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, \([\text{V(O}_2\text{O}_3\text{)}_2\text{H}_2\text{O}] (\text{A} = \text{Na}, \text{K})\), with \(\text{SO}_2(g)\) follow an unprecedented sequence. The deep blue ESR-silent aqueous solution of \([\text{A}(\text{V(O}_2\text{O}_3\text{)}_2\text{H}_2\text{O})_2\text{H}_2\text{O}] (\text{A} = \text{Na}, \text{K})\) readily reacts with \(\text{SO}_2(g)\) to afford a green-blue solution (cf. \(\text{VO}^{2+}\)) solution. The reaction involving \([\text{K}(\text{V(O}_2\text{O}_3\text{)}_2\text{H}_2\text{O})_2\text{H}_2\text{O}] (\text{A} = \text{Na}, \text{K})\) exhibited the isolation of the yellow intermediate characterized as \([\text{K}(\text{V(O}_2\text{O}_3\text{)}_2\text{H}_2\text{O})_2\text{H}_2\text{O}] (\text{A} = \text{Na}, \text{K})\). 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 \([\text{A}(\text{V(O}_2\text{O}_3\text{)}_2\text{H}_2\text{O})_2\text{H}_2\text{O}] (\text{A} = \text{Na}, \text{K})\) with \(\text{SO}_2(g)\) in the presence of \(\text{AF}\) yielded ternary oxo(sulfato)vanadate(IV) species. As a direct sequel to this, and because of the rich diversity and practical utility of peroxo–vanadate(IV) systems, \([\text{A}(\text{V(O}_2\text{O}_3\text{)}_2\text{H}_2\text{O})_2\text{H}_2\text{O}] (\text{A} = \text{Na}, \text{K})\) and \(\text{SO}_2(g)\) are limited to group VIII metals except that of a peroxytitanium(IV) complex. \(\text{SO}_2(g)\) has been shown to be capable of participating in electron-transfer reactions with \(\text{SO}_2(g)\).

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.

Participation of vanadium in stimulating nitrogen fixation, its role as an immediate electron carrier in the oxidation of NADH, active involvement of the vanadium–hydrogen peroxide system in some biochemical processes, and the capacity of peroxovanadium complexes in oxidizing organic substrates are very exciting contributions to the current knowledge of biochemical and catalytic involvement of the metal. Peroxovanadyl complexes are also studied as biomimetic synthetic models.

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 years24–26 reactions of coordinated dioxygen (occurring as peroxide) have been investigated involving carbonyl compounds, olefins, carbon dioxide, sulfur dioxide, etc., and in most of these cases the dioxygen behaved as a nucleophile. It is evident from the earlier reports that coordinated peroxide shows a characteristic reactivity with \(\text{SO}_2(g)\) by way of producing coordinated sulfate. Despite this progress, there did not exist any information concerning reactions of a highly peroxygenated metal complex with \(\text{SO}_2(g)\). Moreover, reactions of peroxovanadyl metalates with \(\text{SO}_2(g)\) were limited to group VIII metals except that of a peroxytitanium(IV) complex. 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 \(\text{SO}_2(g)\) in an aqueous medium.

It was thus imperative to investigate such reactions and to rationalize the reactivity of the isolated products at different stages. Recently, we discovered that a minimum of three \(\text{O}_2\) per vanadium(V) center are required for the formation of a blue color of the \(\text{V–H}_2\text{O}_2\) system owing to the formation of the complex \([\text{V(O}_2\text{O}_3\text{)}_2\text{H}_2\text{O}]_2\) species. As a direct sequel to this, and because of the rich diversity and practical utility of peroxo–vanadate(IV) systems,23–31 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 \(\text{SO}_2(g)\) in preference, when both are capable of participating in electron-transfer reactions with \(\text{SO}_2(g)\).


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Reactivity of Coordinated Peroxide at a V(V) Center

The goal of this paper is to emphasize that quite a different kind of reactivity pattern is observed in the reaction of SO_{2}(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(O_{2})_{2}]^{-} offers potential as a novel synthon in the ternary complex formation reactions.

