J. Phys. Chem. A **1997,** *101,* 4637−4640

Ab Initio Calculations on Water−Peroxovanadium Clusters, $VO(O_2)(H_2O)_n^+$ ($n = 1-5$). Implications for the Structure in Aqueous Solution

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Received: February 4, 1997; In Final Form: March 31, 1997[⊗]

The lack of information on the structure of peroxovanadium complexes in aqueous solution, together with the difficulty to obtain clearcut experimental evidence, prompted us to approach the problem by carrying out *ab initio* calculations (HF/3-21G(*) and B3LYP/LANL2DZ). To the naked oxoperoxocation $[VO(O_2)]^+$, whose preferred structure has been determined to be the "cisoid" one, water molecules have been subsequently added and the resulting geometries optimized. The maximum stabilization due to complexation of the aqua ligands is obtained when three molecules of water are coordinated to vanadium. Further coordination to the metal is characterized by a lower hydration energy, similar to that pertaining to the formation of the second solvation shell. Accordingly, the preferred coordination number is six $[VO(O_2)(H_2O)_3^+]$ with a distorted octahedral geometry and a readily exchangeable fourth water molecule. These results should be compared with those obtained by diffractometric analysis for several monoperoxovanadium complexes in the solid state which exhibit a pentagonal bipyramid geometry and hence a coordination number of seven.

Introduction

Recent investigations on the chemistry of peroxovanadium complexes in aqueous solution, stimulated by the discovery of their biological role,[1,2] improved our understanding of the equilibria and of the oxidative processes in which peroxovanadium complexes are involved.[3] In most of these studies, ^{51}V NMR spectroscopy was successfully employed.[3] *Ab initio* calculations were also carried out, providing results which helped in rationalizing some of the experimental behaviors observed.[4] In spite of all these efforts, however, a fundamental aspect of these systems, *i.e.* the structure of the peroxovanadium species in solution, remains largely obscure.[5] Accordingly, the cationic monoperoxo species formed by addition of hydrogen peroxide to a vanadium(V) precursor in acidic aqueous solution is correctly written as $[VO(O_2)(H_2O)_n]^+$ in order to emphasize that the number of water molecules coordinated to vanadium, and hence the geometry, is unknown.

The solid state structures, determined for various monoperoxovanadium complexes containing different ligands, indicate a pentagonal bipyramid geometry in which the oxo group occupies one of the two apical positions whereas the peroxo group lies in the equatorial plane.[6,7] This would suggest a coordination number of seven. It is well-known, however, that the geometrical arrangements observed in the solid state are not necessarily maintained in solution, particularly in coordinating solvents.[7]

Owing to the difficulty in obtaining even indirect experimental information on the structure in solution of peroxovanadium complexes, we have approached this problem by carrying out *ab initio* calculations. These have been made by using two different levels of theory, *i.e.*, Hartree−Fock with a small all-electron basis set (HF/3-21G(*))[8] and density functional theory (DFT) with effective core potentials (B3LYP/LANL2DZ).[9,10] Both methodologies gave comparable results. On the basis of such results, reported in this paper, we suggest that the preferred coordination number of the aquamonoperoxovanadium complex in acid water is six, *i.e.* $[VO(O_2)(H_2O)_3]^+$, and that the corresponding geometry is a distorted octahedral one.

Methods

All calculations were carried out with Spartan v. 4[11] and Gaussian 92−94,[10] running on IBM RS/6000 workstations. Hartree−Fock calculations were run with the 3-21G(*) basis set.[8] Density functional theory (DFT) calculations were carried out with Becke's hybrid three-parameter functional with Lee−Yang−Parr nonlocal correlation (B3LYP);[9,10] these calculations had to be run with the (99,302) numerical integration grid[10] and full accuracy at all stages in order to achieve SCF convergence. Hay and Wadt's effective core potentials (ECP)[12,13] for vanadium were employed in DFT calculations. However, V(V) compounds have a $3d^0$ configuration, and therefore ECP's incorporating up to the outermost core orbitals ($3s^23p^6$) will not give satisfactory results. Accordingly, the ECP's developed specifically for these cases[13] (*i.e.*, explicitly treating $3s^23p^6$ electrons), were employed; this basis set is denoted as LANL2DZ in Gaussian 9*x*. Atomic charges were calculated by fitting to electrostatic potential maps (CHELPG method).[14]

