Vanadium-51 and Oxygen-17 Nuclear Magnetic Resonance Study of Vanadate(V) Equilibria and Kinetics

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Approximately 15 vanadate(V) and polyvanadate(V) species have been identified by ^{51}V n.m.r. in the range pH 7—14, mostly for the first time. Oxygen-17 n.m.r. spectroscopy confirms in several cases that the vanadium co-ordination is tetrahedral, and that the ^{17}O shifts are correlated closely with formal π-bond order. Most linear and cyclic catenations of VO_4 tetrahedra are found up to V_6, but there is no branched or triprotonated species or cyclic trimer. Several equilibrium constants and pK_a values are reliably measurable. The ion $[HVO_4]^{2-}$ rather than OH^- is shown to be the dominant nucleophile in the two main ring-breaking reactions, and a simple kinetic pathway is proposed for the formation of decavanadate ion.

POPE AND DALE[1] reviewed the aqueous chemistry of isopolyvanadates up to 1967. They reported a general consensus that the only species present in reliably detectable proportions were $[VO_4]^{3-}$, $[HVO_4]^{2-}$, $[H_2VO_4]^-$, $[V_2O_7]^{4-}$, probably $[HV_2O_7]^{3-}$, $[V_3O_9]^{3-}$ and/or $[V_4O_{12}]^{4-}$, the decavanadate ion $[V_{10}O_{28}]^{6-}$ in various states of protonation, and $[VO_2]^+$. Since then there have been several papers concerning the structure,[2,3] protonation sites,[4,5] and kinetics of reactions[6,7] of the decavanadate ion, but no one has challenged the consensus concerning the other species, despite Pope and Dale's comment that it is very unusual to find such a limited range of oligomers in studies involving polymerisation.

This lack of challenge is probably because all the techniques which have been used to date to study the vanadate system have been limited in their ability to resolve the presence of minor species. Even the early 14-MHz ^{51}V n.m.r. studies,[8,9] which in principle might detect several resonances for each distinct vanadium atom present, were limited by the overlapping of lines and by the difficulty of measuring integrals with derivative-mode spectra. Also they needed high overall vanadate concentrations for reasons of sensitivity, which in turn led to inter-species exchange and hence to further line broadening and overlap.

High-field n.m.r. spectroscopy is much less subject to these limitations, although it may still fail to detect a minor species hidden by an accidental coincidence of chemical shifts. In the present study, at 105.2 MHz, an isolated resonance of typical width would be readily detectable at 10^{-4} mol dm^{-3}. In this way, we have detected about nine new vanadate species in the range pH 7—14. If we accept the argument[1,8] that because the observed shifts are correlated linearly with the protonation state of the vanadium they must all follow $[VO_4]^{3-}$ in arising from tetrahedrally co-ordinated vanadium, then the species detected represent most linear and cyclic catenations of VO_4 tetrahedra, subject to the limitation that each vanadium is co-ordinated to at least two terminal oxo-ligands.

EXPERIMENTAL

Vanadium-51 n.m.r. spectra were obtained at 105.2 MHz, and ^{17}O spectra at 54.2 MHz, on a Bruker WH 400 spectrometer. The probe temperature was 273 ± 1 K throughout, this being independently calibrated. The ^{51}V standard was capillary liquid $VOCl_3$ and the ^{17}O standard was solvent water. Although it was just possible to obtain the ^{17}O n.m.r. spectra at natural abundance, most of these spectra were obtained using isotopic enrichment to 5% ^{17}O, using $H_2{}^{17}O$ from Prochem Ltd. The vanadate solutions were prepared from $[NH_4][VO_3]$ (Hopkin and Williams, reagent grade) which had been treated with Na[OH] and recrystallised. All ^{51}V n.m.r. measurements except the few specifically noted below were made in 2.0 mol dm^{-3} $Li[ClO_4]$. The total vanadium concentration for the measurements varied from 0.5 to 0.0004 mol dm^{-3}, and most of the quantitative results were obtained from solutions $\leqslant 0.1$ mol dm^{-3} in V.

The ^{51}V spectra were obtained from the accumulation of 1 000—10 000 transients, at about ten per second. The ^{17}O spectra were similarly obtained, but required up to 200 000 transients. The apparent ^{17}O linewidths were typically 500 Hz for terminal O and 1 000 Hz for bridging O. However, by applying a line narrowing of only 50 Hz, followed by a superimposed Gaussian-decay envelope, to the ^{17}O spectrum of $[VO_4]^{3-}$ it was possible to resolve the ^{51}V coupling and to measure an underlying ^{17}O linewidth of only 50 Hz. (The same resolution enhancement was used for related spectra.) This implies that the linewidth attributable to the ^{17}O T_2 is only of the order of 100 Hz in this case, and that much of the extra linewidth actually observed is due to coupling and exchange.

