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Oxygen and vanadium exchange processes in linear vanadate oligomers

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The existence of the linear tri- and tetra-vanadate anions in aqueous solution has been confirmed by ^{51}V and ^{17}O NMR and potentiometry, yielding the formation constants. Their resonances are mostly broadened by an exchange process which is shown by the linewidths and by magnetisation-transfer experiments to be independent of the monomeric or the dimeric vanadates also present, and also of the solvent oxygens. The broadenings are not consistent with a simple process of exchange, but instead reveal the presence of an intermediate, probably cyclic, having a short but not insignificant lifetime. Also, simple proton transfer between the oxygens in the aqueous monoprotonated monovanadate anion is sufficiently slow to be detectable by NMR spectroscopy.

The aqueous linear tri- and tetra-vanadate anions, $[V_3O_{10}]^{5-}$ (here abbreviated to V_3) and $[V_4O_{13}]^{6-}$ (V_4), were posited in 1981, on the basis of limited ^{51}V and ^{17}O NMR evidence,[1] but their existence has not been universally acknowledged.[2,3] The present study was undertaken in order to settle this question, with the aid of a 14.1 T spectrometer, and also to attempt to explain why the linewidths that were previously reported for these species are substantially larger than those of the mono- and di-vanadate species (V_1 and V_2) which exist alongside them. This observation was especially puzzling, because one- and two-dimensional ^{51}V NMR studies of the exchange processes between vanadate oligomers, at lower pH, show a relatively slower exchange between the more highly charged anions than between those with lower charge, so that one would expect V_3 and V_4 to have narrower resonances than V_1 or V_2. An understanding of the linewidths was initially necessary simply in order to maximise the separation of the vanadium resonances. However, it quickly became apparent that these widths, in both the ^{51}V and the ^{17}O NMR spectra, varied in quite unexpected ways with both temperature and even chemical shift, and that they are clearly inconsistent with any simple analysis of the effects of chemical exchange on NMR linewidths.[4]

Very little has been published to date concerning oxygen-exchange processes in aqueous polyanions, except for the observation of very slow processes using isotopic labelling, and one earlier study of a process on the millisecond time-scale using a rather crude method for partially selective oxygen inversion, which demonstrated the existence of a purely internal three-oxygen exchange in the heptamolybdate anion, together with a solvent-linked exchange between mono- and hepta-molybdate in the same solutions, but at higher temperature.[5] The growing importance of polyoxometalate chemistry and of hydrothermal synthesis suggests that a detailed analysis of such exchange processes is overdue. It is also fortunate that selective inversion pulses for heteronuclei have recently become available, because magnetisation-transfer methods enable one to observe kinetic pathways directly.[4] They are used in the present study to show that the dominant processes of exchange which occur at higher values of pH are intra- rather than inter-ionic. This explains why they are not inhibited by high anionic charge.

Experimental

All solutions for pH and quantitative NMR studies were prepared by mixing stock solutions of $NaVO_3$ and NaOH, so as to contain 3.0 mol dm^{-3} Na(Cl) at 25 °C. Boiled, distilled water was used to prepare all the solutions. Sodium chloride (E. Merck, p.a.) was dried at 180 °C and used without further purification. Sodium metavanadate $NaVO_3 \cdot 2H_2O$ (E. Merck, p.a.) was dissolved in hot water, then cooled, filtered through porous glass G4 and also standardised by evaporation to the anhydrous solid. The NaOH solution was prepared from *oljelut* (50% NaOH and 50% H_2O) and standardised against hydrochloric acid.

All solutions were allowed to equilibrate for at least 1 d at either 25 or 0 °C. The pH values were measured with an Ingold U402-M6-S7/100 combination electrode, calibrated using Merck buffer solutions of known pH at the chosen temperature.

