

Two Crystal Structures Featuring the Tetraperoxovanadate(V) Anion and a Brief Reinvestigation of Peroxovanadate Equilibria in Neutral and Basic Solutions

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Two purple crystals, each containing the tetraperoxovanadate(V) anion, have been characterized by low-temperature X-ray diffraction methods. $\text{Na}_3[\text{V}(\text{O}-\text{O})_4]\cdot\text{H}_2\text{O}_2\cdot 10.5\text{H}_2\text{O}$ crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 9.139(3)$ Å, $b = 11.774(3)$ Å, $c = 9.143(3)$ Å, $\alpha = 105.47(2)^\circ$, $\beta = 104.58(2)^\circ$, $\gamma = 71.65(2)^\circ$, and $Z = 2$. $\text{Na}_3[\text{V}(\text{O}-\text{O})_4]\cdot 14\text{H}_2\text{O}$ also crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 8.667(2)$ Å, $b = 9.010(2)$ Å, $c = 7.520(2)$ Å, $\alpha = 98.41(2)^\circ$, $\beta = 110.59(2)^\circ$, $\gamma = 63.99(2)^\circ$, and $Z = 1$. The peroxo O–O and the V–O_{peroxo} bond distances are in the normal range. The $\text{V}(\text{O}-\text{O})_4^{3-}$ anions exhibit approximately dodecahedral symmetry with the peroxo ligands bound in an η^2 fashion. It is unclear from the literature whether tri- or tetraperoxovanadate(V) should predominate under the experimental conditions used to obtain the crystals. Therefore, we have briefly reinvestigated by spectrophotometry their formation equilibria in neutral and basic solution, respectively. A value of $K = 2 \times 10^{-6}$ has been determined at 25 °C in 0.050 M MOPS buffer at pH 7 for the reaction $\text{VO}(\text{O}-\text{O})_2^- + \text{H}_2\text{O}_2 = \text{V}(\text{OH})(\text{O}-\text{O})_3^{2-} + \text{H}^+$. The equilibrium constant for the reaction $\text{V}(\text{OH})(\text{O}-\text{O})_3^{2-} + \text{HO}_2^- = \text{V}(\text{O}-\text{O})_4^{3-} + \text{H}_2\text{O}$ was determined to be 0.48 at 25 °C in H_2O_2 , HO_2^- buffer solutions at $I = 2.5$ M (NaCl). These results are consistent with previous reports that utilized ^{51}V NMR (*Inorg. Chem.* **1991**, *30*, 3718) and spectrophotometry (*Bull. Soc. Chim. Fr.* **1960**, 819), respectively. In our hands, the syntheses reported to yield the blue solids $\text{Na}[\text{V}(\text{O}-\text{O})_3]$ (*Inorg. Chem.* **1985**, *24*, 2706) and $\text{Na}_2[\text{V}(\text{O}-\text{O})_3\text{F}]$ (*Inorg. Chem.* **1982**, *21*, 4020) afforded instead blue solids that appear to be impure samples of $\text{Na}_3[\text{V}(\text{O}-\text{O})_4]$.

Introduction

Peroxovanadates are formed in aqueous solutions containing hydrogen peroxide and vanadium(V) over nearly the entire pH range. Their compositions and structures have been extensively examined by use of a variety of techniques including cryoscopy, spectrophotometry, ^{17}O and especially ^{51}V NMR spectroscopy, Raman spectroscopy, and single-crystal X-ray diffraction.^{1–9} A limited number of equilibrium studies have been reported.^{1,5,10–12} The peroxo ligands are normally bonded in an η^2 fashion, which we shall consider to be two-coordinate. Mononuclear complexes containing one to four peroxo ligands have been found, although definitive structural evidence is abundant only for mono- and diperoxovanadates. There are several reasons that structural assignments have proved difficult: (1) single crystals are difficult to prepare except when heteroligands are present, (2) the peroxovanadates exhibit extensive acid–base chemistry, and (3) basic solutions, where tri- and tetraperoxovanadates are favored, are unstable due to decomposition of hydrogen

peroxide. Nevertheless, interest in the peroxovanadates remains high, due in large part to their possible biological and medical importance.^{13,14} The reactivity and some structural features of well-defined peroxovanadium(V) systems have recently been reviewed.¹⁵