The ^{51}V spectrum width was normally 20 kHz. The pulse width was 20 μs, which was just small enough to stimulate all the resonances fully. The actual reliability of the integrals depended very much on the relative size and overlap of the peak concerned, and is best judged by the calculated standard deviations of the equilibrium constants which indicate an average uncertainty of ±15%. In the more favourable cases the relative integrals were reproducible to within ±5%. The ^{17}O integrals were less reliable, because of baseline roll. Also, even with a pulse width of only 10 μs, it was difficult to stimulate all resonances equally and simultaneously. However, spectra repeated under various conditions showed that the integral ratios for the terminal ^{17}O resonances were reproducible within 20%. These integrals were not used for obtaining equilibrium constants.

Most of the concentrations used in the calculations were measured directly from integrals. However, there were serious problems of line overlap, especially at the higher concentrations, and therefore some overlapping lines were resolved indirectly. In these cases the integral corresponding to the narrower component was calculated from its width and height, in comparison with an isolated line in the same spectrum, and then the integral of the underlying broad component was found by subtraction. In some cases involving a resonance arising from two species in rapid proton exchange, the proportion of each was calculated either from the pK_a or from the known variation of shift with pH. A computer fit of the overall band shape was not attempted because of the complexity of the underlying exchange processes. The main equilibrium constants were determined from the integrals of between 20 and 32 spectra, plus the use where necessary of the pK_a values reported in the Table.

The ^{51}V chemical shifts reported here are about 5 p.p.m. more negative than those found at 14 [8] and at 22.6 [10] MHz. About 1 p.p.m. of this difference was shown to be due to the Li[ClO$_4$]; the remainder is a bulk magnetic-susceptibility effect arising from the use of a capillary standard. The estimated shift error is $\delta \pm 0.3$, except for the more minor components, where it is larger, and the corresponding ^{17}O error is $\delta \pm 2$.

RESULTS AND DISCUSSION

Figure 1 illustrates the type of spectra obtained. Increasing the pH generally increases the relative proportion of the left-hand peaks, and increasing the concentration increases the right-hand peaks relatively and usually broadens all peaks. It is convenient to discuss the detailed observations in terms of the polymerisation state of the underlying VO$_4$ unit.

Monomers.—In Figure 2 are plotted the ^{51}V chemical shifts of the four major components (excluding decavanadate) against pH. The right-hand two peaks (12 and 14) are pH invariant. The left-hand line (2,3), however, has two pH inflections. One, not measured in this work except at its extremes, is at pH ≈ 12 and corresponds to the equilibrium (1).

$$[VO_4]^{3-} + H^+ \rightleftharpoons [HVO_4]^{2-} \qquad (1)$$
$$\delta_V = -541.2 \qquad \delta_V = -538.8$$

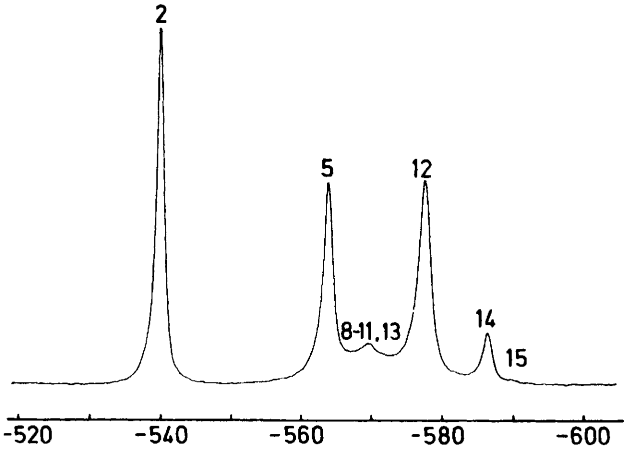


FIGURE 1 Vanadium-51 n.m.r. spectrum of a solution at pH 8.28, overall 0.01 mol dm^{-3} in vanadium. Numbers refer to species in the Table, column 1

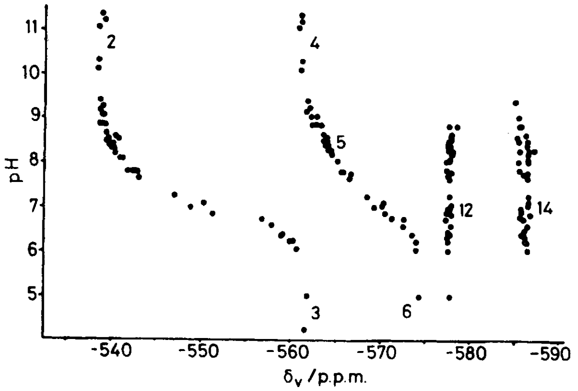


FIGURE 2 Chemical shifts of major species as a function of pH. Numbers refer to the species in the Table, column 1

