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Aromatic Sulfonation by SO_3^{2-} and the Reduction Potential of the Sulfite Radical: Oxidation of Sulfite by the Tetraammine(phenanthroline)ruthenium(III) Cation†

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The reaction of $[Ru(NH_3)_4(phen)]^{3+}$ (phen = 1,10-phenanthroline) with SO_3^{2-} has been studied in aqueous solution at 25 °C and $\mu = 0.1$ M ($NaCF_3SO_3$). Above pH 8 the reaction is $2[Ru(NH_3)_4(phen)]^{3+} + SO_3^{2-} + H_2O \rightarrow 2[Ru(NH_3)_4(phen)]^{2+} + SO_4^{2-} + 2H^+$. Under more acidic conditions an additional reaction occurs: $2[Ru(NH_3)_4(phen)]^{3+} + SO_3^{2-} \rightarrow [Ru(NH_3)_4(phen)]^{2+} + [Ru(NH_3)_4(phen\text{-}SO_3)]^+ + H^+$, where phen-$SO_3$ is 1,10-phenanthroline-4-sulfonate. The rate law is $-d[Ru(III)]/dt = [Ru(NH_3)_4(phen)^{3+}]\{2k_1[S(IV)]/(1 + [H^+]/K_a) + 2k_dQ_d[S(IV)]^2/(1 + K_a/[H^+])^2\}$ with $k_1 = (3.7 \pm 0.2) \times 10^4$ M^{-1} s^{-1}, $k_dQ_d = (3.2 \pm 0.5) \times 10^{-2}$ M^{-2} s^{-1}, and $K_a = (8.0 \pm 0.9) \times 10^{-8}$ M, where K_a is the acid dissociation constant of HSO_3^-. The product distribution follows a pH function quite different from the rate law, indicating that the rate-limiting step is the same for both sets of products. No sulfonation occurs in the presence of allyl alcohol, demonstrating that SO_3^- is an intermediate. In the proposed mechanism, the k_1 pathway represents electron transfer from SO_3^{2-} to Ru(III) to form SO_3^-, which can be further oxidized to SO_4^{2-}. The mechanism of sulfonation is unclear, possibly occurring by attack of HSO_3 or SO_3. The reaction $[Ru(NH_3)_4(phen)]^{2+} + SO_3^- \rightarrow [Ru(NH_3)_4(phen)]^{3+} + SO_3^{2-}$ was studied by pulse radiolysis, and its rate constant was found to be 1.0×10^8 M^{-1} s^{-1}. Combining this rate constant with k_1 and E_f for the $[Ru(NH_3)_4(phen)]^{3+/2+}$ couple leads to a value of $E_f = 0.72$ V for the SO_3^-/SO_3^{2-} redox couple. An effective self-exchange rate constant of 4 M^{-1} s^{-1} is derived for the SO_3^-/SO_3^{2-} redox couple by use of the Marcus cross-relationship, and this is shown to be consistent with a major portion of the barrier arising from the "umbrella" distortional mode.

Introduction

Little is known about the factors that control the electron-transfer rates of tetraatomic free radicals. Smaller radicals such as the iodine atom, O_2^-, ClO_2, and NO_2 have been studied in some detail in aqueous solution.[1-4] The kinetics of their electron-transfer reactions has been discussed in terms of the Marcus theory. The barrier for electron transfer is of course confined to solvent reorganization in the case of the iodine atom, but for diatomics and triatomics inner-sphere reorganization can be significant. The only larger main-group free radicals that have been discussed in this context are $N_2H_4^+$,[5] $ON(SO_3)_2^{2-}$,[6] and SO_3^-.[7] In the case of the $N_2H_4^{+/0}$ couple a self-exchange rate constant less than 0.3 M^{-1} s^{-1} was inferred, which implies a large inner-sphere barrier. In the case of the $ON(SO_3)_2^{2-/3-}$ couple a self-exchange rate constant of 9×10^{-6} M^{-1} s^{-1} was derived from the oxidation of $Fe(CN)_6^{4-}$; such a low rate constant implies a very large barrier, but a detailed analysis in terms of force constants and structural parameters has not yet been conducted. In the third case, the $SO_3^{-/2-}$ system, a self-exchange rate constant of 3×10^4 to 2×10^5 M^{-1} s^{-1} was reported, which implies a rather small inner-sphere barrier; however, the reduction potential of SO_3^- on which this estimate was based has recently been contested.[8] Thus, there are no examples of main-group free radicals larger than triatomics for which a detailed analysis of electron-transfer reactivity has been conducted.

In principle, the sulfite radical (SO_3^-) is an ideal candidate for extending the Marcus theory to reactions of larger inorganic free radicals. In preparing for this development, we have measured the infrared spectrum of matrix-isolated $CsSO_3$, which should resemble that of free SO_3^-, and we have conducted ab initio calculations of SO_3^- in order to predict its structure and to help in assigning the IR spectrum of $CsSO_3$.[9] Moreover, it has been shown that oxidation of SO_3^{2-} by a series of $M(CN)_x^{3-}$ complexes and by a series of $[M(phen)_3]^{3+}$ and IrX_6^{2-} complexes is consistent with the cross-relationship of the Marcus theory.[1,10] Further motivation for studying the SO_3^- radical is its environmental significance.

When we began our study of the SO_3^- radical, it was clear that an accurate value of E_f for the SO_3^-/SO_3^{2-} couple was required. All that was available was an estimate of its upper limit of 0.89 V.[11] In the belief that an accurate E_f value could be obtained by combining pulse-radiolysis data on SO_3^- and stopped-flow data on a related reaction of SO_3^{2-}, we conducted preliminary pulse-radiolysis screening experiments. These showed that the reactions of SO_3^- with $IrBr_6^{3-}$ and $IrCl_6^{3-}$ were too slow to measure. Accordingly we selected a stronger substitution-inert reducing agent: $[Ru(NH_3)_4(phen)]^{2+}$ (phen = 1,10-phenanthroline). This species proved to react with SO_3^- at a detectable rate, and so we conducted a complete study of the $SO_3^{2-}/[Ru(NH_3)_4(phen)]^{3+}$ system. During these studies, two highly discordant reports appeared regarding E_f for the SO_3^-/SO_3^{2-} couple: 0.63 and 0.76 V.[8,12] Our results allow us to support an intermediate value, to conduct a detailed analysis of the reactivity of the SO_3^- radical, and to report an unusual example of aromatic sulfonation.

Experimental Section

Reagents. Distilled deionized water was obtained from Corning MP-1 Mega-Pure and Barnstead Fi-Streem glass stills, and water for pulse radiolysis came from a Millipore Milli-Q three-stage water system. Sodium sulfite was of certified Fisher ACS grade. Trifluoromethanesulfonic acid from 3M was purified by distillation under reduced pressure. Sodium trifluoromethanesulfonate (sodium triflate) was prepared from neutralization of concentrated HCF_3SO_3 with sodium carbonate. After neutralization the solution was boiled to drive off excess CO_2 and the solid was recrystallized from hot water. 1,10-Phenanthroline monohydrate was of Aldrich gold label. The Br_2/CH_3CN solutions used for in situ oxidation of Ru(II) to Ru(III) were prepared by the method of Callahan et al.[13] Argon for the deaeration of solutions was purified by passing through a Catalyst Q1 column (Dow) and then through a tower containing the solvent. Phthalic acid from Eastman Kodak was recrystallized from hot water. Reagent grade malonic acid from Fisher Scientific was also recrystallized from hot water. All other materials of certified or reagent grade were used as such.

Preparation of Sulfite Solutions. Solutions of sulfite were prepared in water that was sparged with argon for at least 1 h prior to the addition of sodium sulfite. Prepared thus, these solutions were iodometrically

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found to be stable[14] over the entire period of their use. All the solutions for kinetic studies were freshly prepared and purged with argon for at least 60 min prior to their use. Standard syringe techniques were employed for transfer of solutions, and platinum syringe needles with Teflon hubs were used to avoid any contamination with iron.

Synthesis of Ruthenium Complexes. $[Ru(NH_3)_6]Cl_3$ was obtained from Alfa Chemicals. $[Ru(NH_3)_5Cl]Cl_2$ was prepared by a modification of Vogt's procedure.[15] A 0.85-g amount of $[Ru(NH_3)_6]Cl_3$ was dissolved in 9 mL of water. A 0.9-mL of volume of concentrated HCl was added to this, and the mixture was refluxed for 4 h. The yellow complex was recrystallized from 60 mL of warm 0.1 M HCl.

