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Peroxovanadium(V) complexes of glycolic acid as studied by NMR spectroscopy

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Abstract

Multinuclear (^{1}H, ^{13}C, ^{17}O, ^{51}V) 1D and 2D NMR spectroscopy has been used to characterize the peroxovanadium(V) complexes of glycolic acid in aqueous solution. One 2:2:2 (metal:ligand:peroxo) complex, together with a 1:1:1 and a 2:2:1 species, are found in the pH range 1–7. The 2:2:2 complex is a monoperoxo (one peroxide unit per vanadium atom) dinuclear species having a $V_2O_3^{4+}$ seven-coordinated metal centre. In this structure, the two vanadium atoms are triple bridged, two of those bridges being formed by oxygen atoms of the hydroxyl group of the acid. The 1:1:1 species has a seven-coordinated VO^{3+} metal centre. Glycolic acid bonds to the vanadium atoms in a bidentate way, through both the carboxylic and the hydroxyl groups. The peroxo groups are bound in the equatorial plane relative to the apical V=O and the geometry around each vanadium atom is close to pentagonal bipyramidal. The 2:2:1 complex is similar to the 2:2:2 species, except for one of the vanadium centres, which is now a five-coordinated oxovanadium centre. Three additional complexes are found in very small amounts for some pH and concentration conditions. Further support for the proposal of monoperoxovanadium species is given by UV–visible spectroscopy results. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Peroxovanadium(V) complexes; Glycolic acid; Multinuclear NMR

1. Introduction

The importance of peroxovanadium(V) complexes has become well established over the past several years. Vanadate and peroxide have been shown to act synergistically to mimic insulin activity [1] and this mimetic ability has also been found for several peroxovanadium complexes [2–5]. These complexes are also known to have antitumour activity [6], and have been studied as functional models for the vanadium haloperoxidase enzymes [7–9]. These enzymes catalyse the oxidation of halides by hydrogen peroxide and are thought to be involved in the biosynthesis of a large number of marine natural products, many of them with potent antifungal, antibacterial, antiviral (e.g. HIV) and antineoplastic properties [10]. In addition to this biological relevance, a large variety of oxidation reactions can be efficiently performed by peroxovanadium(V) complexes. These complexes have been shown to hydroxylate benzene and other aromatics, epoxidize and hydroxylate alkenes and allylic alcohols and oxidize sulfides and primary and secondary alcohols [1].

The solid state structures have been determined for a large number of mono- and di-peroxovanadium(V) complexes by X-ray diffraction. Those studies showed that the most common geometry for the monomeric oxoperoxo complexes is the pentagonal bipyramidal one and that the peroxo groups are always bound in the equatorial plane relative to the axial oxo ligand [1]. The remaining equatorial and apical positions in the coordination shell are occupied by the heteroligand(s).

In view of the interest in peroxovanadium(V) compounds, we are now extending previous work carried out in this group on vanadium complexation with α-hydroxycarboxylic acids [11–13] to these new systems involving hydrogen peroxide. α-Hydroxycarboxylic acids are involved in many biochemical processes, and thus represent an important class of ligands. Following

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our previous study [14] of the peroxovanadium(V) complexes that form with L-lactic acid, we now report on an NMR and UV–visible spectroscopy study of the complexes formed using glycolic acid as the heteroligand. NMR has been intensively used in the study of vanadium(V)–hydrogen peroxide systems, both in the presence and in the absence of heteroligands [14–22], and has proved to be successful in the structural characterization of the species present in solution.

No studies of this system using NMR or any other technique were found in the literature. There are, however, some X-ray diffraction studies concerning peroxovanadium complexes for other α-hydroxycarboxylic acids, such as citric [6], DL-malic [23] and L-tartaric acids [24]. These studies revealed monoperoxo (one peroxide unit per vanadium atom) dinuclear structures with double bridges formed by oxygen atoms of hydroxyl groups (and a third bridge formed by the oxygen of a water molecule in the case of tartaric acid). The peroxo groups are bound in the equatorial plane across from the bridging hydroxyl oxygen atoms and the geometry about each vanadium atom was found to be distorted pentagonal bipyramidal.

