



ELSEVIER

Journal of Molecular Catalysis A: Chemical 104 (1995) 159–169

JOURNAL OF
MOLECULAR
CATALYSIS
A: CHEMICAL

Studies directed toward the prediction of the oxidative reactivity of vanadium peroxo complexes in water. Correlations between the nature of the ligands and ^{51}V -NMR chemical shifts

Valeria Conte, Fulvio Di Furia *, Stefano Moro

Università di Padova, Centro CNR di Studio sui Meccanismi di Reazioni Organiche, Dipartimento di Chimica Organica, via Marzolo 1, 35131 Padova, Italy

Received 9 March 1995; accepted 14 June 1995

Abstract

The ^{51}V -NMR spectroscopic behavior in water of a series of vanadium peroxo complexes was investigated. Monoperoxo vanadium complexes containing bidentate ligands in which the two binding sites are either oxygen atoms ($\text{O}\cap\text{O}$ ligands) or one oxygen and one nitrogen atom ($\text{N}\cap\text{O}$ ligands) and diperoxo vanadium complexes containing variously substituted pyridines or anilines were examined. A direct dependence of the magnetic shielding of the metal, measured by its ^{51}V -NMR chemical shift, on the electronic character of the ligand was observed in all cases. For diperoxo complexes Hammett-type correlations between the ^{51}V -NMR chemical shifts and the σ values of the substituents in the pyridine or aniline rings were established. For monoperoxo complexes, a Ramsey-type correlation between the chemical shifts and the energy of the ligand-to-metal charge transfer electronic transitions was found thus suggesting that the electron donating ability of the ligands and the energy gap HOMO–LUMO of the peroxo complexes are linearly correlated. All these observations indicate that peroxo vanadium complexes containing strongly electron donating ligands should be weak electrophilic oxidants and poor one-electron acceptors. Preliminary data concerning the reactivity of a series of peroxo vanadium species in the simple self-decomposition reaction confirm this prediction.

Keywords: Peroxo vanadium complexes; ^{51}V -NMR spectroscopy; Ligand–magnetic shielding correlations

1. Introduction

The aqueous chemistry of peroxo vanadium complexes is receiving renewed attention in connection with the biological importance of this metal [1]. Vanadium, either in the +4 or +5 oxidation states, is present both in plants and in organisms in concentrations which range from μM to M [2]. In human body trace amounts of vanadium have been found in various organs and

fluids [2]. Peroxo vanadium complexes are key intermediates in the mechanism of action of haloperoxidases [3] and, likely, in other biologically significant oxidations [4]. Their oxidative ability is affected by the nature of the ligands coordinated to vanadium [5]. We [6], and others [7], have already reported that ^{51}V -NMR spectroscopy is the technique of choice for the characterization of peroxo vanadium species in solution. The ^{51}V -NMR chemical shifts are very sensitive to the nature of the coordination sphere of the metal so that quantitative and accurate information on the

* Corresponding author.

magnetic shielding exerted by the ligands can be obtained [8]. The possibility, then, exists to correlate ^{51}V -NMR spectroscopic data with the electronic character of the ligands. An important goal of such correlations is to predict the reactivity of peroxo vanadium species as oxidants. As an example, if peroxo vanadium complexes react as electrophilic oxidants, as it is often the case [9], it might be possible to predict their efficiency on the basis of their ^{51}V -NMR chemical shifts, since an increase of the electron density on the metal should reduce their electrophilicity. Similar considerations apply to oxidative processes in which peroxo vanadium complexes act as one-electron acceptors [10].

In this work we have measured the ^{51}V -NMR chemical shifts of a series of mono- and diperoxo vanadium complexes containing both mono- and bidentate ligands which bind to the metal either by oxygen or nitrogen atoms. At variance with previous reports [11] we find that, at least for the peroxo vanadium species examined, a direct correlation between the electron donating ability of the ligand and the shielding of the metal, measured by its ^{51}V -NMR chemical shift, occurs. In some cases, linear relationships between the two properties have been obtained.

We also found that the ^{51}V -NMR chemical shifts and the wavelengths of the maximum of the absorption in the visible region, attributed to a charge-transfer, $n-d$ transition [12], of a series of monoperoxo vanadium complexes are linearly correlated. Such Ramsey-type correlations [13] allow to estimate the energy gap between the HOMO and LUMO orbitals of the peroxo complexes as a function of the nature of the ligands. We found that such gaps increase with increasing the electron donating character of the ligands. Preliminary reactivity data have been collected concerning the self-decomposition of some peroxo vanadium species in aqueous solutions [14]. The behavior observed agree with the prediction made. Namely, the rates of decomposition decrease with increasing the electron density on the metal.

2. Experimental section

2.1. Reagents

Anhydrous NH_4VO_3 (99.9% Fluka puriss. p.a.) and H_2O_2 (30% w/v Carlo Erba) were used without further purification. All the ligands were commercially available products used without further purification. 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.

2.2. 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 measurements. The amount of dioxygen evolved in the decomposition reactions was determined by means of a thermostated, 10-ml maximum capacity, gas-burette.

