Characterization and Reactivity of Triperoxo Vanadium Complexes In Protic Solvents

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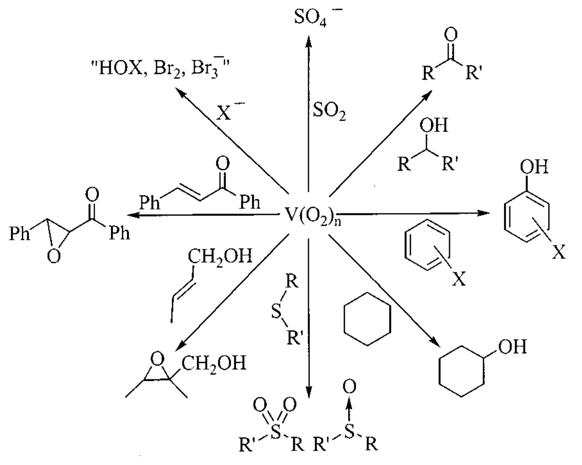
ESI-MS and ^{51}V NMR techniques have been used to detect the formation of vanadium triperoxo complexes in protic solvents. RHF/6-311++G(d,p) ab initio calculations were also carried out to address the structure and the energy requirements of vanadium peroxo species formed from vanadates and hydrogen peroxide. Such studies point to a step-by-step decomposition process involving the triperoxo vanadium complex, as highlighted by ESI-MS^n experiments. The reactivity of the triperoxo compound has been examined in an alcohol/water mixture with the aim of elucidating its oxidative behavior; evidence for the formation of the HOO^- anion as an active oxidant in solution has been obtained.

Introduction

The relevance of peroxo transition metal compounds either in oxidation chemistry[1,2] or in biochemical systems[3,4] is well established. Vanadium peroxides, in particular, are effective oxidants, as demonstrated by their reactions with different inorganic and organic substrates, viz. halides, sulfur dioxide, thioethers, alkenes, alcohols and aromatic or aliphatic hydrocarbons (Scheme 1).[5,6]



Scheme 1. Reactivity of vanadium peroxides with inorganic and organic substrates

These processes, whether stoichiometric or catalytic, where the oxidant can be hydrogen peroxide or an alkyl hydroperoxide, are usually carried out under very mild conditions with good selectivities and chemical yields.

The oxidation of halides with peroxo vanadates is the rate-determining step in the peroxidative halogenation of organic substrates [Equation (1)]:[7]

$$X^- + H_2O_2 + RH + H^+ \xrightarrow{\text{V(V)-peroxides}} RX + 2H_2O \tag{1}$$

Such a process is actually a chemical model of the activity of vanadium-dependent haloperoxidases enzymes.[8,9] Recent studies have shown that in the natural haloperoxidase systems the active peroxidic intermediate for the oxidation of bromide ion is a monoperoxo vanadate stabilized by a histidine residue contained in the active site pocket.[8,9] Conversely, mimicking systems reported in the literature are usually based either on monoperoxo vanadium [10] or on divanadium triperoxo species.[11]

Monoperoxo vanadium compounds are also catalysts for the aerobic oxidation of alcohols to carbonyl compounds [Equation (2)]:

$$R_2CHOH + O_2 \xrightarrow{\text{catalyst}} R_2C{=}O + H_2O_2 \tag{2}$$

In particular, it has been observed[12] that an accumulation of hydrogen peroxide takes place during the course of the oxidation of *i*PrOH with $n\mathrm{Bu_4NVO_3}$ in the presence of $HClO_4$ and excesses of H_2O_2 and H_2O, carried out at 40 °C under a pressure of one atmosphere of oxygen. Interestingly, the kinetic profile of this process is characterized by the presence of a periodic pattern, where the concentration of H_2O_2 oscillates as the result of a balance between subsequent production and decomposition phases. Under certain experimental conditions the efficiency of the process, defined as $([H_2O_2]t_{\max} - [H_2O_2]_0)/[\mathrm{cat}]_0$ where $t_{\max}$ is the reaction time for detection of the first maximum in the H_2O_2 concentration kinetic profile, reaches values higher than 4000.[13] Such a reaction compares well with the re-

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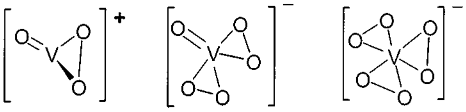
cently reported Pd^{II}-catalyzed process,[14,15] one of the most effective and environmentally friendly methods for the production of hydrogen peroxide.

