

offered for this type of non-Curie behavior in other $S = 1/2$ ¹¹⁶ and $S \geq 1$ ^{117,118} systems. In some cases the SOZ contribution to $(\Delta H/H)^{\text{dip}}$ is believed to be larger than the first-order Zeeman contribution.^{114,115,117} A third explanation, (iii), is possible for $S \geq 1$ systems with a large zero-field splitting (ZFS).^{117,118} In these cases, $(\Delta H/H)^{\text{dip}}$ contains both $1/T$ and $1/T^2$ terms. In principle, this should lead to a nonlinear δ vs. $1/T$ plot. However, the experimental range of temperatures may be too small to detect the curvature. Thus, it is possible for proton resonances having sizable pseudocontact shifts to follow a $1/T$ dependence experimentally but to have a $1/T = 0$ intercept considerably different from the diamagnetic value.^{117,118}

We believe that explanation i is not likely to account for our observations because the $1/T = 0$ intercepts for the methyl protons of Fe(OEC) are very different from the corresponding diamagnetic values (see Table XI). As noted above, the contact contributions to the isotropic shifts should be very small for these protons.^{97,98} If explanation ii accounts for the observed intercepts, then $[\chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})]$ for Fe(OEC) should have a negligible or minor SOZ component while $[\chi_{xx} - \chi_{yy}]$ should have a significant SOZ component. Explanation iii has only been treated theoretically for axial systems with one ZFS term, D .^{117,118} Note that Fe(OEP) has "normal" $1/T = 0$ intercepts, even though it probably has a large D , as does Fe(TPP) (Table XI). Two ZFS parameters, D and E , would be required to describe the rhombic anisotropy of Fe(OEC). Magnetic susceptibility measurements (solution and

solid state) are under way for this compound.

Conclusions

The four-coordinate square-planar molecular structures of Fe(OEC) and Fe(OEP) have been found to be similar. The "small" μ_{eff} and "large" quadrupole splitting of Fe(OEC), however, show that the electronic structures of the two compounds are significantly different despite their common $S = 1$ ground state. Variable-temperature ¹H NMR spectra show that Fe(OEC) possesses rhombic anisotropy. This is the first example of resolvable ring-induced rhombicity in a metallohydroporphyrin. Whether the differences we have discovered between iron porphyrins and hydroporphyrins are to be found for other oxidation states, spin states, and ligation states remains to be seen.

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Registry No. Fe(OEP), 61085-06-1; Fe(OEC), 78319-96-7.

Supplementary Material Available: Table III (anisotropic thermal parameters and hydrogen atom positions for Fe(OEP)), Table IV (anisotropic thermal parameters and hydrogen atom positions for Fe(OEC)), Table V (least-squares planes for Fe(OEP)), Table VI (least-squares planes for Fe(OEC)), Table VII (structure amplitudes for Fe(OEP)), and Table VIII (structure amplitudes for Fe(OEC)) (30 pages). Ordering information can be found on any current masthead page.

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Vanadium(V) Oxyanions: The Esterification of Ethanol with Vanadate

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Abstract: Vanadium-51 nuclear magnetic resonance (NMR) spectroscopy has been used to study the interaction of vanadate, V_i , with ethanol in aqueous solution. At the concentrations employed in this study vanadate existed in water as a monomeric tetrahedral species giving rise to a single resonance in the NMR spectrum. Upon partial replacement of water with ethanol two additional signals appeared. The response of these three resonances to changes in ethanol concentration and pH was consistent with their origin in inorganic vanadate and the esters ethyl vanadate and diethyl vanadate. From the variation in ethanol concentration, the following equilibrium constants were determined: $K_1 = [\text{EtOVO}_3\text{H}^-][\text{H}_2\text{O}]/[\text{EtOH}][\text{VO}_4\text{H}_2^-] = 10.4$ and $K_2 = [(\text{EtO})_2\text{VO}_2^-][\text{H}_2\text{O}]/[\text{EtOH}][\text{EtOVO}_3\text{H}^-] = 2.3$. From the effect of pH on the chemical shifts and the concentration ratio of V_i to ethyl vanadate, the $\text{p}K_a$'s vanadate and ethyl vanadate were determined to be 8.3 and 8.9, respectively. Variable-temperature NMR studies of a solution prepared at pH 7.5 and containing 3.4 M ethanol and 7.8×10^{-5} M V_i showed coalescence of the vanadate and ethyl vanadate resonances at 328 K. From this and the equilibrium constant, a value of $1.2 \times 10^3 \text{ s}^{-1}$ for the pseudo-first-order rate constant of ethyl vanadate hydrolysis at this pH and temperature was determined.

