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Peroxovanadium complexes as radical oxidants in organic solvents and in aqueous solutions [1]

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Abstract

Radical oxidations carried out by peroxovanadium complexes, both in CH_3CN and in water, are presented. A detailed mechanism for the decomposition of, and benzene hydroxylation by, the peroxocomplex $[PicVO(O_2)]$ (Pic = picolinic acid anion) is provided. A very good agreement between calculated and experimental data is observed. Data aimed at establishing a relationship between the nature of peroxovanadium complexes and their reactivity in water are also presented. These include ^{51}V-NMR chemical shifts, Hammett-type and Ramsey-type correlations. Preliminary data obtained from ab initio calculations are also included. A radical chain mechanism, slightly different from that taking place in CH_3CN, is presented for the decomposition of peroxovanadium complexes in water. Also in this case a good agreement between calculated and experimental data is found. Both in CH_3CN, in water and in CH_3CN/water mixtures, the oxidizing agent appears to be the species resulting from the one-electron reduction of the peroxovanadium complexes. Thus, the possible involvement of the $HO^{\cdot}$ radical is at least questionable.

Keywords: Peroxovanadium complexes; Benzene hydroxylation; Reactivity in water; Radical oxidations

1. Introduction

It is well known that complexes or salts of Ti(IV), V(V), Cr(VI), Mo(VI) and W(VI) may add one or more molecules of hydrogen peroxide, either in water or in organic solvents, to form peroxocomplexes [1–3]. These are rather strong oxidants which react with a large variety of organic and inorganic substrates [1–3]. The oxidizing ability of peroxometal complexes accounts for the catalytic effect exhibited by the metal ions mentioned above in the oxidations by hydrogen peroxide, as shown in Scheme 1 for oxo–metal derivatives [1–3].

The mechanism of oxidation by peroxometal complexes which, in many cases, are easily obtainable and fairly stable species, depends on the ligands coordinated to the metal [4–8]. Attempts to correlate the kind of reactivity with some measurable property of the coordination sphere of the peroxocomplexes have been made with some success, particularly for very simple reactions [9,10]. However, a complete understanding of the relationship existing between the nature of the ligands and the reactivity of the

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[1] Dedicated to the late Professor K.I. Zamaraev.

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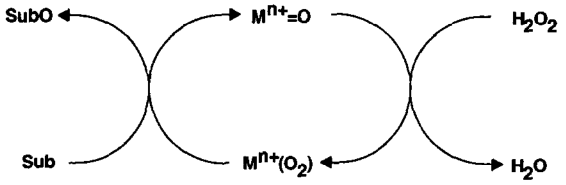
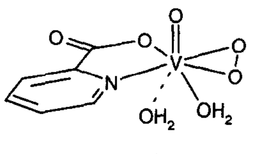


Scheme 1.

peroxocomplexes is not yet available. Two main mechanistic alternatives have been established for the peroxocomplexes of the metals considered here. Namely, they can act either as electrophilic [3] or radical oxidants [5–7,11,12]. This paper focuses on the radical reactivity of peroxovanadium complexes. There are good reasons for this choice: (i) with the possible exception of chromium, vanadium is, among the various metals, the one whose peroxocomplexes display the best documented radical reactivity [11], (ii) radical oxidations by some peroxovanadium complexes are of synthetic relevance in organic chemistry as it will be shown in the case of aromatics hydroxylation [7,8,13], (iii) peroxovanadium complexes play an important role in the biochemistry of plants and lower organisms and, likely, in humans [14,15].

2. Hydroxylation of aromatic compounds in organic solvents

In 1983, the peroxovanadium complex $[PicVO(O_2)]$ [2] was synthesized and fully characterized [5]:



$[PicVO(O_2)]^1$

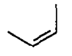
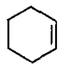
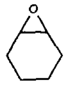
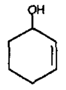
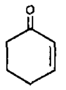
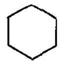
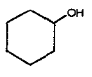
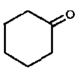
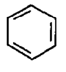
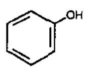
The oxidative ability of $[PicVO(O_2)]$ in CH_3CN was examined with various substrates. Some of the results obtained are reported in Table 1 [5].

It was also observed that, even in absence of substrate, $[PicVO(O_2)]$ decomposes quite rapidly in CH_3CN yielding dioxygen and, likely, a V(V) dimeric species [5].

These pieces of information led to the proposal that $[PicVO(O_2)]$ behaves as a radical oxidant. Further studies, directed toward the definition of the detailed mechanism of benzene hydroxylation, confirmed the radical nature of the oxidations carried out by $[PicVO(O_2)]$ [6,7]. Moreover, it was suggested that such reactions proceed through a radical-chain mechanism [6,7]. An important clue was the sigmoid shape of the curve describing the disappearance of the oxidant as a function of time both in the absence and in the presence of benzene, Fig. 1.

