complexes and hydrogen peroxide coupled with a firm knowledge of the equilibrium parameters and structures of the peroxo complexes should provide important information. At the present time we can only point out that the oxo diperoxo complexes of the d^0 transition-metal ions are much more reactive than the monoperoxo forms. It seems premature to assess the specific effect of the metal ion, but other studies indicate that available coordination sites for the substrate must be present if rate enhancements are to be observed.[31]

Acknowledgment. This research was supported by the U.S. Army Research Office. Preliminary equilibrium studies were performed by Arthur Suits.

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(40) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the numbering: e.g., III → 3 and 13.)

Contribution from the Kenan Laboratories of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Electrochemical Reactivity of Manganese(II) Porphyrins. Effects of Dioxygen, Benzoic Anhydride, and Axial Ligands

S. E. Creager and Royce W. Murray*

Received October 28, 1986

Currents for electrochemical reductions of manganese(III) porphyrins in oxygenated, aprotic media correspond to passage of between one and two electrons per porphyrin, depending on the experimental time scale, the axial base present, and the particular porphyrin. The two-electron process corresponds to an "ECE" reaction sequence involving formation and subsequent reduction of an intermediate Mn(II)–dioxygen adduct. The formal potential of the second electron step is shown to be ca. −0.17 V vs. NaSCE for Mn(TPP)benzoate. Passage of the second electron is suppressed by strong axial bases and by competitive axial binding but is promoted by use of an axial anion that gives the most negative potential for passage of the first electron, Mn(TPP)benzoate being a specific example. The overall rate constant for the intermediate chemical step is estimated. In the presence of the added electrophile benzoic anhydride, and on a slower time scale, reduction by more than two electrons occurs by a process postulated to involve heterolysis of the O–O bond by the electrophile, producing an even more easily reduced, high-valent manganese–oxo porphyrin. The rate of electrophile attack is slower than that for dioxygen binding.

Molecular oxygen is a strong thermodynamic oxidant but reacts only slowly with the many available reducing agents in the environment. Much effort has gone into understanding synthetic and natural catalysts[1,2] that promote the reaction of dioxygen with oxidizable substrates. The heme group is a common component of natural oxygen activation catalysts, which has prompted studies[3,4] on the interaction of dioxygen with model iron(II)

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