Vanadium is a widely dispersed element which, as an essential nutrient, has its major effect on the action of enzymes.^{1,2} The element is important for most biological systems when in the vanadium(IV) and vanadium(V) oxidation states. It has recently

been found that vanadium(V) oxyanions (V_i) strongly activate the glucose dehydrogenase activity of glucose 6-phosphate dehydrogenase and that this activation can be rationalized in terms of the rapid nonenzymic formation of glucose 6-vanadate.³ In

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view of this proposed ester formation it was felt that such non-enzymic formation of vanadate esters should proceed readily with simpler alcohols in aqueous solution.

The sensitivity necessary to quantitatively measure vanadium(V) at concentrations similar to those used for the enzymic studies is provided by vanadium-51 nuclear magnetic resonance (NMR) spectroscopy. ^{51}V NMR spectroscopy has been used to study the oligomerization reactions of vanadate in aqueous solution⁴⁻⁸ and similarly the reaction products of vanadate with hydrogen peroxide.⁹ The reactions of both vanadium(IV) and -(V) with uridine¹⁰ and of vanadium(V) with catechols¹¹ and aromatic diols¹² have also been investigated by using ultraviolet spectroscopy.

The chemistry of aqueous solutions of vanadium(V) oxyanions is exceedingly complex. It was then not surprising that our initial attempts to observe directly glucose 6-vanadate via ^{51}V NMR spectroscopy were not successful. Several new vanadium resonances appeared in the NMR spectra; however, their correlation with a molecular structure was not possible. Various hydroxyl groups in the glucose moiety are available for ester formation so this result was not completely unforeseen. Furthermore, there is the possibility for formation of both cyclic and acyclic esters. Studies done concurrently with those using glucose indicated that there would be distinct advantages to carrying out an intensive investigation of a considerably simpler alcohol such as methanol or ethanol where only one hydroxyl function per molecule is available for esterification. Furthermore, rather high alcohol concentrations can be easily obtained without encountering problems related to aldehyde oxidation as for the glucose solution. This study deals specifically with the use of ethanol as the substrate undergoing esterification, but it is worth mentioning that our preliminary investigations of methanol indicated that there is little difference in behavior of the two alcohols.

Although vanadate complexes have been intensively studied,^{1,8,13} there are few reports of derivatives of simple alcohols. Esters of vanadate and mono- and dichloro vanadate have been prepared and studied in nonaqueous solvents^{14,15} while the interactions of vanadate with aromatic diols in aqueous solution have been studied.^{11,12} The rapid reduction of vanadium in the aqueous systems made it difficult to reach firm conclusions regarding the structure of the vanadium(V) diol derivatives

Experimental Section

Materials. Reagent grade chemicals were used without further purification. Preparation of the vanadate solutions has been described.³

NMR and UV Spectra. ^{51}V NMR spectra were obtained at 105 MHz with the broadbanded probe of a Bruker 400-MHz multinuclear Fourier transform NMR spectrometer. Pulse widths of 50° and ≈ 0.1 -s acquisition times were used for obtaining the spectra. Increase of the acquisition time was found to have no effect on relative peak intensities nor, as well as could be judged, on signal to noise for the same number of acquisitions. Peak areas were obtained with the manufacturer's computer software. Chemical shifts are given with respect to VOCl_3 used as an external reference.

UV spectra were obtained with a Cary 210 UV-vis spectrophotometer and 1 cm path length UV cuvettes. Cuvettes containing solvent without vanadate were used in the reference beam. Unless specifically indicated

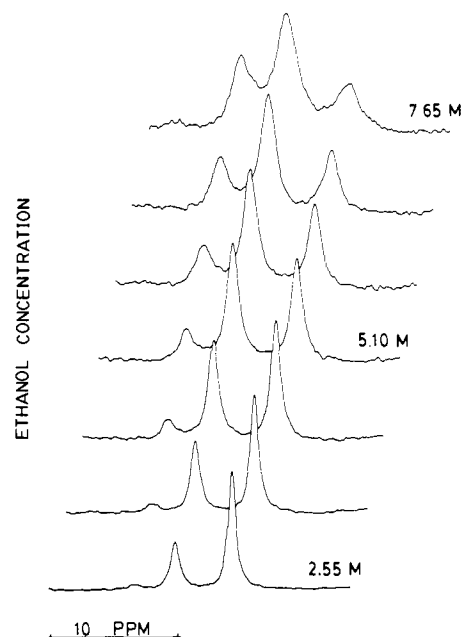


Figure 1. ^{51}V NMR spectra of vanadate/ethanol/water solutions showing the effect of ethanol concentration on the relative intensities of the various vanadium resonances. Solutions contained 3.9×10^{-4} M sodium vanadate, 50 mM Tris-acetate buffer at pH 7.5, and the indicated amount of ethanol.

otherwise, all spectra were obtained from samples at ambient temperature (21 °C).