It should be noted that most of the reactivity data cited above refer to mono- and diperoxo-vanadates. These species are easily formed in neutral or acid solutions upon addition of hydrogen peroxide to V^V precursors according to the equilibria in Equations (3) and (4):[16]

$$VO_2^+ + H_2O_2 \overset{K_1}{\rightleftharpoons} VO(OO)^+ + H_2O \tag{3}$$

$$VO(OO)^+ + H_2O_2 \overset{K_2}{\rightleftharpoons} VO(OO)_2 + 2\,H^+ \tag{4}$$

Nevertheless, together with mono- and diperoxo complexes, other peroxo vanadates may be formed depending upon the pH, and relative concentrations of vanadate and H_2O_2. The nature of the different complexes formed has been studied by ^{17}O and ^{51}V NMR,[17−22] Raman,[23] UV/Vis[24] spectroscopy and, more recently, by electrospray ionization mass spectrometry (ESI-MS).[25−27] The most important monomeric peroxo species are collected in Scheme 2. For the sake of simplicity throughout the paper the peroxo vanadium derivatives will be reported without the solvent molecules bound to the metal center in the first coordination sphere.



1 **2** **3**

Scheme 2. Monomeric peroxo vanadium species with ligands or solvent molecules in the coordination sphere omitted for clarity

The spectroscopic studies cited above provided several details concerning the true structure in solution of the vanadium peroxides,[21,25] even though the actual coordination number for all of them is still uncertain. Further information on the structure of vanadium peroxo derivatives has also been obtained from theoretical calculations. As already reported, considering the coordination ability of the vanadium(V) metal center, the maximum stabilization energy for the naked monoperoxo derivative has been calculated (from both HF and DFT calculations) with three molecules of solvent (H_2O) coordinated to the metal center.[28] Moreover, particular attention has been paid to the identification of the protonation sites for complexes **1** and **2** of Scheme 2. As an example, results obtained for the diperoxo species from RHF/3-21G(*) and B3LYP/LANL2DZ DFT calculations, have indicated that between the two most favorite protonation sites, i.e. the oxo oxygen and one of the peroxidic oxygens, protonation at the latter position is by far the most favored.[29]

It should be noted that very little information, from both experimental and theoretical[30] points of view, is available on species with more than two peroxo ligands.

It has already been mentioned that mono- and diperoxo complexes are well-known as electrophilic oxygen-transfer reagents or as radical oxidants.[5,6] However, the few papers[31,32] present in the literature reporting the reactivity of triperoxo vanadates claim that these species behave as nucleophilic oxidants. In particular, the triperoxo vanadium complexes $M[V(O_2)_3]\cdot 3H_2O$ (M = Na or K) are proposed[32,33] to be efficient oxidants of α,β-unsaturated ketones to the corresponding epoxide, benzonitrile to benzamide and benzil to benzoic acid, reactions which are usually carried out with alkaline hydrogen peroxide.

In the course of our studies on the mechanism[12,13] of the aerobic vanadium-catalyzed oxidation of *i*PrOH cited above [see Equation (2)], we were faced with the possible occurrence in solution of triperoxo vanadium derivatives caused by the high concentration of hydrogen peroxide that accumulates during the reaction. Hence, we decided to analyze alcoholic solutions of vanadates in the presence of high excesses of hydrogen peroxide in more detail in order to ascertain the presence of triperoxo species, and possibly to characterize them. We have also performed reactivity studies in the same media with preformed triperoxo vanadates with the aim of elucidating their oxidative behavior. The results obtained are presented and discussed below.

