tribution to the ^{14}N line width, even at high temperatures, consistent with the Arrhenius plot for ^{14}N being linear over the entire temperature range (Figure 1).

Acknowledgment. R.T.C.B. and A.G.W. thank the Australian

Synthesis of Tetraethylammonium Dithionite and Its Dissociation to the Sulfur Dioxide Radical Anion in Organic Solvents[†]

Samuel M. Lough and John W. McDonald*

The facile synthesis of [Et$_4$N]$_2$[S$_2$O$_4$] from Na$_2$S$_2$O$_4$ and [Et$_4$N]OH has been carried out by using anion-exchange chromatography on Bio-Rex 5. This form of dithionite is soluble in organic solvents, allowing its ability as a reducing agent to be utilized in nonaqueous media. Electronic and EPR spectral studies have shown that the [S$_2$O$_4$]$^{2-}$ ion is extensively dissociated to the sulfur dioxide radical anion in the organic solvents dimethylformamide, dimethyl sulfoxide, and acetonitrile, complementing some,[28] and conflicting with other,[27] previous studies dealing with the electrochemical generation of [SO$_2$]$^-$ from sulfur dioxide in organic solvents. In general, the equilibrium constants for the formation of [SO$_2$]$^-$ from [S$_2$O$_4$]$^{2-}$ in these nonaqueous solvents (DMF, 42.4 mM; Me$_2$SO, 11.3 mM; MeCN, ca. 40 mM) are 10^7 times greater than in aqueous media (1.4 × 10^{-6} mM).[3] The dissociation to the radical anion in nonaqueous media is very dependent on the water content of the solvent, an effect that has been quantitated for the DMF/H$_2$O system. These findings suggest that [S$_2$O$_4$]$^{2-}$ is preferentially stabilized by solvents of higher polarity or perhaps by H$_2$O only. Solid-state EPR studies also indicate that the isolated solid [Et$_4$N]$_2$[S$_2$O$_4$] contains significant, but small (ca. 1%), amounts of [Et$_4$N][SO$_2$].

The dithionite ion ([S$_2$O$_4$]$^{2-}$) is a ubiquitous reducing agent that has been used both in relatively small scale organic synthetic procedures[1] and in larger amounts as a bleach in commercial vat dyeing.[2] However, [S$_2$O$_4$]$^{2-}$ has perhaps been most widely employed in biochemical systems, where it has been used for the in vitro reduction of enzymes and other redox-active proteins such as ferredoxins and/or as an agent for removal of dissolved oxygen from aqueous solutions used in anaerobic biochemical procedures. Although [S$_2$O$_4$]$^{2-}$ itself is occasionally important as an actual reductant, numerous kinetic studies involving metalloproteins,[3-10] synthetic transition-metal complexes,[11-13] organic dyes,[14] and simple inorganic species[15] have shown that usually the sulfur dioxide radical anion, [SO$_2$]$^-$, formed from dissociation of [S$_2$O$_4$]$^{2-}$, is the active species in "dithionite reductions" even though it is present in only small amounts.

Virtually all of the above studies have been carried out in *aqueous solution* on the disodium salt of dithionite, by far the most commonly available and employed form of the reducing agent. By contrast, there is much less information on the properties of the dithionite ion in *nonaqueous solution*, most likely due to the fact that Na$_2$S$_2$O$_4$ is effectively insoluble in most organic solvents. Herein we report a detailed, refined method for the preparation of [Et$_4$N]$_2$[S$_2$O$_4$] and present EPR and electronic spectroscopic data that have been used to quantitate the dissociation of dithionite to the sulfur dioxide radical anion in *N,N*-dimethylformamide (DMF), acetonitrile (MeCN), and dimethyl sulfoxide (Me$_2$SO).

Experimental Section

Materials and Methods. All operations were carried out in the absence of oxygen by using Schlenk tube techniques, glovebox manipulation, or anaerobic chromatographic apparatus and solvents that were degassed prior to use. DMF and MeCN were both vacuum-distilled from CaH$_2$ (the former at reduced pressure) before use. Me$_2$SO was used as received from Burdick and Jackson. Commercial pH 10 borate buffer was from VWR. Electronic spectra were obtained on a Cary 118C instrument, IR spectra on a Beckman IR-20A spectrophotometer, and EPR spectra on a spectrometer system that has been described previously.[16] Bio-Rex 5 anion-exchange resin (200-400 mesh) was purchased from Bio-Rad Laboratories.

