reaction of $M(CO)_2(DCE)(PR_3)_2Br_2$ with CO. It was not possible to test for solvation of the intermediate because of solubility limitations, however it is presumed that the intermediate is solvated. The sluggishness of the tungsten derivatives could then be rationalized as arising from a stronger interaction of the LUMO with a solvent DCE molecule producing a slower reaction with CO.

The free energy relationship of phosphine basicity (χ) and metal effect (ϕ) on the rate constant was examined. Figure 4 shows the plot of $\ln k_{expt}$ vs $g\chi + h\phi + i$ obtained by multiple linear regression. The values for coefficients g and h were 0.28 and 0.13 and the ratio g/h was 2.1. The linearity of the plot suggests the commonality of the reaction mechanism for the derivatives studied. The signs of the coefficients reinforce the previous inference that an electron-donating phosphine at a tungsten metal center inhibits the rate of reaction.

Comparison to the Reaction of $M(CO)_2(DCE)(PR_3)_2Br_2$ with CO. The rate constant for recombination of $M(CO)_3(DCE)(PR_3)Br_2$ with CO is generally 100 times larger than the value for the recombination of the corresponding $M(CO)_2(DCE)(PR_3)_2Br_2$ derivative with CO. Enhancement of the reactivity of the phosphine-deficient tricarbonyl derives from the fact that it has one less phosphine and one more carbonyl than $M(CO)_2(DCE)(PR_3)_2Br_2$. It therefore has less steric bulk to impede an incoming carbon monoxide and less electron density at the metal center. Both would magnify the reactivity of the electron-poor metal center toward CO.

No fast process was observed for the PEt_3 derivatives. Indirect evidence that it occurs for $W(CO)_3(PEt_3)(DCE)Br_2$ is evidenced in the observation that phosphine scrambling was invoked to explain the infrared spectra of $Mo(CO)_3(PPh_3)_2Br_2$ and $W(CO)_3(PEt_3)_2Br_2$ after photolysis. Apparently the transient collapses within the lifetime of the lamp flash and can not be directly observed.

Summary

Flash photolysis of $M(CO)_3(PR_3)_2X_2$ was shown to undergo two independent photoprocesses: CO loss and PR_3 loss. The CO loss products react directly with CO. The intimate mechanism of CO addition for $M(CO)_2(DCE)(PR_3)_2X_2$ depends on the steric bulk of the phosphine. Derivatives with large phosphine ligands appear to react by a single-step CO addition to the solvated dicarbonyl, while derivatives with smaller phosphines require a two-step reaction. The steric bulk of the phosphine affects the rate in a discontinuous fashion. At small phosphine cone angles ($\leq 137°$) there is no effect of cone angle on the rate. Phosphines with larger cone angles show an inhibitory effect on the rate which increases with increasing phosphine steric bulk. The phosphine loss transient, only observed for bromide triarylphosphine derivatives, was analyzed for electronic effects through linear free energy relationships. Its back-reaction with CO was 100-fold faster than for the CO loss transient because of the more open, more electron-poor nature of the transient. The process was photochromic, implying that phosphine freed by photon absorption replaces a CO in the intermediate product reforming the tricarbonyl.

Acknowledgment. We are grateful to Prof. Mauri Ditzler for allowing access to diffuse relfectance instrumentation and to Prof. Warren Giering for helpful discussions on phosphine steric effects. We acknowledge a William and Flora Hewlett Foundation Grant from the Research Corp. and thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation through Grant No. CHE87-12543 for support of this research. R.M.J. acknowledges the National Science Foundation (USE-8852774) for support of the Holy Cross NMR facilities. J.L.H. acknowledges a Vermont EPSCoR-NSF grant for purchase of the X-ray diffractometer (Grant No. R11-8610679) and Dr. C. Campana for helpful discussions.

