High-field Vanadium-51 and Oxygen-17 Nuclear Magnetic Resonance Study of Peroxovanadates(V)

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High-field ^{51}V and ^{17}O n.m.r. spectroscopy has clarified the aqueous chemistry of the peroxovanadates, leading to the identification of five new species, four of which are dimeric. Mono- and di-peroxovanadates undergo a change of co-ordination from octahedral to tetrahedral when their final proton is removed.

An earlier ^{51}V n.m.r. study,[1] at 22.6 MHz, identified eight peroxovanadate species in aqueous solution, and suggested the presence of a further three. The aim of the present work has been to check the previous results using the much higher resolving power of 105.2-MHz ^{51}V n.m.r. spectroscopy, to search for new species, such as asymmetrical dimers whose formation might logically be expected, and in particular to include the use of ^{17}O n.m.r. spectroscopy at 54.2 MHz, not only as a check on the proposed chemistry but also because no information has been published concerning the co-ordination number of the dissolved species. The ^{17}O chemical shifts are also of intrinsic interest, because the wide variation of these for oxy-anions is as yet poorly understood. The peroxovanadate system is well suited to such a study because much of the inter-species exchange is slow on the n.m.r. time-scale.

The present work supports the earlier conclusions.[1] Because species at 10^{-4} mol dm^{-3} can readily be detected when their resonances do not overlap with others, it has been possible to identify small proportions of several new dimers. In general, it is proposed that the mono- and di-peroxo monomeric species present below pH 14 are octahedral, whereas those at very high pH, or with more than two peroxides per vanadium, are tetrahedral. In this context all peroxo-ligands are formally taken to be unidentate.

Experimental

Experimental conditions were exactly as given in a previous paper.[2] Peroxovanadate solutions were prepared by the stoicheiometric addition of repeatedly restandardised *ca.* 8.9 mol dm^{-3} hydrogen peroxide to a vanadate solution of appropriate concentration and pH. In the (final) pH region 1—3 it was found necessary to wait *ca.* 5 min for equilibrium to be reached. All pH variations were effected in both directions, using concentrated $HClO_4$ and NaOH. Results were identical for each direction, except for effects arising from the relatively slow formation of tri- and tetra-peroxo-species noted below. The concentration was varied to assist in the identification of dimeric species. The chemical shifts of individual species were not dependent upon concentration. Overall vanadium concentrations were 0.01—2.0 mol dm^{-3}, mainly in the lower part of this range for quantitative measurements and the upper for ^{17}O n.m.r. The solvent was 2 mol dm^{-3} aqueous Na[ClO$_4$], with 10 atom % ^{2}H, and up to 20 atom % ^{17}O (M.S.D. Isotopes) for ^{17}O n.m.r. As before, the ^{51}V spectra were readily integrable, but the ^{17}O spectra much less so, due to baseline roll and poor sensitivity. The ^{51}V and ^{17}O chemical shifts are accurate to ± 1 p.p.m. and ± 2 p.p.m. respectively except for minor components (± 3 p.p.m.), as linewidths are generally greater than for oxovanadates. The ^{51}V shifts are about 5 p.p.m. more negative than in the previous study,[1] mainly[2] because of a bulk magnetic-susceptibility difference between the sample and the capillary VOCl$_3$ standard. Empirical corrections were made graphically to both high and low measured pH values, as recommended by Bates.[3] These also compensated for the presence of 2 mol dm^{-3} Na[ClO$_4$].

Results and Initial Assignments

Major Species.—The ^{51}V shifts are shown in Figure 1 as a function of pH. The proportion and dependence on stoicheiometry of the major species, which are listed in the Table, is essentially as given in ref. 1. However, the pK_a values, also recorded in the Table, are approximately 1.5 pK_a units lower, presumably because the 2 mol dm^{-3} Na[ClO$_4$] medium favours species with higher charge. The formation of the dimeric species $[\{VO(OO)_2\}_2OH]^{3-}$ is similarly enhanced.