Purification of Sodium Dithionite. A variation of the literature procedure[17] was used. Commercial Na$_2$S$_2$O$_4$ from a variety of sources (10 g) was dissolved in 0.02 M NaOH (55 mL) and an additional 0.40 mL of 3 M NaOH added. This solution was filtered, the filtrate was heated to 65 °C, and MeOH (75 mL) was slowly added. The white granular product was isolated by filtration, washed with hot MeOH, and dried under vacuum. Recovery was typically 60-70%. Repeated reprecipitation gave solids up to 90% pure on the basis of a comparison of their UV spectra with literature[18] values (λ_{max} = 313 nm; ϵ = 8000 M^{-1} cm^{-1}).

Preparation of [Et$_4$N]$_2$[S$_2$O]. A column (2.5 cm in a diameter and 1.5 cm long) of Bio-Rex 5 anion-exchange resin in the Cl$^-$ form was made anaerobic by elution of 300 mL of rigorously degassed H$_2$O. The column was converted to its dithionite form by slow elution of a solution of purified Na$_2$S$_2$O$_4$ (9.0 g; 51.7 mM) in H$_2$O (60 mL) and was then washed with H$_2$O until the eluant showed no capacity to reduce methylviologen. This resin was treated with 0.5 M [Et$_4$N][OH] in H$_2$O and the pH of the eluant carefully monitored. At the first sign of a rise in pH, the elution was discontinued and the eluant evaporated to dryness under vacuum at 30 °C to give an oily, pale yellow residue. This material was then heated for an additional 6 h at 70-80 °C under high vacuum causing both solidification to a well-formed product and a color change to brighter yellow. Reprecipitation of this solid from DMF did not significantly alter its purity as evidenced by both elemental analytical and

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electronic spectral studies. Anal. Calcd for [Et$_4$N]$_2$[S$_2$O$_4$] (C$_{16}$H$_{40}$N$_2$O$_4$S$_2$): C, 49.48; H, 10.31; N, 7.22. Found: C, 49.59; H, 10.54; N, 7.06.

Equilibrium Constant Determinations. Concentrated (ca. 200 mM) dithionite solutions were prepared by dissolving solid [Et$_4$N]$_2$[S$_2$O$_4$] in DMF, Me$_2$SO, and MeCN and the true [S$_2$O$_4$]$^{2-}$ concentrations of these solutions then determined from their absorbance at 313 nm after a 100-fold dilution into pH 10 borate buffer. The literature[18] molar absorptivity value of 8000 M^{-1} cm^{-1} was used in this quantitation. The stock solutions were then diluted with pure solvent to a variety of nominal [S$_2$O$_4$]$^{2-}$ concentrations and these solutions transferred to a ~1-mm-i.d. quartz capillary tube for EPR spectral studies. The intensity of the strong resonance in the $g = 2$ region was quantitated by using computerized double integration as described previously.[16] To avoid errors due to varying tubing thickness, the spectrum of [S$_2$O$_4$]$^{2-}$ under each condition of solvent and concentration was run in the *same* tube, as was quantitation of the integration standard (1.00 mM [Bu$_4$N]$_3$[Mo-(S$_2$C$_4$N$_2$)$_4$][19]). Accurate g values were determined with DPPH as a calibrant.

Electronic and EPR Spectral Studies as a Function of the Aqueous Content of DMF. Various mixtures (300 μL) of degassed pH 10 buffer and DMF were placed in a 1 mm path length cuvette equipped with a septum, and 3 μL of a stock solution of [Et$_4$N]$_2$[S$_2$O$_4$] (ca. 200 mM) in pH 10 borate buffer were added. After the samples were mixed to complete homogeneity, the spectra of these nominally 2 mM [S$_2$O$_4$]$^{2-}$ solutions were recorded in the 400–230-nm region. In separate experiments, the spectrum of [Et$_4$N]$_2$[S$_2$O$_4$] in the complete absence of water was determined by adding 3 μL of a 200–300 mM solution in pure solvent to 300 μL of solvent in a 1 mm path length cuvette. Solutions for EPR studies were prepared as for the electronic spectral studies (but in small vials instead of the cuvette) and then transferred to a quartz capillary EPR tube for spectral determination and analysis as described above.

