Direct Evidence of Solvent-Peroxovanadium Clusters by Electrospray Ionization Mass Spectrometry

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Electrospray Ionization Mass Spectrometry (ESI-MS) measurements and *ab initio* calculations on $[OV(O_2)(H_2O)_m(CH_3OH)_n]^+$ (m,n: 0–4) peroxo cations have been carried out. This experimental technique allowed the direct observation of the above mentioned species for the first time. The results obtained clearly indicate that the exchange reactions between water and methanol molecules, within the coordination sphere of monoperoxo-vanadium complexes, is a conceivable and fast process.

Introduction

The peroxo species formed in aqueous acid solutions by interaction of vanadates with hydrogen peroxide have been studied by several techniques, including heteronuclear NMR[1][2], Raman spectroscopy[3] and ab initio calculations.[4][5] In spite of all these studies, however, a fundamental aspect of these systems, i.e. the nature of the first coordination sphere of the peroxovanadium derivatives present in solution, is still a matter of debate.[1][2] As an example recent ab initio calculations indicate that the oxo-(monoperoxo)vanadium cation likely binds three H_2O molecules to form a species whose structure is a distorted octahedron,[5] whereas in the solid state peroxovanadium complexes prefer the pentagonal bipyramid geometry.[6][7]

In order to obtain direct experimental information on the solution structure of peroxovanadium species, we have undertaken an electrospray ionization mass spectrometry (ESI-MS)[8][9] analysis of water/methanol acid solutions of vanadates in the presence of hydrogen peroxide. The electrospray technique is a gentle ionization method of transferring ions from solution to the gas phase with no apparent fragmentation, and has been successfully applied to the analysis of many inorganic and organometallic systems.[10] In our case the direct observation of $[OV(O_2)(H_2O)_m(CH_3OH)_n]^+$ (m, $n = 0-4$) peroxo cations has been achieved for the first time. Ab initio calculations were also carried out, whose results appear to rationalize most of the experimental behaviors observed.

Results and Discussion

Preliminary data, reported in Table 1, were obtained for solutions containing weighted amounts of ammonium vanadate in CH_3OH/H_2O (1:1; pH = 1, $HClO_4$). The electrospray mass spectrum of this solution, obtained by direct infusion into the ESI source, showed the occurrence of different species[11][12][13] identified as monomeric homo ions $[OV(OH)_3H]^+$ (*m*/*z* 119) and $[OV(OCH_3)_3H]^+$ (*m*/*z* 161), and mixed ions $[OV(OH)_2(OCH_3)H]^+$ and $[OV(OH)(OCH_3)_2H]^+$ (centered at *m*/*z* 133 and 147, respectively). The base peak of the spectrum is associated with the formation of the dimeric species[14] $[OV-O-VO(OH)_4H]^+$ at *m*/*z* 219. Other significant peaks, related to dimeric complexes and formally having the composition reported in Table 1, were found at *m*/*z* 237, 247 and 279.

As expected, addition of an equimolar amount of H_2O_2 to the vanadate solutions produces significant changes in the electrospray mass spectrum. Besides the above-mentioned ions at *m*/*z* 147 and 161, new ionic monoperoxo species at *m*/*z* 117, 131, 135, 181 and 195 were detected (see Table 1). Signals corresponding to the tetraaquo complex $[OV(O_2)(H_2O)_4]^+$ at *m*/*z* 171 and to the mixed $[OV(O_2)(H_2O)_m(CH_3OH)_n]^+$ ($m + n = 4$) cations at *m*/*z* 199 and 213 are also observed, although in low relative intensity.

