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Note

Phosphate complexation of oxovanadium(IV). Evidence of bidentate chelation of orthophosphate

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Abstract

The interaction of VO(IV) with orthophosphate in aqueous solution has been investigated by EPR and electronic absorption. Monodentate coordination of dihydrogenphosphato and monohydrogenphosphato ligands is indicated below pH 4.5. Over the pH range 4.5–8.5 precipitation of VO(IV) orthophosphates depletes the solution of most of the vanadium ions. These are re-dissolved in more basic media to yield, besides polynuclear hydroxo-bridged species, a mononuclear bis-orthophosphate complex with bidentate chelation of the ligands. Finally, a species where the metal ion is chelated by a phosphate group and bound also to two terminal hydroxo groups is detected

Key words Vanadium complexes; Oxo complexes, Orthophosphate complexes

Knowledge of complexation properties of simple phosphate ligands can be of help in understanding the interactions of metal ions with biological phosphates. Oxovanadium(IV) interaction with phosphate, pyrophosphate and peroxodiphosphate was studied in aqueous solution [1–5]. Formation of monodentate, six-membered mono-chelated, and trinuclear complexes was suggested for pyrophosphate by spectrophotometric and EPR studies [4, 5]. As far as the VO(IV)–phosphate system is concerned, an equilibrium model, as studied by ion-exchange methods, included $[VO(HPO_4)]$, $[VO(H_2PO_4)(HPO_4)]^-$ and $[VO(HPO_4)_2]^{2-}$, the first complex being largely the predominant species below pH 3 [1]. The spectrophotometric investigation performed by Copenhafer *et al.* in the pH range 1.9–2.4 introduced the existence of two more species, $[VO(H_2PO_4)]^+$ and $[VO(H_2PO_4)_2]$, which dissociate with pK_a values of 3–4 to $[VO(HPO_4)]$ and $[VO(H_2PO_4)(HPO_4)]^-$, respectively [3]. However, the formation of precipitates hindered the investigation of the system in neutral and basic solution.

We wish to report spectral evidence which complements the above results and provides evidence of further species involving four-membered orthophosphate chelation in basic solution.

The only EPR data available in the literature on the VO(IV)–phosphate system in aqueous solution indicate complexation at pH 2, as suggested by the decrease of the ^{51}V isotropic hyperfine coupling constant from 11.6 mT, typical for the aquaion, to 11.3 mT [3].

Experimental

NaH_2PO_4 and $VOSO_4 \cdot 3H_2O$ were Aldrich products. Aqueous solutions of VO^{2+} 2.4×10^{-2} M and $H_2PO_4^-$ at varying molar ratios were examined as a function of pH. X-band EPR spectra were recorded as either isotropic spectra at room temperature or frozen-solution spectra at 120 K with a Varian E 9 spectrometer. DMSO was used to ensure good glass formation in frozen solutions. Electronic spectra in solution were taken with a Uvidec Jasco 610 instrument, whereas those on solid samples were recorded with a Beckman Acta MIV spectrophotometer using the reflectance technique. IR spectra were recorded with a FT Bruker IFS-66 interferometer.

Results and discussion

The isotropic EPR spectra of a solution of 2.4×10^{-2} M VO^{2+} and $H_2PO_4^-$ at the ligand-to-metal molar ratio of 20:1 are presented in Fig 1. Below pH 2.5 the spectra are very similar to those of the aquaion even if the increase of linewidth is supportive of metal ion complexation. A detectable and continuous decrease of the ^{51}V coupling constant, as compared to that of $[VO(H_2O)_5]^{2+}$ (106×10^{-4} cm^{-1}), is observed over the pH range 2.5–4.5 (104×10^{-4} cm^{-1} at pH 2.7 and 102×10^{-4} cm^{-1} at pH 4.5, with $g_0 \sim 1.964$). Simultaneously, the electronic spectra exhibit a low-energy shift of the absorption maxima typical of the aquaion, 650 and 770 nm, to 660 and 810 nm, respectively.