Supplementary Material Available: Plots of the fast and slow decay traces for both $Mo(CO)_3(PPh_3)_2Br_2$ and $W(CO)_3(PPh_3)_2Br_2$, the plot of observed rate constant vs [CO] for reaction $W(CO)_2(PEt_3)_2Br_2$ and $W(CO)_3(PPh_3)Br_2$ with CO, a linear free energy plot for the reaction of $M(CO)_2(DCE)(PEt_3)Br_2$ with CO, a plot showing a comparison of experimental and predicted spectra for the solution produced by photolysis of $Mo(CO)_3(PPh_3)_2Br_2$ and $W(CO)_3(PEt_3)_2Br_2$, and tables of the atomic coordinates and equivalent isotropic displacement coefficients, the anisotropic displacement coefficients, and hydrogen atom parameters (9 pages); a listing of the observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Formation and Decomposition of Peroxovanadium(V) Complexes in Aqueous Solution

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Received March 13, 1991

^{51}V NMR spectroscopy has been used to characterize the complexes formed between hydrogen peroxide and vanadate under near-neutral conditions in aqueous solution. The formation constants of the mono-, di-, and triperoxovanadates and tetraperoxodivanadate have been measured and the proton requirements for product formation determined. Under the conditions of these studies, the peroxide was found to undergo slow catalytic decomposition. Studies of the decomposition reaction suggested that the monoperoxovanadate is involved in a disproportionation of the hydrogen peroxide, which occurs by a combination of photo- and thermochemical mechanisms. The decomposition reaction is strongly inhibited by the presence of peptides.

Introduction

The interactions that occur between hydrogen peroxide and vanadium oxoanions have been of interest for many years. The studies of these systems are attracting increasing interest in biochemistry because it is becoming increasingly clear that peroxovanadium compounds can have potent biochemical effects.

Over the past 4 years, an insulin mimetic behavior of vanadate in solution with hydrogen peroxide has been well established.[1-4] The insulin-like synergistic effects of hydrogen peroxide with vanadate exceed those seen with vanadate or hydrogen peroxide alone, suggesting strongly that peroxovanadates are responsible for the effects observed. Other work has shown that peroxovanadates have antitumor activity in mice,[5] and efforts are being

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made to understand the biochemistry of peroxovanadium heteroligand complexes.[5,6] In addition to this, vanadium is a component of the prosthetic group of some bromo- and iodoperoxidases of a lichen[7] and of marine brown and red algae.[8] The developing interest in these types of biologically active compounds will undoubtedly lead to the discovery of increasing numbers of such products.

In addition to biochemical interests, intensive studies over many years have concentrated on the function of peroxovanadates as oxygen-transfer agents.[9,10] It may well be that such reactions give rise to significant biochemical effects, both in vivo and in vitro.

It is well-known that a number of peroxovanadates exist in aqueous solution, depending on the pH and the peroxide and vanadate concentrations.[11-13] The various species have been characterized by ^{17}O NMR spectroscopy,[11] ^{51}V NMR spectroscopy,[11-13] and Raman spectroscopy.[13] The various reports identifying and characterizing the derivatives tend to be in good agreement. Formation constants for the various products have generally not been determined, although those for mono- and diperoxovanadates in strongly acidic solution have been reported.[14,15]

Peroxovanadates have a clear biochemical significance, so it is of interest to study the formation of these materials in aqueous solution at physiological pH. In the present investigation, we have undertaken the study of the formation of the mono- and diperoxovanadium(V) products, as well as higher peroxo products, all formed under near-neutral conditions. ^{51}V NMR spectroscopy has been heavily utilized in these studies. The catalytic decomposition of hydrogen peroxide has been followed by UV/vis spectroscopy.

Experimental Section

Materials. Vanadium(V) oxide, 99.99% (Aldrich Chemical Co.), hydrogen peroxide (Fisher Scientific Co.), and *N*-(2-hydroxyethyl)-piperazine-*N'*-ethanesulfonic acid (HEPES) buffer (Boehringer Mannheim GmbH) were used without further purification.

Vanadate stock solutions were prepared by using procedures previously described.[16] Stock solutions of H_2O_2 were standardized against potassium permanganate prior to use. pH calibration was carried out with freshly opened pH standards. The ionic strength of all samples was maintained at 1.0 M with KCl. Peroxovanadate sample solutions were prepared by adding appropriate quantities of the hydrogen peroxide stock solution at pH 7.0 with HEPES buffer to the required volume of vanadate–HEPES buffer–KCl solution, also at pH 7.0, to afford the desired final concentrations. Mixing was done in this order because the forward reaction to form the products is fast compared to the hydrolysis reaction. Application of this procedure allowed equilibrium to be established in a time reasonably short compared to that for the vanadium-catalyzed decomposition of hydrogen peroxide.

