Oxygen Exchange and Protonation of Polyanions: A Multinuclear Magnetic Resonance Study of Tetradecavanadophosphate(9−) and Decavanadate(6−)

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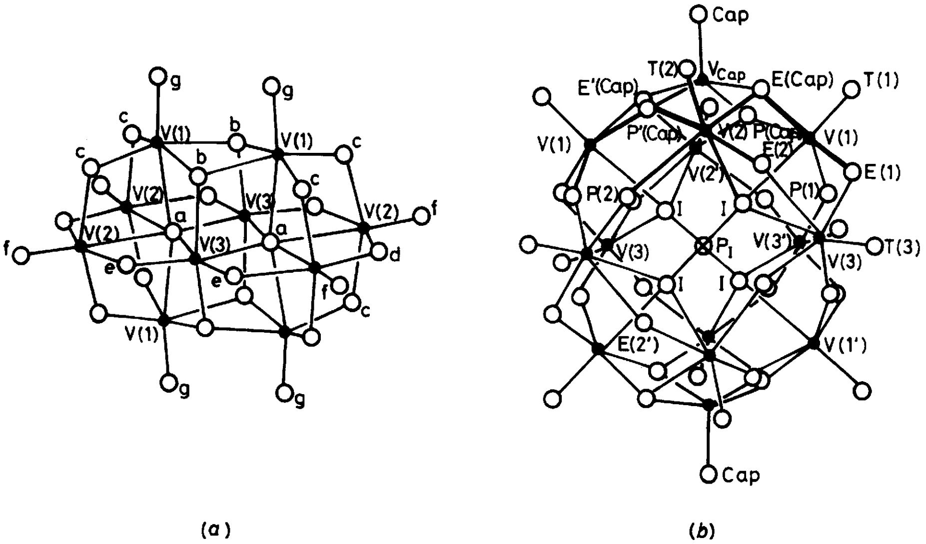
Unlike decavanadate(6−), tetradecavanadophosphate(9−) shows pH-dependent differential rates of exchange of oxygen with solvent water. If the anion's structure is described as a Keggin-type 'sphere' with polar 'caps,' then at pH > 5 the caps are kinetically stabilised with respect to the 'equator,' whereas at pH < 1 the caps are destabilised and only the four half-hemisphere three-octahedron units resist exchange. These observations are related to bulk distortions of the heteropolyanion which can be deduced from the variations of the ^{17}O, ^{51}V, and ^{31}P chemical shifts with pH. The values p*K*a1 = 4.7 and p*K*a2 = 1.3 have been determined for the heteropolyanion. Decavanadate(6−) distorts similarly. The chemical shifts of singly bridging oxygen are shown to increase as the bond angle at oxygen decreases.

Although iso- and hetero-polyanions have been the subject of extensive structural study, relatively little is known at the subunit level about their substitution lability[1,2] or indeed their protonation. Nuclear magnetic resonance (n.m.r.) spectroscopy, particularly of ^{17}O, has proved a powerful method for identifying polyanions in solution,[1–3] but it too is hampered by the lack of any reliable correlation between the chemical shift and the MO bond lengths or MOM angles of oxo-ligands for a given co-ordination number. Even the effect of protonation upon chemical shift is not well defined. One partial exception to the above is the decavanadate anion, $[V_{10}O_{28}]^{6-}$ [Figure 1(*a*)], and its mono- and di-protonated forms. Klemperer and Shum[4] studied the isotopic exchange of this anion with enriched water, and found that all its oxo-ligands reacted at the same rate. They also measured the pH dependence of the ^{17}O shifts over a limited range, and concluded that protonation occurred primarily at two bridging-oxygen sites O_b and O_c. This conclusion was challenged by Howarth and Jarrold,[5] who preferred the terminal oxygen sites O_f and O_g because the central vanadiums shift far less with pH. However, it was partially supported by the reassessment of a crystal structure analysis[6] of $[H_2V_{10}O_{28}]^{4-}$, showing loosened binding of two symmetrically disposed O_c oxygens.