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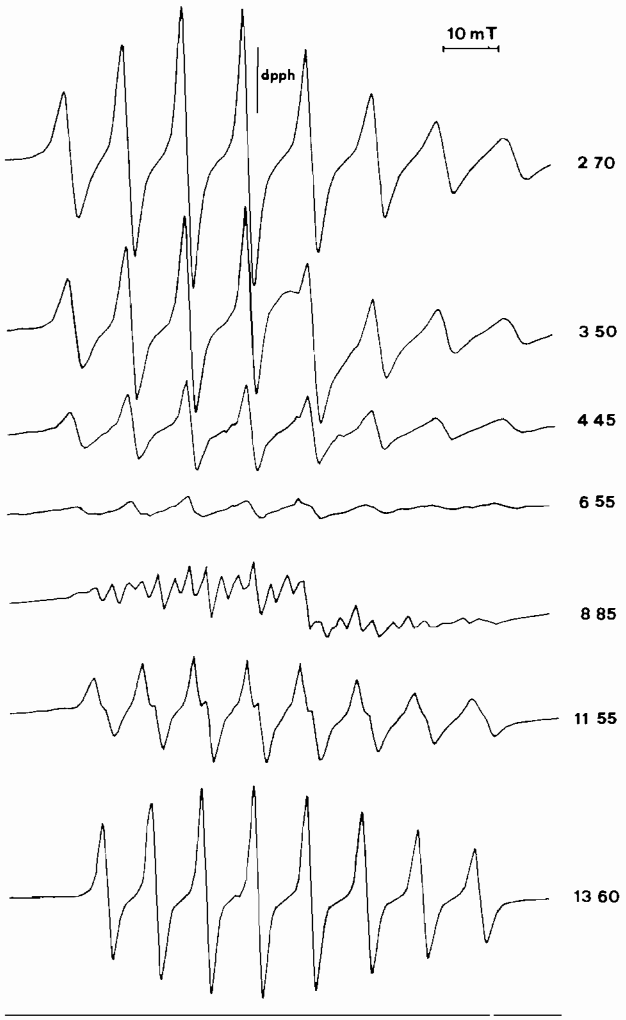

Fig. 1. Isotropic X-band EPR spectra recorded at room temperature on the VO(IV)–$H_2PO_4^-$ system, $c_{VO(IV)} = 2.4 \times 10^{-2}$ M, ligand-to-metal molar ratio = 20:1, as a function of pH

The results can be interpreted in terms of monodentate coordination of dihydrogenphosphato and monohydrogenphosphato below pH 4.5, even if an unambiguous discrimination between the different complexes is not possible on the basis of EPR spectroscopy. Over the pH range 4.5–8.5 precipitation occurs which depletes the solution of most of the vanadium ions. Accordingly, only weak EPR signals are observed at room temperature. IR analysis of the precipitates obtained at different pH values showed that all of them contained VO^{2+} and orthophosphate. The latter one was indicated by an intense absorption centred around 1026–1065 cm^{-1} and two weaker bands in the ranges 532–535 and 673–679 cm^{-1}. These features are characteristic of the ν_3 and ν_4 IR-active modes in the limit of a PO_4^{3-} ion in tetrahedral symmetry, the wavenumber values being close to those of alkali-metal orthophosphates [6]. The difference in the IR absorptions of the precipitates obtained over the pH range 5–8 are likely due to different crystalline forms or to the presence of basic phosphates in the samples obtained at higher pH values.

The precipitates may be re-dissolved in more basic solution (pH > 8). In these conditions, a VO(IV) phosphate complex is detected in the solution with a well-defined EPR spectrum consisting of eight hyperfine lines characteristic of the vanadium nucleus each of them split into three components with an intensity ratio of 1:2:1 arising from the interaction with two equivalent ^{31}P atoms, $A_0(^{51}V) = 82 \times 10^{-4}$ cm^{-1}; $A_0(^{31}P) = 28 \times 10^{-4}$ cm^{-1}, $g_0 = 1.971$. The electronic spectra exhibit an absorption band at 595 nm and another one above 850 nm, which are comparable to those observed on the solid VO(IV) phosphate complex obtained at pH 8 (590 and 880 nm). Further increase in pH (> 11) leads to the detection of another species which exhibits only one ^{31}P superhyperfine interaction, $A_0(^{51}V) = 89 \times 10^{-4}$ cm^{-1}, $A_0(^{31}P) = 21 \times 10^{-4}$ cm^{-1} and $g_0 = 1.968$, and is characterised by a shoulder at 560 nm and a band above 850 nm in the absorption spectra. Finally, above pH 12, the complexes undergo complete hydrolysis to $[VO(OH)_3]^-$ which is EPR detectable.