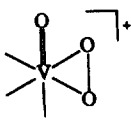
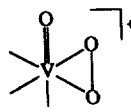
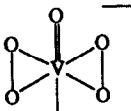
2.3. NMR sample preparation

The peroxo vanadium solutions were prepared by dissolving a weighted amount of ammonium vanadate in 10 ml of water in the presence of the appropriate amount of HClO_4 both in the absence or in the presence of the heteroligands. 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 [6].

2.4. NMR spectroscopy

The ^{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.

Table 1

Complex	#	Ligand	$h/\Delta E$ (nm)
	1	H ₂ O	459.0
	2	O ₂ ²⁻ ; H ₂ O	328.7
	3	oxalic acid; H ₂ O	438.9
	4	α -hydroxy iso-butyric acid; H ₂ O	442.6
	5	lactic acid; H ₂ O	547.9
	10	picolinic N-oxido acid; H ₂ O	454.8
		Ligands	
	11	picolinic acid; H ₂ O	443.0
	11b	3-carboxy picolinic acid; H ₂ O	443.5
	12	3,4-pyrazole dicarboxylic acid; H ₂ O	450.6
	13	pyrazinic acid; H ₂ O	452.2

No field/frequency locking system was used and the spectra were recorded at 21°C. Data sets were obtained with a 2 K time domain. The FIDs were zero filled to 4 K and an exponential line-broadening (20 Hz) was applied before Fourier transformation. Chemical shifts are referred to external VOCl₃ (0 ppm). The line widths were measured by using the standard Bruker software for Lorentzian fitting of the peaks.

2.5. UV–VIS spectroscopy

The electronic spectra were obtained with a Lambda 5 Perkin Elmer instrument with a temperature control better than $\pm 0.05^\circ\text{C}$. The λ_{max} ($h/\Delta E$) values of the various species are collected in Table 1.

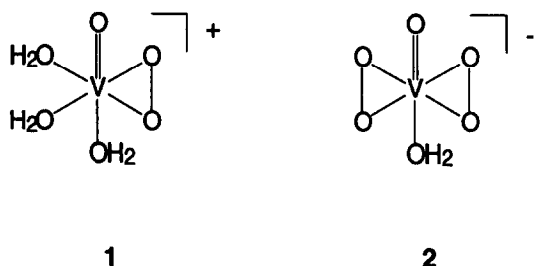
2.6. Kinetic measurements

In a typical decomposition reaction weighted amounts of NH₄VO₃ and of the desired heteroligand, when present, were dissolved in 8 ml of Milli-Q water, containing 0.11 M HClO₄. 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 absorbance of the peroxo complexes at their λ_{max} .

3. Results and discussion

Hydrogen peroxide easily adds to V^V derivatives in aqueous solutions, forming peroxo vanadium complexes [15]. The association equilibria have been extensively studied [6,7,15]. It has been found that the nature of the peroxo species formed is a function of the initial concentrations of the precursors and of the acidity of the medium [6,7,15]. At pH < 2, if equimolar amounts of hydrogen peroxide and of vanadium precursor are used, the monoperoxo species **1** is the only vanadium complex present [6,7]. In the pH region between 4.5 and 7 and in the presence of excess of H₂O₂, again only one vanadium complex is observed, i.e. the diperoxo anion **2** [6,7]. Under intermediate conditions of pH and of excess of hydrogen peroxide both species coexist.

Although direct evidence is not available, in drawing the peroxo complexes **1** and **2** we have chosen the octahedral geometry based on the analogy with the solid state structure determined for some monoperoxo vanadium species [16]. Theoretical studies now in progress in our laboratory support such an arrangement [17].



1 is prepared in water at pH 1.1 (HClO_4) by mixing NH_4VO_3 0.005 mol l^{-1} and H_2O_2 0.005 mol l^{-1} . **2** is obtained by using NH_4VO_3 0.005 mol l^{-1} and H_2O_2 0.01 mol l^{-1} at pH 4.5. The ^{51}V -NMR chemical shifts and band widths values measured for **1** and **2** are respectively -540.5 ppm ($W_{1/2} = 135 \text{ Hz}$) and -691.8 ppm ($W_{1/2} = 198 \text{ Hz}$) from VOCl_3 . In this paper the band widths (b.w.) values for all the peroxo vanadium species examined will be provided. The discussion, however, will be based only on the chemical shifts values.

The peroxo complexes containing heteroligands were prepared in situ by addition of one equivalent of the various ligands to the solutions of **1** or **2**. In the case of monoperoxo complexes, only bidentate ligands belonging to two different classes, i.e. the $\text{O}\cap\text{O}$ ligands, e.g. oxalic acid, α -hydroxy iso-butyric acid, lactic acid, citric acid, tartaric acid and picolinic N-oxido acid, which bind to vanadium by two oxygen atoms [10] (a) [16,18] and the $\text{N}\cap\text{O}$ ligands, e.g. picolinic acid, 3,4-pyrazole dicarboxylic acid and pyrazinic acid, which bind by one oxygen and one nitrogen atom, [6], [10] (a) [16] (a) were used. The remarkable binding ability of such ligands to vanadium in water is documented [6,10,16,18]. A comparison of the behavior of bidentate ligands with that of structurally similar monodentate ones, e.g. pyridine or acetic acid, would have been of interest. Unfortunately, we have found that such monodentate ligands do not bind to **1** under our experimental conditions. Monodentate ligands, which bind through a nitrogen atom [19], i.e. substituted pyridines and anilines, were considered in the case of diperoxo vanadium complexes.