$[Ru(NH_3)_5H_2O](CF_3SO_3)_3$ was prepared from $[Ru(NH_3)_5Cl]Cl_2$ by a modification of Diamond and Taube's method.[16] A 1.0-g amount of $[Ru(NH_3)_5Cl]Cl_2$ was finely ground and added to 100 mL of deaerated water, and the mixture was stirred for 30 min. To this was added 6 mL of deaerated aqueous ammonia (Fisher Scientific) under argon. The mixture was stirred until it dissolved completely. A solution of 2.2 g of $Na_2S_2O_6 \cdot 2H_2O$ in 10 mL of deaerated H_2O was added to the reaction mixture. The mixture was stirred for 2 h. After refrigeration for 6–8 h, $[Ru(NH_3)_5(OH)](S_2O_6)$ separated as an unstable yellow solid. This was dissolved in a minimum amount of warm H_2O (≈40 °C), and an equal volume of 8 M HCF_3SO_3 was added. $[Ru(NH_3)_5(H_2O)](CF_3SO_3)_3$ separated as a white compound, which was washed with ether and dried under vacuum.

$[Ru(NH_3)_4(phen)](CF_3SO_3)_2$ was prepared by modification of the procedure used by Stanbury et al.[17] Under low-light conditions 0.20 g of $[Ru(NH_3)_5(H_2O)](CF_3SO_3)_3$ was added to 10 mL of deaerated methanol in the presence of a few pieces of Zn/Hg and the solution turned bright yellow, indicating the reduction of Ru(III) to Ru(II). To this, 0.61 g of 1,10-phenanthroline was added, and the mixture was allowed to react for 2 h under argon. The dark red solution of Ru(II) was then transferred into a separating funnel, and 5 mL of deaerated water was squirted onto the walls of the degassing flask to remove any adhering ruthenium complex. The unreacted phenanthroline was extracted with 6 × 10 mL portions of methylene chloride, and the aqueous layer was evaporated to dryness, leaving behind a shiny black solid. This was dissolved in a minimum amount of water, and an equal volume of 8 M HCF_3SO_3 was added. Refrigeration of this mixture yielded a mass of glossy black needles, which were washed with ether and dried under vacuum. Anal. Calcd for $Ru(NH_3)_4(C_{12}H_8N_2)(CF_3SO_3)_2$: C, 25.97; H, 3.11; N, 12.981; S, 9.90. Found: C, 26.12; H, 3.12; N, 12.92; S, 9.90. These results support an anhydrous complex, but the sample was subjected to rigorous drying prior to analysis. Monohydrate[17] and trihydrate[18] forms of this complex have also been reported. In the present paper it has been assumed that the complex is anhydrous, although if this assumption is erroneous the consequences should not be significant.

$[Ru(NH_3)_4(phen)]^{3+}$ was generated in situ by oxidation of Ru(II) to Ru(III) with Br_2/CH_3CN. A solution of Ru(II) in triflic acid (pH ≈ 3.0) was taken in a degassing flask, protected from light and deaerated with argon for 30 min. A 0.01 M Br_2/CH_3CN solution was added dropwise until the oxidation was near to completion. The solution was further purged with argon for 15–30 min. Excess addition of Br_2 destroyed the complex, and the typical yields of Ru(III) were maintained spectroscopically to be ≤97%.

$[Ru(NH_3)_4(phen\text{-}SO_3)]Cl$ was prepared by the reaction of $[Ru(NH_3)_4(phen)]^{3+}$ with S(IV). A 0.05-g amount of $[Ru(NH_3)_4(phen)](CF_3SO_3)_2$ was dissolved in 12.5 mL of deaerated HCF_3SO_3 (1 M) in a degassing flask, protected from light and was purged with argon for 30 min. Ru(III) was generated in situ by oxidation with Br_2/CH_3CN, and to this was added 0.04 g of $NaHSO_3$ dissolved in 2.5 mL of deaerated H_2O. This mixture (pH ≈ 4) was passed through a column of Dowex 1-X8 resin (20–50 mesh) in the chloride form, and the anions were exchanged to chloride ions. This solution was further loaded onto a column of Sephadex SP C-25 gel (40–120-μm bead size) in the H^+ form. A small pale pinkish band (assumed to be the disulfonated complex) was eluted with water and was discarded. Upon elution with 0.1 M HCl, a pink band of +1 charge separated. This band was collected, taken to dryness on a rotary evaporator, and used in determining its ^1H NMR and FTIR spectra. A concentrated solution of the (+1) band was further purified by gel filtration on a short column of Sephadex SP G-15-120 gel (40–120-μm particle size) with water as the eluent; this sample was used in the determination of E_f. In order to obtain an accurate value of ϵ_{max} in the UV–vis spectrum, the Sephadex SP C-25 gel was used in its Na^+ form; this modification was required because some decomposition occurred on the column when the H^+ form was used, and because the calculation of ϵ_{max} assumed quantitative conversion of $[Ru(NH_3)_4(phen)]^{3+}$ to a mixture of $[Ru(NH_3)_4(phen)]^{2+}$ and $[Ru(NH_3)_4(phen\text{-}SO_3)]^+$.

Analytical Methods. All UV–visible absorbance data were obtained by using Cary 210 and HP 8452 spectrophotometers with quartz cells of 1.00-cm path length. The resolution of the HP 8452 spectrophotometer was 2 nm. The NMR data were obtained on a Bruker 400-MHz NMR spectrometer with 5 mg of the compound, 0.5 mL of D_2O, and 1.0 mg of DSS (3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt) as internal reference. A small amount of Na_2SO_3 was added to the Ru(II) solutions to maintain the complexes in their reduced states. For the in situ NMR experiments, 5 mg of $[Ru(NH_3)_4(phen)](CF_3SO_3)_2$ was dissolved in 0.5 mL of D_2O in an Ar bubbling flask. Approximately 0.05 mL of 0.01 M Br_2/CH_3CN was then added dropwise to oxidize the sample. To this mixture was added 0.05 g of $NaHSO_3$, the pH of this solution being approximately 4.0. Samples were prepared in 5 mm i.d. NMR tubes with 0.50 mL of sample solutions with DSS as an internal reference. Cyclic voltammograms were recorded on a BAS 100 electrochemical analyzer with an Epson FX-85 printer. Solutions were thermostated at 25.0 ± 0.1 °C under N_2. The working and reference electrodes used were glassy carbon and Ag/AgCl, respectively. The reference electrode was calibrated against two calomel and Ag/AgCl electrodes and was found to have a potential of 0.202 V vs NHE. The medium employed was 0.1 mM triflic acid with $\mu = 0.1$ M ($NaCF_3SO_3$) and [Ru(II)] ≈ 1 mM. pH measurements were made at room temperature on a Corning Model 130 pH meter with a Ross combination electrode.

The ion chromatography experiments for anion analysis were performed on a Wescan Ion Chromatography System-II consisting of a Wescan Versa-Pump II, a Wescan Model 213 conductivity detector, and a Rheodyne Model 7125 syringe loading system with a 100-μL sample loop. To improve the sensitivity to dithionate, only the 3-cm Wescan Anion/R guard cartridge was used as a column. The chromatograms were recorded on an OmniScribe dual pen recorder. The eluent was 4.0 mM potassium phthalate at pH 4.0, and it was filtered through a 0.45-μm Nylon filter before passing through the column. Sulfite was masked from interfering with the analysis by forming an adduct with added formaldehyde. Calibration curves were obtained by measuring the peak heights for known concentrations of sulfate and dithionate, prepared by dissolving sodium sulfate and sodium dithionate in H_2O. The reactions were conducted on an argon bubbling line by injecting a solution of Ru(III) into a solution of S(IV) plus buffer.

The kinetic data were collected on a Hi-Tech Scientific Model SF-51 stopped-flow apparatus, equipped with a SU-40 spectrophotometer unit and C-400 circulating water bath. The reactions were performed under highly anaerobic conditions as the autoxidation of sulfite is well-known.[19-21] The thermostated water bath surrounding the solution and drive syringes was continuously deaerated with nitrogen and was maintained at 25.0 ± 0.1 °C. All the solutions were protected from light and studied by measuring the absorbance of the product at 471 nm with a 1.0-cm path length. The output from the SU-40 unit was digitized by an On Line Instruments System (OLIS) Model 3820 data collection system on a North Star Horizon computer, with data collection routines provided by OLIS. The reactions were conducted by mixing equal volumes of Ru(III) and S(IV)/buffer solutions. Pseudo-first-order rate constants were evaluated on the North Star computer with OLIS subroutines.