Measurements of pH in the ethanol-water solvent mixtures were made with a standard pH meter with a combination electrode which had been standardized in aqueous buffers. It has been shown that hydrogen ion concentrations in ethanol-water mixtures can be measured accurately in this way with a correction factor which varies from -0.032 to 0.221 log units in solvents containing 85.6 or less ethanol (wt %).¹⁶ The correction factor does not vary with pH except at the extremes for a given percent ethanol solvent with dilute solutes. No correction factor was used in this study because it is small, and because it is not necessary either for our calculations or in facilitating studies by other investigators who might wish to verify our observations under similar conditions.

The ethanol-water solvent mixtures were prepared as follows. Ethanol was added to a tared vessel and the mass of ethanol added was recorded. After the solutes and water had been added and the final volume and pH recorded, the vessel with contents was weighed again. This allowed determination of the mass of ethanol and of water in the solution and their molar concentrations, which are given with the figures, could be calculated.

Results and Discussion

Aqueous solutions of sodium vanadate give rise to complex NMR spectra which are dependent on both concentration of vanadate and pH of solution.⁴⁻⁸ The complexity of the spectra arises from the formation of various polymeric forms of the basic tetrahedral species VO_4H^{2-} and VO_4H_2^- . At a concentration of 5×10^{-4} M in water, the observation of a single resonance in the NMR spectrum indicates that essentially all the vanadate occurs as the monomer. The occurrence of this monomer as the mono- or diprotonated ion is a pH-dependent phenomenon. The $\text{p}K_a$ value for the transition from H_2VO_4^- to HVO_4^{2-} is cited as 8.3 in dilute aqueous solution.^{4,13} With stepwise replacement of water by ethanol, NMR spectroscopy indicates the formation of first one then a second additional product. The relative intensities of the three resonances are dependent both on ethanol concentration and on pH. UV spectra obtained from an aqueous solution containing only the vanadate ion provided an absorption with its maximum at 270 nm in agreement with that of other workers.⁵ Samples prepared containing sufficient ethanol (80% by volume) that vanadate ion was present as only a small fraction of the total of all vanadate species present did not significantly shift the

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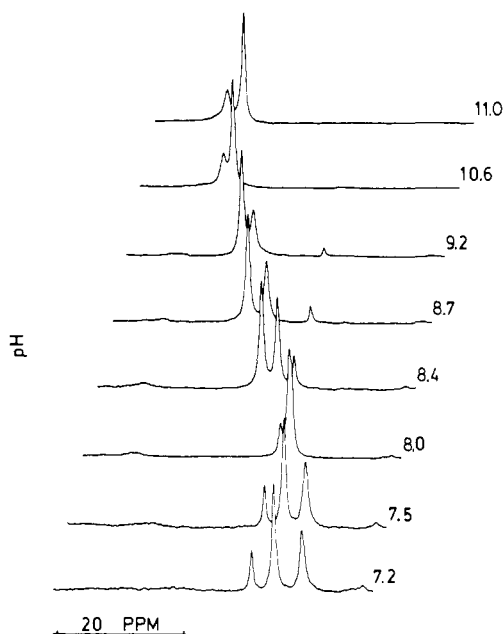
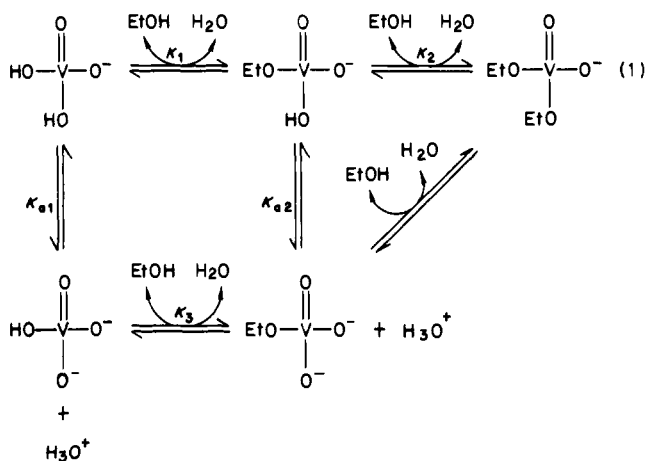


Figure 2. ^{51}V NMR spectra of vanadate/ethanol/water solutions at fixed ethanol concentration showing the effect of pH on resonance positions and relative intensities. Solutions contained 5.10 M ethanol, 5.0×10^{-4} M sodium vanadate, and 50 mM Tris-chloride buffer at the indicated pH.

absorbance maximum. This result is consistent with only minor structural changes, at least with respect to the chromophore.

Figure 1 shows representative ^{51}V NMR spectra from samples in which the ethanol concentration was varied. The large change in relative intensities of the resonances is clearly depicted. Similar results are displayed in Figure 2 where the pH was varied from 7.2 to 11.0. A further point to be made from Figure 2 is that although all three relative intensities are pH dependent, the chemical shifts of only two of the three components are pH dependent, at least in the range studied. The resonances which shift frequency with pH are assigned to vanadate ion (this assignment is supported by dilution studies and agrees with other workers⁴) and ethyl vanadate. The remaining resonance with invariant chemical shift was assigned to diethyl vanadate. With these assignments, the effects of ethanol concentration and of changing pH are quantitatively correlated in terms of the equilibrium expressions of eq 1.



