ppm. These data are consistent with trigonal hydridization of the nitrogen atom with the NO group lying in the symmetry plane of the molecule.

Experimental Section

PnAO and [Ni(PnAO)-6H]. The preparative methods used for these compounds have been described elsewhere.[3]

[Ni(PnAO)-7H(Cl)]. Five grams (0.0154 mol) of [Ni(PnAO)-6H] was dissolved in 200 mL of methanol followed by addition of a small crystal of anhydrous iron(III) chloride. After cooling of this solution to 0 °C, along with rapid magnetic stirring, 285 mL of a 0.0540 M solution of chlorine gas (0.0154 mol) dissolved in methanol was added dropwise while simultaneously adding the same volume of a 0.200 M methanol solution of sodium hydroxide to keep the reaction mixture neutral. The orange, crystalline product that came out of solution was washed with cold water (0 °C) and dried in a vacuum oven at 60 °C; yield 72% of theory. The product was recrystallized twice as follows: it was dissolved in hot chloroform (5 g in 200 mL), activated charcoal was added, and the mixture was filtered followed by addition of 200 mL of carbon tetrachloride to the filtrate with subsequent removal of the chloroform using a water aspirator. Anal. Calcd for $C_{13}H_{21}O_2N_4ClNi$: C, 43.43; H, 5.89; N, 15.59; Cl, 9.86; Ni, 16.33. Found: C, 42.45; H, 5.81; N, 15.25; Cl, 9.83; Ni, 16.23. Molecular weight: calcd 359, found 328.

[Ni(PnAO)-7H(Br)]. Ten grams (0.0308 mol) of [Ni(PnAO)-6H] was dissolved in 400 mL of methanol followed by addition of a small crystal of anhydrous iron(III) chloride. With rapid magnetic stirring at room temperature, 304 mL of 0.100 M bromine (0.0304 mol) dissolved in methanol was added dropwise to this solution while the same volume of a 0.100 M methanol solution of sodium hydroxide was simultaneously added to keep the reaction mixture neutral. The orange crystalline product that came out of solution was washed with cold methanol and dried under vacuum at 60 °C; yield 95% of theory. This complex was recrystallized twice as described for [Ni(PnAO)-7H(Cl)]. Anal. Calcd for $C_{13}H_{21}O_2N_4BrNi$: C, 38.65; H, 5.24; N, 13.87; Br, 19.78; Ni, 14.53. Found: C, 38.16; H, 5.17; N, 13.57; Br, 19.69; Ni, 14.53. Molecular weight: calcd 404, found 380.

[Ni(PnAO)-7H(I)]. Ten grams (0.0308 mol) of [Ni(PnAO)-6H] was dissolved in 400 mL of methanol followed by the addition of a small crystal of anhydrous iron(III) chloride. With rapid magnetic stirring at room temperature, 304 mL of 0.100 M (0.0304 mol) iodine dissolved in methanol was added dropwise to this solution while the same volume of a 0.100 M methanol solution of sodium hydroxide was simultaneously added to keep the reaction mixture neutral. The orange, crystalline product that came out of solution was washed with cold methanol and dried in a vacuum oven at 60 °C; yield 94% of theory. This complex was recrystallized twice as described for [Ni(PnAO)-7H(Cl)]. Anal. Calcd for $C_{13}H_{21}O_2N_4INi$: C, 34.62; H, 4.69; N, 12.42; I, 28.14; Ni, 13.02. Found: C, 34.88; H, 4.57; N, 12.40; I, 28.06; Ni, 13.01. Molecular weight: calcd 451, found 390.

