

SPECTRAL INVESTIGATION OF STABILITY OF THE PEROXO COMPLEXES $M_2[V_2O_2(O_2)_4H_2O] \cdot aq$ ($M = N(CH_3)_4, N(C_4H_9)_4$) IN SOLUTIONS

Peter SCHWENDT¹ and Karol LISCAK

Department of Inorganic Chemistry, Comenius University, 842 15 Bratislava, Slovak Republic;

e-mail: ¹schwendt@fns.uniba.sk

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Infrared spectra of solutions of $M_2[V_2O_2(O_2)_4H_2O] \cdot aq$ ($M = N(CH_3)_4, N(C_4H_9)_4$) in heavy water and acetonitrile indicate that in concentrated solutions ($c \geq 0.5 \text{ mol dm}^{-3}$) the asymmetric structure of the $[V_2O_2(O_2)_4H_2O]^{2-}$ anion remains preserved for some time. Electronic spectra suggest that in more dilute solutions ($c = 10^{-3}$ – $10^{-4} \text{ mol dm}^{-3}$) of the $M_2[V_2O_2(O_2)_4H_2O] \cdot aq$ complexes in water and acetonitrile the dinuclear ion decomposes faster to $[VO(O_2)_2H_2O]^-$, followed by a relatively slow liberation of the peroxidic oxygen and formation of vanadate ions. The dinuclear complex is more stable in dilute chloroform solutions. The ^{51}V NMR spectrum of an aqueous solution of $[N(CH_3)_4]_2[V_2O_2(O_2)_4H_2O]$ ($c = 1.3 \text{ mol dm}^{-3}$) taken after a partial decomposition suggests the simultaneous presence of $[V_2O_2(O_2)_4H_2O]^{2-}$, $[VO(O_2)_2H_2O]^-$, $(V_nO_{3n})^{n-}$ ($n = 4, 5, 6$), $[H_mV_{10}O_{28}]^{(6-m)-}$, and other unidentified species.

Key words: Asymmetric tetraperoxodivanadate; Solution stability; IR spectroscopy; Electron spectroscopy.

The reactivity of vanadium(V) peroxo complexes is being studied extensively with regard to the important role they play in reactions of oxygen transfer to organic substrates as well as in the bioinorganic chemistry of vanadium (modelling vanadium peroxidase enzymes, insulin mimetic effects)¹. Insight into the structure of the complexes in solution is of crucial importance in reactivity studies.

The compounds $M_2[V_2O_2(O_2)_4H_2O] \cdot aq$ where M is $N(CH_3)_4$ (ref.²), K (ref.³), or Cs (ref.⁴) are certainly among the most peculiar peroxovanadates crystallizing from vanadate solutions in dilute hydrogen peroxide solutions. As follows from the crystal structure of the tetramethylammonium² and potassium³ salts, the dinuclear anion $[V_2O_2(O_2)_4H_2O]^{2-}$ is rarely asymmetric and involves the $\mu\text{-}\eta^1\text{:}\eta^2$ peroxidic bridge (Fig. 1). Although over 10 different species have been identified during thorough studies of aqueous solutions of peroxovanadates based on their ^{51}V and ^{17}O NMR spectra, Raman spectra, and electronic spectra⁵⁻⁹, no data have been obtained so far concerning the existence of the $[V_2O_2(O_2)_4H_2O]^{2-}$ ion in solution. The pentagonal pyramidal

$[\text{VO}(\text{O}_2)_2\text{H}_2\text{O}]^-$ ion predominates in slightly acidic solutions, from which the $\text{M}_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot \text{aq}$ complexes crystallize⁹.

The present work was aimed at investigating the stability of the $[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}]^{2-}$ ion in solutions obtained by dissolving the solid complexes. The new complex $[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2 \text{H}_2\text{O}$ was synthesized, allowing less polar solvents to be employed.