The series of solutions for which ethanol concentration was varied was studied at pH 7.5, well below $\text{p}K_{a1}$ and $\text{p}K_{a2}$, therefore the two dianionic species shown in eq 1 are not present at significant concentrations. As a consequence of this, the conservation equation, eq 2, is valid at this pH where V_t refers to total vanadium content. With eq 2 and the equilibrium expressions for K_1 (eq

$$V_t = [\text{VO}_4\text{H}_2^-] + [\text{EtOVO}_3\text{H}^-] + [(\text{EtO})_2\text{VO}_2^-] \quad (2)$$

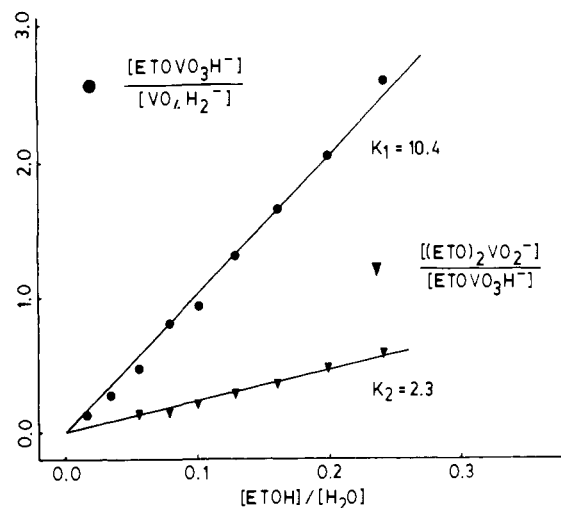


Figure 3. Determination of the equilibrium constants K_1 and K_2 for formation of ethyl vanadate and diethyl vanadate. The ratios $[\text{EtOVO}_3\text{H}^-]/[\text{VO}_4\text{H}_2^-]$ and $[(\text{EtO})_2\text{VO}_2^-]/[\text{EtOVO}_3\text{H}^-]$, obtained from the relative peak intensities of the spectra shown in Figure 1, are plotted against $[\text{EtOH}]/[\text{H}_2\text{O}]$. The slopes give K_1 and K_2 , as shown in eq 3 and 4.

3) and K_2 , (eq 4), the three equations (eq 5–7) which describe how the vanadium is distributed among its three states at equilibrium can be derived.

$$\frac{[\text{EtOVO}_3\text{H}^-]}{[\text{VO}_4\text{H}_2^-]} = K_1 \frac{[\text{EtOH}]}{[\text{H}_2\text{O}]} \quad (3)$$

$$\frac{[(\text{EtO})_2\text{VO}_2^-]}{[\text{EtOVO}_3\text{H}^-]} = K_2 \frac{[\text{EtOH}]}{[\text{H}_2\text{O}]} \quad (4)$$

$$\frac{[\text{VO}_4\text{H}_2^-]}{V_t} = 1 / \left(1 + K_1 \frac{[\text{EtOH}]}{[\text{H}_2\text{O}]} + K_1 K_2 \left(\frac{[\text{EtOH}]}{[\text{H}_2\text{O}]} \right)^2 \right) \quad (5)$$

$$\frac{[\text{EtOVO}_3\text{H}^-]}{V_t} = \frac{K_1 \frac{[\text{EtOH}]}{[\text{H}_2\text{O}]}}{\left(1 + K_1 \frac{[\text{EtOH}]}{[\text{H}_2\text{O}]} + K_1 K_2 \left(\frac{[\text{EtOH}]}{[\text{H}_2\text{O}]} \right)^2 \right)} \quad (6)$$

$$\frac{[(\text{EtO})_2\text{VO}_2^-]}{V_t} = \frac{K_1 K_2 \left(\frac{[\text{EtOH}]}{[\text{H}_2\text{O}]} \right)^2}{\left(1 + K_1 \frac{[\text{EtOH}]}{[\text{H}_2\text{O}]} + K_1 K_2 \left(\frac{[\text{EtOH}]}{[\text{H}_2\text{O}]} \right)^2 \right)} \quad (7)$$

From the ratios of vanadate species in solution provided by the NMR spectra and the known concentrations of ethanol and water, the relevant ratios of eq 3 and 4 were plotted against each other as shown in Figure 3. The slopes of the two lines provided K_1 and K_2 with values of 10.4 ± 0.3 and 2.3 ± 0.2 , respectively. The reliability of these two values was demonstrated by calculating the quantities of eq 5 to 7 and comparing them to the experimentally determined values. The results of this comparison are displayed in Figure 4 from which it is clear that agreement is very good.