The pulse-radiolysis experiments were conducted at the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin. In these experiments, the solutions were subjected to either a 100- or 200-ns pulse of 3 MeV electrons, which were generated by a Van de Graaf accelerator. The reactions were conducted in a 1.8-cm cell at room temperature (≈ 22 °C), and they were monitored by observing the visible absorbance at 471 nm due to Ru(II). Dosimetry was performed with a 10 mM NaSCN solution that was saturated with N_2O. The absorbance at 472 nm attributable to $(SCN)_2^-$ ($\epsilon = 7580\ M^{-1}\ cm^{-1}$) was taken as a measure of the yield of OH + e_{aq}^-.[22] Solutions containing Ru(II) (protected from room light), $NaCF_3SO_3$, and SO_3^{2-}/HSO_3^- as a self-

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Table I. ^{1}H NMR Data for the Various Complexes[a]

compd	proton assignment 2	3	4	5	6	7	8	9
1,10-phenanthroline[b]	9.10 (dd) (4.5, 1.5)	7.51 (dd) (8.1, 4.5)	8.10 (dd) (8.1, 1.5)	7.64 (s)	7.64 (s)	8.10 (dd) (8.1, 1.5)	7.51 (dd) (8.1, 4.5)	9.10 (dd) (4.5, 1.5)
$[Ru(NH_3)_4(phen)]^{2+}$	9.41 (dd) (5.4, 0.86)	7.82 (dd) (8.1, 5.4)	8.36 (dd) (8.1, 1.1)	8.08 (s)	8.08 (s)	8.36 (dd) (8.1, 1.1)	7.82 (dd) (8.1, 5.4)	9.41 (dd) (5.4, 0.86)
$[Ru(NH_3)_4(phen\text{-}SO_3)]^+$	9.60 (d) (5.7)	8.11 (d) (5.7)		8.66 (d) (9.2)	8.20 (d) (9.1)	8.40 (d) (8.1)	7.87 (dd) (8.1, 5.6)	9.42 (d) (5.4)
4-CH_3-phen[b]	8.91 (d) (4.5)	7.28 (d) (4.5)		7.56 (d) (9.0)	7.75 (d) (9.0)	8.02 (dd) (8.1, 1.8)	7.44 (dd) (8.1, 4.5)	9.06 (dd) (4.5, 1.8)

[a] Each value of the proton assignment follows the format δ (ppm) (splitting pattern) (J, Hz). [b] From ref 56.

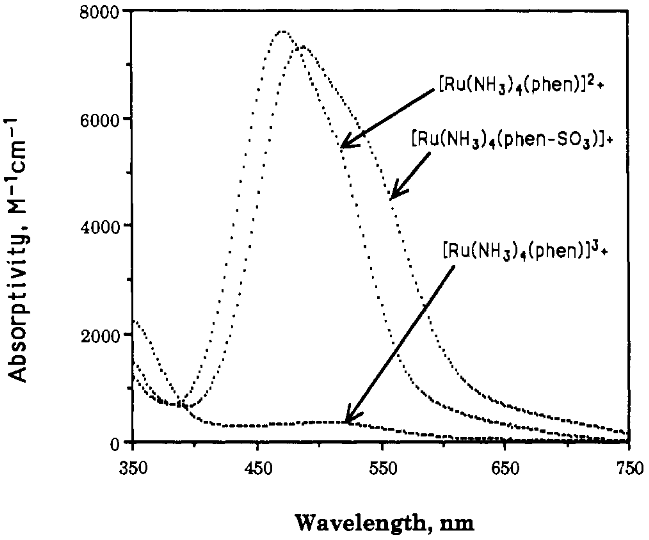


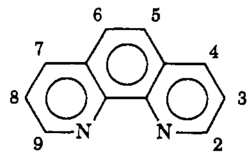
Figure 1. UV–vis spectra of the complexes: $[Ru(NH_3)_4(phen)]^{2+}$; $[Ru(NH_3)_4(phen\text{-}SO_3)]^+$; $[Ru(NH_3)_4(phen)]^{3+}$.

buffer were saturated with N_2O. A 400-nm UV cutoff filter (Schott GG400) was placed in the optical path to minimize photolysis by the monitoring light.

Numerical Methods. The Los Alamos nonlinear least-squares computer program was used to fit the various rate laws to the values of k_{obs} and to fit the product yield as a function of pH. The data were weighted as the inverse square of the dependent variable. Uncertainties are expressed as one standard deviation. Numerical integrations were performed with a local implementation of Hindmarsh and Byrne's subroutine EPISODE (Lawrence Livermore Laboratory, 1977). A Macintosh II computer was used for the integrations and the least-squares optimizations.

Results

Properties of the Compounds. The starting material, $[Ru(NH_3)_4(phen)]^{2+}$, has been described previously.[17] The aromatic ring system is shown as



The UV–vis spectrum of the complex is independent of pH over the range from pH 3 to 8.8 and is displayed in Figure 1. It has an absorbance maximum at 471 nm with a value for ϵ_{max} of 7.61 $\times$ 10^3 M^{-1} cm^{-1}, which is in excellent agreement with the literature value of 7.5 $\times$ 10^3 M^{-1} cm^{-1}.[17] The Ru(III)/Ru(II) couple displayed a reversible cyclic voltammogram when studied in a thermostated cell at 25 °C, μ = 0.1 M. E_f was found to be 0.516 $\pm$ 0.002 V vs NHE with $\Delta E_{p/p}$ of 59.3 $\pm$ 1.5 mV. These values correlated well with the literature values for E_f of 515[23] and 533 mV.[17] The aromatic region of the ^{1}H NMR spectrum, presented in Table I, comprised one singlet, two doublets, and one doublet of doublets. This is as expected for the spectrum of the free ligand when coordinated to a diamagnetic metal ion.

Table II. Ru(II) Product Yields as a Function of pH[a]

pH	shift in λ_{max}, nm	$[Ru(II)^{2+}]$/[total Ru(II)][b]	pH	shift in λ_{max}, nm	$[Ru(II)^{2+}]$/[total Ru(II)][b]
2.89	6	0.62	6.23	2	0.78
4.09	6	0.62	6.78	0	0.89
4.77	6	0.65	8.22	0	0.98
5.42	6	0.65	8.75	0	0.99
5.90	4	0.71			

[a] $Ru(II)^{2+}$ designates $[Ru(NH_3)_4(phen)]^{2+}$. $[Ru(III)]_0$ = 8.67 $\times$ 10^{-5} M, μ = 0.1 M ($NaCF_3SO_3$), $[Ru(II)]_0$ = 5.25 $\times$ 10^{-6} M, T = 25.0 $\pm$ 0.1 °C, $[S(IV)]_t$ = 1.00 $\times$ 10^{-3} M, and [buffer] = 2.5 $\times$ 10^{-2} M. Buffers: malonate (pH 2.89, 5.42, 5.90); succinate (pH 4.09); acetate (pH 4.77); cacodylate (pH 6.23, 6.78); borate (pH 8.22, 8.75). [b] Estimated uncertainty is $\pm$2% as explained in text.

The corresponding Ru(III) complex, $[Ru(NH_3)_4(phen)]^{3+}$, was generated in situ and was never isolated. Its UV–vis spectrum is quite weak in the visible region, as shown in Figure 1. As found for other heterocyclic Ru(III) ammines,[24] this species was unstable in solutions that were not acidic. Accordingly, it was prepared and maintained in acid solution, and when its reactions were examined in nonacidic media, these conditions were attained by mixing with a buffered S(IV) solution.

