

EPR investigations of electron transfer in one-electron reduced **a**-1,4 K₅[PV₂W₁₀O₄₀].3H₂O

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Abstract. Heteropoly blues of **a**-1,2 and **a**-1,4 isomers of [PV₂W₁₀O₄₀]⁵⁻ have been prepared by using the electrochemical technique. EPR spectra, measured as a function of temperature over a wide range (20–300 K), are explicable in terms of electron-hopping processes in heteropoly blues. Temperature dependence of A₀ of the isomers suggest that the activation energy for electron hopping is greater for the **a**-1,4 isomer than the **a**-1,2 isomer. Other parameters like stability of the blues and intra-molecular electron transfer rate constants are also evaluated using EPR as the tool.

Keywords. **a**-1,4 isomer; **a**-1,2 isomer; heteropoly blues.

1. Introduction

In the vast field of heteropolyanion chemistry, greater attention has been focussed on exploiting the catalytic and photocatalytic utility of the Keggin-type heteropoly tungstates and molybdates^{1–7}. These applications are based on the ability of the polyanions to undergo multi-electron redox processes without any modifications in their structures^{8,9}. Among the Keggin-type heteropolyanions, vanadium-substituted mixed addenda heteropoly tungstates and molybdates have qualified as better catalysts for many reactions^{10–16}. Increased interest in these compounds is also due to the fact that the reduced form of these heteropolyanions, known as heteropoly blues, exhibit mixed-valence behaviour similar to class-II type compounds of the Robin and Day scheme¹⁷.

Mixed-valence heteropoly blues with adjacent V(IV)/V(V) centres are convenient systems for studying the intra-molecular electron transfer processes¹⁸. These heteropoly blues have been studied by EPR spectroscopy¹⁹ to get information about their electronic structures, viz., the nature of ground state delocalisation and the mobility of the unpaired electron. Analysis of the *g* and *A* tensors has given important informations about electron delocalisation processes in these heteropoly blues. Heteropoly blues of vanadium-substituted heteropoly tungstates and molybdates have been generally prepared either by electrochemical^{20–22} or by chemical methods^{16,23}. Here, one-electron reduced isomers of Keggin-type polyoxometalates, viz., **a**1,2-K₅[PV₂W₁₀O₄₀].3H₂O and **a**1,4-

*For correspondence

$K_5[PV_2W_{10}O_{40}].3H_2O$ (hereafter referred to as **a1,2** V_2W_{10} and **a1,4** V_2W_{10}) have been prepared by the electrochemical method. **a1,2** V_2W_{10} has been studied in detail. Nevertheless there is no such study on the **a1,4** isomer. Hence in this paper we report a comparative study of **a1,2** and **a1,4** isomers of V_2W_{10} .

2. Experimental

2.1 Materials

Sodium vanadate, sodium tungstate and di-sodium hydrogen phosphate were obtained from Qualigens Fine Chemicals, India. All the chemicals were of AR grade and were used without further purification.

The isomers **a1,2** V_2W_{10} and **a1,4** V_2W_{10} were prepared according to the literature method²⁴. The reduced form of the anions were prepared by controlled potential electrolysis using a CV-27 potentiostat (Bioanalytical System). The cell consisted of a working electrode of graphite packed inside a porous Vycor glass tube (5 mm dia), through which the test solutions were pumped. An outer glass cylinder contained the platinum auxiliary electrode and a Ag/AgCl reference electrode. Typically 0.9975 g of the **a1,2** isomer was dissolved in 10 ml acetate buffer of pH 5 and then reduced (one-electron reduction) by passing 32.21 C of electricity. Similar procedure was adopted for the reduction of **a1,4** isomer also.

2.2 Analytical and physical measurements

Tungsten was estimated by gravimetric method by precipitating as oxinates²⁵. Phosphorus was estimated by gravimetric method by precipitating phosphate as magnesium pyrophosphate. Vanadium was estimated by a spectrophotometric method as the citrate complex²⁵.

X-band EPR spectra were recorded on a Varian E 112 spectrometer equipped with 100 kHz field modulation. DPPH was used as an internal field marker. Spectra at 77 K were recorded by immersing the sample in liquid nitrogen present in a quartz Dewar, whose tail fitted into the EPR cavity.

