Preparation, Spectroscopic Properties, and Characterization of Novel Peroxo Complexes of Vanadium(V) and Molybdenum(VI) with Nicotinic Acid and Nicotinic Acid *N*-Oxide

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Six new compounds, the first peroxo-nicotinic acid and peroxo-nicotinic acid *N*-oxide complexes, have been prepared: K_2-[nicH{VO(O_2)_2}_2](H_2O)$ (1), $MoO(O_2)_2(nicH)(H_2O)$ (2), $MoO_2(O_2)(nicH)(H_2O)$ (3), $MoO_2(O_2)(N\text{-}nicOH)_2(H_2O)$ (4), and $M^I[MoO(O_2)_2(N\text{-}nicO)]$ (M^I = K (5), NH_4 (6)) (nicH = nicotinic acid, *N*-nicOH = nicotinic acid *N*-oxide, *N*-nicO = nicotinate *N*-oxide). These yellow crystalline compounds were characterized by elemental analysis, IR and UV-visible spectroscopy, and ^1H and ^{13}C NMR. Nicotinic acid was oxidized in some peroxo-molybdenum aqueous solutions to *N*-nicOH. Compound **4** was prepared by two methods, starting with nicH or *N*-nicOH. Coordination to the metal via carboxylato groups is present in all the complexes, as indicated by IR and NMR spectra. The presence of a nitrogen-protonated nicotinic acid is indicated in complexes **1-3**. Complex **4** contains two nonequivalently bonded organic ligands in the solid state and the solutions. Peroxo LMCT bands occur between 300 and 330 nm. They undergo a blue shift in aqueous solutions relative to the solid-state spectrum, occur at higher energy in the molybdenum than in the vanadium complex, and have a low molar absorptivity (about 3×10^2). On the basis of all the data six- or seven-coordinated polyhedra are proposed for the structure of these vanadium and molybdenum complexes, containing in the ligand spheres oxygens from oxo, one or two peroxo, nicotinic acid carboxylato, and *N*-oxide groups.

Introduction

A few years ago we reported the preparation, the structure, and the biological activity of several V(V) peroxo complexes with polycarboxylato and amino polycarboxylato heteroligands[1] and a series of $MoO(O_2)_2(\alpha\text{-}AA)H_2O$ complexes,[2] where α-AA = gly, ala, pro, val, leu, and ser. Many aspects of the chemistry of vanadium and molybdenum peroxo heteroligand complexes have been investigated in this laboratory. This research has been motivated to a considerable extent by the idea that the peroxo heteroligand complexes represent a system that will eventually become a useful model for certain biochemical functions of vanadium and molybdenum as well as that this interesting set of complexes will undergo or trigger specific catalytic oxidation and oxygen-transfer reactions.[3-7] Recent investigations involving vanadium bromoperoxidases[8,9] and vanadium nitrogenases,[10,11] which involve V(V), came as an exciting contribution to current knowledge on biological and catalytic participation of vanadium in these enzymes. Vanadium has been investigated for a long time in some marine organisms and plants,[12-14] but its biochemistry still remains poorly understood.[15,16] Complex biochemical interactions are expected in particular for the highest oxidation state, where the stereochemical nonrigidity of V(V) and its ability to display coordinations ranging from tetrahedral and octahedral to trigonal-[17] and pentagonal-bipyramidal[18] combines with the V(V)/V(IV) redox interplay.[19] The formation of intermediates of different thermodynamic and kinetic stability, leading to catalytic conversions,[20,21] is but a logical consequence of these properties. Much the same, and more so, holds true for molybdenum.[22,23]

The peroxo-nicotinic acid V(V) and Mo(VI) systems are complex as well and provide an interesting association of three biochemically relevant entities: the metal ion,[12-16,23] the peroxo group, and the nicotinic acid.[24-26] We have shown that V(V) and Mo(VI) peroxo-nicotinic acid complexes exist as stable species but have also observed the oxidation of nicH to *N*-nicOH and the formation of stable Mo(VI) peroxo-nicotinic acid *N*-oxide complexes. Brief reports of some of this work have already appeared.[27]

Compounds reported here provide an opportunity to study the peroxo-metal and the peroxo-organic ligand interactions in the solid state and solutions, the peroxo-to-metal charge-transfer bands (LMCT) in relation to the reduction potentials observed by cyclic voltammetry, and a correlation with the vibrational energy of the M=O and O—O bonds.[28] Empirical assignments of some characteristic IR vibrational modes were made possible by comparing the spectra of related compounds in this series.

Experimental Section

Materials. Reagent grade V_2O_5, MoO_3, KOH, nicotinic acid, and nicotinic acid *N*-oxide (Aldrich product) and H_2O_2 (30% Mallinckrodt, analytical grade, or 35% Interox, chemical grade) were used. All solvents were reagent grade.

Syntheses. Preparations given below are based on numerous experiments undertaken over the last few years, in order to obtain pure compounds or bigger crystals. The concentration of metals and ligands, the temperature, the pH, and the sequence of adding the reagents all affect the syntheses. Recrystallization from water or organic solvents is im-

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possible, and by recrystallization from the hydrogen peroxide solutions partially decomposed and less pure compounds are obtained. The basic problem is the coprecipitation of oxoperoxovanadates or oxoperoxomolybdates that do not contain the heteroligand and crystallize from solutions where the pH is too high or the precipitation of mixtures containing complexes and excess organic ligands, found in solutions where the pH is too low. So far we did not succeed in getting large enough crystals for an X-ray structure analysis, but by using the given procedures, we have improved the yield and the purity of the products. The pure complexes are much more stable toward decomposition, which is first manifested in a loss of peroxides and later in the reduction of the metals, evident from the color change of the solids. The compounds have a shelf life from a few weeks to several months, some over 1 year.

Preparative work has to be done in the hood with a protective shield, as sometimes unexpectedly violent reactions occur.

