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Epr Spectra of α-1,2,3-[H$_n$PV(IV)V$_2$W$_9$O$_{40}$]$^{(7-n)-}$(n = 1,2 or 3). The Effects of Protonation on the Electron Transfer Rate

Chul Wee Lee and Hyunsoo So*

Department of Chemistry, Sogang University, Seoul 121

Kyu Ryong Lee

Department of Premedical Science, Hallym University, Chuncheon 200, Received October 12, 1985

The solution epr spectra of α-1,2,3-[H$_n$PV(IV)V$_2$W$_9$O$_{40}$]$^{(7-n)-}$ were measured at various pH and three protonated species have been identified. The spectrum of H$_3$PV(IV)V$_2$ consisting of 8 lines indicates that the V–OH–V bridge prevents effectively the electron transfer between the vanadium atoms. The spectrum of H$_2$PV(IV)V$_2$ consisting of 15 lines can be interpreted by assuming that the electron is hopping fast between the two vanadium atoms in the V–O–V sequence. The multi-line spectrum of HPV(IV)V$_2$ is interpreted as a poorly resolved 43–line spectrum which originates from the electron hopping among the three vanadium atoms with the forward and backward transition probabilities of 4:1 in the OH-V–O–V sequence.

Introduction

In our previous epr study[1] we noted that a species in which the unpaired electron interacted with two vanadium nuclei only could be separated from one–electron reduction products of [PV$_3$W$_9$O$_{40}$]$^{6-}$. In order to identify this species we have measured epr spectra of [PV(IV)V$_2$W$_9$O$_{40}$]$^{7-}$ at various pH and obtained evidence that a protonated species [H$_2$PV(IV)V$_2$W$_9$O$_{40}$]$^{5-}$ shows a 15–line spectrum similar to that of [PV(IV)VW$_{10}$O$_{40}$]$^{6-}$.

The effect of protonation on epr spectra of mixed valence heteropoly anions was first reported by Pope *et al.*,[2,3] who investigated the epr spectra of [SiV(IV)VW$_{10}$O$_{40}$]$^{7-}$ and [P$_2$V(IV) V$_2$W$_{15}$O$_{62}$]$^{10-}$. The solution epr spectrum[4] of SiV(IV)V consisting of more than 40 equally spaced hyperfine lines was ascribed to a protonated species [HSiV(IV)VW$_{10}$O$_{40}$]$^{6-}$. The spectrum could be interpreted by assuming that it was split into eight equally intense lines(a_1 = 68G) by one vanadium nucleus(I = 7/2) and each line was split into 15 lines(a_2 = 17G) with relative intensities 1:2:3...8...1 by the two equivalent vanadium nuclei. It was suggested that the unpaired electron is trapped on one vanadium atom but delocalized by about 17% on each of the other two.

The solution epr spectrum of P$_2$V(IV)V$_2$ at pH 11 consists of 22 equally spaced lines, indicating that the unpaired electron interacts equally with the three equivalent vanadium atoms.[3] This spectrum was ascribed to the unprotonated species. On the other hand, the spectrum at pH 4.7 shows 36 lines and it was ascribed to a protonated species, [HP$_2$V(IV) V$_2$W$_{15}$O$_{62}$]$^{9-}$. This spectrum could be interpreted by assuming that it was split into eight lines(a_1 = 63G) and each line was again split into 15 lines(a_2 = 21G). It was suggested that the electron transfer through the V-OH-V bridge is much slower than through V-O-V.

In this paper we present the solution epr spectra of [H$_n$PV(IV)V$_2$W$_9$O$_{40}$]$^{(7-n)-}$(n = 1,2 or 3) and discuss the effect of protonation on the electron transfer rate in this mixed valence complex.

Experimental Section

Preparation of Compounds. α-1,2,3-K$_6$[PV$_3$W$_9$O$_{40}$] was prepared according to the method of Domaille.[5] An aqueous solution of this compound at a desired pH was reduced to one-electron reduction state by adding hydrazine dihydrochloride. The pH of the solution was adjusted by adding hydrochloric acid or potassium hydroxide.

