Protonation of the Decavanadate(6−) Ion: a Vanadium-51 Nuclear Magnetic Resonance Study

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The first protonation site of $[V_{10}O_{28}]^{6-}$ differs both from the second protonation site and from the site of preferential interaction with aqueous manganese(II) ion. It is probably an out-of-plane apex, and not a bridging oxygen as has recently been proposed. The ^{51}V n.m.r. linewidths are almost independent of direct protonation but depend indirectly on more distant protonation.

THE isopolyvanadate ion $[V_{10}O_{28}]^{6-}$ has the structure shown in Figure 1 in all the crystals in which it has so far been identified.[1,2] Recently, high-field ^{51}V n.m.r. studies [3,4] have greatly improved upon early derivative-mode n.m.r. studies [5,6] and have confirmed that the 4 : 4 : 2 population ratio of three distinct vanadium-atom types, present in the solid, also persists in solution. However, the pH dependence of these resonances has not yet been studied in any detail. Conventional pH studies of this system [7,8] have not been easy because of its metastability and sensitivity to ionic strength and counter ion. However, they show successive pK_a values in the ranges pK_1 5.5—6.0, pK_2 3.1—3.7, and $pK_3 \approx 2$. At pH < 2 the ion hydrolyses fairly rapidly to give $[VO_2(OH_2)_n]^+$,[9] and at pH < 6.5 it hydrolyses slowly to give various tetrahedral species.[5,10] Vanadium-51 n.m.r. spectra should give additional information about the separate protonation sites, and should be less sensitive than conventional pH studies to the system's metastability.

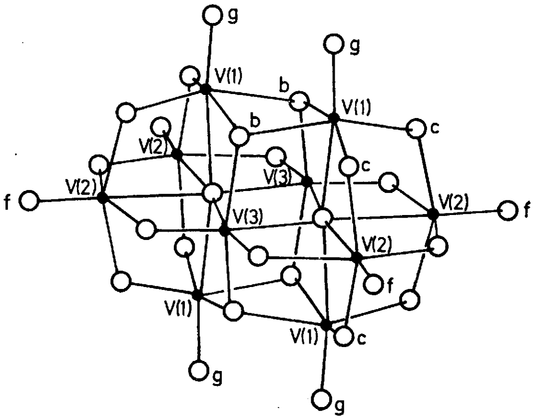

FIGURE 1 Crystal structure of $[V_{10}O_{28}]^{6-}$ (refs. 1 and 2)

Polyoxoanions are generally believed to protonate at terminal oxygens, and therefore some workers have assumed [11,12] that the eight apical sites will be preferred, although a dissentient view has recently been published [13] which will be discussed separately in the final paragraphs. In the present study the chemical shifts and linewidths of the three ^{51}V resonances have been measured as a function of pH. These measurements confirm the assumptions of Griffith and Lesniak and of Corigliano and Di Pasquale, and cast doubt upon Klemperer and Shum's findings. They also offer some progress in the difficult task of providing a detailed semiquantitative account of the protonation behaviour of a large polybasic anion.

EXPERIMENTAL

N.m.r. measurements were made at 22.63 MHz on a Bruker WH90 spectrometer at 299 K. An internal capillary of VCl_3O was used as a standard, and locking was not found to be necessary over the 5 min required for accumulation of each spectrum. Since the spectral lines overlapped somewhat, their peak positions and linewidths (at half-height) were determined accurately by computer fitting of Lorentzian lineshapes to the digitised spectra, with the area ratio fixed at 4 : 4 : 2.

The $[V_{10}O_{28}]^{6-}$ ion was prepared by HCl acidification of a potassium trioxovanadate(V) solution, and was studied at 0.020 mol dm^{-3} and $I = 0.5$ mol dm^{-3}. AnalaR grade chemicals were used. The pH was measured before and after each n.m.r. accumulation, and an average value was used because of pH drift due to hydrolysis. The likely errors are ± 0.05 pH unit between pH 3 and 6, and ± 0.1 pH unit outside this range.

RESULTS AND DISCUSSION

Chemical Shifts.—The variations of peak widths and positions with pH are shown in Figure 2. The peaks are labelled A, B, and C in order of increasing absolute frequency (*i.e.* decreasing upfield shift) relative to VCl_3O. Peak C has half the area of either A or B at all pH values, and the spectra are independent of concentration. It is evident that the first protonation occurs

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[11] W. P. Griffith and P. J. B. Lesniak, *J. Chem. Soc. (A)*, 1966, 1087.