Mononuclear peroxovanadates containing one and two peroxo ligands are normally pentagonal bipyramidal, with an apical oxo ligand, η^2 -bound peroxo and water, hydroxo, or oxo ligand(s) in the equatorial plane, and a weakly bound water molecule in the apical position trans to the oxo ligand. We favor the following formulations, with water ligands omitted: $\{\text{VO}(\text{O}-\text{O})^+\}$, $\{\text{VO}_2(\text{O}-\text{O})^-\}$, and $\{\text{VO}_2(\text{OH})(\text{O}-\text{O})^{2-}\}$ and $\{\text{VO}(\text{O}-\text{O})_2^-\}$, $\{\text{VO}(\text{OH})(\text{O}-\text{O})_2^{2-}\}$, and $\{\text{VO}_2(\text{O}-\text{O})_2^{3-}\}$. Only in the case of dioxo-diperoxovanadate(V) are the coordination number and geometry matters of substantial uncertainty.^{4,7} Triperoxovanadates also appear to be seven-coordinate; two have been characterized by single-crystal X-ray diffraction. The geometry about the vanadium atom in $(\text{NH}_4)_2[\text{V}(\text{O}-\text{O})_3\text{F}]\cdot\text{H}_2\text{O}$ (the data could only be refined to $R = 25\%$)¹⁶ and $[\text{N}(\text{CH}_3)_4]_2[\text{V}(\text{OH})(\text{O}-\text{O})_3]\cdot 4\text{H}_2\text{O}$ ¹⁷ is close to a capped trigonal prism. There is general agreement that the triperoxovanadates formulated as $\text{V}(\text{OH})(\text{O}-\text{O})_3^{2-}$ (pK_a ca. 13) and $\text{VO}(\text{O}-\text{O})_3^{3-}$ are formed in neutral and basic solutions containing excess hydrogen peroxide, and (where mentioned) they are reported to be pale yellow.^{1–7} Blue or purple powders of $\text{K}_3[\text{V}(\text{O}-\text{O})_4]$ have been shown to be isomorphous with the tetraperoxometalates of Cr(V), Nb(V),

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and Ta(V);¹⁸ the much studied chromium compound has distorted dodecahedral geometry.¹⁹

There are reports, however, that appear to be inconsistent with some of these conclusions. For example, compounds identified as the triperoxo complexes $K_3[V(O-O)_3Ox] \cdot H_2O$ (orange) and $(NH_4)[V(O-O)_3bipy] \cdot 3H_2O$ (yellow) have been reported.²⁰ These were shown later to be instead perhydrates containing $[VO(O-O)_2Ox]^{3-}$ and $[VO(O-O)_2bipy]^-$ anions.²¹ More recently, Chaudhuri and co-workers²²⁻²⁵ reported the synthesis of several blue solids containing triperoxovanadates. These include $A[V(O-O)_3]$ ($A = Na$ or K) and $A_2[V(O-O)_3X]$ ($A = NH_4, Na$, or K and $X = F$ or Cl). These solids were all described as microcrystalline and were obtained from aqueous solution by addition of excess ethanol. The characterization was mainly based on elemental analysis, molar conductance measurements, and titration of peroxide content, all of which were in close agreement with the theoretical values. The absence of a $V=O$ bond was shown by means of Raman spectroscopy. An absorption maximum for $V(O-O)_3^-$ was found at 560 nm; Chauveau has reported¹ a maximum at 550 nm for $V(O-O)_4^{3-}$. Chakravorti et al. recently described the synthesis of a blue solid formulated as $K[V(O-O)_3] \cdot 3H_2O$ by a slightly different method.²⁶

We have successfully isolated single crystals of two closely related species, each containing the tetraperoxovanadate(V) anion. These have been characterized at low temperatures by X-ray diffraction methods. The crystals were obtained from solutions in which either $[V(O-O)_4]^{3-}$ should predominate, according to Chauveau,¹ or $V(O-O)_3^-$, on the basis of the results of Chaudhuri and co-workers. We have therefore briefly reinvestigated the interconversions of the di-, tri-, and tetraperoxovanadates by spectrophotometry in an effort to resolve this ambiguity.

