

The chemistry of peroxovanadium species in aqueous solutions. Structure and reactivity of a neutral diperoxovanadium complex as provided by ^{51}V -NMR data, ab initio calculations and kinetic results

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Abstract

The addition of hydrogen peroxide to vanadium (V) precursors in aqueous acidic solutions leads to the formation of a cationic monoperoxospecies $[\text{VO}(\text{O}_2)]^+$ and an anionic diperoxocomplex $[\text{VO}(\text{O}_2)_2]^-$, depending on the pH and on the excess of H_2O_2 . The latter may undergo protonation to form the neutral complex $[\text{HVO}(\text{O}_2)_2]$. ^{51}V -NMR data and ab initio calculations suggest that the neutral complex is formed via protonation of a peroxide oxygen and that in such a species, as well as in the other two peroxovanadium derivatives, the usual η^2 arrangement of the peroxo groups is maintained. The comparison of reactivity data of the three complexes in the self-decomposition reaction and in the oxidation of uracil, indicates that the neutral diperoxocomplex exhibits an oxidizing power considerably larger than that of the other two peroxovanadium species.

Keywords: Peroxovanadium complexes; Oxidations; Ab initio calculations; ^{51}V -NMR spectroscopy

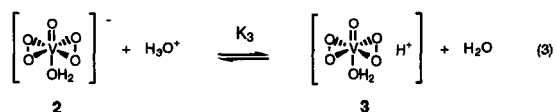
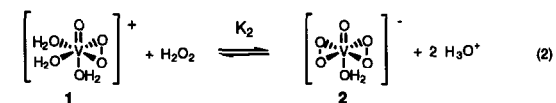
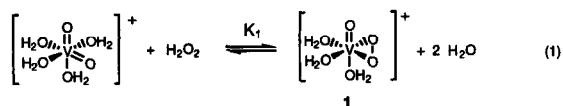
1. Introduction

The renewed interest in the chemistry of peroxovanadium species in acid aqueous solutions [1], stimulated by the recently discovered biochemical significance of such compounds [1,2], led us to reexamine by ^{51}V -NMR spectroscopy the equilibria involving the peroxospecies formed in situ by addition of hydrogen

peroxide to NH_4VO_3 as a function of the vanadium-peroxide ratio and of the pH of the solution [3,4]. Our investigation, whose results are summarized in the series of equilibria of Scheme 1 and graphically shown in the distribution diagram of Fig. 1, while confirming the overall picture established by several previous studies [5] revealed some novel aspects [3,4].

In particular we reported evidence that, together with the cationic monoperoxospecies **1** and the anionic diperoxovanadium one, **2**, al-

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Scheme 1.

readily described, also the almost unprecedented neutral dperoxovanadium complex **3** is formed [3]. The domain of existence of **3** is shown in Fig. 1. As indicated by the pK_a value of 0.43, **3** is a rather strong acid [3].

Previous studies suggest that **1** is a stronger electrophilic oxidant than **2** [3,4,6–8]. This is not surprising in the light of its cationic character. No information is, as yet, available on the oxidizing power of **3**. In this paper we report data on the nature and on the oxidative behavior of **3**. Such information may be useful in interpreting the results of related investigations in which the occurrence of **3** may be envisaged [9].

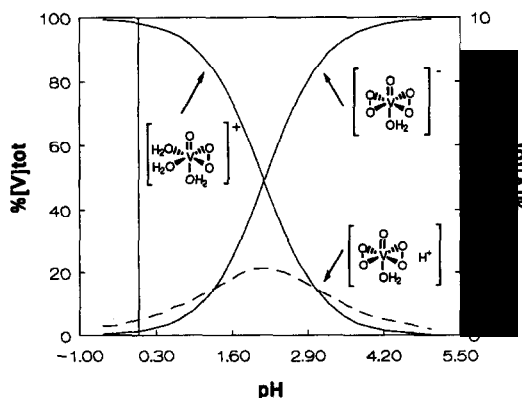


Fig. 1. Distribution diagram of V(V) peroxospecies in water as a function of pH (HClO_4). Total vanadium concentration 0.005 mol L^{-1} , hydrogen peroxide 0.01 mol L^{-1} . (—) left axis, (---) right axis.