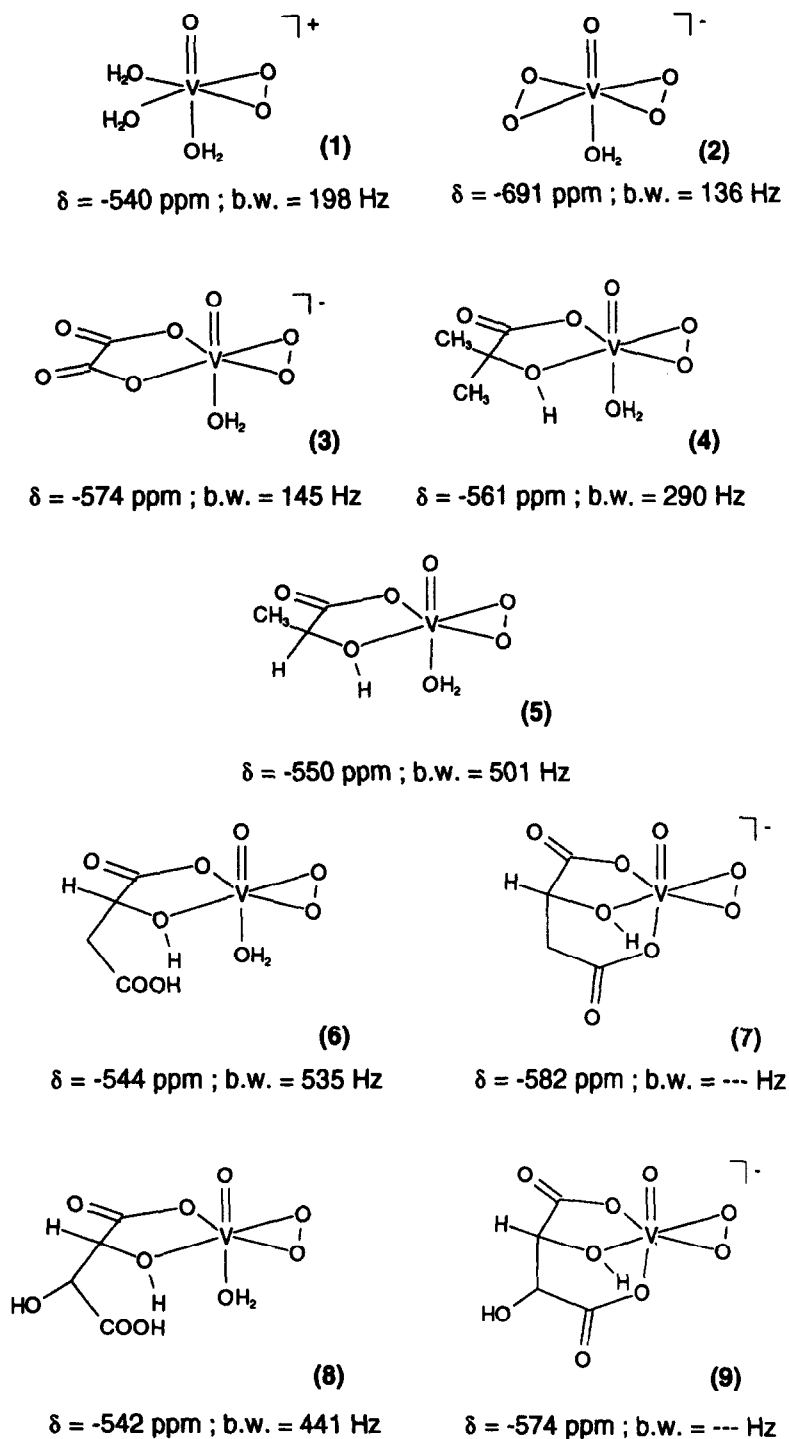
3.1. V^{V} monoperoxo complexes containing $\text{O}\cap\text{O}$ and $\text{N}\cap\text{O}$ ligands

The ^{51}V -NMR parameters of the monoperoxo vanadium complexes **3–6** and **8** containing $\text{O}\cap\text{O}$ ligands are collected in Scheme 1. Also in this case an octahedral geometry has been assumed. The effect of the nature of the ligands on the ^{51}V -NMR chemical shifts may be conveniently discussed by looking first at the differences between **1** and **2**. The signal of diperoxo anion derivative **2** is 152 ppm upfield with respect to the monoperoxo species **1**. The larger magnetic shielding observed in **2**, compared with **1** might simply be explained by the presence in the former species of a second peroxo bridge which places two additional negative charges on the vanadium atom.

However, following this line of reasoning it is difficult to account for the difference of chemical shifts observed between **2** and the anionic monoperoxo complex **3** containing the oxalate ligand ($\delta = -574 \text{ ppm}$). Also in **3**, two additional negative charges brought in by the ligand are present. We suggest that the magnetic shielding of the diperoxo derivative is also due to the transfer of electron density from the filled anti bonding orbitals of the η^2 -bonded O_2^- moiety into the empty d orbitals of vanadium of the appropriate symmetry. In **3** this transfer is less important likely because of a less favorable symmetry of the filled orbitals of the oxalate ligand. Preliminary theoretical calculations support this hypothesis [17].

