Table I. Crystal Data for Complexes **1** and **3**

	1	**3**
formula	$C_{10}H_{18}Cl_4N_2Ti$	$C_{22}H_{28}Cl_6N_4V_2\cdot C_7H_8$
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	9.124 (1)	12.846 (1)
b, Å	17.360 (2)	12.525 (1)
c, Å	11.942 (1)	11.238 (1)
α, deg	90	90
β, deg	108.25 (1)	91.52 (1)
γ, deg	90	90
V, Å^3	1796.4 (3)	1807.5 (3)
Z	4	2
intens meas method	three points, individual profiles	
refinement method	full-matrix least squares	
$R = \sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$	0.042	0.044
$R_w = \sum w^{1/2}\lvert\Delta F\rvert/\sum w^{1/2}\lvert F_o\rvert$	0.046	0.050

Table II. Fractional Atomic Coordinates (×10^4) for Complex **1**

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ti	2815 (1)	3916 (1)	2724 (1)
Cl1	3415 (2)	3119 (1)	1406 (2)
Cl2	1302 (2)	3069 (1)	3261 (2)
Cl3	2984 (2)	4753 (1)	4237 (2)
Cl4	1223 (2)	4651 (1)	1357 (2)
N1	5798 (7)	4969 (3)	2437 (5)
N2	5948 (7)	3093 (3)	4687 (5)
C1	4799 (8)	4604 (4)	2532 (6)
C2	7102 (8)	5431 (4)	2327 (7)
C3	7061 (9)	5398 (5)	1065 (7)
C4	6849 (10)	6229 (5)	2733 (8)
C5	8562 (9)	5061 (5)	3131 (8)
C6	4887 (8)	3365 (4)	4037 (6)
C7	7377 (8)	2773 (4)	5532 (6)
C8	7248 (10)	1906 (5)	5429 (9)
C9	8702 (9)	3078 (6)	5171 (7)
C10	7408 (10)	3046 (6)	6725 (8)

Table III. Fractional Atomic Coordinates (×10^4) for Complex **3**[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*
V	622 (1)	383 (1)	1536 (1)
Cl1	−609 (1)	1106 (1)	177 (1)
Cl2	2014 (1)	1112 (1)	668 (1)
Cl3	1477 (1)	−838 (1)	2667 (1)
N1	481 (3)	1281 (3)	2589 (3)
N2	−1456 (3)	−863 (3)	2425 (3)
C1	426 (3)	2039 (3)	3461 (3)
C2	−285 (3)	1940 (4)	4365 (4)
C3	−318 (4)	2728 (4)	5233 (4)
C4	335 (4)	3586 (4)	5187 (4)
C5	1047 (4)	3674 (4)	4303 (5)
C6	1099 (4)	2915 (4)	3427 (4)
C7	−725 (3)	−475 (3)	2074 (4)
C8	−2414 (3)	−1349 (4)	2871 (4)
C9	−3323 (4)	−742 (4)	2319 (5)
C10	−2370 (4)	−1234 (5)	4203 (4)
C11	−2414 (4)	−2506 (4)	2483 (5)
C1S	5632 (5)	622 (6)	5410 (7)
C2S	4539 (9)	1137 (10)	3655 (11)
C3S	4129 (12)	118 (12)	3784 (13)
C4S	5385 (10)	1216 (10)	4678 (11)
C5S	4725 (11)	460 (11)	4397 (12)

[a] The site occupation factors for the disordered toluene molecule are 1.0 for C1S and C2S and 0.5 for C2S, C3S, and C4S.

