Reactivity of Coordinated Peroxide at a Highly Peroxygenated Vanadium(V) Center in an Aqueous Medium

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Reactions of a highly peroxygenated metal complex, $A[V(O_2)_3]\cdot 3H_2O$ (A = Na, K), with $SO_2(g)$ follow an unprecedented sequence. The deep blue ESR-silent aqueous solution of $A[V(O_2)_3]\cdot 3H_2O$ readily reacts with $SO_2(g)$ to produce a yellow, ESR-inactive solution that on further reaction with $SO_2(g)$ affords a green-blue ESR-active (cf. VO^{2+}) solution. The reaction involving $K[V(O_2)_3]\cdot 3H_2O$ enabled isolation of the yellow intermediate characterized as $K[VO(O_2)_2(H_2O)]$. The product obtained from the ultimate green-blue solution has been identified as an oxo(sulfato)vanadate(IV) species, $A_2[VO(SO_4)_2(H_2O)_3]\cdot H_2O$ (A = Na, K). At the stages of its yellow and green-blue coloration, the reaction medium pH values were recorded to be ca. 6 and ca. 2, respectively. Similarly, reactions of $A[V(O_2)_3]\cdot 3H_2O$ with $SO_2(g)$ in the presence of AF yielded ternary oxofluoro(sulfato)vanadate(IV) compounds, $A_4[VO(SO_4)_2F_2(H_2O)]\cdot 2H_2O$ (A = Na, K). The compounds have been characterized from the results of elemental analyses, chemical determinations of oxidation states of the metals, magnetic susceptibility and ESR measurements, and IR and laser Raman spectroscopic studies. Sulfate is coordinated to the VO^{2+} center in a unidentate manner.

Introduction

Interest related to the binding, interaction, and reactivity of coordinated peroxide at a vanadium(V) center stems from its occurrence as an essential trace element in biological systems.[1-5] Participation of vanadium in stimulating nitrogen fixation,[6] its role as an intermediate electron carrier in the oxidation of NADH,[7] active involvement of the vanadium–hydrogen peroxide system in some biochemical processes,[8,9] and the capacity of peroxyvanadium complexes in oxidizing organic substrates[10-12] are very exciting contributions to the current knowledge of biochemical and catalytic involvement of the metal. Peroxymetal complexes are also studied as biomimetic synthetic models,[13-15] and information obtained thereof is valuable in the context of biomodeling and developing of practically useful catalytic systems.

Information concerning reactivity of coordinated dioxygen is relevant to the understanding of processes involved in the activation of molecular oxygen by metalloenzymes in biological systems. In recent years[16-26] reactions of coordinated dioxygen (occurring as

peroxide) have been investigated involving carbonyl compounds,[27,28] olefins,[29-32] carbon dioxide,[28] sulfur dioxide,[16-23,26,29] etc., and in most of these cases the dioxygen behaved as a nucleophile.[29] It is evident from the earlier reports that coordinated peroxide shows a characteristic reactivity with $SO_2(g)$ by way of producing coordinated sulfate.[16,26,29] Corresponding theoretical studies on the mechanistic details of the steps involved in the formation of SO_4^{2-} were also carried out.[25] Despite this progress, there did not exist any information concerning reactions of a highly peroxygenated metal complex with $SO_2(g)$. Moreover, reactions of peroxymetalates with $SO_2(g)$ were limited to group VIII metals except that of a peroxytitanium(IV) complex.[26] Besides this, most of the earlier results were derived from the studies conducted in nonaqueous medium. An important issue therefore addresses the pattern of reactivity of a highly peroxygenated metal complex with $SO_2(g)$ in an aqueous medium.

It was thus imperative to investigate such reactions and to rationalize the reaction sequence by isolating products at different stages. Recently, we discovered that a minimum of three O_2^{2-} per vanadium(V) center are required for the formation of a blue color of the $V–H_2O_2$ system[33] owing to the formation of the complex $[V(O_2)_3]^-$ species. As a direct sequel to this, and because of the rich diversity and practical utility of peroxy–vanadate(V) systems,[9-12,33-39] it was incumbent on us to provide information on this important issue. An additional interest was to ascertain if the coordinated peroxide or the metal center reacted with SO_2 in preference, when both are capable of participating in electron-transfer reactions with SO_2.

(1) Mertz, W. *Science* **1981,** *213,* 1332.

(2) Ramasarma, T.; Crane, F. L. *Curr. Top. Cell. Reg.* **1981,** *20,* 247.

(3) Chasteen, N. D. *Struct. Bonding (Berlin)* **1983,** *53,* 105.

(4) Gresser, M. J.; Tracey, A. S.; Parkinson, K. M. *J. Am. Chem. Soc.* **1986,** *108,* 6229.

(5) Tracey, A. S.; Gresser, M. J. *Proc. Natl. Acad. Sci. U.S.A.* **1986,** *82,* 609.