In order to obtain the agreement between experiment and the calculated curves of Figures 3 and 4 it is necessary that the term representing formation of water be incorporated into the appropriate equilibrium expressions. This incorporation is consistent with ester formation where water is produced.

The linear correlations shown in Figure 3 are consistent with the proposal that at the relatively low pH of this study eq 1 describes the distribution of vanadate among the three states shown

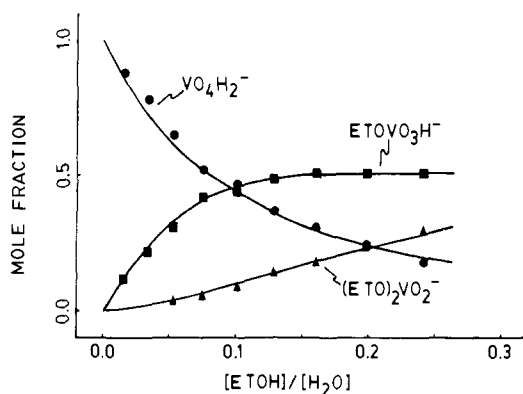


Figure 4. The effect of ethanol concentration on the mole fraction of vanadium existing as inorganic vanadate, ethyl vanadate, and diethyl vanadate at pH 7.5. The experimental points were obtained from relative peak intensities of the spectra shown in Figure 1. The lines were calculated from eq 5-7, using the K_1 and K_2 values shown in Figure 3.

in the top line of eq 1. That the correlations are linear indicates that K_1 and K_2 are constant over the range of solvent composition used. While there is no thermodynamic reason why this must be so for any given reaction, it is frequently found to be the case.¹⁷ This implies that the solvation of the three species in the system is similar or, stating it another way, the free energy of transfer from one solvent mixture to another is the same for all three species over the range of solvent compositions used in this study.

The chemical shifts of both vanadate and ethyl vanadate are pH dependent as shown by Figure 2. The limiting values at low pH are -561 and -555 ppm for the free ion and ester, respectively. There is a positive shift in resonance positions of these two species as the pH increases, to -534 and -532 ppm, respectively. The chemical shift of diethyl vanadate remains constant throughout the range of pH utilized in this study. Both vanadate and ethyl vanadate have ionizable protons with pK_a values within the range of pH studied. The change in ionization state of these two species causes the observed variation in chemical shift. diethyl vanadate carries a single negative charge throughout the pH range studied and consequently does not undergo a change in ionization or the associated shift in resonance frequency. Figure 5 shows the chemical shift as a function of pH for the vanadate and its monoethyl derivative. Curves similar to these have been used to determine pK_a values for vanadate and divanadate.⁴ If the assumption that chemical shift provides an accurate measure of the proportion of an ion in its acidic or basic forms is valid, then the curves in Figure 5 should be correlated by eq 8 where $|\delta_l|$ and $|\delta_h|$ are the absolute values of the limiting chemical shifts at low and high pH, respectively, and $|\delta|$ is the corresponding value for the observed chemical shift. Equation 8 assumes $|\delta_h| < |\delta_l|$.

$$pH = pK_a + \log \left(\frac{|\delta_l| - |\delta|}{|\delta| - |\delta_h|} \right) \quad (8)$$

The solid curves in Figure 5 were calculated from eq 8 by using the indicated limiting values δ_l , δ_h , and the pK_a . The points represent the experimental results.

At high pH diethyl vanadate cannot be stabilized by loss of a proton as can ethyl vanadate and vanadate itself. Furthermore, since $pK_{a1} < pK_{a2}$, the ratio of vanadate to the ethyl ester will be different at pH values above and below the pK_a values of these ions. This effect of pH is shown in Figure 6 where total vanadium and ethanol concentrations are kept constant. In this figure the mole fractions of vanadate, ethyl vanadate, and diethyl vanadate are plotted as a function of pH, the various proportions being provided by the NMR spectra. The solid curves of this figure were calculated according to eq 9 through 11. These equations were derived by extending the conservation equation, eq 2, to include $VO_4H_2^-$ and $EtOVO_3^{2-}$ and by including the equations

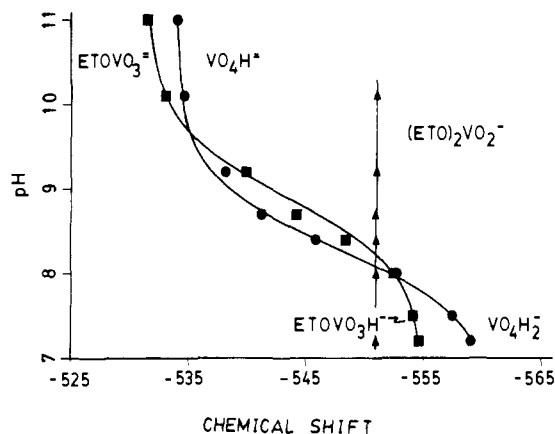


Figure 5. The effect of pH on the resonance positions of the peaks in the ^{51}V NMR spectrum assigned to inorganic vanadate and ethyl vanadate. The experimental points were taken from the spectra shown in Figure 2. The lines were calculated from eq 8, using the following values for the limiting chemical shifts of vanadate and ethyl vanadate, respectively: $\delta_l = -561$ and -555 , $\delta_h = -534$ and -532 , $K_{a1} = 10^{-8.3}$ and $K_{a2} = 10^{-8.9}$.