one of the three possible geometric isomers, two of them having a cis arrangement of the isocyanide ligands. The proposed cis isomer is in agreement with the two $C\equiv N$ stretchings observed in the IR spectrum and the singlet for the Bu^t substituent at the isocyanide ligand. An X-ray analysis was carried out to clarify the structure of **3**. An ORTEP view of **3** is reported in Figure 3, with some relevant structural parameters. Each vanadium atom in the centrosymmetric dimer is six-coordinate in a distorted octahedral arrangement. The bridging chlorine atoms in the equatorial plane are in an unsymmetrical arrangement, the V–Cl distance trans to the multiple V–N bond being 0.33 Å longer than the other one. This bond is in its turn 0.1 Å longer than the vanadium distances to the terminal chlorines, values which are close to that in $[V((Ntol)Cl(O\text{-}2,6\text{-}C_6H_3(CH_3)_2)_2]_2$,[11] [2.240 (1) Å]. The V–C distance is slightly longer than those found in $[VCl_3(Bu^tNC)_3]$.[6] The absence of any insertion of isocyanide into the M–Cl bond of highly acidic early-transition-metal halides prompts us to reexamine the role of Lewis acids, MX_n, in the modified version of the Passerini reaction.[4,5] A fundamental question should be: does $TiCl_4$ assist the Passerini reaction via the interaction with the isocyanide or the carbonylic function?

Experimental Section

Synthesis of Complex 1. Bu^tNC (1.62 g, 19.5 mmol) was added to a toluene solution (100 mL) of $TiCl_4$ (1.73 g, 9.1 mmol). A light yellow solid crystallized in a few minutes from the solution. It was filtered and washed with *n*-hexane (ca. 85%). The same synthesis can be carried out equally well in CH_2Cl_2.[1] Longer reaction times and different Ti:RNC molar ratios in either toluene or CH_2Cl_2[1,4] always gave red solutions from which the isolated solid, washed carefully, was the same yellow diisocyanide derivative. Anal. Calcd for $C_{10}H_{18}N_2Cl_4Ti$: C, 33.74; H, 5.10; N, 7.87. Found: C, 34.01; H, 5.25; N, 7.76. Recrystallization from hot toluene gave crystals suitable for the X-ray analysis.

Synthesis of Complexes 3 and 4. Bu^tNC (0.39 g, 4.69 mmol) was added to a toluene solution (100 mL) of $[PhNVCl_3(THF)_2]$ (0.92 g, 2.35 mmol). The solution color changed from green to deep green. Partial evaporation of the solvent and allowing the solution to stand gave yellow crystals of **3** containing a molecule of toluene per dimer (80%). Anal. Calcd for $C_{29}H_{36}N_4Cl_6N_4V_2$: C, 46.09; H, 4.76; Cl, 9.40; N, 7.41. Found: C, 46.61; H, 4.90; Cl, 9.27; N, 7.36. ^1H NMR (δ, CD_2Cl_2): 7.33 (m, 5 H, Ph), 1.55 (s, 9 H, Bu^t). When the reaction was carried out with a 2:1 Bu^tNC:V molar ratio, a yellow-green crystalline solid formed (70%). Anal. Calcd for $C_{16}H_{23}Cl_3N_3V$: C, 46.34; H, 5.59; Cl, 25.65; N, 10.13. Found: C, 46.14; H, 5.50; Cl, 25.67; N, 10.06. ^1H NMR (δ, CD_2Cl_2): 7.49 (m, 5 H, Ph), 1.53 (s, 18 H, Bu^t).

X-ray Crystallography. Crystal data are given in Table I. A total of 1272 (corrected for absorption) and 2300 unique reflections for complexes **1** and **3**, respectively, were collected at room temperature on a Philips PW 1100 single-crystal diffractometer (Mo Kα radiation, λ = 0.71069 Å). The structures were solved by Patterson and Fourier methods. Final atomic coordinates are listed in Tables II and III.

Acknowledgment. We thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 2000-5.031) for financial support.

Registry No. **1**, 123148-55-0; **2**, 123168-66-1; **3**, 123148-57-2; **4**, 123148-58-3; $[TiCl_4(2,6\text{-}Me_2C_6H_3NC)]_2$, 123148-59-4; $[TiCl_4(C\equiv NCH_2P(O)(OEt)_2)]_2$, 123148-60-7.