(6) Robson, R. L.; Eady, R. R.; Richardson, T. H.; Miller, R. W.; Hawkins, M.; Postgate, J. R. *Nature* **1986,** *332,* 388.

(7) Rau, M.; Patole, M. S.; Vijaya, S.; Ramakrishna Kurup, C. K.; Ramasarma, T.; *Mol. Cell. Biochem.* **1987,** *75,* 151.

(8) Patole, M. S.; Ramakrishna Kurup, C. K.; Ramasarma, T. *Mol. Cell. Biochem.* **1987,** *75,* 161.

(9) Djordjevic, C.; Wampler, G. L. *J. Inorg. Biochem.* **1985,** *25,* 51.

(10) Mimoun, H.; Mignard, M.; Brechot, P.; Saussine, L. *J. Am. Chem. Soc.* **1986,** *108,* 3711.

(11) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983,** *105,* 3101.

(12) Chaudhuri, M. K. *J. Mol. Catal.* **1988,** *44,* 129 and references cited therein.

(13) Karlin, K. D. *J. Chem. Educ.* **1985,** *62,* 983 and references therein.

(14) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds;* Academic Press: New York, 1981.

(15) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986,** *108,* 7834.

(16) Valentine, J. S. *Chem. Rev.* **1973,** *73,* 243.

(17) Chen-Hwa-Yank; Keeton, D. P.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1974,** 1089.

(18) Levison, J. J.; Robinson, S. D. *J. Chem. Soc. A.* **1971,** 762.

(19) Valentine, J. S.; Valentine, D., Jr.; Collman, J. P. *Inorg. Chem.* **1971,** *10,* 219.

(20) Cook, C. D.; Jauhal, G. S. *J. Am. Chem. Soc.* **1967,** *89,* 3066.

(21) Horn, R. W.; Weissberger, E.; Collman, J. P. *Inorg. Chem.* **1970,** *9,* 2367.

(22) Taqui Khan, M. M.; Andel, R. K.; Manoharan, P. T. *J. Chem. Soc., Chem. Commun.* **1971,** 561.

(23) Davies, R.; Hagopian, A. K.; Sykes, A. G. *J. Chem. Soc. A.* **1969,** 623.

(24) Vaska, L. *Acc. Chem. Res.* **1976,** *9,* 175.

(25) Mehandru, S. P.; Anderson, A. B. *Inorg. Chem.* **1985,** *24,* 2570.

(26) Miksztal, A. R.; Valentine, J. S. *Inorg. Chem.* **1984,** *23,* 3548.

(27) Ugo, R.; Conti, F.; Cenini, S.; Mason, R.; Miki, M. *J. Chem. Soc., Chem. Commun.* **1984,** 1498.

(28) Hayward, P. J.; Blake, D. M.; Wilkinson, G.; Nyman, C. J. *J. Am. Chem. Soc.* **1970,** *92,* 5873; *J. Chem. Soc. D* **1969,** 987.

(29) Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981,** *103,* 5832.

(30) Takao, K.; Wayaku, M.; Fujiwara, Y.; Imanaka, T.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1970,** *43,* 3898.

(31) Dudley, C. W.; Read, G.; Walker, P. J. C. *J. Chem. Soc., Dalton Trans.* **1974,** 1926.

(32) Otsuka, S.; Nakamura, A.; Tatsuno, Y.; Miki, M. *J. Am. Chem. Soc.* **1972,** *94,* 3761.

(33) Chaudhuri, M. K.; Islam, N. S. *Inorg. Chem.* **1985,** *24,* 2706.

(34) Clark, R. J. H.; Brown, D. *The Chemistry of Vanadium, Niobium, and Tantalum;* Pergamon Texts in Inorganic Chemistry Vol. 20; Pergamon Press: New York, 1975; p 519.

(35) Djordjevic, C. *Chem. Brit.* **1982,** 554.

(36) Campbell, N. J.; Capparelli, M. V.; Griffith, W. P.; Skapski, A. C. *Inorg. Chim. Acta.* **1983,** *77,* L215.

(37) Stomberg, R. *Acta Chem. Scand.* **1986,** *A40,* 325.

(38) Schwendt, P.; Joniakova, P. *Polyhedron* **1984,** *3,* 287.

(39) Chaudhuri, M. K.; Ghosh, S. K. *Inorg. Chem.* **1982,** *21,* 4020; *Inorg. Chem.* **1984,** *23,* 534; *J. Chem. Soc., Dalton Trans.* **1984,** 507.

(40) Chaudhuri, M. K.; Islam, N. S. *Inorg. Chem.* **1986,** *25,* 3749.