3. Results and discussion

3.1 Electron paramagnetic resonance

The X-band EPR spectra of **a1,2** V_2W_{10} and **a1,4** V_2W_{10} isomers in aqueous acetate buffer show the expected hyperfine interaction with the ^{51}V nuclei. The spin Hamiltonian parameters are extracted from the EPR spectra using the axially symmetric spin Hamiltonian²⁶,

$$= g_{\parallel} \mathbf{H} S_z + g_{\perp} \mathbf{H} (S_x + S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y). \quad (1)$$

3.2 EPR investigations of electrochemically generated heteropoly blues

3.2a *Heteropoly blues of **a1,2** $[PV_2W_{10}O_{40}]^{5-}$ and **a1,4** $[PV_2W_{10}O_{40}]^{5-}$* : EPR spectroscopy has been used to identify different isomers of Keggin anion. The **a b g** and

120°). It has also been suggested that a large M–O–M bond angle in the corner-shared species may increase the $d-p-d$ π interaction, which in turn lowers the activation energy for electron hopping. Variable temperature EPR spectroscopy has been used to examine electron delocalisation and hopping pathways in one-electron reduced tungstovanadophosphates.

3.2b *Stability of reduced species:* X-band, 300 K EPR spectra of one-electron reduced ($pH = 5.0$) $\mathbf{a}1,2$ V_2W_{10} and $\mathbf{a}1,4$ V_2W_{10} are shown in figures 1a and 2a. The spectra consist of 15 lines arising from the interaction unpaired electron with two ^{51}V nuclei. The 15 line spectrum can be readily analysed using the expression ²⁶.

$$h\nu = g\beta B + am + a^2/2(h\nu) [I(I+1) - m^2]. \quad (2)$$

Second-order corrections were made to derive the parameters g and a from the experimental spectra. The second-order corrected lines may be readily related to the experimental lines by working out the magnitude of the second-order shifts to each

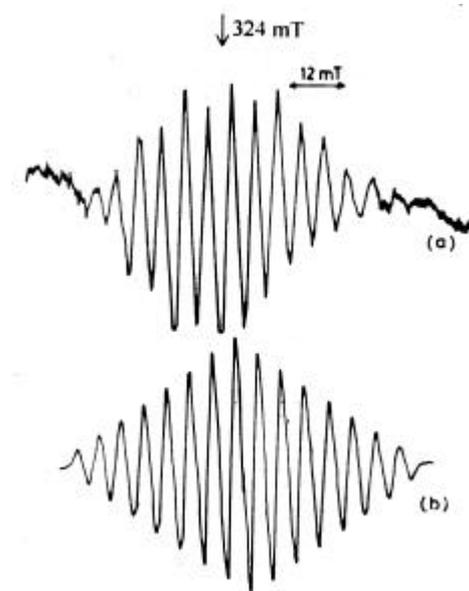


Figure 1. Experimental (a) and simulated (b) X-band 300 K EPR spectra of $\mathbf{a}1,2$ $[PV^{IV}VW_{10}O_{40}]^{5-}$ in aqueous acetate buffer, pH 5. The g_{iso} and a_{iso} values used for the simulation are listed in table 1.

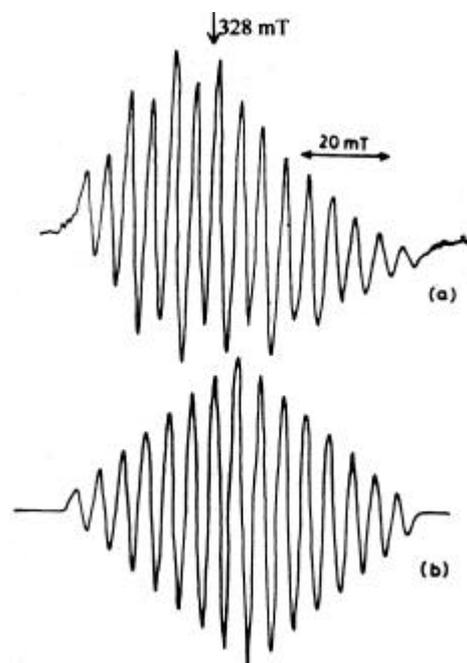


Figure 2. Experimental (a) and simulated (b) X-band 300 K EPR spectra of **a**-1,4 $[\text{PV}^{\text{IV}}\text{VW}_{10}\text{O}_{40}]^{5-}$ in aqueous acetate buffer, pH 5. The g_{iso} and a_{iso} values used for the simulation are listed in table 1.

Table 1. EPR parameters of **a**-1,2 and **a**-1,4 isomers of $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$.

| a -1,2 Isomer | | | a -1,4 Isomer | | |
|----------------------|--|---------------|----------------------|--|---------------|
| Temp. (K) | * A_{\parallel} | * A_{\perp} | Temp. (K) | * A_{\parallel} | * A_{\perp} |
| 300 | $g_{\text{iso}} = 1.963$ $*a_{\text{iso}} = 51.5$ | | 300 | $g_{\text{iso}} = 1.952$ $*a_{\text{iso}} = 46.9$ | |
| 120 | 136.2 | 51.5 | 99.5 | 91.6 | 49.5 |
| 102 | 160.3 | 51.7 | 50 | 122.8 | 50.0 |
| 75 | 163.8 | 54.2 | 30 | 147.9 | 53.1 |
| 60 | 170.6 | 56.0 | 20 | 165.2 | 57.1 |
| 20 | 181.1 | 60.4 | | | |

*In 10^{-4} cm^{-1}

line²⁹. Using the g and a_{iso} values obtained after the second-order correction, the experimental spectra could be readily simulated. The computer simulated spectra are given in figures 1b and 2b. The EPR parameters used for the simulation are given in table 1.