Preparation of $K_2[nicH\{VO(O_2)_2\}_2](H_2O)$ (1). V_2O_5 (0.91 g, 10 mmol) was dissolved in water (10 mL) containing KOH (0.70 g, 12 mmol) by stirring and heating at 40–50 °C. The solution was cooled in ice, and H_2O_2 (30%, 5.0 mL, 48 mmol) was added dropwise with stirring. To this clear ice-cold yellow solution was then gradually added nicotinic acid (1.23 g, 10 mmol). The reaction mixture (pH ∼4) was stirred at room temperature for a few minutes and finally heated with stirring at 40 °C for about 20 min. The almost clear solution was then rapidly filtered (pH ∼3.0), and the yellow prismatic microcrystalline compound (yield 23–28%) obtained in 1–14 h was filtered, washed once with cold water (5 mL) and three times with cold ethanol (5 mL), and dried on Drierite or in vacuo at 40 °C. The compound is soluble in water, DMSO, and DMF. Anal. Calcd for $K_2V_2C_6H_7NO_{13}$: K, 16.3; V, 21.2; C, 15.0; H, 1.5; N, 2.9; O_2^{2-}, 26.6. Found: K, 16.2; V, 21.4; C, 15.5; H, 1.4; N, 3.0; O_2^{2-}, 25.6–26.8.

Preparation of $MoO(O_2)_2(nicH)(H_2O)$ (2) and $MoO_2(O_2)$-$(nicH)(H_2O)$ (3). MoO_3 (1.43 g, 9.9 mmol) was dissolved in H_2O_2 (30%, 10 mL, 97 mmol) with stirring and heating at 50–60 °C. To the filtered warm solution was then gradually added nicotinic acid (1.23 g, 10 mmol) with stirring and the reaction mixture kept stirring at about 50 °C for 6 h. The temperature was then raised to 75 °C, and more H_2O_2 (30%, up to 30 mL) was added to obtain a clear solution, which was filtered hot and left standing at room temperature (pH ∼1). The prismatic microcrystalline complex (45–65% yield) appeared within 30 min to 6 h and was soluble in water, DMSO, and DMF. The compound was filtered, washed, and dried as for 1. Anal. Calcd for $MoC_6H_7NO_8$: Mo, 30.3; C, 22.7; H, 2.2; N, 4.4; O_2^{2-}, 20.2. Found: Mo 31.0; C, 22.1; H, 2.4; N, 4.3; O_2^{2-}, 19.4.

When the precipitate was left in the mother liquor for more than 6 h, the collected crystals, washed and dried as above, showed a very similar IR spectrum but contained less peroxide, corresponding to compound 3. Anal. Calcd for $MoC_6H_7NO_6$: C, 23.9; H, 2.3; N, 4.6; O_2^{2-}, 10.6. Found: C, 23.4; H, 2.3; N, 4.6; O_2^{2-}, 10.2.

Preparation of $MoO_2(O_2)(N\text{-}nicOH)_2(H_2O)$ (4). Method 1. Nicotinic acid (2.46 g, 20 mmol) was dissolved in H_2O_2 (30%, 10 mL, 97 mmol), MoO_3 (1.43 g, 10.0 mmol) was added gradually with stirring at 40–50 °C, and the stirring and heating was continued for 5 h. H_2O_2 (30%, 10 mL, 97 mmol) was added to the cloudy solution, which was then heated and stirred for next 10 h. The temperature was raised to 75 °C, and to the hot solution was added dropwise more H_2O_2 (30%, 10 mL, 97 mmol) and then water (10 mL) to obtain a clear solution, which was heated and stirred for another 6–7 h. The hot solution was then quickly filtered (pH ∼2). The pale yellow microcrystalline complex was obtained within 6 h (yield 25–40%) and was filtered and washed and dried as for 1. The compound was slightly soluble in water and was more soluble in DMSO and DMF. Concentrated DMSO solutions ignited spontaneously.

A second crop of crystals can be obtained from the mother liquor left standing at room temperature for 8–10 h. Sometimes it contained a mixture of 4 and thin, colorless 1–2 mm long needles, which did not contain molybdenum and were identified as nicotinic acid N-oxide.

Method 2. MoO_3 (1.41 g, 9.8 mmol) was dissolved in H_2O_2 (30%, 10 mL, 97 mmol) by heating to 60 °C with stirring for 5–6 h. To the clear solution was gradually added nicotinic acid N-oxide (2.8 g, 20 mmol), and the solution was warmed up to 75 °C and stirred at this temperature for 1 h. H_2O_2 (30%, 2 mL, 19 mmol) was then added and stirring continued. After 1–6 h a crystalline precipitate was obtained, filtered, washed, and dried as described for 1; yield 20–40%. The compound had IR and NMR spectra and an elemental analysis identical with those of the product obtained by method 1. Anal. Calcd for $MoC_{12}H_{12}N_2O_{11}$: Mo, 21.0; C, 31.6; H, 2.6; N, 6.1; O_2^{2-}, 7.0. Found: Mo, 20.5; C, 32.4; H, 2.8; N, 6.5; O_2^{2-}, 6.9.

Preparation of $K[MoO(O_2)_2(N\text{-}nicO)]$ (5). MoO_3 (1.44 g, 10 mmol) was dissolved by heating (65 °C) and stirring in water (5 mL) with KOH (0.84 g, 15 mmol). H_2O_2 (30%, 5 mL, 48 mmol) was then added

Scheme I
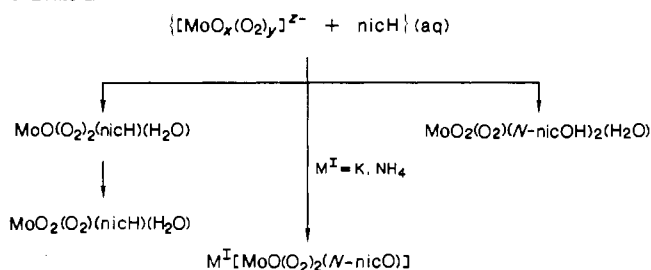
gradually, followed by nicotinic acid (1.23 g, 10 mmol), added in small portions with constant heating and stirring (65–70 °C). The reaction mixture was left heated and was stirred for 5–6 hours, and during this time more H_2O_2 (30%, about 7 mL) was added to maintain the volume at about 10 mL and the pH between 2.5 and 3.5. Bright yellow crystals, soluble in water only, were then obtained on cooling (40–50% yield). They were filtered, washed with cold ethanol (first 50% and then 95%), and dried on Drierite or in vacuo at 40 °C. Anal. Calcd for $KMoC_6H_4NO_8$: K, 11.1;, Mo, 27.2; C, 20.4; H, 1.1; N, 4.0; O_2^{2-}, 18.1. Found: K, 10.7; Mo, 27.8; C, 20.7; H, 1.3; N, 3.8; O_2^{2-}, 17.6.