The [VO$_4$]$^{3-}$ species may be readily identified from its very small linewidth. The second inflection corresponds to equilibrium (2) and has a pK_a of 7.1 under the conditions of this experiment. This is about 1.0 pK_a unit

$$[HVO_4]^{2-} + H^+ \rightleftharpoons [H_2VO_4]^- \qquad (2)$$
$$\delta_V = -538.8 \qquad \delta_V = -560.4$$

less than observed at 293 K in studies at somewhat lower ionic strength,[1] and about 0.9 of a pK_a unit lower than that observed in the present study when the Li[ClO$_4$] was omitted. Evidently the more highly charged species is favoured both by high ionic strength and by low temperature. The assignment of the [H$_2$VO$_4$]$^-$ resonance replaces that in our earlier work,[8] where the pH inflection was not observable.

A peak with the same pH dependence as [HVO$_4$]$^{2-}$ was observed at $\delta_O = +573$ in the ^{17}O n.m.r. spectrum of a solution 0.7 mol dm^{-3} in V and enriched to 5% in ^{17}O. The lineshape under conditions of resolution enhancement corresponded to an underlying $|^1J_{VO}|$ (average) ≈ 34 Hz. The corresponding peak for [VO$_4$]$^{3-}$ could be clearly resolved into the expected octuplet with $|^1J_{VO}| = 62.6$ Hz. Lutz *et al.*[11] report 61.6 ± 2.5 Hz for this coupling. Its shift was at $\delta_O = +565$. As protonation does not affect the average π-bond character of the oxygens, the protonation shift of +8 p.p.m. must be a direct effect, corresponding to +32 p.p.m. on a single oxygen. The sign and approximate magnitude of this protonation shift are as predicted,[5] and help to explain the otherwise unexpected ^{17}O shifts observed on protonation of decavanadate ion.[4]

Dimers.—The second line from the left in Figure 2 (species 4,5,6) has an obvious pH inflection at pH 7.2. However, closer inspection shows that there is a second, shallower inflection at pH ≈ 9. If the rapid equilibration (3) is assumed to take place then the equilibrium

$$[V_2O_7]^{4-} \rightleftharpoons [HV_2O_7]^{3-} \rightleftharpoons$$
$$\delta_V = -561.0 \ \mathrm{p}K_a = 8.9 \ \delta_V = -563.5 \ \mathrm{p}K_a = 7.2$$
$$[H_2V_2O_7]^{2-} \qquad (3)$$
$$\delta_V = -572.7$$

constant log $K = \log_{10}[V_2O_7{}^{4-}] - 2 \log_{10}[HVO_4{}^{2-}]$ may be calculated between pH 6.5 and 11.0 as +1.39 ±0.12 (32 determinations). The quoted root-meansquare (r.m.s.) deviation worsens considerably for a change of more than 0.1 in the higher value of pK_a, and the lower value of pK_a is well determined by the shift data. Thus the combination of the pH curve and the equilibrium-constant calculation defines both pK_a values within 0.1 unit. A previous study at 25 °C and in 3 mol dm^{-3} Na[ClO$_4$] found log $K = 1.68 \pm 0.04$.[12] However, the two pK_a values for $[H_2V_2O_7]^{2-}$ have not previously been reported. The pK_a difference is consistent with reported values (at 25 °C) [13] at lower ionic strengths for $[H_2P_2O_7]^{2-}$, *viz.* 2.0 ($I = 1.0$) or 2.3 ($I = 0.1$ mol dm^{-3}) units. At pH >11 the apparent value of log K based on the area of the monomer resonance is somewhat reduced owing to the presence of $[VO_4]^{3-}$. In the absence of Li[ClO$_4$] the pK_a values increase by *ca.* 0.9 unit, as might be expected.

We obtained further evidence concerning the structure of the $[V_2O_7]^{4-}$ ion from its ^{17}O n.m.r. spectrum. Peaks were observed, showing the appropriate pH dependence, at $\delta_O = +695$ and $+405$, with the respective area ratio within experimental error equal to the 6 : 1 predicted for terminal : bridging oxygens. The shift of the bridging oxygen implies a somewhat bent V–O–V axis (see further discussion). Under resolution enhancement, the terminal-oxygen resonance had an envelope whose shape was consistent with $|^1J_{VO}| = 31$ Hz, which is only half the 62 Hz noted above for $[VO_4]^{3-}$. Although some of this apparent reduction in coupling might be accounted for by ^{51}V relaxation (the ^{51}V linewidth is *ca.* 130 Hz), the residual VO coupling is nevertheless sufficient to leave a dip at the top of the resonance envelope.