The **a**1,2 isomer is found to be stable³⁰ between pH 3 and 5. To compare the stability of the **a**1,4 isomer with that of the **a**1,2 isomer, EPR spectra of **a**1,4 isomer were recorded at different pH values. It is found that **a**1,4 isomer is also stable between pH 3 and 5. The stability is seen by similar EPR spectrum in this spectral region. When the pH

is reduced to below 3, the one-electron reduced **a**-1,4 isomer undergoes decomposition. For example, EPR spectra of both the isomers recorded in aqueous acetate buffer at pH 2 are shown in figures 3 and 4. These spectra consists of 8- and 15-line components. The features indicated by '•' are greater in intensity and they correspond to $g_{\text{iso}} = 1.965$, $a_{\text{iso}} = 105 \times 10^{-4} \text{ cm}^{-1}$ for the **a**-1,4 isomer and $g_{\text{iso}} = 1.962$, $a_{\text{iso}} = 105.9 \times 10^{-4} \text{ cm}^{-1}$ for the **a**-1,2 isomer. These values are comparable with those of VO^{2+} ions¹⁹, indicating the decomposition of the polyoxometalate framework.

3.2c *Variable temperature EPR spectra:* As mentioned earlier, in order to compare the behaviour of both **a**-1,2 and **a**-1,4 isomers, variable temperature EPR spectra were recorded. Typical EPR spectra of **a**-1,2 and **a**-1,4 isomers are shown in figures 5 and 6. The derived g and a values are given in table 1. At low temperatures, the EPR spectra

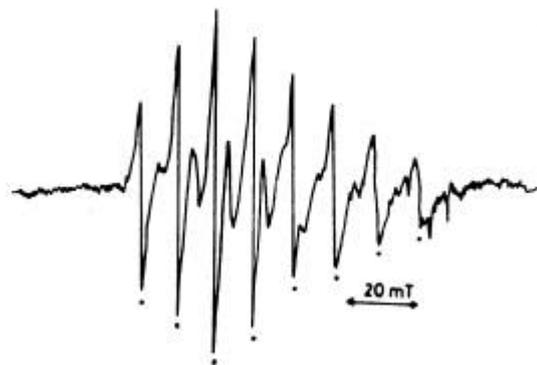


Figure 3. X-band 300 K EPR spectrum of **a**-1,2 $[\text{PV}^{\text{IV}}\text{VW}_{10}\text{O}_{40}]^{5-}$ in aqueous acetate buffer, pH 2. One of the products is indicated by •.

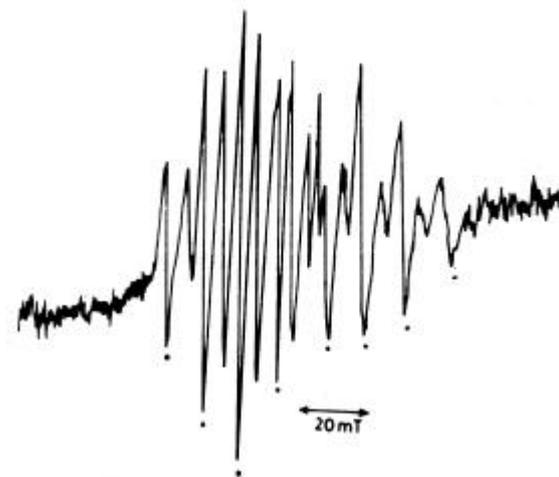


Figure 4. X-band 300 K EPR spectrum of **a**-1,4 $[\text{PV}^{\text{IV}}\text{VW}_{10}\text{O}_{40}]^{5-}$ in aqueous acetate buffer, pH 2. One of the products is indicated by •.