Preparation of $NH_4[MoO(O_2)_2(N\text{-}nicO)]$ (6). MoO_3 (2.85 g, 20 mmol) was dissolved with heating and stirring at 65 °C in H_2O_2 (30%, 15 mL, 145 mmol). A solution of ammonium nicotinate was made by dissolving nicotinic acid (2.53 g, 20 mmol) in water (10 mL) and concentrated ammonia (30%, 2.5 mL, 21 mmol) and boiling the solution until a faint odor of NH_3 was left. The two solutions were mixed cold (pH ∼3.9) and the mixture heated for about 1 h at 70 °C. The crystals (yield about 40%), soluble in water, obtained by standing at room temperature, were filtered, washed, and dried as above for compound 5. Anal. Calcd for $MoC_6H_8N_2O_8$: C, 21.7; H, 2.4; N, 8.4; O_2^{2-}, 19.3. Found: C, 21.8; H, 2.4; N, 8.5; O_2^{2-}, 19.1.

Physical Measurements and Analyses. Infrared spectra were recorded as Nujol or hexachlorobutadiene mulls with a Perkin-Elmer Model 983 spectrophotometer. Electronic absorption spectra were recorded on a Beckman Acta VI spectrophotometer. ^1H and ^{13}C NMR spectra were obtained on a Varian FT-80A 80-MHz spectrometer, at room temperature in tubes of diameter 10 mm, and were measured relative to an external $(CH_3)_4Si$ standard. The data are results of several independent runs, with a precision of ±0.03 ppm or better.

C, H, N, K, V, and Mo analyses were performed by Atlantic Microlab, Inc., and Galbraith Laboratories, Inc. K, Mo, and V were also determined by atomic absorption spectroscopy. In addition, vanadium was obtained by difference from the thiosulfate titration determining the sum of peroxide and vanadium.[29] In compounds 2, 3, 4, and 6 molybdenum was also determined by ignition to MoO_3. Peroxides were determined by Ce(IV) titration on a Brinkmann E536 potentiograph. In the vanadium compound peroxides were also obtained by difference from the thiosulfate titration, which does not work in the presence of molybdenum.

Results

Nicotinic acid (pyridine-3-carboxylic acid) was stabilized in a ligand sphere of V(V) and Mo(VI) containing coordinated peroxo group(s), and crystalline compounds of the formula K_2-$[nicH\{VO(O_2)_2\}_2](H_2O)$ (1), $MoO(O_2)_2(nicH)(H_2O)$ (2), and $MoO_2(O_2)(nicH)(H_2O)$ (3) were prepared. Oxidation of nicotinic acid to the nicotinic acid N-oxide was also observed in aqueous solutions, under relatively mild conditions, and three compounds with ligand spheres containing nicotinic acid N-oxide and coordinated peroxo groups were separated from the solution: $MoO_2(O_2)(N\text{-}nicOH)_2(H_2O)$ (4) and $M^1[MoO(O_2)_2(N\text{-}nicO)]$ (M^1 = K (5), NH_4 (6)). Three different types of complexes, outlined in Scheme I, were thus obtained from aqueous solutions of Mo(VI) containing hydrogen peroxide and nicotinic acid. They include in an oxo–peroxo–molybdate(VI) coordination sphere nicotinic acid or nicotinic acid N-oxide as a neutral ligand or an anionic nicotinate N-oxide. We could not obtain crystals large enough for an X-ray structure analysis and have characterized these new complexes by chemical and spectroscopic evidence. Spectral data are tabulated in Tables I–III.

IR spectra have been very useful for revealing characteristic vibrational bands, associated with a specific type of coordination

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Table I. Relevant Infrared Data for Compounds **1**, **2**, and **4–6** in Comparison with Those of the Free Ligands (cm⁻¹)[a]

nicH	N-nicOH	1	2	4	5	6	assignt
3421 br		3580 sh	3460 s	3480 s		3460 w, br	ν(OH)
		3506 s	3340	3360			
			3191 m			3192 m	ν(NH)
			3141 s			3141 m	
	3117	3109 s	3112 s	3120 s	3127 s		
				3103 m	3114 w	3114	ν(CH)
3080 sh	3088 sh			3088 m			
3042 s	3078 s	3068 m	3064 s	3068 s	3061 w	3065	
1709 br	1710 s, br			1729 vs			
		1634 vs	1664 vs	1649 vs	1674 vs	1664 vs	ν_{as}(COO)
1416 s	1441 vs	1428 vs	1353 vs	1443 vs	1443 s	1441 s	ν_{s}(COO)
				1362 s, br			
		1271 s		1281 vs	1223 s	1218 s	ν(NO)
				1219 vs			
		941 vs	966 vs	963 vs	969 vs	968 vs	ν(M=O)
				946 vs			
		889 sh	870 sh	871 sh	872 s	872 s	ν_{1}(O—O)
		879 vs	859 vs	860 vs	854 vs	857 vs	
		863 m					

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

Table II. Summary of Electron Absorption Spectral Data of the Complexes[a–c]

	λ_{max}, nm						
complex	Nujol mull		DMSO		DMF		H₂O (0.1 M KCl)
$K_2[nicH\{VO(O_2)_2\}_2](H_2O)$ (1)	265 s	350 sh	261	355 w, br	263	360 w, br	261 (3 × 10³) 329 (3 × 10²)
			265				
$MoO(O_2)_2(nicH)(H_2O)$ (2)	263 s	300–350 sh	256	320 (3 × 10²)	264	338 br	260 (4 × 10³) 304 (3 × 10²)
$MoO_2(O_2)(N-nicOH)_2(H_2O)$ (4)	267 s	290–360 sh	280 (9 × 10³)	336 (9 × 10²)	282	343 (9 × 10²)	257 (9 × 10³) 300–350 sh
$K[MoO(O_2)_2(N-nicO)]$ (5)	275–350 br		c		c		258 (4 × 10³) 300–350 sh
$NH_4[MoO(O_2)_2(N-nicO)]$ (6)	277–350 br		c		c		257 (4 × 10³) 300–350 sh

[a] Abbreviations: s = strong, w = weak, sh = shoulder, br = broad. [b] Values in parentheses are molar absorptivities (L mol⁻¹ cm⁻¹), based on the calculated concentrations of the complexes. [c] Insoluble in the solvent.