Combination of the two stock solutions, which were prepared at pH 7.0, provided resultant solutions with pH values varying between 6.6 and 6.8. Because of the problems associated with the decomposition of H_2O_2, the values were not corrected. Stock solutions of different pH values were utilized for the pH studies.

Spectroscopy. ^{51}V NMR spectra were obtained from a Bruker AMX-400 NMR spectrometer operating at 105.2 MHz at ambient temperature. Vanadium chemical shifts are relative to the external reference $VOCl_3$ assigned to 0 ppm. Baseline corrections were applied to all spectra before integrals were obtained. NMR spectral parameters were as follows: pulse widths, 60°; spectral widths, 80 kHz; acquisition times, 0.05 s; line broadening, 40 Hz; frequency domain size, 16K data points.

Kinetic measurements were done on a Hewlett Packard 8952 A diode array UV/vis spectrometer using 1 cm path length cells. The decomposition was monitored both in the light and in darkness. For the dark studies, kinetic measurements were made at 10-min intervals with a 0.5-s sampling time. The experiment was repeated with 30-min intervals and then again with 60-min intervals.

Methods. Equilibrium equations were put into a linear form as outlined in the next section and analyzed by standard least-squares procedures. The reported errors represent the standard deviations. The half-lives for decomposition were estimated from the absorption spectra. The decay is complicated by an induction period, which was allowed for in the estimation of the decomposition half-lives.

Table I. ^{51}V NMR Chemical Shifts for the Peroxovanadium(V) Products of this Study[a]

derivative	δ	derivative	δ
$VO(OH)_2(OO)^-$	−602	$VO_2(OH)(OO)^{2-}$	−625
$V(OH)_2(OO)_2^-$	−686	$VO(OH)(OO)_2^{2-}$	−765
$V(OH)(OO)_3^{2-}$	−733	$(VO(OO)_2)_2OH^{3-}$	−758

[a] All species were identified by varying vanadate, peroxide, or hydrogen ion concentration under conditions of 1.0 M KCl and 20 mM HEPES buffer.

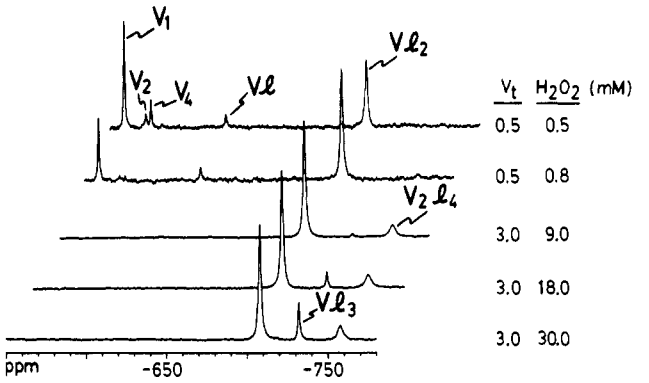

Figure 1. ^{51}V NMR spectra showing the formation of the various peroxovanadates as a function of added hydrogen peroxide. Conditions of the experiments: 1.0 M KCl, 20 mM HEPES buffer, pH 6.7, and the indicated amounts of added vanadate and H_2O_2.

Results

Vanadate undergoes very favorable condensation reactions with hydrogen peroxide. A variety of products are formed as a function of pH and vanadate or hydrogen peroxide concentration. The correspondence between the structure of the product and the signal position in the NMR spectrum has been assigned on the basis of ^{51}V and ^{17}O NMR spectroscopies[11] and ^{51}V NMR and Raman spectroscopies.[13] Those assignments have, in general, been confirmed here by studies of the equilibria established as a function of vanadate or peroxide concentration. The present studies were all done at 1.0 M ionic strength with KCl and at total vanadate concentrations of 5 mM or less so that the minor products observed at the much higher concentrations of the other studies were not observed. The results of mixing vanadate with peroxide are demonstrated in Figure 1. At low vanadate and low peroxide concentrations, the mono- and diperoxo products are the predominant products. With increased vanadate and peroxide concentrations the triperoxovanadate and the tetraperoxodivanadate are the favored products.