Results and Discussion

Synthesis of [Et$_4$N]$_2$[S$_2$O$_4$]. We previously reported[20] the use of ion-exchange chromatography on (2-(diethylamino)ethyl)-cellulose (DEAE) for the preparation of [Et$_4$N]$_2$[S$_2$O$_4$] in a form that was sufficiently pure to allow the isolation and reduction of the iron molybdenum cofactor of nitrogenase.[21–24] We have now refined the synthetic procedure for this reductant, using the higher capacity Bio-Rad Bio-Rex 5 instead of DEAE. Because it is an anion-exchange resin, elution with aqueous Na$_2$S$_2$O$_4$ not only generates the dithionite form of the column but also removes any residual oxygen present in the chromatographic matrix. This resin is then treated with degassed 0.5 M aqueous [Et$_4$N]OH, the pH of the eluant is carefully monitored, and the elution is terminated at the first sign of basicity. Our use of fairly short columns as described in the Experimental Section makes "channelling" of the [Et$_4$N]OH a potential problem that makes the monitoring of pH imperative and also results in some variation in yield. Evaporation of the eluant to dryness under vacuum results first in the formation of a white tacky residue that gradually becomes yellow on further dehydration at higher temperatures. This change in color is reproducible, and in general, the most intensely yellow samples are also of highest purity. On the basis of EPR spectral evidence (vide infra), we speculate that the color is due to the presence of small amounts of the sulfur dioxide radical anion [SO$_2$]$^-$. These samples of [Et$_4$N]$_2$[S$_2$O$_4$] are thermally stable in the solid state at room temperature, but the product is extremely air-sensitive and hygroscopic, becoming oily within seconds after exposure to air, and therefore must be weighed and transferred under anaerobic conditions.

[Et$_4$N]$_2$[S$_2$O$_4$] prepared in this way is characterized by elemental analytical data, which are acceptable for this formulation, and by an IR spectrum, which is consistent with the postulated
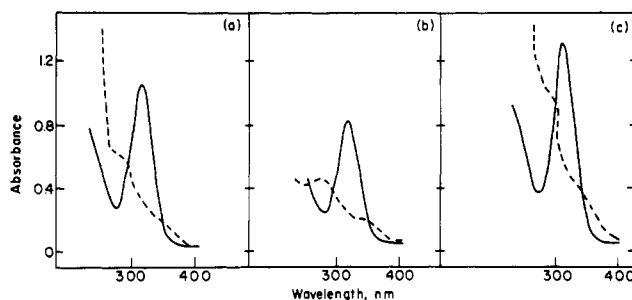
Figure 1. Electronic spectra of ca. 250 mM solutions of [Et$_4$N]$_2$[S$_2$O$_4$] in organic solvents after 100-fold dilution into pH 10 borate buffer (—) and solvent (---): (a) DMF, 1.61 mM; (b) Me$_2$SO, 1.31 mM; (c) MeCN, 1.02 mM. All spectra were obtained in a 1 mm path length cuvette.

product, containing bands at 910 and 1060 cm^{-1}, the positions associated with S–O stretching vibrations in Na$_2$S$_2$O$_4$. The electronic spectrum, as determined in pH 10 borate buffer, contains a strong band at 313 nm characteristic[25] of the dithionite ion. The maximum molar absorptivity observed for this band (6900 M^{-1} cm^{-1}) is somewhat lower than the literature[18] value (8000 M^{-1} cm^{-1}), a fact which suggests that it contains [Et$_4$N]$^+$ salts of impurities from the Na$_2$S$_2$O$_4$ starting material, which was ca. 90% pure after recrystallization on the basis of its electronic spectrum. In any event, [Et$_4$N]$_2$[S$_2$O$_4$] prepared in this way is of higher purity than most unpurified, commercially available samples of Na$_2$S$_2$O$_4$.