The goal of this paper is to emphasize that quite a different kind of reactivity pattern is observed in the reaction of SO₂(g) with a highly peroxygenated metal in which the metal is also known to undergo facile electron-transfer reaction with the chosen substrate. For that we present the results of some of our recently investigated experiments. Apart from this, evidence has also been provided to show that the complex [V(O₂)₃]⁻ offers potential as a novel synthon in the ternary complex formation reactions.

Results and Discussion

Reactions of the complex triperoxyvanadate(V), A[V(O₂)₃]·3H₂O (A = Na, K), with SO₂(g) were studied by following the reaction sequence through the isolation of compounds at various stages of the reactions. It was also our concern to explore the possibility of obtaining mixed-ligand peroxy(sulfato)vanadate(V) compounds that were inaccessible so far.[41] We expected that this would be possible from the interaction of one of the coordinated O_2^{2-} ligands through an insertion of SO₂ into the O—O bond in a manner similar to what happens with monoperoxo complex.[16-22,26,29] Strategically, the reactions were conducted in an aqueous medium because most of the earlier studies were carried out in nonaqueous media. Fortunately, the triperoxyvanadate(V) compounds are stable in water at least under our experimental conditions.

The deep blue A[V(O₂)₃]·3H₂O in solution readily reacted with SO₂(g), as evident from the color changes from deep blue to yellow and finally to green-blue. In separate experiments, the flow of SO₂(g) was discontinued at each stage of color changes, followed by attempts to isolate compounds. The pH values of the yellow and the green-blue solutions have been recorded to be ca. 6 and ca. 2, respectively. From the intermediate yellow solution a yellow solid precipitated spontaneously only in the case of the potassium salt. This was highly soluble and stable in water. The results of chemical analyses suggested the stoichiometry of K:V:O_2^{2-} as 1:1:2, and the molar conductance in water was found to be 135 Ω⁻¹ cm² mol⁻¹, clearly indicating a 1:1 electrolytic nature of the product. On the basis of this information and the results of other physical studies as highlighted below, the yellow intermediate has been characterized as potassium aquaoxodiperoxyvanadate(V), K[VO(O₂)₂(H₂O)].

It is quite significant to note that the intermediate yellow solution and also an aqueous solution of the yellow compound made after it was isolated did not show any ESR signals, suggesting beyond doubt that the metal did not undergo any reduction so far. It may be mentioned in passing that the solid K[V(O₂)₃]·3H₂O and a deep blue aqueous solution of it were ESR silent, as expected for a peroxyvanadate(V) species. The significant features of the IR spectrum of the yellow compound involve bands due to coordinated peroxide and water and V=O stretching (Table I). Interestingly, no characteristic band for sulfate was observed, and its absence was also ascertained independently by chemical tests. This is an unusual kind of observation because all such studies reported to date led to the insertion of SO₂ into the O—O bond of O_2^{2-} leading to coordinated SO_4^{2-}.[16-26] In the present case, however, instead of S—O modes, a strong band appears at 950 cm⁻¹, which has been assigned to ν(V=O). The bands at 860 cm⁻¹ owing to ν(O—O)[39] and at 605 and 520 cm⁻¹ due to complementary ν(V—O₂)[39] modes are characteristic of a chelated (c_{2v}) O_2^{2-} group. Diagnostic laser Raman (LR) signatures for [VO(O₂)₂(H₂O)]⁻ comprise ν(O—O) (ν₁), ν(V—O₂) (ν₂ and ν₃), and ν(V=O) at 870, 590, 528, and 936 cm⁻¹, respectively. The presence of coordinated water[42] was ascertained from the distinct appearance of ν(O—H), δ(H—O—H), and rocking modes occurring at 3120, 1620, and 742 cm⁻¹, respectively.

Although the reaction of Na[V(O₂)₂]·3H₂O with SO₂(g) produced an ESR-inactive yellow solution, however, working up afforded only a yellow oil, which did not solidify. In view of the similarity with the preceding reaction, it may be said that the

Table I. Structurally Significant IR and Raman Bands of K[VO(O₂)₂(H₂O)] and A₂[VO(SO₄)₂(H₂O)₃]·H₂O (A = Na, K)

compd	IR bands, cm⁻¹	Raman bands, cm⁻¹	assgnt
K[VO(O₂)₂(H₂O)]	950 s	936	ν(V=O)
	860 s	870	ν(O—O) (ν₁)
	605 s	590	ν(V—O₂) (ν₃)
	520 s	528	ν(V—O₂) (ν₂)
	1620 m		δ(H—O—H)
	3120 m		ν(O—H)
	742 m		ρᵣ(H₂O)
Na₂[VO(SO₄)₂(H₂O)₃]·H₂O	975 s	978	ν(V=O)
	1046 s	1080	} ν(S—O) (ν₃)
	1140 s	1172	
	619 s	610	} ν(S—O) (ν₄)
	640 s	650	
	483 m	480	ν(S—O) (ν₂)
	1631 m		δ(H—O—H)
	3422 m		ν(O—H)
	740 m		ρᵣ(H₂O)
	360 w		ν(V—O)
K₂[VO(SO₄)₂(H₂O)₃]·H₂O	975 s	966	ν(V=O)
	1049 s	1082	} ν(S—O) (ν₃)
	1152 s	1166	
	616 s	613	} ν(S—O) (ν₄)
	640 s	648	
	479 m	487	ν(S—O) (ν₂)
	1643 m		δ(H—O—H)
	3420 m		ν(O—H)
	750 m		ρᵣ(H₂O)
	340		ν(V—O)

yellow color is due to Na[VO(O₂)₂(H₂O)] but any further comment cannot be supported by experimental results.