Supplementary Material Available: Listings of experimental details associated with the X-ray studies, hydrogen coordinates, anisotropic thermal parameters, and bond distance and angles for **1** and **3** (8 pages); tables of observed and calculated structure factors for complexes **1** and **3** (21 pages). Ordering information is given on any current masthead page.

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Kinetic Study of the Formation of the Oxo Diperoxo Complex of Tungsten(VI) in Aqueous Perchloric Acid Solution

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We have shown that the peroxo ligands in the oxo diperoxo complexes of molybdenum(VI) and tungsten(VI) are impressively activated toward both oxygen atom transfer and inner-sphere, one-electron-reduction reactions in aqueous solution.[1-3] This

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activation extends at least over the pH range 0–7, and in the presence of excess hydrogen peroxide the rate laws are strictly catalytic with respect to the group 6, d^0 metal ion. The oxo diperoxo complexes have been formulated as $MO(O_2)_2$ and $MO(OH)(O_2)_2^-$, with two and one coordinated water molecule omitted, respectively. There is substantial evidence that the complexes have a pentagonal-bipyramidal structure, with an apical oxo ligand and two η^2-peroxo ligands in the equatorial plane.[4,5] The pK_a's of $MoO(O_2)_2$ and $WO(O_2)_2$ are 1.85 and 0.12, respectively.[1,6]

We have been able to determine the equilibrium and kinetic parameters for the formation of the oxo diperoxo complexes of molybdenum(VI) over a wide pH range. This was possible only because the aqueous chemistry of molybdenum(VI), while quite complex, has been thoroughly studied.[7-10] The interconversions of monomeric molybdenum(VI) species—$HMoO_3^+$, MoO_3, $HMoO_4^-$, and MoO_4^{2-}—are rapid; we have worked under conditions where oligomeric forms, mainly dimers and heptamers, are negligible. Our related studies with the oxo diperoxo complexes of tungsten(VI) have been limited to the neutral region, where WO_4^{2-} is the principal form of the uncomplexed metal ion. In acidic solution the chemistry of tungsten(VI) becomes very complex.[11-14] Schwarzenbach and co-workers have determined the first and second protonation constants for tungstate ion by means of rapid-flow potentiometric experiments in which dilute solutions of tungstate ion were rapidly mixed with hydrochloric acid of comparable concentrations.[11] They observed that after 5–10 ms rapid aggregation of the protonated tungsten(VI) monomers began to occur, followed by very slow additional reactions. We have observed that under certain conditions hydrous tungsten oxide eventually precipitates.[6] Spectra of all the monomeric forms of molybdenum(VI) in the UV region have been reported;[10,15] the corresponding spectra for tungsten(VI) under acidic conditions have not been measured to the best of our knowledge.

We wish to report the results of some stopped-flow experiments that have yielded useful information about both the spectrum of a presumably monomeric tungsten(VI) species and its conversion to oxodiperoxotungsten(VI) in acidic solution. Our approach involves rapidly mixing dilute solutions of sodium tungstate in water, where WO_4^{2-} predominates and is stable, with perchloric acid solutions and then monitoring spectral changes in the UV region. We have performed similar experiments with hydrogen peroxide in acidic solution. Our results and interpretation will be compared to the corresponding data presently available for molybdenum(VI).

Experimental Section

A slightly basic stock solution containing 4.00×10^{-3} M $Na_2WO_4 \cdot 2H_2O$ was used in all the experiments. Diluted solutions of W(VI) prepared from this stock were shown to obey Beer's law at $\lambda \geq 220$ nm with $[W(VI)] \leq 4.00 \times 10^{-4}$ M. Solutions of H_2O_2 were assayed by iodometric titration. Deionized water was distilled twice before use; the last distillation was from alkaline permanganate. Reaction solutions contained only Na_2WO_4, $HClO_4$, and often H_2O_2; the variable ionic strength was determined by $[HClO_4]$, which did not exceed 0.10 M. All experiments were conducted at 25.0 ± 0.1 °C.