If the shielding of **2** is the result of two effects, i.e. the presence of the negative charges and the π donation, the similarity of the ^{51}V -NMR chemical shifts of the cation VO_2^+ and the monoperoxo cation $\text{VO}(\text{O}_2)^+$ **1**, -544 ppm and -540 ppm , respectively, suggests that the effect of the oxo and the peroxo groups is also similar. Therefore, the overlap between vanadium 3d orbitals and the $\text{O}_2^- \pi^*$ orbitals of the peroxo ligands should be as effective as that of the $\text{O}^{2-} \pi$ orbitals of the oxo ligands.

In the series of neutral monoperoxo complexes **4–6** and **8**, containing the anions of α -hydroxy iso-butyric, lactic, citric and tartaric acids respec-



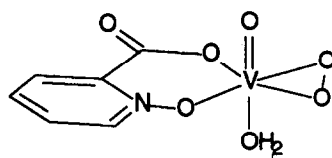
Scheme 1.

tively, a continuous decrease of the ^{51}V -NMR chemical shifts is observed with increasing the basicity of the alkoxo oxygens of the ligands. This

finding allows to establish a correlation between the increase of the magnetic shielding and the increase of the electron donating properties of the

ligands, as it might have been expected. It must be mentioned, however, that in other non peroxidic vanadium species an opposite behavior has been reported [11]. As an example, in the series of the complexes X_3VO ($X = F, Cl, Br$) the ^{51}V -NMR chemical shifts are -760 ppm, 0 ppm and $+432$ ppm, respectively [11]. It may be anticipated that in the series of peroxo vanadium complexes examined in this paper the 'inverse effect' [11,20] found for X_3VO species has never been observed. This allows us to neglect the occurrence of specific [21] ligand–metal interactions thus assuming that the main effect of the ligand is in transferring electron density to the metal. This is also confirmed by the comparison of the chemical shifts values of species **6–7** and **8–9**. In both cases, the substitution of the water molecule with an anionic ligand causes an increase of ca. 30 ppm of the chemical shifts as an indication of an increase of the magnetic shielding.

The ligands considered exhibit a remarkable chelating ability toward **1** likely because they give rise to a five-membered ring in the equatorial plane of the peroxo complex. In fact, such an arrangement appears to be the preferred one. We have established by direct experiments that under the same experimental conditions dicarboxylic acids, such as malonic, succinic and glutaric acid, do not add to **1**. Also *ortho*-hydroxy benzoic acid does not form appreciable amounts of the corresponding mono peroxo complex. This is unfortunate because it could have been of interest to compare the ^{51}V -NMR behavior of monoperoxo vanadium complexes containing a five-membered ring with that of those containing larger rings. This comparison has been possible only with complex **10**. Such a complex has been previously synthesized [18] and its solid state structure has been determined [18]. At variance with all the other species reported in Scheme 1, **10** cannot be prepared in situ simply by adding the ligand to the acid solution of the peroxo vanadium derivative. Even in the presence of more than a ten-fold excess of the picolinic N-oxido acid over vanadium, in solution **10** and **1** are present in the ratio 80/20.



(10)

$\delta = -553$ ppm ; b.w. = 275 Hz

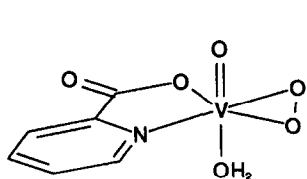
Although based on this single example, it may be suggested that the size of the ring should not have a major effect on the magnetic shielding since the chemical shifts measured for **10** is in the range of those measured for complexes **5** and **6**.

The peroxo species containing $N \cap O$ ligands which have been examined are shown in Scheme 2. Also in this class of ligands the 5-membered ring structure appears to be the preferred one. Accordingly, pyridin-acetic acid does not bind to the monoperoxo vanadium complex.

The species **11a–13** show, in agreement with the observations made for complexes **1–9**, a direct dependence of the ^{51}V -NMR chemical shifts on the electronegativity of the ligand. In fact the electron donating properties of the ligands decrease on passing from the picolinato, **11a**, to the pyrazinato, **13**, anions [22].

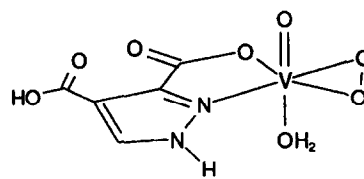
In order to obtain a more quantitative estimate of the effect of the electronic character of the ligand on the shielding of vanadium, the chemical shifts of the series of complexes **11a–e** containing different picolinic acids with a second carboxylic function in the various positions of the ring, were measured. The pertinent data are collected in Table 2, together with the data referring to bis-coordinated complexes (**14a–d**) which under our experimental conditions are formed together with **11**. Only in the case of pyridine 2,6-dicarboxylic acid a bis-coordinated complex is not observed. The contemporary formation of species **1** and **14** has been previously observed [6,23].

