Peroxo-complexes of Vanadium(V); a Vanadium-51 Nuclear Magnetic Resonance Study

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Peroxovanadium(V) species of notional formula $[VO(OO)]^+$, $[HVO_2(OO)_2]^{2-}$, $[H_2VO_2(OO)_2]^-$, $[VO(OO)_3]^{3-}$, $[HVO(OO)_3]^{2-}$, $[V(OO)_4]^{3-}$, $[H\{VO(OO)_2\}_2O]^{3-}$, and $[VO(NH_3)(OO)_2]^-$ have been identified in aqueous solution by ^{51}V n.m.r. spectroscopy; species $[HVO_3(OO)]^{2-}$, $[VO_2(OO)_2]^{3-}$, and $[\{V(OH_2)(OO)_2\}_2O]$ are also indicated. The chemical shifts and pK_a values indicate that peroxo-ligands bind to vanadium less covalently than oxo-ligands, provided that at least one oxo-ligand remains co-ordinated.

THE chemistry of the peroxo-complexes of vanadium(V) was last reviewed in 1965;[1] most of this review depended on extensive studies by Chauveau[2,3] using spectrophotometry and cryoscopy. Since then several crystal structures have been determined by X-ray diffraction, namely those of $[VO(NH_3)(OO)_2]^-$,[4] $[VO(OH_2)(pydca)(OO)_2]^{3-}$ (pydca = pyridine-2,6-dicarboxylate),[5] and $[\{VO(OO)_2\}_2O]^{4-}$.[6] The respective geometries, treating the sideways-co-ordinated peroxodianion as one ligand, are approximately tetrahedral, octahedral, tetrahedral sharing an O^{2-}, and tetrahedral. The species $[V(OO)_4]^{3-}$ was also shown to be pseudotetrahedral[7] *via* an isomorphism with $[Cr^V(OO)_4]^{3-}$,[8] but in this ion the peroxo-ligands are each unsymmetrically co-ordinated.

Vanadium-51 n.m.r. spectroscopy has been applied by a number of workers[9,10] to the oxo-complexes of vanadium(V), and is probably the least ambiguous method for studying them in solution. Here it is applied to the simpler peroxovanadium(V) complexes in aqueous solution; the results generally confirm and extend Chauveau's work, and identify not only the main known species $[VO(OO)]^+$, $[HVO_2(OO)_2]^{2-}$, $[H_2VO_2(OO)_2]^-$, $[VO(OO)_3]^{3-}$, $[HVO(OO)_3]^{2-}$, $[V(OO)_4]^{3-}$, and $[H\{VO(OO)_2\}_2O]^{3-}$, but also the more minor species $[HVO_3(OO)]^{2-}$ and (probably) $[VO_2(OO)_2]^{3-}$, $[VO(NH_3)(OO)_2]^-$, and $[\{V(OH_2)(OO)_2\}_2O]$. These formulae should all be interpreted as possibly omitting some co-ordinated water molecules. Peroxide is printed as $(OO)^{2-}$ for visual clarity.

EXPERIMENTAL

Vanadium-51 n.m.r. spectra were obtained on a Bruker WH90 spectrometer operating at 22.6 MHz and at reduced field. Field-frequency locking was not necessary since spectra of 0.01 mol dm^{-3} species could be obtained in *ca.* 2 min with good signal-to-noise ratio by accumulating *ca.* 1 000 transients. An internal capillary of neat VCl_3O was used as a standard, and shifts are recorded in p.p.m. downfield from this. All measurements were carried out at 273 K, to reduce decomposition to a negligible rate. Because the n.m.r. method is only sensitive to major species, it was found adequate to use AnalaR grade ammonium metavanadate and reagent grade H_2O_2 (May and Baker). The ammonium metavanadate was converted into sodium metavanadate by refluxing with 1 equivalent of sodium hydroxide.