Table III. ¹H NMR Spectral Data and Assignments in D₂O and DMSO-d_6[a]

	chem shift					
	nicH (zwitterion)		$K_2[nicH\{VO-(O_2)_2\}_2](H_2O)$		$MoO(O_2)_2$-(nicH)(H₂O)	
peak assignt[b]	D₂O	DMSO-d_6	D₂O	DMSO-d_6	D₂O	DMSO-d_6
H(5)	7.98	7.58	7.91	7.58	8.07	7.55
H(4)	8.80	8.35	8.69	8.33	8.82	8.29
H(6)	8.79	8.83	8.77	8.77	8.93	8.79
H(2)	9.08	9.15	9.04	9.14	9.13	9.09

[a] δ(TMS) = 0.0. [b] The protons are numbered according to the numbering scheme of the carbon atoms to which they are bound.

of ligands. By comparison of the IR spectra of the novel complexes to the spectra of the free ligands (nicH and N-nicOH), and the available literature data on some metal nicotinate[24,26,30–33] and nicotinate N-oxide[34] complexes, fairly reliable empirical assignments can be derived for the characteristic bands given in Table I. Some other typical vibrational modes, such as δ(NO) expected in the vicinity of 820 cm⁻¹, ν_3(M–O$_p$) and ν_2(M–O$_p$) in the vicinity of 630 and 580 cm⁻¹ and the metal–oxygen stretching frequencies occurring between 400 and 250 cm⁻¹ could have been added as an "educated guess" but were omitted from Table I because of the uncertainty in their assignment among several organic ligand bands. M=O and O—O stretching modes[35,36] of the coordinated

peroxo group are clearly distinguished in the spectra as sharp, very strong bands, and they cannot be mistaken, according to our experience with about 60 peroxo–heteroligand compounds prepared and characterized over the years.

The UV–visible spectra of these complexes contain two important sets of bands in the examined region (200–800 nm): the ligand π–π^* transition and the peroxo–metal charge-transfer (LMCT) bands, which are of much smaller intensity than the π–π^* absorption.[28,37] The spectra were recorded in the solid state as Nujol mulls, in DMSO, DMF, and aqueous (0.1 M KCl) solutions, in the pH range 8–0. Peroxo LMCT bands are broad and weak, but by careful choice of concentrations it was possible to resolve them in most of the solutions. λ_{max} values of these bands are shown in Table II, with an estimated molar absorptivity in brackets.

¹H NMR spectra were obtained in D₂O, DMSO-d_6, and DMF-d_7. They confirm the IR evidence regarding the coordination of organic ligands, which seemed to be retained in the solution. Patterns typical for the nicotinic acid zwitterion were observed. Legg et al. have shown and discussed the NMR spectrum of nicotinic acid in D₂O,[31] observing that by removing electron density from the nitrogen and protonating it in an acid solution, or by coordinating nitrogen to a metal, the ring protons shift and the overlap of H(4) and H(6) resonances occurs. These shifts are small, and Legg et al. later used deuteron NMR of complexes with C(2)D-deuteriated nicotinic acid, observing shifts of ca. 70 ppm.[38] ¹H NMR spectra of V(V) and Mo(VI) complexes show in aqueous solutions some broadening, caused by partial decomposition and hydrolysis in water, but it has still been possible to measure chemical shifts and some spin–spin coupling constants. Sharp and better resolved ¹H spectra were obtained in DMSO-d_6 and DMF-d_7. The ¹³C spectra of the complexes were

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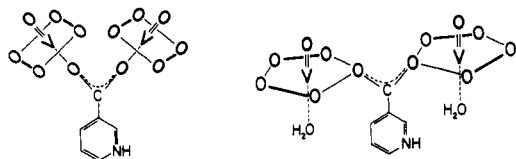
Figure 1. Structural formula of the six- or seven-coordinated V(V) polyhedron expected in $K_2[nicH\{VO(O_2)_2\}_2](H_2O)$.

poor, and even in organic solvents decomposition, indicated by the color change of the solutions, occurred in the time required for the experiment. In spite of numerous attempts we have not found all the carbons, and a stronger magnetic field instrument is needed for ^{13}C NMR spectra of these compounds.

Properties and proposed structures of each specific compound are presented below, supported by combined chemical and spectral evidence.

$K_2[(\mu\text{-nicH})\{VO(O_2)_2\}_2](H_2O)$ **(1)**, the microcrystalline yellow compound, obtained from aqueous solutions at pH 3–4, did not decompose in about 1 year, stored in a dark, dry container. Its formation can be schematically described by the equation

$$2VO_3^- + 4H_2O_2 + nicH \rightarrow [nicH\{VO(O_2)_2\}_2]^{2-} + 4H_2O$$
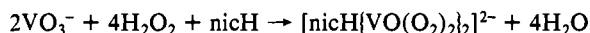
The presence of a carboxylato N protonated and symmetrically bridging zwitterion of nicH is supported by IR and ^1H NMR evidence. In combination with chemical and spectral evidence for the presence of two coordinated peroxo groups and a terminal oxo group, the structure of the complex ion may be represented by six- or seven-coordinated polyhedra, shown in Figure 1. The position of the water molecule cannot be known without an X-ray structure analysis, but a relatively high $\nu(OH)$ band (see Table I) may indicate a loosely bound lattice water. The $\nu(NH)$ band cannot be singled out in the rich spectrum of well-resolved CH stretchings and some bands between 3000 and 2500 cm^{-1}, due to hydrogen-bonded OH or NH. The coordination mode of the nicotinic acid, however, can be safely deduced from the IR spectra, on the basis of the previous experience and spectra of Cr(II-I),[26,30,32,39] Co(III),[31] Cr(II),[30] and Cu(I)[33] complexes, some of which with a known X-ray structure. These complexes have demonstrated that generalization about the relationship between IR vibrational modes of a coordinated carboxylato group, most thoroughly examined in the acetato complexes,[40] can be extended to other monocarboxylic acids, such as nicH. The position of the asymmetric and symmetric COO stretchings and their absolute difference of about 206 cm^{-1} found in the vanadium complex are typical of a bidentate or symmetrically bridging nonprotonated carboxylato group. A larger difference, e.g. 293 cm^{-1} in nicotinic acid, is typical of a free or unidentately coordinated carboxylate.[33,40] Furthermore, it has been suggested that the aromatic CC stretchings (appearing at ca. 1620–1580 cm^{-1}) exhibit absorption intensity of a strength equal to those of COO absorptions only when the carboxylato group is symmetrically coordinated.[40] This is clearly the case in the IR spectrum of complex **1**, as compared to the spectrum of $MoO(O_2)_2(nicH)(H_2O)$ **(2)** in this region, where a considerably less intense aromatic CC stretching band signifies monodentate carboxylato group coordination to molybdenum. The strong bands assigned to V=O and O—O stretchings, shown in Table I, occur at the expected frequency.[18,29]