The origin of the oxo oxygen of the yellow intermediates is believed to be one of the coordinated O_2^{2-} groups. Presumably, SO₂ insertion took place in the O—O bond of the peroxide group to form a sulfatodiperoxyvanadate(V) species, [V(SO₄)(O₂)₂]⁻, which readily underwent hydrolysis to produce the yellow aquaoxodiperoxyvanadate(V) complex, [VO(O₂)₂(H₂O)]⁻, as isolated and H₂SO₄. The formation of an oxo species over that of a sulfato is unusual but certainly not unprecedented. For example, the TiOEP(SO₄) obtained from the reaction of TiOEP(O₂) with SO₂ was hydrolyzed in moisture giving Ti(O)OEP and H₂SO₄.[43] This observation in conjunction with our earlier results[41] of reactions of vanadium(V) with H₂O₂ and SO_4^{2-} or SCN⁻ causes us to state that synthesis of (sulfato)peroxyvanadate(V) is a difficult task, although definitive reasons for this could not be discerned at the moment.

The reaction of A[V(O₂)₃]·3H₂O with SO₂(g), without being arrested at a stage of yellow coloration, ultimately generated a green-blue solution (pH ca. 2) that did not undergo any further color change under our experimental conditions. The ESR spectrum of this solution exhibited a pattern typical of an oxovanadium(IV) species. The blue compound isolated from the solution was different from the yellow one not only in terms of color but also in terms of its physical properties, viz., the magnetic moment, oxidation state of the metal, and the kinds of ligands present. The blue compound was finally characterized as a triaquabis(sulfato)oxovanadate(IV) complex, A₂[VO(SO₄)₂(H₂O)₃]·H₂O (A = Na, K).

The molar conductances of A₂[VO(SO₄)₂(H₂O)₃]·H₂O in water were found to lie between 235 and 262 Ω⁻¹ cm² mol⁻¹, in conformity with the formulae assigned. The room-temperature magnetic moments occurring in the range 1.71-1.74 μ_B support the contention that the vanadium has an oxidation state of +4. The ESR spectra of aqueous solutions of the compounds recorded both at ambient temperatures and at 77 K showed signals at g_{av} = 1.992, typical of an oxovanadium(IV) species, suggesting that the complexes exist as monomers. Further, the similarity of the

(41) Chaudhuri, M. K.; Islam, N. S. *Transition Met. Chem. (Weinheim, Ger.)* **1985**, *10*, 333.

(42) Nakamoto, K. *Infrared Spectra of Inorganic and Co-ordination Compounds*, 3rd ed.; Wiley-Interscience: London, 1978; p 226.

(43) Nakajima, M.; Latour, J. M.; Marchon, J. C. *J. Chem. Soc., Chem. Commun.* **1977**, 763.

spectra with that of vanadyl sulfate, $VO(SO_4) \cdot 5H_2O$, indicates that the coordination polyhedra around the vanadyl (VO^{2+}) center in both cases are similar. The IR and LR spectra of the compounds showed evidence of the complete absence of peroxide, which was further confirmed by chemical tests. The sharp absorption at 975 cm^{-1} must owe its origin to $\nu(V=O)$. For sulfate, the appearance of medium-intensity ν_1 and ν_2 modes of S–O vibrations at 970 and ca. 485 cm^{-1}, respectively, and the splitting of ν_3 and ν_4 into two bands each (Table I) as opposed to the absence of ν_1 and ν_2 and the presence of unsplit ν_3 and ν_4 provide clear evidence for the lowering of symmetry of SO_4^{2-} from T_d to C_{3v},[44] and its occurrence as an unidentate ligand in the complex. Although the reaction of SO_2 with chelated O_2^{2-} invariably gave rise to a chelated SO_4^{2-},[16,26,29] the present observation is apparently peculiar. However, this mode of coordination seems to be rather typical of sulfato complexes of vanadium(IV).[45] The LR spectra of $A_2[VO(SO_4)_2(H_2O)_3] \cdot H_2O$ (A = Na, K) complement their IR spectra by exhibiting S–O signals at 970 and ca. 480 cm^{-1} owing respectively to ν_1 and ν_2, at ca. 1080 and ca. 1160 cm^{-1} due to ν_3, and at ca. 650 and ca. 610 cm^{-1} due to the ν_4 modes of coordinated (C_{3v}) sulfate ligands. Owing to the presence of lattice water, IR spectral information on ν(O–H) and δ(H–O–H)[42] modes are not very significant in so far as the distinction between coordinated and lattice water are concerned. Fortunately, a consistent appearance of the rocking mode of water at ca. 740 cm^{-1}, however, supports the occurrence of coordinated water. Further, pyrolysis studies on $K_2[VO(SO_4)_2(H_2O)_3] \cdot H_2O$, as a representative, showed that whereas one molecule of water per formula weight was lost at 110–120 °C, loss of rest of the water required a much higher temperature, lending support to the notion that one molecule of water occurred as a lattice water.

