

³¹P Magnetic Resonance Study of Phosphate Exchange in Vanadyl Phosphate Complexes*

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Received June 6, 1975

The rate of loss of $H_2PO_4^-$ ligand from bis-dihydrogenphosphato oxovanadium(IV) was determined from analysis of broadening of the ³¹P magnetic resonance line of 1.0M NaH_2PO_4 solutions in the presence of vanadyl ion at pH 2.0. The aquation rate constant at 25° C was found to be $(2.5 \pm 0.3) \times 10^4 \text{ sec}^{-1}$ and the corresponding anation rate constant, estimated from the formation constant of the bis complex, was $2 \times 10^6 M^{-1} \text{ sec}^{-1}$.

The activation energy for the aquation process is 52 kJ/mol. The anation rate indicates that coordinated water in $VO(H_2PO_4)^+$ is much more labile than in the aquo complex. The linewidths of metal-free phosphate solutions at pH 2 were found to be linear in T/η and are thus apparently due to a spin-rotation interaction.

Introduction

In the absence of coordinating ligands, the oxovanadium(IV) or vanadyl ion exists in aqueous acidic solution as the pentaquo complex, $VO(H_2O)_5^{2+}$. Three very different lifetimes for the exchange of inner sphere ligands are observed for this species. The oxo ligand is very strongly bonded to the metal with an exchange lifetime on the order of seconds.¹ The axial water molecule, on the other hand, is extremely labile with an estimated lifetime of 10^{-11} sec .² The four equatorial water ligands have intermediate exchange lifetimes of about 1–2 msec.^{1–3}

Recent studies of ligand exchange on vanadyl ion have shown that replacement of equatorial coordinated water by anionic ligands results in a labilization of the remaining water molecules by two to three orders of

magnitude. This effect has been observed both for strong chelate complexes⁴ and for the very weak chloro complexes.¹ The effect is presumably due, at least in part, to quenching of the high effective charge on the vanadium atom.

We report here a study of the exchange of dihydrogen phosphate on vanadyl ion. The stability constants for the mono and bis complexes have been estimated and are reported in the preceding paper.⁵ The bis complex is the dominant species in 1M $H_2PO_4^-$ solutions at pH 2.

The ³¹P nucleus provides an nmr probe for studies of phosphate exchange processes. It was first exploited in an exploratory study of paramagnetic metal ions in H_3PO_4 solution,⁶ later in investigations of the interactions of paramagnetic cations with phosphate esters of biochemical interest⁷ and recently in a study of paramagnetic metal ions, including the vanadyl ion, in tributyl phosphate solution.⁸

Experimental

Sample Preparation

Stock solutions of vanadyl perchlorate were prepared as described previously.⁹ Phosphate stock solutions were prepared by dissolving 0.25 mol of Fisher $NaH_2PO_4 \cdot H_2O$ and 0.125 mol of perchloric acid in 250 ml of distilled water, followed by adjustment of the pH to 2.0 with a small amount of 4M NaOH solution. Solutions used for nmr measurements were prepared from the stock solutions and had a total phosphate concentration between 0.9 and 1.0M, an ionic strength of approximately 1.0M, and vanadyl ion concentrations in the range 0.65 mM to 6.5 mM.

Viscosity Measurements

The viscosity of a 1.0M phosphate solution was measured as a function of temperature with an Ostwald viscometer. Dust was removed by passing the solution through a sintered glass filter. The temperature was maintained within $\pm 0.2^\circ$. The density of the phosphate solution was 1.103 g/cm³ at 26° C. The experimental

* Taken in part from the Ph. D. Thesis of M. W. K., Brown University, 1973.

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data is represented to within about $\pm 0.5\%$ by the empirical equation

$$\log(\eta) = A + B\left(\frac{1}{T} - \frac{1}{298}\right) + C\left(\frac{1}{T} - \frac{1}{298}\right)^2 \quad (1)$$

where $A = -2.883$, $B = 888 \text{ K}$, $C = 3.2 \times 10^5 \text{ K}^2$ when η is expressed in $\text{kg m}^{-1} \text{ sec}^{-1}$, and the temperature is in the range $5\text{--}55^\circ \text{C}$.