Experimental Section

Reagents. A stock solution of sodium vanadate was prepared by the method of Tracey, Gresser, and Liu.²⁷ Stock solutions made by dilution of hydrogen peroxide (30%, Fisher Certified, stabilizer free) were assayed iodometrically. The biological buffer MOPS (3-morpholinopropanesulfonic acid) was obtained from Aldrich. Highly purified EDTMP (ethylenediaminetetramethylenephosphonic acid) was generously donated by Dow Chemical. All other chemicals were of reagent grade and were used as supplied. Deionized water was distilled twice before use; the last distillation was from alkaline permanganate. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Equilibrium And Kinetic Studies. An HP8452A diode array spectrophotometer, equipped with a thermostated (± 0.1 °C), rapid-mixing (ca. 1 s) sample compartment was used. The decomposition of hydrogen peroxide in the basic solutions required for studies of tetraperoxovanadate was minimized by addition of EDTMP at concentrations $\leq 0.01[V(V)]_{total}$.

Table 1. Crystallographic Data for $Na_3[V(O-O)_4] \cdot H_2O_2 \cdot 10.5H_2O$ (A) and $Na_3[V(O-O)_4] \cdot 4H_2O$ (B)

	A	B
formula	$H_{23}O_{20.5}Na_3V$	$H_{28}O_{22}Na_3V$
fw	471.1	500.1
space group	$P\bar{1}$	$P\bar{1}$
a , Å	9.139(3)	8.667(2)
b , Å	11.774(3)	9.010(2)
c , Å	9.143(3)	7.520(2)
α , deg	105.47(2)	98.41(2)
β , deg	104.58(2)	110.59(2)
γ , deg	71.65(2)	63.99(2)
V , Å ³	885(1)	494(1)
Z	2	1
D_c , g cm ⁻³	1.768	1.681
μ , cm ⁻¹	7.1	6.4
$F(000)$	486	260
radiation		Mo K α
λ , Å (graphite monochromator)		0.71073
diffractometer		Enraf-Nonius CAD4
no. of orienting reflcns;		25; $10 < \theta < 15$
range, deg		
temp. °C		-100 \pm 1
scan method		$\omega-2\theta$
data collcn range, deg	$2.0 < 2\theta < 48$	$2.0 < 2\theta < 50$
no. of data measd	2974	2014
no. of unique data	2772	1722
R_i (data averaging), %	1.7	2.1
no. of obsd data ($I > 2.0\sigma(I)$), N	2335	1571
no. of params, P	323	182
R_w , %	2.6	3.1
R_w , %	3.7	4.3
S , goodness of fit ^c	1.43	1.45
max. shift/error, final	0.10	0.01
largest positive peak, e Å ⁻³	0.51	0.55
largest negative hole, e Å ⁻³	-0.30	-0.25

$$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|. \quad ^b R_w = \{\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}; w = 4(F_o)^2/[\sigma(F_o)]^2. \quad ^c S = [\sum w(|F_o| - |F_c|)^2/(N - P)]^{1/2}.$$

Collection and Reduction of X-ray Data. X-ray diffraction data for crystals of both $Na_3[V(O-O)_4] \cdot H_2O_2 \cdot 10.5H_2O$ (A) and $Na_3[V(O-O)_4] \cdot 4H_2O$ (B) were collected on an Enraf-Nonius CAD4 diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). Both structures were solved by a combination of Patterson and direct methods²⁸ and completed by successive difference Fourier calculations. Following initial refinement of the models, all H atoms were located from difference Fourier maps and the completed structures were refined by least-squares methods, with anisotropic thermal parameters for the non-H atoms and fixed isotropic thermal parameters for the H atoms. All refinements were performed with the SDP program package.²⁹ Details of the X-ray experiment, crystal data, and data collection, reduction, and refinement are given in Table 1.

Results

Single-Crystal X-ray Structures of $Na_3[V(O-O)_4] \cdot H_2O_2 \cdot 10.5H_2O$ (A) and $Na_3[V(O-O)_4] \cdot 4H_2O$ (B). Two X-ray structures featuring the tetraperoxovanadate(V) anion were determined. The methods by which we obtained these crystals only make sense if we confess that we were attempting to obtain crystals of triperoxovanadates. Crystals of A were obtained by storing the cold reaction mixture described in the literature²⁴ for the synthesis of $Na[V(O-O)_3]$ at -5 °C overnight—no ethanol was added. A small portion of the purple crystals that had formed and mother liquor were placed on a microscope slide, and a suitable crystal was removed, rapidly mounted, and placed in a stream of cold N_2 at ca. -110 °C. Gas evolution