defining K_{a1} and K_{a2} . The values of the equilibrium constants K_1 , K_2 , K_{a1} , and K_{a2} used to calculate these curves were 11.4, 2.45, $10^{-8.3}$, and $10^{-8.9}$. These constants were determined by using a nonlinear least-squares program to simultaneously fit the five data sets shown in Figures 5 and 6. The high and low pH limiting values of δ , as well as the values K_1 , K_2 , K_{a1} , and K_{a2} , were varied until a single set of values was obtained which, with eq 8-11, gave the best fit to the five sets of experimental points.

$$\frac{[\text{VO}_4\text{H}_2^-] + [\text{VO}_4\text{H}^-]}{V_t} = \frac{\left(1 + \frac{K_{a1}}{[\text{H}_3\text{O}^+]}\right)}{\left(1 + \frac{K_{a1}}{[\text{H}_2\text{O}^+]} + K_1 \frac{[\text{EtOH}]}{[\text{H}_2\text{O}]}\right) \times \left(1 + \frac{K_{a2}}{[\text{H}_2\text{O}^+]} + K_1 K_2 \left(\frac{[\text{EtOH}]}{[\text{H}_2\text{O}]}\right)^2\right)} \quad (9)$$

$$\frac{[\text{EtOVO}_3\text{H}^-] + [\text{EtOVO}_3^{2-}]}{V_t} = \frac{K_1 \frac{[\text{EtOH}]}{[\text{H}_2\text{O}]} \left(1 + \frac{K_{a2}}{[\text{H}_3\text{O}^+]}\right)}{K_1 \frac{[\text{EtOH}]}{[\text{H}_2\text{O}]} \left(1 + \frac{K_{a2}}{[\text{H}_3\text{O}^+]}\right) + K_1 K_2 \left(\frac{[\text{EtOH}]}{[\text{H}_2\text{O}]}\right)^2} \quad (10)$$

$$\frac{[(\text{EtO})_2\text{VO}_2^-]}{V_t} = \frac{K_1 K_2 \left(\frac{[\text{EtOH}]}{[\text{H}_2\text{O}]}\right)^2}{K_1 \frac{[\text{EtOH}]}{[\text{H}_2\text{O}]} \left(1 + \frac{K_{a2}}{[\text{H}_3\text{O}^+]}\right) + K_1 K_2 \left(\frac{[\text{EtOH}]}{[\text{H}_2\text{O}]}\right)^2} \quad (11)$$

The value of 8.3 ± 0.1 for pK_{a1} agrees very well with the corresponding values obtained for low ionic strength solutions (8.0 to 8.36) reported by other workers.^{4,13} The value of pK_{a2} is 8.9 ± 0.1 . Similar pK_a values for vanadate and ethyl vanadate are to be expected since the substitution of an ethoxy for a hydroxy group is a relatively small structural change. The values of K_1 and K_2 (11.4 ± 0.5 and 2.5 ± 0.5 , respectively) used to fit eq 8-11 to the results shown in Figure 2, 5, and 6 differ slightly from those used to fit eq 3-7 to the data shown in Figure 1, 3, and 4. The differences are small and close to the experimental error; however, they probably result from the fact that in the ethanol concentration study Tris-acetate buffer was used, while in the pH study Tris-chloride buffer was used.

Although on the basis of the results reported here we cannot determine with certainty the coordination geometry of the va-

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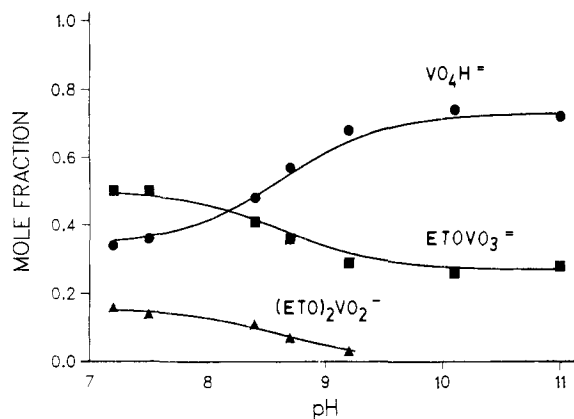


Figure 6. The effect of pH, at a fixed ethanol concentration, on the mole fraction of vanadium existing as inorganic vanadate, ethyl vanadate, and diethyl vanadate. The experimental points were taken from the relative peak intensities of the spectra shown in Figure 2. The curves were calculated from eq 9–11, using the following values: $K_{a1} = 10^{-8.3}$, $K_{a2} = 10^{-8.9}$, $K_1 = 11.4$, $K_2 = 2.45$.

vanadium species which were observed, the results are consistent with tetrahedral structures for all three species. From the ethanol concentration study it can be concluded that the coordination number is constant for all three species. Each time ethanol adds as a reactant, water is produced as a product.