Quantitative ^{51}V NMR spectra were obtained at both 157.7 and 105.3 MHz, and at either 298 or 273 K. The higher field was used for the selective inversion experiments, and the lower for determining linewidths and T_1. Other spectra were obtained at suitable temperatures between 298 and 268 K. It was not possible to control ionic strength in all cases, because of the severe sensitivity requirements for ^{17}O NMR spectroscopy, but 3.0 mol dm^{-3} Na(Cl) was used as far as possible. The ^{17}O spectra, with *ca.* 5% isotopic enrichment, were obtained at 81.2 and 54.2 MHz, using Varian VXR600S and Bruker ACP400 spectrometers respectively. Hard pulse widths were typically 10–20 μs, and the ^{17}O spectra typically required 100 000 transients. Approximate spin–lattice relaxation times T_1 were measured for both nuclei, by the inversion-recovery technique, in order to allow a fuller analysis of the kinetic data. They were typically 3 ms for ^{51}V and 5 ms for ^{17}O, and varied in the expected way with temperature and ionic mass. Thus relaxation normally accounts for a contribution to linewidth of 100 Hz or less, and never exceeding 200 Hz. Selective inversion was achieved with the Varian programmable pulse-modulator unit, using the hrm 180 waveform. The delay between the midpoints of the soft inversion pulse and the hard observation pulse was set as low as possible, because the exchange processes were found to be very rapid. Its effective value was estimated to be *ca.* 1 ms. Thus it was only possible to obtain semiquantitative kinetic information by this means, even though the time allowed for exchange was appreciably shorter than the oxygen relaxation time. Subtraction spectra, which show only those resonances affected by the selective inversion, were obtained by subtracting the normal spectrum from the selectively inverted spectrum.

Other exchange rates were calculated from the excess broadening of the ^{51}V and ^{17}O resonances. The linewidths at half height were measured either directly from the spectrum, or

by deconvolution with curve-fitting. It may reasonably be assumed that $T_1 = T_2$ because the relaxation of both ^{51}V and ^{17}O will be dominated by the quadrupolar term; the large frequency difference between these nuclei ensures that scalar relaxation of the second kind will be very small. The natural linewidths were then calculated from the T_1 values, and hence the exchange broadenings were obtained by subtraction, after due allowance for the effects of any window function. Their accuracy is ±20% at best, but this is quite sufficient for the present semiquantitative analysis, especially as in many cases the exchange broadenings are considerably greater than the natural linewidths.

No allowance was made for possible contributions from two-bond ^{51}V–^{51}V couplings through oxygen.[6] Their magnitudes are not known for tetrahedral vanadate species, although couplings of the order of 5–10 Hz must exist between octahedrally co-ordinated vanadium atoms, in *e.g.* decavanadate, in order for two-dimensional ^{51}V–^{51}V correlation (COSY) spectra to be observable at higher temperatures. If such couplings exist in the present species they should broaden the central vanadium resonance by almost twice the broadening of those of the outer V atoms, and thus, if anything, they will tend to reduce the linewidth anomalies reported below. In any case the couplings in V_3 must be considerably smaller than $1/T_1$ (see Table 2) and thus they are unlikely to make a large contribution to the linewidth.

Spectra for the equilibrium analysis were integrated as quantitatively as possible using the NMRI program.[7] Mathematical analysis of pH plus ^{51}V integral data was accomplished using the least-squares program LAKE.[8] This new program can simultaneously treat data from more than one type of measurement, which considerably refines the equilibrium analysis. Calculations and plots of distribution diagrams were performed using the program SOLGASWATER.[9]

The assignments of peaks in the ^{51}V NMR spectra were in accord with earlier work, and confirmed by the potentiometric analysis, which gave excellent fits to the NMR integral data. The ^{17}O NMR assignments were confirmed by manual cross-correlation of the ^{17}O and ^{51}V integrals for given solutions, and also by the peaks having the shifts anticipated for such oxygens, according to the well known correlation of oxygen shift with bond order.[10]