**Epr Measurements.** Epr spectra were recorded on a

Bruker epr spectrometer (Model ER 200E) operating at 9.7 GHz. The microwave frequency was measured by a Hewlett-Packard frequency counter and DPPH was used as a g-marker. All spectra were recorded at room temperature.

Results and Discussion

The solution epr spectrum at pH 2.0 is an 8-line spectrum($g = 1.967$, $a = 104.3 \times 10^{-4}$ cm^{-1}) typical of a mononuclear vanadyl species(I = 7/2); see Figure 1. As the pH is raised, this spectrum is maintained until pH 3.0 with another series of lines growing between the hyperfine lines.

At pH 3.6 the spectrum looks completely different and quite complicated; see Figure 2. It consists of a series of lines with a hyperfine splitting of 18G and the lines are grouped in triplet-like sets. At a higher pH the triplet-like pattern diminishes, while the hyperfine splitting of 18G remains unchanged. At pH 4.0-9.0 the spectrum is essentially the same; see Figure 3 for a typical spectrum. Above pH 9 the complex was not so stable as an epr spectrum could be recorded.

In order to interpret the epr spectra in terms of the protonated species, we represent the heteropoly anion structures by the following abbreviated forms.[3]
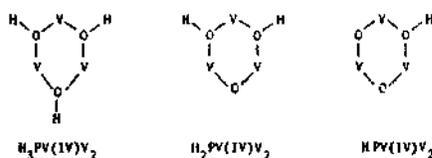
The 8-line spectrum at low pH shows that the unpaired electron is trapped[6] on one vanadium atom. Since the rapid electron transfer through the V–O–V bridge is well established,[3] this spectrum must originate from H₃PV(IV)V₂ in which the V–OH–V bridges effectively prevent electron transfer among the vanadium atoms.

The spectrum at high pH (4.0-9.0) is similar to that of HSiV(IV)V₂, although the outer parts of our room temperature spectrum are not so well resolved as the reported spectrum measured at 80°C. Thus the spectrum may be interpreted in the same way as described in the introduction section. The positions of the hyperfine lines could be calculated by using the following equation:

$$h\nu = g\beta B + \sum_{i=1}^{2}\{a_i m_i + \frac{a_i^2}{2h\nu}(I_i(I_i+1)-m_i^2)\}   \qquad (1)$$

where $I_1 = 7/2$, $I_2 = 7$, and $m_i = I_i, I_i-1,...,-I_i$. We could simulate the central portion of the spectrum using $g = 1.957$, $a_1 = 65.2 \times 10^{-4}$cm^{-1}, $a_2 = 16.3 \times 10^{-4}$cm^{-1}, and a line width[7]
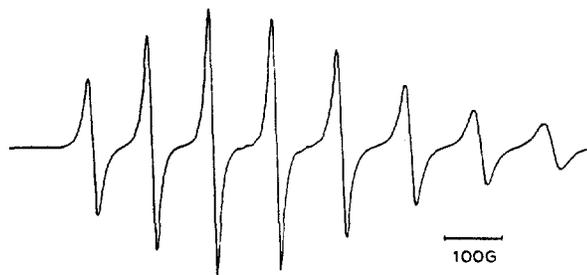
Figure 1. Epr spectrum of α-1,2,3-[H₃PV(IV)V₂W₉O₄₀]⁴⁻ in aqueous solution, pH 2 at room temperature.

$w = 6G$. This simulation produces a total of 43 lines, of which only about half were resolved in the room temperature spectrum. In order to simulate the broad, outer parts of the spectrum, one has to consider the line width variation due to anisotropic hyperfine interactions and other effects. Although we could not simulate the intensity distribution correctly, we feel it safe to ascribe the spectrum to the monoprotonated species, HPV(IV)V₂.

The triplet-like pattern of the spectrum at pH 3.6 could be simulated by combining a 43-line spectrum with a 15-line spectrum[1] similar to that of [PV(IV)VW₁₀O₄₀]⁶⁻. Here again the broad, outer parts of the spectrum cannot be simulated by using the same line width for all hyperfine lines in each component. However, when the experimental spectrum in Figure 3 was mixed with a 15-line spectrum ($g = 1.958$, $a_1 = a_2 = 47 \times 10^{-4}$cm^{-1}, $w = 20G$),[8] a spectrum similar to that in Figure 2 was generated; see Figure 4. The 15-line spectrum was calculated by using Eq.(1) with $I_1 = I_2 = 7/2$.

