Inorg. Chem. **1997,** *36,* 4029−4034

Molecular Modeling of Vanadium Peroxides

Thomas R. Cundari,*[,1] Laura L. Sisterhen, and Chryssanthi Stylianopoulos

Department of Chemistry, University of Memphis, Memphis, Tennessee 38152

Received March 5, 1997[⊗]

A computational study of vanadium peroxides ($L_nV(O_2)_m$; $m = 0-4$), important for their biochemical and catalytic activity, is reported. In the compounds studied, ancillary ligands (L_n) are generally the hard, oxygen- and nitrogen-based donor ligands, e.g., carboxylates and pyridines, prevalent in the coordination chemistry of vanadium peroxides. The utility of estimating missing metal-dependent molecular mechanics (MM) parameters from quantum calculations is demonstrated. Given the limited vibrational data for many families of transition metal complexes, quantum calculations are a viable source for parameters to use in development of force fields. A conformational search of $[V(O_2)_3F]^{2-}$ using MM yielded a geometry inconsistent with experiment, but consistent with *ab initio* geometry optimizations. A reinvestigation of this structure is therefore of interest. Molecular mechanics provides a quick and accurate method for obtaining structural information. The level of agreement for structural prediction is competitive with that obtained using more computationally intensive methods in much less time. In most cases it was seen that MM and quantum predictions reinforced each other, lending greater confidence in modeling results. In other cases, classical and quantum results were in conflict, indicating the need for further higher-level, quantum calculations. Hence, MM and low-level quantum calculations, when used together, provide a valuable method for quickly probing the conformational space of large coordination complexes.

Introduction

Vanadium peroxides ($L_nV(O_2)_m$; $m = 0-4$) are emerging as important compounds and have been implicated in enzymatic and nonenzymatic hydrocarbon oxidation.[2] Vanadium bromoperoxidase (VBrPO) has been isolated from marine algae and shown to catalyze halide oxidation by hydrogen peroxide;[3] biomimetic studies[3,4] have implicated vanadium peroxides as reactive intermediates in the catalytic cycle. Mimoun et al.[5] have reported olefin epoxidation by a vanadium peroxide. More recently, vanadium peroxides have been shown to exhibit antitumor[6] and antidiabetic[7] activity. Mono-, di-, tri-, and tetraperoxide complexes have been modeled in this research with ancillary ligands (L_n) prevalent in vanadium coordination chemistry.

Several groups have investigated molecular mechanics (MM) modeling of transition metals,[8−11] although applications for these elements still lag behind those for main-group elements. To our knowledge, there has been no detailed study of MM for vanadium complexes. A major challenge in extension of MM force fields to transition metals has been development of parameters, particularly vibrational parameters such as force constants, since these data can be limited. Quantum calculations can provide metric and vibrational parameters with sufficient accuracy for use in force field construction.[9a,11,12] Also, simple force fields appear robust and not inordinately sensitive to vibrational parameters over a range that is within the limits of computational accuracy.[8−11,13] A second major challenge in routine application of MM to transition metals is derived from their chemical diversity.[8] In force field parametrization this affects the transferability of parameters from one complex to another (e.g., the V−oxo bond in a square pyramidal vanadyl versus that in a seven-coordinate diperoxide) or even within the same complex (e.g., $V-L_{cis}$ versus $V-L_{trans}$). Vanadium thus provides a very rigorous test of MM schemes for transition metals.

Computational Methods

Quantum Mechanics. Quantum calculations employ the GAMESS program.[14] Effective core potentials (ECPs) and valence basis sets (VBSs) are used for heavy atoms, and the -31G basis set is used for H. ECPs replace the innermost core orbitals for vanadium and all core orbitals for main-group (MG) elements.[15] Thus, the 3s, 3p, 3d, 4s and 4p orbitals are treated explicitly for vanadium;[15] for main-group elements, 2s and 2p orbitals are treated explicitly.[15] The vanadium VBS is quadruple and triple ζ for the sp and d shells, respectively, while MG elements have double-ζ-plus-polarization VBSs.[15] This scheme has been widely applied to transition metal chemistry.[16]

Geometries are optimized at the restricted Hartree−Fock level for closed-shell singlets. Vibrational frequencies are calculated at all stationary points to identify them as minima. Intrinsic stretching frequencies, and the metal−ligand force constants derived from them, are calculated from the normal coordinate analysis formalism described by Boatz and Gordon.[17]

---

* Address correspondence to this author.

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

(1) E-mail: tcundari@cc.memphis.edu.

(2) (a) Chasteen, N. D. *Structure and Bonding*; Springer: Berlin, 1983; Vol. 53, p 105. (b) Sigel, H.; Sigel, A., Eds. *Metal Ions in Biological Chemistry*; Marcel Dekker: New York, 1995; Vol. 31.

(3) Butler, A.; Clague, M. J.; Meister, G. E. *Chem. Rev.* **1994**, *94*, 625.

(4) Colpas, G. J.; Hamstra, B. J.; Kampf, J. W.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1994**, *116*, 3627.

(5) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101.

(6) Djordjevic, C; Wampler, G. L. *J. Inorg. Biochem.* **1985**, *25*, 51.