On the basis of a kinetic analysis of the chain reaction and of other important observations such as the promoting effect of species capable of acting as one-electron donors [6], the various

Table 1
Oxidation of selected substrates (2 mol L^{-1}) with $[PicVO(O_2)]$ (0.04 mol L^{-1} in CH_3CN at 20°C [5]

Substrates	Products (%yield)		
	 19	 8	CH_3CHO 20
	 30	 7	 7
	 17	 8	
	 60		

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[2] In the solid state the $[PicVO(O_2)]$ complex contains 2 molecules of water and its structure is a pentagonal bipyramid. In solution, on the basis of ab initio calculations and spectroscopic data, a distorted octahedral arrangement with only one molecule of water as sixth ligand appears to be the favored one.

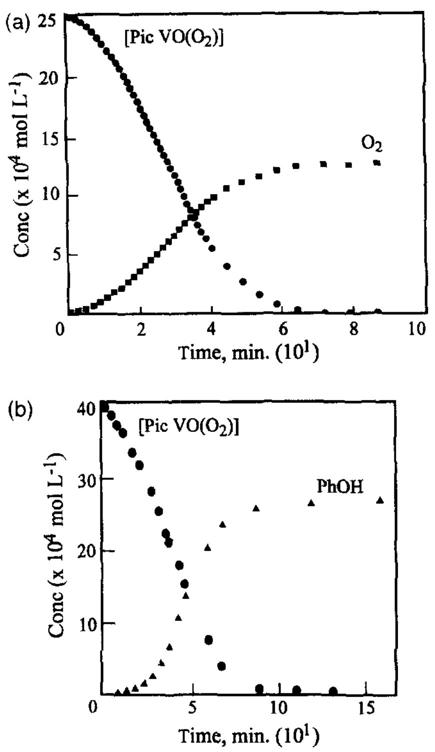


Fig. 1. (a) Disappearance of the oxidant (●) and appearance of dioxygen (■) in the decomposition reaction of [PicVO(O$_2$)] (0.0025 mol L^{-1}) in CH$_3$CN at 25°C. (b) Disappearance of the oxidant (●) and appearance of phenol (▲) in the hydroxylation reaction of benzene (2 mol L^{-1}) by [PicVO(O$_2$)] (0.004 mol L^{-1}) in CH$_3$CN at 25°C.

elementary reactions for the initiation, propagation and termination steps of the process shown in Scheme 2 have been proposed for the self decomposition of [PicVO(O$_2$)] [7]. For the sake of simplicity in this and other schemes the water molecules bound to [PicVO(O$_2$)] (see footnote 1) have been omitted when unnecessary.

The decomposition of the oxidant and the hydroxylation of benzene appear to be closely related reactions. In fact, if [PicVO(O$_2$)] does not decompose, as, for example, in DMF solution [6], phenol is not formed even when large excesses of benzene are added. Therefore, it is reasonable to suggest that the hydroxylation reaction proceeds through a mechanism similar to that of Scheme 2 in which the steps related to the formation of phenol, i.e. steps 6–8 of Scheme 3, are added [7].

The relevant points of the mechanisms presented are the following:

(i) The initiation involves two molecules of [PicVO(O$_2$)], as proved by direct kinetic data. In particular, one molecule of [PicVO(O$_2$)] acts as the one-electron donor and the other one as the one-electron acceptor. The electron transfer takes place *within* a reversibly formed intermediate, likely a dimeric one, whose nature, however, has not been established.

(ii) The result of the inner sphere electron transfer is, formally, the formation of a radical anion and a radical cation. The latter may be regarded as a vanadium (IV) derivative plus dioxygen [16]. In the former, the oxygen–oxygen bond is very likely cleaved as suggested by electrochemical evidence [9]. This species is the radical chain carrier. In the absence of substrate it reacts with [PicVO(O$_2$)] yielding dioxygen while in the presence of benzene, together with the decomposition, the reaction with the aromatic ring takes place.

(iii) The formal radical anion attacks the

$$2\ [\mathrm{Pic\text{-}VO(O_2)}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Dimer}] \qquad (1)$$

$$[\mathrm{Dimer}] \xrightarrow{k_2} [\mathrm{Pic\text{-}VO(O_2)}]^{-\cdot} + [\mathrm{PicV^{IV}O}]^{+} + \mathrm{O_2} \qquad (2)$$

$$[\mathrm{PicV^{IV}O}]^{+} + [\mathrm{Pic\text{-}VO(O_2)}] \xrightarrow{k_3} [\mathrm{Pic\text{-}VO(O_2)}]^{-\cdot} + [\mathrm{PicVO}]^{2+} \qquad (3)$$

$$[\mathrm{Pic\text{-}VO(O_2)}]^{-\cdot} + [\mathrm{Pic\text{-}VO(O_2)}] \xrightarrow{k_4} [\mathrm{Pic\text{-}VO_3}]^{2-} + [\mathrm{PicV^{IV}O}]^{+} + \mathrm{O_2} \qquad (4)$$

$$[\mathrm{Pic\text{-}VO(O_2)}]^{-\cdot} + [\mathrm{PicV^{IV}O}]^{+} \xrightarrow{k_5} [\mathrm{Pic\text{-}VO(\text{-}O\text{-})}]_2 \qquad (5)$$