RESULTS

The results of a range of acid or base titrations of 0.1 mol dm^{-3} metavanadate solutions containing between 1 and 6 equivalents of hydrogen peroxide are summarised in the Figure. The only resonances whose relative intensity was dependent on vanadium concentration were those at $\delta = -747$ and -670; their concentration dependence was consistent in each case with the species being dimeric, on the assumption that the other species are monomeric.

pH >5.—The modest lowering of pH from *ca.* 8 to *ca.* 5.5 on addition of peroxide to metavanadate ion (mainly $[H_2VO_4]^-$ at 0.1 mol dm^{-3}) suggests the formation of a peroxo-species with the same number of protons but a somewhat lower pK_a. Along with Chauveau, we find that the main new species formed ($\delta = -696$) is present in 100% proportion after 2.0 equivalents of hydrogen peroxide have been added, and we therefore assign this resonance to $[H_2VO_2(OO)_2]^-$.

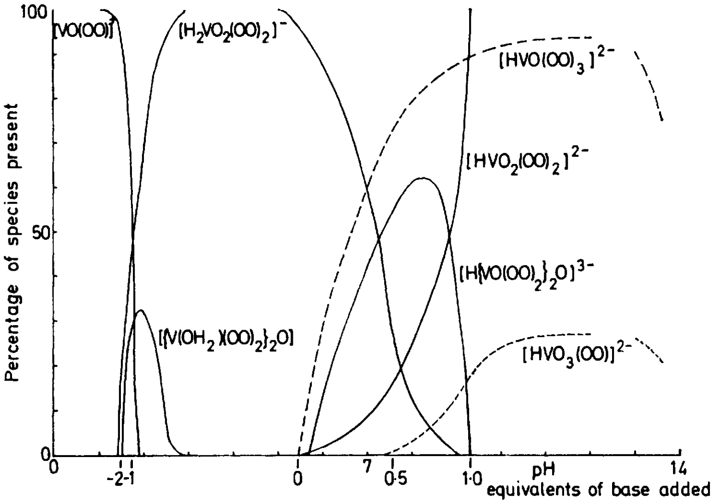
The effect of addition of base is shown in the Figure. When one full equivalent of base has been added to $[H_2VO_2(OO)_2]^-$ the only peak present is at $\delta = -765.6$; we therefore assign this to $[HVO_2(OO)_2]^{2-}$. When half an equivalent of base has been added the largest resonance present (above 0.1 mol dm^{-3} in V) is at $\delta = -757$. At pH <7.5 this peak has a pH-independent shift. In contrast, $[H_2VO_2(OO)_2]^-$ and $[HVO_2(OO)_2]^{2-}$ are in rapid exchange, showing a single n.m.r. peak of averaged shift. At pH >7.5 the dimer peak is in rapid exchange with, or else is unresolvable from, the peak due to $[HVO_2(OO)_2]^{2-}$ at $\delta = -765.6$.

These results are entirely consistent with Chauveau's postulate of a protonated dimer, $[H\{VO(OO)_2\}_2O]^{3-}$. No evidence was found at the concentrations studied for the corresponding unprotonated dimer, whose crystal structure has been published.[6] The relative proton-exchange rates are closely comparable to those in the corresponding oxo-species.

If only 1 equivalent of hydrogen peroxide is used initially the species observed are the same at pH <7, plus 50% of the oxovanadium(V) species appropriate to that pH value.[10] However, above this pH value a new, quite narrow, peak appears at $\delta = -621$, shifting slightly to $\delta = -622.8$ at pH 8 and remaining constantly at this shift at pH >8. From pH 10 its proportion is also constant at 26%, the remainder being $[HVO_2(OO)_2]^{2-}$. We therefore assign the peak at $\delta = -622.8$ to $[HVO_3(OO)]^{2-}$, and believe that the slight lowering of chemical shift at pH <8 may indicate rapid exchange of this species with a small and thermodynamically unstable amount of (probably) $[H_2VO_3(OO)]^-$.

If more than 2 equivalents of peroxide are used a further peak appears at $\delta = -733.2$ at pH >5.5. The proportion of this peak area to that at $\delta = -765$ is essentially constant at pH >10 for a given peroxide concentration, which implies that it arises from $[HVO(OO)_3]^{2-}$. Chauveau also finds this species. However, the triperoxo-species is evidently less thermodynamically stable than the diperoxo-species because some of the latter persists even at high peroxide concentration.