The novel compound $[Ru(NH_3)_4(phen\text{-}SO_3)]^+$ was isolated as the chloride salt but never in sufficient purity to obtain satisfactory elemental analysis. Apparently there was some decomposition during workup, as indicated by the appearance of spurious peaks in the ^{1}H NMR spectra. However, the following three observations support our assignment of the composition of the compound. (1) Its ion-exchange behavior implies that the complex has a charge of +1. (2) ^{1}H NMR spectroscopy of the compound generated in situ showed six doublets and one doublet of doublets in the aromatic region, as shown in Table I; these seven resonances require a monosubstituted phenanthroline. The splitting pattern requires the substitutent to be either at the 2- or 4-position, and the δ and J values preferentially support sulfonation at the 4-position. If substitution were to occur at the 2-position, there might be significant steric hinderance. (3) FTIR studies of the isolated salt revealed a characteristically strong absorption feature at 1030 cm^{-1} due to the S–O stretch.[25] Throughout the remainder of this paper it is assumed that the complex is indeed $[Ru(NH_3)_4(phen\text{-}SO_3)]^+$. Cyclic voltammetry studies showed that this complex gave reversible behavior with E_f = 0.586 $\pm$ 0.002 V vs NHE and $\Delta E_{p/p}$ = 62 $\pm$ 2 mV. As shown in Figure 1, the UV–vis spectrum of this complex exhibited a peak maximum at 488 nm, with ϵ_{max} = 7.31 $\times$ 10^3 M^{-1} cm^{-1}. This spectrum was pH-independent over the range from pH 3 to 8.8.

Stoichiometry. Visually, the reaction of excess [S(IV)] with $[Ru(NH_3)_4(phen)]^{3+}$ in acidic media was found to yield a Ru(II) product different from the starting Ru(II). This was confirmed

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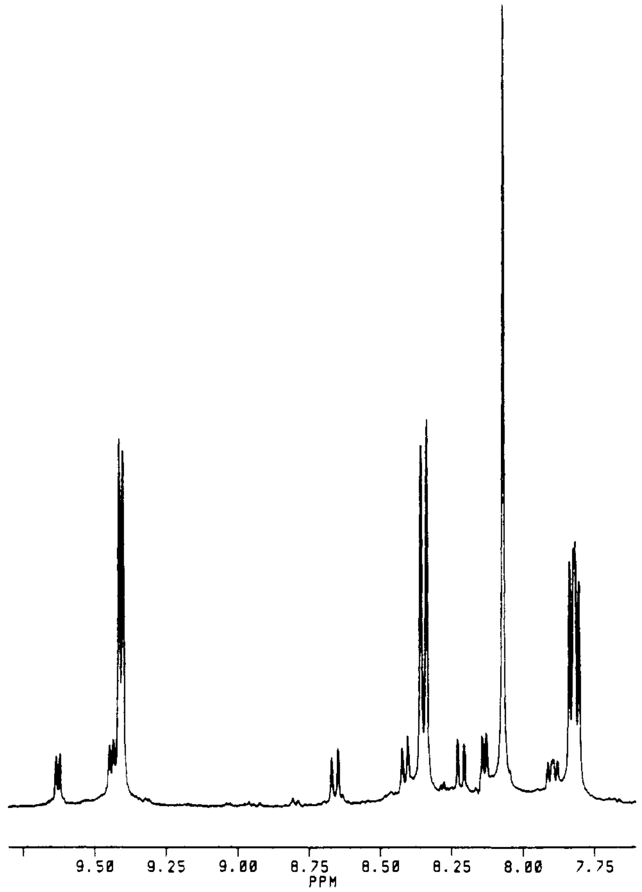

Figure 2. In situ ^{1}H NMR spectrum of the products from the reaction of S(IV) with $[Ru(NH_3)_4(phen)]^{3+}$. Chemical shifts are relative to DSS, pH ≈ 4, in D_2O.

by UV–vis spectra of the product solutions that showed a shift in the peak maximum from 472 to 478 nm with decreasing pH of the reaction, as shown in Table II. At higher pH (pH ≥ 8.0) the product was similar to the initial Ru(II), but at lower pH the spectrum shifted and became distorted, indicative of a product mixture.

The Ru(II) products were separated on a cation-exchange column. After the product solution was loaded onto the column a minor pale pinkish band was eluted with water. This showed an absorption maximum of 496 nm and is tentatively identified as the zerovalent disulfonated Ru(II) complex. The yield of this species was stoichiometrically negligible. Upon elution with 0.1 M NaCl, a dark pink band moved down the column with properties characteristic of a monovalent cation. This species exhibited UV–vis and ^{1}H NMR spectra characteristic of $[Ru(NH_3)_4(phen\text{-}SO_3)]^+$. With 0.2 M NaCl a red band moved down the column; this species was identified as $[Ru(NH_3)_4(phen)]^{2+}$ by its ^{1}H NMR and UV–vis spectra. An in situ ^{1}H NMR spectrum of the reaction mixture in D_2O, displayed in Figure 2, was found to be identical with the superimposed spectra of these two complexes.

The relative yields of the two Ru(II) products were determined from the UV–vis spectra of the product mixtures. Absorbances were measured at 556 and 446 nm, where the differences between the spectra of the two Ru(II) complexes are minimum and maximum, respectively. The composition of the product mixture was determined from the relationships

$$A_{446} = \epsilon_1[Ru(NH_3)_4(phen\text{-}SO_3{}^+] + \epsilon_2[Ru(NH_3)_4(phen)^{2+}] \quad (1)$$

$$A_{556} = \epsilon_3[Ru(NH_3)_4(phen\text{-}SO_3{}^+] + \epsilon_4[Ru(NH_3)_4(phen)^{2+}] \quad (2)$$

where $\epsilon_1 = 3.87 \times 10^3$ and $\epsilon_3 = 4.61 \times 10^3$ M^{-1} cm^{-1} refer to $[Ru(NH_3)_4(phen\text{-}SO_3)]^+$ at 446 and 556 nm, while $\epsilon_2 = 5.84 \times 10^3$ and $\epsilon_4 = 2.09 \times 10^3$ M^{-1} cm^{-1} correspond to $[Ru(NH_3)_4(phen)]^{2+}$ at the same wavelengths. The simultaneous eqs 1 and 2 were solved for the unknown concentrations of the two Ru(II) products. The fractional yields of the two products as a function of pH are shown in Table II. An estimate of the uncertainties in these results (±2%) was obtained by conducting similar calculations with other pairs of wavelengths. The maximum yield of $[Ru(NH_3)_4(phen\text{-}SO_3]^+$ was 36% and obtained at pH 2.89. Integration of the peaks in the in situ ^{1}H NMR spectrum obtained at pH ≈ 4 gave a product ratio quite similar to that derived from the UV–vis spectra.

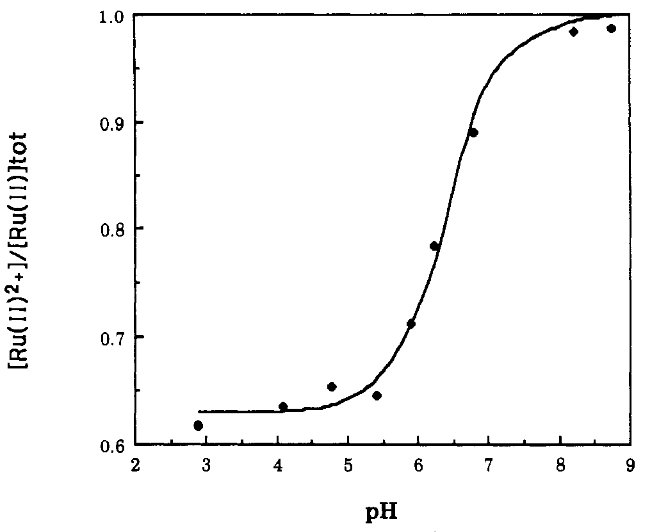

Figure 3. Relative yield of $[Ru(NH_3)_4(phen)]^{2+}$ as a function of pH. Data are from Table III. The solid line is calculated from eq 3 with fitted parameters as specified in the text.

The fractional yield of $[Ru(NH_3)_4(phen)]^{2+}$ was found to fit the equation

$$\frac{[Ru(II)^{2+}]}{[total\ Ru(II)]} = \frac{A + (1 + B/2)[H^+]}{A + (1 + B)[H^+]} \quad (3)$$

where A and B were $(1.42 \pm 0.25) \times 10^{-6}$ M and 2.86 ± 0.24, respectively. Here $[Ru(II)^{2+}]$ represents the yield of $[Ru(NH_3)_4(phen)]^{2+}$, while [total Ru(II)] is the sum of the two products. Observed and calculated values of $[Ru(II)^{2+}]/[total\ Ru(II)]$ from this fit are illustrated in Figure 3. The uncertainties indicated above for A and B represent the scatter in the data; because of potential systematic errors in the ϵ values, the actual uncertainty in B could be substantially larger. However, a finite value for B is required by the yield of $SO_4{}^{2-}$ in acidic media as described below.