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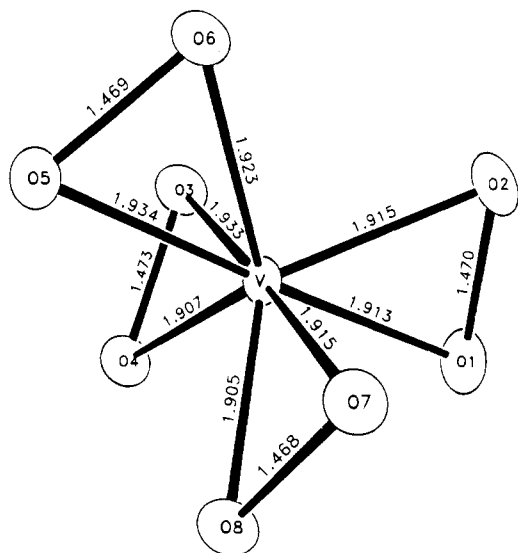


Figure 1. Structure of the tetraperoxovanadate(V) anion in $\text{Na}_3[\text{V}(\text{O}-\text{O})_4]\cdot\text{H}_2\text{O}_2\cdot 10.5\text{H}_2\text{O}$. Errors in the bond lengths were 0.001–0.002 Å.

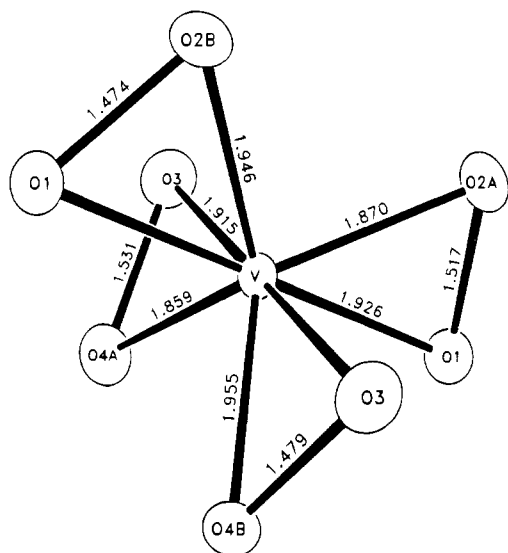


Figure 2. Structure of the tetraperoxovanadate(V) anion in $\text{Na}_3[\text{V}(\text{O}-\text{O})_4]\cdot 14\text{H}_2\text{O}$. Errors in the bond lengths were 0.001–0.004 Å.

was observed in the mother liquor while the crystal was removed, but the crystals themselves appeared to be moderately stable. Samples of the crystals from the cold solution were filtered off under suction, thoroughly dried in a vacuum desiccator, and submitted for Na and V analysis. Anal. Calcd for $\text{Na}_3[\text{V}(\text{O}-\text{O})_4]$: Na, 27.82; V, 20.55. Found: Na, 27.01; V, 20.00. Crystals of **B** were obtained in an identical manner from a cold reaction mixture described in the literature²² for the synthesis of $\text{Na}_2[\text{V}(\text{O}-\text{O})_3\text{F}]$. Again, samples of the purple crystals were filtered off, thoroughly dried, and submitted for Na, V, and F analysis. Anal. Calcd for $\text{Na}_3[\text{V}(\text{O}-\text{O})_4]$: Na, 27.82; V, 20.55; F, 0.00. Found: Na, 26.63; V, 18.73; F, 0.30.

The ORTEP drawings of the complex anion $[\text{V}(\text{O}-\text{O})_4]^{3-}$ together with the atomic numbering scheme and selected bond distances are shown in Figures 1 and 2. Final atomic coordinates are given in Table 2, and selected bond angles are summarized in Table 3. In both crystals the structures show disorder. In **A**, the complex anion is well ordered, but one Na^+ in a general position is present at half-occupancy. The solvent structure about this cation includes overlapping half-occupancy water and H_2O_2 molecules. In **B**, V is on an inversion center, and the $\text{O}-\text{O}^{2-}$ ligands are necessarily disordered about this