Results

Equilibrium calculations

The 157.7 MHz ^{51}V NMR spectra were obtained at 298 and 273 K, between pH 10 and 12. At pH 12 the only significant vanadate species are the well known dimer, $[V_2O_7]^{4-}$ (V_2), and the monoprotonated monomer $[HVO_4]^{2-}$ (V_1). Below pH 9.9 the resonances, particularly those from the linear trimer and tetramer, become unresolvably broad, with linewidths > 2 kHz. However, within this range the integrals and linewidths can be measured fairly reliably, although as Fig. 1 shows the resonance appearing around δ −586 at 273 K is composite. This resonance is shown by integration to arise from the 'central' VO_2 vanadium atoms in both the linear trimer and the linear tetramer, for its area is never less than half that of the 'terminal' VO_3 vanadium atom resonance at δ −554, nor is it ever larger than this resonance. Fig. 2(*a*) and 2(*b*) show the results of a quantitative LAKE analysis[8] of the four peak areas at either temperature. The fit to the proposed speciation is of good quality at both temperatures, and the formation constants are given in Table 1, relative to the monoprotonated monomer. This convincingly confirms the proposed formulations.

The ^{17}O NMR spectrum at a similar pH, but from a more concentrated solution at 273 K, is shown in Fig. 3(*a*). The various oxygen resonances are identified. One may note that

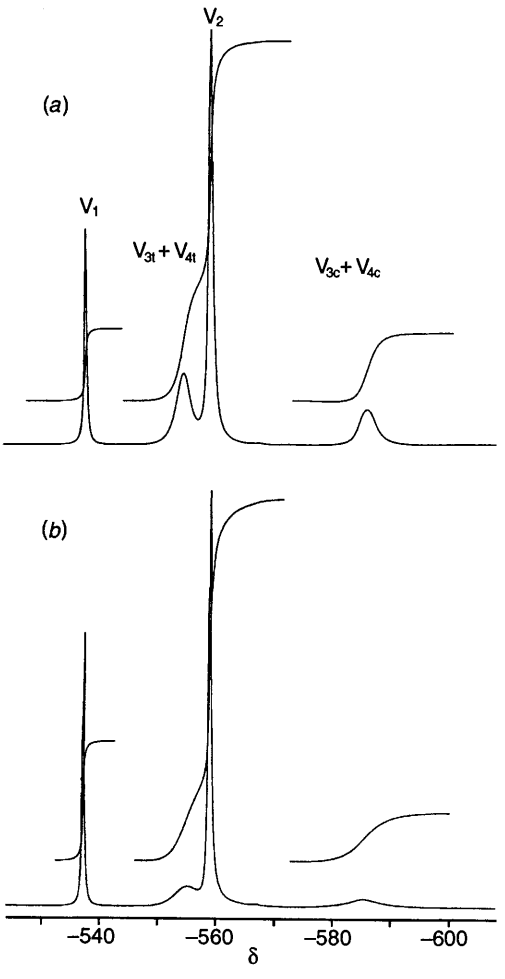


Fig. 1 The 157.7 MHz ^{51}V NMR spectra at (*a*) 273 K, pH 10.65 and (*b*) 298 K, pH 10.20, labelled as in the text

the resonance of the monoprotonated monomer oxygens is so broad at this temperature that it can barely be distinguished from the rolling baseline when this is digitally removed. However, the presence and area of this V_1 resonance is confirmed at 298 K [Fig. 3(*b*)] where it is considerably narrower. Conversely, the trimer and tetramer oxygen resonances at 298 K are extremely broad, with the marked exception of the terminal VO_3 resonances, particularly those of the V_4 species at δ 728. These oxygen NMR spectra confirm the presence of both the V_3 and the V_4 oligomers at high concentrations and at the lower end of the useful pH range. However, Fig. 2(*a*) and 2(*b*) show that V_4 is not formed significantly above pH 10.8.

The ^{51}V NMR shifts at 273 K are listed in Table 1. Small increases in shift were observed in the V_3/V_4 resonances at pH < 10, although they are difficult to measure because of the striking increase in all the V_3 and V_4 linewidths with decreasing pH. This increase is discussed in a later section. The sign of the shift change upon protonation is unexpectedly opposite to that for V_1 and V_2.