(7) Posner, B. I.; Faure, R.; Burgess, J. W.; Bevan, A. P.; Lachance, D.; Zhang-Sun, G.; Fantus, I. G.; Ng, J. B.; Hall, D. A.; Soo Lum, B.; Shaver, A. *J. Biol. Chem.* **1994**, *269*, 4596.

(8) Comba, P.; Hambely; T. W. *Molecular Modeling of Inorganic Compounds*; VCH: Weinheim, 1995.

(9) (a) Allured, V. S.; Kelly, C. M.; Landis, C. R. *J. Am. Chem. Soc.* **1991**, *113*, 1. (b) Rappé, A. K.; Colwell, K. S.; Casewit, C. J. *Inorg. Chem.* **1993**, *32*, 3438. (c) Mayo, S. L.; Olafson, B. D.; Goddard, W. A., III. *J. Phys. Chem.* **1990**, *94*, 8897.

(10) (a) Hay, B. P. *Coord. Chem. Rev.* **1993**, *126*, 177. (b) Comba, P. *Coord. Chem. Rev.* **1993**, *123*, 1.

(11) Cundari, T. R.; Moody, E. W.; Sommerer, S. O. *Inorg. Chem.* **1995**, *34*, 5989.

(12) Raby, P. D. M.S. Thesis, University of Memphis, 1996.

(13) Cundari, T. R.; Fu, W.; Klinckman, T. R.; Moody, E. W.; Slavin, L. L.; Snyder, L. A.; Sommerer, S. O. *J. Phys. Chem.* **1996**, *100*, 18057.

(14) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Matsunaga, N. M.; Gordon, M. S.; Nguygen, K. A.; Su, S.; Windus, T. L.; Elbert, S. T. *J. Comput. Chem.* **1993**, *14*, 1347.

(15) Krauss, M.; Stevens, W. J.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612.

(16) Cundari, T. R.; Gordon, M. S. *Coord. Chem. Rev.* **1996**, *87*, 87.

S0020-1669(97)00266-8 CCC: $14.00

Molecular Mechanics. The molecular mechanics force field includes the terms shown in eq 1.[10] The steric energy, U_{steric}, of a complex is the sum of individual bond stretching, U_s; angle bending, U_b; bond torsion, U_t; and van der Waals interactions, U_{vdW}. A steepest descent algorithm is used for geometry optimization;[18] optimizations are carried out until the RMS gradient is ≤ 0.002 kcal Å^{-1}.

$$U_{\mathrm{steric}} = \sum U_s + \sum U_b + \sum U_t + \sum U_{\mathrm{vdW}} \qquad (1)$$

Fifty to one hundred conformations are generated using molecular dynamics for each complex depending on its conformational flexibility. The complex is heated up to 1000 K at a rate of 2.0 kcal atom^{-1} ps^{-1}; 2 fs time steps are used. Conformations are sampled every 1 ps. These conformations are then optimized using a two-step protocol. First, geometries are loosely MM-optimized (RMS gradient < 0.025 kcal Å^{-1}). Second, only unique conformations are MM-optimized with the standard tight convergence criterion (RMS gradient < 0.002 kcal Å^{-1}).

Force Field Preliminaries. Our driving motivation is to accurately predict the structure of V peroxides using a minimum of terms beyond the basic Allinger MM2 force field.[19] Test calculations were carried out on several V peroxides. First, geometry optimizations were carried out using cubic and quartic terms in U_s as well as stretch–bend (U_{sb}) terms, and a sextic correction to the harmonic U_b potential. Second, geometry optimizations were rerun with harmonic U_s and U_b potentials and neglecting U_{sb}. In both cases torsional potentials are described using a standard, three-term Fourier series expansion, while vdW terms are calculated using a Buckingham potential ($U_{\mathrm{vdW}} = A \exp(-Br) - C/r^6$, A, B, and C are adjustable parameters). Both sets of calculations yield nearly identical geometries so the second approximation was used in all subsequent calculations.

Results and Discussion

1. Force Field Derivation. The peroxides studied, apart from $[\mathrm{V(O_2)_4}]^{3-}$, possess a seven-coordinate vanadium (atom type 237).[20] In general, ancillary ligands for vanadium peroxides are oxygen- and nitrogen-based donor ligands. Thus, we focused on eight new ligating atom types: fluoride (atom type 11), carboxylate O (atom type 86), water O (atom type 85), oxide O (atom type 77), imine N (atom type 800), alkoxide O (atom type 808), peroxide O (atom type 822), and amino N (atom type 888). There are two types of force field parameters: metal-dependent and metal-independent. Metal-independent parameters are assumed not to change upon coordination of the ligand to the metal, and thus standard MM2 parameters are used.[19] Derivation of metal-dependent parameters is outlined below. A complete table of new parameters is available as Supporting Information.

van der Waals. The van der Waals parameters for ligating atom types (N, O, and F) are taken from corresponding nonligating congeners (e.g., coordinated amine N, atom type 888, and amine N, atom type 8) contained in the modeling program.[18]

Bond Stretching. Equilibrium bond lengths and force constants[17] for V–ligand bonds are estimated from quantum calculations on model compounds: C_{2v}-$\mathrm{VO_2F_2}$; C_{3v}-$\mathrm{VOF_3}$; C_{2v}-$[\mathrm{VO_2F_4}]^{2-}$; D_{2d}-$[\mathrm{V(O_2)_4}]^{3-}$; C_1-$\mathrm{V({=}NH)_2(NH_3)(CH_3)}$. Methods used in quantum calculations are outlined in Computational Methods and described in detail elsewhere.[16] X-ray data and ECP-based quantum calculations are used in estimation of V–ligand equilibrium bond lengths.