Acid catalysis appears to play a fundamental role in the chemistry of peroxovanadium species, particularly when they are involved in the catalytic cycle of bromoperoxidase

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Table 1. Percentage of ion abundances in Electrospray Ionization Mass Spectra of vanadates and peroxovanadates in water methanol acid solutions[a]

ion	m/z	rel. abund. (%)
vanadates		
$[OV(OH)_3H]^+$	119	14
$[OV(OH)_2(OCH_3)H]^+$	133	5
$[OV(OH)(OCH_3)_2H]^+$	147	2
$[OV(OCH_3)_3H]^+$	161	20
$[OV{-}O{-}VO(OH)_4H]^+$	219	100
$[OV{-}O{-}VO(H_2O)(OH)_4H]^+$	237	12
$[OV{-}O{-}VO(OCH_3)_2(OH)_2H]^+$	247	7
$[OV{-}O{-}VO(OCH_3)_3(H_2O)(OH)H]^+$	279	85
peroxo vanadates		
$[OV(O_2)]^+$	99	24
$[OV(O_2)(H_2O)]^+$	117	100
$[OV(O_2)(CH_3OH)]^+$	131	60
$[OV(O_2)(H_2O)_2]^+$	135	18
$[OV(O_2)(H_2O)(CH_3OH)]^+$	149	25
$[OV(O_2)(H_2O)_3]^+$	153	10
$[OV(O_2)(CH_3OH)_2]^+$	163	[b]
$[OV(O_2)(H_2O)_4]^+$	171	2
$[OV(O_2)(H_2O)(CH_3OH)_2]^+$	181	20
$[OV(O_2)(CH_3OH)_3]^+$	195	25
$[OV(O_2)(H_2O)_2(CH_3OH)_2]^+$	199	[b]
$[OV(O_2)(H_2O)(CH_3OH)_3]^+$	213	5

[a] NH_4VO_3 (0.0005 M), in CH_3OH/H_2O (1:1; pH = 1, $HClO_4$), and NH_4VO_3 (0.0005 M), H_2O_2 (0.0005 M), in CH_3OH/H_2O (1:1; pH = 1, $HClO_4$). – [b] Relative peak intensity less than 2%.

enzymes.[15] In that respect the knowledge of the protonation site of peroxovanadium complexes is an important piece of information. In the present work, where cationic peroxovanadium species are studied in acid solutions, we have addressed such a problem by carrying out ab initio calculations on the oxoperoxo complexes $[OV(O_2)(H_2O)]^+$ and $[OV(O_2)(CH_3OH)]^+$. The calculations have been made by using two different levels of theory, i.e. Hartree-Fock with a small all-electron basis set (HF/3-21G(*))[16] and density functional theory (DFT) with effective core potentials (B3LYP/LANL2DZ),[17][18] and are shown in a pictorial way in Figure 1. As it can be seen, the differences in energies of the three possible protonation sites, i.e. the oxo oxygen atom , the peroxo oxygen atom and solvent molecule, for both peroxo complexes are rather small, thus suggesting the occurrence of equilibria among them. Details on the calculations are reported in the experimental section.[19]

Although in the case of vanadium derivatives a comparison between the theoretically calculated and experimentally found isotopic cluster in ESI-MS spectra is hampered by the lack of vanadium isotopes, further support to the identification of the ions reported in Table 1 was obtained with tandem (MS^2) analysis and deuteration experiments.

The preferential decomposition patterns of the peroxidic species, as obtained by MS^2 experiments, are the loss of

Figure 1. Relative-energy diagrams for the gas-phase proton-migration reactions of species $[OV(O_2)(H_2O)]^+$ (**A**) and $[OV(O_2)(CH_3OH)]^+$ (**B**); energy values are given in kcal/mol