Kinetics

The results of two typical ^{17}O magnetisation-transfer experiments, on a more concentrated solution, are shown in Fig. 4(*a*) and 4(*b*). In Fig. 4(*a*), the central trimer oxygen resonance at δ 852 was inverted. It is clear from this subtraction spectrum that the transfer of oxygen atoms to the other two V_3 positions, at δ 720 (terminal O) and 440 (bridging O), is substantial within the 1 ms time-scale. At the same time no transfer whatever is detected to the V_1 or to the V_2 oxygens, or to solvent water. The reverse experiment at this temperature

Table 1 Formation constants

Species	log K^a 273 K	298 K	δ_V [b]
$[V_2O_7]^{4-}$ (V_2^{4-})	1.44	1.11	−558.8
$[HV_2O_7]^{3-}$ (V_2^{3-})	11.56[c]	10.95[c]	−559.9
$[V_3O_{10}]^{5-}$ (V_3^{5-})	13.12	12.13	−554.3 (2V), −586.6 (1V)
$[V_4O_{13}]^{6-}$ (V_4^{6-})	24.39	*d*	−554.3 (2V), −585.4 (2V)

[a] From H^+ and $[HVO_4]^{2-}$ (V_1^{2-}, δ_V −537.2). [b] At 273 K in 3.0 mol dm^{-3} NaCl. [c] *i.e.* pK_a = 10.12 and 9.84 respectively. [d] Not determined, because of severely overlapping V_2 and V_{3t} resonances.

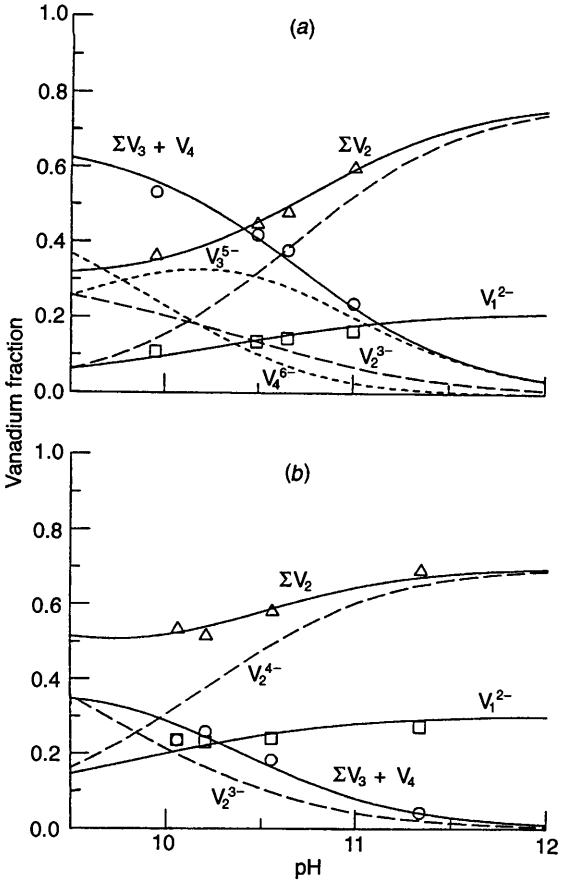


Fig. 2 Experimental (points) and calculated (lines) proportions of vanadium derived from 157.7 MHz ^{51}V NMR spectra of 0.3 mol dm^{-3} vanadates in 3.0 mol dm^{-3} Na(Cl) solution at (*a*) 273 and (*b*) 298 K. Labels as in the text