The stoichiometry of the oxidation of S(IV) by Ru(III) was also examined by anion chromatography measurements. In order to avoid saturating the column, it was necessary to conduct these experiments at low ionic strength, and thus they are not strictly comparable with the spectrophotometric experiments described above. With excess S(IV), analyses for sulfate and dithionate were made by assuming these two were the only possible anionic sulfur-containing oxidation products. These studies revealed that sulfate was the major oxidation product, with no detectable yield of dithionate even at lower pH where it is a significant product of sulfite radical recombination.[26,27] Our detection limit for $S_2O_6{}^{2-}$ was 1.8×10^{-6} M. The quantitative results of these experiments are presented in Table III, which shows that at pH 8.5 the stoichiometry can be represented as

$$2[Ru(NH_3)_4(phen)]^{3+} + SO_3{}^{2-} + H_2O \rightarrow 2[Ru(NH_3)_4(phen)]^{2+} + SO_4{}^{2-} + 2H^+ \quad (4)$$

At lower pH the yield of $SO_4{}^{2-}$ is diminished (but still significant) and $[Ru(NH_3)_4(phen\text{-}SO_3)]^+$ becomes a significant product.

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Table III. Yield of Sulfate in the Reaction of $[Ru(NH_3)_4(phen)]^{3+}$ with S(IV)[a]

pH	$[Ru(III)]_0$, μM	$[SO_4^{2-}]_{calc}$, μM[b]	$[SO_4^{2-}]_{obs}$, μM[c]
5.08	91.1	16.2 ± 1.6	15.8 ± 0.8
6.54	83.4	32.7 ± 1.5	35.2 ± 1.8
8.50	87.4	41.8 ± 2.9	44.0 ± 2.2

[a] $\mu = 6.50 \times 10^{-3}$ M (sodium triflate), $[Ru(II)]_0 \approx 4.6 \times 10^{-6}$ M, $T = 25.0 \pm 0.1$ °C, $[S(IV)]_t = 5.00 \times 10^{-4}$ M, and [buffer] = 5 mM. Buffers: acetate (pH 5.08); cacodylate (pH 6.54); borate (pH 8.50). [b] As predicted by eq 6 from the spectrophotometric yield of the two Ru(II) products. [c] Determined by ion chromatography.

Table IV. pH Dependence of the Kinetics[a]

	k_{obs}, s^{-1}			k_{obs}, s^{-1}	
pH	exp	calc	pH	exp	calc
4.09	9.16×10^{-2}	7.26×10^{-2}	6.23	11.0	8.76
4.77	3.93×10^{-1}	3.44×10^{-1}	6.78	28.1	23.8
5.42	1.22	1.51	8.22	55.5	68.3
5.90	4.57	4.37	8.75	72.1	71.8

[a] $[Ru(III)]_0 = 7.91 \times 10^{-5}$ M, $[Ru(II)]_0 = 1.03 \times 10^{-5}$ M, $[S(IV)]_t = 1.00 \times 10^{-3}$ M, $\mu = 0.1$ M (sodium triflate), $T = 25.0 \pm 0.1$ °C, and [buffer] = 2.5×10^{-2} M. Buffers: succinate (pH 4.09); malonate (pH 5.42, 5.90); acetate (pH 4.77); cacodylate (pH 6.23, 6.78); borate (pH 8.22, 8.75).

These results can be explained if reaction 4 occurs in parallel with the reaction

$$2[Ru(NH_3)_4(phen)]^{3+} + SO_3^{2-} \rightarrow [Ru(NH_3)_4(phen)]^{2+} + [Ru(NH_3)_4(phen\text{-}SO_3)]^{+} + H^{+} \quad (5)$$

with their relative contributions being pH-dependent. Mass conservation requires that

$$[SO_4^{2-}] = \{[Ru(NH_3)_4(phen)^{2+}] - [Ru(NH_3)_4(phen\text{-}SO_3)^{+}]\}/2 \quad (6)$$

and as shown in Table III this condition is satisfied by the data. A blank experiment verified that sulfonation is intrinsic to the redox reaction; i.e., in a mixture of $[Ru(NH_3)_4(phen)]^{2+}$ with S(IV) at pH 4.1 no sulfonation occurred, even after several hours.

Kinetics. All the reactions were studied under pseudo-first-order conditions with [S(IV)] ≫ [Ru(III)] by observing the formation of products. Kinetic data were analyzed by constructing plots of log $(A_\infty - A_t)$ vs time. The pseudo-first-order rate constants, k_{obs}, defined by the equation

$$d[Ru(II)]/dt = k_{obs}[Ru(III)] \quad (7)$$

were obtained from the slopes of these plots. These plots showed slight curvature toward lower rate constants at long times, the effect being most significant at higher pH. This curvature was attributed to disproportionation of the Ru(III) complex, as noted above; consequently, rate constants were determined from the first half-life, over which the semilog plots were linear. Addition of 1×10^{-5} M EDTA or 2×10^{-5} M $Cu(ClO_4)_2$ had no perceptible effect on the kinetics. On the other hand, the reactions were highly sensitive to contamination by atmospheric dioxygen. Such contamination led to apparent induction periods, with the subsequent formation of Ru(II) occuring more slowly than for rigorously deoxygenated solutions. This sensitivity to O_2 is entirely consistent with other reports of reactions of S(IV) with metal complexes, and it is attributed to a chain autoxidation of S(IV) induced by the Ru(III).[11,28]

The oxidation of [S(IV)] by Ru(III) was studied over the pH range from 4.09 to 8.75 at a constant S(IV) concentration. The pH-dependent data presented in Table IV and Figure 4 show an inverse acid dependence that reaches a limiting regime at high pH. The dependence on [S(IV)] was studied at pH 8.75, 4.77, and 2.89, and the data are presented in Table V. At pH 8.75 the reaction showed a clear first-order dependence on [S(IV)]; the small intercept in a plot of k_{obs} vs [S(IV)] at 9.13 s^{-1} is attributed to the slow decomposition of Ru(III) in alkaline medium. The order in [S(IV)] was also found to be unity at pH 4.77, and there was no evidence of a [S(IV)]-independent term. At pH 2.89 the order with respect to [S(IV)] was greater than unity; as shown in Figure 5 a plot of k_{obs}/[S(IV)] vs [S(IV)] was linear with a finite intercept, indicating a rate law with terms first and second order in [S(IV)].

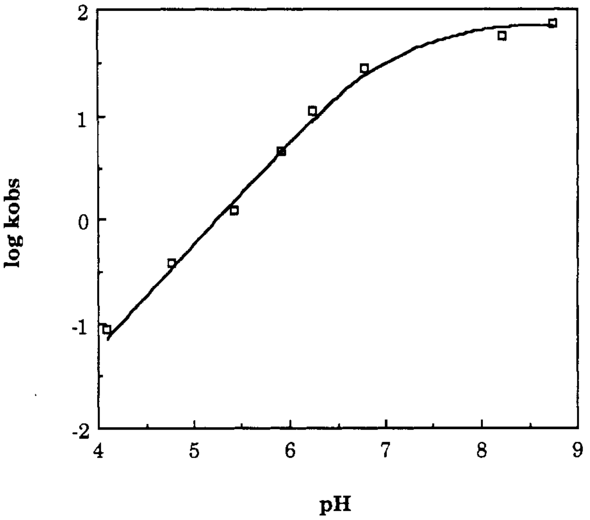

Figure 4. pH dependence of the kinetics of oxidation of S(IV) by $[Ru(NH_3)_4(phen)]^{3+}$ at 1.0 mM S(IV). Data are as in Table IV. The solid line is as calculated from the fit to eq 8 with constants as noted in the text.

Table V. Dependence of the Kinetics on [S(IV)][a]

		k_{obs}, s^{-1}	
pH	$[S(IV)]_t$, mM	exp	calc
8.75	0.25	22.3	18.0
8.75	0.50	44.0	35.9
8.75	1.00	72.1	71.8
8.75	1.50	112	108
8.75	2.00	133	144
8.75	2.50	171	180
4.77[b]	1.00	0.276[c]	
4.77[b]	1.25	0.400[c]	
4.77[b]	2.50	0.712[c]	
4.77[b]	5.00	1.43[c]	
2.89	3.00	0.0158	0.0194
2.89	3.50	0.0207	0.0238
2.89	6.00	0.050	0.050
2.89	8.25	0.081	0.081
2.89	10.5	0.130	0.119
2.89	13.2	0.212	0.172

[a] $[Ru(III)]_0 = 7.91 \times 10^{-5}$ M, $[Ru(II)]_0 = 1.03 \times 10^{-5}$ M, $\mu = 0.1$ M ($NaCF_3SO_3$), $T = 25.0 \pm 0.1$ °C, and [buffer] = 2.5×10^{-2} M. Buffers: malonate (pH 2.89); acetate (pH 4.77); borate (pH 8.75). [b] $[Ru(III)]_0 = 8.66 \times 10^{-5}$ M, $[Ru(II)]_0 = 1.63 \times 10^{-5}$ M, $\mu = 0.15$ M ($NaCF_3SO_3$), and buffer = 0.1 M acetate. [c] These were not included in the least-squares calculation because of the differing ionic strength.