These three monoprotonated species remain unchanged as the pH is raised to *ca.* 13. However, at very high pH (*e.g.* $\geqslant 0.5$ mol dm^{-3} Na[OH]), when the free peroxide is mainly present as $[HO_2]^-$, some further shift changes were observed. The triperoxo-species reduces to *ca.* 10% in proportion, despite the high peroxide concentration, and a further small peak appears at $\delta \approx -845$. The resonance of the diperoxo-species seems to undergo a slight upfield shift to $\delta \approx -760$ (although a shift of this size could be attributable to a substantial solvent effect). The mono-peroxo-species disproportionates to $[VO_4]^{3-}$ ($\delta = -536.2$) and the diperoxo-species. These somewhat qualitative observations are consistent with deprotonation under extreme conditions to the species $[VO_2(OO)_2]^{3-}$ and $[VO(OO)_3]^{3-}$.



pH dependence of the concentrations of major species as estimated from n.m.r. integrals. All solutions contain 0.1 mol dm^{-3} vanadium. [peroxide] = 0.2 (——), 0.6 (— — —), and 0.1 mol dm^{-3} (- - -); in the latter two cases the concentrations of the other species are reduced in appropriate proportion

All the above peroxide-containing solutions were pale yellow. However, the purple species $[V(OO)_4]^{3-}$ can be made [1] in solutions containing comparable proportions of H_2O_2 and $[HO_2]^-$ in substantial excess relative to vanadium. Under these conditions, $[OO^{2-}]$ is at a maximum relative to $[O^{2-}]$. We found $[V(OO)_4]^{3-}$ to be apparently the sole species present under optimum conditions, with $\delta = -734$ and a width of 480 Hz, which indicates that the solution structure, like the inferred crystal structure,[7,8] is not strictly tetrahedral. However, the presence of some $[HVO(OO)_3]^{2-}$ cannot be entirely ruled out because of its very similar shift.

Some differences were also noted in the pH dependence of the peaks arising from the oxovanadium(V) species, compared with an earlier study. Several further peaks were resolved, because of the reduced concentration and temperature and increased magnetic field. These peaks were entirely consistent with the equilibria postulated earlier [10] but permit the following improved shift and pK_a determinations: $[V_2O_7]^{4-}$, $\delta = -552.5$; $[HV_2O_7]^{3-}$, $\delta = -562$, p$K_a = 9.2 \pm 0.2$. They also imply that at a given pH the exchange between $[HVO_4]^{2-}$ and $[V_2O_7]^{4-}$ (and $[HV_2O_7]^{3-}$) is more rapid than that between $[HVO_4]^{2-}$ and $[H_2VO_4]^-$ (or $[VO_3]^-$).

pH <5.—A very small addition of concentrated perchloric acid changes a solution of $[H_2VO_2(OO)_2]^-$ at pH 5 to one of pH 3, without affecting the chemical shift or colour, or introducing new peaks. Below this pH, however, the solution reddens. The red species at a pH value of about zero is generally agreed [1,3] to be $[VO(OO)]^+$, at some unknown level of hydration. The n.m.r. observations confirm this in that the deep red solution at pH <1, corresponding to the addition of at least 2 equivalents of acid, shows only one n.m.r. peak at $\delta = -543$.

This shift value is inconveniently close to $\delta = -545$ observed with $[VO_2]^+$. However, the species may be distinguished by their very different colours and linewidths. They were also distinguished by a further qualitative experiment. A solution of sodium metavanadate (pH 7) was saturated with $Na_2[H_2edta]$ (disodium dihydrogen-ethylenedinitrilo-*NNN'N'*-tetra-acetate). This resulted in 20% of the vanadium appearing as a peak of width 1 000 Hz at $\delta = -518$, presumably due to the formation of the H_2edta complex of $[VO_2]^+$.[11] Then an excess of hydrogen peroxide was added. A red-brown colour characteristic of $[VO(OO)]^+$ was formed immediately, and an additional peak appeared at $\delta \approx -543$, whose area was *ca.* 20% of the remaining overlapping resonance at $\delta = -518$ and whose width was also consistent with the formation of $[VO(OO)]^+$.

Although this experiment is not conclusive, because of the inaccuracy in measuring chemical shift, due to line overlap and also the possibility that edta complexation of $[VO(OO)]^+$ produces no change in δ, it nevertheless suggests that $[VO(OO)]^+$ is distinct from $[VO_2]^+$ in that it cannot readily be chelated by edta. The ion $[VO_2]^+$ has a *cis* co-ordination geometry [11] which permits its chelation by edta; almost any other co-ordination geometry would preclude such chelation.