Trimers.—There has been argument for years [1] over whether the main species present in a neutral solution of ' metavanadate ' is primarily the cyclic trimer $[V_3O_9]^{3-}$ or the cyclic tetramer $[V_4O_{12}]^{4-}$. In this pH region the dominant peak at all concentrations greater than 10^{-3} mol dm^{-3} is at $\delta_V = -577.6$. It is difficult to distinguish between whether this arises from a trimer or a tetramer because in equilibrium (4) the constants $x_n = (\log_{10}$-

$$n\,[H_2VO_4]^- \rightleftharpoons [V_nO_{3n}]^{n-} + nH_2O \qquad (4)$$

$[V_nO_{3n}{}^{n-}])/n$ ($n = 3$ or 4) differ by only $\log_{10}[V_nO_{3n}{}^{n-}]/12$. Nevertheless we present evidence below which on balance suggests that the peak at $\delta_V = -577.6$ arises from a cyclic tetramer rather than a trimer, and that the peaks at $\delta_V = -585.0$ and -598.4 arise from higher oligomers.

The only clear evidence for a trimeric species is in the region pH 9—11, where one might expect to find only unprotonated species. The dominant peaks in this region arise from $[HVO_4]^{2-}$ and $[V_2O_7]^{4-}$, but two other peaks appear at $\delta_V = -556.3$ and -590.4, as illustrated in Figure 3. The area ratio of the last two peaks is not easy to measure because of overlap with the peak at $\delta_V = -561.0$, but is constant and entirely consistent with the value of 2 : 1 expected for the linear trimer $[V_3O_{10}]^{5-}$. The shift for the terminal vanadiums is, as expected, close to that for $[V_2O_7]^{4-}$, and the shift of the central vanadium is close to that of the larger cyclic species. The equilibrium constant, obtained from eight determinations, was $\log_{10}K = \log_{10}[V_3O_{10}{}^{5-}] - 3\log_{10}[HVO_4{}^{2-}] + \text{pH} = +21.1 \pm 0.2$.

Further support for the presence of $[V_3O_{10}]^{5-}$ comes from the ^{17}O n.m.r. spectrum of a 0.7 mol dm^{-3} solution at the same pH, where in addition to the resonances for $[V_2O_7]^{4-}$ and $[HVO_4]^{2-}$ we observed two fairly sharp resonances approximately in the area ratio 2 : 6 at $\delta_O = +852$ and $+721$, and another broader resonance at $\delta_O = +438$ of area and shift consistent with its arising from the two bridging oxygen atoms.

The trimer resonances broaden substantially below pH 9, and the resonance from the terminal vanadiums shifts to lower frequency, as would be expected for protonation by analogy with $[V_2O_7]^{4-}$. The pK_a for the first protonation step of the trimer appears to be very similar to the 8.9 observed for the dimer, although unfortunately the shift cannot be traced against pH owing to exchange broadening and overlap.

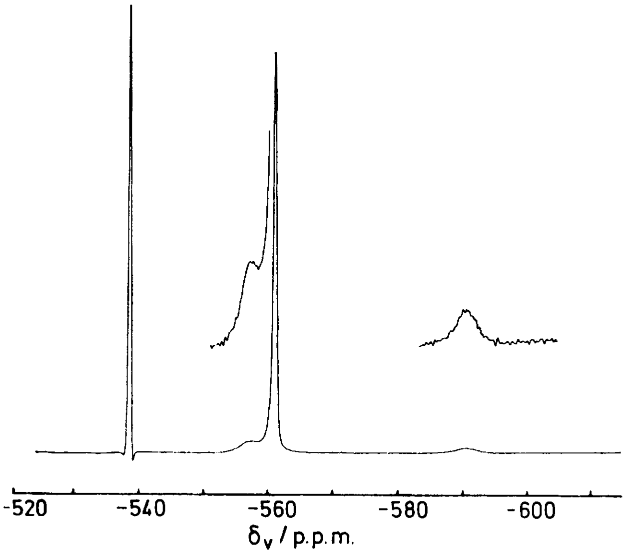


FIGURE 3 Vanadium-51 n.m.r. spectrum of an 0.1 mol dm^{-3} solution, pH 10.09, with resolution enhancement, showing two small resonances arising from $[V_4O_{12}]^{4-}$ in addition to larger resonances from $[HVO_4]^{2-}$ and $[V_2O_7]^{4-}$. Vertical expansions × 7