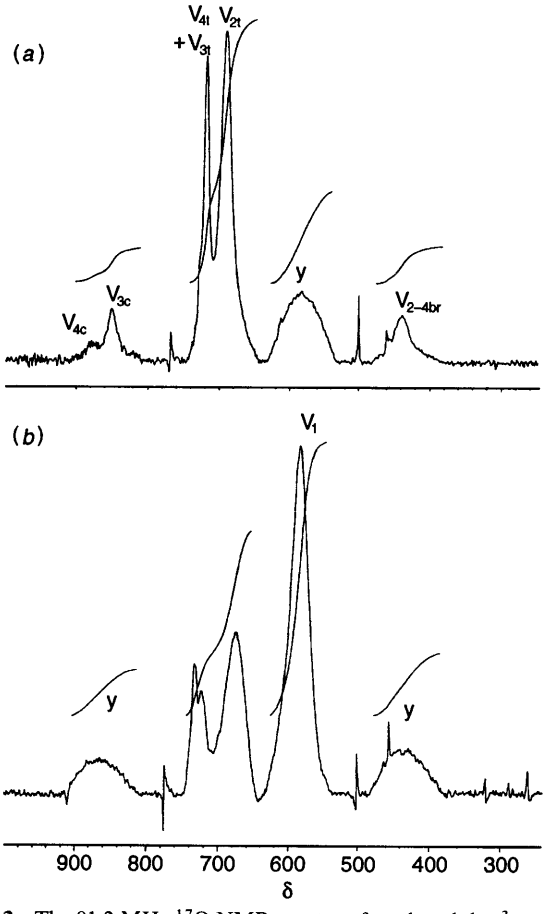


Fig. 3 The 81.2 MHz ^{17}O NMR spectra of *ca.* 1 mol dm^{-3} vanadate solutions at pH 10. Labels as in the text. Peaks marked y are almost too broad to be separable from the originally rolling baseline, and their areas are exaggerated here. (*a*) 273, (*b*) 298 K

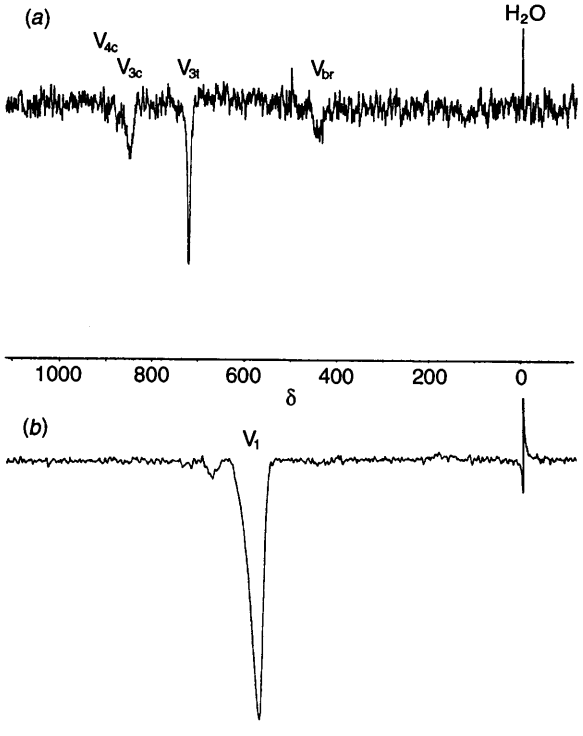


Fig. 4 Oxygen-17 NMR subtraction spectra of the same solution as that in Fig. 3. The normal spectrum was subtracted from a spectrum obtained *ca.* 1 ms after a selective inversion pulse. (*a*) Selective pre-inversion at V_{3c}, 273 K; (*b*) selective pre-inversion at V_1, 298 K