Table I. Kinetic Results for the Formation of the Oxo Diperoxo Complex of Tungsten(VI) at 25 °C[a]

$[HClO_4]$, M	$10^4[W(VI)]_0$, M	$10^2[H_2O_2]_0$, M	k_{obs}, s^{-1} [b]	$10^{-3}k_{obs}/[H_2O_2]_{av}$ [c]
0.10	1.00	0.50	9.13	1.9
0.10	1.00	1.00	18.8	1.9
0.10	1.00	1.00	21.7	2.2
0.10	1.00	1.50	35.3	2.4
0.10	1.00	2.00	43.4	2.2
0.10	1.00	2.00	48.9	2.4
0.10	1.00	2.00	46.8	2.3
0.10	0.50	2.00	43.7	2.2
0.10				2.2 ± 0.3[d]
0.10				2.1 ± 0.1[e]
0.050	1.00	0.50	10.3	2.1
0.050	1.00	1.00	24.0	2.4
0.050	1.00	1.50	39.5	2.6
0.050	1.00	2.00	52.4	2.6
0.050	0.50	2.00	55.3	2.8
0.010	1.00	0.50	10.1	2.1
0.010	1.00	1.00	25.3	2.6
0.010	1.00	1.50	35.0	2.3
0.010	1.00	2.00	55.7	2.8
0.010	0.50	2.00	50.5	2.5
0.010				2.6 ± 0.4[f]
0.010				2.9 ± 0.5[g]
0.0050	1.00	0.50	10.7	2.2
0.0050	1.00	1.00	23.4	2.4
0.0050	1.00	1.50	35.9	2.4
0.0050	1.00	2.00	53.9	2.7
0.0050	0.50	2.00	52.3	2.6

[a] Monitored at 280 nm unless otherwise indicated. [b] Values are slopes of plots of $-\ln (A_\infty - A)$ vs time. [c] $[H_2O_2]_{av} = [H_2O_2]_0 - [W(VI)]_0$. [d] Average value of five runs monitored at 270 nm. [e] Average value of five runs monitored at 260 nm. [f] Average value of four runs monitored at 290 nm. [g] Average value of four runs monitored at 260 nm.

Routine spectra of stable species were collected on a Cary 14 spectrophotometer. A Durrum D-110 stopped-flow instrument was used for all the rapid-mixing experiments. The path length was 2 cm, and a 1.0-mm slit width was used. The W(VI) solution was always in water; hydrogen peroxide, if present, was in the perchloric acid solution. Each experiment was repeated until three consecutive traces were superimposable. The data were collected by use of a Nicolet 3091 digital oscilloscope equipped with a bubble memory that allowed collection of multiple runs. The data consisting of 2000 voltage–time pairs per experiment were transferred to a Macintosh SE microcomputer for analysis.

The range of $[H_2O_2]$ used in studies of the formation kinetics of the oxo diperoxo complex of W(VI) was limited at the low end by competition of aggregation of W(VI) and at the high end by the speed of reaction. We were initially worried about the formation of colloidal, hydrous tungsten(VI) oxide in the stopped-flow instrument in the experiments without added hydrogen peroxide, but this proved not to be a problem under our experimental conditions.

Results

The results of some typical experiments monitored at 280 nm in which dilute tungstate solutions were rapidly mixed with aqueous perchloric acid are shown in Figure 1. We note first that the observed spectral changes at a given acidity (0.010 M H^+ in Figure 1a) are extraordinarily dependent on [W(VI)]. Second, the spectral changes at a given [W(VI)] (1.0×10^{-4} M in Figure 1b) are significantly dependent on the acid concentration. We make no claim to understanding the chemistry that is occurring; we have observed previously that slow additional absorbance changes lasting at least many hours occur subsequent to the stopped-flow data shown in Figure 1.[6] However, the *initial* absorbance at a fixed wavelength is independent of acidity over the range 0.0050–0.10 M and, in addition, is proportional to [W(VI)] provided it is $\leq 1.0 \times 10^{-4}$ M. This feature is observed over the range 200–300 nm.[16] In Figure 2 we present the apparent