Angle Bending. There are two types of metal-dependent, angle-bending potentials, X–V–Y and V–X–Y. The X–V–Y potentials are replaced by 1,3-van der Waals interactions.[10,21] The V–X–Y potentials are estimated from organic analogues (e.g., $\mathrm{C_{alkane}}$–X–Y), and the equilibrium bond angle and force constant are modified as needed to improve geometric prediction. The efficacy of replacing X–V–Y angle-bending potentials with 1,3-nonbonded interactions in high coordination number complexes has been described previously.[21] Alternative approaches have been developed.[9] Peroxide is treated as a bidentate ligand (with appropriate angular parameters) as opposed to a monodentate ligand coordinated by a bond from V to the OO bond midpoint.

Torsion. There are two varieties of metal-dependent torsions: X–Y–Z–V and X–Y–V–Z. The latter involve rotation about metal–ligand bonds and are often assumed to be small and set to zero.[10a] The former are approximated by assuming that the metal plays a spectator role in determining the torsional potential about the X–Y bond; V–X–Y–Z torsional potentials are estimated from $\mathrm{C_{alkane}}$–X–Y–Z potentials,[10a] which are usually available when X, Y, and Z are non-metal atoms.

Out-of-Plane Bending. This term describes the energy needed for pyramidalization of planar atom types (alkene C, carbonyl C, amide N, coordinated imine N). A quadratic potential is used; out-of-plane bending force constants are given in the Supporting Information.

2. Prediction of Lowest Energy Conformations. To fully exploit a force field in computer-aided design, it must predict structure when there are no experimental data to provide a starting guess. Also, there is no guarantee that solid- and solution-phase structures are identical. Finally, for complexes with flexible ligands it is possible, particularly in solution, that multiple conformational states are populated. As a result, efficient and accurate conformational space searching is of importance. Conformational analysis of organic molecules with MM, employing molecular dynamics (MD) and Monte Carlo methods, has been widely studied.[22] Application of new and existing methods to transition metal complexes is of interest. MD searches were begun with a random geometry without recourse to X-ray data.

Root mean square deviations in atomic positions for corresponding inner coordination sphere ($\mathrm{RMS_{ic}}$) and heavy ($\mathrm{RMS_{heavy}}$) atoms give a straightforward estimate of the quality of the MM-predicted geometries, Table 1. Comparisons are made between MM-predicted and X-ray structures except for $[\mathrm{V(O_2)_4}]^{3-}$ and $[\mathrm{V(O_2)_3F}]^{2-}$, where experimental data is lacking or uncertain.

2.1. Tetraperoxides. The tetraperoxide $[\mathrm{V(O_2)_4}]^{3-}$ has been reported and its vibrational spectra recorded. To our knowledge, no crystal structure has been reported.[3,23] Hence, ECP quantum calculations[16] were carried out on D_{2d} -$[\mathrm{V(O_2)_4}]^{3-}$ which is a minimum: V–O = 1.92 and 1.90 Å, O–O = 1.42 Å, **1**. A conformational search (73 conformations) of $[\mathrm{V(O_2)_4}]^{3-}$ using MM yielded only a dodecahedral (D_{2d}) geometry with no evidence for cubic or square antiprismatic coordination geometries. The MM-predicted geometry of $[\mathrm{V(O_2)_4}]^{3-}$ is in good agreement with that obtained from ECP calculations: $\mathrm{RMS_{ic}} = \mathrm{RMS_{heavy}} = 0.06$ Å. Related tetraperoxides, e.g., $[\mathrm{Cr(O_2)_4}]^{3-}$, have been structurally characterized and possess D_{2d} symmetry.[24] Infrared and Raman data are consistent with a D_{2d} geometry

---

(17) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1986**, *7*, 385.

(18) *Chem 3D Plus User's Manual*; Cambridge Scientific: Cambridge, 1992.

(19) Allinger, N. L.; Burkert, U. *Molecular Mechanics*; American Chemical Society: Washington, D.C., 1982.

(20) Type 237 was used for $[\mathrm{V(O_2)_4}]^{3-}$.

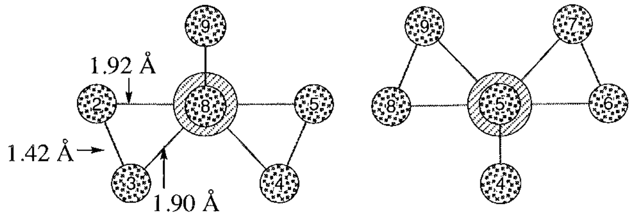
(21) Hay, B. P. *Inorg. Chem.* **1991**, *30*, 2786.

(22) Gunsteren, W. F.; Berendsen, H. J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 992.

(23) Campbell, N. J.; Dengel, A. C.; Griffith, W. P. *Polyhedron* **1989**, *8*, 1379.