[Ni(PnAO)-7H(NO_2)]. One gram (0.00308 mol) of [Ni(PnAO)-6H] was dissolved in 60 mL of carbon tetrachloride. After cooling of this solution to 0 °C, concentrated nitric acid was added in a dropwise stream which caused the solution color to change from orange to a pale red. After the addition of 7 mL of acid, the solution color changed to a dark red at which point 3 mL of concentrated nitric acid was added with no further color change. After 3 or 4 s, the reaction mixture was quenched with 200 mL of 0.500 M sodium hydroxide (0.100 mol) solution which resulted in the immediate formation of a green crystalline product. Prolonging the neutralization time results in lower yields of this complex. The pH was adjusted to 7 with additional 0.500 M sodium hydroxide solution after which the green compound was washed with water and dried in a vacuum oven at 60 °C; yield 78% of theory. This compound was recrystallized twice as described for [Ni(PnAO)-7H(Cl)] and chromatographed several times (basic alumina, BA-1) to remove a small quantity of purple impurity. Anal. Calcd for $C_{13}H_{21}O_4N_5Ni$: C, 42.19; H, 5.72; N, 18.93; Ni, 15.86. Found: C, 42.05; H, 5.53; N, 18.81; Ni, 15.90. Molecular weight: calcd 370, found 384.

[Ni(PnAO)-7H(NO)]. Two grams of [Ni(PnAO)-6H] (0.00615 mol) was dissolved in 100 mL of carbon tetrachloride followed by addition of 20 mL of aqueous 1.0 M sodium nitrite (0.020 mol) solution. At room temperature, with rapid magnetic stirring, 2.0 mL of concentrated hydrochloric acid (0.024 mol) was added dropwise within a 3-min period during which time green crystals precipitated from the reaction mixture. The green product was washed with water and dried in a vacuum oven at 60 °C; yield 96% of theory. This compound was recrystallized twice as described for [Ni(PnAO)-7H(Cl)] and chromatographed several times (basic alumina, BA-1), to remove a small quantity of purple impurity. Anal. Calcd for $C_{13}H_{21}O_3N_5Ni$: C, 44.10; H, 5.98; N, 19.78; Ni, 16.58. Found: C, 43.96; H, 5.88; N, 19.66; Ni, 16.59. Molecular weight: calcd 354, found 330.

All chemicals were of reagent grade. The water was deionized by a double-bed column. Infrared spectra were taken as KBr pellets on a Perkin-Elmer Model 237B instrument. Proton NMR measurements were made on solutions in deuterated solvents at room temperature with a Varian T-60 ^1H NMR spectrometer. Magnetic susceptibility measurements were made with a conventional Gouy apparatus at two field strengths at room temperature (27 °C). The field strength was calibrated using solid $Hg[Co(NCS)_4]$. The diamagnetic corrections were approximated from Pascal's constants. Conductance measurements were made with a Beckman conductivity bridge, Model RC16B2, and an immersion type conductivity cell. Analyses for C, H, and N and molecular weight determinations were made by Galbraith Laboratories, Knoxville, Tenn., and the nickel and the halogen analyses were carried out gravimetrically using DMG and Ag^+, respectively.

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Registry No. [Ni(PnAO)-6H], 18195-22-7; [Ni(PnAO)-7H(Cl)], 68707-94-8; [Ni(PnAO)-7H(Br)], 68707-95-9; [Ni(PnAO)-7H(I)], 68738-43-2; [Ni(PnAO)-7H(NO_2)], 68707-96-0; [Ni(PnAO)-7H(NO)], 68707-97-1.

References and Notes

(1) The designation -*n*H implies the removal of *n* hydrogens from the complexed ligand.
(2) PnAO is an abbreviation for 2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone) dioxime.
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Kinetics of the Diperoxovanadate(V)-Monoperoxovanadate(V) Conversion in Perchloric Acid Media

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It has long been recognized that yellow diperoxovanadate(V) complexes are not stable in acidic solution but are converted to red monoperoxo species.[1] VO_2^+(aq) forms in aqueous acidic solution red 1:1 monoperoxo- and in neutral solution 2:1 diperoxovanadates(V); the precise structures in solution are are not known.[1] Orhanovič and Wilkins have investigated briefly the kinetics of the very rapid formation of the monoperoxo species from diperoxo species.[2] Their scant data indicated an acid-catalyzed transformation which was found to be likely *independent* of hydrogen peroxide concentration.[2] In the reaction of *cis*-dioxodipicolinatovanadate(V)[3] with H_2O_2 at low H^+ concentrations transient diperoxo species have been