2. Experimental section

2.1. Reagents

Anhydrous NH_4VO_3 (99.9%, Fluka), H_2O_2 (30% w/v, Carlo Erba) and uracil (Sigma) were used as received. Deionized water was passed through a Milli-Q/Organex-Q system (Millipore). The hydrogen peroxide solutions were prepared by dissolving the appropriate amount of 30% w/v H_2O_2 in water.

Authentic samples of the products of the experiments on uracil oxidation were obtained as follows: 5,6-*cis*-dihydroxy-5,6-dihydrouracil and 5,6-*trans*-dihydroxy-5,6-dihydro-uracil were synthesized by oxidation of uracil with KMnO_4 [10]. The *trans*-diol was obtained by acid catalyzed isomerization of the *cis*-diol [10]. *N*-formyl-5-hydroxy-hydantoin was synthesized by oxidation of 5,6-*cis*-dihydroxy-5,6-dihydrouracil with NaIO_4 [11]. The IR and NMR spectroscopic data of all the synthesized products are in good agreement with those reported in the literature [12].

2.2. NMR sample preparation

The solution of peroxovanadium complexes were prepared by dissolving a weighted amount of NH_4VO_3 in 10 mL of water in the presence of the appropriate amount of HClO_4 . H_2O_2 was added immediately before the registration of the spectra in order to minimize possible decomposition reactions. No electrolytes were added in this study in order to avoid potential coordination of anions to vanadium [3]. ^{51}V -NMR spectra were recorded on a 4.69 Tesla Bruker AC 200 MHz spectrometer for ^1H . The ^{51}V -NMR spectra were obtained from the accumulation of about 10000–15000 transients with a 3500 Hz spectral window, an accumulation time of 0.03 s, and a relaxation delay of 0.01 s. The probe temperature was maintained at 21°C . Data sets were obtained with a 2 K time domain and were zero filled to 4 K prior Fourier transformation. Exponential line-broadening (20 Hz) was ap-

plied to FID before Fourier transformation. Chemical shifts are referred to external VOCl_3 (0 ppm).

2.3. Methodologies

The peroxide content was determined by standard iodometric titration. pH measurements (± 0.02) have been obtained with a pH-meter Metrohm 632 standardized at pH 4 and 7 before each measurement. The amount of dioxygen evolved in the decomposition reactions was determined by means of a thermostated, 10 mL maximum capacity, gas-burette. The electronic spectra were obtained with a Lambda 5 Perkin Elmer instrument with a temperature control better than $\pm 0.05^\circ\text{C}$.

Ab initio calculations were performed by using Spartan 3.11 [13] and GAUSSIAN 92 [14] on an IBM Risk 6000, model 250.

2.4. Kinetic measurements

In a typical decomposition reaction weighted amounts of NH_4VO_3 , were dissolved in 8 mL of Milli-Q water, containing HClO_4 when needed. To such a solution, thermostated at 37°C , the appropriate volume of a standardized (iodometry) hydrogen peroxide solution was added. The reaction mixture was then made up to 10 mL. The kinetic behavior of the decomposition reactions was obtained by following the decrease with the time of the peroxide content by iodometry. Quantitative yields of dioxygen, based on the peroxide consumed, were observed.

When uracil was present the oxidation products were detected, after 100% conversion of the substrate, by TLC. Such analyses were carried out on Kieselgel F_{254} thin layer plates (Merck). The eluent was a mixture of ethyl acetate:2-propanol:water 75:16:9, and the developing agent was a $\text{NaOH}-\text{AgNO}_3-\text{NH}_4\text{OH}$ solution in water. The R_f values relative to uracil are: 5,6-*cis*-dihydroxy-5,6-dihydrouracil, 0.45; 5,6-*trans*-dihydroxy-5,6-dihydrouracil, 0.89; uracil, 1.00; *N*-formyl-5-hydroxy-hydantoin, 1.62 [15].