Scheme 2.

$$[\text{Pic-VO}(O_2)]^{\cdot -} + \text{ArH} \xrightarrow{k_6} \left[[\text{Pic-VO}(O_2)]^{\cdot -}/\text{ArH}\right] \quad (6)$$

$$\left[[\text{Pic-VO}(O_2)]^{\cdot -}/\text{ArH}\right] + [\text{Pic-VO}(O_2)] \xrightarrow{k_7} \text{ArOH} + [\text{Pic-VO}]^{2+} + [\text{Pic-VO}(O_2)]^{\cdot -} \quad (7)$$

$$\left[[\text{Pic-VO}(O_2)]^{\cdot -}/\text{ArH}\right] + [\text{Pic-VO}(O_2)] \xrightarrow{k_8} \text{ArH} + [\text{Pic-VO}_3]^{2-} + [\text{PicV}^{IV}\text{O}]^{+} + O_2 \quad (8)$$

Scheme 3.

substrate forming an intermediate which, in turn, has two alternatives. Namely, it may either react with [PicVO(O_2)] through a chain reaction which produces dioxygen or it may form phenol again through a chain mechanism.

On the basis of the mechanistic schemes proposed for the self decomposition of [PicVO(O_2)] and for the hydroxylation of benzene by [PicVO(O_2)], respectively, the behaviors of the disappearance of the oxidant and of the formation of dioxygen and of dioxygen and phenol may be calculated by using the appropriate mathematical methods [17]. These calculated curves are then compared with the experimental results as shown in Fig. 3.

An excellent agreement between the calculated and the experimental values is observed. Moreover, it may be noted in Fig. 2 that, if the reversible formation of the 'dimeric' species by interaction of two molecules of [PicVO(O_2)] is not considered in the calculations, the curve indicated by the dotted line is obtained which does not fit with the experimental points. Accordingly, if the formation of an intermediate between the formal radical anion and benzene is not included in the calculations (Eqs. (6)–(8) Scheme 3), the curves 1 and 2 of Fig. 3 are obtained which do not account for the experimental behavior observed.

Therefore, the information collected may be summarized as follows: [PicVO(O_2)] and, likely, other peroxovanadium complexes, display in CH_3CN and other organic solvents a definite radical character when they act as oxidants. The oxidizing species is the formal radical anion deriving from the transfer of one electron to [PicVO(O_2)]. The oxidizing ability of such radical anion is rather strong as demonstrated by the fact that it oxidizes aromatic and even aliphatic compounds.

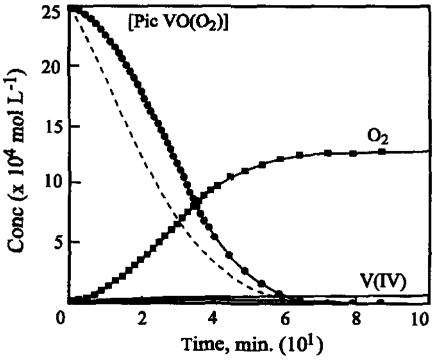


Fig. 2. Calculated curves for the disappearance of the oxidant and appearance of dioxygen in the decomposition reaction of [PicVO(O_2)] (0.0025 mol L^{-1}) in CH_3CN at 25°C, under the hypothesis that the initiation process is a bimolecular outer sphere one-electron transfer (dotted line) or under the hypothesis of a preliminary formation of an intermediate as reported in Schemes 2 (see text), solid lines. (●) and (■) are experimental points, see Fig. 1a.