Nmr Spectra

Phosphorus-31 magnetic resonance spectra were obtained with a modified Varian HA-60 spectrometer equipped with a 24.3 MHz probe. The 24.3 MHz signal was synthesized from a 15 MHz standard. A proton nmr "piggyback" probe was used to stabilize the magnetic field by locking the field to the water proton resonance at 60 MHz. The field was swept by varying the 60 MHz oscillator frequency. The system is more fully described by Kaufman.¹⁰ The spectra were recorded and calibrated in frequency units using the 100 Hz sidebands of 85% phosphoric acid. Typical field sweep reproducibility was $\pm 0.4\%$. Nmr samples were contained in spinning 5 mm ground glass tubes.

The temperature of the nmr samples was maintained with a Varian variable temperature accessory employing heated or cooled nitrogen gas. The temperature of the nmr sample was measured by replacing the nmr tube with an identical tube containing mineral oil and a copper-constantan thermocouple. Although care was taken to insulate the assembly with glass wool, temperature gradients of up to 3° were found over the length of the nmr tube. Thus the temperature in the vicinity of the r. f. coils was known at best to $\pm 1^\circ$.

Measurement of Linewidths

The nmr spectra obtained in most cases had relatively low signal-to-noise ratios so that direct measurement of the linewidths was difficult and subject to considerable error. To obtain the best possible estimate of the widths and a reasonably reliable estimate of the error, each spectrum was digitized, taking 30–100 points, and fitted, using a non-linear least-squares procedure,¹¹ to a Lorentzian line shape function,

$$G(\omega) = \alpha_1 + \frac{\alpha_2}{1 + \alpha_3^2(\omega - \alpha_4)^2}, \quad (2)$$

where the fitted parameters are α_1 , the y-axis offset of the baseline, α_2 , the amplitude, α_3 , the squared reciprocal of the linewidth, and α_4 , the position of the center of the line. After appropriate application of the field sweep calibration, the parameter α_3 can be identified as the square of the desired relaxation time T_2 . The details of the non-linear least-squares procedure are given elsewhere.¹²

As an example of the experimental data and the results obtained, Figure 1 shows the ^{31}P magnetic resonance spectra of 0.9M phosphate at pH 2.0 and

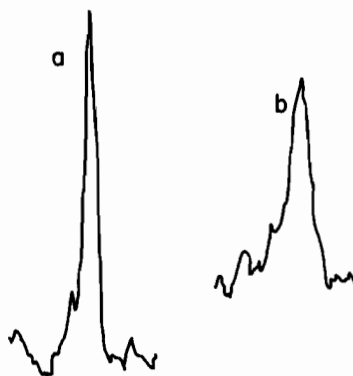


Figure 1. ^{31}P magnetic resonance spectrum of 0.90M phosphate at pH 2.0, 20°C ; (a) no added metal; (b) 0.65 mM vanadyl perchlorate.

20°C in the absence of metal and in the presence of 0.65 mM vanadium. Although the broadening on addition of the metal is certainly noticeable, direct measurement of the widths is obviously not easy or accurate. After digitization and least-squares analysis, the linewidth parameters for the two spectra were found to be $T_2^{-1} = 10 \pm 6$ and $34 \pm 6 \text{ sec}^{-1}$, respectively. Here and elsewhere in this paper, the quoted error limits are $\pm \sigma$ (standard deviation).

Results and Discussion

Theory

Solution of the modified Bloch equations for exchange of a nucleus between bulk solution and a dilute paramagnetic site yields for the transverse relaxation times:¹³

$$T_{2p}^{-1} = T_{2o}^{-1} + T_{2p}^{-1} \quad (3)$$

where

$$T_{2p}^{-1} = p_m \tau_m^{-1} \frac{T_{2m}^{-2} + (\tau_m T_{2m})^{-1} + \Delta\omega_m^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + \Delta\omega_m^2} \quad (4)$$

In eq (4), p_m is the probability of finding the nucleus at the paramagnetic site and τ_m is the average lifetime of the nucleus at that site; $\Delta\omega_m$ is the contact shift and T_{2m} is the transverse relaxation time of the nucleus at the paramagnetic site. Limiting cases may be obtained depending upon the relative magnitudes of the quantities in eq (4). When exchange is fast such that τ_m^{-2} is large compared with both $\Delta\omega_m^2$ and T_{2m}^{-2} , the broadening is given by

$$T_{2p}^{-1} = p_m(T_{2m}^{-1} + \tau_m \Delta\omega_m^2). \quad (5)$$

On the other hand, when exchange is slow such that τ_m^{-2} is small compared with either T_{2m}^{-2} or $\Delta\omega_m^2$, the broadening is given by