2. Experimental

Analytical-grade ammonium vanadate(V) and commercially available glycolic acid and hydrogen peroxide (35%) were used. The samples were prepared by adding the appropriate amounts of vanadate, glycolic acid and hydrogen peroxide stock solutions (the hydrogen peroxide stock solution was prepared immediately prior to use in order to avoid uncertainties regarding concentrations). The pH was adjusted (cautiously, to reduce the possibility of drastic local disturbances of equilibria that may be slow to disappear) by addition of solutions of DCl and NaOD; the pH* values quoted are the direct pH-meter readings (at room temperature) after standardization with aqueous (H_2O) buffers.

The ^{1}H, ^{13}C, ^{17}O and ^{51}V NMR spectra were obtained on a Varian UNITY-500 NMR spectrometer. The residual water signal was reduced by using the Presat sequence. The ^{13}C NMR spectra were recorded using proton-decoupling techniques with suppression of the nuclear Overhauser effect. A relaxation delay of 30 s was used in order to allow the complete relaxation of the carboxylate ^{13}C nuclei, so that signal intensities can be compared. The 2D NMR spectra, HETCOR [25], were also recorded on the Varian UNITY-500 NMR spectrometer. For more detailed information on the NMR conditions see Ref. [14]. The experimental conditions of these studies were the following: concentration of complexing species ranging from 0.15 to 2.0 M, metal:ligand and H_2O_2:metal molar ratios ranging from 3:1 to 1:3 and 5:1 to 1:1 respectively, and pH values ranging from 1.0 to 9.6.

UV–visible spectra were recorded on a Spectronic Genesys 2PC spectrophotometer. Spectra of the 330–650 nm region were obtained from a 14 mM:14 mM:14 mM V(V)–glycolic acid–H_2O_2 aqueous solution at pH 4.2, prepared by dilution of a stock 50 mM:50 mM:50 mM aqueous solution at pH 4.4.

3. Results and discussion

The formation of peroxovanadium(V) complexes of glycolic acid results from a competition of several equilibria, since the metal is simultaneously involved in the formation of peroxovanadates, oxocomplexes, free metal species (hydrolysis and polymerization reactions) and peroxocomplexes. In spite of this, the system is relatively simple, with the formation of three major species and three other complexes in very low concentrations, as discussed below. Fig. 1 shows a typical ^{13}C NMR spectrum. The signals of the three major peroxocomplexes, **a**, **b** and **c**, one vanadium(V) oxocomplex of glycolic acid and free ligand are identified.

Four sets of ligand signals are observed in this spectrum, two of them being attributed to the same species, complex **c**. This attribution is based on the observation that, irrespective of concentration and pH conditions, the two carboxylate ^{13}C signals always have equal intensities, which suggests that complex **c** has two ligand molecules in different magnetic environments. On the other hand, the signals labelled **a** and **b** appear to arise from separate molecules, each containing a single type of ligand, or ligands that are magnetically equivalent. Similarly, the ^{1}H NMR spectra (AB spectra) show two sets of ligand signals for complex **c** and only one set for each of the complexes **a** and **b**.

Table 1 shows the ^{1}H and ^{13}C NMR parameters for complexes **a**, **b**, **c** and, additionally, a weaker complex, **d**. Owing to its low concentration, it was not possible to detect complex **d** by ^{13}C NMR spectroscopy. HETCOR experiments were performed in order to confirm the assignment of the proton and carbon shifts of complexes **a**, **b** and **c**.