The formation of the various products can be written as in eq 1–4, where V refers to vanadate and ℓ to the peroxide ligand.

$$V_1 + \ell \overset{K_1}{\rightleftharpoons} V\ell \qquad [V_1][\ell]K_1 = [V\ell] \tag{1}$$

$$V\ell + \ell \overset{K_2}{\rightleftharpoons} V\ell_2 \qquad [V\ell][\ell]K_2 = [V\ell_2] \tag{2}$$

$$V\ell_2 + \ell \overset{K_3}{\rightleftharpoons} V\ell_3 \qquad [V\ell_2][\ell]K_3 = [V\ell_3] \tag{3}$$

$$2V\ell_2 \overset{K_4}{\rightleftharpoons} V_2\ell_4 \qquad [V\ell_2]^2K_4 = [V_2\ell_4] \tag{4}$$

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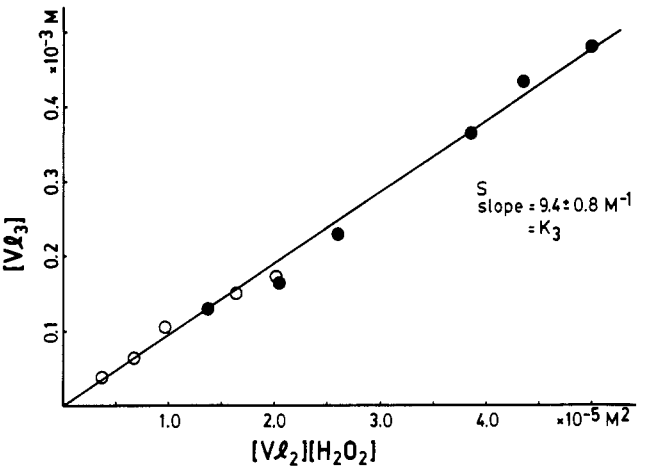

Figure 2. Graphical display of the formation of hydroxotriperoxovanadium(V) according to eq 3. Conditions of the experiments: (●) 3.0 mM total vanadate, 1.0 M KCl, 20 mM HEPES buffer, pH 6.7, and variable amounts of H_2O_2 (9.0–30.0 mM); (○) 15.0 mM total H_2O_2, 1.0 M KCl, 20 mM HEPES buffer, pH 6.7, and variable amounts of added vanadate (0.3–5.0 mM).

Product formation is very favorable, so that, in order to determine the formation constants, the conservation equation (5) must be

$$c(\ell_t) = [\ell] + [V\ell] + 2[V\ell_2] + 3[V\ell_3] + 4[V_2\ell_4] \quad (5)$$

utilized. The concentration of free peroxide is then given by the total peroxide added and the product concentrations as determined from the ^{51}V NMR spectra. This procedure yields considerable error in the free-ligand concentrations when the total added peroxide is comparable to the total vanadate concentration. However, repetitions of the concentration study provided similar equilibrium constants.

The formation constants obtained by plotting the appropriate parameters of eq 1 and 2 were $K_1 = (3 \pm 1) \times 10^3\ M^{-1}$ and $K_2 = (1.7 \pm 0.6) \times 10^5\ M^{-1}$. The value for K_1 is about 100 times larger than the formation constant for mono(oxalato)vanadate, while K_2 is about 1000 times larger than the corresponding value for formation of the bis(oxalato)vanadate.[17,18] This comparison illustrates the very favorable formation of the peroxo products relative to oxalate, which is a reasonably good ligand for vanadate.

At peroxide concentrations higher than utilized in the above study (up to 30 mM for 3 mM vanadate), the $V\ell_3$ and $V_2\ell_4$ products become increasingly important. Incorporation of an additional peroxide into $V\ell_2$ is much less favorable than incorporation into $V\ell$. The ratio $[V\ell_3]/[V\ell_2]$ was plotted against $[H_2O_2]$ as required by eq 3 to yield a good linear relationship. The results, depicted in Figure 2, gave the value $9.4 \pm 0.8\ M^{-1}$ for K_3, to be compared to $1.7 \times 10^5\ M^{-1}$ for K_2. The dimerization of $V\ell_2$ to give $V_2\ell_4$ proceeds favorably, the dimerization constant as defined by eq 4 being $49 \pm 5\ M^{-1}$.