3. Results and discussion

3.1. ^{51}V -NMR data

In a previous study [4] we have established a direct correlation, which holds for several peroxovanadium complexes [4], between the shielding of vanadium, as measured by its ^{51}V -NMR chemical shift, and the electron density on the metal. This latter property is, in turn, related to the oxidizing power of the peroxo-complexes, either when they act as electrophiles or as one-electron acceptors. Such relationships hold only for structurally similar species in which no other effects than the electron donating ability of the ligands need to be considered [4]. By applying the approach outlined above to the three complexes **1**, **2** and **3**, the behavior indicated by the data of Table 1 is obtained.

While the difference between the chemical shifts of **1** and **2** indicates a larger shielding effect for the latter in accordance with its anionic nature, the chemical shift observed for **3** is clearly out of trend. In fact, it would imply that the shielding is larger for a neutral species such as **3** than for an anionic one such as **2**. This is taken as evidence that in **3** structural differences from both **1** and **2** exist. It is conceivable that such differences involve the mode of binding of the peroxo groups. In order to deal with this problem ab initio calculations, described in the next paragraph, were carried out.

3.1.1. Ab initio calculations

The formation of **3** can be described as the result of two subsequent equilibria, i.e. the association of H_2O_2 to **1** forming **2** (Eq. (2)), and the protonation of **2** leading to **3** (Eq. (3))

Table 1
 ^{51}V -NMR chemical shifts for peroxovanadium complexes

Complex	^{51}V -NMR chemical shift δ (ppm)
1	- 540
2	- 692
3	\approx - 702

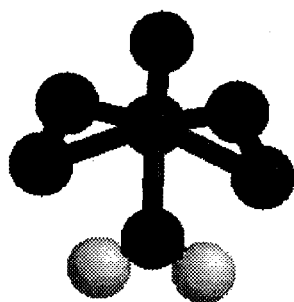


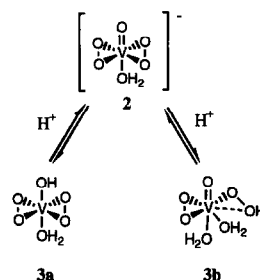
Fig. 2. Optimized structure at the B3LYP/LANL2DZ level for $[\text{VO}(\text{O}_2)_2\text{H}_2\text{O}]^-$.

[3,7,16]. Therefore, a key point in determining the structure of **3** is the identification of its site of protonation¹. This, in turn, requires a detailed knowledge of the structure of **2** in solution. The η^2 coordination of hydrogen peroxide to V(V) and other transition metals such as Ti(IV), Mo(VI) and W(VI) is ubiquitous in the solid state structures [8,17] of the corresponding peroxometal complexes as revealed by diffractometric analysis. There are several pieces of evidence, ranging from ¹⁷O-NMR spectra [18] to thermodynamic and kinetic data [8], that such a triangular arrangement is maintained also in solution including protic solvents.

Moreover, ab initio calculations recently carried out [19] indicate that the preferred geometry of peroxovanadium complexes in water is the octahedral one in which one of the two apical ligands is the oxo group. On the basis of such calculations, which have been made by using both RHF/3-21G(*) [20] and B3LYP/LANL2DZ density functional methods [21], the structure of **2** shown in Fig. 2 has been obtained.

All the above observations, taken together, suggest that the two possible sites of protonation of **2** are either the oxo-oxygen to form **3a** or the peroxo-oxygen to form **3b** as shown in Scheme 2.

¹ Attempts to establish the protonation site by Raman spectroscopy failed, owing to the too long times required by this methodology. In fact, an extensive decomposition of the peroxide is experienced in the course of the spectroscopic experiments.



Scheme 2.

Protonation of the water molecule of **2**, though possible, was considered unlikely. At any rate, in the calculations reported below, this possibility was taken into account. The results will be discussed later. Initially, the calculations were carried out by optimizing all geometries without geometry constraints by using the RHF/3-21G(*) basis set [20]. Vibrational frequencies calculations at the RHF/3-21G(*) level were used to characterize all minima stationary points (zero imaging frequencies). Subsequently, the calculations have been repeated by using the more sophisticated B3LYP/LANL2DZ density functional method, which takes into consideration correlation effects [21]. The results are presented in Table 2.