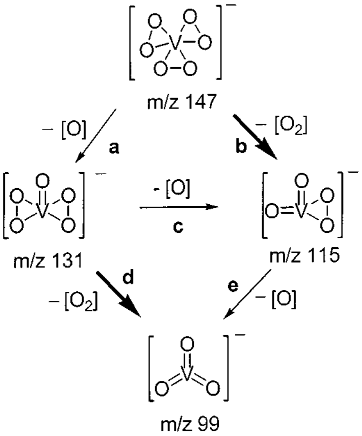
Results and Discussion

Characterization

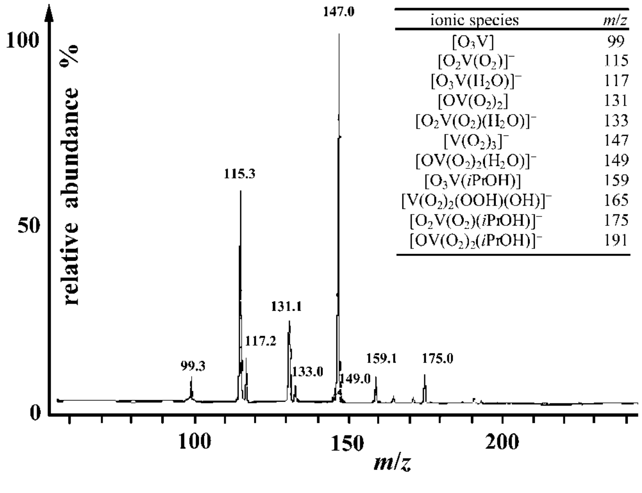
Vanadium derivatives undergo fast and favorable addition reactions with hydrogen peroxide producing peroxo complexes whose nature depends on the concentration of the reagents and on the pH. The negative-ion mode ESI mass spectra of nBu_4NVO_3 (5×10^{-4} $molL^{-1}$) solutions in *i*PrOH containing 0.5 $molL^{-1}$ H_2O and increasing amounts of H_2O_2 from 0.025 up to 0.35 $molL^{-1}$, are characterized and increasing amounts of H_2O_2 from 0.025 up to 0.35 $mol\cdot L^{-1}$, are characterized by the presence of two major ions at $m/z = 131$ and 147. Less intense, but equally important, ionic species are found at $m/z = 99$, 115, 133, 149 and 165. For relatively low excesses of H_2O_2 over V^V (50−150 equivalents) the $m/z = 131$ ion, corresponding to the oxo diperoxo derivative,[26] is dominant, however it is progressively overtaken by the species centered at $m/z = 147$ as the hydrogen peroxide concentration is increased. By analogy with previous studies carried out using either ethanol or *i*PrOH as mobile phases, the system under investigation was studied in both solvents and no significant dependence on the alcohol used was observed.

The different species were identified on the basis of labeling experiments and MS^n spectra[25−27] and are summarized in the inset of Figure 1. Among them, the species at *m*/*z* = 147, identified as the vanadium triperoxo derivative $[V(O_2)_3]^-$, and that at *m*/*z* = 115, assigned to the unprecedented dioxo monoperoxo compound $[O_2V(O_2)]^-$, are of particular interest. Labeling experiments were used to confirm this assignment. As expected, the replacement of water with $H_2{}^{17}O$ (ca. 50% isotope content) has no effect on the triperoxo anion, whereas formation of new peaks at *m*/*z* = 116 and 117 is observed next to the species at *m*/*z* = 115. In agreement with literature data,[5] this evidence indicates a fast exchange of the two oxo oxygens.

When the triperoxo derivative is mass selected within the ion-trap analyzer and allowed to decompose by increasingly higher tickling voltages, the CID decompositions observed are the fragmentations of one and two of the three peroxidic bridges, thus affording the oxo diperoxo derivative $[OV(O_2)_2]^-$ (*m*/*z* = 131, path **a**), and the dioxo monoperoxo derivative $[O_2V(O_2)]^-$ (*m*/*z* = 115, path **b**) of Scheme 3, including its water- and alcohol-containing homologues $[O_2V(O_2)(ROH)]^-$ (R=H, Et, *i*Pr). The decomposition implicating two peroxo moieties is the most favorable pattern. This fragmentation is also the major decomposition observed with the oxo diperoxo derivative $[OV(O_2)_2]^-$, path **d** of Scheme 3.



Scheme 3. Decomposition patterns of mono-, di- and triperoxo derivatives as obtained by MS^n experiments; wate-r or alcohol-containing adducts of ions at *m*/*z* = 131, 115 and 99 are not shown



ionic species	*m*/*z*
$[O_3V]$	99
$[O_2V(O_2)]^-$	115
$[O_3V(H_2O)]^-$	117
$[OV(O_2)_2]$	131
$[O_2V(O_2)(H_2O)]^-$	133
$[V(O_2)_3]^-$	147
$[OV(O_2)_2(H_2O)]^-$	149
$[O_3V(i\text{PrOH})]$	159
$[V(O_2)_2(OOH)(OH)]^-$	165
$[O_2V(O_2)(i\text{PrOH})]^-$	175
$[OV(O_2)_2(i\text{PrOH})]^-$	191