The three complexes involve both the carboxylate and the hydroxyl groups in bonding to the metal, as shown by the high-frequency shifts, relative to the free ligand, observed for the carbinol protons and for the carboxylic and carbinol carbon nuclei of complexes **a**, **b** and **c**. It is found that one of the two ligand molecules of complex **c** undergoes significantly smaller ^{1}H shifts on complexation (0.74 and 0.45 ppm) than the other (1.19 and 1.12 ppm). These shifts are also smaller than those of the ligand molecules in complexes **a**, **b** and **d** (0.88–1.28 ppm). This is expected if there is a significant structural difference between the metal centres. It is noted that those smaller ^{1}H shifts are characteristic of vanadium(V) glycolic acid oxocomplexes [11,13].

In order to find the influence of the metal:ligand and hydrogen peroxide:metal molar ratios on the concentrations of the several peroxocomplexes, some studies were carried out at pH 3–4 in which these ratios were varied. The metal:ligand and hydrogen peroxide:metal molar ratios were varied from 3:1 to 1:3 and from 5:1 to 1:1 respectively. These results show that the metal:ligand molar ratio has no significant effect on the relative concentrations of the three peroxocomplexes **a**, **b** and **c**, which is an indication that the three complexes have similar metal:ligand stoichiometries. Concerning complexes **a** and **b**, simple determinations involving ^{51}V and ^{1}H signal intensities in free and bound species point to the conclusion that these are n:n species ($n \geq 1$). This determination could not be carried out for complex **c** because of the influence of the Presat sequence (used for the suppression of the residual water signal) on the intensities of ^{1}H signals close to the HDO resonance.

Regarding the results of the variation of the hydrogen peroxide:metal molar ratio, it is found that, when this ratio is high, complexes **a** and **b** are favoured relative to **c**. The strongest influence of this factor is found, however, when considering the relative concentrations of glycolic acid peroxocomplexes and the remaining species in solution, as follows. Glycolic acid peroxocomplexes are present only if the hydrogen peroxide:metal molar ratio is equal or smaller than two. If an excess of peroxide over metal larger than two is used, the main species in solution is the diperoxovanadate $[VO(O_2)_2(H_2O)_n]^-$. If the ratio is two, the major species initially present is the diperoxovanadate, but, over time, as the peroxide concentration decreases due to disproportionation catalysed by vanadium(V) [17], glycolic acid peroxocomplexes become the dominant species. Finally, when equal molar amounts of vanadium and hydrogen peroxide are used, the peroxocomplexes are already the major species present immediately after preparing the solution.

The results above suggest that no more than one peroxide unit is involved for each metal centre. ^{51}V NMR results support this conclusion. ^{51}V chemical shifts in vanadium complexes are known to be sensitive to the coordination number of the metal centre and to the nature of the ligands. For α-hydroxycarboxylic acids, such as glycolic acid, chemical shifts close to -595 ppm have been attributed [26] to monoperoxo seven-coordinated VO^{3+} metal centres, whereas diperoxovanadium seven-coordinated centres give rise to signals approximately at -695 ppm [26]. Fig. 2 shows a time-course ^{51}V NMR study were the signals of the three major complexes are observed approximately at -580 ppm, suggesting that these complexes have monoperoxovanadium centres. There is, however, a signal at -514.2 ppm that is also attributed to complex **c** (Fig. 2 and Table 2) on the basis that, as the two complexes **a** and **b** disappear, both signals at -580.4 and -514.2 ppm increase. Also, as the glycolic acid oxocomplex becomes the dominant species, they both decrease.