Table 2. Positional Parameters and Isotropic Equivalent Thermal Parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Crystal A				
V	0.15550(3)	0.28380(3)	0.21203(3)	0.765(6)
Na1	0.500	0.500	0.000	1.38(2)
Na2	0.18769(8)	-0.05406(6)	-0.42150(8)	1.51(2)
Na3	0.65527(8)	-0.71838(6)	-0.29222(8)	1.35(2)
Na4 ^b	-0.4985(2)	0.0669(1)	0.0831(2)	2.30(4)
O1	0.3462(1)	0.3331(1)	0.2756(2)	1.49(3)
O2	0.3231(1)	0.2704(1)	0.1126(1)	1.50(3)
O3	0.2643(1)	0.1299(1)	0.2751(1)	1.34(3)
O4	0.1950(1)	0.2258(1)	0.3978(1)	1.27(3)
O5	-0.0348(1)	0.2305(1)	0.1404(1)	1.36(3)
O6	0.0598(1)	0.1987(1)	0.0197(1)	1.30(3)
O7	0.0438(2)	0.4382(1)	0.1562(1)	1.31(3)
O8	0.0442(2)	0.4374(1)	0.3166(1)	1.31(3)
O9	-0.5213(1)	-0.4876(1)	0.2593(2)	1.34(3)
O10	-0.2721(1)	-0.4255(1)	0.0876(2)	1.50(3)
O11	-0.6616(2)	-0.2967(1)	0.0242(2)	1.63(3)
O12	-0.7991(2)	-0.0750(1)	0.3111(2)	1.69(3)
O13	-0.6530(2)	-0.2558(1)	0.5615(2)	1.67(3)
O14	0.0268(1)	0.1434(1)	-0.4547(2)	1.39(3)
O15	-0.4254(2)	0.0072(2)	0.3125(2)	3.34(4)
O16	-0.1151(2)	0.0422(1)	0.1833(2)	2.42(3)
O17	0.0938(2)	-0.3262(1)	0.2154(1)	1.34(3)
O18	0.4004(2)	-0.7486(1)	-0.3272(2)	1.82(3)
O19 ^b	-0.2328(3)	0.0298(2)	0.0461(3)	1.37(6)
O20 ^b	-0.4273(3)	0.1126(2)	0.0236(3)	1.72(6)
O21 ^b	-0.4463(4)	-0.0813(3)	0.1851(4)	2.91(8)
O22	-0.7838(2)	-0.4386(1)	-0.4257(2)	1.85(3)
Crystal B				
V	0.000	0.000	0.000	0.965(8)
Na1	0.500	0.500	0.500	1.36(2)
Na2	0.77967(8)	0.62276(8)	0.36051(9)	1.39(1)
O1	0.1473(2)	-0.0270(1)	0.2637(2)	1.59(3)
O2A ^b	0.1434(3)	0.1051(3)	0.1558(4)	1.58(5)
O2B ^b	0.0554(3)	-0.1388(3)	0.2092(4)	1.44(5)
O3	0.2010(2)	-0.1715(1)	-0.0641(2)	1.72(3)
O4A ^b	0.0688(3)	-0.2262(3)	-0.0313(4)	1.58(6)
O4B ^b	0.2037(3)	-0.0085(3)	-0.0639(3)	1.38(5)
O5	0.5775(2)	-0.2963(2)	0.0497(2)	2.17(3)
O6	0.5086(2)	-0.2484(1)	-0.5567(2)	1.57(3)
O7	0.1491(2)	0.1406(2)	0.6060(2)	2.33(3)
O8	0.2421(2)	-0.3608(1)	-0.3861(2)	1.60(3)
O9	0.0539(2)	-0.5693(1)	0.3043(2)	1.49(3)
O10	0.2769(2)	-0.4742(1)	0.2036(2)	1.66(3)
O11	0.5389(2)	-0.0859(2)	-0.2092(2)	1.99(3)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

^b Disordered atoms with occupancy of 0.5.

Table 3. Selected Angles (deg) in $\text{V}(\text{O}-\text{O})_4^{3-}$ Anions^a

crystal A		crystal B	
O1–V–O2	45.18(5)	O1–V–O2A	47.1(1)
O3–V–O4	45.07(5)	O1–V–O2B	44.74(9)
O5–V–O6	44.79(5)	O3–V–O4A	47.8(1)
O7–V–O8	45.18(5)	O1–V–O4B	44.92(8)
O1–V–O5	177.81(5)	O1–V–O1	180.0
O2–V–O6	87.87(5)	O2A–V–O2B	88.2(1)
O3–V–O7	177.81(5)	O3–V–O3	180.0
O4–V–O8	87.64(5)	O4A–V–O4B	87.2(1)

^a Numbers in parentheses are estimated standard deviations.