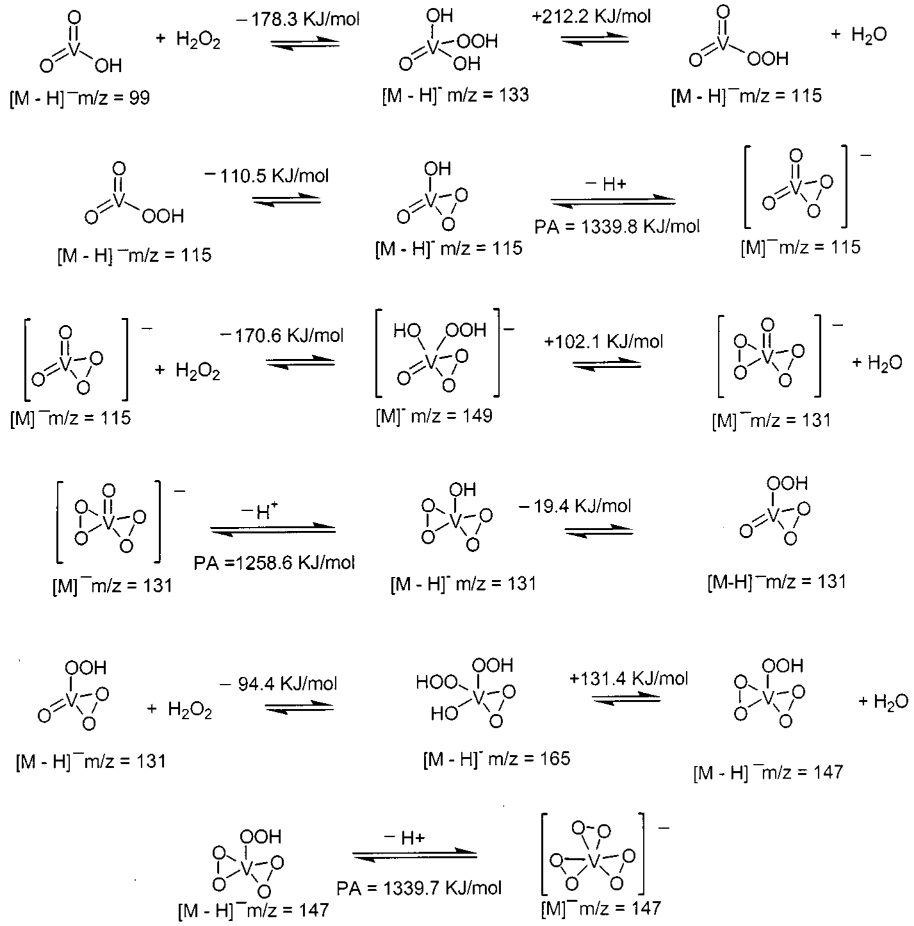
Figure 1. Negative-ion mode ESI-MS full scan spectrum of solutions of 5 × 10^{-4} mol·L^{-1} *n*Bu_4NVO_3 in *i*PrOH-0.5 mol·L^{-1} H_2O and H_2O_2 (0.25 mol·L^{-1}); the identification of the different ions is reported in the inset

The direct decomposition of both peroxidic bridges, formally corresponding to the expulsion of an O_2 molecule (pathways **b** and **d** of Scheme 3) probably occurs by a two-step mechanism consisting of two subsequent oxygen atom losses; this has been confirmed by experiments at increasing tickling energies.

Ab initio calculations have been carried out in order to address the structure and the energy requirements for the various intermediates detected by MS^n experiments and outlined in Scheme 3. Calculations have been carried out at the RHF/6-311++G(d,p) level of theory,[34−39] and the fully optimized species are collected in Scheme 4. The formation of all the peroxidic species results from a sequence of addition of H_2O_2, release of H_2O and proton transfer equilibria. In particular, proton-transfer processes are thermodynamically connected with the corresponding proton affinity (PA) of vanadium peroxo species, defined as the standard heat of ion dissociation to form a proton and the conjugate base in the gas phase (see Scheme 4).