It was possible to obtain information concerning proton stoichiometry and pK_a values of the various products by varying the pH while constant total vanadate and total peroxide concentrations were maintained. The pH studies were restricted to the range of about pH 6–10, and products that are favored outside this range of pH values were not investigated. When the pH was varied, it was evident that some products had pH-dependent chemical shifts, a property also utilized by other workers.[11,12] These pH-dependent shifts derive from changes in protonation/deprotonation equilibrium positions and are related to the acidity constants, K_a, by eq 6, where δ_O is the observed shift while δ_L is the chemical shift at low pH and δ_H is that at high pH. A plot of pH versus the logarithm term provides a line of intercept, pK_a, and unit slope.

$$pH = pK_a + \log\left(\frac{\delta_L - \delta_O}{\delta_O - \delta_H}\right) \quad (6)$$

The products that were observed to have pH-dependent shifts were $V\ell$ and $V\ell_2$. The pK_a values were 6.2 ± 0.1 and 7.2 ± 0.1, respectively. The latter value is close to that previously reported for a 2 M $NaClO_4$ solution,[11] $pK_a = 6.98$, while the former value has not previously been reported. The other pK_a of interest for this study is that of $VO_4H_2^-$, which is 8.21 ± 0.03 under conditions of 1 M ionic strength with KCl,[16] the same as this study.

Utilization of the above pK_a values in conjunction with pH studies allows the protonation states of all products to be identified and allows pH-independent equilibrium constants to be obtained. These equilibrium constants in conjunction with the pH and the known pK_a values allow the formation constants of eq 1–4 to be calculated for any pH. The present studies are consistent with the speciation already reported for these derivatives.[11,13] The pH-independent equilibrium constants corresponding to eq 1–4 are as follows:

$$\begin{array}{ccc} VO_2(OH)_2^- + HOOH & \overset{K'_1}{\rightleftharpoons} & VO(OH)_2(OO)^- \\ K_a \downarrow\!\!\uparrow H^+ & & K'_a \downarrow\!\!\uparrow H^+ \\ VO_3(OH)^{2-} & & VO_2(OH)(OO)^{2-} \end{array} \quad (7)$$

$$\begin{array}{ccc} VO(OH)_2(OO)^- + HOOH & \overset{K'_2}{\rightleftharpoons} & V(OH)_2(OO)_2^- \\ K'_a \downarrow\!\!\uparrow H^+ & & K''_a \downarrow\!\!\uparrow H^+ \\ VO_2(OH)(OO)^{2-} & & VO(OH)(OO)_2^{2-} \end{array} \quad (8)$$

$$\begin{array}{ccc} VO(OH)_2(OO)_2^- + HOOH & \overset{K'_3}{\rightleftharpoons} & V(OH)(OO)_3^{2-} + H^+ \\ K''_a \downarrow\!\!\uparrow H^+ & & \\ VO(OH)(OO)_2^{2-} & & \end{array} \quad (9)$$

$$\begin{array}{ccc} 2V(OH)_2(OO)_2^- & \overset{K'_4}{\rightleftharpoons} & (VO(OO)_2)_2OH^{3-} + H^+ \\ K''_a \downarrow\!\!\uparrow H^+ & & \\ VO(OH)(OO)_2^{2-} & & \end{array} \quad (10)$$

The values obtained for these formation constants are as follows: $K'_1 = (6 \pm 2) \times 10^2\ M^{-1}$; $K'_2 = (6 \pm 2) \times 10^5\ M^{-1}$; $K'_3 = (2.7 \pm 0.4) \times 10^{-6}$; $K'_4 = (1.7 \pm 0.2) \times 10^{-5}$.

From eq 7–10, the values of K_1, K_2, K_3, and K_4 of eq 1–4 can be calculated as follows for any pH value:

$$K_1 = K'_1([H^+] + K'_a)/([H^+] + K_a) \quad (11)$$

$$K_2 = K'_2([H^+] + K''_a)/([H^+] + K'_a) \quad (12)$$

$$K_3 = K'_3/([H^+] + K''_a) \quad (13)$$

$$K_4 = K'_4[H^+]/([H^+] + K''_a)^2 \quad (14)$$

The various equilibrium constants that were obtained from this study are summarized in Table II.