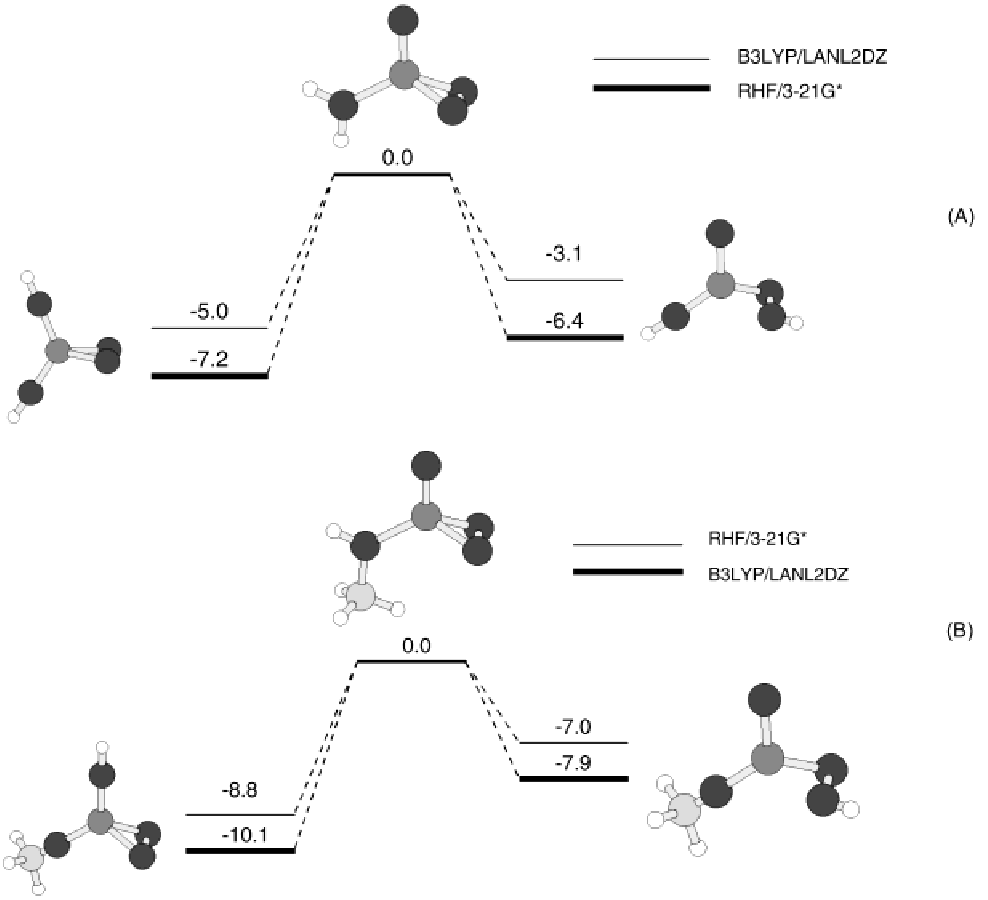


Figure 2. MS/MS mass spectrum of $[OV(O_2)(H_2O)(CH_3OH)_2]^+$ (m/z 181) using 2 V tickling voltage