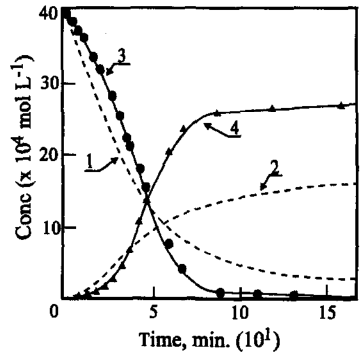


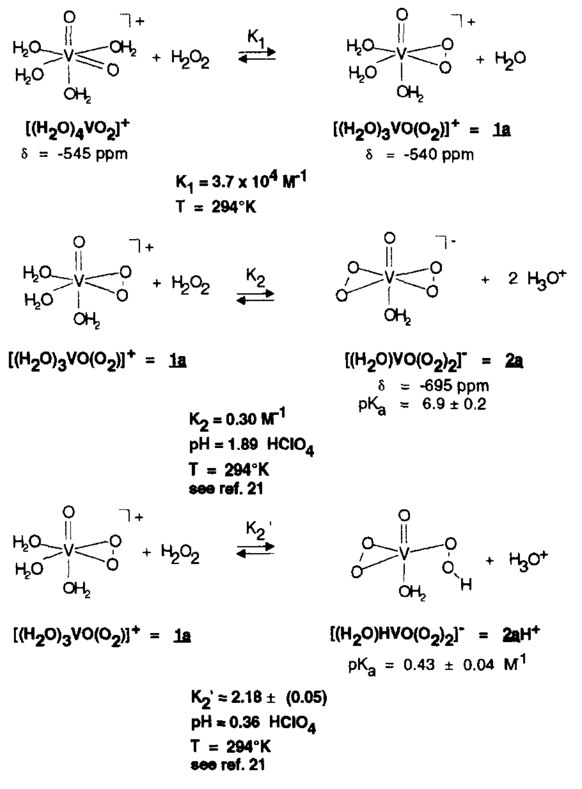
Fig. 3. Calculated curves for the disappearance of the oxidant and appearance of phenol in the hydroxylation reaction of benzene (2 mol L^{-1}) by [PicVO(O_2)] (0.004 mol L^{-1}) in CH_3CN at 25°C, under the hypothesis that the decomposition of the peroxocomplex and the formation of phenol are parallel processes (dotted lines 1 and 2) or under the hypothesis of the formation of a substrate–oxidant intermediate as reported in Scheme 3 (solid lines 3 and 4). (●) and (▲) are experimental points, see Fig. 1b.

3. Chemistry of peroxovanadium complexes in aqueous solution

As mentioned earlier in this paper, the biological role of peroxovanadium complexes is receiving increasing attention [14,15]. As an example, it has been established that peroxovanadium complexes are key intermediates in the mechanism of action of haloperoxidases [18]. These enzymes, found in algae and other marine organisms, catalyze the oxidation of halide ions to the corresponding halogens which, then, brominate organic compounds [18]. The proposal that peroxovanadium complexes may participate into oxidation reactions occurring in animals including the humans has also been made [14,19]. On this basis, the aqueous chemistry of such peroxospecies is enjoying a renewed interest [15]. In fact, in spite of the several investigations carried out in the past [20–23] on the formation and stability of peroxovanadium complexes obtained in water by addition of hydrogen peroxide to vanadium (V) derivatives, there are still some aspects which remain unclear.

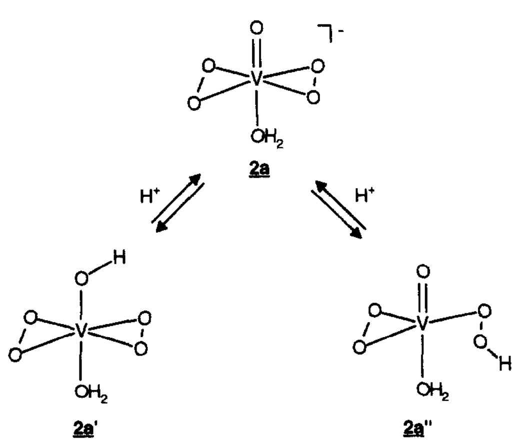
The technique of choice for this kind of studies appears to be ^{51}V-NMR spectroscopy which became readily available only in recent years. Therefore, we have reinvestigated the association equilibria of H_2O_2 to V(V) ($NaVO_3$) in acid ($pH = 1$, $HClO_4$) aqueous solutions which lead to the formation of aqua-peroxovanadium complexes and their acid–base equilibria [24]. The pertinent data are shown in Scheme 4.

According to the data of Scheme 4, the formation of the monoperoxovanadium complex **1a** is pH-independent whereas that of the diperoxospecies **2a** depends on the acidity of the solution. The very large value of K_{ass} supports the hypothesis that, under biological conditions, the simultaneous presence of vanadium(V) derivatives and of hydrogen peroxide may lead to the formation of peroxovanadium complexes. It may also be mentioned that there is very little information regarding the structures of the various species in solution [25]. Not only the coordination number and hence the geometry of the species in solution, but even the site of protonation of the diperoxospecies **2** are virtually unknown.

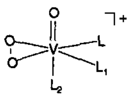


Scheme 4.

Species 2a' and 2a''



Ab initio calculations now in progress in our



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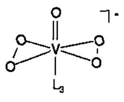
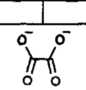
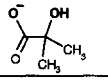
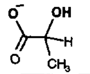
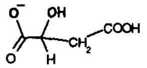
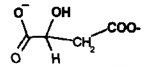
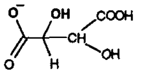
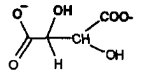
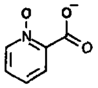
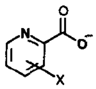
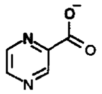
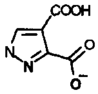
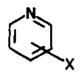
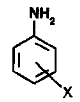