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detected which are converted to the corresponding monoperoxo complex.[3] This process is also acid catalyzed, but contrary to Orhanovič and Wilkins' results an inverse dependence on H_2O_2 concentration has been established. A plausible interpretation of these contradicting results is seriously hampered because in both studies the precise structures of the diperoxo species present in solution are not known. In order to obtain a set of internally consistent kinetic data, we have studied the conversion of several oxo-diperoxovanadate(V) complexes containing bidentate organic ligands in acidic media. The structure of $[VO(O_2)_2C_2O_4]^{3-}$ has been determined by an X-ray analysis,[4] and we feel that the basic respective arrangement of the oxo, peroxo, and bidentate organic ligands will be essentially the same for all complexes of the present investigation despite the fact that due to different charges of the bidentate ligands (0, −1, −2) the overall negative charge of the complex anion varies from −1 to −3.

Experimental Section

Preparation of Complexes. The complexes $K[VO(O_2)_2(bpy)]\cdot 5H_2O$, $K[VO(O_2)_2(phen)]\cdot 3H_2O$, and $K_3[VO(O_2)_2(C_2O_4)]\cdot 2H_2O$ (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, $C_2O_4^{2-}$ = oxalate) were prepared by the method described by Vuletić and Djordjević.[5]

$K[VO(O_2)_2(Me_4phen)]\cdot 5H_2O$ (Me_4phen = 3,4,7,8-Tetramethyl-1,10-phenanthroline). Quantities of 0.46 g of V_2O_5 and 0.33 g of KOH were dissolved in 10 mL of H_2O. To the cooled and filtered solution (15 °C), 5 mL of 30% H_2O_2 and a solution of 1.2 g of 3,4,7,8-tetramethyl-1,10-phenanthroline in 20 mL of ethanol were added. The solution was kept at 0 °C for a few hours. Yellow crystals were filtered off and washed with ethanol and ether. Anal. Calcd: K, 7.60; (O_2^{2-}), 13.14; V, 10.26; C, 38.71; H, 5.28; N, 5.67. Found: K, 7.9; (O_2^{2-}), 13.0; V, 10.3; C, 38.1; H, 5.2; N, 5.7.

$K_2[VO(O_2)_2(pic)]\cdot H_2O$ (pic = Picolinic Acid). Quantities of 1.8 g of V_2O_5 and 3.0 g of KOH and 2.5 g of picolinic acid were dissolved in 30 mL of H_2O. To the cooled and filtered solution (15 °C), 10 mL of 30% H_2O_2 was added. Within a few hours yellow crystals precipitated at 0 °C, which were filtered off and washed with ethanol and ether. Anal. Calcd: K, 22.32; (O_2^{2-}), 18.32; V, 14.54; C, 20.57; H, 2.01; N, 4.00. Found: K, 22.6; (O_2^{2-}), 18.7; V, 14.0; C, 21.3; H, 2.4; N, 3.9.

$(NH_4)_2[VO(O_2)_2(isoquin)]\cdot 5H_2O$ (isoquin = 1-Isoquinolinecarboxylic Acid). Quantities of 0.6 g of NH_4VO_3 and 0.85 g of 1-isoquinolinecarboxylic acid in 40 mL of H_2O and 10 mL of concentrated NH_3 were dissolved. To the cooled and filtered solution, 5 mL of 30% H_2O_2 was added. The solution was kept for 24 h in the refrigerator. Yellow crystals were filtered off and washed with ethanol and ether. Anal. Calcd: N, 11.48; C, 32.80; H, 4.68; V, 13.91; (O_2^{2-}), 17.48. Found: N, 12.4; C, 32.4; H, 5.0; V, 14.3; (O_2^{2-}), 16.6.