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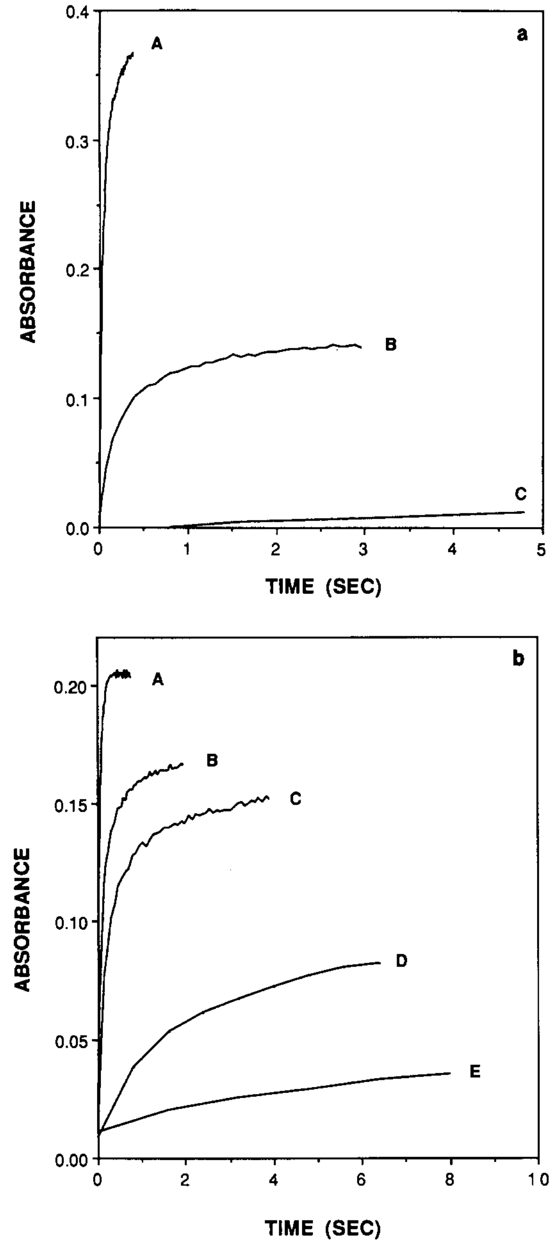

Figure 1. (a) Stopped-flow kinetic traces observed at 280 nm and 25 °C for tungsten(VI) in 0.010 M $HClO_4$. [W(VI)] was 0.20, 0.10, and 0.040 mM in traces A–C, respectively. (b) Stopped-flow kinetic traces observed at 280 nm and 25 °C for 0.10 mM W(VI) in perchloric acid solution. [$HClO_4$] was 1.0, 5.0, 10.0, 50.0, and 100 mM in traces A–E, respectively.

extinction coefficient (initial absorbance)/(path length × [W(VI)]) observed over this region measured with 0.1 mM W(VI) and 0.050 and 0.10 M $HClO_4$. We have included a spectrum of tungstate ion measured in water by conventional spectrophotometry.

The experiments designed to measure the formation kinetics for the oxo diperoxo complex of W(VI) were usually monitored at 280 nm but were also checked from 260 to 290 nm. Linear plots of $-\ln(A_\infty - A_t)$ vs time were obtained under the conditions 0.0050–0.10 M $HClO_4$, [W(VI)] ≤ 1.0×10^{-4} M, and [H_2O_2] = (0.50–2.00) × 10^{-2} M. The slopes of these plots, k_{obs}, and the experimental details are summarized in Table I. The values of $k_{obs}/[H_2O_2]_{av}$ listed in the last column are reasonably constant not only at a given acidity but also over the entire acidity range listed and appear to be independent of the wavelength used to monitor the reactions. Nonlinear rate plots were obtained at lower acidities, where the absorbance changes in the absence of hydrogen peroxide are very rapid. With higher [W(VI)] either nonlinear, pseudo-first-order kinetic plots or linear plots but with resulting values of $k_{obs}/[H_2O_2]_{av}$ that decreased with increasing [H_2O_2] were observed, depending on the acidity.