2

L	L₁	L₂	X	Complex
H_2O	H_2O	H_2O		**1a**
		H_2O	-	**1b**
		H_2O	-	**1c**
		H_2O	-	**1d**
		H_2O	-	**1e**
			-	**1f**
		H_2O	-	**2g**
			-	**1h**
		H_2O	-	**1i**
		H_2O	H 3-COOH 4-COOH 5-COOH 6-COOH	**1k** **1l** **1m** **1n** **1o**
		H_2O	-	**1p**
		H_2O	-	**1q**
H_2O	-	-		**2a**
	-	-	$p-NH_2$ $m-NH_2$ p-Me m-Me H m-OMe p-Br p-Cl mCl	**2b** **2c** **2d** **2e** **2f** **2g** **2h** **2i** **2j**
	-	-	$p-N(Me)_2$ p-tBu p-Et p-Me m-Me $m-NH_2$ H p-Cl $m-CONH_2$ m-COMe p-COMe m-Br	**2k** **2l** **2m** **2n** **2o** **2p** **2q** **2r** **2s** **2t** **2u** **2v**

Scheme 5.

laboratory suggest that the geometry of the diperoxo complex **2** is a distorted octahedron and that **2″** is the result of the protonation of **2** [26].

We have also investigated the equilibria formation of peroxovanadium complexes containing heteroligands, again by using ^{51}V-NMR spectroscopy [10]. The experiments are simply carried out by adding one equivalent of the ligand to the solution containing the aqua–vanadium peroxocomplexes. In the case of monoperoxovanadium derivatives bidentate ligands, which bind either through two oxygen atoms or an oxygen and a nitrogen atom, were used. For diperoxospecies, monodentate ligands binding through a nitrogen atom were examined. The ligands used are shown in Scheme 5. For some of these, the association constants were determined. The pertinent values are reported in Table 2.

It may be observed that the association constants of the bidentate ligands reported in Table 2 are remarkably large and comparable with the association constants of hydrogen peroxide to vanadium to form monoperoxo derivatives [24,27]. Thus, also for such heteroligands, whose structure resembles that of some biomolecules [28], the formation of complexes with vanadium in biological systems may be considered a very likely process.

The next step in the study of the chemistry of peroxovanadium complexes in aqueous solutions has been the investigation of their reactivity [10]. Under the reasonable assumption that an increase of the negative charge on the metal brought in by the ligands would reduce the electrophilicity of the peroxocomplexes and also their ability to act as one-electron acceptors, the dependence of the ^{51}V-NMR chemical shifts of various peroxovanadium complexes on the nature of the ligands has been studied. By taking the aqua–monoperoxo complex as the reference compound, it has been observed that an increase of the electron-donating properties of the ligands results in a larger magnetic shielding and, therefore, in a lower chemical shift [10]. This is shown by the data of Table 3 which include some of the data presented in Scheme 5. Indeed,

Table 2
Association constants for picolinic acid or pyrazinic acid to the mono and di-peroxo complexes **1** and **2** in water at 21°C [24]

$$\left[(H_2O)_3VO(O_2))^+\right] + LH \overset{K_a}{\rightleftarrows} [(H_2O)VO(O_2)L] + H_3O^+$$

$$[(H_2O)VO(O_2)L] + LH \overset{K_b}{\rightleftarrows} \left[(VO(O_2)L_2)^-\right] + H_3O^+$$

$$\left[(H_2O)VO(O_2)_2^-\right] + LH \overset{K_c}{\rightleftarrows} \left[(VO(O_2)_2L)^{2-}\right] + H_3O^+$$

L = picolinic acid anion or pyrazinic acid anion

Constant	Picolinic acid	Pyrazinic acid
K_a	5.8×10^3	2.5×10^3
K_b	1.39	0.8
K_c	5.7×10^{-3}	1.7×10^{-2}

in the case of diperoxocomplexes containing variously substituted monodentate ligands, e.g. species **3b–3j** or **3k–3v** of Scheme 5, Hammett-type plots of the ^{51}V-NMR chemical shifts against the σ values of the substituents gave straight lines with $\rho = 29.8 \pm 0.1$ ($r = 0.995$) slope for pyridines containing complexes and $\rho = 5.5 \pm 0.2$ ($r = 0.993$) slope for anilines containing species, thus confirming that there is a direct correlation between the electron-donating character of the ligand and the charge density on vanadium [10].

An estimate of the reactivity of peroxovanadium complexes may also be obtained by using Ramsey-type correlations [29]. In its most simplified formulation such correlations, applied to peroxovanadium complexes, predict that the magnetic shielding of vanadium depends on the energy of the ligand-to-metal charge-transfer excitations $\Delta E(n \rightarrow d)$ according to Eq. (9).