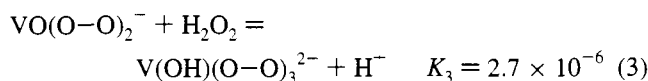
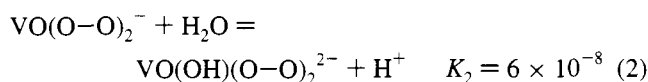
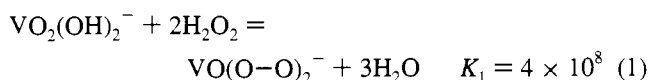
center. O2A, O2B, O4A, and O4B are present at half-occupancy, and the drawing in Figure 2 represents one of the two possible chemically reasonable anions combined in the disordered structure. The solvent and cation structure is well ordered.

The best plane through O1, O2, O5, and O6 (see Figure 1) is perpendicular to that containing O3, O4, O7, and O8. The metal atom lies in these planes within experimental error, a feature

common to the tetraperoxoperoxo complexes of Cr(V), Mo(VI), and W(VI).¹⁹ The O1–V–O5 and O3–V–O7 bond angles are 178°, while the O2–V–O6 and O4–V–O8 angles are 88°. In the oxo diperoxo complexes one O–V–O angle is ca. 150°, whereas the other is nearly 90°. In our structures the peroxy O–O bond distances are within the normal range. There is a fair correlation between deviations in equivalent V–O_{peroxy} distances (e.g., those at 180° to each other) and the strength and number of hydrogen bond interactions with the solvent molecules in the ordered [V(O–O)₄]^{3–} anion in A.

Literature Synthesis and Analysis of Sodium Triperoxovanadate(V) and Sodium Triperoxofluorovanadate(V). Blue solids reported to be Na[V(O–O)₃]²⁴ and Na₂[V(O–O)₃F]²² were prepared and dried as described and submitted for analysis. Anal. Calcd for Na[V(O–O)₃]: Na, 13.53; V, 29.98. Found: Na, 28.98; V, 19.73. Calcd for Na₂[V(O–O)₃F]: Na, 21.70; V, 24.04; F, 8.97. Found: Na, 26.69; V, 16.89; F, 0.76. Clearly, in our hands the reported syntheses failed. The solids we did obtain correspond much better to impure samples of Na₃[V(O–O)₄].

Formation Constants for Tri- and Tetraperoxovanadates. The following equilibria, written in terms of predominant species at pH 7, have been carefully studied by means of ⁵¹V NMR:



The equilibrium constants listed have been taken from the work of Jaswal and Tracey⁵ and were determined in 1 M KCl with HEPES buffer at ambient temperature. The value of K_1 is consistent with that determined by Secco in a spectrophotometric study under more acidic conditions.¹² The value of K_2 is in reasonable agreement with that determined by Harrison and Howarth.⁴ We sought to estimate the value of K_3 independently by spectrophotometry. On the basis of the equilibrium data, it should be relatively easy to identify conditions where either VO(O–O)₂[–] or V(OH)(O–O)₃^{2–} is the principal V(V) species. This was confirmed by spectrophotometry in the sense that a constant spectrum was obtained for each peroxy complex over a range of conditions consistent with those calculated.³⁰ The spectral differences between di- and triperoxovanadate are small but at 400 nm are sufficient to allow a measurement of K_3 . We chose conditions where essentially all the V(V) is complexed as a mixture of the two peroxy complexes. It can be shown that a plot of $(\epsilon_{\text{di}} - \epsilon_{\text{obs}})/(\epsilon_{\text{obs}} - \epsilon_{\text{tri}})$ vs [H₂O₂] should be linear with a slope of $K_3/([H^+] + K_2)$. The predicted linear plot was obtained at pH 7.00 (0.050 MOPS buffer), [V(V)]_{total} = 5.00 × 10^{–4} M, [H₂O₂]₀ = 0.0050–0.10 M, and $T = 25.0$ °C. The resulting value of K_3 was 2 × 10^{–6}, in quite satisfactory agreement with Jaswal and Tracey's result. Our study is not intended to improve on the published value but rather to confirm that it is at least approximately correct.