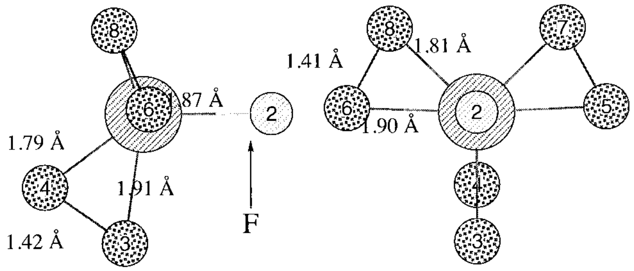
(24) Dickman, M. H.; Pope, M. T. *Chem. Rev.* **1994**, *94*, 569.

for $[V(O_2)_4]^{3-}$.[23] Hence, there is a consensus among theory and experiment about the structure of $[V(O_2)_4]^{3-}$.



1

2.2. Triperoxides. In a recent review[3] the only V triperoxide listed as structurally characterized is $[V(O_2)_3F]^{2-}$. However, the experimental structure has large estimated standard deviations in the X-ray positional parameters.[25] Hence, ECP calculations were carried out on C_2-$[V(O_2)_3F]^{2-}$, the symmetry that was indicated by experiment. ECP optimization of C_2-$[V(O_2)_3F]^{2-}$ indicates that it is not a local minimum; there is an imaginary frequency (183i cm^{-1}) leading to a C_s minimum (**2**, 44 kcal mol^{-1} lower in energy): V−F = 1.87 Å, V−O = 1.81 and 1.90 Å for the symmetry-related peroxides, and V−O = 1.79 and 1.91 Å for the unique peroxide, **2**. The electronic origins of the difference in V−O bond lengths for η^2-peroxides have been discussed, although it is smaller for mono- and diperoxides that make up the bulk of the structural database.[26] An MM search of $[V(O_2)_3F]^{2-}$ (54 conformations) yielded only a C_s geometry with no evidence for a C_2 isomer, consistent with ECP results. The MM-predicted geometry of $[V(O_2)_3F]^{2-}$ is in good agreement with that obtained from ECP optimization (**2**): $\mathrm{RMS_{ic}} = \mathrm{RMS_{heavy}} = 0.08$ Å. Reinvestigation of the structure of $[V(O_2)_3F]^{2-}$ and analysis of other vanadium triperoxides, would be of great interest.



2

2.3. Diperoxides. Several vanadium diperoxides have been characterized by X-ray crystallography.[3,27] The crystal and MM-predicted structures of $VO(O_2)_2(pic)^{2-}$, $VO(O_2)_2(ox)^{3-}$, $VO(O_2)_2(bpy)^{-}$, and $VO(O_2)_2(picOH)^{2-}$ are in good agreement; pic = picolinate, ox = oxalate, bpy = 2,2′-bipyridine, picOH = 3-hydroxypicolinate, Table 1. An overlay of the experimental and theoretical structures of $VO(O_2)_2(pic)^{2-}$ is shown in Figure 1 as an example. A comparison of the root mean square deviations in atomic positions for inner coordination sphere atoms ($\mathrm{RMS_{ic}}$) and all heavy atoms ($\mathrm{RMS_{heavy}}$) for diperoxides is given in Table 1. For the four diperoxides the average theory−experiment deviations are very good: $\mathrm{RMS_{ic}} \approx 0.11$ Å, and $\mathrm{RMS_{heavy}} \approx 0.12$ Å.

Table 1. Comparison of MM-Predicted and Experimental Geometries

structure[a]	$\mathrm{RMS_{ic}}$[b] (Å)	$\mathrm{RMS_{heavy}}$[c] (Å)
$VO(O_2)(pic)(bpy)$	0.182	0.166
$VO(O_2)(ox)_2^{3-}$	0.120	0.134
$VO(O_2)(dpc)(OH_2)^{-}$	0.117	0.123
$VO(O_2)(pic)(OH_2)_2$	0.129	0.146
$VO(O_2)_2(bpy)^{-}$	0.108	0.122
$VO(O_2)_2(picOH)^{2-}$	0.115	0.146
$VO(O_2)_2(pic)^{2-}$	0.112	0.110
$VO(O_2)_2(ox)^{3-}$	0.096	0.107
$V(O_2)_3F^{2-}$	0.083[d]	0.083[d]
$V(O_2)_4^{3-}$	0.060[d]	0.060[d]

[a] Abbreviations for the different ligands are given in the text. [b] This is the root mean square deviation in corresponding atomic positions for the inner coordination sphere atoms, i.e., vanadium and the atoms directly ligated to it, for the MM predicted lowest energy conformer and that subsequently obtained from X-ray crystallographically determined atomic positions. [c] This is the root mean square deviation in corresponding atomic positions for all heavy atoms in the complex for the MM-predicted lowest energy conformer and that subsequently obtained from X-ray crystallographically determined atomic positions. [d] These comparisons are made with ECP-optimized geometries since experimental structures are either unavailable (tetraperoxide) or uncertain (triperoxide).

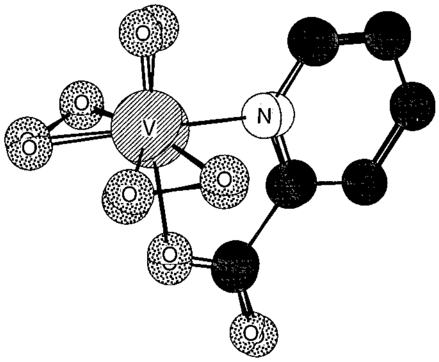


Figure 1. Overlay of MM-predicted and X-ray geometries of $[VO(O_2)_2(pic)]^{2-}$. In this and the subsequent overlays, hydrogen atoms are omitted from the figure for the sake of clarity.