At least one further peak was observed between pH 0.5

and 3, at $\delta = -670$, which reached maximum intensity at pH 1.9, when 1 equivalent of acid had been added. The peak at $\delta = -670$ approximately doubled in relative intensity when the experiment was repeated with a solution 0.3 mol dm^{-3} in vanadium and 0.6 mol dm^{-3} in peroxide. When only 1 equivalent of peroxide was added, the equilibration shifted in favour of the peak at $\delta = -543$. Unfortunately, quantitatively accurate measurements were not possible around pH 1.9 because there was appreciable effervescence due to peroxide decomposition, which interfered with pH measurement and limited the time available for the establishment of equilibrium. Also the linewidths were large (700 Hz for the peak at $\delta = -670$) resulting in overlap.

Species observed at 273 K

Peroxo-ligands per V	0	1	2	3	4
Formula [a]	$[VO_4]^{3-}$		$[VO_2(OO)_2]^{3-}$?	$[VO(OO)_3]^{3-}$	$[V(OO)_4]^{3-}$
δ [b]	-536.2		-760	-845	-734
Width/Hz [c]	<10		250	380	480
Colour	colourless		yellow	yellow?	purple
Formula	$[HVO_4]^{2-}$	$[HVO_3(OO)]^{2-}$	$[HVO_2(OO)_2]^{2-}$	$[HVO(OO)_3]^{2-}$	
δ	-533.5	-622.8	-765.6	-733.2	
Width/Hz	50	85	240	160	
Colour	colourless	colourless or yellow	yellow	yellow	
pK_a [d]	>14	v. large	>14	*ca.* 13	
Formula	$[H(VO_3)_2O]^{3-}$		$[H\{VO(OO)_2\}_2O]^{3-}$		
δ	-562		-757		
Width/Hz	160		650		
Colour	colourless		yellow?		
pK_a	9.2		6.8		
Formula	$[H_2VO_4]^-$	$[H_2VO_3(OO)]^-$?	$[H_2VO_2(OO)_2]^-$		
δ	-573.6	-621	-696		
Width/Hz	80		260		
Colour	colourless		yellow		
pK_a	9.5	<7.7	7.9		
Formula	decavanadate [e]		$[\{V(OH_2)(OO)_2\}_2O]$?		
δ	-420 to -530		-650		
Width/Hz	100—600		700		
Colour	yellow		red-brown		
Formula	$[VO_2]^+$	$[VO(OO)]^+$			
δ	-545	-543			
Width/Hz	850	340			
Colour	yellow	red-brown			
Formula	$[VO_2(H_2edta)]^-$		$[VO(NH_3)(OO)_2]^-$?		
δ	-518		-746		
Width/Hz	1 000		165		
Colour	yellow		yellow		

[a] May omit co-ordinated water. Query indicates tentative identification. [b] Downfield from internal VCl_3O capillary. [c] At half-height. [d] Approximate value (for loss of one proton) based on n.m.r. integrals. [e] See ref. 9 for details.

A reasonable interpretation of the peak at $\delta = -670$ would be the formation of a symmetrical dimeric species, containing two peroxides per vanadium, and probably neutral in charge judging by the stoicheiometry of its formation. It may be that the presence of the peroxo-ligands prevents the formation of more highly condensed species. A possible formula would be $[\{V(OH_2)(OO)_2\}_2O]$.

The chemical shift of $[H_2VO_2(OO)_2]^-$ was also found to be slightly variable with vanadium concentration at pH <2, indicating the possible presence of further species in rapid exchange with it.