During the investigations of these materials, it was noted that the hydrogen peroxide slowly decomposed with a half-life of approximately 1 h for concentrations of 0.4 mM for both vanadate and hydrogen peroxide. The vanadium-catalyzed decomposition of peroxide has been known for many years. In strongly acidic solution, the decomposition is light catalyzed, the peroxide being stable in the dark.[19] At the higher pH levels of this study, it was found that the decomposition was slowed but not stopped in the absence of light. Very preliminary results of kinetic experiments are presented in Table III. Actually, a simple kinetics equation

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Table II. Formation and Acidity Constants Obtained for the Peroxovanadium(V) Products

equilibrium eq[a]	equilibrium const[b]
pH 6.7	
$V + \ell \rightleftharpoons V\ell$	$(3 \pm 1) \times 10^3\ M^{-1}$
$V\ell + \ell \rightleftharpoons V\ell_2$	$(1.7 \pm 0.6) \times 10^5\ M^{-1}$
$V + 2\ell \rightleftharpoons V\ell_2$	$(5 \pm 2) \times 10^8\ M^{-2}$
$V\ell_2 + \ell \rightleftharpoons V\ell_3$	$9.4 \pm 0.8\ M^{-1}$
$2V\ell_2 \rightleftharpoons V_2\ell_4$	$49 \pm 5\ M^{-1}$
pH Independent	
$VO_2(OH)_2^- + HOOH \rightleftharpoons VO(OH)_2(OO)^-$	$(6 \pm 2) \times 10^2\ M^{-1}$
$VO(OH)_2(OO)^- + HOOH \rightleftharpoons V(OH)_2(OO)_2^-$	$(6 \pm 2) \times 10^5\ M^{-1}$
$V(OH)_2(OO)_2^- + HOOH \rightleftharpoons V(OH)(OO)_3^{2-} + H^+$	$(2.7 \pm 0.4) \times 10^{-6}$
$2V(OH)_2(OO)_2^- \rightleftharpoons (VO(OO)_2)_2OH^{3-} + H^+$	$(1.7 \pm 0.2) \times 10^{-5}$
$VO(OH)_2(OO)^- \rightleftharpoons VO_2(OH)(OO)^{2-} + H^+$	$10^{-6.2 \pm 0.1}$
$V(OH)_2(OO)_2^- \rightleftharpoons VO(OH)(OO)_2^{2-} + H^+$	$10^{-7.2 \pm 0.1}$

[a] Water stoichiometry was not considered in these equilibrium equations because it was not possible to observe uptake or release of water under the conditions of these studies. [b] All constants were determined for 1 M KCl–20 mM HEPES buffer solutions from variable vanadate or peroxide concentrations or from changes in pH.

Table III. Half-Life for the Decomposition of Hydrogen Peroxide under Various Conditions[a]

pH	c(V), mM	$c(H_2O_2)$, mM	half-life, min[b]
7.0	0.2	0.4	50
	0.4	0.4	50
	0.4	1.0	140
7.0 (in the dark)	0.4	0.4	130
7.0 (under nitrogen)	0.4	1.0	120
8.0	0.2	0.4	60
	0.4	0.4	50
	0.4	1.0	120

[a] Solutions contained 1.0 M KCl and 20 mM HEPES buffer and the indicated total concentrations of vanadate or hydrogen peroxide. [b] Half-lives were estimated from the decay curves of the UV spectra.

does not fit the complete decay curve at all well. At longer times the amount of decay becomes proportionately more than that calculated from initial rates, the indication being that the decay accelerates with decrease in residual H_2O_2 concentration. This behavior is evident from the results given in Table III, from which it can be seen that decreasing the concentration of hydrogen peroxide by about a factor of 2 increases the rate by a similar factor.

During the course of our studies of the reactions between peroxovanadates and peptides,[20] it was observed that the peroxide decomposition was greatly slowed or even stopped when peptides were present in solution. Preliminary ^{51}V NMR studies of the glycylglycine-inhibited decomposition reaction revealed that in addition to the much more rapidly formed products there was slow formation of an additional peroxovanadate peptide derivative. Presumably, it is this material that prevents peroxide decomposition. The formation of this compound is shown in Figure 3, which also shows peptide products formed with vanadate (−505 ppm) and diperoxovanadate (−747 ppm).