The only equilibrium study, to the best of our knowledge, of the formation of tetraperoxovanadate is Chauveau's.¹ Her interpretation of the spectrophotometric results, obtained at ice temperatures and an ionic strength of ca. 4 M, is summarized

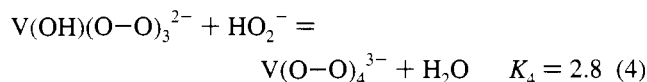
Table 4. Equilibrium Results for the Interconversion of Tri- and Tetraperoxovanadate(V)^a

[OH [–]] ₀ , M	[H ₂ O ₂] ₀ , M	abs	[OH [–]] ₀ , M	[H ₂ O ₂] ₀ , M	abs
1.5	3.0	0.563	0.50	1.0	0.276
1.3	3.0	0.506	1.5	3.0	0.218 ^b
1.0	3.0	0.425	0.75	2.0	0.696 ^c
1.0	2.0	0.436	0.35	1.0	0.391 ^c
1.0	1.5	0.438	0.25	1.0	0.292 ^c
0.75	2.0	0.362	0.20	1.5	0.240 ^c
0.50	2.0	0.265	0.20	0.7	0.233 ^c

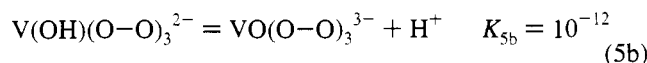
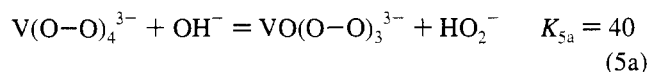
<i>I</i> , M (salt)	[OH [–]] ₀ , M	[H ₂ O ₂] ₀ , M	abs
3.0 (NaCl)	1.5	3.0	0.666
2.8 (NaCl)	1.3	3.0	0.610
2.25 (NaCl)	0.75	2.0	0.332
2.5 (NaNO ₃)	1.0	2.0	0.411
2.5 (NaClO ₄)	1.0	2.0	0.452

^a Conditions: [V(V)] = 5.00 × 10^{–3} M, [EDTMP] = 0.01[V(V)], $I = 2.5$ M (maintained with NaCl), $T = 25.0$ °C, path length = 1.0 cm, and $\lambda = 560$ nm unless otherwise indicated. ^b [V(V)] = 2.00 × 10^{–3} M. ^c [V(V)] = 1.00 × 10^{–2} M.

in eq 4. The formulations are ours but are consistent with her



notation; it should be remembered that at the time of her investigation not a single X-ray structure of a peroxy complex was available. According to this result, the tetraperoxo complex will only be formed in solutions containing high concentrations of a H₂O₂–H₂O[–] buffer; with excess [OH[–]] relative to [H₂O₂], the complex is destroyed as shown in eq 5a. This was a truly



remarkable study. Among other features, it explains why the blue or purple tetraperoxo complex is observed only in peroxide buffers and not in strongly basic solution. The approximate value of K_{5b} was later confirmed by NMR and Raman studies.^{3,7} Considerable decomposition of hydrogen peroxide occurs under the experimental conditions required; Chauveau worked at low temperatures to minimize problems arising from bubble formation.

We were able to make equilibrium measurements at 25 °C by partially sequestering the trace metal catalyzed decomposition of hydrogen peroxide through the use of EDTMP (ethylenediaminetetramethylenephosphonic acid).³¹ Bubble formation was still troublesome, but stable absorbance values could be measured. The results obtained at the 560 nm absorption maximum found for V(O–O)₄^{3–} are summarized in Table 4. We find, in agreement with Chauveau, that the equilibrium absorbance values are extraordinarily dependent on ionic strength but importantly depend far less on the nature of the salt used, provided the anion is only weakly coordinating toward vanadium(V). The strong base added is almost completely converted to HO₂[–] under our conditions, and essentially all the V(V) is present in the tri- and tetraperoxo complexes. Under these conditions, eq 6 should hold. The appropriate plot was linear, and from the slope and intercept we obtained values of $K_4 = 0.48$ and $\epsilon_{\text{tetra}} = 270 \text{ M}^{-1} \text{ cm}^{-1}$. We view our value of

(30) The spectra of VO(O–O)₂[–] and VO(OH)(O–O)₂^{2–} are very similar.