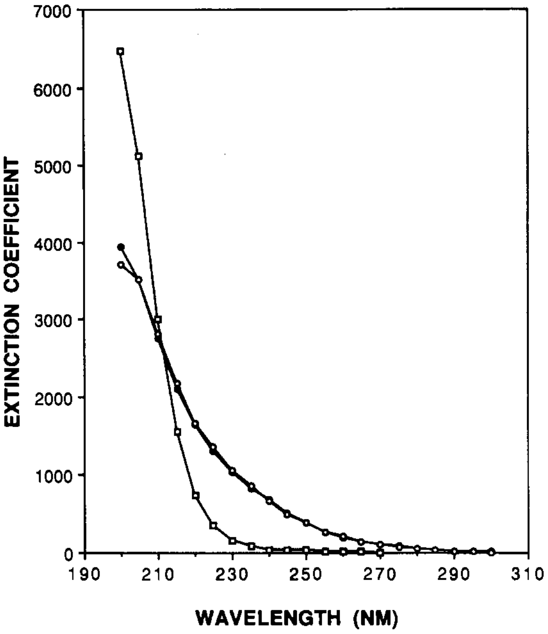

Figure 2. UV spectra of the product formed immediately after mixing dilute Na_2WO_4 solutions with perchloric acid ([$HClO_4$] after mixing is 0.10 M (closed circles) and 0.050 M (open circles)). The spectrum of WO_4^{2-} in water is also shown (squares).

Discussion

The spectral changes in the UV region we observed after mixing tungstate ion with perchloric acid are in qualitative agreement with the potentiometric changes reported by Schwarzenbach,[11] although the acid concentration in our experiments was much greater than in the earlier experiments. Schwarzenbach assigned the very rapid condensation reaction to the formation of a tetramer, probably $H_5W_4O_{16}^{3-}$, with the subsequent formation of a heptameric species within minutes on the basis of the work of Sasaki.[17] It is quite possible that we observed similar chemistry; our data indicate a high order dependence on [W(VI)] in the rapid reaction (cf. Figure 1a). The spectrum shown in Figure 2 is probably that of the neutral tungsten(VI) monomer, which may be formulated as WO_3 with three water ligands omitted or $WO_2(OH)_2(H_2O)_2$ according to the analysis by Tytko.[18] The spectrum of the neutral molybdenum(VI) monomer is similar except shifted to higher wavelengths, with a maximum at 220 nm.[10,15] This shift in the charge-transfer spectra would be anticipated on the basis of the greater oxidizing power of molybdenum(VI). The spectral differences seen for WO_4^{2-} and presumably $WO_2(OH)_2(H_2O)_2$ are in line with those seen with molybdenum(VI), although, as Cruywagen has pointed out, little information about the structures of the various protonated species is revealed by their spectra.[10]

The kinetic data for the formation of $WO(O_2)_2(OH)(H_2O)^-$, the predominant oxo diperoxo complex over the acidity range employed, are consistent with the simple rate expression given in eq 1 at 25 °C. However, the determination of this rate law

$$d[WO(O_2)_2(OH)(H_2O)^-]/dt = ((2.4 \pm 0.3) \times 10^3\ M^{-1}\ s^{-1})[W(VI)][H_2O_2] \quad (1)$$

required careful attention to the experimental conditions since increasing absorbance in the UV region was seen also in the absence of hydrogen peroxide. Competition from condensation reactions of the unstable tungsten(VI) formed immediately after mixing was effectively eliminated only with sufficiently low [W-

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(16) Plots of $A_t - A_{initial}$ vs λ were constructed at 4-s time increments (up to 36 s after mixing) for the experiments in 0.10 M $HClO_4$; broad peaks centered at ca. 230 and 265 nm were observed.