More recently, Kato *et al.*[7] published the crystal structure and ^{51}V n.m.r. solution spectrum of the first well-characterised heteropolyphosphovanadate, $[HPV_{14}O_{42}]^{8-}$ [Figure 1(*b*)]. The present study confirms the preliminary spectra[7,8] showing that the solid-state structure persists in solution. It also yields pH *vs.* chemical shift curves that bear a striking similarity to those for decavanadate, but which enable a refinement of earlier explanations of these shifts.[2,9]

As Kato *et al.*[7] have identified the structure of the heteropolyphosphovanadate anion as being of symmetrically bicapped Keggin type, there was also the hope that different oxo-ligands might exchange at different and measurable rates. For example, one might predict that the capping VO units, whose function is to reduce the anion's net charge, would be less necessary and hence more readily exchanged at low pH. Our results confirm this hypothesis, and contribute to an understanding of regional stability within the anion.



(*a*) (*b*)

Figure 1. Structures of (*a*) decavanadate, $[V_{10}O_{28}]^{6-}$, and (*b*) the heteropolyphosphovanadate, $[HPV_{14}O_{42}]^{8-}$ (ref. 7)

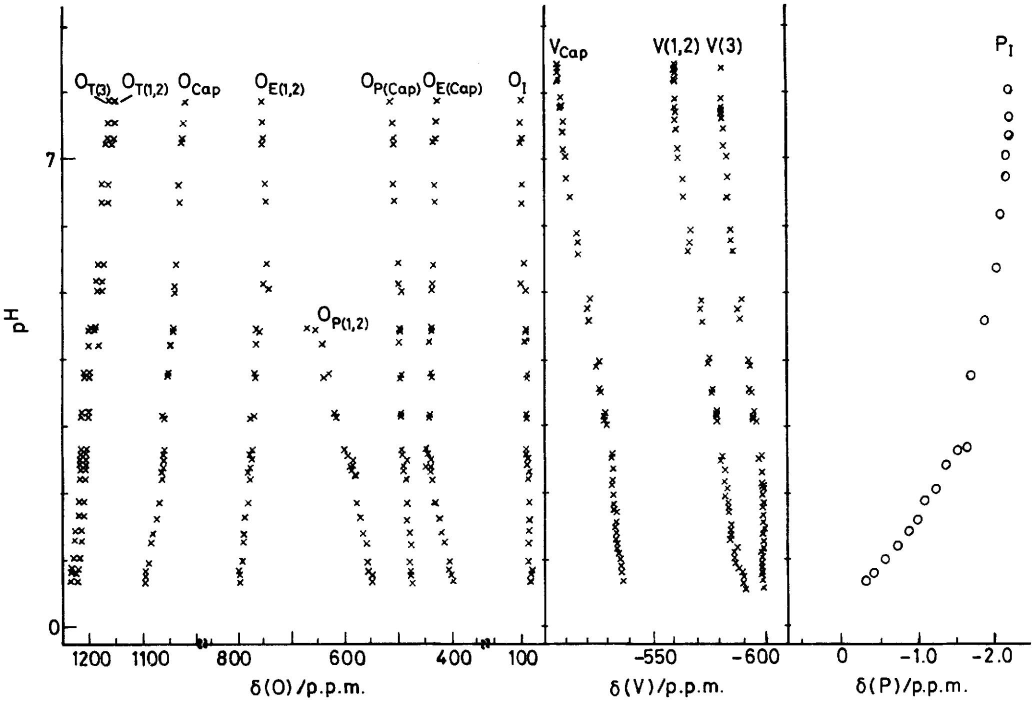


Figure 2. Chemical shift *vs.* pH for the heteropolyphosphovanadate ^{17}O, ^{51}V, and ^{31}P nuclei. At pH >5 the resonances for $O_{P(1,2)}$ and $O_{E(1,2)}$ merge