The agreement between the results of the two rather different methods of calculations is, somehow surprisingly, very good. The same information that **3b** is favored over **3a** is provided. It can be mentioned that if calculations are carried out by assuming protonation at the apical water molecules of **2** the optimized structure converges to **3b**.

The same calculations allow to obtain the various bond distances for **3a** and **3b**. These

Table 2
Energy values for structures **3a** and **3b** calculated by using RHF/3-21G(*) and B3LYP/LANL2DZ DFT methods

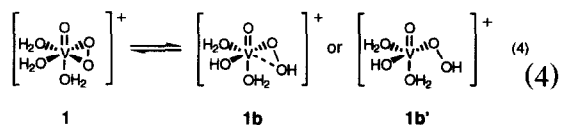
Structure	Energy (u.a.) RHF	Energy (u.a.) DFT
3a	-1386.649378	-475.364589
3b	-1386.660866	-475.372698
	$\Delta E(\mathbf{3a} - \mathbf{3b})_{\text{RHF}} =$	$\Delta E(\mathbf{3a} - \mathbf{3b})_{\text{DFT}} =$
	1.72 kJ/mol	1.41 kJ/mol

values are reported in Scheme 3 in which, for comparison purposes, the bond distances of the O–O bond of H₂O₂, calculated by the same methods, are reported.

It should be noted that in the hydroperoxo-like structure **3b**, which on the basis of the calculations is the preferred one, the O–O bond distance is considerably larger than that of H₂O₂ which, on the contrary, is very similar to that of **3a**. This could have some effect on the reactivity of **3b** as an oxidant in a process which involves the cleavage of the peroxidic bond. In particular, one could expect a larger oxidizing power of **3b** compared with H₂O₂. Reactivity data, presented in the next paragraph, appear to be in line with such a prediction.

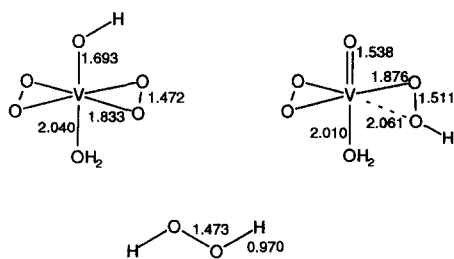
The observation of a hydroperoxo-like structure in a peroxovanadium complex may shed some shadows on an important point made above, i.e. that the η^2 coordination of the peroxo group is the preferred one also in solution for all the peroxovanadium complexes.

We have briefly examined this aspect by taking into account the possibility for complex **1** of the equilibrium of Eq. (4) and by calculating the difference in energy among the three structures.



The results are presented in Table 3.

It may be seen that complex **1b'** in which no interaction between the distal peroxo-oxygen



Scheme 3.

Table 3

Energy values for structures **1b'** and **1b** calculated by using RHF/3-21G(*) and B3LYP/LANL2DZ DFT methods

Structures	Energy (u.a.) RHF	Energy (u.a.) DFT
1b'	-1236.935203	-373.121016
1b	-1236.925097	-373.116073
	$\Delta E(\mathbf{1b}' - \mathbf{1b})_{\text{RHF}} =$	$\Delta E(\mathbf{1b}' - \mathbf{1b})_{\text{DFT}} =$
	-1.53 kJ/mol	-0.75 kJ/mol

and vanadium is considered is very high in energy. By contrast, **1** and **1b** both corresponding to a η^2 coordination of the peroxo-group, in which the only difference is the distance between the distal peroxo-oxygen and vanadium, have comparable energies. Therefore, it appears that the triangular geometry of peroxovanadium complexes is indeed the preferred one also in solution. In addition, it has to be mentioned that starting the calculations from structure **1b'** the system converges to **1b**.