Kinetic Measurements. Stock solutions of hydrogen peroxide, perchloric acid, and lithium perchlorate were prepared and standardized as described previously.[3] The kinetics of the reaction of diperoxovanadate(V) species with perchloric acid were studied on a Durrum stopped-flow spectrophotometer. Formation of the red monoperoxo species was followed by measuring the increase in absorbance at λ 440 nm as a function of time or alternatively the decrease in absorbance at λ 350 nm. An aqueous solution containing the respective diperoxovanadate(V) complex (0.5×10^{-3} M) and the desired concentration of H_2O_2 was rapidly mixed at 25 ± 0.2 °C with a second solution containing the desired concentrations of perchloric acid and lithium perchlorate as supporting electrolyte (μ = 1.0 M). Solid samples of the complexes were dissolved prior to kinetic experiments. No free peroxo or bidentate ligand is present in aqueous solution.[5] Values of pseudo-first-order rate constants were obtained from the slopes of ln ($A_t - A_\infty$) vs. time plots, where A_t is the absorbance at time t and A_∞ that after the reaction is complete. Such plots were linear for ca. 5 half-lives. After the first rapid step of the reaction is completed, a very slow and small decrease of absorption at λ 440 nm was observed for all complexes due to slow decomposition of the primary monoperoxovanadate(V) product (presumably loss of the organic ligand). Consequently, it has not been possible to isolate a crystalline monoperoxovanadate(V) complex. The kinetics of this process have not been investigated in any detail. The visible absorption spectra of the diperoxo complexes and their reaction products with H^+ (monoperoxo complexes) are summarized in Table II.

Table I. Summary of Kinetic Data of the Conversion of Oxo-diperoxovanadate(V) Complexes in Acidic Media (25 °C, μ = 1.0 M ($LiClO_4$)), Equations 2 and 3

$[VO(O_2)_2L]^{n-}$	a, M s	b, s	c, $M^{-1}\ s^{-1}$
oxalato	$(1.5 \pm 0.2) \times 10^{-3}$	0.19 ± 0.1	
bipyridine	$(1.5 \pm 0.2) \times 10^{-3}$	0.25 ± 0.1	
phenanthroline	$(2.4 \pm 0.2) \times 10^{-3}$	0.52 ± 0.1	
tetramethylphenanthroline			$(3.0 \pm 0.2) \times 10^3$
picolinato			$(0.75 \pm 0.1) \times 10^3$
1-isoquinolinecarboxylato			$(0.73 \pm 0.1) \times 10^3$

Table II. Visible Absorption Spectra of Complexes (>300 nm)

	diperoxo complexes		monoperoxo complexes[a]	
	λ, nm	ε, L mol⁻¹ cm⁻¹	λ, nm	ε, L mol⁻¹ cm⁻¹
oxalato	329	681	440	~308
bipyridine	335 sh	669	446	~250
phenanthroline	326 sh	1206	451	~257
tetramethylphenanthroline	330 sh	2420	465	~290
picolinato	330	601	443	~290
1-isoquinolinecarboxylato	335 sh	1405	446	~210

[a] Slow decomposition in 0.1 M perchloric acid solutions at 25 °C.

Results

The kinetics of the reaction (1) were measured at 25 °C

$$[VO(O_2)_2L]^{n-} + 2H^+ + H_2O \rightarrow H_2O_2 + [VO(O_2)L\ OH_2]^{(n-2)-} \quad (1)$$

and 1.0 M ionic strength over the concentration ranges $[H^+]$ = 0.01–0.3 M, $[H_2O_2]$ = 0–0.01 M, and [complex] = 0.5×10^{-3} M. The functional dependencies of measured pseudo-first-order rate constants on $[H^+]$ and $[H_2O_2]$ conform to either eq 2 or eq 3. The rate of transformation exhibits a first-order dependence on $[H^+]$ for all complexes under investigation, and an *inverse* dependence on $[H_2O_2]$ for only three complexes whereas the rate of conversion appears to be independent of $[H_2O_2]$ for three other complexes over the $[H_2O_2]$ range investigated. Equation 2 holds for the oxalato, bipyridine, and 1,10-phenanthroline complexes, whereas eq 3 is valid for the tetramethylphenanthroline, picolinato, and isoquinolinecarboxylato complexes (Figure 1).