The values of k_{obs} illustrating the pH dependence and the dependence on [S(IV)] at pH 2.89 and 8.75 were fit by the equation

$$k_{obs} = \frac{2k_1[S(IV)]_t}{1 + [H^+]/K_a} + \frac{2k_dQ_d[S(IV)]_t^2}{(1 + (K_a/[H^+]))^2} \quad (8)$$

where we have defined $[H^+]$ as 10^{-pH}. The fit resulted in values of $(7.34 \pm 0.47) \times 10^4$ M^{-1} s^{-1}, $(6.4 \pm 1.0) \times 10^{-2}$ M^{-2} s^{-1}, and $(8.0 \pm 0.8) \times 10^{-8}$ M for $2k_1$, $2k_dQ_d$, and K_a, respectively, and the values of k_{calc} presented in the various tables correspond to this function. The data at pH 4.77 showing the [S(IV)] dependence were omitted from the fit because the ionic strength differed

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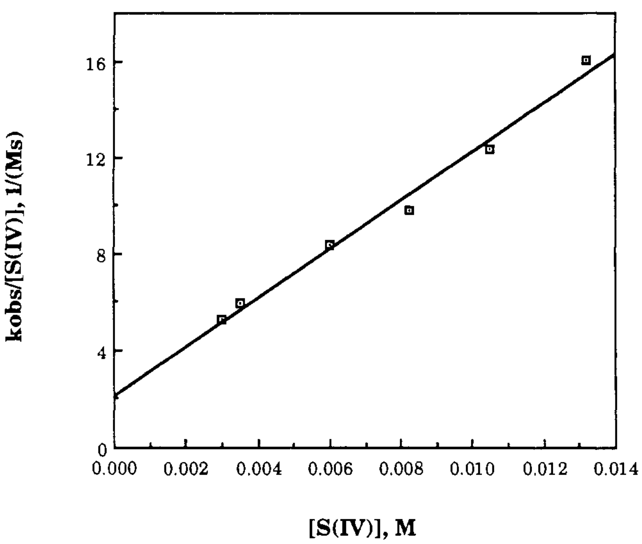

Figure 5. S(IV) dependence of the kinetics of oxidation of S(IV) by $[Ru(NH_3)_4(phen)]^{3+}$ at pH 2.89. A plot of $k_{obs}/[S(IV)]$ as a function of [S(IV)] is shown, illustrating a rate law having terms first and second order in [S(IV)]. Data are as in Table V.

Table VI. Kinetic Inhibition by [Ru(II)]

pH	k_{obs}, s^{-1}	$[Ru(II)]_0$, mM	pH	k_{obs}, s^{-1}	$[Ru(II)]_0$, mM
8.75	23.1	0.181	4.77	0.155	0.051
5.90	1.33	0.181	8.75	30.4	0.027
4.77	0.145	0.181	5.90	1.41	0.027
8.75	27.6	0.103	4.77	0.171	0.027
5.90	1.32	0.103	8.75	44.6	0.0103
4.77	0.152	0.103	5.90	1.79	0.0103
8.75	24.2	0.051	4.77	0.214	0.0103
5.90	1.26	0.051			

[a] $[Ru(III)]_0 = 1.41 \times 10^{-5}$ M, $[S(IV)]_t = 1.00 \times 10^{-3}$ M, $\mu = 0.1$ M ($NaCF_3SO_3$), $T = 25.0 \pm 0.1$ °C, and [buffer] $= 2.5 \times 10^{-2}$ M. Buffers: acetate (pH 4.77); malonate (pH 5.90); borate (pH 8.75).

from the other experiments. Our derived value of 7.10 for pK_a (the acid dissociation constant of HSO_3^-) compares well with the literature value of 6.91 (this is a Brønsted constant including both activity and concentration terms and was obtained by adding 0.11 to the reported value of 6.8[29]). Under our experimental conditions no evidence could be discerned for a pathway first-order in $[HSO_3^-]$.

An attempt was made to fit the data with a version of eq 8 modified by including the term $k'/[H^+]$ so as to account for the intercept in the pH 8.75 data. This resulted in the following values: $2k_1 = (6.59 \pm 0.59) \times 10^4$ M^{-1} s^{-1}, $2k_dQ_d = (6.4 \pm 1.0) \times 10^{-2}$ M^{-2} s^{-1}, $K_a = (8.9 \pm 1.1) \times 10^{-8}$ M, and $k' = (1.28 \pm 0.69) \times 10^{-8}$ M s^{-1}. Due to the high uncertainty in k_4, this modified rate law was rejected in favor of eq 8.

Addition of $[Ru(NH_3)_4(phen)]^{2+}$ mildly suppressed the reaction rates, and at higher pH the semilog plots were more linear than in its absence. Unfortunately, because of the strong absorption by Ru(II), it was not possible to attain very high concentrations of Ru(II). These results are presented in Table VI. Essentially identical results were obtained when Ru(III) was generated by oxidation of Ru(II) with Ce(IV) instead of Br_2.

Effect of Allyl Alcohol. The reaction was studied at pH 4.75 with 1.0 mM S(IV) in the presence of added 0.1 M allyl alcohol, a known scavenger of the sulfite radical.[30] This addition did not interfere with the kinetics of the reaction. The pseudo-first-order rate constant in the presence of allyl alcohol was 0.39 s^{-1}, which was essentially the same as in its absence (0.41 s^{-1}). On the other hand, addition of allyl alcohol did have a profound effect on the product ratio. The product solution exhibited a λ_{max} of 472 nm, resembling the unsulfonated Ru(II). In the absence of allyl alcohol under similar conditions the product solution showed a maximum absorbance at 478 nm. A detailed analysis according to eq 1 and 2 showed that the product ratio of $[Ru(NH_3)_4(phen)^{2+}]/[Ru(NH_3)_4(phen\text{-}SO_3)^+]$ in the presence of allyl alcohol was 6.9 whereas in its absence the ratio was 1.9.

Pulse Radiolysis. Pulse radiolysis of N_2O-saturated solutions of S(IV) leads to generation of SO_3^- by a well-documented sequence of reactions.[12,31] The reaction of $[Ru(NH_3)_4(phen)]^{2+}$ with SO_3^- was investigated by irradiating mixtures of Ru(II), S(IV), and N_2O, where the Ru(II) concentration was held in large excess over that of the SO_3^-. All reactions were performed at ≈22 °C with $\mu = 0.1$ M ($NaCF_3SO_3$). Under these conditions the reactions displayed good psuedo-first-order kinetics for the loss of $[Ru(NH_3)_4(phen)]^{2+}$. However, the total absorbance change was typically only about 60% of that expected from the dosimetry for the reaction

$$[Ru(NH_3)_4(phen)]^{2+} + SO_3^- \rightarrow [Ru(NH_3)_4(phen)]^{3+} + SO_3^{2-} \quad k_{-1} \quad (9)$$

Consequently, it is inferred that the reaction

$$[Ru(NH_3)_4(phen)]^{3+} + SO_3^- \rightarrow [Ru(NH_3)_4(phen)]^{2+} + SO_3 \quad k_2 \quad (10)$$

is also occurring, although to a lesser degree. Reaction 10 specifies the product as $[Ru(NH_3)_4(phen)]^{2+}$, but it is possible that both $[Ru(NH_3)_4(phen)]^{2+}$ and $[Ru(NH_3)_4(phen\text{-}SO_3)]^+$ are formed. Moreover, it is possible that in acidic media the radical exists in its protonated form. In one series of experiments the pH was held at 3.0, 3.6, 6.4, and 7.5, with $[Ru(II)] = 8 \times 10^{-5}$ M, $[S(IV)] = 0.01$ M, and $[SO_3^-]_0 \approx 5 \times 10^{-6}$ M; the pseudo-first-order rate constants were pH-independent. In another series of experiments at pH 3.0 the concentration of Ru(II) was varied from 6×10^{-5} to 1.36×10^{-4} M; these results showed a first-order dependence of k_{obs} on [Ru(II)], with the apparent second-order rate constant having a value of $(1.8 \pm 0.3) \times 10^8$ M^{-1} s^{-1}. The integrated rate law arising from reactions 9 and 10 does not appear to have an analytical solution. Numerical integration, however, shows that the observed behavior (half-life and overall absorbance change) is consistent with values of 1.0×10^8 M^{-1} s^{-1} for k_{-1} and 1.0×10^9 M^{-1} s^{-1} for k_2. Because of the considerable imprecision in the ratio of $\Delta[Ru(II)]/\Delta[SO_3^-]$, the value of k_2 could be in error by as much as a factor of 2.