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(VI)], relatively large [H_2O_2], and acidities ≥ 0.0050 M.

The simple rate law summarized in eq 1 is remarkable in view of the corresponding formation kinetics determined for the molybdenum(VI) system over the same acidity range.[3,6] Here the rate law was second order with respect to [H_2O_2] at 0.10 M H^+ but first order at [H^+] $\leq$ ca. 0.005 M. In 0.1 M acid, $HMoO_3^+$ and MoO_3 are the predominant monomeric Mo(VI) species; in 0.005 M acid, MoO_3 is the principal form. The formation rate constants are pH dependent both in the strongly acidic region and in dilute acid, where the order with respect to hydrogen peroxide is second and first, respectively. This feature arises in part from the changing speciation with respect to Mo(VI).

We propose the scheme given in eq 2–4 to account for the rate law observed for the tungsten(VI) system. We have formulated

$$WO_2(OH)_2(H_2O)_2 + H_2O_2 \rightarrow WO_2(O_2)(H_2O)_3 + H_2O \quad \text{slow, } k_2 \quad (2)$$

$$WO_2(O_2)(H_2O)_3 \rightleftarrows WO_2(O_2)(OH)(H_2O)_2^- + H^+ \quad \text{rapid, } K_a > 0.1 \quad (3)$$

$$WO_2(O_2)(OH)(H_2O)_2^- + H_2O_2 \rightarrow WO(O_2)_2(OH)(H_2O)^- + 2H_2O \quad \text{rapid} \quad (4)$$

the neutral W(VI) monomer according to the preference of Tytko, although the exact formulation is not critical, provided it remains as a neutral species over our acidity range. Similarly, the precise formula for the monoperoxo intermediate formed in the first reaction is not important as long as it is largely deprotonated at acidities ≤ 0.10 M, as shown in eq 3. This scheme is consistent with the observed rate law, but we must attempt to justify some of the assumptions that have been made and also to account for the differences seen in the molybdenum(VI) system.

We have proposed[3] that K_a for the monoperoxo complex of Mo(VI) is ca. 0.01. In the acid range where the neutral form is predominant, we suggest that entry of the first peroxo ligand is reversible and entry of the second peroxo ligand is rate determining. Conversely, when the monoperoxo intermediate is largely hydrolyzed, the reaction scheme is analogous to that shown above for W(VI), except for speciation changes of the free Mo(VI) with pH. At pH values near 2 the order with respect to hydrogen peroxide would lie between 1 and 2, as is observed experimentally.

In the case of W(VI) we propose that the formula of monomeric W(VI), presumably $WO_2(OH)_2(H_2O)_2$, does not change from 0.005 to 0.10 M H^+ and that the monoperoxo intermediate is largely deprotonated over the same acidity range as shown in eq 2 and 3. Some experimental support is provided by our spectral data for monomeric W(VI) and the rate expression for the formation of oxohydroxodiperoxotungsten(VI), respectively. If we are correct, then the species we have formulated as $WO_2(OH)_2(H_2O)_2$, $WO_2(O_2)(H_2O)_3$, and $WO(O_2)_2$ are each more acidic than their molybdenum(VI) counterparts. Only in the case of oxodiperoxotungsten(VI) is there direct experimental confirmation of this conclusion.[1,6] Paradoxically, WO_4^{2-} and HWO_4^- are probably more *basic* than MoO_4^{2-} and $HMoO_4^-$.[18]

The first-order rate constant for the formation of oxohydroxodiperoxomolybdenum(VI) is about twice as great as that for the W(VI) analogue in 0.005 M H^+ and in the neutral region. The formation constants[3] are also comparable around pH 7. It appears that the principal differences in the equilibrium and kinetic parameters for these oxo diperoxo complexes are the instability of monomeric tungsten(VI) in acidic solution and the greater acidity of the mono- and diperoxo complexes of tungsten(VI). We have also observed that the activation of peroxide toward reducing agents by the oxo diperoxo complexes of W(VI) and Mo(VI), is similar, though the effect is slightly more pronounced with W(VI).[1,3]

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Registry No. WO_4^{2-}, 14311-52-5; H_2O_2, 7722-84-1.