This parallel behaviour suggests that both signals arise from the same species and the finding that the ratio of their intensities is unity supports the conclusion. Taking into account that ^{51}V signals at -514.2 ppm are not expected for peroxocomplexes, but they are for five-coordinated vanadium(V) oxocomplexes [26], these results suggest that **c** is a dimeric

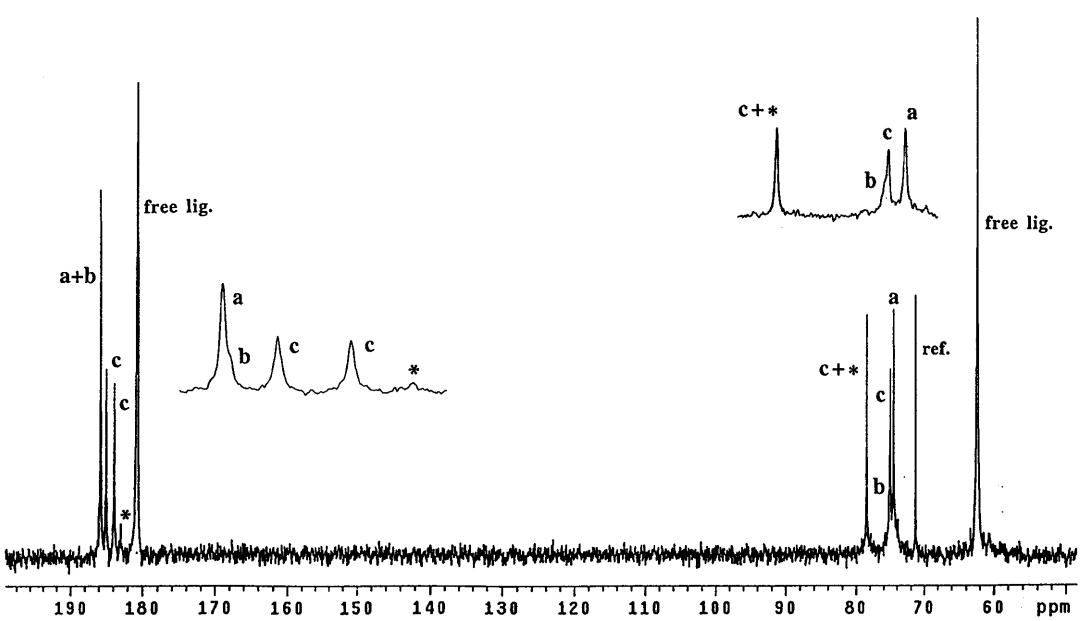


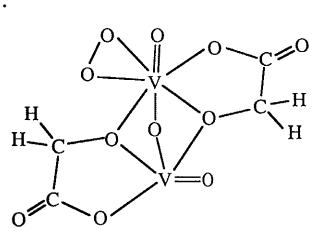
Fig. 1. ^{13}C NMR spectrum (125.692 MHz) of a 0.25 M:0.50 M:0.25 M aqueous solution (30% D_2O) of V(V)–glycolic acid–H_2O_2; pH* 4.1; temp. = 294K; (*): oxocomplex (δ_{CO_2H} 183.02, δ_{CH_2} 78.52).

Table 1
^{1}H and ^{13}C NMR parameters for V(V)+glycolic acid+H_2O_2 at pH* 3.3 (^{1}H) and pH* 4.1 (^{13}C) (298 K)

	δ_H[a]	J_{HH} (Hz)	δ_C[a]
Glycolic acid			
	4.13 (CH_2)		62.39 (CH_2)
			180.72 (CO_2H)
V(V)+glycolic acid+H_2O_2			
Complex **a**[c]			
δ	5.32 (CH_2, A)[g]	16.2	74.56 (CH_2)
$\Delta\delta$[h]	1.19		12.17
δ	5.23 (CH_2, B)[g]		185.80 (CO_2H)
$\Delta\delta$	1.10		5.08
Complex **b**[c]			
δ	5.41 (CH_2, A)	16.1	75.16 (CH_2)
$\Delta\delta$	1.28		12.77
δ	5.01 (CH_2, B)		185.69 (CO_2H)
$\Delta\delta$	0.88		4.97
Complex **c**[d]			
δ	5.32 4.87 (CH_2, A)	16.4 16.2	75.06 78.50 (CH_2)
$\Delta\delta$	1.19 0.74		12.67 16.11
δ	5.25 4.58 (CH_2, B)		184.99[f]/183.89 (CO_2H)
$\Delta\delta$	1.12 0.45		4.27 3.17
Complex **d**[e]			
δ	5.17 (CH_2, A)	16.0	–[b] (CH_2)
$\Delta\delta$	1.04		
δ	5.03 (CH_2, B)		–[b] (CO_2H)
$\Delta\delta$	0.90		