Other Species.—Solutions containing 0.1 mol dm^{-3} metavanadate plus 2 equivalents of hydrogen peroxide plus 0.1 mol dm^{-3} NH_3 were studied between pH 7 and 11. An additional peak was observed at $\delta = -747$, present in up to 40% proportion at the lower end of this pH range. The addition of more ammonia does not significantly affect these observations. We tentatively attribute this further peak to the species $[VO(NH_3)(OO)_2]^-$ whose crystal structure has been described previously.[4]

DISCUSSION

The properties of the observed peroxovanadium(V) species are summarised in the Table, along with those of some oxovanadium(V) species. A crude rationalisation of the shifts is as follows: the protonation of an O^{2-} ligand affects δ by less than 50 p.p.m. (generally increasing it unless there is a change of co-ordination number at vanadium [10]). However, protonation of the final O^{2-} ligand adds *ca.* 100 p.p.m. to δ. The replacement of $[OH]^-$ by $[OO]^{2-}$ also adds up to 100 p.p.m. to δ. For the purposes of this rationalisation, $[VO(OO)]^+$ is taken to be $[V(OH)_2(OO)]^+$. (The linewidth and the edta co-ordination experiment shows it to be unlike $[VO_2]^+$, which has two *cis* oxo-ligands.[11])

The effect of protonation on δ was previously explained [9,10] as increasing the energy of the ligand-to-metal charge-transfer transition, which is taken to be the dominant contributor to the paramagnetic part of the chemical shift. This explanation holds for the peroxo-complexes provided that at least one O^{2-} remains co-ordinated. If the final O^{2-} is either protonated or replaced by $[OO]^{2-}$, as in $[V(OH)_2(OO)]^+$ or $[V(OO)_4]^{3-}$, it would seem that a significant structural rearrangement occurs. In $[V(OO)_4]^{3-}$, for example, the difference in the V–O bond lengths for a given peroxo-ligand is *ca.* 0.01 nm,[5,7,8] compared with *ca.* 0.002 nm in the other vanadium(V) peroxo-complexes. The corresponding electronic rearrangements are shown by the marked reductions in charge-transfer absorption frequency, which correlate with the otherwise unexpectedly low values of δ.

At first sight it may seem a little surprising that the replacement of O^{2-} or $[OH]^-$ by $[OO]^{2-}$, in the presence of another O^{2-} ligand, should decrease δ, *i.e.* increase the charge-transfer transition energy. However, this is consistent with four other observations. (*i*) A typical $V–O^{2-}$ distance is 1.6 nm, and $V–OCH_3^-$ in $[VO(OCH_3)_3]$ is 1.74 nm,[12] whereas a typical $V–(OO)^{2-}$ distance is 1.9 nm. (*ii*) The protonation of a co-ordinated peroxo-ligand, which is analogous to a charge transfer to metal, does not occur, judging by the non-detection of $[HV(OO)_4]^{2-}$ and $[H_2VO(OO)_3]^-$. It would presumably involve an alteration in the co-ordination of the peroxo-ligand from its preferred 'sideways-on' geometry. (*iii*) Similarly, $[OO]^{2-}$ is not available for catenation. This may explain the observation that most of the vanadium peroxo-complexes are monomers. (*iv*) The species $[H_2VO_2(OO)_2]^-$, $[H_2VO_3(OO)]^-$, and $[H\{VO(OO)_2\}_2O]^{3-}$ all have pK_a values lower than the corresponding oxo-species by 2—3 units, implying less effective covalent compensation of the metal ion's charge by the peroxo-ligand.

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REFERENCES

[1] J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Chem. Radiochem.*, 1965, **6**, 292.

[2] F. Chauveau, *Bull. Soc. chim. France*, 1960, 819.

[3] P. Souchay and F. Chauveau, *Compt. rend.*, 1957, **245**, 1434.

[4] I.-B. Svensson and R. Stomberg, *Acta Chem. Scand.*, 1971, **25**, 898.

[5] R. E. Drew and F. W. B. Einstein, *Inorg. Chem.*, 1973, **12**, 829.

[6] R. E. Drew and F. W. B. Einstein, *Inorg. Chem.*, 1972, **11**, 1079.

[7] J. E. Fergusson, C. J. Wilkins, and J. F. Young, *J. Chem. Soc.*, 1962, 2136.

[8] R. Stomberg, *Acta Chem. Scand.*, 1963, **17**, 1563.

[9] O. W. Howarth and M. Jarrold, *J.C.S. Dalton*, 1978, 503 and refs. therein.

[10] O. W. Howarth and R. E. Richards, *J. Chem. Soc.*, 1965, 864.

[11] L. W. Amos and D. T. Sawyer, *Inorg. Chem.*, 1972, **11**, 2692.

[12] C. N. Caughlan, H. M. Smith, and K. Watenpaugh, *Inorg. Chem.*, 1966, **5**, 2131.