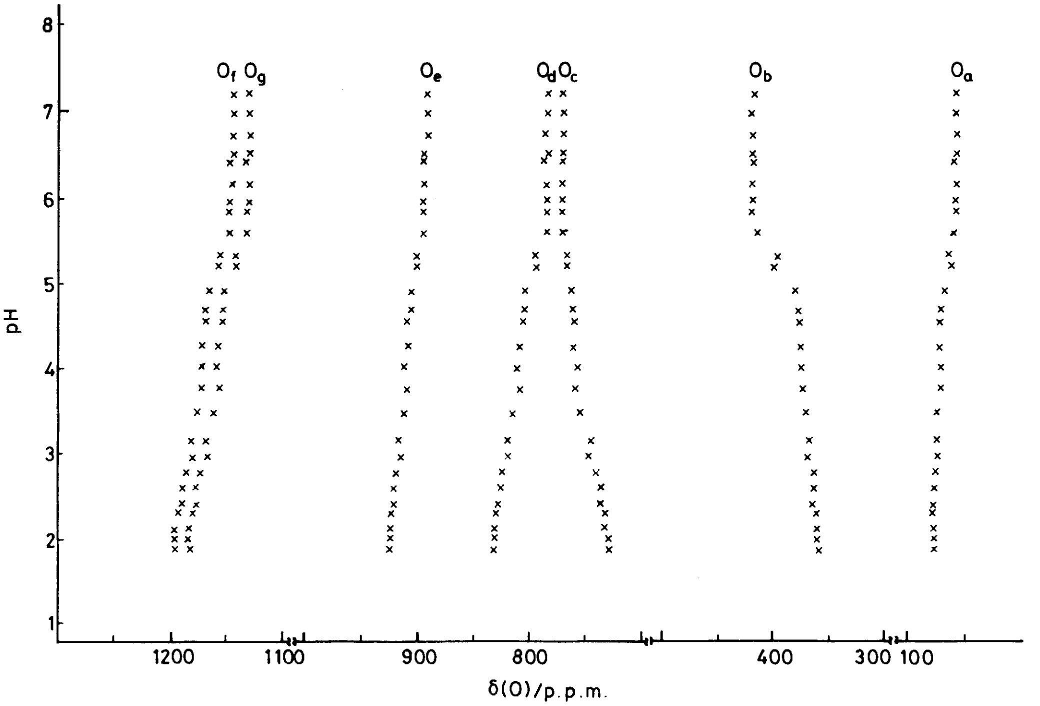


Figure 3. Chemical shift *vs.* pH for decavanadate ^{17}O nuclei

Experimental

Preparations.—(*i*) $Na_8[HPV_{14}O_{42}]\cdot 9H_2O$. Phosphoric acid (prepared by adding $POCl_3$ to water and warming to remove HCl) was added to a sodium metavanadate solution in a stoicheiometric ratio P:V between 1:2 and 1:12. The pH was adjusted to between 2 and 3 using $HClO_4$, and cooling overnight gave solid $Na_8[HPV_{14}O_{42}]\cdot 9H_2O$. Oxygen-17 enrichment required the use of up to 20 atom % $H_2{}^{17}O$.

(*ii*) *Decavanadate.* ^{17}O-Enriched decavanadate was prepared by dissolving $NaVO_3$ in $H_2{}^{17}O$ ($[V] = 2$ mol dm^{-3}) followed by

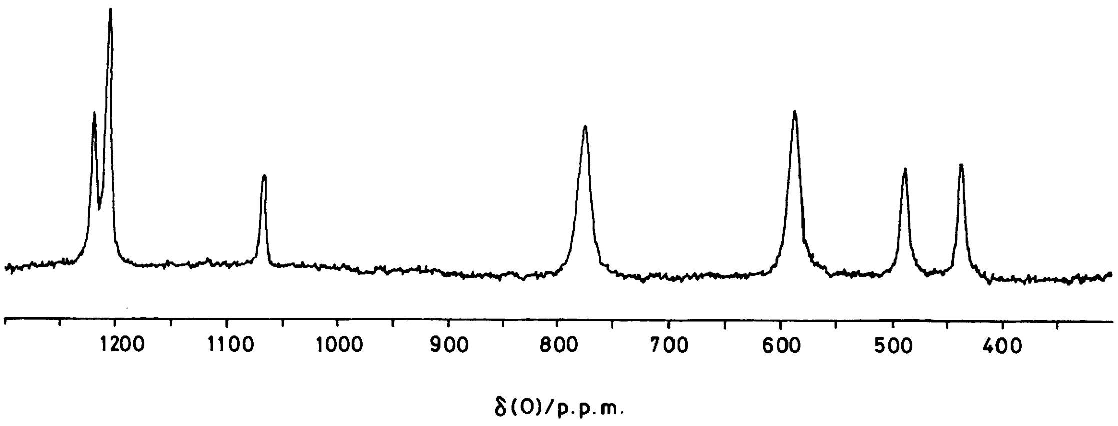


Figure 4. Oxygen-17 n.m.r. spectrum of the heteropolyphosphovanadate, omitting O_l