Also consistent with tetrahedral structures are the observations that the species assigned the diethyl vanadate structure is not stabilized by proton loss, presumably because it does not have a proton to lose. There is also no evidence from the ethanol concentration study that more than two hydroxy groups can be replaced by ethoxy. Formation of triethyl vanadate would not be expected to be significant except at pH values near or below the pK_a for protonation of the oxyanion of diethyl vanadate. Since the pK_a for ionization of H_3VO_4 is about three,^{4,13} the pK_a for diethyl vanadate is expected to be well below the pH values used in this study.

Enzymic studies have led to the inference that vanadate can esterify glucose nonenzymically to produce the ester glucose 6-vanadate, which is accepted as a substrate by an enzyme whose physiological substrate is glucose 6-phosphate.³ A kinetic analysis of the enzymic study led to the conclusion that the second-order rate constant for formation of glucose 6-vanadate from glucose and vanadate is approximately 10^{10} times that for glucose 6-phosphate formation from glucose and phosphate, and 10^5 times that for glucose 6-arsenate formation from glucose and arsenate. Because of the importance of this result, it was decided that exchange rates of vanadate between the free ion and the ethyl ester should be determined. The occurrence of individual NMR resonances at ambient temperature ($\approx 21^\circ\text{C}$) put an upper limit on the rate of exchange but not a lower limit. It was found that a moderate elevation in temperature was sufficient to increase the exchange rate to that sufficient for measurement by normal NMR techniques. Figure 7 shows the results obtained. The concentration and pH were such that the proportion of diethyl vanadate was sufficiently low to neglect its presence and treat this as a two-site exchange process between sites of unequal populations. As is clear from Figure 7, coalescence occurs at close to 328 K. No attempt to obtain a temperature dependence of the exchange rate by line shape fitting was made so that it cannot be said with certainty that coalescence does occur at 328 K; however, it must occur near this temperature. From the peak separation of 488 Hz at 298 K and from the assumption that this separation is not significantly temperature dependent, an exchange rate constant, k , of $1.1 \times 10^3 \text{ s}^{-1}$ at coalescence is obtained. With the added assumption that the change in the ratio of vanadate to ethyl vanadate is small on increasing the temperature from 298 to 328 °K, the pseudo-first-order rate constants for ester formation and hydrolysis can be determined.

From the NMR spectrum obtained at 298 K, $[V_i]/[EtOVO_3H^-] = 1.24$ so that V_i and $EtOVO_3H^-$ are present in

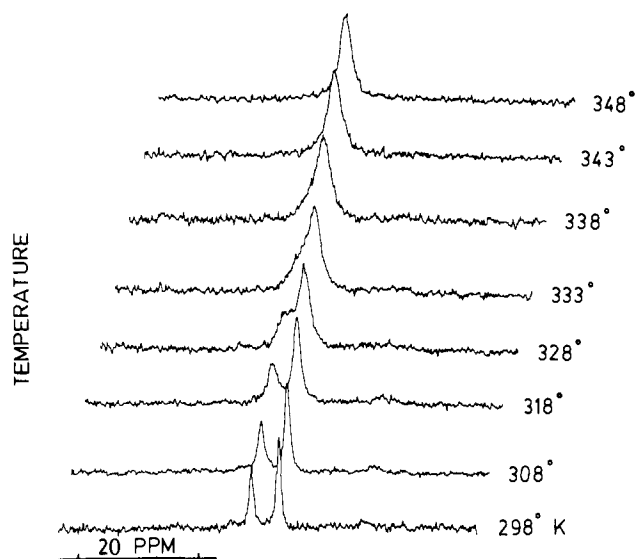


Figure 7. The effect of temperature on the ^{51}V NMR spectrum of a vanadate/ethanol/water solution. The solution contained 3.4 M ethanol, 3.9×10^{-4} M sodium vanadate, and 50 mM Tris-acetate buffer at pH 7.5. Temperatures were as indicated.

fractional amounts of 0.56 and 0.44 of the total vanadate, respectively. Since the system is at equilibrium, the rates of ester formation and hydrolysis are equal so that $k_f[V_i][EtOH] = k_h[EtOVO_3H^-][H_2O]$, where k_f and k_h are the corresponding second-order rate constants. From this and the expression relating the exchange rate constant to the fractional populations,¹⁸ the pseudo-first-order rate constants for formation, $k_f[EtOH]$, and hydrolysis, $k_h[H_2O]$, are obtained. $k_f[EtOH] = 2 \times 0.44 \times 1.1 \times 10^3 \text{ s}^{-1} = 0.95 \times 10^3 \text{ s}^{-1}$ and $k_h[H_2O] = 2 \times 0.56 \times 1.1 \times 10^3 \text{ s}^{-1} = 1.2 \times 10^3 \text{ s}^{-1}$ are the values obtained for these two rate constants under the conditions of this experiment: pH 7.5, 3.4 M ethanol, 44.8 M water, 50 mM Tris-acetate buffer, and 3.9×10^{-4} M vanadate.