The shifts of the ^{17}O peaks whose pH- and concentration-dependences correlate with the ^{51}V spectra are shown in Figure 2, using the same identification numbers as in the Table. Because of the lower sensitivity, minor species are not detected. Where possible, ^{51}V and ^{17}O spectra were recorded successively for the same solution, although a lower concentration was generally preferred for ^{51}V spectra to obtain quantitative data. Figure 3 shows some typical spectra. As no equilibrium constant has yet been reported for the formation of the previously noted dimer $[\{VO(OO)_2\}_2OH]^{3-}$, we obtained pK_c = -10.1 ± 0.33 (27 observations) for the nominal formation reaction (1). In the absence of Na[ClO$_4$], this figure drops to *ca.* -9.9.

$$2[VO(OH)(OO)_2(OH_2)_2]^{2-} + H^+ \rightleftharpoons [\{VO(OO)_2\}_2OH]^{3-} + 5H_2O \quad (1)$$

There is one major discrepancy between the ^{17}O spectra and the major ^{51}V species as set out in the earlier publication.[1] No clear evidence had been found for the deprotonated mono-peroxo-species, $[VO_3(OO)]^{3-}$, at high pH. Instead, the only major feature of the spectrum (except in the presence of high peroxide concentration) was a peak at $\delta_V = -770.6$ p.p.m. (after making the shift correction noted above) with a slight shift towards *ca.* δ -769 p.p.m. at very high pH, attributed to deprotonation of $[HVO_2(OO)_2]^{2-}$. This proposal left the question of why the monoperoxo-species $[HVO_3(OO)]^{2-}$ should gain peroxide on deprotonation, to give $[VO_2(OO)_2]^{3-}$, in preference to the more plausible deprotonation reaction $[HVO_3(OO)]^{2-} \longrightarrow [VO_3(OO)]^{3-}$. The ^{17}O spectra suggest an answer. Above pH 12 the two resonances of equal area at δ_O = 1 021 and 83 p.p.m. which are assigned to hydrated $[HVO_2(OO)_2]^{2-}$ (see below) become broadened and are progressively replaced by resonances at 568 and 602 p.p.m. The resonance at 568 p.p.m. then grows at the expense of that at 602 p.p.m. as the pH is increased further, and replaces it as the major peak. In the ^{51}V spectrum under these conditions, more than