Table 3
Spectroscopic parameters for monoperoxovanadium complexes containing various ligands (see Scheme 4), in acid water ($HClO_4$, pH ≈ 1) at 21°C

Complex	δ (ppm) [a]	γ (MHz T^{-1})	$h/\Delta E$ (nm)
1a	−540	9.667	459.0
1b	−574	9.571	438.9
1c	−561	9.608	442.6
1d	−550	9.639	457.9
1e	−544		
1g	−542		
1j	−553	9.631	454.8
1k	−600	9.498	443.0
1l	−595	9.513	443.5
1m	−596		
1n	−596		
1o	−597		

[a] From $VOCl_3$.

$$\gamma = \gamma_0(1 - \sigma^d) + \gamma_0 \frac{B}{\Delta E_{(n \rightarrow d)}} \tag{9}$$

in which the value of γ, i.e. the magnetogyric ratio for a given nucleus, is easily obtained from the γ_0 value of the compound taken as reference, i.e. $VOCl_3$, by using the relationship [$\gamma = \gamma_0(1 + d)$] and σ^d is the diamagnetic contribution to the total shielding of the nucleus, which can be considered a constant value for all the peroxovanadium complexes because it is mostly determined by the electrons located in the internal orbitals of the metal. Therefore, in terms of measurable parameters, a dependence of ^{51}V-NMR chemical shifts on the λ_{max} values of the lowest energy electronic transition may be expected. The energy of such electronic transition corresponds to the difference of energy between the HOMO and LUMO of the peroxo complexes. Satisfactory Ramsey-type correlations are obtained for peroxovanadium complexes as shown by the linear plots of Fig. 4, referring to monoperoxo vanadium complexes containing various ligands (see also Table 3). Two straight lines (slopes: $3.1 \times 10^{-3} \pm 6 \times 10^{-5}$, $r = 0.997$ and $2.8 \times 10^{-3} \pm 1 \times 10^{-4}$, $r = 0.951$) are obtained for the two families of O ∩ O and N ∩ O ligands, respectively. Interestingly, the first correlation contains also the diperoxo anion **2**.

The value of the intercept of the two straight lines is 8.24 MHz T^{-1}. According to the Ramsey theory [29] this value provides the amount of diamagnetic shielding of vanadium which is independent of the nature of the ligands.

The occurrence of Ramsey-type correlations is a direct evidence that the nature of the ligands affects the difference of energy of the HOMO and LUMO of the various complexes. If the reasonable assumption is made that the HOMO orbital resembles the π^* orbital of the O_2^{2-} peroxo group, and the LUMO the d orbitals of the metal, the information provided by the Ramsey-type correlation is that the HOMO energy should be less affected by the ligands than that of the LUMO ones. Therefore, one might conclude that the LUMO energy is enhanced by increasing the electron-donating ability of the ligands.

Thus, the prediction can be made that the aqua–peroxoderivative should be the most reactive among the various peroxovanadium complexes. This, at least as far as the decomposition reaction is concerned, has been confirmed, as shown in Fig. 5.

The shape of the decomposition curves is very similar to that observed in CH_3CN. Thus, a similar mechanism might be suggested including only minor modifications, such as the occurrence, in water, of the acid–base equilibria of Eqs. (10) and (11):

$$[\text{Pic–VO}(O_2)]^{-} + H_3O^+ \xrightarrow{k_9} [\text{Pic–VO}_2] + HO^{\cdot} + H_2O \quad (10)$$

$$[\text{Pic–VO}(O_2)] + HO^{\cdot} + H_3O^+ \xrightarrow{k_{10}} [\text{PicV}^{IV}O]^+ + O_2 + 2H_2O \quad (11)$$

It may be observed that the sum of Eqs. (10) and (11) corresponds to Eq. (4) of Scheme 2.

Also in this case, the validity of the mechanistic hypothesis has been tested by comparing the experimental data with those calculated by using Scheme 2 modified as discussed above. This has been made by considering the aqua–monoperoxo complex and the picolinato one, **2k**. The results of the decomposition reactions for the two complexes are shown in Figs. 6 and 7.

Particularly in the case of the picolinato complex, the agreement between experimental and calculated data is not a satisfactory one. In fact, the experimental data clearly show that V(IV) is one of the products of the reaction. This forced us to modify the mechanism of the decomposition as shown in Scheme 3, by taking into account different termination steps.

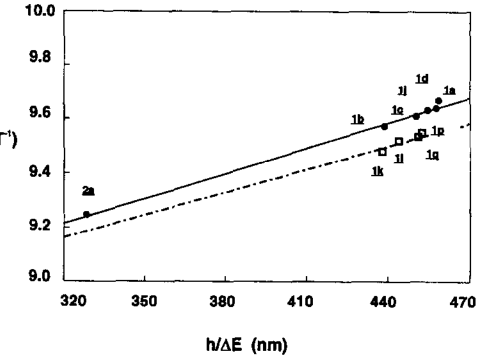


Fig. 4. Correlations between ^{51}V magnetogyric ratios and electronic transition (n → d) wavelengths for monoperoxovanadium complexes containing O∩O (●) and N∩O (□) ligands (see Table 3). Slope for O∩O species $= 3.1 \times 10^{-3} \pm 6 \times 10^{-5}$, $r = 0.997$; slope for N∩O species $2.8 \times 10^{-3} \pm 1 \times 10^{-4}$, $r = 0.951$. The two lines give an intercept value of 8.24 MHz T^{-1}.