One would not expect the pK_a for the second protonation of $[V_3O_{10}]^{5-}$ to be less than the 7.1 observed for $[V_2O_7]^{4-}$, and therefore it would seem reasonable to assume that the diprotonated trimer is present at neutral pH. But if one guesses the pK_a values to be 8.9 and 7.4, then using the other equilibrium constants reported below one can calculate that the solutions observed would be at least 10% in $[H_2V_3O_{10}]^{3-}$ at pH < 7.0. No additional peaks of this intensity are observed. Therefore, unless an accidental overlap occurs with the main peaks at $\delta_V = -577.6$ and -586.0, one must conclude that the second pK_a of $[V_3O_{10}]^{5-}$ is unexpectedly low. The alternative possibility of very rapid exchange between cyclic and diprotonated species is ruled out by the fixed chemical shift of the dominant species, and by its two clearly distinct ^{17}O resonances. It remains likely, however, that other exchange processes broaden the resonances of $[H_2V_3O_{10}]^{3-}$ and thus make it hard to detect.

Tetramers.—The linear tetramer $[V_4O_{13}]^{6-}$ corresponds to a slightly higher mean protonation level per vanadium atom than that of the linear trimer, and it is therefore not surprising to find that it is not observed at pH >9. At or near pH 9, however, we observed a very small, quite sharp resonance (*ca.* 0.5% of total V) at $\delta_V = -569.1$. At pH <9 this peak broadens and merges with the underlying broad resonances. We assign it tentatively to the terminal resonances of $[V_4O_{13}]^{6-}$, since this species should be the next to appear after $[V_3O_{10}]^{5-}$ on lowering the pH. We associate its broadening at lower pH with diprotonation and consequent cyclisation to $[V_4O_{12}]^{4-}$.

The broad group of resonances observed between pH 9 and 7 extends from $\delta_V = -560$ to -590. It is reasonable to assume that around pH 9 this represents at least some monoprotonated linear trimer. In general, between pH 7.7 and 8.9, the area of the broad peak has a pH and concentration dependence that fits best with its arising from $[V_4O_{13}]^{6-}$. The equilibrium constant was found to be $\log_{10}K = -\log_{10}[\text{broad peak}] + \log_{10}[V_4O_{12}{}^{4-}] + 2\ \text{pH} = 16.51 \pm 0.22$ (from 20 determinations). However, the broadness of the peak belies the simplicity of this formula, which can only be regarded as an average.

One other way of determining the average state of protonation of the species giving rise to the broad peak is to study the stoicheiometry of the overall reaction with base. The calculation does not give very accurate results, but suggests a somewhat higher average protonation state than the equilibrium constant would imply. Unfortunately, the ^{17}O resonances in this pH region do not allow further elucidation of the nature of the species because of their breadth.

The above argument depends on identifying the dominant resonance at $\delta = -577.6$ as that of the cyclic tetramer $[V_4O_{12}]^{4-}$. Our evidence for this, based on 26 determinations, is that the reduced equilibrium constant $\log_{10}K = \frac{1}{4}\ (4\ \log_{10}[HVO_4{}^{2-}] - \log_{10}[V_4O_{12}{}^{4-}] + 4\ \text{pH}) = -10.004 \pm 0.074$ whereas, assuming the same data correspond to the formation of a cyclic trimer, we obtain $\log_{10}K' = \frac{1}{3}\ (3\ \log_{10}[HVO_4{}^{2-}] - \log_{10}[V_3O_9{}^{3-}] + 3\ \text{pH}) = -9.865 \pm 0.099$. In addition, the fit for the tetramer–pentamer equilibrium described below is marginally more satisfactory than for a trimer–tetramer equilibrium. Hence, we tentatively identify the resonance at $\delta = -577.6$ as that of the tetramer. It is possible that the apparently total absence of the cyclic trimer is connected with the unexpectedly difficult second protonation of the linear trimer, and also with the close approach required for the three V atoms.

The ^{17}O n.m.r. spectrum of an 0.9 mol dm^{-3} vanadate solution at pH 7 shows only two resonances, at $\delta_O = +472$ and $+928$, with the latter being narrower and having twice the area of the former. This is entirely and solely consistent with the dominating presence of cyclic oligomers. Unfortunately, the ^{17}O n.m.r. spectrum was not able to resolve the various cyclic oligomers that were resolved in the ^{51}V spectrum.