Results and Discussion

Structure of $VO(O_2)^+$. Our first approach to the problem was to determine the structure of the "naked" oxoperoxo cation $VO(O_2)^+$ **1** (Figure 1). For this species either a "transoid" (planar, **1a**) or a "cisoid" geometry (**1b**) can be envisaged.

The structures of **1a**−**b** were firstly optimized at the HF/3-21G(*) level.[10] The results (energy and geometrical parameters) are collected in Table 1 and show the cisoid structure **1b** to be more stable than **1a** by 48 kcal/mol.

However, a large effect of electron correlation on the structure and stability of transition metal species is expected. On the other hand, such an effect can hardly be evaluated by perturbation methods (like MP2) with a basis set as small as 3−21G(*). Therefore, as a further step, electron correlation was taken into account using a DFT method (B3LYP hybrid functional).[9,10] In order to improve the electronic description without excessively increasing the size of the calculations, we employed a basis set using ECP's for vanadium in DFT calculations. The use of ECP's originally derived from HF calculations has been found to be acceptable for DFT calculations too.[15]

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

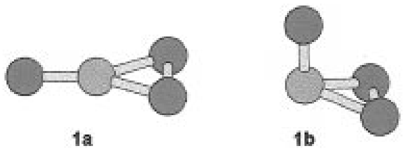

Figure 1. Transoid (**1a**) and cisoid (**1b**) geometries of the $VO(O_2)^+$ ion.

TABLE 1: Calculated Energies (au) and Geometrical Parameters of Structures 1a and 1b[a]

	$VO(O_2)^+$ *transoid* **1a**	$VO(O_2)^+$ *cisoid* **1b**
	RHF/3-21G(*)	
energy	−1161.119963	−1161.196492 $\Delta E_{1a-1b} = -48.0$ kcal mol^{-1}
q(V)	2.05	2.05
r(V=O)	1.531	1.499
r(V−O)	1.722	1.766
r(O−O)	1.514	1.449
∠O=V−O	159.9	107.8
∠O−V−O	52.1	48.5
	B3LYP/LANL2DZ	
energy	−296.620262	−296.581537 $\Delta E_{1a-1b} = -24.3$ kcal mol^{-1}
r(V=O)	1.569	1.562
r(V−O)	1.871	1.787
r(O−O)	1.411	1.492
∠O=V−O	157.8	111.7
∠O−V−O	44.3	49.2

[a] Energies in atomic units (1 au = 627.5 kcal mol^{-1}), distances in Å, angles in deg.

The results of the B3LYP/LANL2DZ geometry optimization are also collected in Table 1, whereby one sees that the energy gap between **1a** and **1b** is substantially reduced, although the overall energy balance still indicates that the cisoid form is more stable by 24 kcal/mol.

Structure of the $[VO(O_2)(H_2O)_n]^+$ Clusters. Once the geometry of **1** was established, we proceeded by calculating the geometry of the species obtained by stepwise addition of water molecules to **1b**. The calculations were carried out at both the RHF/3-21G(*)[8] and B3LYP/LANL2DZ[9,10] levels. All structures were checked to be minima on the potential energy surface by RHF/3-21G(*) vibrational analysis. The structures are represented in Figure 2.

A noteworthy feature is that the geometry optimization of the most flexible species (**6**) succeeded only when carried out in redundant coordinates (implemented only in Gaussian 94[10]), whereas optimization in Cartesian coordinates failed to converge to any minimum.

The structures of **2**−**5** feature a rather straightforward arrangement of the water molecules around vanadium. However, in the species containing five molecules of water (**6**), the fifth molecule was assumed to lie in the second solvation shell (*i.e.*, to act as a solvent molecule hydrogen-bonded to the oxo oxygen, rather than as a ligand), because the maximum coordination number of seven has been already reached by addition of four water molecules.