EXPERIMENTAL

Preparation of $[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2 \text{H}_2\text{O}$

V_2O_5 (0.455 g) was dissolved in a stirred solution (6.25 ml) of $\text{N}(\text{C}_4\text{H}_9)_4\text{OH}$ (1 mol dm^{-3}), gently heated in a water bath. The resulting solution (dark-green colour due to the presence of $\text{V}(\text{IV})$) was evaporated to dryness on a water bath. The residue was cooled to 0°C and dissolved in a solution of hydrogen peroxide (3 ml of 30% $\text{H}_2\text{O}_2 + 2 \text{ ml}$ of water). The yellow solution obtained was filtered and allowed to crystallize in a thin layer on a Petri dish at 5°C . The crystalline complex was collected in 24 h. For $\text{C}_{32}\text{H}_{78}\text{N}_2\text{O}_{13}\text{V}_2$ (800.8) calculated: 47.99% C, 9.82% H, 3.50% N, 15.98% O_2^{2-} , 12.72% V; found: 50.05% C, 9.75% H, 3.50% N, 15.96% O_2^{2-} , 12.50% V. The $[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{D}_2\text{O}] \cdot 2 \text{D}_2\text{O}$ complex was prepared analogously using heavy water and a D_2O_2 solution in heavy water (Isocommerz, Germany).

The complex is stable at 6°C : no changes in its IR spectrum were observed in 3 months. The substance is well soluble in water, acetonitrile, methanol, chloroform, and other solvents. Its molar conductivity in acetonitrile ($c = 1 \text{ mmol dm}^{-3}$) at 20°C was $236 \text{ S cm}^2 \text{ mol}^{-1}$.

Attempts at replacing the water molecule in the complex anion with a molecule of a different solvent (methanol, acetonitrile, pyridine) by recrystallization failed.

The $[\text{N}(\text{CH}_3)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2 \text{H}_2\text{O}$ complex was synthesized following ref.².

Spectral Measurements

The infrared spectra were scanned on a Specord M-80 instrument (Zeiss, Jena) in Nujol mulls across the $4000\text{--}200 \text{ cm}^{-1}$ region. KRS-5 cells were employed to measure solutions in heavy water and acetonitrile ($c = 0.5\text{--}1.3 \text{ mol dm}^{-3}$). Both the solutions and cells were cooled to 0°C prior to measurement. The IR spectrum of the chloroform solution could not be measured due to a rapid decom-

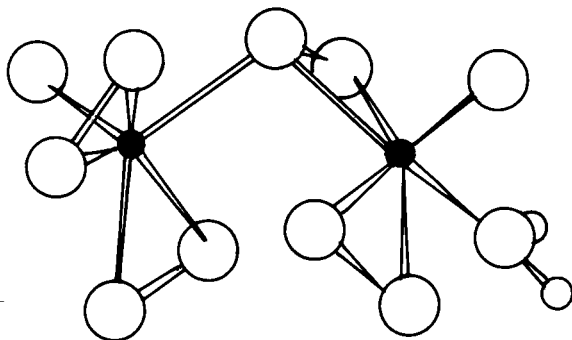


FIG. 1
Structure of the $[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}]^{2-}$
anion

position of the complex. The Raman spectrum was measured on a JEOL JRS 1 spectrometer (He-Ne laser). Electronic spectra were run on a Hewlett-Packard 84-52 A spectrophotometer at 20 °C. The ^{51}V NMR spectrum of an aqueous solution of $[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2 \text{H}_2\text{O}$ ($c = 1.3 \text{ mol dm}^{-3}$, temperature 23 °C) was scanned on a Bruker AM-300 spectrometer at 78.94 MHz, using VOCl_3 as the internal standard. Due to a vigorous evolution of oxygen from the solution, the spectrum could only be measured in 30 min after preparation.