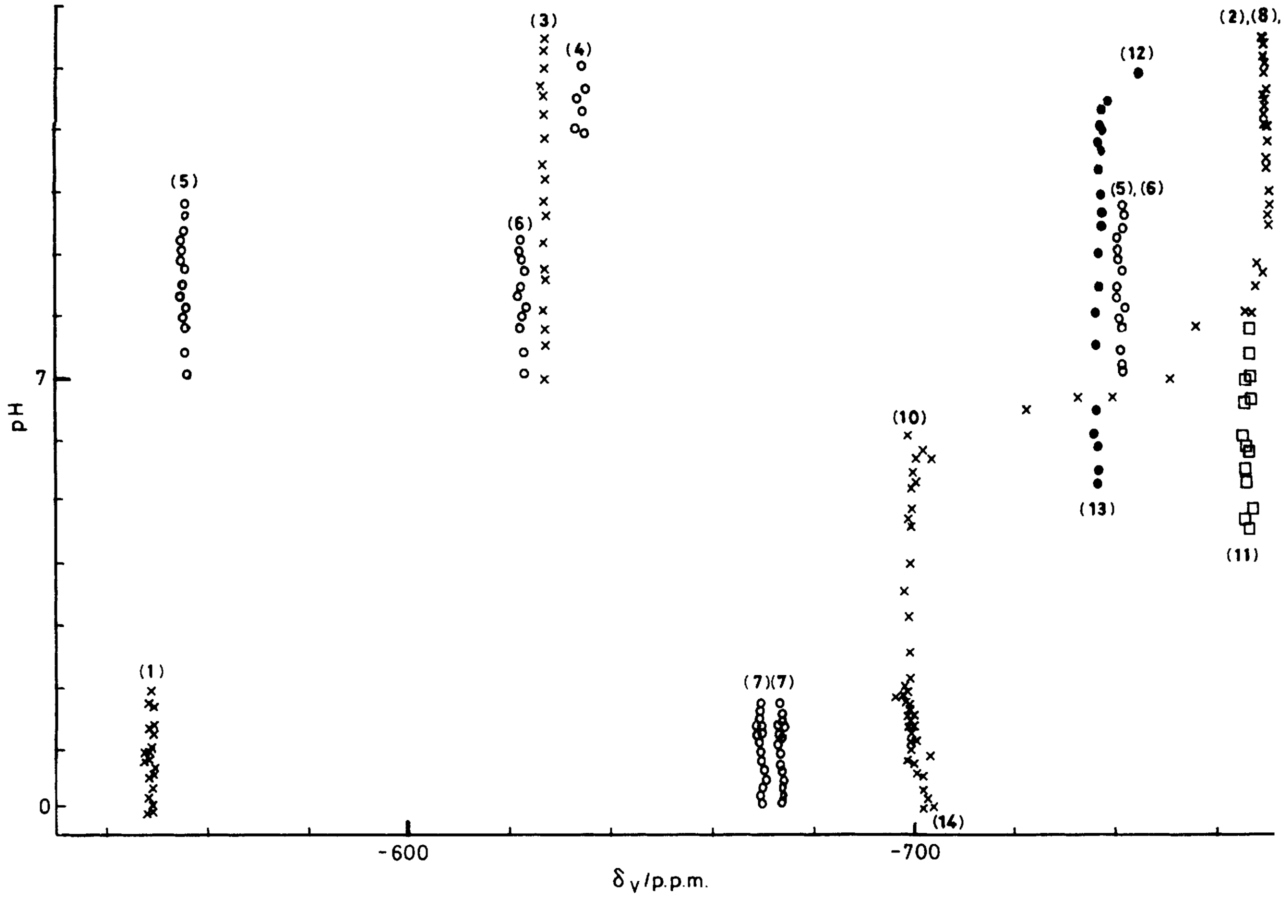

Figure 1. Plot of ^{51}V chemical shifts *vs.* pH. Typical conditions were OO:V = 2:1, 0.1 mol dm^{-3} in vanadium. Species are numbered as in the Table

75% of the total area lies in a single resonance at −769.3 p.p.m. We propose that this arises from two species whose resonances overlap, namely $[VO_3(OO)]^{3-}$ at δ_O = 568 p.p.m. and $[VO_2(OO)_2]^{3-}$ at δ_O = 602 p.p.m. That this deprotonation is slow on the n.m.r. time-scale suggests a change of co-ordination number.

It was also noted that under the present conditions the triperoxo-species take several minutes to reach their equilibrium concentrations following a pH change. Previously this had only been observed for the tetraperoxo-species $[V(OO)_4]^{3-}$. Apart from these, all the equilibria are rapidly reversible.

Low pH Region.—Peak (**10**), assigned to hydrated $[H_2VO_2(OO)_2]^-$, shifts to lower ^{51}V frequency at pH <1. A further protonation is likely, either at OH or [4] at OO, to give hydrated $[H_3VO_2(OO)_2]$. At the same time various broad transient peaks appear, but then decay within minutes to give two peaks of equal area at δ_V = −670.6 and −674.0 p.p.m., in the range pH 1.7—0.1. The combined area of these peaks reaches a maximum of 38% total V at pH 1, 0.5 mol dm^{-3} total V, and an OO:V ratio of 1.5:1. (At higher vanadium concentrations the effervescence is too great for accurate measurements.) Also the dependence of their area on concentration is consistent with a dimeric species. We therefore assign both peaks to $H_4[(OO)_2OVOVO_2(OO)]$, with the sites of protonation remaining uncertain. For reaction (2), pK_c = −0.97 ± 0.27 (23 observations) in 2 mol dm^{-3} Na[ClO$_4$]. An identical value is obtained (27 observations) in the absence of perchlorate. Other attempted formulations of the dimer give substantially poorer standard deviations for pK_c. At lower pH only one peak is observed for the red-brown solution, at δ_V = −549.3 and δ_O = 1 240 p.p.m. This is assigned as before to $[VO(OO)(OH_2)_4]^+$ or $[V(OH)_2(OO)(OH_2)_3]^+$.

$$[V(OH)_2(OO)_2(OH_2)_2]^- + [VO(OO)]^+ \rightleftarrows H_4[(OO)_2OVOVO_2(OO)] + H_2O \quad (2)$$

Minor Species.—When less than 2 equivalents of peroxide per vanadium are added, several new peaks are detected in the ^{51}V spectrum. None of these is ever present at more than 5% total V, and all of them have a concentration dependence consistent only with a dimeric species. In the range pH 7—10, the ^{51}V shifts are −556, −624, and −743 p.p.m., with the peak at −624 p.p.m. having a marginally smaller pH range. A further peak appears at −636 p.p.m. in the range pH 10.5—12. The peaks all show maximum intensity at a peroxide to vanadium ratio between 1:1 and 1.5 to 1. Also, insofar as they can be accurately measured, the areas of the peaks at −556 and −624 p.p.m. are different, but their sum equals the area of the peak at −743 p.p.m.