The species responsible for the 15-line spectrum must be the diprotonated species, [H₂PV(IV)V₂W₉O₄₀]⁵⁻. In this species the electron can be either trapped on the vanadium atom of the OH–V–OH group or interacting with the two vanadium atoms of the V–O–V sequence. If the electron were trapped on one vanadium atom, an 8-line spectrum would be observed. There is no indication that such a species coexists with the species showing the 15-line spectrum.

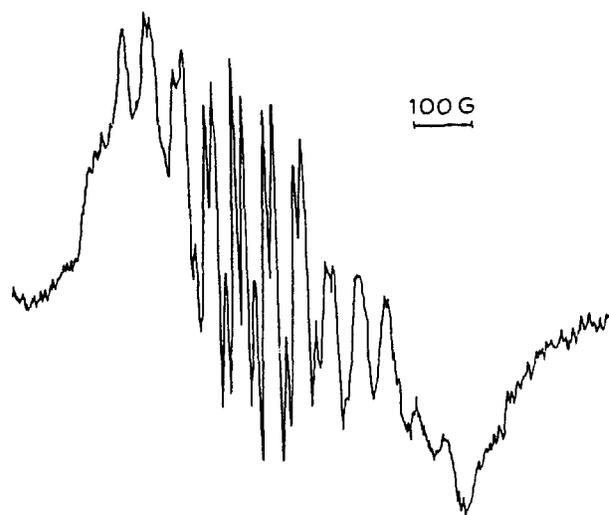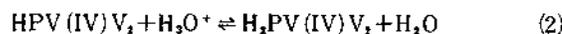The composite spectrum in Figure 2 indicates that two protonated species are in equilibrium at pH 3.6.

$$HPV(IV)V_2 + H_3O^+ \rightleftharpoons H_2PV(IV)V_2 + H_2O   \qquad (2)$$

Figure 2. Epr spectrum of a mixture of α-1,2,3-[H₂PV(IV)V₂W₉O₄₀]⁵⁻ and α-1,2,3-[HPV(IV)V₂W₉O₄₀]⁶⁻ in aqueous solution, pH 3.6 at room temperature.
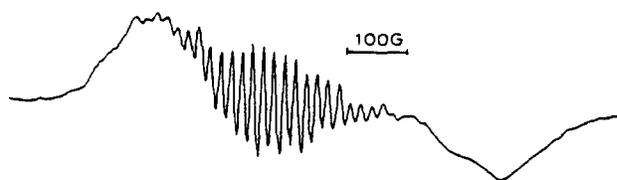

Figure 3. Epr spectrum of α-1,2,3-[HPV(IV)V₂W₉O₄₀]⁶⁻ in aqueous solution, pH 5.5 at room temperature.
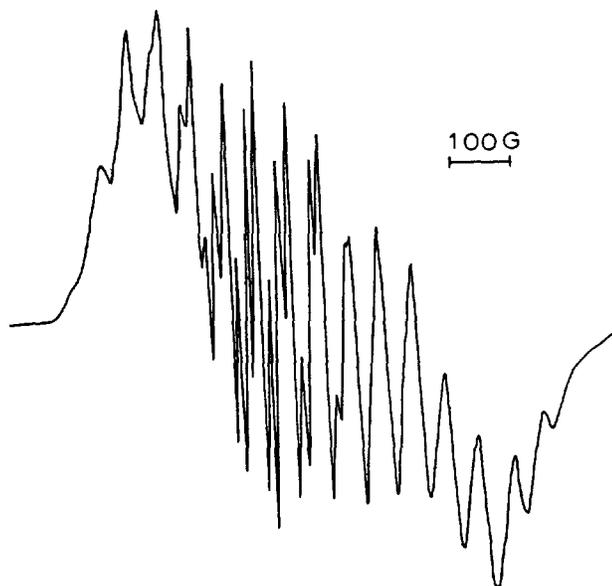
Figure 4. Simulation of the spectrum in Figure 2 obtained by mixing the spectrum in Figure 3 and a 15-line spectrum. See the text.