$$T_{2p}^{-1} = p_m \tau_m^{-1}. \quad (6)$$

The limiting cases may be distinguished experimentally by the expected temperature dependences. Since τ_m^{-1} is in effect a rate constant, it should show an Arrhenius temperature dependence with an activation energy on the order of 40–60 kJ/mol. The relaxation time T_{2m} contains contributions from the dipolar interaction of the nucleus with the unpaired electron of the metal ion, modulated by tumbling in solution and by electronic relaxation processes. The temperature dependence thus is expected to be at most that of η/T , which in this case has an activation energy of about 20 kJ/mol. The contact shift is related to the electron-nuclear isotropic hyperfine coupling constant A by

$$\Delta\omega/\omega = (\gamma_e/\gamma_N)(A/4kT) \quad (7)$$

where γ_e and γ_N are the magnetogyric ratios of the electron and the ^{31}P nucleus. Thus $\Delta\omega_m$ decreases slowly with increasing temperature.

In the fast exchange limit, eq (5), the broadening is expected either to decrease with increasing temperature (second term dominant) or to increase slowly. In the slow exchange limit, eq (6), the broadening is expected to increase with increasing temperature.

Results of Linewidth Measurements

Up to ten separate spectra were recorded for each concentration and temperature studied. The spectra were separately digitized and subjected to least-squares analysis. Values of T_2^{-1} , given in Table I, were obtained by taking weighted averages of the measured linewidths, with weights inversely proportional to the variances obtained from the least-squares fits.

Nmr linewidths of the phosphate solutions in the absence of vanadyl ion were observed to increase with increasing temperature. The variation is linear in T/η within experimental error,

$$T_{2,0}^{-1} = A + B(T/\eta) \quad (9)$$

where $B = (7.4 \pm 0.6) \times 10^{-5} \text{ kg m}^{-1} \text{ sec}^{-2} \text{ K}^{-1}$ and the temperature independent part, $A = 3 \pm 2 \text{ sec}^{-1}$, is nearly negligible.

The linearity in T/η suggests that the linewidths are due to a spin-rotation interaction which is given theoretically by¹⁴

$$T_{2,0}^{-1} = \frac{8\pi^2 I \langle C^2 \rangle kT}{h^2} \tau_{sr} \quad (10)$$

TABLE I. Nmr Linewidth Data.

$T(^{\circ}\text{C})$	C_P^a	C_V^b	No. of Spectra	T_2^{-1c}	T_{2p}^{-1c}
6	1.00	0.00	7	11.2 ± 2.1	—
6	1.00	0.65	3	19.6 ± 1.5	8.4 ± 2.6
6	0.93	0.65	1	26.6 ± 8.1	15.4 ± 8.4
6	0.99	1.29	3	27.9 ± 2.8	16.7 ± 3.5
6	0.99	1.95	2	44.8 ± 2.4	33.6 ± 3.2
6	0.98	2.61	4	45.9 ± 7.6	34.7 ± 7.9
6	0.98	3.20	6	57.8 ± 4.6	46.6 ± 5.0
6	0.98	3.84	3	76. ± 21.	65. ± 21.
6	0.97	4.46	1	66.6 ± 5.3	55.4 ± 5.7
6	0.90	6.46	1	140. ± 12.	129. ± 12.
11	1.00	0.00	1	17.1 ± 3.9	—
11	0.93	0.65	2	24.8 ± 3.3	7.7 ± 5.1
20	1.00	0.00	1	19.1 ± 6.3	—
20	0.93	0.65	1	33.5 ± 3.6	14.4 ± 7.2
33	1.00	0.00	10	31. ± 11.	—
33	1.00	0.65	3	84. ± 9.	53. ± 14.
33	0.93	0.65	2	77. ± 6.	47. ± 13.
33	0.99	1.29	3	123. ± 15.	92. ± 19.
33	0.99	1.93	3	242. ± 62.	211. ± 63.
33	0.98	2.57	4	224. ± 25.	193. ± 27.
33	0.98	3.84	3	348. ± 71.	317. ± 72.
63	1.00	0.00	1	40. ± 4.	—
63	0.93	0.65	1	422. ± 30.	382. ± 30.
91	1.00	0.00	1	80. ± 13.	—

^a Total phosphate concentration, M . ^b Total vanadium concentration, mM . ^c Linewidth parameters in sec^{-1} ; uncertainties quoted correspond to one standard deviation.