It is worth pointing out that MM calculations compare favorably with more computationally intensive quantum calculations. For example, optimization using a semiempirical INDO method parametrized for transition metals yielded poor results (e.g., peroxides dissociate, V=O bonds are much too long, etc.)[28] while ECP optimization of $VO(O_2)_2(pic)^{2-}$ required ≈19 days on a high-performance workstation.[29] These results are not

---

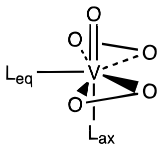
(25) Westerman, K.; Leimkühler, M.; Mattes, R. *J. Less-Common Met.* 1988, *137*, 181.

(26) Cundari, T. R.; Drago, R. S.; Zerner, M. C. *Inorg. Chem.* **1988**, *26*, 4239. Analysis of the Cambridge Structural Database (version 5.1.3: Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31) yields an average difference in $V-O_{peroxide}$ bond lengths of <0.03 Å (1%) for 36 samples.

(27) (a) $K_2[VO(O_2)_2(pic)]\cdot 2H_2O$ and $K_2[VO(O_2)_2(picOH)]\cdot 3H_2O$: Shaver, A. Ng, J. B.; Hall, D. A.; Soo Lum, B.; Posner, B. I. *Inorg. Chem.* **1993**, *32*, 3109. Shaver et al. (Shaver, A.; Hall, D. A.; Ng, J. B.; Lebuis, A. M.; Hynes, R. C.; Posner, B. I. *Inorg. Chim. Acta* **1995**, *229*, 253) have also reported the structure of two more complexes with derivatized picolinates. All four complexes have nearly identical core geometries. (b) $K_3[VO(O_2)_2(ox)]\cdot H_2O_2$ and $NH_4[VO(O_2)_2(bpy)]\cdot 4H_2O$: Campbell, N. J.; Capparelli, M. V.; Griffith, W. P.; Skapski, A. C. *Inorg. Chim. Acta* **1983**, *77*, L215. (c) Synthesis of V diperoxides is described by Vuletic and Djordjevic although no structures are reported. Vuletic, N.; Djordjevic, C. *J. Chem. Soc., Dalton Trans.* **1973**, 1137. (d) $NH_4[VO(O_2)_2(bpy)]\cdot 4H_2O$: Szentivanyi, H.; Stomberg, R. *Acta Chem. Scand.* **1983**, *A37*, 553. Szentivanyi and Stomberg also report the structure of this anion with a bipyridinium counterion (Szentivanyi, H.; Stomberg, R. *Acta Chem. Scand.* **1984**, *A38*, 121). The experimental geometries of both $VO(O_2)_2(bpy)^{-}$ anions is very similar. (e) $K_3[VO(O_2)_2(ox)]\cdot H_2O$: Begin, D.; Einstein, F. W. B.; Field, J. *Inorg. Chem.* **1975**, *14*, 1785. (f) Shaver et al. have reported the crystal structure of a V−oxo diperoxide with a 5-nitrophenanthroline ligand: Shaver, A.; Ng, J. B.; Hynes, R. C.; Posner, B. I. *Acta Crystallogr. C* **1994**, *50*, 1044). MM optimization of $VO(O_2)_2(phen)^{-}$ yields $\mathrm{RMS_{ic}} = 0.10$ Å and $\mathrm{RMS_{heavy}} = 0.15$ Å (NO_2 group not included), values comparable to those of other diperoxides.

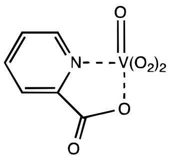
surprising given the stringent requirements needed for accurate quantum modeling of coordination complexes of first-row transition metals.[30]

One trend evident from MM conformational searching is that the preferred geometry of $VO(O_2)_2$ is with the peroxides perpendicular to the oxo and parallel to each other, **3**. Geometries in which the $VO(O_2)_2$ moiety is distorted from that depicted in **3** are considerably higher in energy using the present force field. Semiempirical extended Hückel[31] and INDO calculations (at MM geometries) also point to a clear preference for **3** over other geometric isomers. Computational results are consistent, therefore, with all structurally characterized V−oxo diperoxides.

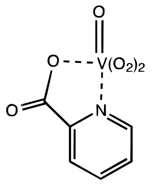


3

For diperoxides with an asymmetric bidentate ligand like picolinate,[27a] there are two coordination isomers: one in which the carboxylate oxygen is trans to the oxo ligand (**4a**) and another in which the pyridine nitrogen is trans to the oxo (**4b**). Experimentally, the solid-state structures of $VO(O_2)_2(pic)^{2-}$ and derivatives[27a] are as depicted in **4a**. The MM force field predicts the correct isomer, although the difference in steric energies between **4a** and **4b** is very small (0.01 kcal mol^{-1}). Electronic factors play an important role in determining which ligand occupies the L_{ax} coordination site due to the strong trans influence of the oxo ligand.[32] Quantum calculations (at MM geometries) are inconclusive in that **4a** is predicted to be lower in energy than **4b** using extended Hückel theory (EHT), while the situation is reversed using the INDO method.