Discussion

Oxidation of S(IV) by $[Ru(NH_3)_4(phen)]^{3+}$ leads to two sets of products, depending on pH. The rate law and the effects of allyl alcohol show that the two sets of products derive from a common transition state: pH-dependent events occurring after the transition state determine the reaction stoichiometry. Our understanding of the reaction mechanism at high pH, where SO_4^{2-} is the product, is relatively unambiguous and will be presented first. At low pH, where coordinated phenanthroline becomes sulfonated, the mechanism is less clear.

Reaction Mechanism Leading to SO_4^{2-}. Formation of SO_4^{2-} during the oxidation of S(IV) by substitution-inert oxidants is a rather common process. Scheme I is the proposed mechanism, and it is essentially the same as reported in other studies.[11,28,32,33] Protonation of SO_3^{2-} as in reaction 11 is well-established and rapid and is required by the rate law for oxidation of S(IV) by Ru(III). The second protonation, to form SO_2, is also well-established,[29] but because its pK_a is 1.6, it is not a significant species under the conditions of this study. The other intrinsic reaction of S(IV), formation of $S_2O_5^{2-}$ as in reaction 15, is also reasonably well-established,[34] and it is invoked to explain the term in the rate law

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Scheme I

$$HSO_3^- \rightleftarrows H^+ + SO_3^{2-} \qquad K_a \qquad (11)$$

$$[Ru(NH_3)_4(phen)]^{3+} + SO_3^{2-} \rightleftarrows [Ru(NH_3)_4(phen)]^{2+} + SO_3^- \qquad k_1, k_{-1} \qquad (12)$$

$$[Ru(NH_3)_4(phen)]^{3+} + SO_3^- \rightarrow [Ru(NH_3)_4(phen)]^{2+} + SO_3 \qquad k_2 \qquad (13)$$

$$SO_3 + H_2O \rightarrow SO_4^{2-} + 2H^+ \qquad k_{hyd} \qquad (14)$$

$$2HSO_3^- \rightleftarrows S_2O_5^{2-} + H_2O \qquad Q_d \qquad (15)$$

$$[Ru(NH_3)_4(phen)]^{3+} + S_2O_5^{2-} \rightarrow [Ru(NH_3)_4(phen)]^{2+} + SO_2 + SO_3^- \qquad k_d \qquad (16)$$

second order in [S(IV)]. The forward steps in reactions 12 and 16 represent the two rate-limiting steps corresponding to the two terms in the rate law. The reverse step in reaction 12 is included to accommodate the pulse-radiolysis data. Redox reaction 13 is the path by which SO_3^- is consumed. Hydrolysis of SO_3 as in reaction 14 is of course rapid and irreversible.

Scheme I is consistent with rate law 8 under conditions where the reverse reaction, k_{-1}, can be neglected and where the steady-state approximation applies to the concentration of SO_3^-. Under this interpretation the rate constants in rate law 8 are identified with the corresponding reactions in Scheme I. In summary, the following values have been determined: $k_1 = 3.7 \times 10^4$ M^{-1} s^{-1}, $k_dQ_d = 3.2 \times 10^{-2}$ M^{-2} s^{-1}, $K_a = 8.0 \times 10^{-8}$ M, $k_{-1} = 1.0 \times 10^8$ M^{-1} s^{-1}, $k_2 = 1.0 \times 10^9$ M^{-1} s^{-1}.

The above mechanism and rate constants are consistent with the experiments in which mild kinetic inhibition by Ru(II) was observed. Thus, the experiments in Table VI at pH 8.75 were simulated by numerical integration. An excellent fit to the data was found for the first 3 half-lives when the value for A_∞ was adjusted appropriately.

One conceivable alternative mechanism would have the sulfite radical be consumed by self-reaction. The stoichiometry of this process has been investigated in a γ-radiolysis study by Eriksen, and it is pH-dependent.[27] In alkaline media the product is sulfate, and no dithionate is produced. The mechanism is proposed to be

$$2SO_3^- \rightarrow SO_3 + SO_3^{2-} \qquad (17)$$

$$SO_3 + H_2O \rightarrow SO_4^{2-} + 2H^+ \qquad (14)$$

Over the pH range 7.55 to 4.1 the yield of dithionate increases at the expense of sulfate. Eriksen depicts this as

$$2SO_3^- \rightarrow S_2O_6^{2-} \qquad (18)$$

From our ion chromatography experiments at pH 5.08 and 6.54, the ratio of dithionate to sulfate produced in the reaction of Ru(III) with S(IV) is much lower than the ratio calculated from Eriksen's data. Therefore, in the present case the sulfite radical cannot be consumed by self-reaction. At pH 8.5 the self-reaction of SO_3^- yields so little dithionate that our ion chromatography measurements do not distinguish between the possible fates of the radical. However, the mild kinetic inhibition by Ru(II) at this pH requires that the radical be consumed much more rapidly than would be the case if self-reaction were the mechanism.

The second term in the rate law for oxidation of S(IV) by Ru(III) is interpreted as a direct oxidation of $S_2O_5^{2-}$ by Ru(III). Terms second order in [S(IV)] have been reported for other reactions. For example, in the oxidation by Cr(VI), [S(IV)] also appeared in the denominator of the rate law, and so the mechanism was interpreted in terms of formation of a Cr(VI)/S(IV) complex.[35] In the case of oxidation by Mn^{III}CyDTA the second-order dependence on [S(IV)] was attributed to association of S(IV) with the complex.[36] Only one case, oxidation by $[Fe(phen)_3]^{3+}$, is directly comparable to the present study.[32] When the study of the $[Fe(phen)_3]^{3+}$ reaction was published, the magnitude of Q_d, the formation constant of $S_2O_5^{2-}$, was unknown; Q_d is now believed to have a value of 0.088 M^{-1} at μ = 1 M.[34] From this and the published rate constant[32] a value of 8.2×10^4 M^{-1} s^{-1} is calculated for the rate constant of oxidation of $S_2O_5^{2-}$ by $[Fe(phen)_3]^{3+}$. Likewise, a value of 0.36 M^{-1} s^{-1} is calculated for oxidation by $[Ru(NH_3)_4(phen)]^{3+}$. The faster of these two reactions has the stronger oxidant, and this trend suggests that the mechanism is indeed electron transfer, as indicated in reaction 16.

Reduction Potential of SO_3^-. A consequence of Scheme I is that it is possible to calculate the ratio k_1/k_{-1}. The ratio, 3.7×10^{-4}, is the equilibrium constant for reaction 12. From this and the E_f value for the $[Ru(NH_3)_4(phen)]^{3+/2+}$ couple (0.516 V) the reduction potential for the sulfite radical as in

$$SO_3^- + e^- \rightleftarrows SO_3^{2-} \quad E_f \qquad (19)$$

can be calculated: E_f = 0.72 V vs NHE. There have been various prior estimates of this parameter. The first of these was 1.1 V;[37] it is not clear how this result was obtained, but it is now clearly incorrect. The second estimate was that E_f was less than 0.89 V,[11] which is in agreement with all subsequent reports. A value of 0.63 V was reported by Huie and Neta on the basis of pulse-radiolysis studies in which an apparent electron-transfer equilibrium was established between SO_3^- and certain organic compounds.[12] This is the value that was selected in a recent review of free radical reduction potentials.[38] The present investigation suggests a potential source of error in such measurements: since SO_3^- can undergo oxidation as well as reduction, a reaction studied by pulse radiolysis may reach a steady state in which the rates of oxidation and reduction by SO_3^- are equal, rather than a genuine equilibrium. Recently, a value of 0.76 V was obtained by investigating the kinetics of the reaction of SO_3^{2-} with ClO_2;[8] the authors of this work present good arguments as to why the prior value of 0.63 is in error. On the other hand, we note that the reaction of ClO_2 with SO_3^{2-} apparently proceeds both by electron and atom transfer,[39] and thus there is reason to doubt the value of 0.76 V. We believe that the present result, 0.72 V, is the most reliable estimate of E_f for the $SO_3^{-/2-}$ couple.