Reactions of $A[V(O_2)_3] \cdot 3H_2O$ (A = Na, K) with $SO_2(g)$ in the Presence of F^- as an Access to Ternary Complexes of Vanadium(IV). Consequent upon the observations made from the reactions of $A[V(O_2)_3] \cdot 3H_2O$ with $SO_2(g)$, it was anticipated that similar reactions in the presence of a suitable ligand might afford ternary complexes of vanadium(IV). It has been known that vanadyl, VO^{2+}, binds the most electronegative atoms very effectively, of which fluoro complexes are especially stable.[46] Accordingly, the reactions of $A[V(O_2)_3] \cdot 3H_2O$ with $SO_2(g)$ were conducted in the presence of alkali-metal fluoride, AF, maintaining the atom ratio of V:F at 1:2. Here again, the spectrum of color changes was similar to that observed earlier, ultimately producing a green-blue ESR-active (cf. VO^{2+}) solution. Working up of the solution afford a blue solid containing both F^- and SO_4^{2-} as anticipated. On the basis of the results of elemental analyses, chemical determinations of oxidation states of the metals, magnetic susceptibility (1.71 μ_B) and molar conductance (510–522 Ω^{-1} cm^2 mol^{-1}) measurements, the compound has been formulated as $A_4[VO(SO_4)_2F_2(H_2O)] \cdot 2H_2O$ (A = Na, K).

The ESR spectra of aqueous solutions of the compounds, recorded both at ambient and at liquid-nitrogen (77 K) temperatures, were identical with those of $A_2[VO(SO_4)_2(H_2O)_3] \cdot H_2O$ with g_{av} being 1.996, typical of an oxovanadium(IV) species. The absence of any hyperfine coupling precluded the possibility of V–V interaction, suggesting in turn that $[VO(SO_4)_2F_2(H_2O)]^{4-}$ exists as a monomer. The IR and LR spectral features originating from the presence of coordinated SO_4^{2-}, coordinated and lattice water, and terminally bonded V=O including the positions of the related modes are similar to those observed for $A_2[VO(SO_4)_2(H_2O)_3] \cdot H_2O$, except for a new band at ca. 520 cm^{-1} (Table II). The absorption at ca. 520 cm^{-1} is significant as this provides clear evidence for the occurrence of coordinated fluoride.[47] The results

(44) Nakamoto, K. *Infrared Spectra of Inorganic and Co-ordination Compounds*, 3rd ed.; Wiley-Interscience: London, 1978; p 239.

(45) Balhausen, C. J.; Djurinskij, B. F.; Waston, K. J. *J. Am. Chem. Soc.* **1968**, *90*, 3305.

(46) Clark, R. J. H.; Brown, D. *The Chemistry of Vanadium, Niobium, and Tantalum*; Pergamon Texts in Inorganic Chemistry Vol. 20; Pergamon Press: New York, 1975; p 514.

(47) Chaudhuri, M. K.; Ghosh, S. K.; Subramanian, J. *Inorg. Chem.* **1984**, *23*, 4439.

Table II. Structurally Significant IR and Raman Bands of $A_4[VO(SO_4)_2F_2(H_2O)] \cdot 2H_2O$ (A = Na, K)

compd	IR bands, cm^{-1}	Raman bands, cm^{-1}	assgnt
$Na_4[VO(SO_4)_2F_2(H_2O)] \cdot 2H_2O$	980 s	972	$\nu(V=O)$
	1060 s	1080	$\nu(S—O)$ (ν_3)
	1140 s	1165	
	620 s	609	$\nu(S—O)$ (ν_4)
	640 s	648	
	485 m	510	$\nu(S—O)$ (ν_2)
	520 m		$\nu(V—F)$
	3420 m		$\nu(O—H)$
	1640 m		$\delta(H—O—H)$
	740 m		$\rho_r(H_2O)$
	365 w		$\nu(V—O)$
$K_4[VO(SO_4)_2F_2(H_2O)] \cdot 2H_2O$	980 s	967	$\nu(V=O)$
	1050 s	1073	$\nu(S—O)$ (ν_3)
	1120 s	1171	
	610 s	620	$\nu(S—O)$ (ν_4)
	620 s	633	
	480 m	469	$\nu(S—O)$ (ν_2)
	530 m		$\nu(V—F)$
	3419 m		$\nu(O—H)$
	1653 m		$\delta(H—O—H)$
	743 m		$\rho_r(H_2O)$
	340 w		$\nu(V—O)$