acidification to pH 6.5 to give 100% vanadium as decavanadate (checked by ^{51}V n.m.r. spectroscopy). Solid $Na[ClO_4]$ was added to 2 mol dm^{-3}.

N.M.R. Measurements.—The phosphovanadate $Na_8[HPV_{14}O_{42}]\cdot 9H_2O$ was dissolved in 2 mol dm^{-3} $Na[ClO_4]$ to give a concentration between 0.06 and 10^{-3} mol dm^{-3}. $^{31}P-\{^1H\}$ N.m.r. spectra were obtained at 162 and 36.4 MHz using Bruker WH400 and WH90 spectrometers respectively, referenced to capillary trimethyl phosphite at -140.2 p.p.m. (298 K). Up to 1 000 transients were accumulated at a rate of one per second.

The ^{51}V n.m.r. spectra at 105.2 MHz, referenced to external $VOCl_3$, required up to 3 000 transients. Similarly, the ^{17}O data were obtained at 54.2 MHz, referenced to solvent water, and required up to 100 000 transients at a rate of 100 per second with a spectral width of 100 kHz and a pulse length of 8 μs to allow equal stimulation over the whole range. For kinetic experiments, ^{17}O n.m.r. data were measured for 30-min periods up to 8 h at 295 K, rate constants being extracted by least-squares fitting. The pK_a values are computer-fitted averages based on those curves in Figure 2 and 3 having reasonably well-defined protonation shifts, errors being $\pm$ 0.05 for pK_{a1} and $\pm$ 0.01 for pK_{a2}.

Results and Discussion

Figures 2 and 3 show titration curves for the heteropolyphosphovanadate and decavanadate respectively. Figure 4 gives a typical spectrum of the heteropolyanion, omitting in this case the resonance from O_l, the oxygen bound to P, which can only be observed easily by the initial use of enriched phosphate. The pK_a values are 4.7 and 1.3 for the heteropolyanion, compared with 5.2 and 3.0 for decavanadate, whose values are close to those obtained elsewhere at different ionic strengths.[5] The areas of the peaks in Figure 4 permit immediate assignments, except for the pairs $O_{E(1,2)}/O_{P(1,2)}$ and $O_{E(Cap)}/O_{P(Cap)}$ (see Figure 1 for nomenclature). As the latter assignments are required for interpreting the kinetic results below, it is necessary first to extend the theory of ^{17}O shifts for oxo-ligands.

Theory of ^{17}O Shifts.—Several authors[2,9] have already noted the inverse dependence of the ^{17}O shift for terminal oxygens upon the metal–oxygen distance. However, attempts to extend this to multico-ordinate oxygen have met with less success. If the oxygen co-ordination is dominated by one nearby metal ion then it may be treated as pseudo-monoco-ordinate. More commonly, there are two or more metal ions co-ordinated at similar distances, both of which must clearly affect the ^{17}O shift. In such cases ^{17}O shifts for a given co-ordination number may