Dissociation of Dithionite to the Sulfur Dioxide Radical Anion in Organic Solvents. As presented in Figure 1, the 313-nm band, which is characteristic of the dithionite ion in H$_2$O, does not appear in the spectrum of [Et$_4$N]$_2$[S$_2$O$_4$] in the organic solvents DMF, Me$_2$SO, or MeCN. This behavior suggests (a) that dithionite itself is not present in solution under these conditions, (b) that dithionite has a very different electronic spectrum in nonaqueous media, or (c) that both of these possibilities are relevant. Addition of small amounts of concentrated solutions of [Et$_4$N]$_2$[S$_2$O$_4$] (100–200 mM) in these solvents to pH 10 buffer results in solutions that indeed exhibit the 313-nm band, a finding which shows conclusively that either [S$_2$O$_4$]$^{2-}$ or a species that is its precursor on dilution into H$_2$O is present in the nonaqueous solutions. One explanation for this behavior is that the dithionite ion is much more dissociated to the sulfur dioxide radical anion (eq 1) in these

$$[S_2O_4]^{2-} \rightleftharpoons 2[SO_2]^- \tag{1}$$
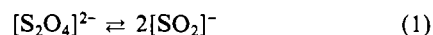
nonaqueous solvents than in H$_2$O. As noted above, the presence of small amounts of the sulfur dioxide radical anion in *aqueous* solutions of [S$_2$O$_4$]$^{2-}$ has been implicated from a variety of kinetic studies.[3–15] In addition, the EPR spectrum of the radical has been observed[3] under these conditions, making it possible to evaluate the equilibrium constant for the dissociation of dithionite to [SO$_2$]$^-$ (eq 1) via double integration of this spectrum. Under a variety of conditions, K_{eq} for eq 1 was found[3] to be (1.4 $\pm$ 0.4) $\times$ 10^{-6} mM, a value which confirms that the equilibrium in eq 1 lies far to the left in aqueous solution.

In fact, this equilibrium constant has also been estimated in nonaqueous solution from experiments on the reductive electrochemistry of sulfur dioxide in organic solvents. A wide range of values, albeit determined under different solvent and temperature conditions, have been reported for K_{eq} by using these voltammetric and coulometric methods. Thus, Bonnaterre and Cauquis found[27] a value of 0.01 mM for the dissociation in Me$_2$SO at 55 °C while Martin and Sawyer reported[28] a value of 41.7 mM for the same

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Table I. Values of K_{eq} for $[S_2O_4]^{2-} \rightleftharpoons 2[SO_2]^-$ in DMF, Me$_2$SO, and MeCN at Ambient Temperature

solvent[a]	init $[S_2O_4]^{2-}$ concn, mM	K_{eq}, mM
DMF	0.93	30.7
(36.7)	9.32	204
	21.1	44.0
	26.4	45.3
	93.2	49.8
Me$_2$SO	1.30	10.3
(46.6)	13.0	15.3
	130	8.2
MeCN	1.44	20.4
(36.2)	11.2	10.7
	14.4	8.1
	112	3.8
	144	3.5
H$_2$O[b]		1.4×10^{-6}
(78.5)		

[a] Dielectric constant in parentheses. From: Schneider, R. L. *Eastman Org. Chem. Bull.* **1975**, *47*, 1. [b] From ref 3.

Table II. Effect of the Aqueous Content of DMF on the Equilibrium Constant for $[S_2O_4]^{2-} \rightleftharpoons 2[SO_2]^-$ at Ambient Temperature and $[S_2O_4^{2-}]_{init} = 1.97$ mM

% H$_2$O[a]	UV/vis[b]	[H$_2$O], M	K_{eq}, mM
0.0	332 (2130)	0.000	42.4
1.0	332 (2120)	0.056	13.9
2.7	330 (3090)	0.149	2.75
4.3	330 (3990)	0.243	1.03
10.9	322 (5840)	0.616	0.068
20.8	313 (6300)	1.18	ca. 10^{-4}
100	313 (6400)	55.5	