^1H NMR spectra provide additional support for the presence of a bridging zwitterion in the solution, as proposed in Figure 1. Spectra in D_2O, DMSO-d_6, and DMF-d_7 display a signal pattern and chemical shifts typical of a nicotinic acid zwitterion. A significant downfield shift of the H(4) proton in D_2O, as compared to its position in the spectra in DMSO-d_6 and DMF-d_7, shown in Table III, probably indicates a fast hydrolysis of the ligand. In DMSO-d_6 and DMF-d_7 spectra four distinct proton signal patterns are observed, without an overlap of H(4)–H(6). The spectra in both solvents are very similar and consistent with the
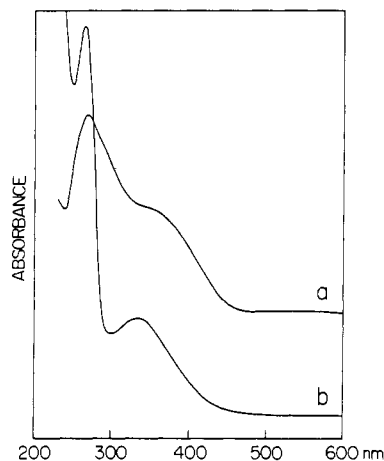

Figure 2. Absorption spectrum of $K_2[nicH\{VO(O_2)_2\}_2]$ in (a) Nujol and (b) 0.1 M KCl.
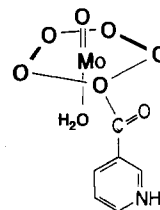

Figure 3. Proposed structural formula of $MoO(O_2)_2(nicH)(H_2O)$.

existence of a carboxylato-coordinated nicotinic acid zwitterion, which displays similar chemical shifts in these solvents. Significant changes in the chemical shifts of aromatic proton signals in the complex relative to those of the free zwitterion are neither expected nor observed, because coordination via the carboxylato group removes the electron density on the carboxylato oxygens, which are four atoms away from the nearest proton. Proton spin–spin coupling constants were assigned. The largest value of about 8 Hz is naturally observed for the ortho $J(5-4)$ and $J(4-5)$ protons; the constant for the ortho $J(5-6)$ and $J(6-5)$ protons amounts to about 5 Hz; the meta $J(4-6)$, $J(4-2)$, and $J(6-4)$ protons show a value of about 2 Hz. The weakest coupling constant of about 1 Hz is, of course, observed for the para $J(5-2)$ and $J(2-5)$ protons.

The UV–visible spectrum of this complex (see Table II) contains the $\pi\text{--}\pi^*$ transition of the organic ligand and the solvent-dependent LMCT bands from the peroxo group. The former appears much like in the free ligand[37] at about 260 nm and has been observed to split into two maxima (255 and 263 nm) at pH >6. The more important peroxo LMCT bands are of general interest in relation to dioxygen bonding to metal centers in proteins and metalloenzymes, as well as to catalytic oxidations. In this vanadium complex the peroxo LMCT band was found in water at $\lambda_{max} = 329$ nm. No other nicH or nicotinato LMCT bands were observed in this region in the spectra of Cr(III) and Co(III) nicotinato complexes,[24-26,30,38] Figure 2 illustrates the comparison of the spectra in the solid-state and aqueous solutions. The position and intensity of the peroxo LMCT band remain unchanged in aqueous solutions of pH 8–2. At pH <2 a new band at 458 nm appears, with a molar absorptivity of 510–550 L mol^{-1} cm^{-1}. This value amounts to approximately twice that found for the $VO(O_2)^+$ cation (280 L mol^{-1} cm^{-1}) reported previously for acid peroxide solutions of V(V),[41] in agreement with the proposed stoichiometry of the vanadium complex **1**.

$MoO(O_2)_2(nicH)(H_2O)$ **(2) and** $MoO_2(O_2)(nicH)(H_2O)$ **(3).** The yellow, prismatic, microcrystalline compound **2** is most likely a monomeric seven-coordinated complex, similar to the pentagonal-bipyramidal compounds $MoO(O_2)(\alpha\text{-AA})(H_2O)$, where α-AA = glycine, proline. In the pentagonal plane of these com-

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(39) Gonzalex-Vergara, E.; Hegenauer, J.; Saltman, P.; Sabat, M.; Ibers, J. A. *Inorg. Chim. Acta* **1982**, *66*, 115.

(40) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

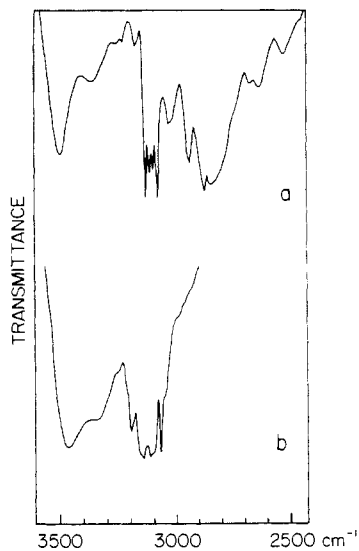(41) Orhanovic, M.; Wilkins, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 278.

Figure 4. IR spectra of (a) $MoO_2(O_2)(N\text{-nicOH})_2(H_2O)$ and (b) $MoO\text{-}(O_2)_2(nicH)(H_2O)$.
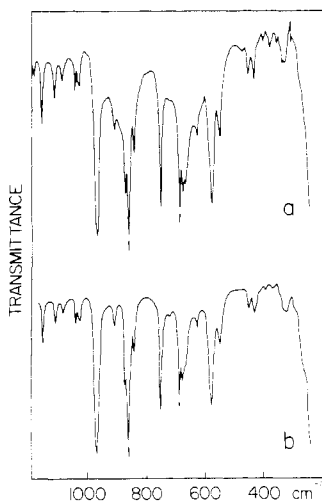
Figure 5. IR spectra of (a) $MoO(O_2)_2(nicH)(H_2O)$ and (b) $MoO_2\text{-}(O_2)(nicH)(H_2O)$, with the arrows indicating the $\nu_1(O—O)$ and $\nu_3(O—O)$ bands.