where I is the moment of inertia, $\langle C^2 \rangle$ is the mean-square spin-rotation coupling constant, and τ_{sr} is the correlation time for molecular angular velocity. Assuming that τ_{sr} may be related to the correlation time for reorientation by

$$\tau_{sr} = I/6kT\tau_r \quad (11)$$

and that τ_r may be approximated by the Debye relation,

$$\tau_r = 4\pi a^3 \eta / 3kT \quad (12)$$

where a is the hydrodynamic radius, we have

$$T_{2,0}^{-1} = \frac{\pi I^2 \langle C^2 \rangle k T}{h^2 a^3 \eta} \quad (13)$$

Eq (13) invites a theoretical estimate of the parameter B . The mean-square spin-rotation coupling constant is expected to be on the order of 10^4 sec^{-1} by analogy with ^{31}P coupling constants in molecules of size similar to phosphate.¹⁵ The moment of inertia of PO_4 is $1.7 \times 10^{-45} \text{ kg m}^2$ (P-O bond length of 0.154 nm¹⁶). Assuming a hydrodynamic radius of 0.25 nm, we obtain a predicted value of $B = 1.8 \times 10^{-9} \text{ kg m}^{-1} \text{ sec}^{-2} \text{ K}^{-1}$, more than four orders of magnitude smaller than observed! A number of factors contribute to this discrepancy: eq (12) is known to introduce serious errors for small molecules;¹⁷ eq (11) is known experimentally to introduce errors of as much as a factor of four;¹⁵ and the effective moment of inertia of a solvated phosphate anion is probably substantially larger than that computed for an isolated PO_4 molecule. Although all of these factors tend to underestimate B , the size of the error is difficult to reconcile.

Nmr linewidths, measured for phosphate solutions in the presence of small amounts of vanadyl ion, were found to increase with metal concentration as expected. The behavior observed at 6° and 33° C is shown in Figure 2. At constant ligand-to-metal ratio, f , the broadening is found to increase with increasing temperature. Figure 3 shows an Arrhenius plot of the logarithm of the normalized excess linewidths, $T_{2p}^{-1}f$, against reciprocal temperature. The error limits on the 6° and 33° points are reduced compared with the other points by the more numerous data available at those temperatures. A least-squares fit of these data, weighting the points in proportion to the reciprocal of their variances, results in an activation energy of $52 \pm 5 \text{ kJ/mol}$ for the process which produces the line broadening. This result, together with the straight line Arrhenius plot (within experimental error, which is admittedly large), suggests that the data are indeed in the slow exchange limit and that the broadening may be interpreted using eq (6).

If we assume that the slow exchange limit is satisfied over the entire temperature range studied, wherein τ_m^{-1} ranges from 5×10^3 to $2 \times 10^5 \text{ sec}^{-1}$, the condition for the validity of eq (6) is that either T_{2m}^{-1} or $|\Delta\omega_m|$ must be substantially greater than 10^5 sec^{-1} .

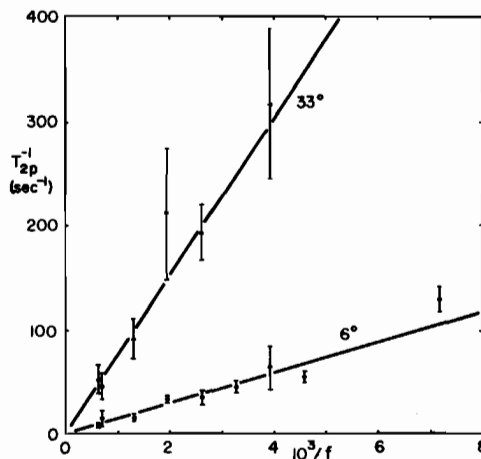


Figure 2. Excess linewidths of ^{31}P magnetic resonance as a function of the vanadyl to phosphate mole ratio, $1/f$.

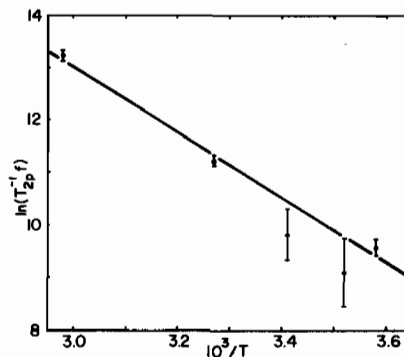
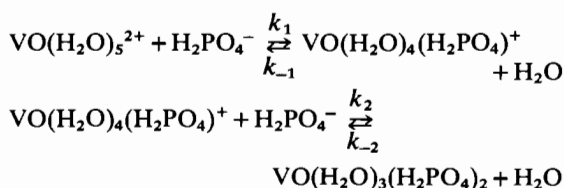


Figure 3. Arrhenius plot of the logarithm of the normalized excess linewidths vs. the reciprocal of the absolute temperature.