Contribution from the Radiation Laboratory,
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Intermediates in the Charge-Transfer and Ligand-Labilization Photoreactions of Molybdenum(V) μ-Oxo Dimers[†]

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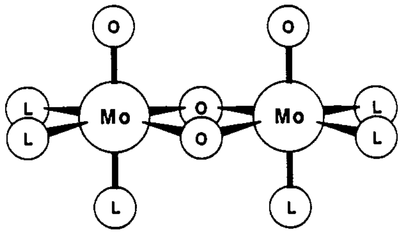
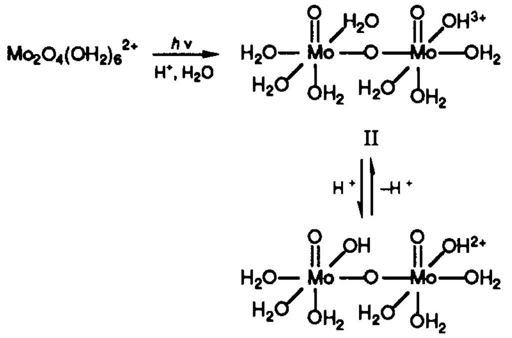
There has been considerable interest in the chemistry of Mo complexes because of its occurrence in biological systems as an essential component of enzymes and its potential applications as a catalyst.[1–7] Recent studies have dealt with the photochemical properties of Mo in its VI, V, IV, III, and II oxidation states, but little is known yet about such properties in molybdenum(V) oxo complexes.[6] In a flash-photochemical study of the (μ-oxo)bis(oxomolybdenum(V)) aquo ion dimer (I),[8] it has been established that photolabilization induces the formation of a single-bridged μ-oxo dimer (II and III in eq 1–3) that experiences dissociative disproportionation into very reactive monomeric Mo(IV) and Mo(VI) species.[9]



I (basic $M_2O_4^{2+}$ core; O = oxygen, L = ligand)



(1)

II

(2)

III

$$\text{II, III} \rightarrow Mo^{IV}O(OH)^+ + Mo^{VI}(OH)_6 + H^+ \quad (3)$$

Such a reactivity suggests that photochemical primary charge-transfer processes leading to the reduction of the metal center and the oxidation of a ligand may have a significant role in the photochemistry of the Mo(V) complexes. These photoprocesses have been investigated in this work by flash photolysis and pulse radiolysis of $Mo_2O_4(OH_2)_6^{2+}$ and $Mo_2O_4Cl_6^{4-}$.

Experimental Section

Photochemical Procedures. The apparatus used for flash photolysis has been described elsewhere.[10] Two FP-8-100C lamps were fired in series at energies adjusted to values between 250 and 40 J/pulse. A lifetime of 30 μs was measured for the flash pulse under these conditions. Hence, points for either kinetic or spectral determinations were collected for times equal to or longer than 50 μs. The wave-form recorder, Biomation 805, was interfaced to a computer, VAX 11/780, for data analyses. Solutions were irradiated at preselected wavelengths, i.e. $\lambda_{exc} > 210$ or 240 nm, respectively, by using appropriate cutoff filters. Streams of ultrapure N_2 or ethylene were used for the deaeration of the solutions prior to the irradiations.

Pulse-Radiochemical Procedures. The apparatus and procedures used for pulse radiolysis have been described in previous literature reports.[11,12] The investigated reactions were initiated by oxidizing the Mo(V) complex

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