Results and Discussion
Reactions of the complex triperoxyvanadate(V), A[V(O_{2})_{3}]·3H_{2}O (A = Na, K), with SO_{2}(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 peroxysulfato(oxovanadate)(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 SO_{2} 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(O_{2})_{3}]·3H_{2}O in solution readily reacted with SO_{2}(g), as evident from the color changes from deep blue to yellow and finally to green-blue. In separate experiments, the flow of SO_{2}(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 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 so far have not been significant features of the IR spectrum of the yellow compound.

Physical Studies
Silent, as expected for a peroxyvanadate(V) species. The significant features of the IR spectrum of the yellow intermediate have been characterized as potassium aquoxodiperoxyvanadate(V), K[V(O_{2})_{2}(H_{2}O)].

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(O_{2})_{3}]·3H_{2}O 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 SO_{2} into the O=O bond of O_{2}^{2-} leading to coordinated SO_{2}^{2-}. \(^{18,19,24-26}\) In the present case, however, instead of S=O modes, a strong band appears at 950 cm\(^{-1}\), which has been assigned to v(V=O). The bands at 860 cm\(^{-1}\) owing to v(O=O) and at 605 and 520 cm\(^{-1}\) due to complementary ν(V=O)\(^{39}\) modes are characteristic of a chelated (c_{5}) O_{2}^{2-} group. Diagnostic laser Raman (LR) signatures for [V(O_{2})_{3}(H_{2}O)]\(^{3-}\) comprise v(O=O) (ν_{1}), v(V=O) (ν_{2} and ν_{3}), and v(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(O_{2})_{3}]·3H_{2}O with SO_{2}(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 yellow color is due to Na[V(O_{2})(H_{2}O)] 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, SO_{2} insertion took place in the O=O bond of the peroxide group to form a sulfatodiperoxyvanadate(V) species, [V(SO_{4})(O_{2})_{2}]\(^{-}\), which readily underwent hydrolysis to produce the yellow aquoxodiperoxyvanadate(V) complex, [V(O_{2})(H_{2}O)]\(^{2+}\), as isolated and H_{2}SO_{4}. The formation of an oxo species over that of a sulfato is unusual but certainly not unprecedented. For example, the TiOEP(SO_{4}) obtained from the reaction of TiOEP(O_{2}) with SO_{2} was hydrolyzed in moisture giving Ti(OEP)EP and H_{2}SO_{4}. This observation in conjunction with our earlier results \(^{41}\) of reactions of vanadium(V) with H_{2}O and SO_{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(O_{2})_{3}]·3H_{2}O with SO_{2}(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, A_{3}[V(SO_{4})_{2}(H_{2}O)]\(^{3-}\) (A = Na, K).

The molar conductances of A_{3}[V(SO_{4})_{2}(H_{2}O)]\(^{3-}\) in water were found to lie between 235 and 262 \(\text{Ω}^{-1} \cdot \text{cm}^{2} \cdot \text{mol}^{-1}\), in conformity with the formulae assigned. The room-temperature magnetic moments occurring in the range 1.71-1.74 \(\mu_{B}\) 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 \(g_{\text{av}}\) = 1.992, typical of an oxovanadium(IV) species, suggesting that the complexes exist as monomers. Further, the similarity of the

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Table I. Structurally Significant IR and Raman Bands of K[V(O_{2})(H_{2}O)] and A_{3}[V(SO_{4})(H_{2}O)]\(^{3-}\) (A = Na, K)