$$[\text{Pic–VO}(O_2)]^{-} + [\text{PicVO}_2] \xrightarrow{k_{11}} [\text{PicV}^{IV}O]^+ + [\text{Pic–VO}(O_2)] \quad (12)$$

$$[\text{Pic–VO}(O_2)] + [\text{PicVO}_2] \xrightarrow{k_{12}} 2[\text{PicV}^{IV}O]^+ + O_2 \quad (13)$$

Under this hypothesis, a good agreement between calculated and experimental data is again

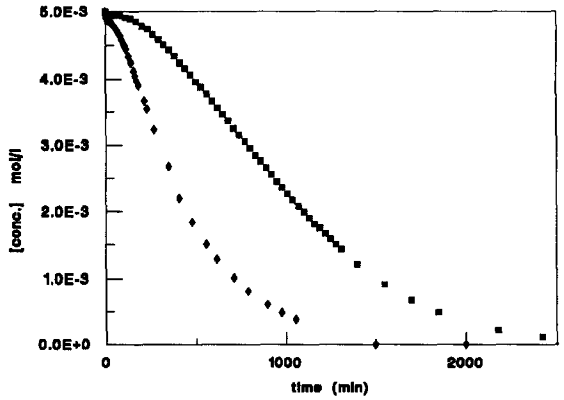


Fig. 5. Disappearance of the oxidant as a function of time, measured by the decrease of the absorbance at the λ_{max} values, in the decomposition reactions of $[(H_2O)_3VO(O_2)^+]$ (♦) and of $[(H_2O)PicVO(O_2)]$ (■) 0.005 mol L^{-1} in acid water (pH = 1, $HClO_4$) at 37°C.

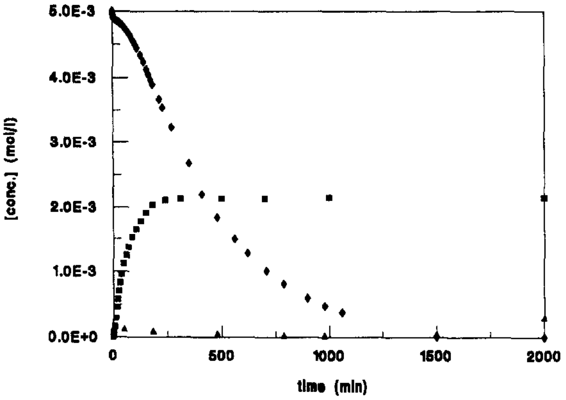


Fig. 6. Disappearance of the oxidant (◆) and appearance of dioxygen (■) and V(IV) (▲) in the decomposition reaction of $[(H_2O)_3VO(O_2)^+]$ 0.005 mol L^{-1} in acid water (pH = 1, $HClO_4$) at 37°C.

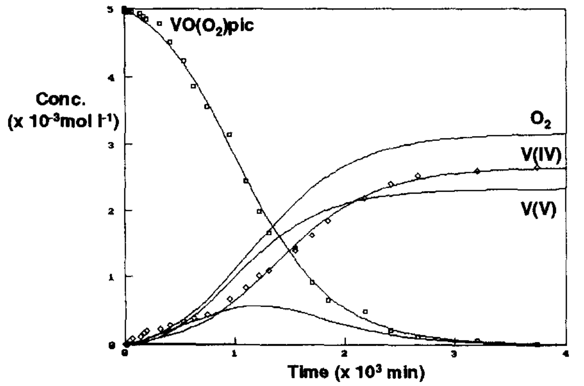


Fig. 8. Calculated curves for the disappearance of the oxidant and appearance of dioxygen and V(IV) in the decomposition reaction $[(H_2O)PicVO(O_2)]$ 0.005 mol L^{-1} in acid water (pH = 1, $HClO_4$) at 37°C, under the mechanistic hypothesis including Eqs. (10)–(13) (see text). (□) and (◇) are experimental points.

found also for the picolinato complex, see Fig. 8.

The observation that V(IV) is one of the products of the reaction, in the light of the fact that V(IV) can act as one-electron donor, suggested the possibility to accelerate the decomposition reaction by adding V(IV) from the beginning. This should occur without changing the overall mechanistic scheme. The data of Fig. 9, referring to the aquacomplex, confirm that indeed V(IV) may act as an initiator of the decomposition.