The theoretical calculations showed that the addition of one molecule of hydrogen peroxide to vanadate, to form the hydroxo-monoperoxo derivative, is a favorable process with an energy balance of −76.6 kJ/mol. Similarly, the coordination of hydrogen peroxide to such a monoperoxidic adduct to produce the oxo-diperoxo species is an exothermic process by −68.5 kJ/mol. Such theoretical evidence agrees well with the experimental studies carried out on the complexation of vanadate by hydrogen peroxide, where an almost quantitative formation of mono and diperoxo vanadium complexes is observed under a range of conditions.[5]

Interestingly, the further reaction of protonated diperoxo vanadates with hydrogen peroxide yielding the triperoxo complex is clearly endothermic (see Scheme 4). In fact, the protonated triperoxo species lies 33.5 kJ/mol higher in energy than the diperoxo precursor. The capped trigonal prismatic geometry expected for the triperoxo complex[30,33] does not retain the V=O bond originally present in all mono and diperoxo vanadium complexes, and this probably destabilizes the triperoxo structure. However, the hydroperoxy-diperoxo vanadium complex can be formed in solution by protonation of the triperoxo derivative, and it could also represent one of the predominant structures of the triperoxo vanadate in alkaline solution. Moreover, the structure of this hydroperoxy-diperoxo vanadium complex may explain the peculiar oxidative behavior of vanadium species formed in highly basic solutions in the presence of large excesses of hydrogen peroxide (seebelow). The optimized structures of both protonated and unprotonated triperoxo vanadium complexes are shown in Figure 2. It should be noted that all the minimized species shown in Scheme 4 have been observed experimentally, as anions or as [M − H]$^-$ if neutrals, in the full scan ESI mass spectrum of Figure 1.



Scheme 4. Calculated relative energies (kJ/mol) for the formation of peroxo species from hydrogen peroxide and vanadate derived by RHF/6-311++G(d,p) ab initio calculations; calculated proton affinities (PA) for vanadium peroxo species, defined as the standard heat of ion dissociation to a proton and the conjugate base in the gas phase, are also included; all the species reported here have been observed experimentally, either as anions or as $[M - H]^-$ if neutrals, in the full scan ESI mass spectrum of Figure 1

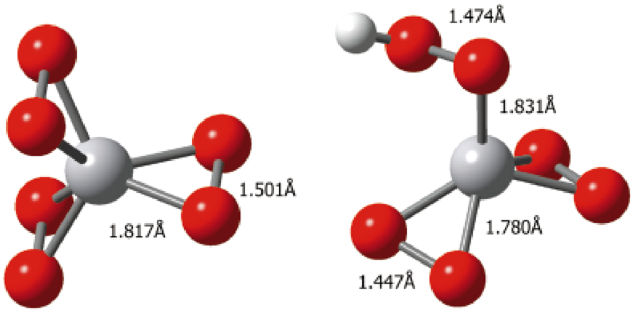


Figure 2. Structures of $[V(O_2)_3]^-$ (*left*) and of $[V(O_2)_2OOH]$ (*right*) optimized at the RHF/6-311++G(d,p) level; atomic distances are reported in Å

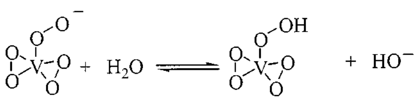
As pointed out in previous paragraphs, ESI-MS experiments were conducted to investigate the possible direct relationship occurring between diperoxo and triperoxo species as a function of hydrogen peroxide excess. The full-scan mass spectra of the system under investigation, recorded at different initial concentration of hydrogen peroxide, (5×10^{-4} molL^{-1} nBu$_4$NVO$_3$ in iPrOH containing 0.5 molL^{-1} H_2O, $[H_2O_2]$ from 0.025 up to 0.35 mol·L^{-1}, apparent pH ca. 7), showed that, as the concentration of H_2O_2 is increased, the vanadium diperoxo derivatives are progressively replaced by the triperoxo species. In addition, the ratio of the relative abundances of the diperoxo compounds (and related fragments) with the relative abundances of the triperoxo compounds (and related fragments) correlates linearly with the hydrogen peroxide concentration. Such a linear behavior suggests a direct equilibrium between the two peroxo species, even though a quantitative measure of the related K_{eq} is hampered by the non-equilibrium, low-pressure and solvent free conditions that pertain to ion traps.