There is no reliable way of estimating the anticipated proportions of the diprotonated linear tetramer in neutral solutions. However, two very small peaks, each *ca.* 0.2% of the total peak area, were observed for most solutions at pH <7.5, at δ -597 and -605. Their proportion appears to be independent of both pH and overall vanadium concentration, which is consistent with their arising from the central and terminal resonances of $[H_2V_4O_{13}]^{4-}$. At pH >7 the resonances broaden substantially, especially at high overall concentrations.

Pentamers.—There is no direct evidence for linear pentameric species, although they probably contribute to the broad peak described above. However, the single peak at $\delta_V = -586.0$ must arise from a symmetrical cyclic species, and one would reasonably suppose this to be a pentamer from its relation to the peak of the cyclic tetramer. The reduced equilibrium constant $\log_{10}K = \frac{1}{9}\ (5\ \log_{10}[V_4O_{12}{}^{4-}] - 4\ \log_{10}[V_5O_{15}{}^{5-}]) = -0.015 \pm 0.029$ (31 determinations) whereas the corresponding constant for a tetramer–hexamer equilibrium has a much larger standard deviation (± 0.068). The corresponding reduced equilibrium constant for an assumed trimer–tetramer equilibrium is $\log_{10}K' = \frac{1}{7}\ (4\ \log_{10}[V_3O_9{}^{3-}] - 3\ \log_{10}[V_4O_{12}{}^{4-}]) = -0.061 \pm 0.035$ which is slightly less convincing. We therefore assign the peak at $\delta_V = -586.0$ to the cyclic pentamer $[V_5O_{15}]^{5-}$ and note that its ^{17}O n.m.r. shifts coincide with those of $[V_4O_{12}]^{4-}$.

Brief measurements at 290 and 313 K indicate that ΔH (five tetramers $\longrightarrow$ four pentamers) ≈ -10 kJ mol^{-1}, which is almost negligible.

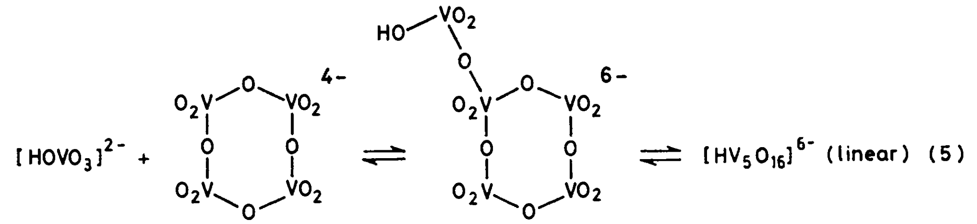
Hexamers.—The one remaining peak found in the ^{51}V spectra, at pH <8, is at $\delta_V = -589.4$. Its area is *ca.* 10% of the peak at $\delta_V = -586.0$ with which it overlaps and is independent of pH, but increases measurably at high concentrations and additionally at high ionic strength. Its overlap prevents an accurate calculation such as in the previous section, but it may reasonably be assigned to the cyclic hexamer, $[V_6O_{18}]^{6-}$, on the basis of the above data and the way it fits into a chemical-shift and area sequence with $[V_4O_{12}]^{4-}$ and $[V_5O_{15}]^{5-}$.

If this assignment is correct, then it may solve a long-standing puzzle in vanadate chemistry, namely how does the decavanadate ion, with its complex structure, assemble with such kinetic ease on acidification of alkaline vanadate solutions? The cyclic hexamer $[V_6O_{18}]^{6-}$ could readily form the planar 3×2 arrangement of vanadium atoms in the decavanadate ion, with the remaining four out-of-plane vanadiums coming from, *e.g.*, $[H_2VO_4]^-$, with subsequent loss of OH^-. This proposal need not conflict with Murmann and Giese's different explanation of the much slower dissociation of decavanadate.[14]

Chemical Shifts.—The ^{51}V chemical shifts are all entirely consistent, despite the present reassignments, with a graph[8] showing a linear dependence of shift on the mean vanadium protonation state, plus a change in co-ordination number at pH <7. The total range of shifts for tetrahedral vanadates is only 70 p.p.m., whereas the total range including peroxovanadates[10] and vanadium(V) sulphide complexes[15] is over 2 200 p.p.m. We therefore do not feel able to attempt further analysis of the oxovanadate shifts.