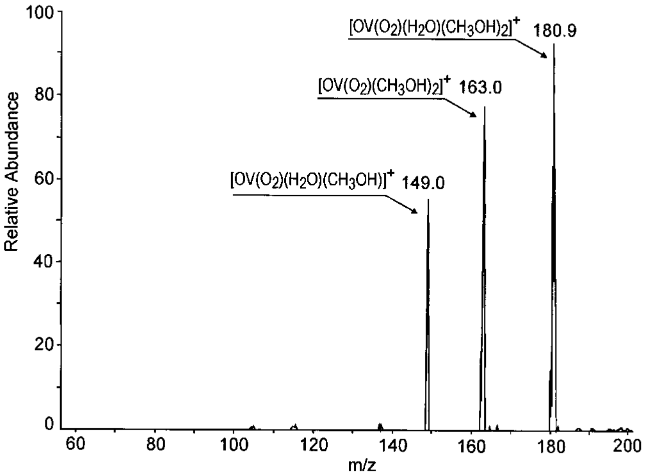
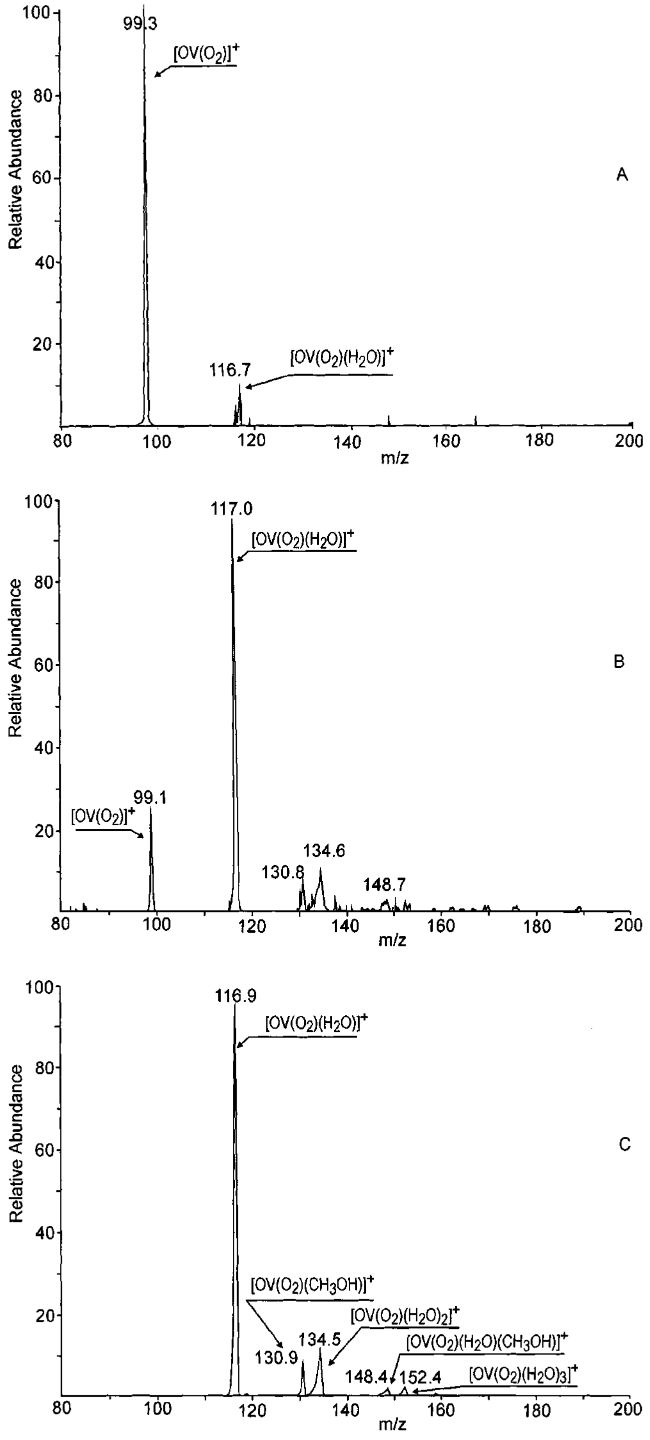


Figure 3. MS/MS mass spectra of $[OV(O_2)(H_2O)]^+$ using tickling voltages of: 3 V (**A**), 1 V (**B**) and 15 mV (**C**), respectively

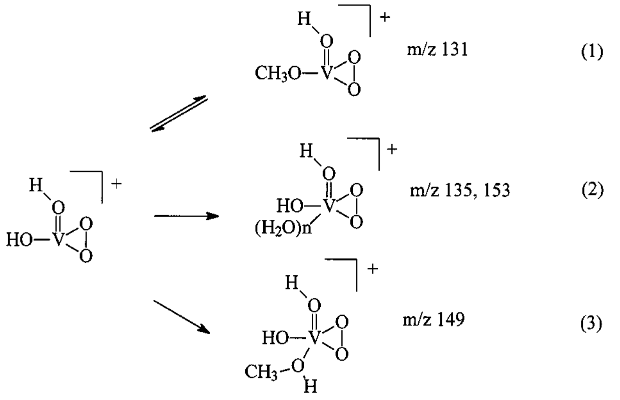


H_2O and/or CH_3OH molecules. As an example, at 2 V tickling voltage, the mixed species $[OV(O_2)(H_2O)(CH_3OH)_2]^+$ (m/z 181) fragments through expulsion of H_2O and CH_3OH, affording the ions at m/z 163 and 149, respectively (see Figure 2). On the other hand, the aquo(oxo)peroxovanadium cation $[OV(O_2)(H_2O)]^+$ (m/z 117) decomposes to the "naked" ion $[OV(O_2)]^+$ (m/z 99) by using 3 V tickling voltage (Figure 3A). Most noteworthy however, ionic species at higher mass-over-charge values are detected upon isolation of the ion under analysis. This is shown for ion $[OV(O_2)(H_2O)]^+$ (m/z 117), which has been isolated and trapped within the ion-trap analyzer in the presence of relatively small tickling voltages (10−15 mV), for times of about 0.1 ms. Under these conditions (Figure 3C) no fragmentation products, but formation of ions at m/z 131, 135, 149, 153 is observed. A likely explanation for such a result is the reaction of the ion $[OV(O_2)(H_2O)]^+$ with solvent molecules present in the ion trap (see Scheme 1), i.e. exchange between H_2O and CH_3OH (eq. 1), coordination of water [eq. 2 (n = 1, 2)] or coordination of methanol (eq. 3). At intermediate tickling voltage (1 V) formation of these ions is reduced and collision-induced decomposition product ions prevail (Figure 3B). An analogous behavior has been recently reported for (allyl)Pt^{II} compounds.[20]