If it is assumed that the pH range of these dimers parallels that of the known dimer,[1] and that the chemical shift of each vanadium is interpretable similarly to those of the monomers, then the data above are entirely consistent with the presence of $[HO_3VOVO(OO)_2]^{3-}$, having δ_V = −743 p.p.m. for the diperoxovanadium and −556 p.p.m. for the other, and also of $[HO_2(OO)VOVO(OO)_2]^{3-}$ (δ_V = −743 and −624 p.p.m.). In addition the peak at −636 p.p.m. can be assigned to the unprotonated bis(monoperoxovanadium) dimer $[\{VO_2(OO)\}_2O]^{4-}$. Other dimers may be present in smaller quantities, or undetected because of overlap. It was fortuitous that the

Table. Chemical shifts and pK_a values for the peroxovanadates(v) and related species

(*a*) Monomers

Peroxo-ligands per V	0	1	2	3	4
Species		**(2)**	**(8)**	**(12)**	
Formula	$[VO_4]^{3-}$	$[VO_3(OO)]^{3-}$	$[VO_2(OO)_2]^{3-}$	$[VO(OO)_3]^{3-}$	$[V(OO)_4]^{3-}$
δ_V/p.p.m.	−541.2	−769.3	−769.3	< −830	−737.6
δ_O/p.p.m.	565	568	602	<990	*a*
Species		**(3)**	**(9)**	**(13)**	
Formula	$[VO_3(OH)]^{2-}$	$[VO_2(OH)(OO)]^{2-}$	$[VO(OH)(OO)_2(OH_2)_2]^{2-}$	$[V(OH)(OO)_3]^{2-}$	
δ_V/p.p.m.	−538.8	−627.6	−770.6	−737.2	
δ_O/p.p.m.	573[b]	1 041,[b] <75	1 021,[b] 83	1 014	
pK_a[c]	12	>14	>14	>14	
Species			**(10)**		
Formula	$[VO_2(OH)_2]^-$		$[V(OH)_2(OO)_2(OH_2)_2]^-$		
δ_V/p.p.m.	−560.4		−699.9		
δ_O/p.p.m.	*a*		1 057, <75		
pK_a[c]	7.1		6.98 ± 0.25		
Species		**(1)**	**(14)**		
Formula	$VO_2{}^{+d}$	$[VO(OO)]^{+d}$	$[HV(OH)_2(OO)_2(OH_2)_2]$		
δ_V/p.p.m.	−545.9	−549	< −705		
δ_O/p.p.m.	*a*	1 240, <75	>1 065, <75		

(*b*) Dimers

Species	**(4)**		
Formula	$[\{VO_2(OO)\}_2O]^{4-}$		
δ_V/p.p.m.	−636.3		
δ_O/p.p.m.	*a*		
Species	**(5)**	**(6)**	**(11)**
Formula	$[HO_3VOVO(OO)_2]^{3-}$	$[HO_2(OO)VOVO(OO)_2]^{3-}$	$[\{VO(OO)_2\}_2OH]^{3-}$
δ_V/p.p.m.	−556.2, −742.8	−624.3, −742.8	−766.5
δ_O/p.p.m.	*a*	*a*	1 057
Species	**(7)**		
Formula	$H_4[(OO)_2OVOVO_2(OO)]$		
δ_V/p.p.m.	−670.6, −674.0		
δ_O/p.p.m.	? 1 208, ? 924		

[a] Not observed. [b] Average due to rapid H transfer. [c] For loss of one proton, in 2 mol dm^{-3} $NaClO_4$. [d] Species probably also has co-ordinated H_2O.

peak at 556 p.p.m. could be observed, as most of the −535 to −595 p.p.m. region contains vanadate resonances, at low peroxide:vanadium ratio. Indeed, if such an overlap occurred then the peak at −636 p.p.m. peak could equally well arise wholly or in part from $[O_3VOVO_2(OO)]^{4-}$.