The magnetic shielding in the series of complexes **14** is in all cases larger than that of complexes **11**, in agreement with the anionic character of the former. Within the two series, the presence



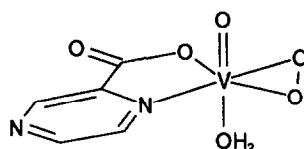
(11a)

$\delta = -600.6$ ppm ; b.w. = 195 Hz



(12)

$\delta = -592.2$ ppm ; b.w. = 269 Hz



(13)

$\delta = -585.5$ ppm ; b.w. = 203 Hz

Scheme 2.

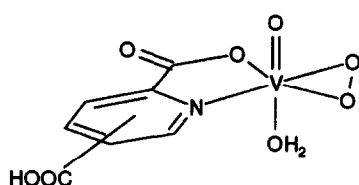
of the electron-withdrawing substituent $-\text{COOH}$ in the ring decreases the magnetic shielding again in agreement with the direct correlation established between the electronic character of the ligands and the chemical shift values.

3.2. V^V diperoxo complexes containing nitrogen binding ligands

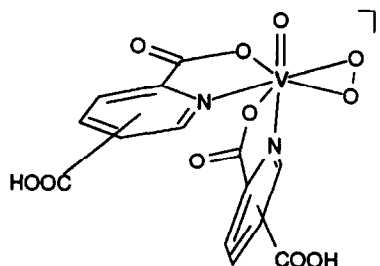
It may be anticipated that the analysis of the ^{51}V -NMR behavior of diperoxo vanadium com-

Table 2

^{51}V -NMR parameters for monoperoxo vanadium complexes containing various carboxypicolinic acids



(11)a-e



(14)a-e

Substituent	Complex	δ (ppm)	$W_{1/2}$ (Hz)	Complex	δ (ppm)	$W_{1/2}$ (Hz)
–	(11a)	–600.6	196	(14a)	–632.6	171
3-COOH	(11b)	–595.1	284	(14b)	–617.8	299
4-COOH	(11c)	–596.3	292	(14c)	–624.0	344
5-COOH	(11d)	–595.9	288	(14d)	–622.3	395
6-COOH	(11e)	–597.5	207	(14e)	^a	

^a Formation of complex 14e was not detected.

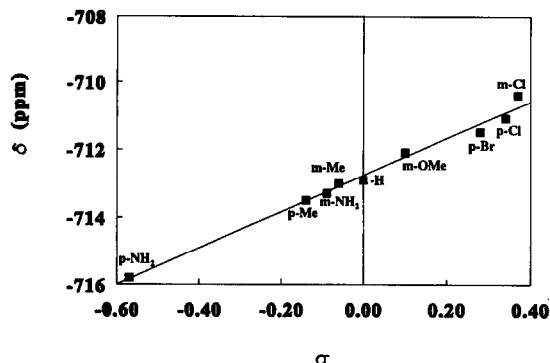


Fig. 1. Hammett plot of ^{51}V -NMR chemical shifts (downfield from VOCl_3) of diperoxo vanadium complexes containing as ligands *meta* and *para* substituted pyridines vs. σ constants. $\rho = 29.8 \pm 0.1$, $r = 0.995$.

plexes confirms the conclusions reached for the monoperoxo species. The octahedral geometry appears to be the preferred one in solution also for diperoxo complexes since monodentate ligands form stable complexes by substituting the water molecule in **2**. It has been established by direct experiments that such substitution equilibrium is favored when neutral rather than anionic nucleophilic molecules, e.g. pNO_2^- benzoic acid anion or acetate anion, are used. The small binding ability of the latter ligands is likely related to the fact that they would form dianionic derivatives.

Meta and *para* substituted pyridines and anilines were used to obtain two Hammett-type correlations in which the ^{51}V -NMR chemical shifts are plotted against the σ values of the substituents as shown in Fig. 1 and Fig. 2. The correlations obtained are satisfactory. It may be observed that by increasing the electron density on the metal nucleus i.e. by placing electron donating substituents in the aromatic rings, the value of the chemical shift of the complexes decreases. This confirms that also in the diperoxo vanadium derivatives the magnetic shielding increases with the increase of the negative charge on the metal.

The absolute value of the ρ obtained in the series of the diperoxo complexes containing substituted pyridines ($\rho = 29.8 \pm 0.1$, $r = 0.995$) is larger than that of substituted anilines ($\rho = 5.5 \pm 0.2$, $r = 0.993$) as it might have been expected since the effect of the substituent decreases with the

distance from the reaction center which is the nitrogen atom.

3.3. Ramsey-type correlation for V^{V} peroxo derivatives

Further information on the role of the ligands in determining the general properties of peroxo vanadium complexes may be obtained if Ramsey-type correlations [24] can be established. In its most simplified formulation the theoretical description developed by Ramsey, applied to peroxo vanadium complexes, predicts that the magnetic shielding of vanadium should depend on the energy of the ligand-to-metal charge-transfer excitations $\Delta E(n \rightarrow d)$ according to Eq. 1.