The same ion-molecule reactions have been observed with the corresponding deuterated ion $[OV(O_2)(D_2O)]^+$ (m/z 119) and with other oxoperoxo species with different coordination-sphere composition. Thus, after the isolation of the ion $[OV(O_2)(H_2O)_2]^+$ (m/z 135), the ionic species at m/z 167 (addition of methanol) and 185 (addition of water and methanol) are formed, whereas the complex $[OV(O_2)(H_2O)(CH_3OH)]^+$ (m/z 149) gives rise to ions at m/z 163 (exchange water/methanol), 167 (addition of water) and 181 (addition of methanol). Furthermore, the occurrence of these ion-molecule reactions upon trapping the selected ions in the ion trap and the high tickling voltages that must be used (up to 3 V, see Figures 2 and 3C) to have complete collision-induced decomposition of peroxovanadium compounds $[OV(O_2)(H_2O)_m(CH_3OH)_n]^+$ (m, n = 0−4), likely suggest[20] the binding of water and/or methanol to the vanadium center.

^{51}V-NMR studies in mixed H_2O/CH_3OH solvents, revealed for oxo(monoperoxo)vanadium species the presence of a single broad peak ($\delta \approx -540$, ca. 1200 Hz at half width),[1b] thus suggesting the occurrence of fast equilibria, on the ^{51}V-NMR time scale, between water and methanol molecules for complexation to the metal center. A direct observation of the rapidly exchanging species by lowering

Scheme 1



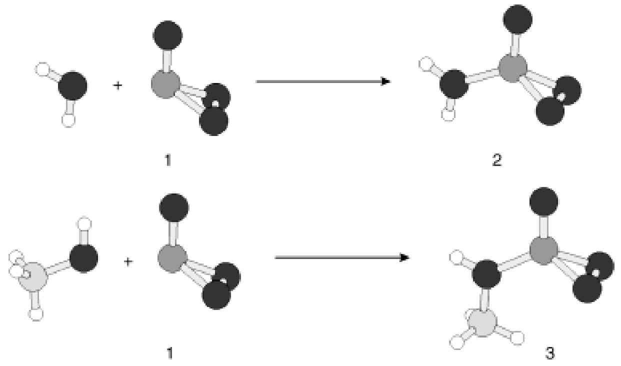
the temperature is hampered by the simultaneous increase of the line width due to the increase of the correlation time. The ESI-MS results here reported, however, show that the substitution of water molecules with methanol, and vice versa, in the coordination sphere of monoperoxovanadium complexes, is a conceivable and detectable process which leads to several peroxo complexes. The tandem use of ESI-MS and low-temperature NMR spectroscopy in the investigation of rapidly exchanging organometallic systems has been recently reported.[21]

In order to obtain further support to the occurrence of exchange process between water and methanol molecules in the coordination sphere of oxo(monoperoxo)vanadium complexes, ab initio calculations were also carried out. The reactions taken into consideration are the addition to the “naked” ion $[OV(O_2)]^+$ of either H_2O or CH_3OH molecule. As in the calculations reported above, two different levels of theory were used[16][17][18] and the relevant results are collected in Table 2.

The binding of a methanol molecule to the “naked” oxo(peroxo) ion involves a larger degree of stabilization as compared with that observed in the binding of a water molecule [99.6 kcal/mol against 86.4 kcal/mol with RHF/3-21G(*) calculation]. Such a result, supported also by the good agreement with that obtained with the DFT level of theory (see Table 2), may indeed substantiate the evidence that exchange between water and methanol molecules in the coordination sphere of oxo(monoperoxo)vanadium complexes is a likely process. If this were not the case, the exchange reaction between water and methanol detected upon isolation in the ion trap of the previously reported cations, could not be observed (see eq. 1, Scheme 1).