(31) Evans, D. F.; Upton, M. W. *J. Chem. Soc., Dalton Trans.* **1985**, 1151, 2525.

$$[V(V)]_{\text{total}}/A_{\text{obs}} = 1/\{\epsilon_{\text{tetra}}K_4[HO_2^-]\} + 1/\epsilon_{\text{tetra}} \quad (6)$$

K_4 to be in reasonable agreement with that determined by Chauveau, given the temperature and ionic strength differences.

Survey Kinetic Studies of the Formation of Tetraperoxovanadate(V). The principal V(V) species at pH 7 with $[H_2O_2] = 0.70\text{--}2.0$ M is $V(OH)(O-O)_3^{2-}$, on the basis of the equilibrium data. These solutions are relatively stable if small amounts of EDTMP ($\leq 0.01[V(V)]_{\text{total}}$) are present. The rather slow rate of conversion to the tetraperoxo complex was monitored at 560 nm after addition of strong base. Plots of $-\ln(A_\infty - A_t)$ vs t were linear; the slopes of these plots (k_{obs}) showed an approximately linear dependence on $[H_2O_2]$ with a slope of $0.013 \text{ M}^{-1} \text{ s}^{-1}$. Efforts to study the reverse reaction were frustrated by the instability of the tetraperoxovanadate(V) solutions.

Qualitatively, the rate of conversion of $VO(O-O)_2^-$ or $VO(OH)(O-O)_2^{2-}$ to $V(OH)(O-O)_3^{2-}$ is quite rapid; a kinetic study was not undertaken.

Discussion

Our equilibrium results lend support to the contention that reliable formulations, formation constants, and protonation constants for mononuclear peroxovanadium(V) complexes are available. Except for that of tetraperoxovanadate, the formation rates are rapid. A number of heteroligand (amino carboxylates, 2,2'-bipyridine, 1,10-phenanthroline, fluoride, oxalate, carbonate, etc.) complexes of mono- and diperoxovanadates have been studied. Their structures are usually analogous to those of the hydrated forms, but in a few cases the dissociation rate of peroxide can be quite slow. The most impressive example reported to date is $VO(O-O)(nta)^{2-}$.³²

(32) Sivak, M.; Joniakova, D.; Schwendt, P. *Transition Met. Chem.* **1993**, *18*, 304.

Unfortunately, we were unable to repeat the reported syntheses of $Na[V(O-O)_3]$ and $Na_2[V(O-O)_3F]$.^{24,22} The preparations utilized $H_2O_2\text{--}H_2O^-$ buffers in which $V(O-O)_4^{3-}$ and to a lesser extent $V(OH)(O-O)_3^{2-}$ have been reported as predominant species by other workers, although in the absence of F^- .^{1,3,4,7} The $[V(V)]$ used in the syntheses was much higher than that used in our equilibrium studies but comparable to that employed in some NMR and Raman studies. That we obtained crystals containing tetraperoxovanadate from solutions made as described^{22,24} could conceivably be due to the slightly different experimental conditions (no ethanol, a colder temperature, and longer standing). Of more concern is our inability to reproduce the elemental analysis for solids prepared exactly as described in the literature. The Na/V ratio should be independent of the degree of hydration or possible presence of perhydrates; this ratio is 2.99 for the filtered and dried crystals from **A** and 3.15 for **B**. For the blue solids obtained by the literature methods, the ratio was 3.25 for $Na[V(O-O)_3]$ and 3.50 for $Na_2[V(O-O)_3F]$. All are consistent with solids containing $Na_3[V(O-O)_4]$ contaminated to varying degrees with other sodium salts.

Theoretical investigations of peroxo complexes have often centered on tetraperoxometalates due to their simplicity and symmetry.^{33,34} Crystal structures are now available for two additional complexes— $W(O-O)_4^{2-}$ and $V(O-O)_4^{3-}$.¹⁹

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Supporting Information Available: Tables of anisotropic thermal parameters, least-squares planes, and hydrogen coordinates for **A** and **B** (6 pages). Ordering information is given on any current masthead page.

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(33) Cundari, T. R.; Zerner, M. C.; Drago, R. S. *Inorg. Chem.* **1988**, *27*, 4239.

(34) Roch, M.; Weber, J.; Williams, A. F. *Inorg. Chem.* **1984**, *23*, 4571.