Tracey et al.[40] have reported a thermodynamic measure of a pH dependent K_{eq} (9.4 L·mol^{-1}) in water measured in ^{51}V NMR experiments (1.0 mol·L^{-1} KCl, 2×10^{-2} mol·L^{-1} HEPES buffer, pH 6.7), referring to the equilibrium $Vl_2 + l \rightleftarrows Vl_3$ (l = peroxide). We have tried to determine the equilibrium constant for the formation of triperoxo derivatives in experimental conditions as close as possible to those employed for ESI experiments by recording ^{51}V NMR spectra in mixed solvents (alcohol/water) in the absence of buffers and without controlling the ionic strength. Under our experimental conditions, in contrast to Tracey's results, the presence of an alcohol-containing diperoxo derivative (signal at $\delta = -642$, $W_{1/2} = 240$ Hz) is detected irrespective of the excesses of hydrogen peroxide. Furthermore, upon increasing the water content in the solvent a second signal ($\delta = -663$, $W_{1/2} = 260$ Hz) appears, probably due to a water-containing diperoxo complex. The occurrence of a slow equilibrium between these species was confirmed previously by the coalescence of these two signals at 348 K.[12] It should be noted that the high ionic strength of the solutions (buffers and/or KCl as used in Tracey's experiments) is compelling for the formation of triperoxo vanadium complexes.[41]

The observation, during ESI-MS experiments in almost neutral solutions, of the triperoxo derivative as the major ionic species in the presence of large excesses of hydrogen peroxide may be explained by the particular conditions that pertain to the electrospray ionization technique. The electrospray process of aqueous or mixed alcohol-water solutions of various analytes has been reported to produce a marked pH change in the nebulized droplets with respect to the bulk.[42,43] In particular, droplets formed under the ESI negative-ion mode may undergo a considerable pH increase, favoring the formation of the triperoxo derivative, which is stable under fairly basic conditions, as discussed below.

Reactivity

The blue-violet complex $Na[V(O_2)_3]$ has been synthesized by using a slightly modified literature procedure[31−33] (see Experimental section for details). $Na[V(O_2)_3]{\cdot}3H_2O$ is not stable in aqueous solution at millimolar concentrations. Accordingly, a fast change of color from blue-violet (triperoxo vanadate) to yellow (diperoxo vanadate) is observed while preparing the solutions. The yellow solution thus obtained has a pH of about 11 due to the hydrolysis of the triperoxo derivative.[31−33] Such equilibria may be indicated schematically as in Equation (5)−(7), where the triperoxo species is reported with one end-on peroxy anion in order to unravel the hydrolysis equilibria. Indeed, the structural data available[7] indicate that such a species contains three side-on peroxo moieties. Similarly, the theoretical calculations reported above indicate that the triperoxo complex has a capped trigonal prismatic geometry with three side-on peroxo moieties.



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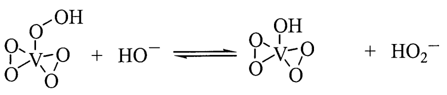

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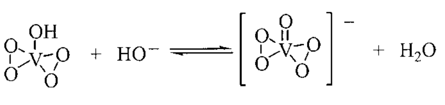

(7)

The formation of the yellow diperoxo complex from the blue triperoxo derivative has been further confirmed by ^{51}V NMR spectroscopy.[17−22] When $Na[V(O_2)_3]{\cdot}3H_2O$ (1×10^{-3} mol·L^{-1}) is dissolved in aqueous solution (giving a solution of pH 11), the triperoxo complex quickly decomposes to form the diperoxo vanadium derivative identified by a signal at $\delta = -764$. On the other hand, when strongly basic water (pH 14) is used to dissolve the same amount of $Na[V(O_2)_3]{\cdot}3H_2O$, the decomposition reaction described above is slowed down, although not blocked. In fact, in the ^{51}V NMR spectrum a peak is observed at $\delta = -847$ due to the triperoxo derivative together with the signal at $\delta = -764$.

The scarce data present in the literature[31,32] regarding the reactivity of triperoxo vanadium complexes indicate that they react as nucleophilic oxidants. Correspondingly, the oxidation of benzonitrile to benzamide by $Na[V(O_2)_3]{\cdot}3H_2O$ and Baeyer−Villiger-type oxidations of benzil to benzoic acid, as well as the epoxidation of (*E*)-chalcone, have been reported. These authors also reported that the reduction product of the triperoxo derivative is the anionic diperoxo vanadate $[OV(O_2)_2(H_2O)]^-$.[32]

In the present work the behavior of the complex $Na[V(O_2)_3]{\cdot}3H_2O$ toward cyclobutanone was studied. The triperoxo complex is almost insoluble in most organic solvents therefore its oxidative ability toward the selected substrate was examined in mixed alcohol/water solvents, even though the oxidant was still not completely dissolved at the desired concentration in this medium (see below).