The higher affinity of methanol molecules for peroxovanadium center as compared with that of water is also confirmed by various experiments such as that shown in Figure 2. In particular, the relative abundance of ion $[OV(O_2)(CH_3OH)_2]^+$ at *m*/*z* 163, corresponding to the expulsion of a water molecule from $[OV(O_2)(H_2O)(CH_3OH)_2]^+$ (*m*/*z* 181), is higher than that of the ion at *m*/*z* 149, $[OV(O_2)(H_2O)(CH_3OH)]^+$, corresponding to the loss of methanol, despite of the statistical factor of 2 which would favor the latter process. The use of closely related experiments for measuring the relative affinities toward cationic species has been recently reviewed.[22]

Table 2. Calculated reaction energies for the addition of water and methanol molecules to $OV(O_2)^+$ ion (**1**)[a]



Species	RHF/3−21G(*) Energy[a]	RHF/3−21G(*) ZPE[b]	B3LYP/ LANL2DZ Energy[a]
H_2O	−75.585959	0.019391	−76.4143166
CH_3OH	−114.398019	0.048494	−115.705434
1	−1161.196492	0.009055	−296.581537
2	−1236.925096	0.033333	−373.116073
3	−1275.750310	0.060562	−412.423621
$\Delta E_{(\mathbf{2}-\mathbf{1}-\mathrm{H2O})}$[c]		−86.4	−75.4
$\Delta E_{(\mathbf{3}-\mathbf{1}-\mathrm{CH3OH})}$[c]		−99.6	−83.9

[a] Energies in atomic units (1 au = 627.5 kcal/mol). – [b] Zero-point vibrational energy (ZPE) scaled by 0.89. – [c] Reaction energies in kcal/mol.

Conclusion

In conclusion the possibility to select and trap ions in a defined region of space with relatively simple devices (ITMS), together with the development of electrospray ionization, has added interesting new perspectives to the study of inorganic and organometallic compounds for the possibility to perform collisional experiments and/or gas-phase ion-molecule reactions on the isolated ionic species. Furthermore, this technique is particularly useful in the analysis of highly labile and reactive intermediates, such as peroxidic species[23] and of rapidly exchanging systems.[21]

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Experimental Section

General Remarks: The ESI-MS measurements were obtained using a Finnigan MAT LCQ instrument (San Jose, CA). The samples were introduced by direct injection of NH_4VO_3 (0.0005 M), dissolved in CH_3OH/H_2O (1:1; pH = 1, $HClO_4$), in the absence or in the presence of an equimolar amount of H_2O_2. The same experiments were also performed using perdeuterated solvents, in the presence of $DClO_4$. Solution flow rate 8 $\mu l\ min^{-1}$, capillary temperature 145°C, spray voltage 2.4 kV, capillary voltage 14 V, nebulizing gas N_2 (40 units flow rate). The parameters related to octapoles and detector were those achieved by the automatic set-up procedure. Collision-induced decompositions of selected ions were obtained by applying a supplementary r.f. voltage (tickling voltage) to the end-cap electrodes of the ion trap (resonance activation). Typical V_{tickle} values for fragmentation were up to 3 V. For ion-molecule reaction studies, a tickling voltage of 15 mV was employed. − All calculations were carried out with *Spartan* v. 4[24] and *Gaussian 94*,[25] running on IBM RS/6000 workstations. Hartree-Fock calculations were run with the 3-21G(*) basis set.[16] Density functional theory (DFT) calculations were carried out with Becke's hybrid 3-parameter functional with Lee-Yang-Parr non-local correlation (B3LYP);[17][26] these calculations had to be run with the (99,302) numerical integration grid[25] and full accuracy at all stages in order to achieve SCF convergence. Hay and Wadt's effective core potentials (ECP)[18][26] 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[26] (i.e., explicitly treating $3s^23p^6$ electrons), were employed; this basis set is denoted as LANL2DZ in *Gaussian 9x*. Atomic charges were calculated by fitting to electrostatic potential maps (CHELPG method).[27] NMR experiments were carried out as already described.[1]

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