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with an overall pK of *ca.* 5.5, as expected, and affects the shift of peak B substantially, that of A somewhat, and that of C hardly at all. The second protonation is also at the predicted $pK_2 \approx 3.6$ (as confirmed by the pH-fitting calculation described below). However, although peak C is again barely affected, peak A is now more shifted than B.

The relative insensitivity to protonation of peak C confirms that only V(1) and V(2) (Figure 1) are affected by protonation. This strongly supports the hypothesis that protonation is predominantly at the apical oxygens; if it occurred readily at bridging oxygens there is no good reason why it should not also occur at the oxygens bonded to V(3). That the protonation shift is to lower absolute frequency is consistent with known ^{51}V n.m.r. shifts; protonation increases the energy of a ligand-to-metal charge transfer, and hence decreases the absolute resonance frequency by reducing the deshielding contribution of temperature-independent paramagnetism. Similarly, it is to be expected that peak C is to higher absolute frequency, because V(3) has two closely bound oxygens, rather than one. This should decrease the lowest excitation energy and indeed make V(3) the polyanion's chromophore.

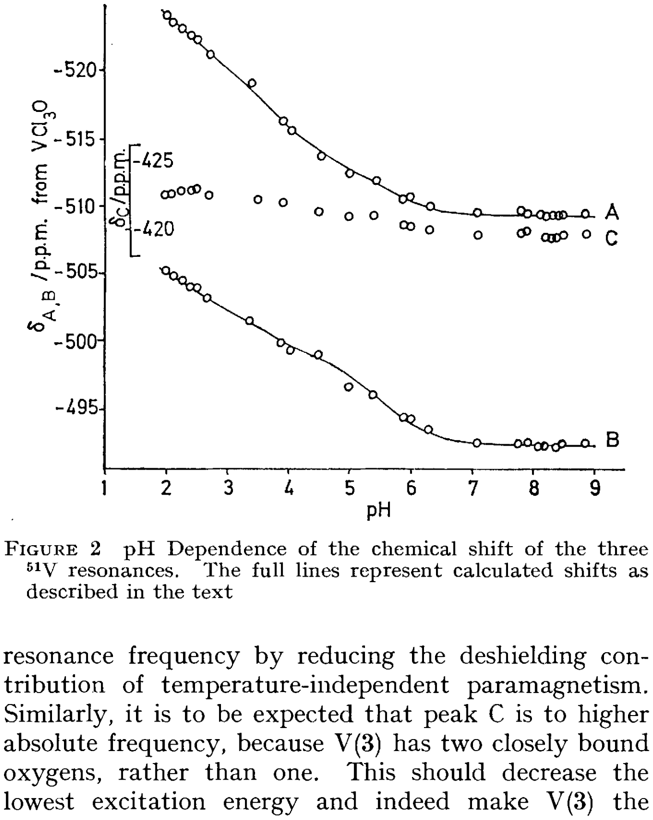

FIGURE 2 pH Dependence of the chemical shift of the three ^{51}V resonances. The full lines represent calculated shifts as described in the text

There are so many possible variables that an automatic computer pK fit to the experimental points in Figure 2 is not realistic. However, using certain simplifying assumptions, a manual fit is feasible and gives meaningful pK data because of the adequate separation of pK_1 and pK_2 for each titration curve. The full lines in Figure 2 were calculated on the undoubtedly approximate assumptions that protonation occurs exclusively at the eight apical oxygens, and then only affects the shift of the vanadium to which that oxygen is bound. Each of the four sites of type A was given one pK_1, and the four of type B another pK_1, and then three independent pK_2 values were assumed for the three diprotonated species AA, AB, and BB. It was also assumed that the shift arising from one protonation was the same at either type of protonation site, and that each individual site could only be protonated once. This one-shift value was an adjustable variable in the curve fitting.

The resulting ' best-fit ' pK_a values for the individual apices, together with their estimated reliabilities, were: monoprotonation at an A site, pK_1 4.50 ± 0.05; monoprotonation at a B site, pK_1 4.70 ± 0.05; diprotonation at A and B sites, pK_2 2.14 ± 0.1; diprotonation at A sites only, pK_2 2.64 ± 0.1; and diprotonation at B sites only, pK_2 2.36 ± 0.1 where site A refers to the site corresponding to resonance A. The low-pH section of the curve (pH < 3) also includes a contribution from $[H_3V_{10}O_{28}]^{3-}$.