When 0.45 mmol of $Na[V(O_2)_3]{\cdot}3H_2O$ was allowed to react with 0.3 mmol of cyclobutanone in 2.5 mL of *i*PrOH/H_2O (2:1, heterogeneous conditions) at room temperature, complete consumption of the substrate and the formation of 4-hydroxy butyric acid as the main product were observed in about four days. It has also been confirmed that the initially formed γ-butyrolactone is not stable in the basic reaction conditions. By a careful GC check of the reaction mixture, it was observed that oxidation of *i*PrOH to acetone occurs as well as oxidation of the cyclobutanone. Thus, in order to simplify the system under analysis the solvent was changed to a mixture of CH_3OH/H_2O (1:2), where a similar oxidation of cyclobutanone to 4-hydroxy butyric acid takes place.

It is well-known that Baeyer−Villiger-type oxidations are carried out by the hydroperoxy anion.[44] It is conceivable that in the hydrolytic equilibria of Equation (5)−(7), the triperoxo vanadium species may act as a source of HOO^-. Therefore a more detailed analysis of the oxidation of cyclobutanone with $Na[V(O_2)_3]{\cdot}3H_2O$ was required in order to elucidate the nature of the active nucleophilic oxidant.

Figure 3 shows the disappearance of cyclobutanone (0.12 mol·L^{-1}) as a function of time, observed under different experimental conditions. A very fast reaction (●) is observed when the substrate is reacted with basic H_2O_2 [CH_3OH/H_2O (1:2), pH 11]. On the other hand, slower processes have been observed with the triperoxo complex in CH_3OH/H_2O (1:2) (○) or in CH_3OH/H_2O (1:2; pH 11) (▲).

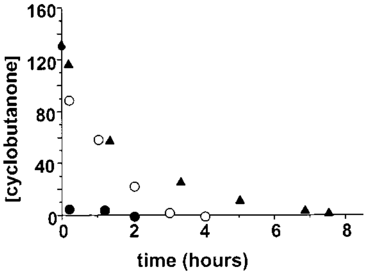

Figure 3. Behavior of cyclobutanone concentration as a function of time: (•) reaction with basic H_2O_2 in CH_3OH/H_2O (1:2), pH 11, room temp.; (○) reaction with $Na[V(O_2)_3]\cdot 3H_2O$ in CH_3OH/H_2O (1:2), room temp.; (▲) reaction with $Na[V(O_2)_3]\cdot 3H_2O$ in CH_3OH/H_2O (1:2), pH 11 (NaOH) room temp.

The behaviors detected can be explained by taking into consideration that, in all cases, the real oxidant is the hydroperoxy anion. Indeed, when the oxidant is $[V(O_2)_3]^-$, HOO^- is slowly released in solution upon hydrolysis of the vanadium triperoxide. This process [see Equation (5)−(7)] is in fact inhibited in the presence of added base. Accordingly the reaction performed at pH 11 (▲) is the slowest.

In order to verify this hypothesis further, two reactions with $Na[V(O_2)_3]\cdot 3H_2O$ in basic water (pH 14) were performed in the presence and in the absence of cyclobutanone. These processes were monitored by UV/Vis spectroscopy by measuring the decrease of the absorbance of the triperoxo vanadium complex at 561 nm. Interestingly, an identical kinetic behavior is observed both in the presence and in the absence of cyclobutanone, which is clear evidence that the substrate is not involved in the rate-determining step of the oxidation. Furthermore, taking into account that $[V(O_2)_3]^-$ decomposes to form $[OV(O_2)_2]^-$, and that the acid-base equilibria reported in Equation (5) and (7) are fast, it is likely that the ligand exchange process HO^-/HOO^- [Equation (6)], where the hydroperoxy anion is released in solution, is the rate determining step in the oxidation of cyclobutanone.