In contrast, the ^{17}O shifts cover a wide range, and fit well with the shifts observed for other oxy-anions. Kidd[16] plotted the ^{17}O shifts for various chromate species against the average π-bond character of the Cr=O bond, based on simple valence-bond formulae. The vanadate ^{17}O shifts fit with Kidd's predictions (given in brackets) as follows: $-VO_2^{-}$– 852, 928 (900); $-VO_3^{2-}$ 695, 721 (710); VO_4 565, 573 (620); and -VOV- 405, 438, 472 (340). If the small discrepancy in the last set of figures is meaningful, this may imply that the V–O–V bridge to which they refer is rather less bent than the Cr–O–Cr bridge, and hence has some π character. It may even be that the preferred V–O–V angle is too large to permit a cyclic trimer. Observed V–O–V angles vary between 117 and 180° in crystals.[17]

Kinetics.—The ^{51}V linewidth of $[V_4O_{12}]^{4-}$ is constant at 80 Hz below pH 7, but then increases with pH. The reciprocal of the extra linewidth (above pH 7) is a direct measure of the lifetime of the cyclic tetramer under conditions where the resonance is well resolved. Surprisingly, it does not correlate at all well with $[OH^-]$. Instead, increased concentration at fixed pH broadens the resonance. The extra linewidth does, however, correlate well with $[HVO_4^{2-}]$, calculated where necessary from the equilibrium constants given above (Figure 4, closed circles). The ring-breaking reaction must therefore involve $[HVO_4]^{2-}$ as nucleophile in preference to OH^-, perhaps because of its greater concentration.



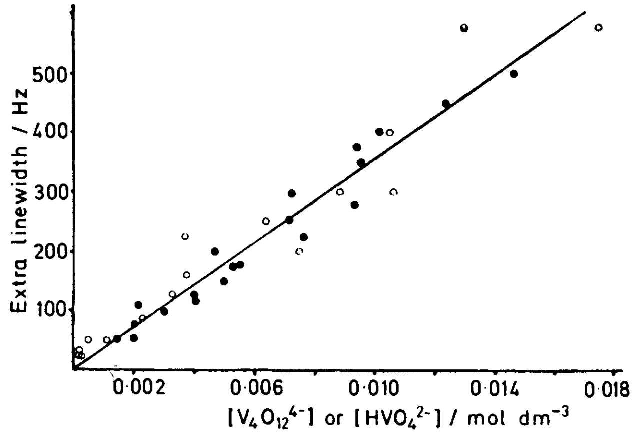


FIGURE 4 Plot of extra line broadening of other species against concentration: (●), broadening of $[V_4O_{12}]^{4-}$ against $[HVO_4^{2-}]$; (○), broadening of $[HVO_4]^{2-}$ against $[V_4O_{12}^{4-}]$

This is confirmed by the observation that the $[HVO_4]^{2-}$ resonance is broadened in proportion to $[V_4O_{12}^{4-}]$. However, we were surprised to find that the corresponding plot of the extra $[HVO_4]^{2-}$ linewidth against $[V_4O_{12}^{4-}]$ fits closely (Figure 4, open circles) the same slope as found for that of $[V_4O_{12}]^{4-}$ against $[HVO_4^{2-}]$ (full circles), given that the scatter of points is worse because of the lower peak intensity. If the reaction between the two species were a simple exchange, *i.e.* $A^* + A_4 \rightleftharpoons A + A_3A^*$, then the slope for the $[HVO_4]^{2-}$ width should be four times that for the $[V_4O_{12}]^{4-}$ width, so that peaks of equal intensity would have equal broadening. The equal slopes that are observed must arise because each collision between the two species produces a third species, presumably the linear pentamer, which lasts for a substantial time, *i.e.* $A^* + A_4 \rightleftharpoons A_4A^*$ (long lived) $\rightleftharpoons A + A_3A^*$. In this scheme, one collision dephases the precession of all the $[V_4O_{12}]^{4-}$ vanadium spins instead of just one of them. A similar observation was made by Kidd and co-workers[18] in an ^{17}O n.m.r. study of chromate species. The coincidence of the two slopes confirms that $[V_4O_{12}]^{4-}$ is indeed a tetramer rather than a trimer, subject to the caution outlined below. We propose the mechanism in equation (5), or else the corresponding concerted processes.

The cyclic pentamer shows a line broadening which is also proportional to $[HVO_4^{2-}]$, but is only *ca.* 30% of that observed for $[V_4O_{12}]^{4-}$. The collision is presumably less effective because of the increased repulsion between the ions. The same repulsion may explain what is evident from Figure 3, namely that $[HVO_4]^{2-}$ does not act as an efficient nucleophile towards the unprotonated linear trimer $[V_3O_{10}]^{5-}$.

The monoprotonated dimer shows a line broadening approximately proportional to $[V_4O_{12}^{4-}]$, and *ca.* 70% of that observed for $[HVO_4]^{2-}$. As the broadening of the $[V_4O_{12}]^{4-}$ peak does not correlate well with $[HV_2O_7^{3-}]$, and as $[HV_2O_7^{3-}]$ is generally only half that of $[HVO_4^{2-}]$, we have ignored any contribution to the tetramer linewidth from nucleophilic attack by the dimer, and attribute the broadening of the $[HV_2O_7]^{3-}$ resonance to the formation of, *e.g.*, linear tetramer species.