<table>
<thead>
<tr>
<th>compd</th>
<th>IR bands, cm(^{-1})</th>
<th>Raman bands, cm(^{-1})</th>
<th>assgnt</th>
</tr>
</thead>
<tbody>
<tr>
<td>K[V(O_{2})(H_{2}O)]</td>
<td>950 s 936</td>
<td>ν(V=O)</td>
<td></td>
</tr>
<tr>
<td>860 s 870</td>
<td>ν(O=O) ((\nu_{1}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>605 s 590</td>
<td>ν(V=O) ((\nu_{3}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>520 s</td>
<td>ν(V=O) ((\nu_{2}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1620 m</td>
<td>δ(H-O-H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3120 m</td>
<td>ν(O=O)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>742 m</td>
<td>ν(0-H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>975 s 978</td>
<td>ν(V=O)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1046 s 1080</td>
<td>ν(S-O) ((\nu_{a}))</td>
<td></td>
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</tr>
<tr>
<td>1140 s 1172</td>
<td>ν(S-O) ((\nu_{b}))</td>
<td></td>
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<tr>
<td>619 s 610</td>
<td>ν(S-O) ((\nu_{c}))</td>
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<td></td>
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<tr>
<td>640 s 650</td>
<td>ν(S-O) ((\nu_{d}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>483 m 480</td>
<td>ν(S=O) ((\nu_{a}))</td>
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<td></td>
</tr>
<tr>
<td>1651 m</td>
<td>δ(H-O-H)</td>
<td></td>
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</tr>
<tr>
<td>3422 m</td>
<td>ν(0-H)</td>
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<tr>
<td>740 m</td>
<td>ν(H-O)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>360 w</td>
<td>ν(V=O)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K_{3}[V(SO_{4})(H_{2}O)](^{3-})·H_{2}O</td>
<td>975 s 966</td>
<td>ν(V=O)</td>
<td></td>
</tr>
<tr>
<td>1049 s 1082</td>
<td>ν(S-O) ((\nu_{a}))</td>
<td></td>
<td></td>
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<tr>
<td>1152 s 1166</td>
<td>ν(0-H)</td>
<td></td>
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</tr>
<tr>
<td>616 s 613</td>
<td>ν(S-O) ((\nu_{c}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>640 s 648</td>
<td>ν(S-O) ((\nu_{d}))</td>
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<tr>
<td>647 m 487</td>
<td>ν(S=O) ((\nu_{a}))</td>
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<tr>
<td>1643 m</td>
<td>δ(H-O-H)</td>
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<tr>
<td>3420 m</td>
<td>ν(0-H)</td>
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<tr>
<td>750 m</td>
<td>ν(H-O)</td>
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<tr>
<td>340 m</td>
<td>ν(V=O)</td>
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spectra with that of vanadyl sulfate, VO(SO_4)_2·5H_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 v(\nu=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_1 and ν_2 into two bands each (Table I) as opposed to the absence of ν_1 and ν_2 and the presence of unsplit ν_1 and ν_2 provide clear evidence for the lowering of symmetry of SO_4^{2-} from T_d to C_2v, and its occurrence as an undentate ligand in the complex. Although the reaction of SO_2 with chelated O_2 invariably gave rise to a chelated SO_4^{2-}, the present observation is apparently peculiar. However, this mode of coordination seems to be rather typical of sulfato complexes of vanadium(IV). The LR spectra of A[V(O_2)_{3}·3H_2O]·H_2O (A = Na, K) in the Presence of F^- as an Access to Ternary Complexes of Vanadium(IV). Consequently, observations made from the reactions of A[V(O_2)_{3}·3H_2O]·H_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. According to the results of elemental analyses, one molecule of water occurred as a lattice water. Further, pyrolysis studies on K_4[VO(SO_4)_2·F·(H_2O)]·2H_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.

**Table II. Structurally Significant IR and Raman Bands of**

<table>
<thead>
<tr>
<th>compd</th>
<th>IR bands, cm^{-1}</th>
<th>Raman bands, cm^{-1}</th>
<th>assign</th>
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<tbody>
<tr>
<td>Na_4[VO(SO_4)_2·F·(H_2O)]·2H_2O</td>
<td>980 s 1060 s 1140 s 620 s 640 s 485 s 520 s 3420 s 1640 s 740 s</td>
<td>972 s 1080 s 1165 s 609 s 648 s 510 s 670 s 2700 s 950 s 450 s</td>
<td>ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4)</td>
</tr>
<tr>
<td>K_4[VO(SO_4)_2·F·(H_2O)]·2H_2O</td>
<td>980 s 1050 s 1120 s 610 s 620 s 480 s 530 s 3419 s 1653 s 743 s</td>
<td>967 s 1073 s 1171 s 660 s 633 s 469 s 670 s 2700 s 950 s 450 s</td>
<td>ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4) ν(S-O) (ν_4)</td>
</tr>
</tbody>
</table>