RESULTS AND DISCUSSION

Synthesis and Vibrational Spectra of $[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2 \text{H}_2\text{O}$

The $[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2 \text{H}_2\text{O}$ complex can be prepared from a solution obtained by dissolving $\text{N}(\text{C}_4\text{H}_9)_4\text{VO}_3$ in dilute H_2O_2 . The crystals are yellow platelets, soluble in the majority of conventional solvents. The infrared spectrum (Table I and Fig. 2, curve 1) involves all characteristic bands of the $\text{VO}(\text{O}_2)_2$ group (refs¹⁰⁻¹³). The rather rich spectral patterns in the region of the $\nu(\text{O}_p-\text{O}_p)$ and $\nu(\text{V}-\text{O}_p)$ vibrations (O_p

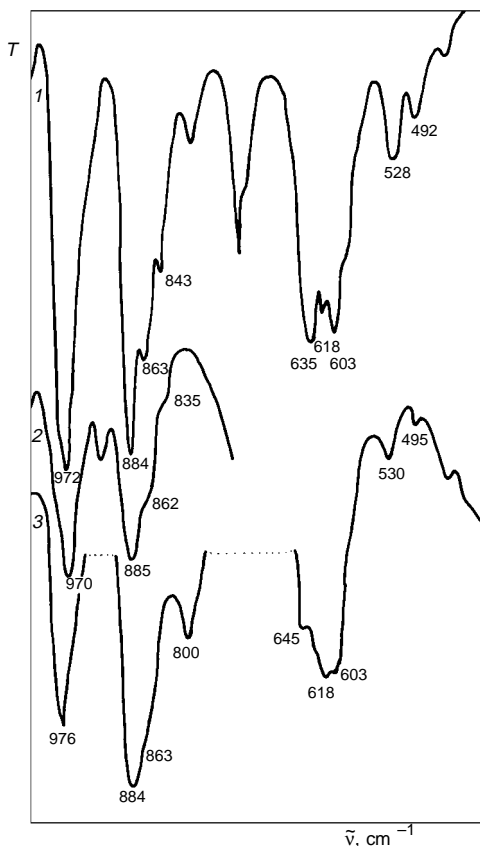


FIG. 2
Infrared spectra of $[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2 \text{H}_2\text{O}$; 1 solid in Nujol mull, 2 solution in D_2O , 3 solution in acetonitrile (regions of CH_3CN absorption are omitted)

is peroxidic oxygen) give evidence of non-equivalence of the $V(O_2)$ groups, consistent with the assumed structure (Fig. 1). The coordination of the water molecule to the central atom is borne out by the $550\text{--}300\text{ cm}^{-1}$ range of the infrared spectrum (Fig. 3). Deuteration brings about a 15 cm^{-1} shift of the band at 407 cm^{-1} , as expected for the band due to the $\nu(V-OH_2)$ stretching vibration⁴.

Infrared Spectra of Solutions of $M_2[V_2O_2(O_2)_4H_2O] \cdot aq$

The infrared spectrum of the solution of $[N(C_4H_9)_4]_2[V_2O_2(O_2)_4H_2O] \cdot 2 H_2O$ in D_2O ($c = 0.5\text{ mol dm}^{-3}$), as shown in Fig. 2, resembles closely that of the solid complex over the $800\text{--}1\,000\text{ cm}^{-1}$ range (Fig. 2, curve 1). Characteristic is particularly the $\nu(O_p-O_p)$

TABLE I

Characteristic bands in the infrared and Raman spectra of $[N(C_4H_9)_4]_2[V_2O_2(O_2)_4H_2O] \cdot 2 H_2O$

IR spectrum	Raman spectrum	Assignment
972 vs	980 vs	$\nu(V=O)$
884 vs ^a , 863 s, 843 m	883 vs	$\nu(O_p-O_p)$
635 s, 618 w, 603 s	610 m	$\nu(V-O_p)$
587 sh ^b		$\rho_w(H_2O)$
528 m ^a	515 vs	$\nu(V-O_p)$
492 m	480 w	$\nu(V-O_p)$
407 w ^c		$\nu(V-OH_2)$

^a The band shape may be affected slightly by the band of the cation; ^b absent from the spectrum of the deuterated sample; ^c shifted in 392 cm^{-1} in the spectrum of the deuterated sample.