of physicochemical studies cause us to state that the SO_4^{2-} binds the VO^{2+} center in a unidentate manner, and the complex $[VO(SO_4)_2F_2(H_2O)]^{4-}$ species occurs as a hexacoordinated monomer.

Conclusions

The interaction of a highly peroxygenated vanadium(V) species, $[V(O_2)_3]^-$, with $SO_2(g)$ follows a novel reaction sequence. While both coordinated peroxide and the metal center are prone to undergo ready electron-transfer reactions with the chosen inorganic substrate, the present experiments clearly demonstrate that it is one of the edge-bound peroxide ligands that participates in the reaction in preference to vanadium(V). The reaction proceeds through distinct steps such that first one of the coordinated peroxides undergoes a two-electron irreversible cleavage of the O–O bond leading to a diperoxymono(sulfato)vanadate(V) intermediate, $[(O_2)_2V–O–SO_3]$, that readily undergoes hydrolysis to produce H_2SO_4 and aquaoxodiperoxyvanadate(V) complex, $[VO(O_2)_2(H_2O)]^-$, as isolated in the solid state as its K^+ salt. The latter complex reacts with more $SO_2(g)$ causing reduction of vanadium(V) to vanadium(IV) and conversion of coordinated peroxide to coordinated sulfate producing bis(sulfato)vanadyl complex $[VO(SO_4)_2(H_2O)_3]^{2-}$, which has also been isolated and characterized.

The reaction of $A[V(O_2)_3] \cdot 3H_2O$ (A = Na, K) with $SO_2(g)$ in the presence of the corresponding AF afforded a ternary fluoro(sulfato)oxovanadate(IV) complex $A_4[VO(SO_4)_2F_2(H_2O)] \cdot 2H_2O$. This serves as a paradigm for the synthesis of ternary complexes of vanadyl, VO^{2+}. It is also evident *inter alia* that the $[V(O_2)_3]^-$ species offers potential as a novel synthon.

Experimental Section

Reagents and solvents used were of commercially available reagent grade quality. Alkali-metal triperoxyvanadate(V) trihydrates, $A[V(O_2)_3] \cdot 3H_2O$ (A = Na, K), were prepared following the method described in ref 33 with a slight modification made only in the process of drying of the products. Thus, the deep blue products after isolation (vide ref 33) were dried in vacuo over concentrated H_2SO_4 instead of P_4O_{10}. This provides the trihydrates, $A[V(O_2)_3] \cdot 3H_2O$.

The water used for reactivity studies was deoxygenated by the following procedure. The water sample was first boiled for ca. 30 min under N_2 atmosphere and cooled to room temperature followed by bubbling of N_2 gas through it for a period of ca. 15 min. The deoxygenated water was stored in an airtight container. Preparation of solutions of sodium or potassium triperoxyvanadate(V) trihydrates were performed under N_2.

Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer. The laser Raman (LR) spectra were recorded on a SPEX Ramalog Model 1403 spectrometer. The 4880-Å laser line from a Spectra-Physics Model 165 argon laser was used as the excitation source. The light scattered at 90° was detected with the help of a cooled RCA

31034 photomultiplier tube followed by a photon-count processing system. The spectra were recorded at ambient temperatures by making pressed pellets of the compounds. Magnetic susceptibilities were measured by the Gouy method by using Hg[Co(NCS)$_4$] as the calibrant. ESR spectra of the solids as well as of aqueous solutions of the compounds were recorded by using a Varian E109, X-band ESR spectrometer with 100-K$_c$ field modulator. Molar conductance measurements were made by using a Philips PR 9500 conductivity bridge. Conductivity grade water was used for the purpose. pH values of the reaction solutions were measured by using a Systronics Type 335 digital pH meter and also by BDH indicator paper.

Elemental analyses were performed following the methods described in our earlier papers.[33,40]

Reaction of Alkali-Metal Triperoxyvanadate(V) Trihydrates, A[V-(O$_2$)$_3$]·3H$_2$O (A = Na, K), with SO$_2$(g). **(a) Isolation of Yellow Potassium Aquaoxodiperoxyvanadate(V), K[VO(O$_2$)$_2$(H$_2$O)].** The deep blue microcrystalline K[V(O$_2$)$_3$]·3H$_2$O (1.5 g; 6.25 mmol) was dissolved in 10 cm^3 of water. SO$_2$(g) was slowly bubbled through the blue solution with occasional shaking until the solution attained a uniform yellow color and deposited a yellow microcrystalline product. The pH of the solution at this stage was ca. 6. The compound was separated by filtration, washed repeatedly with ethanol, and finally dried in vacuo over concentrated H$_2$SO$_4$.