A few measurements at 290 and 313 K indicate that $\Delta H^{\ddagger}$ for the $[HVO_4]^{2-} + [V_4O_{12}]^{4-}$ reaction is *ca.* +15 kJ mol^{-1}.

Proposed assignments and equilibrium constants

Number	Species	δ_V/p.p.m.	$\Delta\nu_{\frac{1}{2}}$(V)/Hz	δ_O/p.p.m.	$\lvert{}^1J_{VO}\rvert$/Hz	K or pK_a
1	$[VO_4]^{3-}$	−541.2	<5	+565	62.6	
2	$[HVO_4]^{2-}$	−538.8	100	+573	34	p$K_a \approx 12$
3	$[H_2VO_4]^-$	−560.4	200			p$K_a = 7.1$
4	$[V_2O_7]^{4-}$	−561.0	130	+405 (br), +695 (t)	31 (t)	$\log_{10}(4/2^2)^* = 1.39$
5	$[HV_2O_7]^{3-}$	−563.5	180			p$K_a = 8.9$
6	$[H_2V_2O_7]^{2-}$	−572.7	150			p$K_a = 7.2$
7	$[V_3O_{10}]^{5-}$	−556.3, −590.4	<400, 350	+438 (br), +721 (t), +852		$\log_{10}(7/2^3.H)^* = 1$
8	$[HV_3O_{10}]^{4-}$ (?)	*ca.* −570				p$K_a = 8.9$
9	$[V_4O_{13}]^{6-}$	−569.1, *ca.* −585				$\log_{10}($' 9 '$/12.H^2)^* = 16.5$
10	$[HV_4O_{13}]^{5-}$	−560 to −590				p$K_a \approx 9$
11	$[H_2V_4O_{13}]^{4-}$ (?)	−597, −605	<300			
12	$[V_4O_{12}]^{4-}$	−577.6	130	−472 (br), +928 (t)		$\log_{10}(12/2^4.H^4)^* = 40.01$
13	$[V_5O_{16}]^{7-}$ (?)	−570				
14	$[V_5O_{15}]^{5-}$	−586.0	150	−472 (br), +928 (t)		$\log_{10}(15^4/12^5)^* = 0.14$
15	$[V_6O_{18}]^{6-}$	−589.4	150			$\log_{10}(16^5/15^6)^* \approx -7$

* The numbers in parentheses represent concentrations of species as numbered in column 1, and H = [H$^+$].

Conclusions.—The chemical shifts and the unbroadened linewidths at 273 K of the various species identified above are recorded in the Table for convenience, together with equilibrium constants and pK_a values. Because it is not easy to visualise actual concentrations from equilibrium constants, we have in Figure 5 plotted the observed concentrations (as % V) of all but the most minor species against pH, for a solution overall 0.1 mol dm^{-3} in V.

Our study confirms the generally accepted conclusion that tetrahedral vanadium(V) is unwilling to be co-ordinated to less than two non-bridging oxide ligands. There are exceptions to this rule, such as $VOCl_3$ and $[V(O_2)_4]^{3-}$, but even with peroxovanadate complexes there is a marked thermodynamic preference for two rather than three or four peroxo-ligands.[10] In oxovanadates the effect of attempting to protonate or catenate the third or fourth oxo-ligand is to increase the vanadium co-ordination number, whereas this may not be possible with bulkier ligands, such as Cl$^-$ and O_2^{2-}.

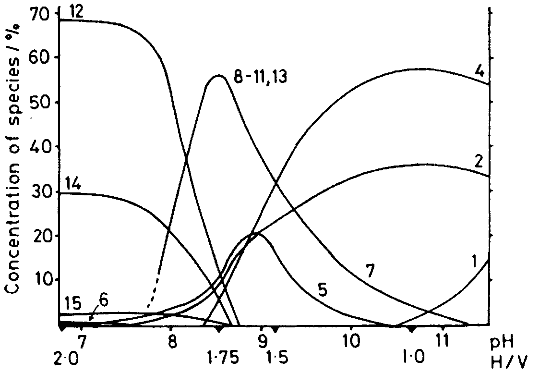


FIGURE 5 Observed percentage concentrations of species (as % V), 0.1 mol dm^{-3} overall, as a function of pH. The minor species $[H_2VO_4]^-$ and $[H_2V_4O_{13}]^{4-}$ are omitted, and no attempt is made to resolve the broad peak into its underlying components

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