This first-order rate constant for hydrolysis, $1.2 \times 10^3 \text{ s}^{-1}$, would presumably be slightly higher in 55.5 M water; however, this value is adequate for comparison with that for the corresponding phosphate ester. At 398 K, the rate constant for ethyl phosphate hydrolysis is $6.09 \times 10^{-6} \text{ s}^{-1}$ when measured under conditions such that the ester exists essentially entirely as the monoanion.¹⁹ Thus, it is apparent that ethyl vanadate hydrolyzes in the order of 10^8 times as rapidly as does ethyl phosphate.

Literature values for the rate constant for formation of ethyl phosphate or the equilibrium constant for this process do not appear to be available so that comparisons with the vanadate system cannot be made at this time. However, it is apparent that the rate constant for formation of ethyl vanadate must be many orders of magnitude larger than that for ethyl phosphate formation.

Conclusions

From these studies it is concluded that ethyl vanadate and diethyl vanadate are formed rapidly and reversibly from ethanol and vanadate contained in aqueous solution. The rate of formation of such vanadate esters is many orders of magnitude faster than those for phosphate ester formation. These observations support the inference from studies of the vanadate-activated glucose dehydrogenase activity of glucose 6-phosphate dehydrogenase that glucose 6-vanadate is formed from glucose and vanadate much more rapidly than the corresponding process with glucose and phosphate.³

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Registry No. VO_4H_2^- , 34786-97-5; ethanol, 64-17-5; vanadium, 7440-62-2.

Kinetics and Mechanism of the Permanganate Ion Oxidation of Sulfite in Alkaline Solutions. The Nature of Short-Lived Intermediates

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Abstract: The oxidation of sulfite by permanganate ion has been studied by the stopped-flow technique combined with rapid scan spectrophotometry. The overall reaction involves manganate(VI) as an intermediate, whose fate depends on the pH. The formation and disappearance of manganate(VI) represent two distinct phases: (1) reduction of permanganate to manganate(VI) via outersphere electron transfer; (2) slower disproportionation of manganate(VI) to permanganate and a soluble manganese(IV) product. The direct oxidation of sulfite by manganate(VI) is too slow to compete with the permanganate route. Manganate(V) has been detected for the first time by rapid scan spectrophotometry as an intermediate of manganate(VI) disproportionation. The first phase obeys overall second-order kinetics, the rate constant being pH-independent between 13 and 9.5. Disproportionation is second order in manganate, and the observed rate constant increases with decreasing pH.

Mechanistic studies on permanganate oxidations of both organic and inorganic substrates are invariably encumbered by difficulties due to the multitude of possible oxidation states, which may be involved as intermediates in the reduction of manganate(VII). Thermodynamic stabilities of the individual oxidation states, though known from available redox potentials, do not always represent usable information for judging whether or not a given valence state will play the role of an intermediate. The lifetime together with the accessible techniques of detection will ultimately determine the degree of certainty with which a transient manganese species can be assigned an oxidation state.

It is relatively easy to detect and identify manganese(III) intermediates, as has been done in permanganate oxidations of unsaturated compounds in acidic solutions.²⁻⁵ The manganese(IV) state is detectable by chemical techniques.⁶⁻⁸ Manganate(V) esters have been invoked as intermediates in a variety of reactions

between unsaturated compounds and permanganate ion in both acidic⁴⁻⁶ and alkaline^{2,9-15} media as well as in nonaqueous solvents.^{11,12} The difficulties encountered in the detection of this oxidation state as a transient have led to disagreement over the identity of some short-lived intermediates, a case in point being cinnamic acid oxidation.^{6,12,13} As no stable compounds of the manganate(V) ester type have been reported, it is not known what spectral characteristics should be expected for an intermediate of that structure. The evidence presented thus far for manganate(V) ester intermediates is of indirect nature. The MnO_4^{3-} ion, however, has been prepared in strongly alkaline aqueous solution,¹⁶ and its UV-vis spectrum is known.^{2,17} We have recently communicated the detection of MnO_4^{3-} as a short-lived intermediate in the oxidation of sulfite ion by alkaline permanganate.¹⁸ This appears to be the first case in which a manganese(V) species has been positively identified by a spectroscopic technique as a transient in a permanganate oxidation. We now report a kinetic study of this reaction with special reference to the nature and sequence of short-lived intermediates.

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