The yield of the compound was 0.8 g (70%). Anal. Calcd for K-[VO(O$_2$)$_2$(H$_2$O)]: K, 20.74; V, 27.13; peroxide (O$_2^{2-}$), 34.04. Found: K, 20.33; V, 26.92; peroxide (O$_2^{2-}$), 33.88.

(b) Isolation of Blue Alkali-Metal Triaquabis(sulfato)oxovanadate(IV) Monohydrates, A$_2$[VO(SO$_4$)$_2$(H$_2$O)$_3$]·H$_2$O (A = Na, K). A[V(O$_2$)$_3$]·3H$_2$O (6.6 mmol) was dissolved in 10 cm^3 of water. Bubbling of SO$_2$(g) through this solution resulted in different color changes. First, the solution changes color from deep blue to yellow, then to deep green, and ultimately to green-blue and does not undergo anymore change on further bubbling of SO$_2$(g) (in the case of the reaction of K[V(O$_2$)$_3$]·3H$_2$O with SO$_2$ a yellow microcrystalline solid precipitated from the yellow solution, which redissolved on further bubbling of SO$_2$). The pH of the solution at this stage was recorded to be ca. 2. Bubbling of SO$_2$(g) was stopped and the solution filtered to remove any undissolved residue. To the clear solution was slowly added ethanol until a blue oily mass was formed. Addition of an excess of ethanol is detrimental as this contaminates the product with white alkali-metal sulfate, A$_2$SO$_4$. The blue oily mass was separated by decantation, treated several times with an ethanol–acetone (1:1) mixture, and finally dried in vacuo over concentrated H$_2$SO$_4$ to afford blue solid A$_2$[VO(SO$_4$)$_2$(H$_2$O)$_3$]·H$_2$O.

The yields of Na$_2$[VO(SO$_4$)$_2$(H$_2$O)$_3$]·H$_2$O and K$_2$[VO(SO$_4$)$_2$(H$_2$O)$_3$]·H$_2$O were 1.2 g (48%) and 1.3 g (51%), respectively. Anal. Calcd for K$_2$[VO(SO$_4$)$_2$(H$_2$O)$_3$]·H$_2$O: K, 19.07; V, 12.46; SO$_4^{2-}$, 46.94. Found: K, 18.87; V, 12.12; SO$_4^{2-}$, 47.3. Calcd for Na$_2$[VO(SO$_4$)$_2$-(H$_2$O)$_3$]·H$_2$O: Na, 12.20; V, 13.52; SO$_4^{2-}$, 50.92. Found: Na, 12.36; V, 13.24; SO$_4^{2-}$ 51.18.

The reaction was monitored by ESR spectrometry. Whereas the deep blue solution of A[V(O$_2$)$_3$]·3H$_2$O was completely ESR silent, as expected, the ultimate green-blue solution, obtained through SO$_2$(g) reaction, was ESR active, giving characteristic signals of vanadium(IV). It is also important to mention that the yellow solution obtained at an intermediate stage of color changes was ESR inactive.

Reactions of A[V(O$_2$)$_3$]·3H$_2$O (A = Na, K) with SO$_2$(g) in the Presence of AF (A = Na, K) and Synthesis of Ternary Complex Alkali-Metal Aquabis(sulfato)difluorooxovanadate(IV) Dihydrates, A$_4$[VO(SO$_4$)$_2$F$_2$-(H$_2$O)]·2H$_2$O (A = Na, K). A[V(O$_2$)$_3$]·3H$_2$O (6.6 mmol) and AF (13.3 mmol) were dissolved in about 15 cm^3 of water, maintaining the atom ratio of V:F at 1:2. SO$_2$(g) was bubbled through this solution in a manner similar to that described under the preceding reaction. The color changes were also similar to those observed therein. Here again, the ultimate green-blue solution was found to be ESR active (cf. vanadium-(IV)). The green-blue solution was worked up in an analogous manner as described earlier for the isolation of A$_2$[VO(SO$_4$)$_2$(H$_2$O)$_3$]·H$_2$O (polyethylene apparatus was used in this reaction). The products obtained in the present reaction have been analyzed as blue A$_4$[VO-(SO$_4$)$_2$F$_2$(H$_2$O)]·2H$_2$O. The yields of Na$_4$[VO(SO$_4$)$_2$F$_2$(H$_2$O)]·2H$_2$O and K$_4$[VO(SO$_4$)$_2$F$_2$(H$_2$O)]·2H$_2$O were 1.5 g (52%) and 1.6 g (49%), respectively.