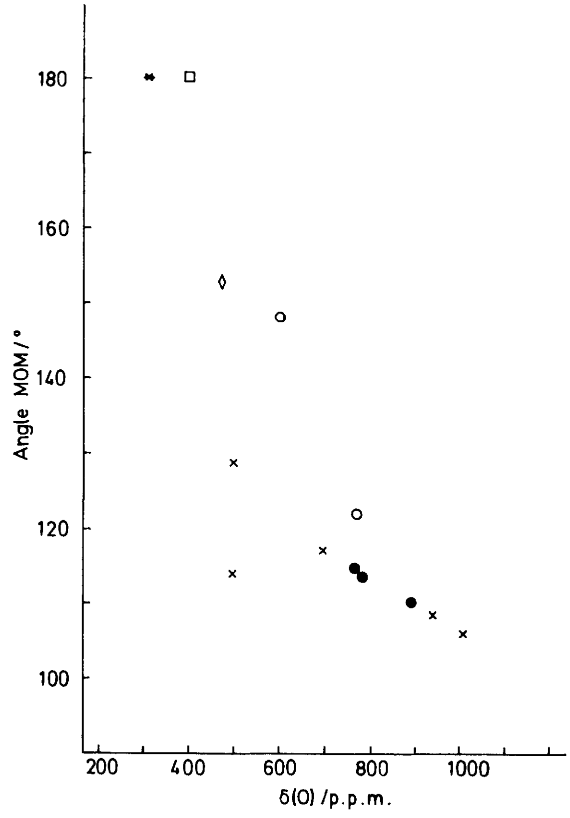


Figure 5. Plot of ^{17}O chemical shift *vs.* angle VOV or MoOMo (shift scaled × 1.24) for two-co-ordinate oxygen atoms. Points: ●, decavanadate (O_c, O_d, and O_e); ○, heteropolyphosphovanadate [$O_{E(1,2)}$ and $O_{P(1,2)}$]; ×, $[Mo_6O_{19}]^{2-}$ and $[Mo_7O_{24}]^{6-}$ [3,4] (reassigned to fit published integrals); □, $[V_2O_7]^{4-}$; ⋇, $[Mo_2O_7]^{2-}$; and ◇, $[HV_4O_{12}]^{3-}$. For the latter three compounds the relevant angle has been assumed to reach its maximum possible value in solution

differ markedly despite very similar average M–O distances (see Figure 2 especially). Clearly a further factor operates at least as strongly as modest variations in M–O distance.

We propose that this factor is the angle M–O–M, at least for bidentate oxygen. It is already well known[10] that the ^{15}N shifts in M–NO complexes increase by up to 500 p.p.m. when MNO becomes bent, because of the increased availability of the nitrogen lone pair as a highest occupied molecular orbital (h.o.m.o.) for paramagnetic induced electron circulation. In

Figure 5 the angles VOV and MoOMo are plotted against $\delta(^{17}O)$ scaled *via* the shifts of typical terminal-oxygen resonances.[2] It gives a reasonable inverse correlation despite substantial variations in M–O distance, and some uncertainties in angle. (The plot includes the assignment used below for $O_{P(1,2)}/O_{E(1,2)}$ and $[Mo_7O_{24}]^{6-}$ is reassigned to be more consistent with the peak areas in the spectrum;[11] $[Mo_2O_7]^{2-}$, $[V_2O_7]^{4-}$, and $[V_4O_{12}]^{4-}$ are given their maximum possible angles at oxygen, which may be overestimates.)

pH *Dependence.*—If the correlation of Figure 5 is established it may explain the otherwise unexpected general features of Figures 2 and 3, namely the similarity between the anions, the large protonation shifts, and the apparent balance of these between negative and positive. It is immediately apparent that most of the protonation shifts are too large to be explained solely by changes in bond length and co-ordination at a single protonation site, averaged over all such sites as are available. For example, a single protonation step alters each of the eight $O_{P(1,2)}$ resonances in Figure 2 by −160 p.p.m., corresponding to an impossible shift of −1 280 p.p.m. for a one-site protonation, before exchange-averaging. It seems probable that this shift arises from a net increase in the angle $VO_{P(1,2)}V$, as would occur if protonation caused a marked extension of the entire heteropolyanion along its 'polar' axis. A similar unidirectional extension in decavanadate, involving the four V(1) units and their associated terminal oxygens O_g, would also explain the negative shifts in Figure 3, for it would result in angle increases at O_b and O_c.

Increases in δ(O) on protonation are most noticeable for all the terminal oxygens. They probably arise from decreases in V–O(terminal) distance arising from the lengthening of bonds to other oxygens in the same vanadium co-ordination sphere. These oxygens compete for the *d* orbitals on V.[12]

Protonation Sites.—The precise types of oxygen undergoing protonation are still unclear: $O_{P(1,2)}$ in the heteropolyphosphovanadate and O_c in decavanadate seem most strongly indicated. The latter would satisfy both the *X*-ray crystallographic data[6] and the data (but not the conclusions) presented by Howarth and Jarrold.[5] For the former the protonation of the heteropolyanion would be as far as possible from the positive charge of the two VO caps. It is also consistent with the greater difference between the two pK_a values. However, what is described as protonation should more properly be regarded as corresponding changes in the net hydrogen-bond network around the anions, averaged on the n.m.r. time-scale.