Discussion

Neither ^{51}V nor ^{17}O shifts in vanadates are well understood.[1,2,5] The ^{51}V shifts generally but not invariably increase upon protonation, and upon substitution of OO^{2-}. They also tend to be *ca.* 100 p.p.m. higher for octahedral V than for tetrahedral V, at comparable pH.[5] The ^{17}O shifts for the oxo-ligand are not much affected by protonation. They can increase somewhat,[2] but have also been claimed to decrease.[6] They do correlate fairly well with the formal double-bond character in tetrahedral vanadates,[2] and in polyvanadates and other isopolyanions with octahedral metal co-ordination they decrease with an increase in oxygen co-ordination number. However, these correlations are of limited value. Formal double-bond character is not well defined in polyanions or anions with other ligands such as peroxide. Also, as Klemperer[6] notes, a given oxygen co-ordination by a given metal can result in ^{17}O shifts over a range of at least 300 p.p.m.

The ^{51}V shifts for the present series of compounds are all consistent with the proposed substitutions by peroxide, using the criteria outlined above. As noted before,[1] the protonation shifts can be surprisingly large, with signs opposite to those observed for vanadates.[2] However, the ^{17}O shifts are unexpected. Unlike those of vanadates, they fall into three very distinct regions, namely 0—100, 550—650, and 1 000—1 250 p.p.m. We propose that these regions arise respectively from co-ordinated H_2O, tetrahedrally co-ordinating O^{2-} or OH^-, and octahedrally co-ordinating O^{2-} or OH^-.

It is not surprising that H_2O, even when co-ordinated to a transition-metal ion, should exhibit shifts relatively little changed from its value as a solvent ($\delta_O = 0$). Its bond to the metal ion is relatively weak, and the ligand-to-metal charge transfer from which the shift largely arises will be strongly inhibited by the involvement of both of the remaining oxygen *p* orbitals in covalent bonding to H. The only other oxo-ligands recorded in this range are octahedrally co-ordinated O in polyanions, where all M–O distances are very long.[6]

The 550—650 p.p.m. region corresponds to the ^{17}O resonances in the tetrahedral anions $[VO_4]^{3-}$ and $[HVO_4]^{2-}$. For octahedrally co-ordinated V it lies between the ranges expected for oxygen co-ordination by two and by three vanadiums. We conclude that the present observed shifts of 568 and of 602 p.p.m. arise from tetrahedrally co-ordinated complexes, in which the V–O multiple-bond character is only weakly