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

in which the value of γ , i.e. the magneto-gyric 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 ($\gamma = \gamma_0 \cdot (1 + \delta)$) [25] and σ^d is the diamagnetic contribution to the total shielding of the nucleus, which can be considered a constant value for all the peroxo vanadium complexes because it is mostly determined by the electrons located in the internal orbitals of the metal [24].

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 elec-

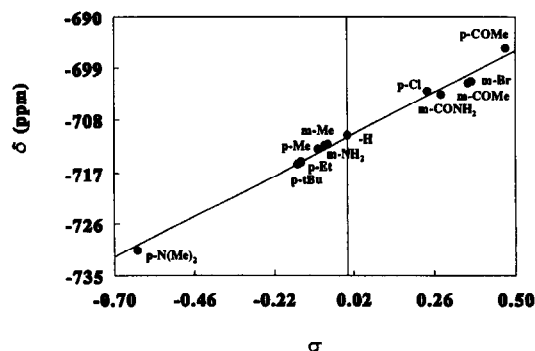


Fig. 2. Hammett plot of ^{51}V -NMR chemical shifts (downfield from VOCl_3) of diperoxo vanadium complexes containing as ligands *meta* and *para* substituted anilines vs. σ constants. $\rho = 5.5 \pm 0.2$, $r = 0.993$.

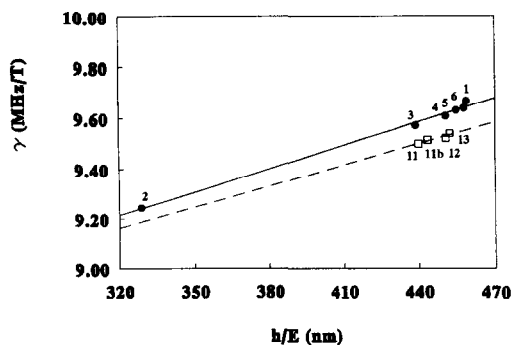


Fig. 3. Correlations between ^{51}V magneto-gyric ratios and electronic transition ($n \rightarrow d$) wavelengths for monoperoxo vanadium complexes containing $\text{O}\cap\text{O}$ (\bullet) and $\text{N}\cap\text{O}$ (\square) ligands. Slope for $\text{O}\cap\text{O}$ class = $3.1 \times 10^{-3} \pm 6 \times 10^{-5}$, $r = 0.997$; slope for $\text{N}\cap\text{O}$ class = $2.8 \times 10^{-3} \pm 1 \times 10^{-4}$, $r = 0.951$. The two straight lines give an intercept value of 8.24 MHz T^{-1} .

tronic transition corresponds to the difference of energy between the HOMO and the LUMO of the peroxo complexes. Satisfactory Ramsey-type correlations are obtained for peroxo vanadium complexes as shown by the linear plots of Fig. 3, referring to monoperoxo vanadium complexes containing various ligands.

Two straight lines, characterized by slightly different 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 $\text{O}\cap\text{O}$ and $\text{N}\cap\text{O}$ ligands, respectively. Interestingly, in the family of $\text{O}\cap\text{O}$ ligands also the diperoxo anion **2** lies in the correlation.

The slopes of the Ramsey-type correlations contain the B values of Eq. 1, which provide an estimate of the contribution of the d orbitals of the metal to the HOMO and LUMO orbitals of the complex [24]. Although the difference of the slope values, and hence of the B values, is small, the larger value for $\text{O}\cap\text{O}$ ligands is in agreement with the larger electron withdrawing effect of these ligands compared with those of $\text{N}\cap\text{O}$ [24].

The value of the intercept of the two straight lines is 8.24 MHz T^{-1} . According to the Ramsey theory this value provides the amount of diamagnetic shielding of vanadium which is independent of the nature of the ligands [24].

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-} peroxy group, and the LUMO the d orbitals of the metal [26], the HOMO energy should be less affected by the ligands than those of the LUMO. Therefore, one might conclude that the LUMO energy is enhanced by increasing the electron donating ability of the ligands [17].

4. Conclusions

This investigation was aimed at establishing quantitative relationships between the nature of the ligands of peroxo vanadium complexes and an easily accessible experimental parameter such as ^{51}V -NMR chemical shift. Our results indicate that such relationships exist. Thus, we have demonstrated that the electronic character of the ligands may be quantitatively correlated with the magnetic shielding of the metal and, consequently, with the chemical shift values. In particular, the shielding increases with the electron donating ability of the ligand. In addition we have also found that the increase of the electron density of the metal leads to a larger separation of the energies of the HOMO and LUMO of the complexes and, very likely, to an increase of the energy of the LUMO.

In terms of reactivity some predictions can be made. In fact, a comparison of the ^{51}V -NMR chemical shifts of peroxo vanadium complexes allows to select the ones in which the electron density of the metal and the energy gap of the frontier orbitals are both sufficiently small. In these complexes, in principle and neglecting all the kinetic factors which often dominate the scene [9,27], an electrophilic oxidative reactivity and a one-electron acceptor ability should be found. The kinetic behavior of the self-decomposition of the four peroxo complexes **1**, **3**, **11a** and **13**, leading to dioxygen, [10,14] shown in Fig. 4, is in agreement with the expectation.