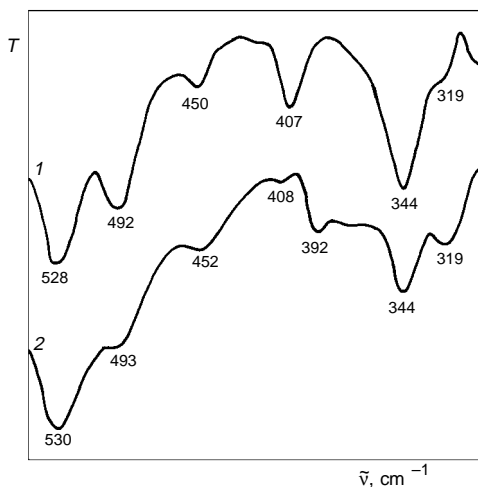


FIG. 3

Infrared spectra ($550\text{--}300\text{ cm}^{-1}$) of the solid complexes: 1 $[N(C_4H_9)_4]_2[V_2O_2(O_2)_4H_2O] \cdot 2 H_2O$, 2 $[N(C_4H_9)_4]_2[V_2O_2(O_2)_4D_2O] \cdot D_2O$

band splitting (885, 862, 835 cm^{-1}). The intensity of the band at 927 cm^{-1} increases with time: apparently, this band is due to (intermediate) products of the decomposition*

ratios lower than 2 can be expected, the system is too complex to allow us to decide whether the band at 927 cm^{-1} (and the analogous band at 800 cm^{-1} for the acetonitrile solution) belongs to intermediates or to the final polyvanadate ion mixture. The spectrum of the solution of the complex in acetonitrile (Fig. 2, curve 3) displays rather marked signs of decomposition (expressive band at 800 cm^{-1} , change in the $\nu(\text{V}-\text{O}_p)$ band intensity ratio in the 620 cm^{-1} range). The overall spectral patterns, on the other hand, allow us to conclude that in this solvent, too, a fraction of vanadium at least remains in the $[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}]^{2-}$ form for 15 min (which is the time required to scan the spectrum). A still more pronounced analogy between the spectra of the complex in D_2O solution and in the solid phase was observed for the $[\text{N}(\text{CH}_3)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2 \text{H}_2\text{O}$ complex (Fig. 4). The spectral patterns were similar not only over the $\nu(\text{V}=\text{O})$ and

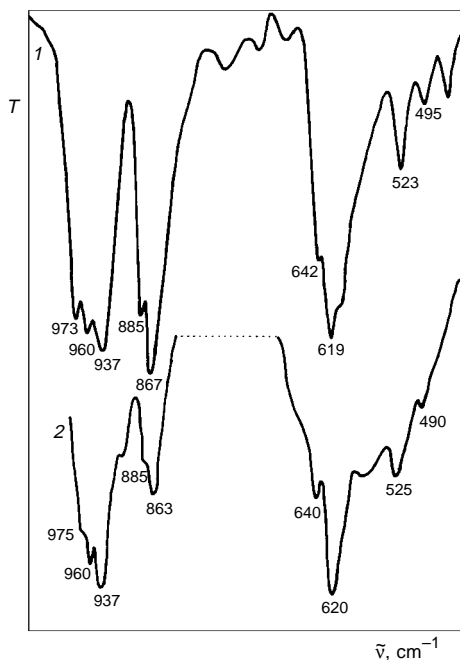


FIG. 4
Infrared spectrum of $[\text{N}(\text{CH}_3)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2 \text{H}_2\text{O}$; 1 solid complex, 2 solution in D_2O ($c = 1.3 \text{ mol dm}^{-3}$)

* Although the formation of intermediate products with the $n(\text{O}_2^-)/n(\text{V})$ ratios lower than 2 can be expected, the system is too complex to allow us to decide whether the band at 927 cm^{-1} (and the analogous band at 800 cm^{-1} for the acetonitrile solution) belongs to intermediates or to the final polyvanadate ion mixture

$\nu(\text{O}_p-\text{O}_p)$ ranges ($1\,000\text{--}800\text{ cm}^{-1}$) but also on the background of the broad D_2O absorption band with a maximum in the 600 cm^{-1} range, where bands belonging to the $\nu(\text{V}-\text{O}_p)$ vibrations can be clearly detected. The spectra can be regarded as the first experimental evidence of the existence of the $[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}]^{2-}$ ion in solution.