At variance with literature data,[32] our reactivity studies provide conclusive evidence that the triperoxo anion is a mere precursor of the hydroperoxy anion, which is the active species in the Baeyer−Villiger-type oxidation here examined. Furthermore, this result fits in well with the accepted knowledge that nucleophilic reactivity for d^0 metal peroxides is rarely observed.[45]

Conclusion

In summary, the association of ESI-MS spectrometry with ^{51}V NMR spectroscopy and ab initio calculations has allowed the definition of the nature and the speciation of peroxidic vanadium compounds, and in particular, of the triperoxo vanadium derivative that is formed in highly basic protic solutions in the presence of large excesses of hydrogen peroxide. Furthermore, the oxidation of cyclobutanone to 4-hydroxy butyric acid carried out with the preformed triperoxo compound in alcohol/water mixtures clearly indicates that the triperoxo complex does not itself act as a nucleophilic oxidant, but only as a source of the HOO^- anion.

Experimental Section

The synthesis of nBu_4NVO_3 has been reported previously.[27,46] $Na[V(O_2)_3]$ was synthesized by using a slightly modified literature procedure:[31,33] V_2O_5 (2.6 mmol) was suspended in 1 mL of water and stirred. A large excess of hydrogen peroxide (ca. 50 equivalents, 14.8 mL of 30% v/v solution) was then added slowly and the solution stirred at 0° C until it turned dark red. Subsequently, 11 equivalents of NaOH (1.144 g) were slowly added whilst stirring at 0 °C. The reaction mixture changed color from red to yellow and, finally, to blue-violet, thus indicating the formation of the triperoxo derivative. The reaction was left at 0 °C for 30 min. and the precipitation of the complex was obtained by addition of cold ethanol (10 mL). The product was collected by filtration, washed twice with cold ethanol, dried and characterized as $Na[V(O_2)_3]\cdot 3H_2O$ (86% yield). IR (KBr): ν_{O-O} 854 cm^{-1}, ν_{V-O_2} 617 and 565 cm^{-1}. − UV/Vis: $\lambda'_{max} = 192$ nm, $\lambda''_{max} = 560$ nm ($\varepsilon = 230$). The active oxygen content was determined quantitatively by cerimetric titration.

The ESI-MS measurements were obtained using an LCQ instrument (Thermoquest, San Jose, CA). The peroxovanadium solutions were prepared by dissolving nBu_4NVO_3 (5×10^{-4} mol·L^{-1}) in *i*PrOH (or EtOH for the experiments conducted in this solvent) in the presence of increasing amounts of H_2O_2 from 0.025 up to 0.35 mol·L^{-1}. The concentration of water was adjusted to 0.5 mol L^{-1}. The apparent pH for these solutions is about 7. For labeling experiments, $H_2{}^{17}O$ with an isotope content of ca. 50% was used ($H_2{}^{18}O$ less than 4%). Solution flow rate: 8μL min^{-1}; capillary temperature: 80 °C; spray voltage: 2.2 kV; capillary voltage: −5 to −10 V; tube lenses offset: −55 V; nebulizing gas: N_2 (40 units flow rate). The parameters related to the octapoles and detector were achieved by the automatic set-up procedure. Collision-induced decompositions of selected ions were obtained by applying a supplementary r.f. voltage (tickle voltage) to the end-cap electrodes of the ion trap (resonance activation).

All calculations were carried out with Gaussian 98,[34] running on an SGI O2 R10000 workstation. Hartree−Fock calculations were run with the 6-311++G(d,p) basis set. The latter includes the Wachters−Hay all-electron basis set for vanadium,[34,35] and the standard triply split valence basis set for H and O.[36,37] Only singlet states were considered. Harmonic vibrational frequencies were obtained from RHF/6-311++G(d,p) calculations and used to characterize local energy minima (all frequency real). Atomic charges were calculated by fitting to electrostatic potential maps (CHELPG method).[38]

Oxidation Reactions: The desired amount of cyclobutanone was dissolved in the alcoholic solvent (*i*PrOH or CH_3OH, typically 0.3 mmol in 1.5 mL *i*PrOH or CH_3OH). Subsequently, the appropriate amount of an aqueous (natural pH or basic pH obtained with NaOH) solution of $Na[V(O_2)_3]\cdot 3H_2O$ (typically 0.45−0.6 mmol) was slowly added. The reaction mixture was stirred at room temperature. The consumption of the substrate was followed by quantitative GC analysis [external standard n-C14 on a Carbowax 20M 15% on Chromosorb WAW-DMCS (1.8 m × 2 mm) column, FID detector]. Identification of the products was accomplished by ^1H NMR spectroscopy of the solid material isolated from the reaction mixtures.

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