$$k_{\text{obsd}} = \frac{1}{a + b[H_2O_2]}[H^+] \quad (2)$$

$$k_{\text{obsd}} = c[H^+] \quad (3)$$

Values of a and b were obtained graphically from plots of $(1/k_{\text{obsd}})[H^+]$ vs. $[H_2O_2]$ which are linear. Slopes (b) of straight lines and intercepts (a) were determined by means of a least-squares program (Table I). It would appear that a is relatively independent of the nature of the reacting species (oxalato, bpy, or phen complex).

If $b[H_2O_2] << a$ the $[H_2O_2]$-dependent term in eq 2 is not significant and eq 2 reduces to eq 4. If we bear in mind the structural similarity of all diperoxo complexes of the present study, it is plausible to assume that eq 3 represents this special case of eq 2, and therefore $c = 1/a$. Numerical values of the reciprocals of a (Table I) are very similar to those obtained

$$k_{\text{obsd}} = \frac{1}{a}[H^+] \quad (4)$$

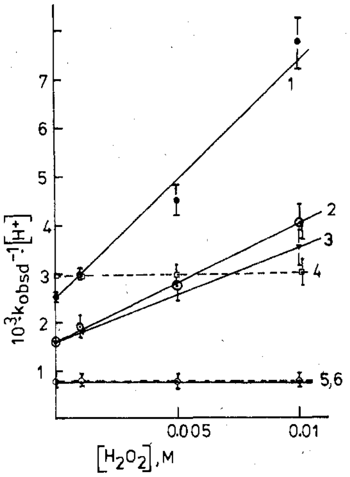


Figure 1. Plot of $k_{obsd}^{-1}[H^+]$ vs. $[H_2O_2]$ for the reaction of $[VO(O_2)_2(L\text{-}L)]^{n-}$ complexes with protons at 25 °C ($\mu = 1.0$ M ($LiClO_4$)). (L-L): 1, phenanthroline; 2, bipyridine; 3, oxalato; 4, tetramethylphenanthroline; 5, picolinato; 6, 1-isoquinolinecarboxylato. Each data point represents the average value of four individual experiments where $[H^+] = 0.05$, 0.1, 0.2, and 0.3 M.

for c and support the above assumption. An upper limit of b can therefore be estimated, 0.02 s, for the experimentally established H_2O_2 independent reactions.

Discussion

From the kinetic data a simple first-order dependence on $[H^+]$ has been detected for all complexes under investigation. A mechanism where the monoprotonated hydroperoxo ligand, O_2H^-, is the actual leaving group leads to rate law eq 5 which

$$[VO(O_2)_2L]^{n-} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [VO(O_2)L]^{(n-2)-} + HO_2^-$$

$$H_2O_2 \rightleftarrows HO_2^- + H^+ \qquad K_a$$

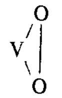
$$[VO(O_2)L]^{(n-2)-} + H_2O \xrightarrow{k_2} [VO(O_2)L(H_2O)]^{(n-2)-}$$

$$\frac{d[VO(O_2)L(H_2O)]}{dt} = \left(\frac{k_1 k_2'}{k_2' + (k_{-1}K_a[H_2O_2]/[H^+])}\right)[H^+][VO(O_2)_2L] \quad (5)$$

$$k_2' = k_2[H_2O]$$

is not consistent with the observed data for the phenanthroline–, oxalato–, and bipyridine–diperoxo complexes. It is noted that for the tetramethylphenanthroline–, picolinato–, and 1-isoquinolinecarboxylato–diperoxo complexes, eq 5 is of the observed form (eq 3) if $k_2' >> (k_{-1}K_a[H_2O_2][H^+]^{-1})$ ($c = k_1$). But it seems highly improbable to us that two different mechanisms should be operative for a series of structurally so similar complexes.