[a] By volume. [b] Peak positions in nanometers with molar absorptivities in parentheses.

reaction in DMF at ambient temperature. More recently, Gardner and co-workers described[30b] the effect of counterion variation on the dissociation of dithionite, reporting a K_{eq} value of 4.3×10^{-5} mM in DMF in the presence of 0.1 M Li$^+$. The determination of the equilibrium constant in these studies was complicated by the fact that the electrochemically generated $[SO_2]^-$ also reacts with unreduced sulfur dioxide to yield the radical $[S_2O_4]^-$ (eq 2)

$$SO_2 + [SO_2]^- \rightleftharpoons [S_2O_4]^- \qquad (2)$$
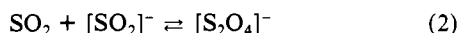
in addition to undergoing dimerization to dithionite (eq 1). This problem is difficult to avoid in reactions where SO$_2$ is the starting material, but it is not a factor in our system, where $[Et_4N]_2[S_2O_4]$ can be dissolved in the nonaqueous media in the complete absence of SO$_2$. We have therefore characterized this dissociation behavior of dithionite in organic solvents using EPR spectroscopy to confirm the presence of $[SO_2]^-$ and to *directly* determine the equilibrium constant for eq 1 in the absence of the effects of eq 2.

EPR spectra of solutions of $[Et_4N]_2[S_2O_4]$ in DMF, Me$_2$SO, and MeCN indeed exhibit a strong, symmetric resonance at $g = 2.006$, the position being independent of solvent within the accuracy of our measurements. This g value and the line width of the resonance (2.9 G) are almost identical with those reported[29] by Kastening and Gostisa-Mihelcic for $[SO_2]^-$, the latter value being particularly diagnostic in differentiating between the resonances due to the radicals $[SO_2]^-$ and $[S_2O_4]^-$. Thus, the presence of significant amounts of the sulfur dioxide radical anion in nonaqueous solutions of dithionite, postulated[25-30] on the basis of electrochemical experiments, is confirmed by these measurements. In addition, accurate quantitation of $[SO_2]^-$ could be carried out directly by double integration of its ambient-temperature solution spectra and, on the basis of simple stoichiometry, the equilibrium constant for eq 1 determined according to eq 3. These mea-

$$K_{eq} = [SO_2^-]^2/([S_2O_4^{2-}]_{init} - 0.5[SO_2^-]) \qquad (3)$$

surements were made as a function both of solvent and of initial $[Et_4N]_2[S_2O_4]$ concentration with the results presented in Table I. The K_{eq} values in DMF and Me$_2$SO are effectively independent of concentration, with the former average value (42.4 mM) in remarkably good agreement with that reported by Martin and Sawyer[28] (41.7 mM), considering the different methods of determination. Our average value of 11.3 mM for K_{eq} at ambient temperature (ca. 25 °C) in Me$_2$SO is not in good agreement with the value previously[27] reported in this solvent at 55 °C (0.01 mM), the discrepancy being much too large to be explained by the temperature differential. The lower value was obtained[27] from

analysis of voltammetric data, seemingly a more complex method, and therefore perhaps one more susceptible to error, than ours. In addition, our work (vide infra) indicates that traces of moisture in the solvent can dramatically lower the apparent K_{eq}, and this effect could also contribute to the difference.

The K_{eq} data for eq 1 in MeCN (Table I) indicate that the apparent equilibrium constant in this solvent, unlike those for DMF and Me$_2$SO, is dependent on the initial concentration of $[Et_4N]_2[S_2O_4]$, becoming larger as the concentration is decreased. Extrapolation of the data to infinite dilution would indicate that the actual equilibrium constant in MeCN is similar to that in DMF and larger than that in Me$_2$SO. The reasons for this deviation from ideality are not known, but one possible explanation could involve preferential stabilization of $[S_2O_4]^{2-}$ at high concentrations in MeCN due to ion pairing, a phenomenon that has been postulated[30b] to be important in determining the effect of electrolyte and solvent on the mechanism of electroreduction of SO$_2$.