The chemical shift of this slowly formed product is similar to that of monoperoxovanadate, indicating that it is a monoperoxide derivative, probably containing one glycylglycine. Diperoxopeptidovanadates give rise to NMR signals at considerably higher field than observed for this product, as indicated in Figure 3.[20]

Discussion

The formation of vanadate complexes with hydrogen peroxide occurs readily and favorably in aqueous solution. Identification of the charge states of reactants and products suggested that a V–O^- moiety in the precursor was required in order for condensation to occur. If this functionality was not available, a proton was released as the product formed from a V–OH precursor. This suggests that a V(OO) group is seen much like a V(O^-) group. It is perhaps, then, not surprising that peroxovanadates, when the

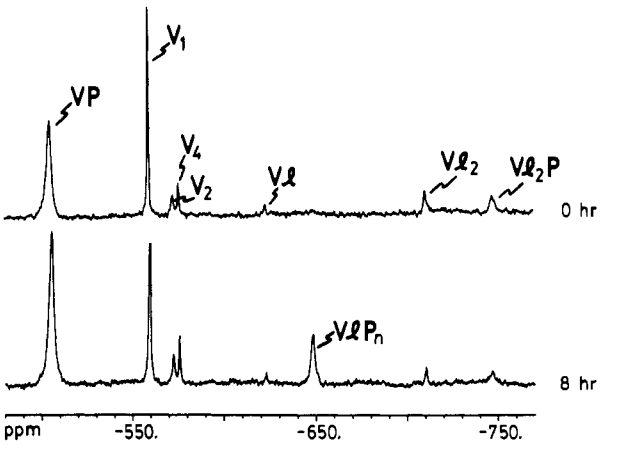

Figure 3. ^{51}V NMR spectra showing the slow formation of a peroxovanadate complex with glycylglycine. The lower spectrum was obtained approximately 8 h after the upper trace, which was measured immediately after preparing the solution. Conditions of the experiments: 0.5 mM total vanadate, 0.2 mM total H_2O_2, 100 mM glycylglycine, 1.0 M KCl, 20 mM HEPES buffer, and pH 7.0.

Table IV. Effects of the Addition of Peroxo Ligands on the ^{51}V Chemical Shifts of the Product Complexes[a]

complex	no. of peroxo groups	δ	Δδ
$VO_2(OH)_2^-$	0	−560	
$VO(OH)_2(OO)^-$	1	−602	−42
$V(OH)_2(OO)_2^-$	2	−686	−84
$VO_3(OH)^{2-}$	0	−536	
$VO_2(OH)(OO)^{2-}$	1	−625	−89
$VO(OH)(OO)_2^{2-}$	2	−765	−140
$V(OH)(OO)_3^{2-}$	3	−733	+32

[a] The chemical shifts quoted are the limiting shifts obtained from pH-variation studies.

peroxides are formally considered as unidentate ligands, often have tetrahedral coordination about vanadium. However, higher coordination is more typical.

The present study cannot establish water stoichiometry, so it cannot be determined whether coordination geometry changes as any of the products studied here are formed. It has been proposed, on the basis of ^{17}O and ^{51}V NMR studies, that the mono- and diperoxovanadates have coordinated water to form octahedral products, while the triperoxide is tetrahedral.[11] Some corroborating evidence for this comes from the ^{51}V chemical shifts when they are arranged in a homologous series based on charge as in Table IV. It appears from this table that the triperoxo product has an anomalous chemical shift, suggesting a coordination change from that of the mono- and diperoxo products. Evidence from X-ray structure work supports a tetrahedral coordination for $V(OH)(OO)_3^{2-}$ in solution, as that is what is observed for the solid.[21] It is not clearcut that the diperoxovanadates have octahedral coordination since they could well have trigonal bipyramidal coordination. This, in essence, is the coordination in $(VO(OO)_2)_2O^{4-}$,[22] $VO(OO)_2(C_2O_4)^{3-}$,[23] and a number of other diperoxovanadates.[23] It should however be noted that if the peroxide ligand is regarded as bidentate, then all the products discussed above are heptacoordinated but of different geometries. The role of the structure of these peroxo derivatives in the delineation of their biological and biochemical effects is not yet understood, but clearly is of interest and importance.