**Conclusions**

The interaction of a highly peroxygenated vanadium(V) species, VO(PO_3)_{2}·3H_2O, with SO_2(g) follows a novel reaction sequence. While both coordinated peroxide and the metal center are prone to undergo electron-transfer reactions with the chosen inorganic substrate, the present experiments clearly demonstrate that it is one of the edge-bound peroxide ligands that participate 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 diperoxyxomono(sulfato)vanadate(V) intermediate, [(O_2)V-O-SO_3]^{-}, that readily undergoes hydrolysis to produce H_2SO_4 and aqua oxo diperoxovanadate(V) complex, [VO_2H_2(H_2O)_4]^-, 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)]^{2+}, which has also been isolated and characterized.

The reaction of A[V(O_2)_{3}·3H_2O]·H_2O (A = Na, K) with SO_2(g) in the presence of the corresponding AF afforded a ternary fluoride(sulfato)oxovanadate(IV) complex A[V(O_2)_{3}·F·(H_2O)]·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}]^{2+} species offers potential as a novel synthon.

**Experimental Section**

Reagents and solvents used were of commercially available reagent grade quality. Alkaline-metal triperoxovanadates(V) trihydrates, A[V-O_2]_{3}·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_2O_5. This provides the trihydrates, A[V(O_2)_{3}·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 air-tight container. Preparation of solutions of sodium or potassium triperoxovanadates(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 Ramanalog 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 HgCo(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 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.30,45

Reaction of Alkal-Metal Triphosphonate (V) Triborylides, A[V-O(0)]₃H₂O (A = Na, K), with SO₂(g). (a) Isolation of Yellow Potassium Aquoxygenotriphosphonate(V), K[V(0)(0)(H₂O)]. The deep blue microcrystalline K[V(O₂)₃]H₂O 1.5 ng; 6.25 mmol) was dissolved in 10 cm³ of water. SO₂(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 H₂SO₄.

The yield of the compound was 0.8 g (70%). Anal. Caled for K\[V(O₂)(H₂O)]: K, 20.74; V, 27.13; peroxide 34.83; water 21.06. Found: K, 20.73; V, 27.17; peroxide: 34.85. (b) Isolation of Blue Alkal-Metal Triquinazolium(sulfato)oxovanadate(VII) Monoaldoxicals, A[V(SO₄)₂(H₂O)]₃H₂O A [V(O₂)₃]H₂O (A = Na, K). A[V(O₂)₃]H₂O (6.6 mmol) was dissolved in about 15 cm³ of water, maintaining the atom ratio of SO₂:H₂O, 1:1, and deposited a yellow microcrystalline solid precipitated from the yellow solution, which redissolved on further bubbling of SO₂. The pH of the solution at this stage was recorded to be ca. 2. Bubbling of SO₂(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 alkal-metal sulfate, A₂SO₄. 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 H₂SO₄ to afford blue solid A₂[V(SO₄)₂(H₂O)]₃H₂O.

The yields of Na₂[V(SO₄)₂(H₂O)]₃H₂O and K₂[V(SO₄)₂(H₂O)]₃H₂O were 1.2 g (48%) and 1.3 g (51%), respectively. Anal. Caled for K₂[V(SO₄)₂(H₂O)]₃H₂O: K, 19.07; V, 12.46; SO₄²⁻, 46.94. Found: K, 18.87; V, 12.12; SO₄²⁻, 47.3. Caled for Na₂[V(SO₄)₂(H₂O)]₃H₂O: Na, 20.72; V, 13.52; SO₄²⁻, 49.92. Found: Na, 20.36; V, 13.24; SO₄²⁻, 51.18.