[a] δ values relative to TMS, using *tert*-butyl alcohol (δ_H 1.2, δ_C 31.2) as internal reference.
[b] Not observed due to its small intensity.
[c] 0.05 M:0.10 M:0.05 M (^{1}H) and 0.25 M:0.25 M:0.50 M (^{13}C) V(V)–glycolic acid–H_2O_2 solutions.
[d] 0.05 M:0.05 M:0.05 M (^{1}H) and 0.25 M:0.25 M:0.50 M (^{13}C) V(V)–glycolic acid–H_2O_2 solutions.
[e] 0.15 M:0.05 M:0.15 M V(V)–glycolic acid–H_2O_2 solution.
[f] Possibility of a reverse assignment.
[g] The CH_2 group gives rise to AB spectra.
[h] $\Delta\delta = \delta_{\text{bound lig}} - \delta_{\text{free lig}}$ at the same pH* and temperature conditions.

complex in which one of the metal centres is a five-coordinated oxovanadium centre and the other is a seven-coordinated monoperoxovanadium centre. This proposal is in accordance with the non-equivalence of the two vanadium atoms and of the two ligands and equally explains the ^{1}H shifts observed for one of the ligand molecules in complex **c**, which, as we noted before, are characteristic of oxovanadium complexes. Based on these observations, we can propose **c** as being a 2:2:1 (metal:ligand:peroxo) species. A possible structure for **c** is **1**.



1

The bipyramidal pentagonal geometry and the equatorial position (relative to the axial V=O) for the peroxo groups are proposed based on the solid state structures found for most peroxovanadium complexes [1,6,23,24]. In addition, OH bridging is expected to be preferred to CO_2H bridging, as found for numerous peroxovanadium(V) complexes [6,23,24]. This kind of dinuclear peroxovanadium complex, in which one of the metal centres is an oxovanadium centre, was first reported by the authors in the case of L-lactic acid [14].

Concerning complexes **a** and **b**, their ^{51}V chemical shifts are characteristic of monoperoxo seven-coordinated metal centres [26]. As mentioned before, by combining ^{1}H and ^{51}V NMR data, both **a** and **b** are found to be *n*:*n* (metal:ligand) species. Since a 1:1:1 species requires two water molecules bound to the metal, a 2:2:2 species, involving only molecules of a strong ligand, is expected to be favoured. Thus, we can propose **a** and **b** as being a 2:2:2 and a 1:1:1 species respectively. The kinetic behaviour observed (Fig. 2) for