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It seems evident from the kinetic studies, taken in conjunction with the equilibrium studies, that the decomposition of H_2O_2 does not involve a diperoxide or higher peroxide of monovanadate. At the higher peroxide concentrations of Table III, the diperoxide is the predominant product in solution and the decomposition proceeds slower than at the lower concentrations, where a major product is the monoperoxide. At even higher peroxide concentrations the decomposition reaction is almost stopped. Interestingly enough, under low peroxide concentrations similar to those utilized here, the decomposition of hydrogen peroxide is slowed or even stopped in the presence of small peptides, apparently because of the formation of a monoperoxovanadate/peptide complex. This aspect of the chemistry of peroxovanadates is of continuing interest.[20]

The decomposition observed here appears to be activated by both photochemical and thermal reactions, as the degradation is only slowed in the absence of light. The photochemical pathway for decomposition recently discussed[19] apparently does not operate efficiently under the conditions of the present study. The information here is not sufficiently detailed to provide a basis for a proposal for a mechanistic pathway. It is, however, perhaps worth noting that the results obtained here do not rule out the possibility that the hydrogen peroxide decomposition is catalyzed by a diperoxodivanadate.

Acknowledgment. Thanks are gratefully extended to the Medical Research Council of Canada for its financial support of this work.

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Excited-State Acid-Base Chemistry of (α-Diimine)cyanotricarbonylrhenium(I) Complexes

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Received October 25, 1990

The excited-state acid-base photophysics of rhenium(I) complexes of the form $LRe^{I}(CO)_3CN$ (L = 1,10-phenanthroline, 2,2'-bipyridine, and 4,7-dimethyl-1,10-phenanthroline) was investigated. The emitting state can be tuned from a metal-to-ligand charge-transfer type to $\pi-\pi^*$ phosphorescence by varying the acidity, L, and temperature. This alteration of excited-state type results in large changes in emission spectra and lifetimes, which suggest use as environmental probes. In low-temperature glasses, site heterogeneity must be invoked to account for the luminescence decay data.

Introduction

Highly luminescent transition-metal complexes are currently being investigated for their practical applications in solar energy conversion and catalysis,[1] molecular probes,[2-4] and sensors.[5] The most frequently studied are $Ru(II)L_3^{2+}$ complexes, where L = 2,2'-bipyridine, 1,10-phenanthroline, and substituted derivatives. However, there is also interest in other d^6 or d^8 complexes as photosensitizers including Os(II), Ir(III), Mo(0), W(0), Pt(II), and Re(I) complexes.[2a,6,7] In some cases these metal sensitizers exhibit more desirable excited-state properties than their Ru(II) counterparts.

In this study, we were interested in the excited-state acid-base photophysics of rhenium(I) complexes of the form $LRe^{I}(CO)_3CN$, where L = 1,10-phenanthroline (phen), 2,2'-bipyridine (bpy), and 4,7-dimethyl-1,10-phenanthroline (Me_2phen).

In particular, we investigated the effects of protonation of the cyanide ligand by varying the acidity in methanol/sulfuric acid solutions. We found the excited-state acid-base characteristics of the $LRe(CO)_3CN$ complexes to be very similar to those of $Ru^{II}L_2(CN)_2$ complexes. Earlier studies of the Ru(II) compounds indicated that the complexes are stronger acids in the excited state, and protonation can invert the order of the lowest MLCT and $\pi-\pi^*$ excited states with radical changes in the luminescence properties.[8a,b] The Re(I) complexes exhibit solvent-insensitive MLCT emission bands, which blue shift with increasing acidity. Room-temperature emissions were typically MLCT in character although by suitable choice of α-diimine ligand and acidity, a strong component or even dominant $\pi-\pi^*$ emission arose. Low-temperature (77 K) studies indicate emissions from two different types of electronic excited states for $(Me_2phen)Re(CO)_3CN$ (even without acid) and for the other two complexes at high acid concentrations. One emission is a $^3(\pi-\pi^*)$ phosphorescence, and the other is an MLCT emission.

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