4a



4b

For $VO(O_2)_2(picOH)^{2-}$, the solid-state structure has been interpreted in terms of placing the phenol hydrogen proximal to the carbonyl oxygen of the carboxylate.[27a] Hydrogen bonding is a plausible justification for this preference. Since hydrogen bonding is not included in the present force field, we expect such systems to present some difficulty. The MM force field predicts the hydrogen-bonded isomer (**5a**) to be ≈0.65 kcal mol^{-1} higher than the non-hydrogen-bonded isomer (**5b**). However, extended Hückel and INDO calculations suggest that **5a** is lower in energy than **5b** by 2 kcal mol^{-1} and 17 kcal mol^{-1}, respectively.

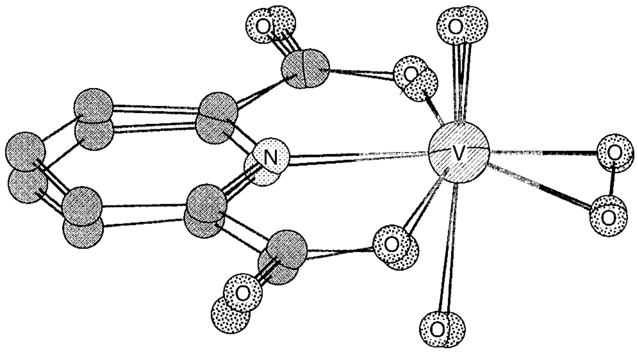
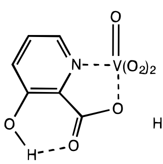
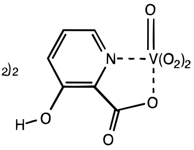


Figure 2. Overlay of MM-predicted and X-ray geometries of $[VO(O_2)(dpc)(OH_2)]^-$.



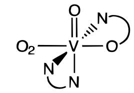
5a



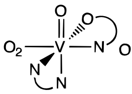
5b

2.4. Monoperoxides. Several V monoperoxides have been structurally characterized.[3,5,33] Solid-state and MM-predicted structures of $VO(O_2)(pic)(bpy)$, $VO(O_2)(ox)_2^{3-}$, $VO(O_2)(pic)(OH_2)_2$, and $VO(O_2)(dpc)(OH_2)^-$, dpc = 2,6-pyridine-dicarboxylate, are in good agreement, Table 1. An overlay of the MM-predicted and experimental geometries of $VO(O_2)(dpc)(OH_2)^-$ is shown in Figure 2. Using RMS_{ic} and RMS_{heavy} as a measure of the predictive ability suggests that the theory−experiment agreement is equal for vanadium monoperoxides and diperoxides.

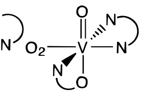
An MM conformational search of $VO(O_2)(pic)(bpy)$ (50 conformations) yields four isomers, **6a**−**d**, within 1 kcal mol^{-1} of the lowest steric energy structure (**6b**). Submission of the four candidates to quantum calculation (EHT and INDO) indicated that **6a** has a lower electronic energy than the other three by ≥8 kcal mol^{-1}. Complex **6a** is consistent with



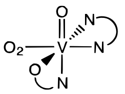
6a



6b



6c



6d

---

(28) Anderson, W. P.; Edwards, W. D.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 2728. INDO calculations were run using HyperChem (version 4.5, Hypercube, Inc., 1994).

(29) Quantum calculations (see Computational Methods) were run in direct mode on an IBM RS-6000/250 workstation using GAMESS[14] and assumed C_s symmetry. The V−O(carboxylate) bond trans to the oxo ligand is predicted to be much too long (≈3.05 Å).

(30) Frenking, G.; Antes, I.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Jonas, V.; Neuhaus, A.; Otto, M.; Stegmann, R.; Veldkamp, A.; Vyboishchikov, S. F. In *Reviews in Computational Chemistry*; Boyd, D. B., Lipkowitz, K., Eds.; VCH: New York, 1996; p 63.

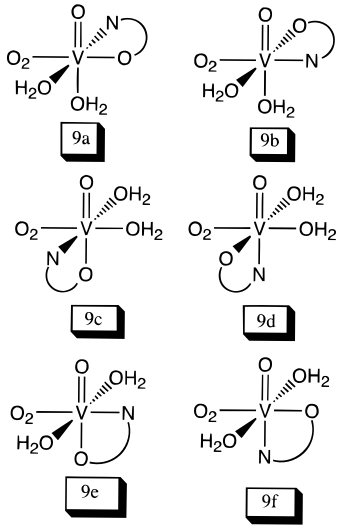
(31) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Extended Hückel calculations were run using HyperChem (version 4.5, Hypercube, Inc., 1994).

(32) Benson, M. T.; Cundari, T. R.; Lim, S. J.; Nguyen, H. D.; Pierce-Beaver, K. *J. Am. Chem. Soc.* **1994**, *116*, 3955.