Anal. Calcd for K$_4$[VO(SO$_4$)$_2$F$_2$(H$_2$O)]·2H$_2$O: K, 30.76; V, 10.06; SO$_4^{2-}$, 37.86; F$^-$, 7.49. Found: K, 31.07; V, 9.89; SO$_4^{2-}$, 37.21; F$^-$, 7.63. Calcd. for Na$_4$[VO(SO$_4$)$_2$F$_2$(H$_2$O)]·2H$_2$O: Na, 20.76; V, 11.51; SO$_4^{2-}$, 43.34; F$^-$, 8.57. Found: Na, 20.39; V, 11.43; SO$_4^{2-}$, 43.81; F$^-$, 8.61.

Registry No. Na[V(O$_2$)$_3$], 96760-79-1; K[V(O$_2$)$_3$], 96760-80-4; SO$_2$, 7446-09-5; K[VO(O$_2$)$_2$(H$_2$O)], 74994-34-6; Na$_2$[VO(SO$_4$)$_2$(H$_2$O)$_3$]·H$_2$O, 120544-91-4; K$_2$[VO(SO$_4$)$_2$(H$_2$O)$_3$]·H$_2$O, 120544-92-5; Na$_4$[VO-(SO$_4$)$_2$F$_2$(H$_2$O)]·2H$_2$O, 120544-93-6; K$_4$[VO(SO$_4$)$_2$F$_2$(H$_2$O)]·2H$_2$O, 120544-94-7; H$_2$O$_2$, 7722-84-1.

Optical versus Thermal Electron Transfer between Iridium(I) Maleonitriledithiolate Complexes and Methyl Viologen

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Acetonitrile solutions of the anionic Ir(I) complexes IrLL'(mnt)$^{n-}$ [mnt = maleonitriledithiolate; n = 1, L = L' = CO, P(OPh)$_3$; n = 1, L = CO, L' = PPh$_3$; n = 2, L = CO, L' = CN$^-$] with methyl viologen (MV^{2+}) exhibit outer-sphere electron-transfer behavior ranging from optical to thermal. The type of electron-transfer behavior observed correlates with the reducing ability of the Ir(I) complexes as determined by their irreversible oxidation waves. The least reducing system, Ir(CO)$_2$(mnt)$^-$, undergoes optical charge transfer with MV^{2+} while the most reducing system, Ir(CO)(CN)(mnt)$^{2-}$, reduces MV^{2+} to the MV$^{•+}$ radical cation thermally. The other complexes, Ir(CO)(PPh$_3$)(mnt)$^-$ and Ir(P(OPh)$_3$)$_2$(mnt)$^-$, show optical CT bands with MV^{2+} and undergo photoassisted and photoinduced electron transfer, respectively. The charge-transfer ion-pair MV[Ir(CO)$_2$(mnt)]$_2$ crystallizes in the monoclinic space group C2/c in a unit cell of dimensions a = 14.754 (4) Å, b = 10.063 (3) Å, c = 19.985 (7) Å, and β = 103.73 (3)° with Z = 4. The structure consists of square-planar Ir(I) anions and MV^{2+} cations of C_2 symmetry that are twisted by 37.8° about the C–C bond between methylpyridinium rings. The dihedral angle between the methylpyridinium ring of MV^{2+} and the nearest neighbor Ir(I) anion is 9.2° with a cation–anion separation in the range 3.2–3.6 Å. The nature of the one-electron-oxidation product for the thermal electron-transfer process was established by oxidation of Ir(CO)(P(p-tol)$_3$)(mnt)$^-$ (p-tol = p-tolyl) using the ferrocenium cation and determination of the crystal structure of the Ir(II) product. This dark red crystalline product was determined to be [Ir(CO)(P(p-tol)$_3$)(mnt)]$_2$ with chelating mnt ligands bridging the Ir–Ir bond. It crystallizes in the monoclinic space group P2$_1$/n in a unit cell of dimensions a = 14.874 (8) Å, b = 17.394 (5) Å, c = 19.99 (1) Å, and β = 96.46 (5)° with Z = 4. The structure shows square-pyramidal coordination at each Ir atom and overall C_{2v} symmetry for the complex. The Ir–Ir bond length is 2.706 (2) Å. On the basis of the position of the CT band for the Ir(P(PPh$_3$)$_2$(mnt)$^-$/MV^{2+} system, the reorganization energy for the Ir(I/II) couple in this complex is estimated to be large (40–44 kcal/mol).

Introduction

Optical-electron-transfer processes have attracted the interest of chemists for many years. Initially, this interest was stimulated by the formation of colors in solution that none of the solution components exhibited individually. More recently, optical electron transfer has been shown to be intimately related to thermal electron transfer, and the impetus to study charge-transfer systems has been provided by their relevance to testing electron-transfer