Based on our previous studies [10,14], the decomposition reaction involves as a key step an

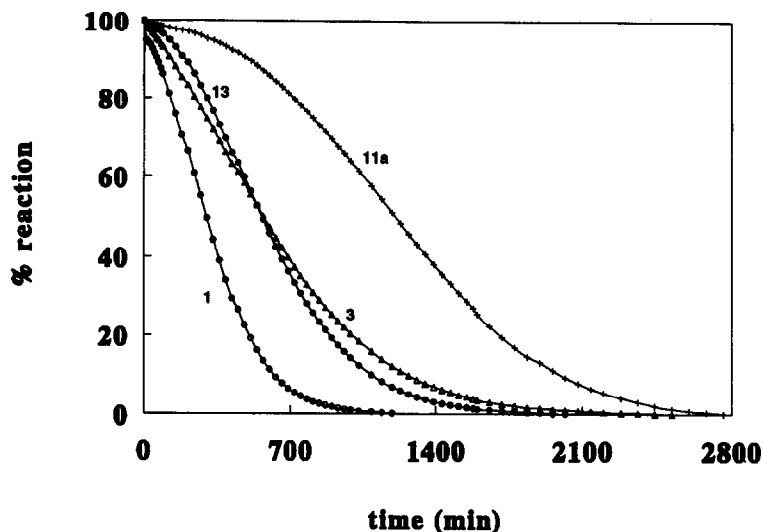


Fig. 4. Disappearance of the oxidant with the time, measured as decrease of the absorbance at the λ_{\max} values, in the decomposition reaction of $5 \times 10^{-3} \text{ mol l}^{-1}$ of **1** (○), **3** (△), **11a** (+) and **13** (●), in water (HClO_4 , pH 1) at 37°C .

electron transfer to vanadium. Accordingly, it may be observed that the complexes in which the electron density on the metal is small and the energy of the LUMO is low, e.g. complex **3** in the $\text{O}\cap\text{O}$ series and complex **11a** in the $\text{N}\cap\text{O}$ series, decompose more rapidly than complexes **1** and **13**, respectively.

Acknowledgements

This work has been carried out with the financial support from MURST, Italian ministry of Research and from 'Progetto Strategico: Tecnologia Chimiche Innovative' of Italian National Research Council. We also thanks the INTAS Association for INTAS 94/1515 grant.

References

- [1] N.D. Chasteen, Vanadium in Biological Systems, Kluwer Academic Publishers, Dordrecht, 1990.
- [2] (a) N.D. Chasteen, *Struct. Bonding*, 53 (1983) 104; (b) B.R. Nechay, *Ann. Rev. Toxicol.*, 24 (1984) 501; (c) H. Michibata, H. Sakurai and N.D. Chasteen, in N.D. Chasteen (Editor), *Vanadium in Biological Systems*, Chap. IX, Kluwer Academic Publishers, Dordrecht, 1990, p. 153.
- [3] (a) R. Wever and B.E. Krenn, in N.D. Chasteen (Editor), *Vanadium in Biological Systems*, Chap. V, Kluwer Academic Publishers, Dordrecht, 1990, p. 81; (b) A. Butler and C.J. Carrano, *Coord. Chem. Rev.*, 109 (1991) 61; (c) A. Butler and J.V. Walker, *Chem. Rev.*, 93 (1993) 1937.
- [4] (a) T. Ramasarma, W.C. Mac Keller and F.L. Crane, *Biochem. Biophys. Acta*, 646 (1981) 88; (b) M.S. Patole, C.K.R. Kurup and T. Ramasarma, *Biochem. Biophys. Res. Commun.*, 141 (1986) 171; (c) R.A. Coulombe, D.P. Briskin, R.J. Keller, W.R. Thornlry and H.P. Sharma, *Arch. Biochem. Biophys.*, 255 (1987) 267; (d) S. Liochev, E. Ivancheva and I. Fridovich, *Arch. Biochem. Biophys.*, 269 (1989) 188; (e) D. Heffetz, I. Bushkin, R. Dror and Y. Zick, *J. Biol. Chem.*, 265 (1990) 2896; (f) C. Djordjevic, B. Puryear, N. Vuletic, C. Abelt and S.J. Sheffield, *J. Inorg. Chem.*, 27 (1988) 2926; (g) A. Sharer, J.B. Nj, D.A. Hall, B.G. Lum and B.I. Posner, *Inorg. Chem.*, 32 (1993) 3109.
- [5] A.F. Ghiron and R.C. Thompson, *Inorg. Chem.*, 29 (1990) 4457.
- [6] V. Conte, F. Di Furia and S. Moro, *J. Mol. Catal.*, 94 (1994) 323.
- [7] (a) O.W. Howarth and A.T. Harrison, *J. Chem. Soc. Dalton Trans.*, (1985) 388; (b) N.J. Campbell, A.C. Dengel and W.P. Griffith, *Polyhedron*, 8 (1989) 1379; (c) A.S. Tracey and J.S. Jaswal, *J. Am. Chem. Soc.*, 114 (1992) 3835.
- [8] D. Rehder, in *Transition Metal Nuclear Magnetic Resonance*, Elsevier, Amsterdam, Chap. 4.1, 1991.
- [9] V. Conte, F. Di Furia and G. Modena, in W. Ando (Editor), *Organic Peroxides*, John Wiley&Sons, Chichester, 1992, Chap. 11.2, p. 559.
- [10] (a) M. Bonchio, V. Conte, F. Di Furia, G. Modena, S. Moro, T. Carofiglio, F. Magno and P. Pastore, *Inorg. Chem.*, 32 (1993) 5797; (b) M. Bonchio, V. Conte, F. Di Furia, G. Modena, S. Moro and J.O. Edwards, *Inorg. Chem.*, 33 (1994) 1631; (c) M. Bonchio, V. Conte, F. Di Furia, G. Modena and S. Moro, *J. Org. Chem.*, 21 (1994) 6262.
- [11] D. Rehder, in N.D. Chasteen (Editor), *Vanadium in Biological Systems*, Chap. X, Kluwer Academic Publishers, Dordrecht, 1990, p. 173.