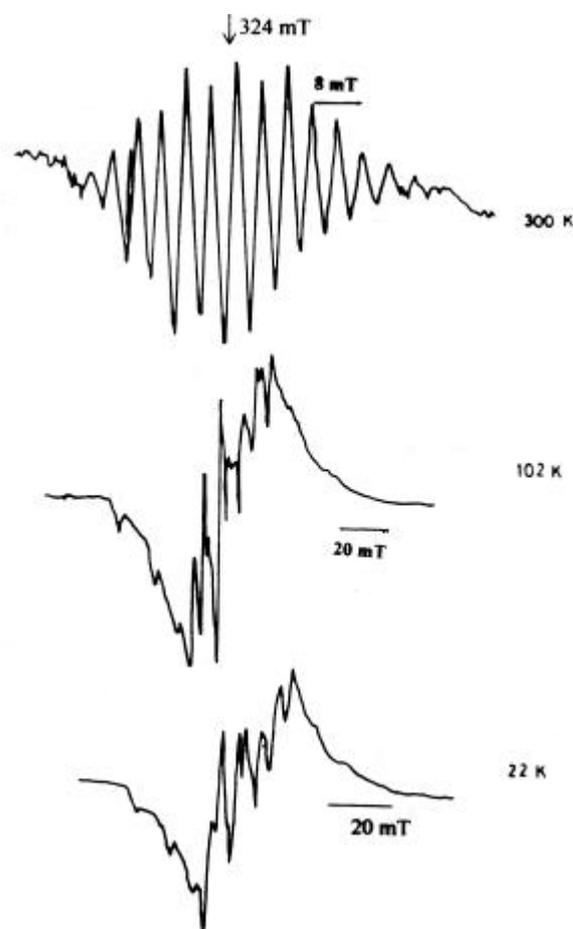


Figure 5. Temperature variation EPR spectra of **a**-1,2 [PV^{IV}VW₁₀O₄₀]⁵⁻ in aqueous acetate buffer, pH 5.

showed gradual coalescence to normal anisotropic forms typical of mononuclear vanadium (IV) with broader lines. The appearance of broader lines may be due to the partial delocalisation of the trapped electron with the neighbouring vanadium (IV) atoms.

In the literature, extent of delocalisation has been evaluated from the intra-molecular electron transfer rate constants³¹. Mono-, di- and tri-vanadium substituted **a** [P₂(W,V)₁₈O₆₂]ⁿ⁻ have been differentiated using intramolecular electron transfer rate constants³¹. Intramolecular electron transfer rate constants can be calculated using the equation³¹,

$$k = (3)^{1/2} \rho g \beta h \Delta B e \text{ s}^{-1}, \quad (3)$$

where $\Delta B e$ is the contribution to the EPR linewidth from the exchange process. The value of $\Delta B e$ used for the calculation has been obtained by subtracting the estimated linewidth under the conditions of no exchange, ΔB_0 ³¹. The estimated linewidth, 15G has been used

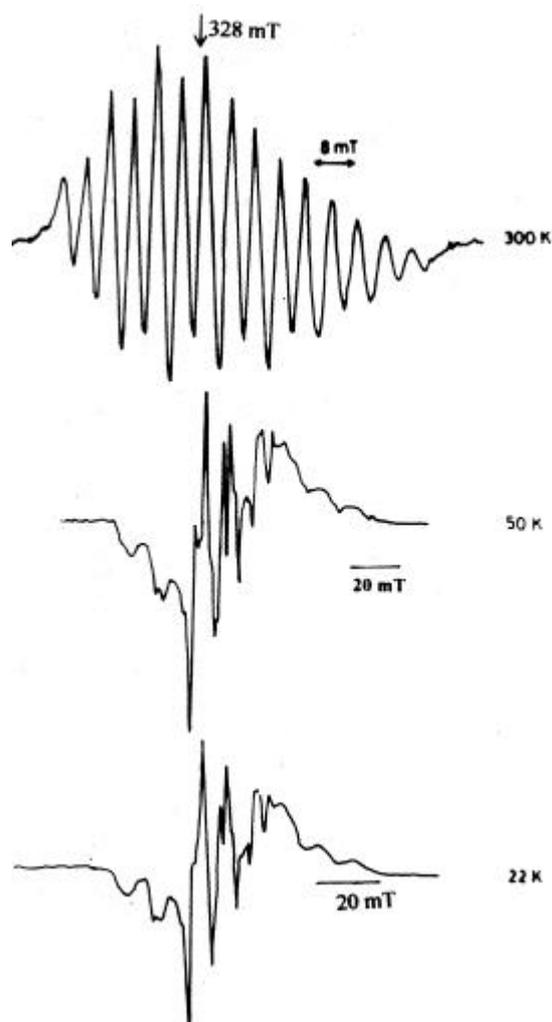


Figure 6. Temperature variation EPR spectra of **a-1**, $[\text{PV}^{\text{IV}}\text{VW}_{10}\text{O}_{40}]^{5-}$ in aqueous acetate buffer, pH 5.

to calculate value of ΔBe^{31} . Using a similar approach the rate constants are evaluated to be $3.23 \times 10^8 \text{ s}^{-1}$ and $1.62 \times 10^8 \text{ s}^{-1}$ for **a1,2** and **a1,4** isomers respectively. These results support the formulation that in corner-shared species (**a1,2** isomer) the *d-p-dp* interaction is enhanced and hence it shows faster electron hopping.

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