If the rate of protonation is assumed to be diffusion-controlled, the lifetime of HPV(IV)V$_2$ is 10^{-7}'s, which is long enough for the two protonated species to show two distinct epr spectra instead of an average spectrum.

In our previous epr study[1] we observed that H$_2$PV(IV)V$_2$ was selectively coprecipitated at pH 4.7 when K$_6$[HSiV$_3$W$_9$O$_{40}$][9] was added. This indicates that the precipitate was mainly K$_6$[H$_2$SiV$_3$W$_9$O$_{40}$], the anion of which had the same charge as H$_2$PV(IV)V$_2$.

Although we have not mentioned specifically how the unpaired electron interacts with more than one vanadium nucleus, Eq.(1) is based on a delocalization model. Here the isotropic hyperfine coupling constant is a measure of the unpaired electron density on the given vanadium atom. The hyperfine coupling constants are summarized below:
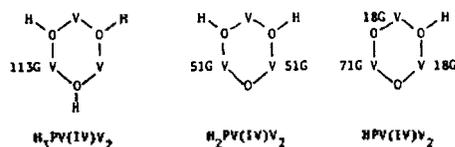
It is noted that the sums of hyperfine coupling constants are approximately the same for all species.

However, the fact that the unpaired electron in HP$_2$V(IV)V$_2$ is trapped on one vanadium atom at 77K suggests that the electron is hopping fast among the vanadium atoms at room temperature.[3] The "hopping electron" model can also explain both the 15- and 43-line spectra. If the electron is hopping

between two equivalent vanadium atoms of the V–O–V sequence, the hyperfine line will appear at the average magnetic field of the two hyperfine lines expected for the two uncoupled vanadium atoms. The average lines will constitute a 15-line spectrum with relative intensities 1:2:3...8...1.

There are two sets of non-equivalent vanadium atoms in HPV(IV)V$_2$. If the position of a hyperfine line expected for V$_i$ in the absence of electron transfer is represented by B$_i$, and the transition probability from V$_i$ to V$_j$ by P$_{ij}$, the average magnetic field in the presence of electron transfer in the OH–V$_a$–O–V$_b$–O–V$_c$–OH sequence is given by the following equation:

$$B_{avg} = \frac{B_a P_{ba} + B_b P_{ab} + B_c P_{ba}}{2P_{ba} + P_{ab}} \tag{3}$$

A 43-line spectrum can be obtained when the ratio of P$_{ab}$ and P$_{ba}$ is 4:1 and the electron transfer rate through the V–OH–V bridge is negligible on the epr time scale.

Concluding Remarks

In this work we have identified three protonated species, H$_3$PV(IV)V$_2$, H$_2$PV(IV)V$_2$, and HPV(IV)V$_2$ by their epr spectra. If we can simulate the composite spectra accurately, we shall be able to measure the concentration of each species existing in equilibrium with other species and determine formation constants of these protonated species.

Accurate simulation of the spectra will also make it possible to decide which model is correct, since the calculated spectra based on the delocalization model and the hopping electron model may give somewhat different intensity distributions.

References and Notes

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3. S.P. Harmalker, M.A. Leparulo, and M.T. Pope, *J. Am. Chem. Soc.,* **105**, 4286 (1983).
4. When there is no confusion, tungsten and oxygen have been omitted from the chemical formula of the complexes.
5. P.J. Domaille, *J. Am. Chem. Soc.,* **105**, 4286 (1983).
6. "Trapped" here means the electron transfer rate is much smaller than the hyperfine coupling constant, $10^8 s^{-1}$.
7. This is the line width at half maximum absorption.
8. This line width was obtained from the spectrum of [PV(IV)VW$_{10}$O$_{40}$]$^{6-}$; see the reference 1.
9. When this complex is recrystallized from a hot, pH 1.5 water/methanol solution, K$_4$[H$_3$SiV$_3$W$_9$O$_{40}$]·3H$_2$O is obtained. (Private communications with R.G. Finke and B. Rapko)