These equilibrium measurements show that the visible spectra in nonaqueous solution in Figure 1 represent a mixture of $[S_2O_4]^{2-}$ and $[SO_2]^-$ (although the latter species is predominant). It is thus difficult to determine the spectrum of either of these species or to define whether the shoulders observed at 275 and 350 nm are due to the radical or its precursor. Martin and Sawyer[28] reported a peak at 350 nm with a maximum molar absorptivity of 4800 M^{-1} cm^{-1} for electrolyzed solutions containing relatively high initial concentrations of SO$_2$, which they assigned to $[S_2O_4]^{2-}$ in DMF. Our results, obtained at lower $[S_2O_4]^{2-}$ concentrations, are not inconsistent with this assignment, the shoulder at 350 nm possibly corresponding to their peak. We did not obtain solid-state electronic spectral data for our product, but we did consider the possibility that the isolated product was, in fact, $[Et_4N][SO_2]$ rather than $[Et_4N]_2[S_2O_4]$. The EPR spectrum of the solid indeed exhibited a resonance at $g = 2.007$, suggesting the presence of the radical anion, but quantitation by double integration showed that it corresponded to <1% of the anticipated spin concentration if the solid were $[Et_4N][SO_2]$. As noted above, the yellow color of the product may be due to the presence of small amounts of this latter salt in the predominant $[Et_4N]_2[S_2O_4]$.

The dielectric constant data included in Table I indicate that the equilibrium constant for dissociation of dithionite to $[SO_2]^-$ varies inversely with the solvent polarity. This phenomenon is also evident from electronic spectral studies as a function of the aqueous content in DMF. The data presented in Table II show that the major peak in the spectrum both increases in intensity (from a molar absorptivity of 2130 to 6400 M^{-1} cm^{-1} based on dithionite concentration) and shifts in position (from 332 to 313 nm) as the percentage of H$_2$O is increased, changes which indicate a decrease in the amount of $[SO_2]^-$ (i.e., a shift of eq 1 to the left). This hypothesis is substantiated by an EPR study of the integrated intensity of the $[SO_2]^-$ resonance under these conditions. As presented in Table II, K_{eq} decreases from 13.9 mM at 1% to ca. 10^{-4} mM at 21% H$_2$O, although the latter value was difficult to determine with any quantitative certainty due to the lack of intensity of the resonance when measured in a capillary tube. At the present time, we have no ready explanation for the dramatic increase in K_{eq} in pure nonaqueous media. However, in the solid state, the dithionite ion has a relatively long S–S bond, which seems

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to invite dissociation to $[SO_2]^-$. It may be, therefore, that the unusual situation occurs in *aqueous* media, where $[S_2O_4]^{2-}$ is the predominant species, and that H_2O and/or OH^- can somehow stabilize the dimeric S–S-bonded species. Anticipated studies of the temperature dependence of K_{eq} will result in enthalpy and entropy data, which should provide additional information about the solvation of the radical anion by organic solvents, another obvious possibility to explain the much increased dissociation in these media.

A form of dithionite which is soluble in nonaqueous media may be a useful reagent for many organic synthetic procedures that now involve $Na_2S_2O_4$. As we have shown, the use of solvents that contain limited amounts of (or no) H_2O will result in dramatically higher concentrations of $[SO_2]^-$, a situation that either could make a known "dithionite reduction" more facile or could result in the formation of new products. $[Et_4N]_2[S_2O_4]$ may also be an effective reductant for various transition-metal species, which are insoluble in water and therefore not susceptible to reduction by $Na_2S_2O_4$. Finally, the characterization of the dithionite/sulfur dioxide radical anion system may be relevant to the design and development of the lithium–sulfur dioxide battery,[31] the driving force for some[30] of the above work on the electroreduction of SO_2. In this context, additional knowledge of the nature of the products formed on reaction of SO_2 with mixtures of $[S_2O_4]^{2-}$ and $[SO_2]^-$, where both $[S_2O_4]^{-\,25-30}$ and $[S_3O_6]^{2-\,28}$ have been implicated, is particularly important.