pounds are two peroxo groups and a carboxylato oxygen from the zwitterion, with the axial positions occupied by the Mo=O group and the water molecule.[2,4] An analogous structure for complex **2**, supported by spectral evidence, is proposed in Figure 3. Most of the structural features can be deduced from the IR spectrum (see Table I). The broad band at 3460 cm^{-1} indicates the presence of a coordinated water molecule. Clearly esolved is the NH stretching, shown in Figure 4 within a distinct pattern of bands in this region and compared to the CH stretchings observed in complex **4**. The position and the difference between ν_{as}(COO) and ν_s(COO) indicate a unidentate coordination of a nonprotonated carboxylato group, supported in addition by the moderate intensity of the aromatic ν(CC) band[40] at 1589 cm^{-1}. The very strong band at 966 cm^{-1} is assigned to ν(Mo=O), and the assignment of the peroxo bands (ν_1 and ν_3), which usually occur as strong, easy to detect bands, has been confirmed by comparison of the spectra of complexes **2** and **3**. In Figure 5 IR spectra of **2** and **3** are shown in the region of 1100–250 cm^{-1}. The spectra are practically identical, except for the intensity ratio of the two sets of strong bands: 966 ↔ 859 and 750 ↔ 687 cm^{-1}. The intensity of the bands at 859 and 687 cm^{-1} is clearly reduced in the spectrum of complex **3**, the monoperoxo analogue of complex **2**. The dependence of the intensity of the two bands upon the peroxo content confirms the assignment of the 859- and 687-cm^{-1} bands and the ν_1 and ν_3 peroxo group vibrational modes, respectively.[29,36] The band at 966 cm^{-1}, however, is totally inde-
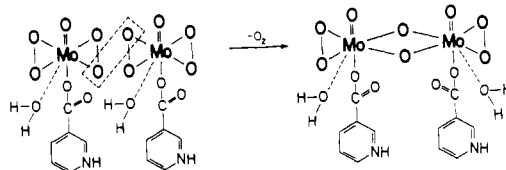

Figure 6. Plausible formation of a bis(μ-oxo) dimer from two MoO-$(O_2)_2(nicH)(H_2O)$ monomers upon oxygen release.

pendent of the peroxo content, representing a pure Mo=O stretching mode.[42]

There was no difference in ^1H NMR spectra of complexes **2** and **3**, run in D_2O, DMSO-d_6, and DMF-d_7. A pattern typical of a nicotinic acid zwitterion was observed, in agreement with IR spectra. Compared to the zwitterion spectrum, a slight downfield shift of H(4) and a more significant upfield shift of H(6) exist in the DMSO-d_6 and DMF-d_7 spectra, resulting in a 0.11–0.50 ppm splitting of the two resonances. Four distinct signal patterns are also observed without any overlap of H(4)–H(6) in DMSO-d_6 and DMF-d_7 (see Table III). The proton coupling constants were calculated for D_2O, DMSO-d_6, and DMF-d_7 spectra and proved to be of the same order of magnitude as the constants given for the vanadium complex **1**. The constant of 6 Hz for J(6–5) is, however, about 1 Hz stronger than that observed in the vanadium complex.

The peroxo LMCT bands are clearly resolved in aqueous solutions at 304 nm, as shown in Table II. In the pH range 7–2 they appear between 304 and 310 nm, and a red shift to 324–330 nm is obserbed below pH 2. The λ_{max} value of these bands depends upon the solvent, but a blue shift definitely exists on comparison with the spectrum of the vanadium complex **1**.

$MoO_2(O_2)(nicH)(H_2O)$ (**3**) was obtained by a modified preparative procedure of the synthesis for **2** or from complex **2** by loss of peroxide on standing. It was much more stable toward deoxygenation than complex **2**, and some samples remained in fact unchanged on standing in a dark dry container for a period of over 2 years. Such a behavior confirms our general observation that, in the solid state and in solution, the diperoxo complexes lose the first peroxo group much easier and the remaining one is bonded much more strongly. This process can be described by the equation

$$2MoO(O_2)_2(nicH)(H_2O) \rightarrow 2MoO_2(O_2)(nicH)H_2O + O_2$$
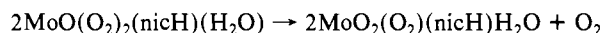
In the solid state favorable orientations of coordination polyhedra may allow the loss of oxygen and subsequent rearrangement of molybdenum–oxygen bonds without destruction of the lattice. In Figure 6 oxygen release involving two polyhedra and an interaction between two adjacent coordinated peroxo groups, followed by the formation of two bridging μ-oxo groups, is shown as an example. No change in the coordination number is required by such dimerization, involving a relatively small distortion of ligand polyhedra. The almost identical IR spectra of compounds **2** and **3** are in excellent agreement with a phenomenon of this kind, because the

$$Mo\overset{O}{\diagdown}\diagup Mo$$
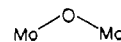
bridging does not involve a vibrational mode generating characteristic IR band.[35] Loss of one peroxide group is reflected in the decreased intensity of the peroxo bands, as demonstrated in Figure 5. The whole event does not require a change in the orientation of the nicotinic acid ligand, which then accounts for the observed similarity of IR and NMR spectra.

$MoO_2(O_2)(N\text{-nicOH})_2(H_2O)$ (**4**) is a crystalline, yellow compound and is stable for months. It has the richest and the most complex IR spectrum among all these compounds, as shown in Table I. The carboxylato stretching region suggests that two dissimilar organic ligands are present, with two nonequivalent

(42) Almond, M. J.; Crayston, J. A.; Downs, A. J.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1986**, *25*, 19.

carboxylato groups. The presence of a coordinated water molecule is indicated by ν(OH), and a number of weak- to medium-intensity bands in the region 2900–2500 cm^{-1} imply the existence of strong hydrogen bonding. The distinct aromatic CH stretching pattern shown in Figure 4 does not contain a band above 3120 cm^{-1}, found as ν(NH) in complex **2**. Two sets of ν_{as}(COO) and ν_{s}(COO) bands appear, as shown in Table I. Two strong additional bands at 1281 and 1219 cm^{-1} (on comparison of the spectrum with the spectra of nicotinic acid and its complexes) are assigned to δ(NO), a characteristic frequency found in nicotinic acid *N*-oxide at 1271 cm^{-1} and shifted to about 1220 cm^{-1} in its M(II) complexes.[34] The existence and positions of these two bands, along with the observed carboxylato stretchings, indicate the presence of two nonequivalent nicotinic acid *N*-oxide molecules, of which one is coordinated via *N*-oxide oxygen (ν(NO) shifted to 1219 cm^{-1}) and the other via an oxygen of the carboxylato group. Two very strong bands at 963 and 946 cm^{-1} imply the presence of two cis-oriented Mo=O groups, and the ν(O—O) stretchings occur at 860 cm^{-1}. Two additional bands in the region between 860 and 800 cm^{-1} must be due to δ(NO) (found in *N*-nicOH at 828 cm^{-1}), but to assign a particular band in this crowded region to a given mode would be possible only by an isotopic shift study. ν_{3}(Mo–O$_{p}$) is, likewise, part of the complex absorption between 675 and 653 cm^{-1}.