(33) (a) $K_2[VO(O_2)(nta)]\cdot 2H_2O$: Djordjevic, C.; Wilkins, P. L.; Sinn, E.; Butcher, R. J. *Inorg. Chim. Acta.* **1995**, *239*, 241. (b) $NH_4[VO(O_2)(H_2O)(dpc)]\cdot xH_2O$: Drew, R. E.; Einstein, F. W. B. *Inorg. Chem.* **1973**, *12*, 829. (c) $[VO(O_2)(pic)(bpy)]\cdot H_2O$: Szentivanyi, H.; Stomberg, R. *Acta Chem. Scand.* **1983**, *A37*, 709. (d) $K_3[VO(O_2)(ox)_2]\cdot {}^1/_2H_2O$: Stomberg, H. *Acta Chem. Scand.* **1986**, *A40*, 168. (e) $NH_4[VO(O_2)(ida)]$: Djordjevic, C.; Craig, S. A.; Sinn, E. *Inorg. Chem.* **1985**, *24*, 1283. This complex is polymeric in the solid state. (f) Four $V(O)(O_2)(nta)^{2-}$ structures have been reported, nta = nitrilotriacetate.[34] The MM-predicted lowest energy conformer for $V(O)(O_2)(nta)^{2-}$ is consistent with experiment, except for a complex in which barium forms a strong association with coordinating carboxylate and peroxide oxygens.[34b]

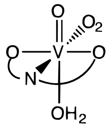
(34) (a) $K_2[V(O)(O_2)(nta)]\cdot 2H_2O$: Laphsin, A. E.; Smolin, Y. I.; Shepley, Y. F.; Sivak, M.; Gyepesova, S. *Acta Crystallogr. C* **1993**, *49*, 867. (b) $Ba[V(O)(O_2)(nta)]\cdot 3H_2O$: Kuchta, L.; Sivak, M.; Pavelcik, F. *J. Chem. Res.* **1993**, *393*, 2801. (c) $Na_2[V(O)(O_2)(nta)]\cdot 2H_2O$: Da-Xu, W.; Xin-Jian, L.; Rong, C.; Mao-Chun, H. *J. Huaxue* **1992**, *11*, 65. (d) $K_2[V(O)(O_2)(nta)]\cdot 2H_2O$: Wei, Y. G.; Zhang, S. W.; Huang, G. Q.; Shao, M. C. *Polyhedron* **1994**, *13*, 1587.

Scheme 1

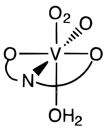


experiment,[33c] and this MM-predicted geometry is in good agreement with experiment, Table 1.

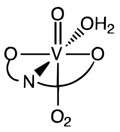
For $VO(O_2)(dpc)(OH_2)^-$, three low-energy conformations are found by MM/MD searching (55 conformations), **7a**−**7c**. Sterically, **7a** is favored over the other isomers by ≥1 kcal mol^{-1}. Electronic structure calculations at the MM2 geometries reinforce the preference for **7a** as its electronic energy is 23 kcal mol^{-1} (INDO) and 3 kcal mol^{-1} (EHT) lower than that of any other isomer.



7a

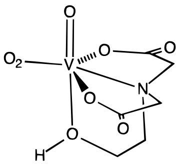


7b

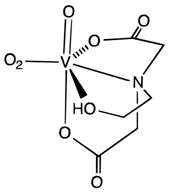


7c

Colpas et al. have reported the structure of $K[V(O)(O_2)(heida)]\cdot 2H_2O$, heida = ((2-hydroxyethyl)imino)diacetate.[4] A molecular dynamics search (105 conformations) yields two low-energy conformations in which the ligand trans to the oxo is hydroxyethyl (**8a**) or acetate (**8b**); the latter is predicted to be lower by ≈0.3 kcal mol^{-1}. The experimental structure is most consistent with **8a**.[4] EHT calculations also predict a small energetic difference (≤0.2 kcal mol^{-1}) between **8a** and **8b**, while INDO calculations suggest that isomer **8a** is preferred by 11 kcal mol^{-1} over **8b**. Agreement of the MM-predicted structure of **8a** with that reported by Colpas et al.[4] is less than for the other monoperoxides, although respectable: $RMS_{ic} = RMS_{heavy} = 0.22$ Å.

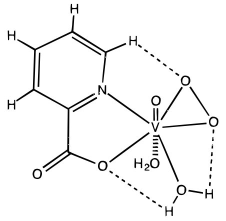


8a



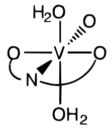
8b

As stated above, complexes with hydrogen bonding may be problematic since such terms are not included in the MM2 force field. This is evident in the case of $VO(O_2)(pic)(OH_2)_2$. There are six isomers whose steric energies cover a range of only 0.6 kcal mol^{-1}, Scheme 1. The MM-predicted geometry of $VO(O_2)(pic)(OH_2)_2$ consistent with experiment (**9a**, Scheme 1) is 0.6 kcal mol^{-1} above the lowest energy isomer (**9e**, Scheme 1). Mimoun et al.[5] indicate that there are three intramolecular hydrogen bonds in the solid-state structure (dotted lines in **10**).[5] Single-point INDO calculations on all low-energy conformers at the MM geometries indicate a preference for a structure like that reported[5] by ≥3 kcal mol^{-1} over any other geometric isomer, suggesting an electronic preference for conformer **9a**. RMS_{ic} and RMS_{heavy} for **9a** and the experimental structure are 0.13 and 0.15 Å, respectively, Figure 3.