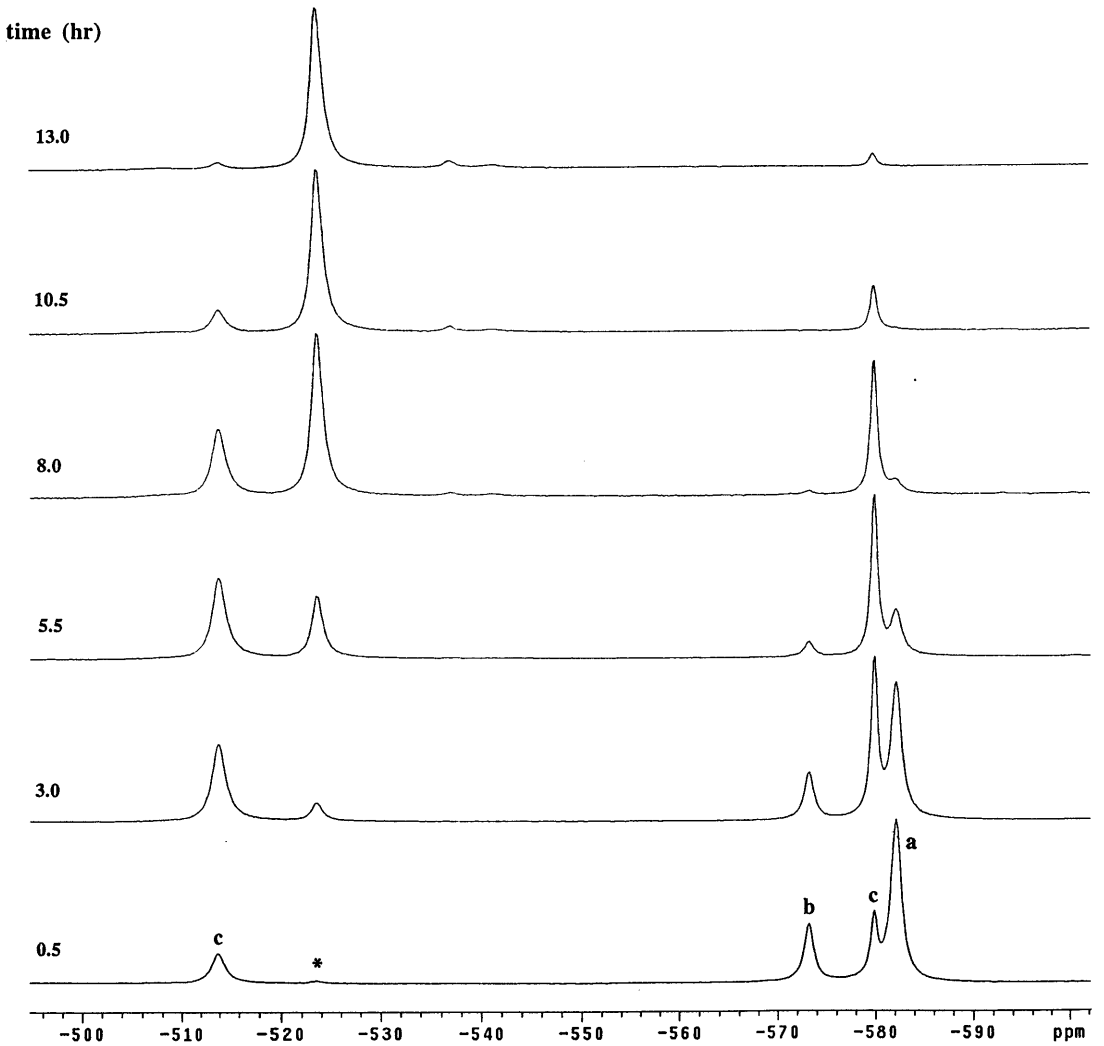
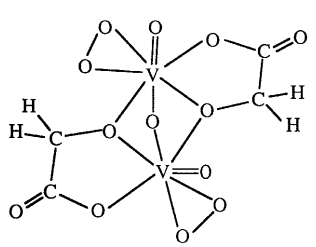


Fig. 2. Time-course ^{51}V NMR study (131.404 MHz) of a 0.05 M:0.10 M:0.05 M aqueous (30% D_2O) solution of V(V)–glycolic acid–H_2O_2 showing that as complexes **a** and **b** disapear, the concentration of complex **c** and of an oxovanadium complex of glycolic acid increase; pH* 3.9; temp. 298 K; (*): oxocomplex.

the system supports this proposal. In fact, complex **a** can convert into a 2:2:1 species (complex **c**) by losing one of its peroxo groups, and one of the seven-coordinated monoperoxovanadium centres becomes then a five-coordinated oxovanadium centre. Complex **b** converts into an oxovanadium complex of glycolic acid when it loses its peroxo group. This was confirmed by some experiments that showed that the addition of hydrogen peroxide to a solution containing **c** and oxocomplexes leads to the formation of **a** and **b**. Based on these considerations, and on the fact that the ^{1}H and ^{13}C NMR results require that the two ligand molecules in complex **a** are magnetically equivalent, we propose **2** for **a**. A possible structure for **b** is **3**.