It is important in analysing the behaviour of this polybasic system to distinguish overall pK (such as one might measure by a pH titration) from individual site pK values. The former values will exceed the latter by a substantial statistical factor. The overall pK values of the polyanion (*i.e.* the pH values at which 0.50 and 1.50 protons are on average attached) are thus 5.54 and 3.65, and the shift on monoprotonation at a single site would be 42.4 ± 1.5 p.p.m. to lower absolute frequency {*cf.* 95 p.p.m. between V(3) of the polyanion and $[VO_2(OH_2)_n]^+$}.

But does site A correspond to vanadium atoms V(1) or V(2) in Figure 1? The sites are quite similar both structurally and in chemical shift, and an unequivocal assignment is likely to be difficult. However, we propose that site A corresponds to V(2). The main evidence for this comes from the pK_2 values given above. That all of these are appreciably less than the pK_1 values indicates some kind of proton–proton repulsion in $[H_2V_{10}O_{28}]^{4-}$. A simple electrostatic-energy calculation was performed, by assuming that the actual population of each pairwise protonation configuration was calculable from its energy (relative to monoprotonation) using Boltzmann's law. If this assumption is valid then pK_2(average) — pK_1 may be calculated straightforwardly from the partition function. The pairwise repulsion energy for each diprotonated configuration was assumed to be that arising from the placing of a positive charge on the apical oxygen. The mean dielectric constant of the interproton medium was adjusted to the (physically reasonable) value of 15.6 in order to normalise the ' AA ' value to 2.64. The calculation predicts that the pK_2 for ' BB ' (per configuration) is 2.50 (obs. 2.36) and for ' AB ' is 2.24 (obs. 2.14). Qualitatively, AA is favoured over AB and over BB because there are two ways in which a second proton can be added at an A [*i.e.* V(2)] site without coming particularly close to the other proton, and a third way which is only moderately close. In contrast, the corresponding AB and BB distances are appreciably shorter.

If this assignment is correct, then it remains to explain why site B [V(1)] is favoured by 0.20 pK units for initial protonation. The relevant V–O distances are closely similar (both 0.161 nm) and so it seems likely that the favouring is either an effect of solvent structure or else is attributable to favourable hydrogen bonding between neighbouring sites B (O–O distance in crystal, 0.299 nm). A similar hydrogen-bonding stabilisation has been invoked[5] to explain the unexpectedly slow proton exchange between the solvent and the $[HV_2O_7]^{3-}$ ion.

Linewidths.—It is immediately apparent from Figure 3 that the pH variation of the linewidths bears little resemblance to that of the shifts. The width of peak B is barely affected by protonation, whereas the changes in A and C are quite similar, at least for the first two protonations. The broken curve superimposed on the data for peak C in the Figure is calculated from the protonation curve for peak B, with the experimental linewidths for zero and one proton at sites B taken as the basis points of the calculation. (The linewidths, like the shifts, will be the weighted average of those for the various species present, under the condition of rapid proton exchange.) That the linewidth curves for A and C follow the protonation of B shows that the effect of protonation on linewidth is long rather than short range.

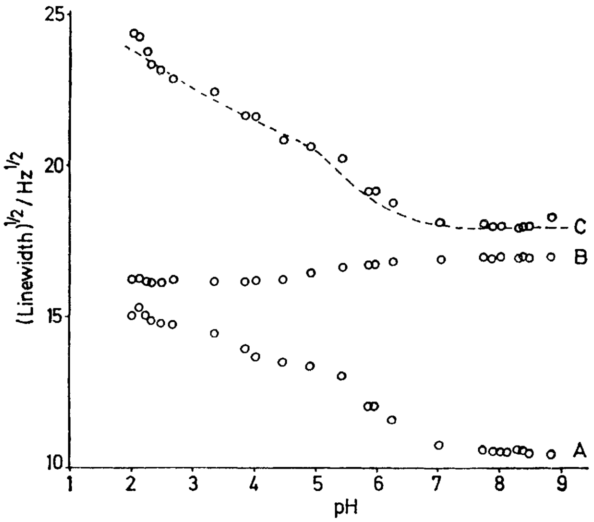

FIGURE 3 pH Dependence of the square root of the linewidth of the three ^{51}V resonances. The broken line is the calculated (linewidth)$^{\frac{1}{2}}$ assuming that this depends only on the degree of protonation at site B

Figure 3 plots the square roots of the linewidths because these are proportional to the electric-field gradients (e.f.g.s) at the various ^{51}V nuclei provided that the tumbling of the polyanion in solution is reasonably isotropic.[14] The e.f.g.s have two main origins, namely co-ordination asymmetry and the asymmetry of the local electronic environment due to covalent bonding. The former is hard to estimate because the most obvious effect of protonation on an O_6 octahedron, namely a charge reduction on one oxygen, will only affect the ^{51}V linewidth in the second order of the distortion. This explains the apparently surprising insensitivity of peak B to direct protonation. In contrast, a small tetragonal distortion has a first-order effect on the linewidth.