As for all weakly bonded species, a large conformational flexibility of the ligands can be expected.[16] Thus, one can expect **2**−**6** to present more minima, corresponding to various rotational arrangements of water molecules relative to the $VO(O_2)^+$ moiety. However, we believe that the stationary points located are indeed representative of the species investigated, because (a) geometry optimizations were run with no symmetry constraint and converged to the reported structures also with different starting geometries; (b) the potential energy surface for rotation of a water molecule in Ca^{2+}−water clusters has been shown to be rather flat, a bending of 20−30° requiring only 1−2 kcal/mol.[16b]

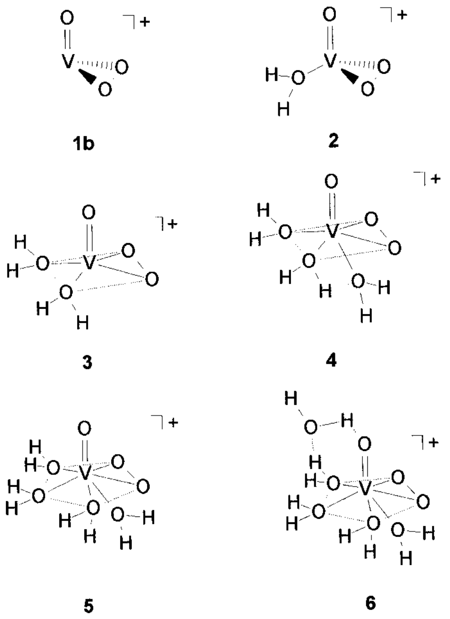

Figure 2. Geometries of hydrated peroxovanadium complexes.

Energetics of Hydration of $VO(O_2)^+$. The absolute energies of **2**−**6**, total and stepwise hydration energies of $VO(O_2)^+$ are collected in Tables 2 and 3.

For species **2**−**6** a reasonable agreement between the two methods of calculation is observed, hydration energies differing by *ca.* 10 kcal/mol for the addition of the first water molecule and decreasing to about 1 kcal/mol.

An important issue related to the energetics of water binding is the possibility that the binding energy is overestimated because of the basis set superposition error (BSSE). Although the need of correcting for the BSSE has been widely recognized, there has been considerable controversy with regard to the method to adopt. In particular, the counterpoise method (CP) has been deemed rough or inadequate for this purpose; however, van Duijneveldt *et al.*[17] recently reviewed the topic and expressed the view that the CP method is a reliable and physically consistent way of correcting the BSSE. CP calculations have indeed been carried out in several other theoretical studies dealing with the hydration of metal cations;[16,18] the general picture that can be drawn from such data is that the BSSE amounts to *ca.* 10% of the binding energy, tends to increase for correlated (MP*n*) wave functions and to decrease if effective core potentials are used. Because we have employed ECP's in conjunction to a correlated (DFT) method, the magnitude of the BSSE is uncertain, and hence we have also estimated the BSSE in the binding energies of the complexes studied by the CP method; these are also listed in Table 2.

The addition of the first water molecule to $VO(O_2)^+$ takes place with a hydration energy of −75.4 kcal/mol, which is reduced to −70.4 kcal/mol by the CP correction. This places the BSSE for this reaction at 5.0 kcal/mol, *i.e.*, about 10% of the binding energy. This value is slightly larger than the values recently reported for similar metal ion−water clusters (0.3−2 kcal/mol).[16b,c] For higher clusters (**3**−**6**), the BSSE amounts to 4 kcal/mol per water molecule and remains below 10% of the binding energy. Although the definition of BSSE becomes ambiguous when applied to the binding energy of two interacting species, one of which is also subjected to BSSE,[17] the constancy of its value allows us to correct the stepwise hydration energies of Table 3 by adding 5 kcal/mol to the binding energy of the

TABLE 2: Energies of Hydrated Peroxovanadium Species[a]