The contact shift is related by eq (7) to the nuclear hyperfine coupling. The ^{31}P hyperfine coupling for tributyl phosphate coordinated to vanadyl ion is $|A/h| = 9.8 \times 10^6 \text{ sec}^{-1}$; if we take tributyl phosphate as a reasonable model for H_2PO_4^- , we anticipate a contact shift of about 10^5 sec^{-1} . Thus at low temperatures the slow exchange limit should be satisfied, but at the high end of the temperature range, it is apparently necessary that relaxation of the ^{31}P nucleus at the metal site be very rapid.

Mechanism of the Exchange Process

The observed nmr line broadening can apparently be explained by exchange of H_2PO_4^- between bulk solution and a coordination site on the paramagnetic vanadyl ion. There are, however, two exchange processes, either of which could be responsible for the observed effects:

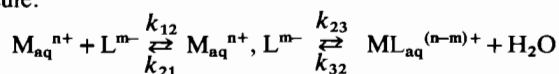


The least-squares plot of Figure 3, extrapolated to 25°C, gives

$$T_{2p}^{-1}f = p_m f \tau_m^{-1} = (4.9 \pm 0.5) \times 10^4 \text{ sec}^{-1}.$$

Given the approximate formation constants at 25°C,⁵ the probability of finding a phosphate ligand at a 1:1 complex site in a 1M phosphate solution is $p_m(1:1) \sim 0.018/f$, and the probability of finding a ligand at a site in a 1:2 complex is $p_m(1:2) = 1.96/f$. If we assume that only the first process, involving H_2PO_4^- loss from a 1:1 complex, contributes to the line broadening, we have $\tau_m^{-1} \sim 3 \times 10^6 \text{ sec}^{-1}$ which, with the formation constant $K_1 \sim 2000$, gives an impossibly large value for the anation rate constant. It is more reasonable to assume that only the second process, involving H_2PO_4^- loss from the 1:2 complex, is responsible for line broadening; we then obtain $\tau_m^{-1} = (2.5 \pm 0.3) \times 10^4 \text{ sec}^{-1}$.

Ligand substitution reactions on transition metal ions are describable in many cases by a mechanism involving ion-pair formation followed by interchange of an outer-sphere ligand with an inner-sphere water molecule:¹⁸



If we assume that the ion-pair formation step is a rapid equilibrium, the aquation rate constant may be identified with k_{32} and the anation rate constant with $K_0 k_{23}$, where K_0 is the ion-pair formation constant. If the transition state of the interchange step involves a substantial degree of bond breaking, then the mechanism may be described as dissociative interchange, I_d . In this case, the rate constant k_{23} should be on the order of or slightly less than the water exchange rate in the corresponding system. When the mechanism tends toward bond formation in the transition state (associative interchange, I_a), k_{23} may exceed the water exchange rate, by a substantial margin if the ligand is a sufficiently strong nucleophile.

If we identify the value of τ_m^{-1} found above with k_{32} , we can use the formation constant $K_2 \sim 100^5$ to estimate $K_0 k_{23} \sim 2 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$. Ion-pair formation constants for (1+), (1-) pairs seem to lie in the range $K_0 \sim 1-10$,¹⁹ so that k_{23} is on the order of $(2-20) \times 10^5 \text{ sec}^{-1}$. This range is considerably above the water exchange rate for the aquo vanadyl ion, $k_{\text{ex}} = 570 \text{ sec}^{-1}$.^{2,3} The result suggests that either (1) the water exchange rate on $\text{VO}(\text{H}_2\text{O})_4(\text{H}_2\text{PO}_4)^+$ is substantially greater than that on the aquo ion, or (2)

the interchange step takes place by a strongly associative mechanism. The first explanation seems the more likely in light of the greatly enhanced water exchange rates observed in vanadyl complexes with iminodiacetic acid, sulfosalicylic acid, and TIRON⁴ as well as in the bis chloro complex.¹ We thus tentatively conclude that coordinated H_2PO_4^- , like these other ligands, exerts a strong labilizing effect on the remaining water molecules in the coordination sphere.

Acknowledgements

The authors are indebted to J. O. Edwards and M. R. Hoffmann for some stimulating discussions and to M. M. Iannuzzi, R. G. Lawler, and H. Klos for assistance with details of the experiments. Financial support from the National Science Foundation is gratefully acknowledged.

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