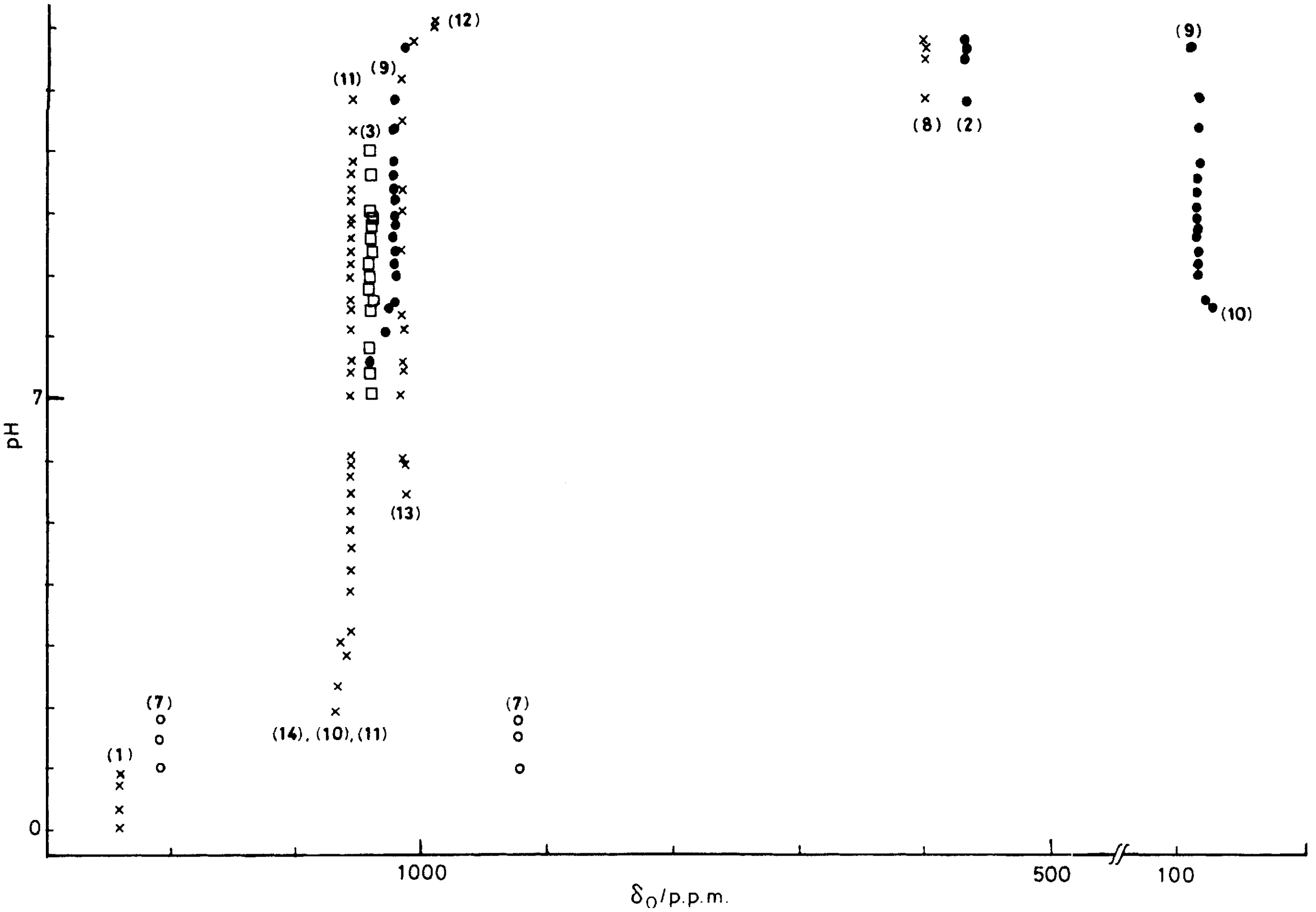

Figure 2. Plot of ^{17}O chemical shifts *vs.* pH. Typical conditions were OO:V = 2:1, 1.5 mol dm^{-3} in vanadium. Species are numbered as in the Table

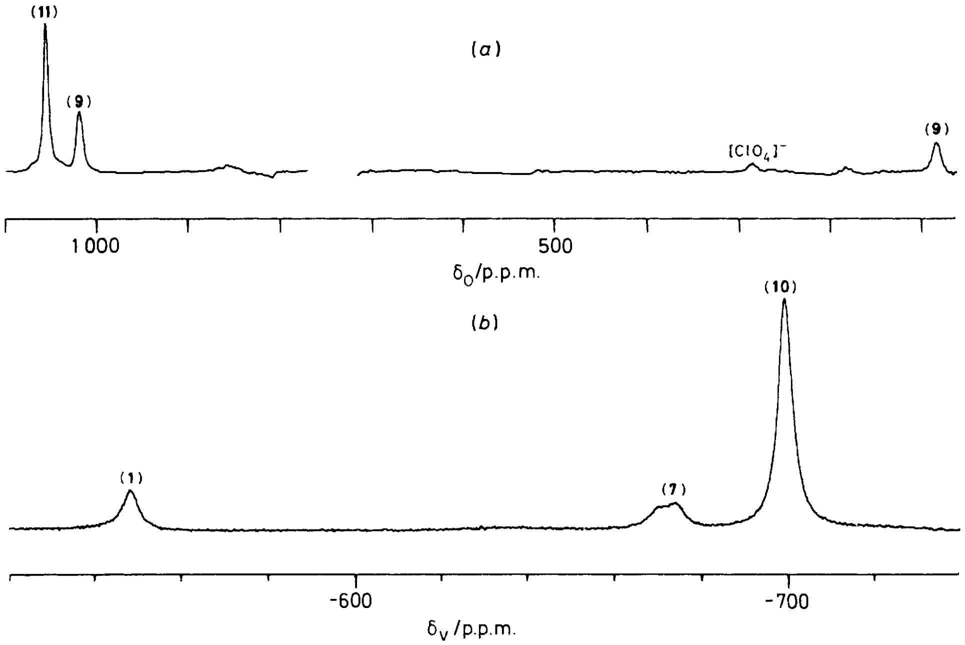

Figure 3. Typical spectra: (*a*) ^{17}O([V] = 1.4 mol dm^{-3}, pH 9.79, OO:V = 2:1); (*b*) ^{51}V([V] =0.07 mol dm^{-3}, pH 0.45, OO:V = 2:1). Species numbering as in the Table

increased when other oxo-ligands are replaced by peroxo. This of course also implies some double-bond character in the metal–peroxo linkage. The marked difference between tetrahedral and octahedral co-ordination is thought to arise because in the tetrahedron there is often competition between tightly bound O^{2-} or OH^- ligands for the same *d* orbital on vanadium, whereas in the octahedron the *trans* ligand may well be either H_2O or octahedrally co-ordinated O^{2-}, both of which have a relatively long M–O bond. In support of this proposal of a change in co-ordination number, it was noted that the unprotonated species gave a markedly paler yellow solution than the protonated ones.