Electronic Spectra

The electronic spectrum of the $[\text{N}(\text{CH}_3)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$ complex in aqueous solution exhibits in the UV region the LMTC band, typical of vanadium(V) diperoxo complexes. The fact that the observed spectrum corresponds to $[\text{VO}(\text{O}_2)_2\text{H}_2\text{O}]^-$ ($\lambda_{\text{max}} = 330\text{ nm}$, $\epsilon_{\text{max}} = 660\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) (refs.^{8,14}) suggests that the dinuclear anion decomposes in dilute solutions as follows:



The $[\text{VO}(\text{O}_2)_2\text{H}_2\text{O}]^-$ ion is relatively stable in aqueous solutions: the absorbance at 330 nm decreases about 10% in 4 h at room temperature. The behaviour is similar in dilute acetonitrile solutions, only the decomposition of the ion to vanadate ions (particularly $\text{H}_2\text{VO}_4^{2-}$ and $\text{V}_4\text{O}_{12}^{4-}$), associated with the vanishing of the characteristic band of $\text{VO}(\text{O}_2)_2$ at 345 nm , proceeds faster to be complete in 50 min.

The electronic spectrum of the solution in chloroform is different. The LMCT band at 338 nm is broader (Fig. 5, curve 1) and probably corresponds to the initial dinuclear $[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}]^{2-}$ ion, possessing non-equivalent peroxy groups. Time changes in the

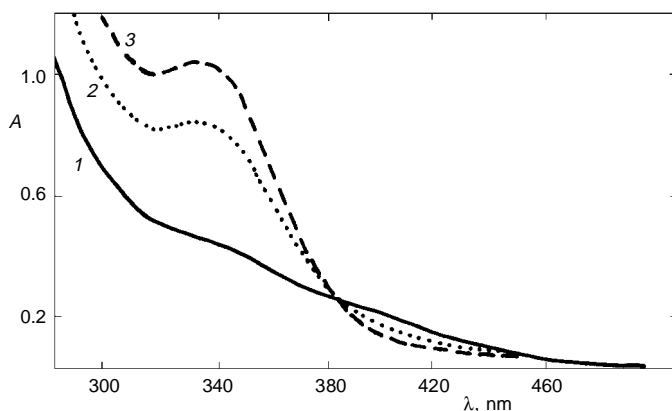


FIG. 5

Electronic spectra of $[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$ solution in chloroform. Time after dissolution (min): 1 0, 2 5, 3 10

spectrum included absorbance increase in the band maximum on account of absorbances at wavelengths over 400 nm and a slight shift of the band maximum to 334 nm (Fig. 5, curves 2 and 3). Such "narrowing" of the characteristic band of the $\text{VO}(\text{O}_2)_2$ group can be interpreted in terms of decomposition of the asymmetric dinuclear ion by pathway (A). Only in the subsequent stage predominates the decomposition of the $[\text{VO}(\text{O}_2)_2\text{H}_2\text{O}]^-$

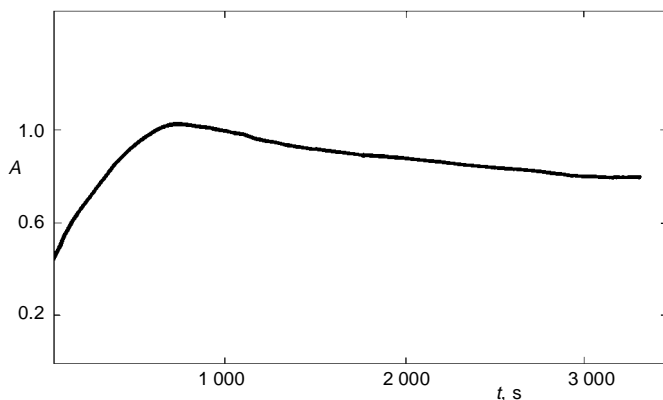


FIG. 6

Time dependence of absorbance at 340 nm for a solution of $[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2 \text{H}_2\text{O}$ in chloroform ($c = 2.75 \cdot 10^{-4} \text{ mol dm}^{-3}$) at 20 °C; optical pathlength 1 cm