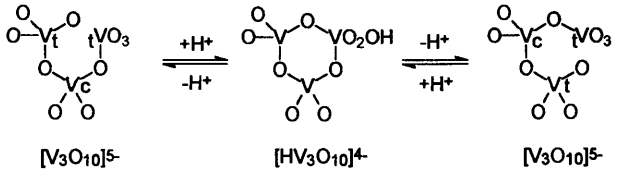
also confirmed the absence of $V_1 \longleftrightarrow V_{3,4}$ exchange. The V_4 oxygens may also be similarly separated from those of V_3, but there is insufficient shift separation for the experiment to confirm this. In confirmation, Fig. 4(*b*) shows that no exchange involving any other species, not even solvent water, occurs with the V_1 oxygens on this time-scale. The only peak to appear, other than the inverted one, is a very weak resonance from V_2 at δ 680. This probably arises either from slower, V_1–V_2 exchange or from the weak, direct transfer of bulk magnetisation between resonances that overlap at their bases. Thus the dominant V_3, and probably also the V_4, exchange processes are likely to be intramolecular, since any intermolecular process involving two V_3 anions, but not V_1 or V_2 anions, is statistically improbable.

This deduction is supported by the ^{51}V NMR linewidths of the V_3 and V_4 resonances, for these are typically an order of magnitude greater than those of V_1 and V_2, whereas their T_1 values are only about $\frac{2}{3}$ those of V_2. The exchange contributions to the linewidths are listed in Table 2 for a series of solutions at 298 and 280 K, all at a pH of 12.3, which is high enough to minimise the formation of V_4. It is evident from this table that the rate of vanadium exchange is small for the V_1 and V_2

Table 2 Relaxation and exchange contributions to ^{51}V NMR linewidths

		c/mol dm^{-3}							
		2.0	1.0	0.5	0.125		2.0	1.0	0.5	0.125
Species	Average T_1/ms	Excess widths * at 280 K				Average T_1/ms	Excess widths * at 298 K			
V_1	4.9	10	10	10	10	9.0	20	20	20	20
V_2	2.9	30	20	10	10	5.5	40	20	20	20
V_{3t}	1.6	230	190	220	230	3.5	270	230	250	280
V_{3c}	2.5	170	220	230	290	4.2	300	330	360	450
V_{3c}/V_{3t}		0.74	1.16	1.05	1.26		1.11	1.43	1.44	1.61

* In Hz, all at pH 12.3.



Scheme 1 Local anionic charges are ignored

anions, but is very significant, and also essentially independent of concentration, for V_3. The only concentration effect that is probably shown in the table is a modest inverse dependence of the exchange rate upon ionic strength. These observations argue for an intramolecular exchange process, the transition state of which has a lower charge than that of V_3.

The pH dependence of the rate could not be determined precisely, because of the overlap of V_3 and V_4 resonances towards lower pH values. However, the rate increases very approximately six-fold between pH 11 and 10. This along with the ionic strength evidence implicates a transition state involving a protonated species.

It is noted here that the linewidth ratios for the two V_3 resonances, given in the table, differ markedly from the 1:2 normally expected for simple exchange involving peaks with area ratio 2:1. Thus both the ^{51}V and the ^{17}O NMR linewidths are anomalous.

Discussion

Since most of the linewidths are anomalous they cannot be used for quantitative calculation of the exchange rates, nor can quantitative comparisons be made between the vanadium and the oxygen widths, although these must be governed by the same exchange processes. It can be noted, however, that the broadest oxygen resonances (V_1 excepted) have exchange broadenings entirely consistent with those of the broadest vanadium resonances. It is the narrow peaks that are unexpected.

If one accepts the above arguments for an intramolecular exchange process in V_3, involving a protonated intermediate, then a kinetic scheme such as that in Scheme 1 can be proposed. The intermediate in this scheme can either revert to the starting anion, or break at the other equivalent V–O bond to form the same chemical species, but with one of the terminal vanadiums, V_t, now exchanged with the central vanadium V_c. A third alternative might be for it to lose OH^-, giving a cyclic trimer. However, much earlier studies[1,2] have demonstrated that this cyclic trimer does not exist stably in aqueous solution, unlike the corresponding cyclic tetramer. Also, the cyclic anions only form at a lower pH.