This argument leaves indeterminate the co-ordination number in $[HVO(OO)_3]^{2-}$ (δ_O = 1 014 p.p.m.) and in $[\{VO(OO)_2\}_2OH]^{3-}$ (δ_O = 1 057 p.p.m.). In the triperoxo-species there can be no competing oxo- or hydroxo-ligand, and in the dimeric species, which is known to have tetrahedral co-ordination of V in the crystal,[7] the only non-peroxo-ligand competing with O^{2-} is an oxygen bound to both H and V. This oxygen is thus like co-ordinated H_2O in having no unused *p* orbitals, and a relatively long bond to V (2.01 Å, *cf.* 1.61 Å for the other two oxo-ligands).

Octahedral co-ordination of V complexed by peroxide is known in the hydrated oxodiperoxopyridine-2,6-dicarboxylato-complex,[8] where the sixth co-ordination position, opposite oxo, is occupied by the H_2O. Here V–O = 1.58 Å and V–OH_2 = 2.21 Å, which underlines the disparity in co-ordination between these ligands. Terminal oxo-ligands on octahedrally co-ordinated V have not so far been found with shifts below *ca.* 1 100 p.p.m.,[6,9] and similar shifts are found for polymolybdates and polytungstates[6] after a scaling allowance for the change of metal. Hence the present ^{17}O shifts in the δ 1 000—1 250 p.p.m. range can be attributed to octahedral complexes, with the possible exception of the triperoxo-anions and the diperoxo-dimer.

The above argument implies the presence of co-ordinated water. However, this will only be observable by n.m.r. spectroscopy if its exchange with solvent is sufficiently slow, and its shift adequately separated from that of the very large solvent peak. These conditions hold for species (**9**), where the peaks at 1 021 and 83 p.p.m. have equal area within the accuracy of measurement. We therefore assign this species to $[VO(OH)(OO)_2(OH_2)_2]^{2-}$, with O^{2-} and OH^-, and each other ligand pair, probably being mutually *cis*, by analogy with other complexes of known structure.[2,8] Similarly, an octahedral co-ordination is proposed for species (**10**), $[V(OH)_2(OO)_2(OH_2)_2]^-$, because its exchange with species (**9**) is rapid, and because although a separate resonance is not observed for co-ordinated water, there is a distinct reduction of the shift of co-ordinated H_2O of species (**9**) as this begins to protonate.

Octahedral co-ordination is also proposed for the species $[VO_2(OH)(OO)(OH_2)_2]^{2-}$, (**3**), on the basis of its ^{17}O shift. In contrast, the deprotonated species (**8**) and (**2**), assigned to $[VO_2(OO)_2]^{3-}$ and to $[VO_3(OO)]^{3-}$ respectively, have tetrahedral co-ordination, both on the basis of their ^{17}O shifts as argued above and also of the slow exchange with their octahedral protonated forms. A change from octahedral to tetrahedral co-ordination with increasing negative overall charge is of course known for many metals. The species $[V(OH)(OO)_3]^{2-}$, (**13**), should also be tetrahedral, because of its rapid exchange with its deprotonated form, (**12**).

At present, further elucidation of the different ^{17}O shift variations in the 1 000—1 100 p.p.m. range is probably not possible. However, the rather high shift of 1 240 p.p.m. for species (**1**) is noted, and attributed to a further reduction in the number of ligands able to compete in π bonding with O^{2-}. This trend is emphasized in $VOCl_3$ (δ_O = 1 350 p.p.m., neat liquid) and $VO(NO_3)_3$ (δ_O = 1 398 p.p.m., in CH_3CN).[10] Several attempts were also made to detect the ^{17}O resonance of VO_2^+, but these were unsuccessful, probably because of rapid exchange with solvent.

Conclusions

The present study increases the understanding of peroxo-vanadate(V) species. Our observations of dimeric species confirm the earlier contention[1] that vanadium(V) markedly prefers two peroxo-ligands, except at pH extremes.

Acknowledgements

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