^{1}H NMR spectra in D$_{2}$O, DMSO-d_{6}, and DMF-d_{7} confirm the IR evidence by indicating the presence of two nonequivalent organic ligands. The resonances of all the eight aromatic protons can be distinguished in the four signal pattern regions, which gave an integration ratio of 1:1:3:3. In D$_{2}$O chemical shifts are broad and time-dependent, implying an ongoing hydrolysis process. ^{1}H NMR spectra of compound **4** prepared from nicotinic acid or nicotinic acid *N*-oxide are identical.

The UV–visible spectrum of compound **4** shows distinct differences from the spectra of complexes **2** and **3** as shown in Table II. The molar absorptivity of the π–π^{*} band indicates a 1:2 molybdenum-to-ligand ratio. The important difference occurs in the LMCT region between 300 and 350 nm, where nicotinic acid *N*-oxide displays a n–π^{*} band at 303–312 nm and 3d transition metal ion complexes of nicotinate *N*-oxide show in addition LMCT bands between 337 and 363 nm.[34] As a consequence, peroxo LMCT transitions are not resolved in the spectrum of complex **4**, because they overlap with the additional n–π^{*} and LMCT bands.

Chemical and spectral evidence therefore shows that, in the aqueous peroxo–Mo(VI) solutions under conditions used for the synthesis of complex **4**, oxidation of nicotinic acid occurs and the product of the oxidation, nicotinic acid *N*-oxide, coordinates to molybdenum. Peroxo complexes of V(V) with nicotinic acid *N*-oxide were not obtained by analogous procedures. This difference between V(V) and Mo(VI) systems is probably due to different reactivities of nicotinic acid in the presence of the two metals; however, a favorable solubility and lattice energy of the molybdenum complexes is another important factor.

M^{I}[MoO(O$_{2}$)$_{2}$(*N*-nicO)] (M^{I} = K (**5**), NH$_{4}$ (**6**)) represent a set of peroxo complexes with a ligated nicotinate *N*-oxide ion. Their compositions are derived from chemical analysis and spectral evidence. Characteristic features of IR spectra are given in Table I. The spectrum of the potassium salt is transparent in the region 3000–1700 cm^{-1} in the absence of hydrogen bonding. The band assigned to ν_{as}(COO) is much stronger than the aromatic ν(CC) band following it, which along with the frequency difference between ν_{as} and ν_{s} (about 230 cm^{-1}) implies the presence of a deprotonated, free, or unidentately coordinated carboxylate of the nicotinate *N*-oxide ligand. ν(NO) is well resolved at 1223 and 1218 cm^{-1}, and δ(NO) appears most likely at 818 and 819 cm^{-1}. The red shift of ν with regard to that for *N*-nicOH (48 and 53 cm^{-1} for the potassium and ammonium salts, respectively) strongly indicates that the *N*-oxide oxygen of the nicotinate *N*-oxide is coordinated to the molybdenum.[34] The strong ν(O—O) stretchings are clearly resolved near 855 cm^{-1}, and the ν_{3} peroxo mode absorbs within the complex band at 689–645 cm^{-1}.

Much like the UV–visible spectrum of complex **4**, the spectra of complexes **5** and **6** display a broad absorption between 300 and

350 nm. The peroxo LMCT bands could not be resolved because of the overlap with the n–π^{*} and LMCT bands of nicotinate *N*-oxide ion. The molar absorptivity of the π–π^{*} band amounts to about half of that observed for complex **4**, in agreement with the proposed formula. Spectra in DMSO and DMF were not obtained because of the insolubility of the compounds.

Discussion

The peroxo complexes obtained from aqueous solutions of V(V) and Mo(VI) containing nicotinic acid and hydrogen peroxide nicely demonstrate the common property of peroxides to readily enter heteroligand spheres of these two metal ions. Peroxo ligands then modify the coordination mode and proton association of the heteroligand in a way that leads to the formation of a stable complex metal species.

Aqueous solutions of vanadates(V) and molybdates(VI) containing nicotinic acid and hydrogen peroxide are governed by complex equilibria involving protonated and deprotonated nicotinic acid, nicotinic acid *N*-oxide (as shown by this work), and a number of complex metal species of various labilities and stabilities.[43,44] Equilibrium between these species depends upon the factors that we have found important when preparing a particular compound, such as pH, temperature, and concentrations of metals and ligands. The lattice energy of the crystalline product is an additional component responsible for the solubility and crystallization of a particular compound. With this in mind, we can understand how under seemingly analogous conditions the peroxo–nicotinic acid or the peroxo–nicotinic acid *N*-oxide complexes can be obtained. The complex metal species, prevailing in the solution equilibria, need not necessarily crystallize and be separated in the solid state, and a very small variation in experimental conditions can bring about crystallization of a different compound. Since it is rather difficult to characterize the mixture of complex metal species in aqueous solutions, the separation of individual components into the solid state remains one of the best ways to learn and understand better the chemistry of such systems.

Interaction of nicotinic acid itself with the transition-metal ions has been attracting the attention of chemists for a long time.[31,32,39,45] More recently this interest has increased because of the possible chromium–nicotinic acid connection with the glucose tolerance factor (GTF) obtained from brewer's yeast.[24,25,30] X-ray structure analysis of some complexes shows that various coordination modes are possible for this pyridine-3-carboxylic acid: the molecule can coordinate in the protonated or deprotonated form,[31,38] monodentately via nitrogen, e.g. in Cr^{II}(nic)$_{2}$(H$_{2}$O)$_{4}$,[30] or oxygen, as in *trans*-[Cr^{III}(nicH)$_{2}$(NH$_{3}$)$_{4}$](ClO$_{4}$)$_{3}$·2H$_{2}$O.[26] A symmetric binuclear carboxylate bridging exists in the [Cr$_{3}$O-(nicH)$_{6}$(H$_{2}$O)$_{3}$]$^{7+}$ ion,[39] and the binuclear bridging via carboxylate and nitrogen is present in the polymeric [(Ph$_{3}$P)$_{2}$Cu^{I}(nic)].[33] The first three of these coordination types have been proposed to occur in solutions as well.[24,25,32,38] In the absence of an X-ray structure analysis, IR spectra have been widely used to assess the coordination site, and complexes have also been characterized by electron absorption spectra and ^{1}H NMR. Some peroxo complexes of V(V) and Mo(VI) containing polydentate pyridinecarboxylate ligands have been reported and characterized.[46,47]

The presence of peroxides in the aqueous nicotinic acid solutions of V(V) and Mo(VI) assures that the metals remain in the highest oxidation state and in some molybdenum systems brings about the oxidation to nicotinic acid *N*-oxide. This oxidation is not surprising, but it is unusual for it to occur under such mild conditions in an aqueous solution of pH 1–4. Normally, it proceeds in glacial acetic acid.[48] The molybdenum presence obviously

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(44) Persdotter, I.; Trysberg, L.; Stomberg, R. *Acta Chem. Scand., Ser. A* **1986**, *A40*, 83.
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catalyzes the oxidation process, and it is notable that under analogous conditions oxidation has not been detected in V(V) systems.