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Synthesis and Redox Properties of the Unsymmetrical, Oxo-Bridged Complex [(bpy)₂(py)Ru^III ORu^III(H₂O)(bpy)₂]^4+

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The μ-oxo ions $[(bpy)_2(L)Ru^{III}ORu^{III}(py)(bpy)_2]^{4+}$ (bpy = 2,2′-bipyridine, py = pyridine, L = py or H_2O) have been prepared and their redox properties in water and acetonitrile investigated by electrochemical techniques. The bis(pyridine) μ-oxo ion is unstable toward ligand loss in acetonitrile or water, giving initially the solvated ions $[(bpy)_2(S)Ru^{III}ORu^{III}(py)(bpy)_2]^{4+}$ (S = CH_3CN, H_2O). In water the mixed aqua pyridine ion undergoes successive 1-electron oxidations to give successively the Ru(I-V)–Ru(III) and then the Ru(V)–Ru(III) ion $[(bpy)_2(O)Ru^VORu^{III}(py)(bpy)_2]^{4+}$. Comparisons with related aqua/oxo monomeric couples suggest that the $[(bpy)_2(py)Ru^{III}–O–]^+$ group acts as an electron-rich "substituent" and is important in allowing the aqua site to reach Ru(V) within the oxidative limits of the solvent. The Ru(V)–Ru(III) form of the μ-oxo ion acts as an effective electrocatalyst for the oxidation of Cl^- to Cl_2 at pH <4 and of Cl^- to OCl^- at pH >11.8 where the oxidations are thermodynamically spontaneous. Water is slowly oxidized to O_2 in acidic solutions containing the mixed aqua pyridine μ-oxo ion and a large excess of Ce(IV).

Introduction

From the results of pH-dependent electrochemical studies, the μ-oxo ion $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$ (bpy is 2,2′-bipyridine) undergoes a sequence of electron–proton losses, ultimately to reach $[(bpy)_2(O)Ru^VORu^V(O)(bpy)_2]^{4+}$. The Ru(V)–Ru(V) ion in turn oxidizes water to oxygen and provides a basis for the catalytic oxidation of water to oxygen via[2]
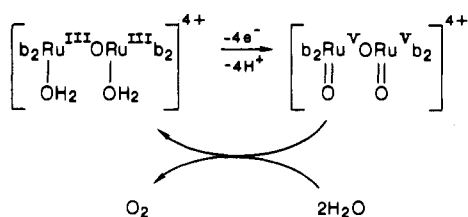

(b = bpy). The μ-oxo structure appears to play an important role in water oxidation in the following ways: (1) The $4e^-/4H^+$ requirement for water oxidation

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+$$
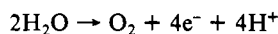
is met by the sequential loss of electrons and protons in the oxidation of the III,III ion to the V,V ion. (2) If there is an O–O

coupling requirement in the mechanism, it is met by the close proximity of the $Ru^V{=}O$ groups.

We report here the preparation of the unsymmetrical μ-oxo ion $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(py)(bpy)_2]^{4+}$ and a comparison of its redox properties with those of the diaqua ion. With the comparison we hoped to explore the implied importance of having two reactive sites in close proximity for water oxidation[3] and in the aqua pyridine dimer to investigate the $Ru^{III}–OH_2 \rightarrow Ru^V{=}O$ redox characteristics of the individual sites. A second basis for our interest in the unsymmetrical μ-oxo ion was the possibility of having access to a $Ru^V{=}O$ site in a chemically linked structure like
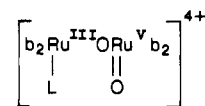
which opens the possibility of synthesizing a family of μ-oxo ions where systematic variations in L could lead to controlled perturbations at the $Ru^V{=}O$ site and possibly to the control of reactivity based on electronic, electrostatic, steric, or chiral effects.

Experimental Section

Materials. All reagents were reagent or ACS grade and used without purification. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. The water used in analytical measurements was Aldrich HPLC grade.

Preparations. $[(bpy)_2(OH_2)RuORu(OH_2)(bpy)_2](ClO_4)_4 \cdot 2H_2O$ (1) was prepared as previously described.[2c]

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