The reaction was monitored by ESR spectrometry. Whereas the deep blue solution of A[V(O₂)₃]H₂O was completely ESR silent, as expected, the ultimate green-blue solution, obtained through SO₂(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(O₂)₃]H₂O (A = Na, K) with SO₂(g) in the Presence of AF (A = Na, K) and Synthesis of Ternary Complex Alkal-Metal Aquabis(sulfato)di fluorooxovanadate(IV) Dihydroxy, A[V(SO₄)₂F₂(H₂O)]H₂O (A = Na, K). A[V(O₂)₃]H₂O 6.6 mmol) and AF 13.3 mmol) were dissolved in about 15 cm³ of water, maintaining the atom ratio of AF:V₂F₄ at 1:2. SO₂(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 A₂[V(SO₄)₂(H₂O)]₃H₂O (polyethylene apparatus was used in this reaction). The products obtained in the present reaction have been analyzed as blue A₂[V(SO₄)₂F₂(H₂O)]H₂O and K₂[V(SO₄)₂F₂(H₂O)]H₂O were 1.5 g (52%) and 1.6 g (49%), respectively.

Anal. Caled for K₂[V(SO₄)₂F₂(H₂O)]H₂O: K, 20.76; V, 10.06; SO₄²⁻, 37.86; F, 7.49. Found: K, 20.71; V, 10.39; SO₄²⁻, 37.21; F, 7.63. Caled for Na₂[V(SO₄)₂F₂(H₂O)]H₂O: Na, 20.76; V, 11.51; SO₄²⁻, 43.34; F, 8.57. Found: Na, 20.39; V, 11.43; SO₄²⁻, 43.81; F, 8.61.

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Registry No. Na₂[V(O₂)₃]H₂O, 96760-79-1; K₂[V(O₂)₃]H₂O, 96760-80-3; SO₄²⁻, 7446-09-5; K₂[V(O₂)₂(H₂O)]; 74994-34-6; Na₂[V(SO₄)₂(H₂O)]; H₂O, 120544-91-4; K₂[V(SO₄)₂(H₂O)]; H₂O, 120544-92-5; Na₂[V(SO₄)₂F₂(H₂O)]; H₂O, 120544-93-6; K₂[V(SO₄)₂F₂(H₂O)]; H₂O, 120544-94-7; H₂O₂, 7722-84-1.

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

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Acetonitrile solutions of the anionic Ir(I) complexes IrL'\[^{mmt}\] \[^{mmt} = \text{maleonitrilidithiolate}; n = 1; L' = CO, L = \text{PPPh}_{3}\]^n \[^{mmt} = \text{methyl viologen} (MV²\text{⁻})\] 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(II) complexes as determined by their irreversible oxidation waves. The least reducing complex, Ir(CO)(mmt)\[^{n = 1; L = CO, L' = CN}\] undergoes optical charge transfer with MV²\text{⁻} while the most reducing system, Ir(CO)(CN)(mmt)\[^{n = 2; L = CO, L' = CN}\] reduces MV²\text{⁻} to the MV²⁺ radical cation thermally. The other complexes, Ir(CO)(PPPh₃)(mmt)\[^{n = 1; L' = CO, L' = CN}\] and Ir(P(OPh)₃)\[^{L' = CN}\] show optical CT bands with MV²⁺ and undergo photoassisted and photoinduced electron transfer, respectively. The charge-transfer ion-pair MV{Ir(CO)\[^{L' = CO, L' = CN}\]} crystallizes in the monoclinic space group C2/c with chelating mnt ligands bridging the Ir-Ir bond. It crystallizes in the monoclinic space group C2/c in a unit cell of dimensions a = 14.754 (4) Å, b = 17.394 (4) Å, c = 19.985 (7) Å, and β = 103.73 (3)° with Z = 4. The structure consists of square-planar Ir(I) anions and MV²⁺ cations of C₂ symmetry that are twisted by 37.8° about the C-C bond between methyliumpyridinium rings. The dihedral angle between the methyliumpyridinium ring of MV²⁺ 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=tol)(mmt)\[^{L = \text{P=tol}}\] (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 \(^{1}^{1} \text{Ir}\)(CO)(P=tol)(mmt)\[^{n = 1; L' = CO}\] with chelating mnt ligands bridging the Ir-Ir bond. It crystallizes in the monoclinic space group P2₁/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 C₂ 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=PPPh₃)(mmt)/MV²⁺ 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