Several metal complexes of nicotinic acid *N*-oxide have been synthesized in aqueous and nonaqueous solvents.[34,49] X-ray structure analysis has been done for some,[49] showing that the ligand can coordinate in a monodentate manner via *N*-oxide oxygen or an oxygen of the carboxylato group. In addition, the ligand can be bidentate through both carboxylato oxygens or by bridging via a carboxylato oxygen and the *N*-oxide oxygen. Only an X-ray structure analysis could reveal the structure of molybdenum complexes **4–6**. However, the spectral and chemical data

given have provided satisfactory evidence for the composition of the ligand sphere and the most likely mode of ligation to the molybdenum ion.

The ligand spheres containing the combination of coordinated peroxo groups along with nicotinic acid or its *N*-oxide represent interesting example of peroxo–heteroligand V(V) and Mo(VI) complexes, where unusual electron transfers may be facilitated and where three biochemically relevant components are combined in a compound. The structure, spectral properties, and reactivity of this type of compound are of interest and importance for biochemistry, as well as for many catalytical oxidations involving vanadium or molybdenum.

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Kinetics of Electron-Transfer Reactions between Transition-Metal Complexes and the Methyl Viologen Radical Cation

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Kinetic data for the reactions between MV$^{\bullet+}$ and eight transition-metal complexes (of cobalt, ruthenium, chromium, and iron) and the uranyl ion were determined at pH 4 in 0.1 M perchlorate medium by pulse radiolysis. All the oxidants investigated are outer-sphere reagents with known standard reduction potentials and self-exchange rate constants. The measured rate constants are in agreement with those predicted by the Marcus theory after allowances are made for the diffusion control and electrostatics.

Introduction

The reactions of the 1,1'-dimethyl-4,4'-bipyridinium ion (abbreviated methyl viologen cation or MV^{2+}) and of its radical cation, MV$^{\bullet+}$, have been of considerable recent interest. Among other considerations that motivated this study is the widespread use of this couple as an "indicator" pair in chemical and photochemical reactions, since the radical cation is so brightly colored ($\epsilon_{max} \sim 13\,000$ L mol^{-1} cm^{-1} at 600 nm).
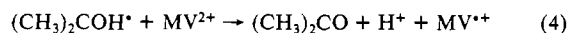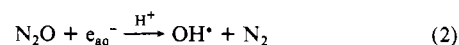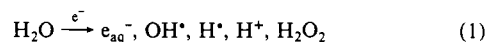
This report concerns the kinetics of a series of nine reactions; the analysis of the data also incorporates three additional reactions from the literature. Tsukahara and Wilkins[2] have studied the reactions of several viologens with a range of cobalt(III) complexes. They noted a considerable anion effect on the rates of reaction. In the present study a constant 0.10 M perchlorate medium is used. The methyl viologen radical cation is a good outer-sphere reductant ($E° = -0.45$ V), and the series of oxidants used have known standard reduction potentials and self-exchange rate constants, making it possible to correlate the data in terms of the equations of the Marcus theory. We relied on the self-exchange rate for the MV^{2+}/MV$^{\bullet+}$ couple directly determined by NMR line broadening,[3] although other estimates[4,5] were also considered.

Experimental Section

Reagents. Methyl viologen was obtained from Aldrich and used without further purification. Most of the other chemicals were available from earlier investigations.[6]

Pulse Radiolysis. The principal reducing agent for MV^{2+} was $^{\bullet}$C-(CH$_3$)$_2$OH, generated by radiolysis of O$_2$-free, N$_2$O-saturated water in the presence of 0.10 M 2-propanol.

The important reactions occurring are shown in eq 1–4.

$$H_2O \xrightarrow{e^-} e_{aq}^-, OH^{\bullet}, H^{\bullet}, H^+, H_2O_2 \qquad (1)$$

$$N_2O + e_{aq}^- \xrightarrow{H^+} OH^{\bullet} + N_2 \qquad (2)$$

$$OH^{\bullet} + (CH_3)_2CHOH \rightarrow (CH_3)_2COH^{\bullet} + H_2O \qquad (3)$$

$$(CH_3)_2COH^{\bullet} + MV^{2+} \rightarrow (CH_3)_2CO + H^+ + MV^{\bullet+} \qquad (4)$$

An acidity of 10^{-4} M was used, and an ionic strength of 0.10 M was achieved through the addition of NaClO$_4$. All solutions were prepared with triply distilled water. Pulse radiolysis was carried out with a beam of 15-MeV electrons at a 4-ns pulse length. A 2-cm reaction cell was used, and the decay of [MV$^{\bullet+}$] was monitored at 600 nm. Pseudo-first-order rate constants were calculated from the absorbance–time data obtained by the use of a nonlinear least-squares fitting program.

Results and Discussion

Kinetic Data. The experiments were conducted so that a given oxidizing agent (an acceptor, A) was present in large stoichiometric excess over the methyl viologen radical cation. In each case the pseudo-first-order rate constant (k_{obsd}) varied linearly with the average concentration of A present in a given experiment. Typical plots are shown in Figure 1.

The slopes of the plots of k_{obsd} vs [A] give the second-order rate constants for the cross-reactions, k_{measd}, to a precision of around 5%, and are given in Table I. They range from $\sim 1 \times 10^6$ for Co(sep)$^{3+}$ to 3×10^9 M^{-1} s^{-1} for Cr(phen)$_3^{3+}$; with the literature values[2,7] for Co(NH$_3$)$_6^{3+}$ and Co(en)$_3^{3+}$ included, the range ex-

(1) (a) Iowa State University. (b) Argonne National Laboratory.
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