An attempt was made to calculate the relative field gradients at each ^{51}V atom using the crystal co-ordinates of a supposedly ionic $[V_{10}O_{28}]^{6-}$. The results bore little relation to observation, which probably implies that covalency is at least as important as co-ordination asymmetry. This would explain why V(3), which from its shift appears to be the most covalent vanadium atom, also has the largest linewidth.

Why should the linewidths of the 'in-plane' vanadium atoms V(2) and V(3) correlate with 'out-of-plane' protonation? It may be relevant that all the π orbitals associated with the short covalent bonds between oxygen and the in-plane vanadiums also have out-of-plane axes. Distortion of these orbitals would affect the linewidths of the in-plane vanadiums.

A final, odd, feature of Figure 3 is that the first inflection for both peaks A and C is at slightly higher pH (0.2—0.5 unit) than that calculated from the shift curves. The significance of this is not yet clear.

Selective Broadening.—In a separate qualitative experiment $MnCl_2$ was added to the solution at a concentration of 0.04—0.12 mol dm^{-3}. This caused substantial line broadening (*ca.* 100 Hz), especially at higher pH. Concurrent relaxation mechanisms affect a linewidth additively, and so the extra broadening should reflect the average inverse sixth power of the distance of approach of the aqueous manganese(II) ion to each vanadium atom. Qualitatively, peak A was broadened appreciably more than B by this mechanism and C was broadened least. This may occur simply because V(2) is the most sterically accessible to a bulky ion, as well as being of similar basicity to V(1) in the absence of contributions from hydrogen bonding.

Comparison with ^{17}O N.M.R. Study.—In a very recent paper Klemperer and Shum[13] investigated the protonation of the $[V_{10}O_{28}]^{6-}$ anion by ^{17}O n.m.r. spectroscopy. They reached conclusions diametrically opposite to those made above, and suggested that the main protonation sites are at the oxygens labelled b in Figure 1, rather than at the apical oxygens f and g. Theoretically, they argued that the undoubtedly greater covalency of the apical oxygens, which is reflected in the ^{17}O n.m.r. shifts and in the V–O bond lengths, makes these less basic and hence unlikely as protonation sites. Experimentally, they found that oxygens b and, to a lesser extent, c shift upfield between pH 6.0 and 4.5 (corresponding approximately to a single protonation) whereas all the other oxygens shift downfield. An upfield shift should result from a weakening of the V–O bond and a downfield shift from its strengthening.

The theoretical rationalisation is incomplete. If all the oxygens were fully ionic then on the above argument each oxygen should be equally basic. But in fact, in this case, the apices (f and g) would clearly be the preferred

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protonation sites on electrostatic grounds; the conversion of O^{2-} into $[OH]^-$ will lead to the least loss of attraction energy if the oxygen is singly co-ordinated. It is by no means certain that this apical preference will in fact be overcompensated by the observed covalency of the V–O linkages. The experimental evidence as presented considers only the indirect effect of protonation on the V–O bond, and not its direct effect on the ^{17}O n.m.r. shift. The actual protonation shift of $^{17}O^{2-}$ is not known, but it will probably be substantial,[15] and in view of the fact that even partially covalent O^{2-} can have an upfield shift [16] relative to water it is probably downfield. Thus the observed downfield protonation shift of the terminal oxygens may in fact be a combination of a substantial downfield protonation shift and a smaller upfield shift due to the perturbation of the V–O bond. If this were the case, it would explain Klemperer and Shum's otherwise rather surprising observation that the net ^{17}O shift on protonation, summed over all the oxygens in $[V_{10}O_{28}]^{6-}$, is downfield. In the absence of any direct protonation shift this would imply a net V–O π-bond strengthening on protonation, which seems unlikely. The i.r. evidence quoted to support this net shortening [11,12] in any case only concerns the unprotonated terminal oxygens, and not all of them, as Klemperer and Shum imply.

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