	RHF/3-21G(*)		B3LYP/LANL2DZ				
species	E	ZPE[b]	E	E (CP)[c]	E_b[d]	E_b (CP)[c,d]	BSSE[e]
H_2O	−75.585 959 6	0.019 391	−76.414 316 6				
1b	−1161.196 492	0.009 055	−296.581 537				
2	−1236.925 096	0.033 333	−373.116 073	−373.003 883	−75.4	−70.4	5.0
3	−1312.628 400	0.058 719	−449.619 766	−449.422 963	−131.5	−123.5	8.0
4	−1388.287 973	0.083 823	−526.099 313	−525.843 139	−172.5	−160.7	11.7
5	−1463.930 273	0.107 225	−602.563 988	−602.263 186	−204.0	−188.7	15.3
6	−1539.571 836	0.133 180	−679.025 317	−678.685 220	−233.5	−213.4	20.1

[a] In atomic units. [b] Zero-point vibrational energy (ZPE) scaled by 0.89. [c] Sum of the energies of $VO(O_2)^+$ and the appropriate number of water molecules with BSSE correction by the counterpoise method. [d] Total binding energy calculated as $E_b = E$ - $(E_{VO3} + nE_{H2O})$, in kcal/mol. [e] Basis set superposition error in kcal/mol.

TABLE 3: Stepwise Hydration Energies (E_{hyd}, kcal/mol) of Peroxovanadium Species

	E_{hyd}[a]		
process	RHF/3-21G(*)[b]	B3LYP/LANL2DZ[b]	B3LYP/LANL2DZ + BSSE + ZPE[c]
$VO(O_2)^+ \rightarrow [VO(O_2)(H_2O)]^+$	−86.4	−75.4	−67.4
$[VO(O_2)(H_2O)]^+ \rightarrow [VO(O_2)(H_2O)_2]^+$	−69.9	−56.1	−48.3
$[VO(O_2)(H_2O)_2]^+ \rightarrow [VO(O_2)(H_2O)_3]^+$	−42.6	−40.9	−33.3
$[VO(O_2)(H_2O)_3]^+ \rightarrow [VO(O_2)(H_2O)_4]^+$	−32.8	−31.6	−25.1
$[VO(O_2)(H_2O)_4]^+ \rightarrow [VO(O_2)(H_2O)_5]^+$	−30.8	−29.5	−21.4

[a] $E_{hyd} = E_n - (E_{n-1} + E_{H_2O})$. [b] No BSSE correction included. [c] Including RHF/3-21G(*) zero-point energies and BSSE correction (see text).

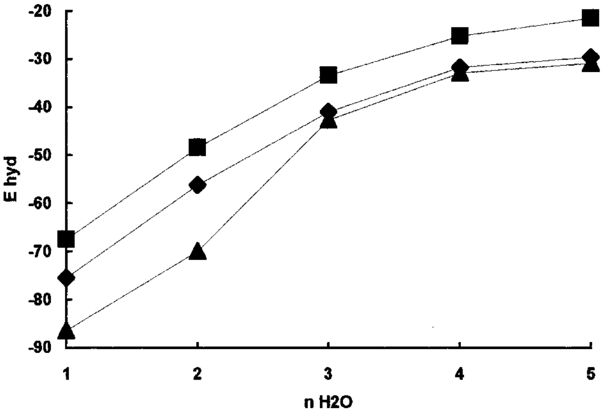

Figure 3. Hydration energies of peroxovanadium complexes as a function of the number of water molecules at the HF/3-21G(*) (▲), B3LYP/LANL2DZ (◆), B3LYP/LANL2DZ including BSSE correction and ZPE's (■) levels.

1b → **2** process, and 4 kcal/mol to the other binding energies. Owing to the similar values found, the CP correction does not significantly affect the conclusions of this study concerning the structure of the solvation shell of **1b** (see below).

An improved estimate of the hydration energy can be made by including the zero-point energies obtained by RHF/3-21G(*) vibrational analysis reported in Table 2. Thus, the stepwise hydration energies listed in the last column of Table 3 include both the BSSE correction and ZPE's and constitute the best estimates of this quantity.