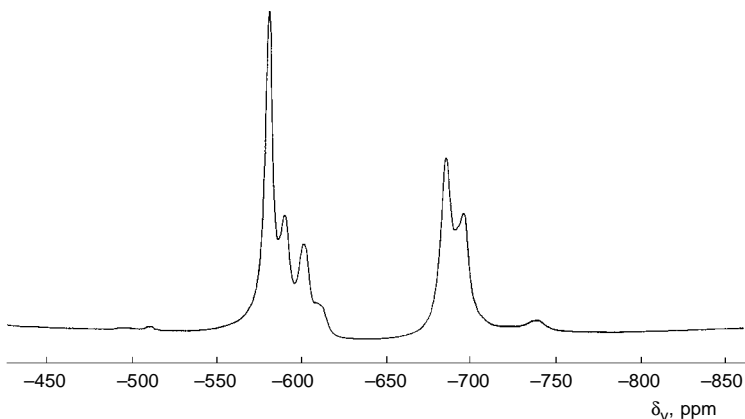


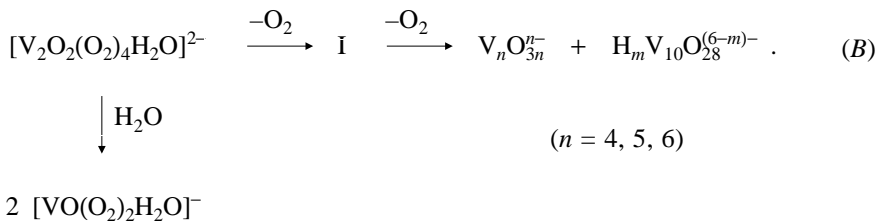
FIG. 7

^{51}V NMR spectrum of an aqueous solution of $[\text{N}(\text{CH}_3)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2 \text{H}_2\text{O}$ ($c = 1.3 \text{ mol dm}^{-3}$) measured 30 min after dissolution

ion associated with the liberation of the peroxidic oxygen, bringing about absorbance decrease in the peak range (Fig. 6).

NMR Spectrum

The ^{51}V NMR spectrum of the aqueous solution of $[\text{N}(\text{CH}_3)_4]_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}] \cdot 2 \text{H}_2\text{O}$ after a partial decomposition of the complex is shown in Fig. 7. In the region around -690 ppm, where a single signal only, corresponding to the $[\text{VO}(\text{O}_2)_2\text{H}_2\text{O}]^-$ ion, has hitherto been observed^{5-7,15}, two signals appear, viz. at -685 and -695 ppm. Since the position of the signal of the $[\text{VO}(\text{O}_2)_2\text{H}_2\text{O}]^-$ ion has been reported to lie within the region of -686 to -699 ppm in dependence on the conditions, the signal corresponding to that ion cannot be assigned unambiguously. The occurrence of two signals, however, is indicative of the presence of the $[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}]^{2-}$ ion in the solution. The complexity



of the decomposition process is documented by the series of signals at higher ppm values: -511 ($\text{H}_m\text{V}_{10}\text{O}_{28}^{(6-m)-}$), -581 ($\text{V}_4\text{O}_{12}^{4-}$), -590 ($\text{V}_5\text{O}_{15}^{5-}$), -601 ($\text{V}_6\text{O}_{18}^{6-}$) (ref.¹⁶). The signal at -612 ppm, which has not been observed before, as well as that at -740 ppm, can be attributed to the decomposition intermediates (I) containing peroxidic oxygen. The pathway of reactions involved in the decomposition of the $[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}]^{2-}$ ion in concentrated aqueous solutions can be expressed as follows:

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