Such a role may be possibly played also in living organisms. Moreover, it may be envisaged that, by analogy with the behavior in CH_3CN, peroxovanadium complexes, while decomposing, may oxidize organic molecules. Thus, the problem must be addressed of the nature of the real oxidizing species. In fact this could be either the formal radical anion as in the case of benzene hydroxylation discussed previously in this paper or the very reactive, and very toxic $HO^{\cdot}$ [19] species, as shown in Eqs. (10) and (11). A first approach to the solution of this

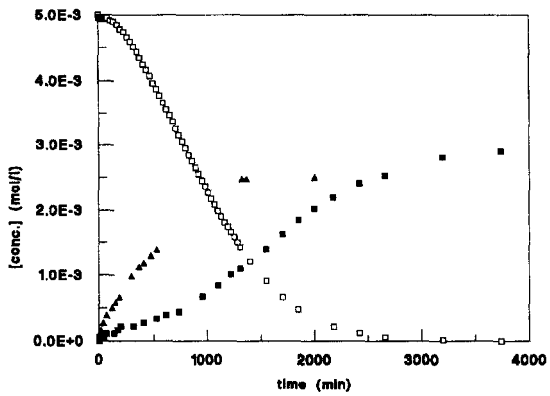


Fig. 7. Disappearance of the oxidant (□) and appearance of dioxygen (■) and V(IV) (▲) in the decomposition reaction of $[(H_2O)PicVO(O_2)]$ 0.005 mol L^{-1} in acid water (pH = 1, $HClO_4$) at 37°C.

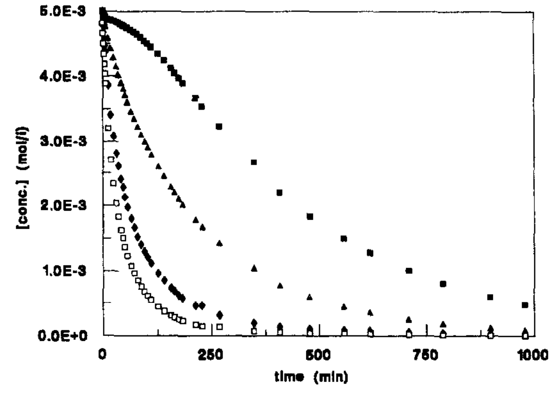
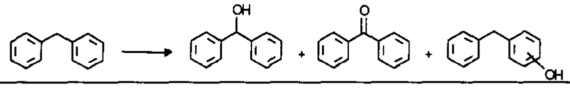


Fig. 9. Disappearance of the oxidant as a function of time in the decomposition reactions of $[(H_2O)_3VO(O_2)^+]$ 0.005 mol L^{-1} in acid water (pH = 1, $HClO_4$) at 37°C in the presence of increasing amounts of V(IV). (■) $VOSO_4 = 0$ mol L^{-1}; (▲) $VOSO_4 =$ 0.00005 mol L^{-1}; (◆) $VOSO_4 = 0.00025$ mol L^{-1}; (□) $VOSO_4$ = 0.0005 mol L^{-1}.

Table 4
Oxidation of diphenyl–methane with different oxidants (0.005 mol L^{-1}) in mixed solvents CH_3CN/H_2O ($HClO_4$ = 0.11 mol L^{-1}) at 37°C



Oxidant	Solvent	Time (h)	% yield [a]	n/c [b]
$[(H_2O)_3VO(O_2)^+]$	$CH_3CN/H_2O = 50/50$ $X_{H_2O} = 0.75$	24	21	0.12 ± 0.02
$[(H_2O)_3VO(O_2)^+]$	$CH_3CN/H_2O = 80/50$ $X_{H_2O} = 0.45$	12	4.8	0.45 ± 0.02
$[(H_2O)PicVO(O_2)]$	$CH_3CN/H_2O = 50/50$ $X_{H_2O} = 0.75$	360	54	0.15 ± 0.02
$[(H_2O)PicVO(O_2)]$	$CH_3CN/H_2O = 80/50$ $X_{H_2O} = 0.45$	168	24	0.79 ± 0.02
Fe^{+2}/H_2O_2	$CH_3CN/H_2O = 50/50$ $X_{H_2O} = 0.75$	12	18	0.38 ± 0.02
Fe^{+2}/H_2O_2	$CH_3CN/H_2O = 80/50$ $X_{H_2O} = 0.45$	12	18	0.14 ± 0.02

[a] Diphenyl methane oxidation products total yield.

[b] nucleus/chain oxidation ratio (= mol Ph_2CHOH + mol Ph_2CO/mol $PhCH_2Ph(OH)$), not corrected for statistical factors.

problem has been found in the study of the oxidation of diphenyl–methane in CH_3CN/H_2O. In particular, the behavior of the aqua–monoperoxovanadium complex has been compared with that of classical $HO^{\cdot}$-forming systems like $Fe(II)/H_2O_2$ [30]. The results are presented in Table 4.

It appears that the behavior of the peroxovanadium complex is different from that of $Fe(II)/H_2O_2$ thus suggesting that also in this case the real oxidizing agent is the formal radical anion rather than $HO^{\cdot}$. The implication of such an observation which would suggest the occurrence, in living organisms, of unprecedented oxidizing species with peculiar properties in now under investigation.

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