- [12] (a) A.B.P. Lever and H.B. Gray, *Acc. Chem. Res.*, 9 (1978) 348; (b) K.I. Hagen, C.M. Schwab, J.O. Edwards and D.A. Sweigart, *Inorg. Chem.*, 25 (1986) 978; (c) K.A. Jorgensen and R. Hoffmann, *Acta Chem. Scand. B*, 40 (1986) 411.
- [13] C.R. Cornman, G.J. Colpas, J.D. Hoeschele, J. Kampf and V.L. Pecoraro, *J. Am. Chem. Soc.*, 114 (1992) 9925 and references cited therein.
- [14] S. Rabbolini, Thesis of 'Laurea', Padova University, 1994.
- [15] (a) G.A. Dean, *Can. J. Chem.*, 39 (1961) 1174; (b) M. Orhanovic and R.G. Wilkins, *J. Am. Chem. Soc.*, 89 (1967) 278; (c) F. Secco, *Inorg. Chem.*, 19 (1980) 2722.
- [16] (a) H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fisher and R. Weiss, *J. Am. Chem. Soc.*, 105 (1983) 3101; (b) C. Djordjevic, S.A. Craig and E. Sinn, *Inorg. Chem.*, 24 (1985) 1283; (c) C. Djordjevic, M. Lee and E. Sinn, *Inorg. Chem.*, 28 (1989) 719; (d) P. Schwendt, K. Liscak and L. Duris, *Chem. Papers*, 47 (1993) 288; (e) L'ubomir Kuchta, M. Sivak and F. Pavelcik, *J. Chem. Res.*, (1993) 393; (f) P. Schwendt, M. Sivak, A.E. Lapshin, Y. Smolin, Y. Shepelev and D. Gyepesova, *Trans. Met. Chem.*, 19 (1994) 34.
- [17] A. Bagno, V. Conte, F. Di Furia and S. Moro, RHF/3-21G(*) ab initio calculation, in progress.
- [18] M. Bonchio, Thesis of 'Laurea', Padova University, 1992.
- [19] R.R. Drew and F.W.B. Einstein, *Inorg. Chem.*, 11 (1972) 1079.
- [20] (a) J. Mason, *Chem. Rev.*, 87 (1987) 1299; (b) J. Mason, *Polyhedron*, 13/14 (1989) 1657.
- [21] J.P. Collman, L.S. Hegeudus, J.R. Norton and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, 1987, Chap. 2.2, p. 43.
- [22] S. Clementi, F. Genel and G. Marino, *J. Chem. Soc. Chem. Commun.*, (1967) 498.
- [23] E.P. Talsi and K.V. Shalyaev, *J. Mol. Catal.*, 92 (1994) 245.
- [24] (a) N.F. Ramsey, *Phys. Rev.*, 78 (1950) 699; (b) N.F. Ramsey, *Phys. Rev.*, 86 (1952) 243; (c) J.S. Griffith and L.E. Orgel, *Trans. Faraday Soc.*, 53 (1957) 601; (d) C.J. Jameson and H.S. Gutowsky, *J. Chem. Phys.*, 40 (1964) 1714; (e) A.D. Buckingham and P.J. Stephens, *J. Chem. Soc.*, 2447 (1964) 4583; (f) K.D. Becker and U. Berlage, *J. Magn. Reson.*, 54 (1983) 272; (g) R. Bramley, M. Brorson, A.M. Sargenson and C.E. Schaffer, *J. Am. Chem. Soc.*, 107 (1985) 2780; (h) K. Kanda, H. Nakatsuji and T. Yonezawa, *J. Am. Chem. Soc.*, 106 (1984) 5888.
- [25] J. Mason, *Multinuclear NMR*, Plenum Press, 1987, Chap. 3, p. 51.
- [26] M. Camporeale, L. Cassidei, R. Mello, O. Sciacovelli and R. Curci, in W. Ando and Y. Moro-oka (Editors), *The Role of Oxygen in Chemistry and Biochemistry*, Vol. 33, Studies in Organic Chemistry, Elsevier, Amsterdam, 1987, p. 201.
- [27] M. Bonchio, V. Conte, F. Di Furia, T. Carofiglio, F. Magno and P. Pastore, *J. Chem. Soc. Perkin Trans.*, 2 (1993) 1923.