3.1.2. Reactivity experiments

The reactivity of the peroxocomplex **3b** has been estimated by examining two different reactions, i.e. the self-decomposition leading quantitatively to dioxygen and the oxidation of uracil which affords the corresponding *cis*- and *trans*-diols and *N*-formyl-5-hydroxy hydantoin [15]. These processes have been selected not only on the basis of their biological significance but also because results collected in previous investigations on the behavior of complexes **1** and **2** in the same reactions allow a comparison among the three complexes. On the basis of the information provided by ⁵¹V-NMR data [3], we are able to establish the experimental conditions, i.e. pH and reagent concentrations which allow the presence in solution of only **1** or only **2**. As indicated by the distribution diagram of Fig. 1 this is hardly feasible for **3b**. Therefore, the data presented below concerning the reactivity of **3b** actually refer to solutions containing both **2** and **3b**. At any rate, it may be clearly seen from the results shown in Fig. 3 that the reactivity of **3b** appears to be significantly larger than that of **1** and **2**.

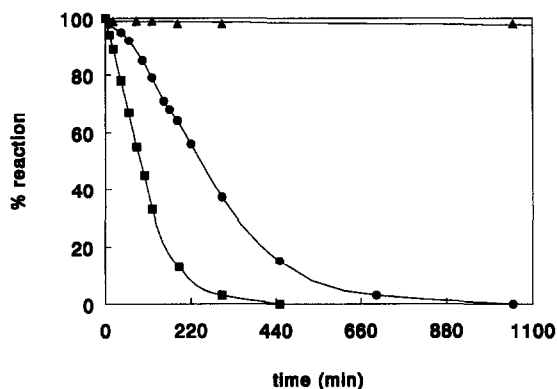


Fig. 3. Disappearance of the oxidant in the decomposition reaction of H_2O_2 0.046 mol L^{-1} in the presence of NH_4VO_3 0.002 mol L^{-1} , in water at various pHs (HClO_4) at 37°C . (●) $\text{pH} \approx 0$, (■) $\text{pH} = 0.8$, (▲) $\text{pH} = 5.1$.

Thus, the disappearance of the oxidant in the absence of substrate is complete in ca. 7 h for the solution containing **2** and **3b** while the same process requires 18 h for **1**. **2** is practically unreactive.

As far as the oxidation of uracil is concerned the salient features of such a process are collected in Table 4.

It may be pointed out that a superior oxidizing power of **3b** over **2** might have been predicted since the comparison is made between a

neutral and an anionic species in processes which likely require that the peroxide acts as a one electron acceptor.

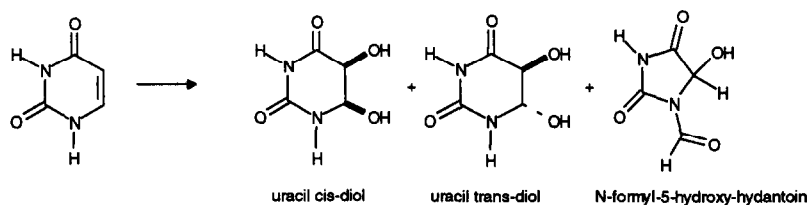
By contrast, the observation that, in the same processes, **3b** is even more effective than **1** is somehow unexpected and, at the moment, not easily rationalized. While we are looking for further examples of the strong oxidizing character of **3b** and for an interpretation of this feature, we think that our findings on the occurrence of **3b**, on its structure and on its remarkable reactivity may help in analyzing the behavior of other systems in which organic and inorganic substrates are oxidized by peroxovanadium complexes.

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Table 4

Oxidation of uracil with peroxovanadium ($0.0046 \text{ mol L}^{-1}$) species in water at different acid concentrations (see text) at 37°C



peroxocomplex	pH	time min.	uracil conversion %
1	≈ 0	800	100
2	0.8	350	100
3	5.1	n.r. ^b	0

^a This value is obtained by using HClO_4 , 1 mol L^{-1} and it is outside the interval of confidence of the glass electrode.

^b No disappearance of uracil after several days.

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