Oxygen-exchange Kinetics.—Figure 6 shows the pH dependence of the rate constants for exchange of ^{17}O with solvent $H_2{}^{16}O$, under pseudo-first-order conditions. Peaks are assigned by the foregoing criteria, which are also assumed to be able to distinguish $O_{P(Cap)}$ from $O_{E(Cap)}$.

The capping oxygen, O_{Cap}, exchanges relatively rapidly at all pH values. This confirms the general concept of Kato *et al.*[7] that the caps are cationic elements added to stabilise an underlying Keggin structure, which in itself carries too high a negative charge. Furthermore, the exchange of O_{Cap} is slow enough to be measurable at pH > 6.5, presumably because the species then carries a higher charge.

One would expect the caps preferentially to stabilise the oxygen ions near them, both thermodynamically and kinetically. On this basis the kinetic lability of the anion at pH > 5 should be most pronounced at oxygens other than O_{Cap}, $O_{E(Cap)}$, and $O_{P(Cap)}$. This would also agree with the deductions above from the protonation data. Figure 6 shows the increased lability in this region for $O_{E(1,2)}$, $O_{P(1,2)}$, and $O_{T(1,2)}$, as predicted. The relative stability of $O_{T(3)}$ is, however, unexplained. It may arise simply because any distortion which could detach it will instead result in the exchange of a neighbouring oxygen.

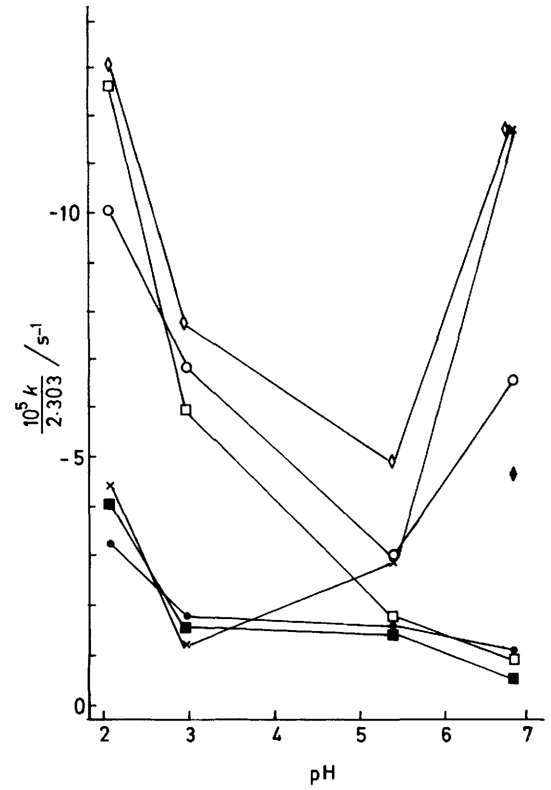


Figure 6. pH Dependence of pseudo-first-order rate constant for ^{17}O exchange with solvent $H_2{}^{16}O$ for the heteropolyphosphovanadate: ◇, $O_{P(1,2)}$; □, $O_{P(Cap)}$; ○, $O_{T(1,2)}$; ×, $O_{E(1,2)}$; ■, $O_{T(3)}$; ●, $O_{E(Cap)}$; ◆, O_{Cap}

At lower pH a different order is observed. All oxygens become labilised, but some residual stability is apparent for $O_{E(1,2)}$, $O_{E(Cap)}$, and $O_{T(3)}$. This may indicate some preferential persistence of the four triangular units made up from V(1), V(2), and V(3) octahedra.

Conclusions

The structure of the decavanadate anion, and even more so the relatively open structure of the heteropolyphosphovanadate anion, is evidently quite sensitive to variations in pH, affecting bond lengths and angles and hence kinetic stability. Most of these variations can be understood qualitatively in terms of simple electrostatics.

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