Complementary information was provided by examination of frozen solution EPR spectra recorded on the same system as that described above (Fig. 2). In this case, the increase of pH produced a small decrease (179×10^{-4} and 178×10^{-4} cm^{-1} at pH 3.0 and 5.1, respectively) in the ^{51}V parallel coupling constant whereas the $g_\parallel$ values were ~1.932. These spectral features can be taken as distinctive of VO(IV)–$H_2PO_4^-$ and –HPO_4^{2-} coordination. Simultaneously, over the pH range 3.5–11, besides magnetically dilute, coupled species were also detected, as indicated by broad resonances centred at $g \sim 2$. As is usual, these are due to polynuclear species with hydroxo bridging between metal ions. The presence of these broad EPR absorptions hindered a clear resolution of the ^{51}V and ^{31}P couplings in the monomeric species existing between pH 8 and 11. However, splittings of ~5 mT were observed. Instead, above pH 11, the monomeric species with vanadium coupling to only one ^{31}P nucleus exhibited a well resolved spectrum with $g_\parallel = 1.946$, $A_\parallel(^{51}V) = 166 \times 10^{-4}$ cm^{-1} and $A_\parallel(^{31}P) = 18 \times 10^{-4}$ cm^{-1}. Finally, the anisotropic spectrum of $[VO(OH)_3]^-$ is observed.

The results of this spectral study demonstrate clearly that, below pH 5, VO(IV)–hydrogenphosphate complexes are formed wherein the metal ion is likely monodentately coordinated to $H_2PO_4^-$ and/or HPO_4^{2-}. Due to the weakness of the ligands, these species exhibit EPR parameters only slightly different from those of the aquaion, whereas electronic spectra are more supportive of metal coordination. The complete deprotonation of the ligand above pH 5 is supported by the

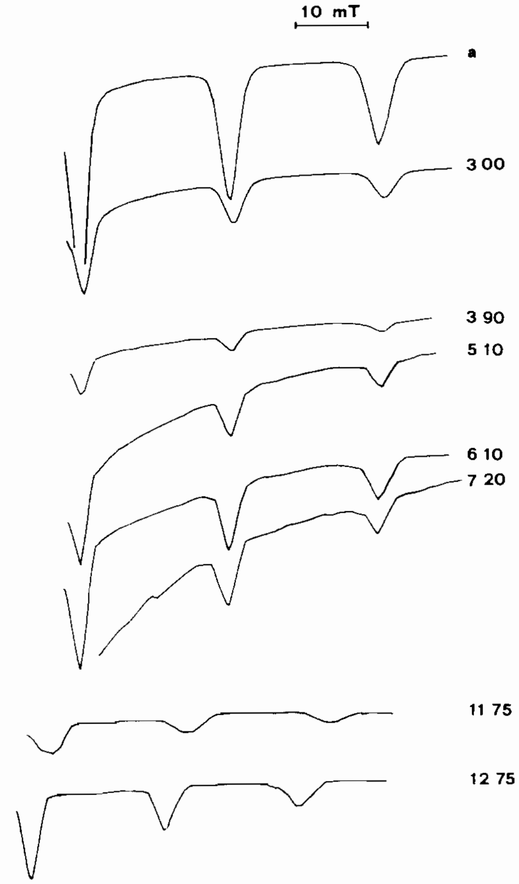

Fig 2 High-field parallel region of frozen-solution X-band EPR spectra recorded at 120 K on the VO(IV)-$H_2PO_4^-$ system, $c_{VO(IV)}=2.4\times10^{-2}$ M, ligand-to-metal molar ratio=20 1, as a function of pH. Spectrum a is that of $[VO(H_2O)_5]^{2+}$

isolation of solid complexes containing orthophosphate. These are re-dissolved in more basic solutions and in these conditions, polynuclear hydroxo-bridged species and a mononuclear bis-orthophosphate VO(IV) complex are detected. The latter one is substantiated by the detectable ^{31}P magnetic interaction with two phosphorus atoms Noticeably, the magnitude of this splitting is typical for VO(IV) complexes of phosphorus ligands, e.g. dithiophosphinates and dithiophosphates [7, 8], carrying coordination units involving four-membered chelated structures. Therefore, the ^{31}P splitting is indicative of bidentate chelation of orthophosphate to oxovanadium(IV).

The species showing interaction with only one phosphorus atom is likely the complex where the metal ion is chelated by a phosphate group and bound also to two terminal hydroxo groups. Accordingly, its $A_{\parallel}$ value is lower than that of the monochelated complex of catecholato(2−) [9], confirming the presence of at least two strong donors, e.g. two hydroxyls, in the metal coordination environment.

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