A second mechanism envisages the rapid acid-catalyzed transformation of a one-coordinated peroxo moiety



to a coordinated, monodentate hydroperoxo ligand, V–O–OH. Under our experimental conditions (lowest employed $[H^+] = 0.01$ M) the entire reactant is believed to be converted to this form. In the rate-determining step the hydroperoxovanadium(V) species undergo an acid-catalyzed substitution reaction—H_2O_2 being the leaving group.

$$[VO(O_2)_2L]^{n-} + H^+ \xrightarrow{\text{rapid}} [VO(O_2)(OOH)L]^{(n-1)-}$$

$$[VO(O_2)(OOH)L]^{(n-1)-} + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} [VO(O_2)L]^{(n-2)-} + H_2O_2$$

$$[VO(O_2)L]^{(n-2)-} + H_2O \xrightarrow{k_4} [VO(O_2)L(H_2O)]^{(n-2)-}$$

A rate law as in eq 6 can be derived which is of the form of eq 2, where $a = 1/k_3$ and $b = k_{-3}/k_3k_4'$ and $k_4' = k_4[H_2O]$.

$$\frac{d[VO(O_2)L(H_2O)]}{dt} = \left(\frac{k_3 k_4'}{k_4' + k_{-3}[H_2O_2]}\right)[H^+][VO(O_2)_2L] \quad (6)$$

Thus a in eq 2 represents reciprocal second-order rate constants (c in eq 3 is k_3) for the substitution of a complex-bonded HO_2^- ligand. Values for k_3 for all six complexes are very similar and do not seem to be affected by the electronic properties of the bidentate organic ligand (O,O-, O,N-, and N,N-coordination) or by the steric requirements of the ligand or by the actual overall charge of the diperoxo anion (−1, −2, −3). b in eq 2, on the other hand, is composite, and a more pronounced variation of the values of b within the series of complexes is plausible—leading to relatively small values of b in some cases, producing thereby an H_2O_2-independent experimental rate law.

The proposed mechanism implies that the basicity of a given peroxo ligand coordinated to V(V) is greatly affected by the total number of peroxo groups coordinated to the same V(V) center. This is qualitatively supported[1] by the fact that the tetraperoxovanadate(V) ion is only stable in strongly alkaline solutions and diperoxovanadium(V) species are stable in neutral solutions, whereas some monoperoxovanadium(V) complexes are known to be stable in 2 M perchloric acid.[3]

Acknowledgment. Financial support of this research from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. $K[VO(O_2)_2(Me_4phen)]$, 68782-45-6; $K_2[VO(O_2)_2(pic)]$, 68782-46-7; $(NH_4)_2[VO(O_2)_2(isoquin)]$, 68782-47-8; $[VO(O_2)_2(C_2O_4)]^{3-}$, 68782-48-9; $[VO(O_2)_2(bpy)]^-$, 68832-77-9; $[VO(O_2)_2(phen)]^-$, 68832-78-0; $[VO(O_2)_2(Me_4phen)]^-$, 68782-49-0; $[VO(O_2)_2(pic)]^{2-}$, 68782-50-3; $[VO(O_2)_2(isoquin)]^{2-}$, 68782-51-4; $[VO(O_2)(C_2O_4)OH_2]^-$, 68782-52-5; $[VO(O_2)(bpy)OH_2]^+$, 68782-53-6; $[VO(O_2)(phen)OH_2]^+$, 68782-54-7; $[VO(O_2)(Me_4phen)OH_2]^+$, 68782-55-8; $[VO(O_2)(pic)OH_2]$, 68782-56-9; $[VO(O_2)(isoquin)OH_2]$, 68782-57-0; H_2O_2, 7722-84-1.

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Synthesis of Tris(difluorophosphino)amine and (Trimethylsilyl)bis(difluorophosphino)amine

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A recent publication by Neilson, Lee, and Cowley[1d] prompts us to report on some related studies of ours, concerned with the cleavage of Si–N and Sn–N bonds by phosphorus(III) halides, PF_2X (X = Cl or Br). This method is known to