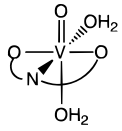


10

2.5. Related Non-Peroxide Vanadium Complexes. A logical extension of the study of peroxides is other important vanadium complexes. Two non-peroxide complexes (with ligand types similar to those studied above) were chosen from the large database of vanadium−oxo species: $VO(OH_2)_2(dpc)$ and $[V(O)_2(ox)_2]^{3-}$. For $[V(O)_2(ox)_2]^{3-}$ there are two low-energy structures, i.e., the O═V═O moiety is cis or trans. The steric energy of the cis isomer is lower than that of the trans by 0.6 kcal mol^{-1}. Reported structures of $[V(O)_2(ox)_2]^{3-}$ have a cis dioxo geometry.[35] Agreement between MM-predicted and X-ray structures for $[V(O)_2(ox)_2]^{3-}$ is of similar quality to agreement for V peroxides: $RMS_{ic} = 0.10$ Å, $RMS_{heavy} = 0.17$ Å. The complex $VO(OH_2)_2(dpc)$ has two low-energy conformations (**11a** and **11b**) since the tridentate dpc ligand has meridional coordination. The MM calculations predict that **11a** is lower in energy than **11b** by 0.8 kcal mol^{-1}, consistent with experiment ($RMS_{ic} = 0.11$ Å, $RMS_{heavy} = 0.10$ Å).[36] Vanadium−oxo species comprise a large family with hundreds of structurally characterized examples. Our limited analysis suggests that parameters developed for V peroxides should be easily extended to related families of vanadium complexes, and that more work in this direction is warranted.



11a



11b

Summary and Conclusions

A molecular mechanics investigation of vanadium peroxides, important for their biochemical and catalytic properties, is reported. Several important conclusions resulted from this research, the most important of which are summarized below.

(1) The utility of deriving missing metal-dependent MM parameters from quantum calculations is demonstrated again in this research. Given the paucity and unreliability of vibrational data for many families of transition metal complexes,

---

(35) Three $[V(O)_2(ox)_2]^{3-}$ structures have been reported. The MM comparison is with the newest structure.[33d] (a) Scheidt, W. R.; Tsai, C.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3867. (b) Drew, R. E.; Einstein, F. W. B.; Gransden, S. E. *Can. J. Chem.* **1974**, *52*, 2184.

(36) Two structures for $[VO(OH_2)_2(dpc)]\cdot 2H_2O$ have been reported with different unit cell symmetries; both structures are very similar. The comparison is with the newer structure. (a) Bersted, B. H. *Inorg. Chem.* **1968**, *7*, 1557. (b) Sundheim, A. *Z. Nat. B* **1993**, *48*, 125.

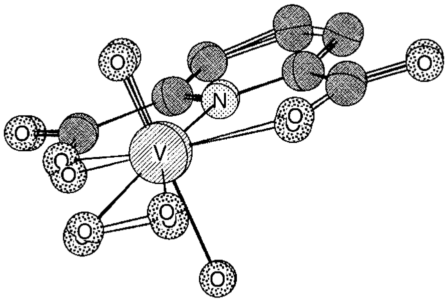


Figure 3. Overlay of MM and X-ray geometries of [VO(O_2)(pic)(OH_2)$_2$].

quantum calculations are a viable source of parameters for force field development.

(2) A conformational search of $[V(O_2)_3F]^{2-}$ using MM yielded a geometrical isomer inconsistent with experimental data, but consistent with quantum mechanical geometry optimizations. A reinvestigation of this structure is therefore of great interest.

(3) As can be seen in the cases of $VO(O_2)(pic)(OH_2)_2$ and $VO(O_2)_2(picOH)^-$, complexes with considerable hydrogen bonding, intermolecular or intramolecular, can be problematic since these terms are not included in the MM2 force field and its extensions. Hydrogen-bonding interactions are included in force fields such as AMBER,[37] and it may be desirable to implement the present force field in such a program if hydrogen bonding is expected to be of importance.

(4) Molecular mechanics can provide a quick and accurate methodology for obtaining structural information. This information is often the starting point in any computer-aided design and analysis scenario. One of the motivations in studying vanadium peroxides is that they provide the potential for numerous conformational and coordination geometry isomers. The ability of a simple MM model to yield reliable predictions in the face of this chemical diversity is encouraging for the more widespread application of MM to transition metal chemistry. The level of agreement for structural prediction is also competitive with if not superior to that which can be obtained using much more computationally intensive methods in much less time. In several cases it was seen that MM and QM calculations reinforced each other, lending greater confidence in modeling results. In other cases, classical and quantum results were in conflict, suggesting the need for higher-level calculations with larger basis sets and appropriate treatment of electron correlation effects. In this regard, MM (in combination with low-level quantum calculations) can quickly screen out unlikely structural types and conformations. More expensive *ab initio* methodologies can then be employed on a much reduced set of target complexes.

Acknowledgment. The authors thank the National Science Foundation (CHE-9614346) for support of this research. The help of Professor Gerard Parkin and Tina Trnka (Chemistry, Columbia University) in obtaining structural information on vanadium peroxides is gratefully acknowledged. L.S. thanks the University of Memphis and the Society of Cosmetic Chemists for scholarship support.

Supporting Information Available: MM and ECP optimized geometries, plus steric energies for the former, for systems studied (15 pages). Ordering information is given on any current masthead page.

IC970266F

---

[37] Weiner, S. J.; Kollman, P. A.; Nguyen, D. T.; Case, D. A. *J. Comput. Chem.* **1986**, *7*, 230.