If a scheme like this applies, then the exchange broadenings will depend on whether the intermediate species is merely a transition state, or alternatively a species with a significant lifetime of its own. If any exchange process $2A \longleftrightarrow B$ occurs without any long-lived intermediate species, then the exchange broadening of A will be half that of B, because A exists for twice as long, on average. This holds true provided that the shift separation of A from B, in Hz, is significantly larger than the exchange rate, and it may be considered to be a consequence of the uncertainty principle, closely analogous to the uncertainty in frequency of a finite wave packet. For smaller shift separations the line broadenings will fall below these values, and the resonances will eventually overlap. In the extreme case of zero shift separation no broadenings can be detected at all, however slow the exchange.

However, if the above intermediate lasts for a significant time, then we must consider not the exchange of V_t with V_c, but rather the separate exchanges of each of these with the corresponding vanadium atom in the intermediate. The same will apply to the oxygens. The intermediate species need not be present in major proportion for this to hold true. Indeed, it may remain undetected, because if it is present only as a minor species, with shifts distinct from those of V_3, then its own exchange broadenings will be considerably larger than those of V_3, and thus become indistinguishable from the baseline. In this case the exchange broadenings of V_t and V_c will be equal. This accords approximately with the 280 K data in Table 2. A more complex possibility is that some of the vanadium resonances of the intermediate are only slightly separated in shift from either V_t or V_c. This will lead to further relative reductions of exchange broadening, which may be apparent in Table 1 at the highest ionic strengths, where the V_c/V_t linewidth ratio even appears to fall below unity.

Table 2 also shows that the exchange-broadening ratios are less anomalous at 298 K, although even here the V_c/V_t linewidth ratio never rises as far as 2:1. It is likely that the intermediate lasts less long at the higher temperature, and thus becomes more like a true transition state.

Similarly anomalous vanadium linewidths have been noted previously,[1] in vanadate solutions at lower pH, for the exchange between the monoprotonated monomer and the cyclic tetramer. The resonances from these anions were shown to have almost equal exchange broadenings, and thus they were also explained in terms of a mutual intermediate having a significant lifetime.

The above arguments can also be applied qualitatively to explain the rather narrow widths of the terminal VO_3 oxygens in the ^{17}O NMR spectrum, at 298 K [Fig. 3(*b*)]. In this case it is probable that some of the oxygen atoms in the intermediate, associated with the original V_t atoms, do not alter greatly in shift during the course of one or more passages through the exchange process depicted in Scheme 1. The time spent by these O atoms at a given resonance frequency will thus be substantially increased, and so their linewidths will be correspondingly decreased. If this argument is valid, then we have detected one of the approximate oxygen-shifts of the

intermediate, even though its resonances are all too broad or too overlapped to see.

The monoprotonated monomer

A quite different explanation must be necessary for the observation, based on Fig. 3(*a*), that the oxygen resonances of V_1 broaden remarkably at the lower temperature. Exchange with either solvent or with the other vanadate oligomers can be ruled out as a contributing mechanism, from the data in Fig. 4(*b*). Also, there is little exchange broadening of the vanadium resonance. An earlier ^{18}O-exchange study by Murmann[11] showed the oxygen-exchange rate with solvent to be as low as 2.4×10^{-2} s^{-1} at 273 K. Almost the only remaining possibility is a significantly slowed rate at which the proton in V_1 jumps between the four oxygens. The order of magnitude of this rate may be estimated if the shift of the OH oxygen is guessed to be about 450 ppm, by analogy with the bridging oxygens, and that the shift of the remaining three oxygens is *ca.* 700 ppm, by analogy with the corresponding oxygens in V_2. Thus the putative frequency separation of the two types of oxygen is 20 kHz at the higher field used, whereas the linewidth at this field, and at 273 K, is at least 2 kHz. Application of the well known equations for fast exchange in NMR spectra leads to a predicted rate of *ca.* 2×10^5 s^{-1} for the proton jumps. This is surprisingly slow, especially as there is no obvious hindrance to a solvent-assisted Grotthus-type mechanism for proton transfer. The slowing may relate to the *ca.* 0.3 Å difference between the V–O and the V–OH bond lengths.

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