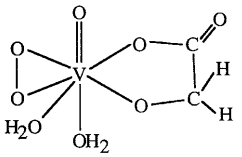


2

Table 2
^{51}V NMR chemical shifts for V(V)+glycolic acid+H_2O_2 at 298K.

Complex	δ_V (ppm)[a]
a[b] (pH* 4.1)	−582.8
b[b] (pH* 4.1)	−574.0
c[b] (pH* 4.1)	−514.2, −580.4
d[c] (pH* 5.7)	−610.9
e[c] (pH* 5.7)	−638.6
f[c] (pH* 5.7)	−652.4

[a] δ values relative to $VOCl_3$ as external reference.
[b] 0.05 M:0.05 M:0.05 M V(V)–glycolic acid–H_2O_2 solution.
[c] 0.40 M:0.20 M:0.40 M V(V)–glycolic acid–H_2O_2 solution.



3

A structure similar to **2** has been previously proposed for the complex $[\{VO(O_2)(L\text{-lactic})\}_2(\mu\text{-}O)]^{2-}$ [14] and has been found by X-ray diffraction for $K_2[\{VO(O_2)(L\text{-tart}H_2)\}_2(\mu\text{-}H_2O)]\cdot 5H_2O$ [24]. In complex **b** the ligand will probably be bound in the equatorial plane, as found by X-ray diffraction for $VO(O_2)(Pic)\cdot 2H_2O$ [27].

In accordance with the presence of two equivalent V=O groups in complex **a**, an ^{17}O signal is found at 1184.2 ppm, in the region expected for V=O terminal O atoms in peroxovanadium(V) complexes [28]. Complexes **b** and **c** could not be detected by ^{17}O NMR, nor any V–O–V resonance.

UV–visible spectroscopy results are in accordance with the proposal of monoperoxovanadium species. The UV–visible spectrum of an aqueous solution of complexes **a**, **b** and **c** shows the [peroxo → vanadium] charge transfer band at $\lambda_{max} = 383$ nm, which is close to reported values for other monoperoxovanadium(V) complexes [6,23,29]. The band is broad and overlapped with bands from $HV_{10}O_{28}^{5-}$ and $[VO(O_2)_2(H_2O)_n]^-$. Owing to overlapping with these species, the presence of weak bands close to 200 and 325 nm, which are expected for diperoxovanadium complexes [30–32], cannot, however, be ruled out.

A minor species, complex **d**, is formed for pH values between 4.5 and 7 and high metal:ligand molar ratios. Two other minor complexes (**e** and **f**) are formed, a few hours after preparation, if the solution is concentrated. The complete assignment of those species was not, however, possible, due to their low concentrations and to some experimental difficulties related to the formation of O_2 resulting from the decomposition of the complexes.

4. Conclusion

There are some differences between the system studied and the complexation of L-lactic acid with V(V) and hydrogen peroxide, reported in a previous paper [14]. Namely, only one 2:2:1 complex is found in the case of glycolic acid, whereas two of those species are found with L-lactic acid. Also, a 1:1:1 seven-coordinated species is now found for pH values between 1 and 7, whereas a 1:1:1 six-coordinated species was found only for very low pH values with L-lactic acid. However, there is a common pattern to the two systems, which is their kinetic behaviour, involving the conversion of 2:2:2 species into 2:2:1 species over time.

5. Note added in proof

An independent paper recently published reached similar conclusions [33].

Acknowledgements

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