In any event, the first hydration energy of **1b** is much higher than that involved in hydrogen bonding between neutral species (see *e.g.* the dimerization energy of water, which amounts to 5.5 kcal mol^{-1}),[19] and also of hydration energies of monovalent inorganic cations. For example, the enthalpy of hydration of alkali metal ions $[M^+ \rightarrow M(H_2O)^+]$ (M = Li, Na, K) is 20−34 kcal/mol and decreases to 10−12 kcal/mol for higher clusters, *e.g.* for the process $M(H_2O)_5^+ \rightarrow M(H_2O)_6^+$.[16e,20] On the other hand, the first hydration energy of first-row transition metal ions (Sc^+, Ti^+, V^+, Fe^+, Cu^+)[21−23] is substantially higher (30−40 kcal/mol). While the water binding for alkali metal ions is clearly electrostatic in origin, the data for transition metals point out that their stronger energetics of hydration derives from a coordination to the metal. Even with these data in mind, the first hydration energy of $VO(O_2)^+$ is much higher than that of the above reference points, being comparable with that of alkaline earth metal ions (*e.g.* −78 kcal/mol for $Mg^{2+} \rightarrow Mg(H_2O)^{2+}$).[24] This finding agrees with the result (Table 1) which places a formal charge of *ca.* +2 on the vanadium atom. Hence, the above data are consistent with a high first hydration energy of $VO(O_2)^+$ as a result of coordination to the metal and strong electrostatic attraction due to a high atomic charge.

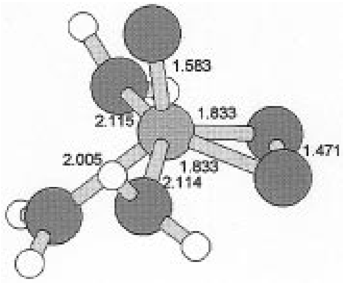

Figure 4. Structure of $[VO(O_2)(H_2O)_3]^+$ (**4**), optimized at the B3LYP/LANL2DZ level.

Solvation Shell of $VO(O_2)^+$. The addition of water molecules causes a continuous stabilization of the peroxovanadium species. The differences in energy of the species obtained by stepwise addition of water are plotted as a function of the number of water molecules in Figure 3, which illustrates the key information provided by these calculations.

It can be seen that the gain in energy obtained on going from three molecules of water to four (**4** → **5**) is similar to the stabilization observed on going from four to five water molecules (**5** → **6**). The latter, as previously mentioned, is due to the solvation of the coordinatively saturated peroxocomplex **6** operated by a water molecule in the second solvation shell. By contrast, the gain in energy on going from two to three water molecules is significantly larger, and similar to that observed on going from one to two coordinated water molecules.

The conclusion that can be reached from these data is that, although the fourth water molecule may still lie in the first solvation shell, the stabilization brought about by it is just comparable with that involved in the formation of the second solvation shell (**5** → **6**). Accordingly, we can envision the preferred structure of aquamonoperoxovanadium species as **4**, with a coordination number of six and the geometry of a distorted octahedron. However, the weaker energetics of hydration of **4** suggests that the remaining coordination position is occupied by water but that it can be readily made available for exchange with other ligands.[6,7] The optimized geometry of **4** (B3LYP/LANL2DZ) is shown in detail in Figure 4.

Additional insight, especially on the thermochemistry of hydration, has been gained by running calculations in which metal ion−water clusters with predefined structure are placed in a solvent, modeled by continuum methods.[25] Although the solvent reaction field affects to some extent the geometry of the cluster (notably the metal−oxygen distance),[25a] it is, however, unlikely to alter the structure of the first solvation shell.

In conclusion, our data lead to a different conclusion from that suggested by the solid state structures of isolated monoperoxovanadium complexes. Although some caution is in order, owing to the fact that our calculations were carried out on discrete water clusters as models of solvated species, the coordinatively unsaturated nature of monoperoxovanadium complexes in aqueous solution fits with the known oxidative ability of such species.

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