Certain thermodynamic data can be derived from the above E_f value. Thus, by use of the NBS value of −486.5 kJ mol^{-1} for $\Delta_fG°$ of SO_3^{2-},[40] a value of −413 kJ mol^{-1} is derived for $\Delta_fG°$ of SO_3^-. The value of 0.07 V for the two-electron $S_2O_6^{2-}/(2SO_3^{2-})$ couple[41] leads to a value of −960 kJ mol^{-1} for $\Delta_fG°$ of $S_2O_6^{2-}$ and hence a value of 3×10^{-24} M for the dissociation constant of $S_2O_6^{2-}$ as in

$$S_2O_6^{2-} \rightleftarrows 2SO_3^- \qquad (20)$$

This result shows quantitatively that the bond in dithionate is much stronger than the bond in $S_2O_4^{2-}$ ($K_{diss} = 1 \times 10^{-9}$ M).[42] This difference in bond strength accounts for the much greater reactivity of $S_2O_4^{2-}$. A rationalization for the difference is that the unpaired electron in SO_3^- resides in a σ orbital whereas in SO_2^- it is in a π orbital. On the other hand, Atkins and Symons attribute the difference to the relative degrees of delocalization of the unpaired electrons.[43]

It is also of interest to calculate the reduction potential of SO_3 as in

$$SO_3 + e^- \rightleftarrows SO_3^- \qquad (21)$$

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Table VII. Cross-Exchange Kinetics Data

oxidant	k_{12}, $M^{-1}\,s^{-1}$	$E°$, V	k_{22}, $M^{-1}\,s^{-1}$	r, Å[r]	log k_{11}[s]
$[Ru(NH_3)_4(phen)]^{3+}$	3.7×10^4[a]	0.52[a]	1.2×10^7[k]	4.4	2.15
MnO_4^-	1.3×10^5[b]	0.56[f]	7.2×10^2[l]	3.5	10.26
$[Os(bpy)_3]^{3+}$	9.0×10^3[c]	0.79[c]	2.0×10^9[m]	6.8	−5.04
$*[Ru(bpy)_3]^{2+}$	3.0×10^5[c]	0.84[c]	1.0×10^8[n]	6.8	−0.65
$IrBr_6^{2-}$	3.2×10^5[d]	0.84[g]	2.0×10^8[g]	4.5	0.70
$IrCl_6^{2-}$	5.6×10^4[d]	0.89[h]	2.0×10^5[o]	4.4	1.39
$[Fe(bpy)_3]^{3+}$	2.1×10^8[d]	1.06[i]	5.0×10^8[p]	6.8	0.20
$[Fe(phen)_3]^{3+}$	4.6×10^6[e]	1.09[j]	5.0×10^8[q]	6.8	−2.31
$[Ru(bpy)_3]^{3+}$	2.2×10^9[c]	1.26[c]	4.0×10^8[q]	6.8	−0.27

[a] This work. [b] Reference 60. [c] Reference 59. [d] Reference 28. [e] Reference 32; μ = 1.0 M. [f] Reference 61. [g] Reference 1. [h] Reference 62. [i] Reference 63, page 118. [j] Reference 63. [k] Reference 18. [l] Reference 64. [m] Reference 65. [n] Reference 66. [o] Reference 67. [p] Reference 68. [q] Reference 69. [r] Estimated. [s] Calculated from eq 29.

Because SO_3 is rapidly hydrolyzed, there is no accurate value of its $\Delta_f G°$. One estimate, $\Delta_f G° = -371.06$ kJ mol^{-1}, can be derived from the NBS data for gaseous SO_3 under the assumption that the hydration free energy of SO_3 is zero.[40] Guthrie estimates that the free energy of hydration is -34 ± 13 kJ mol^{-1},[44] which leads to a value of −405 kJ mol^{-1} for $\Delta_f G°$ of aqueous SO_3; however, it is difficult to understand why SO_3 should have such a favorable hydration free energy relative to other species such as SO_2. Under the assumption of zero hydration energy we obtain $E_f = 0.43$ V, while Guthrie's estimate leads to $E_f = 0.08$ V. Both calculations lead to E_f values that are lower than the reduction potential of SO_3^-, and therefore SO_3^- is unstable with respect to disproportionation to SO_3^{2-} and SO_3. This may explain why $S_2O_6^{2-}$ is not a significant product in the self-reaction of SO_3^- at high pH. A similar situation is found in the self-reaction of Hg^+.[45] The low value of E_f also explains why k_2 (the oxidation of SO_3^- by Ru(III)) is so large: the reaction has a large driving force. For this reason it is to be expected that in most chemical reactions where SO_3^- is generated by oxidation of SO_3^{2-}, the radical will undergo further oxidation rather than self-reaction.

The reduction potentials of SO_3^- and SO_3 derived above also permit a deeper analysis of the reaction of SO_3^{2-} with copper(III) tetraglycine ($Cu^{III}(H_{-3}G_4)^-$) reported by Anast and Margerum.[11] The reported mechanism was

$$Cu^{III}(H_{-3}G_4)^- + SO_3^{2-} \rightleftarrows Cu^{II}(H_{-3}G_4)^{2-} + SO_3^- \quad k_3, k_{-3} \tag{22}$$

$$Cu^{III}(H_{-3}G_4)^- + SO_3^- \rightleftarrows Cu^{II}(H_{-3}G_4)^{2-} + SO_3 \quad k_4, k_{-4} \tag{23}$$

$$SO_3 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad k_5 \tag{24}$$

with $k_3 = 3.7 \times 10^4$ $M^{-1}\,s^{-1}$, $k_4/k_{-3} = 1.66$, and $k_{-4}/k_5 = 177$ M^{-1}. The reduction potential of Cu(III) is 0.63 V. By the combining of this reduction potential with that for SO_3^- and the value for k_3, a value of 1.2×10^6 $M^{-1}\,s^{-1}$ is calculated for k_{-3}. Thus, k_4 has a value of 2×10^6 $M^{-1}\,s^{-1}$. The equilibrium constant of reaction 23 can be calculated from the relevant reduction potentials, and accordingly it lies between 2×10^3 and 2×10^9. From this we find that k_{-4} lies between 1×10^3 and 1×10^{-3}, and k_5 lies between 6 and 6×10^{-6} s^{-1}. This is an admittedly wide range of values for k_5, but it is important because there have been no prior estimates of this fundamental rate constant. On one hand, the rate constant must be greater than 6×10^{-6} s^{-1} because it is known that the hydrolysis of SO_3 is rapid. On the other hand, it is known that the gas-phase reaction of SO_3 with H_2O is some 5 orders of magnitude slower than the collision limit.[46] Further investigation of the hydrolysis of SO_3 is clearly warranted.

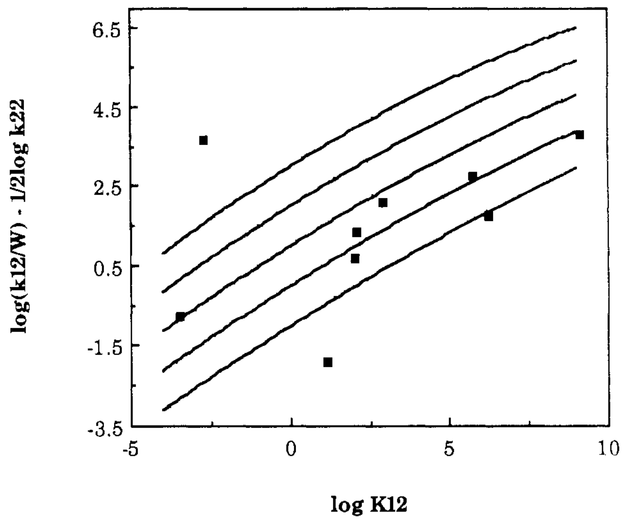

Figure 6. Plot of log $(k_{12}/W_{12}) - {}^1/_2 \log k_{22}$ as a function of log K_{12} for the various reactions in Table VII. The solid lines are drawn according to eq 29 under the approximation that k_{22} is 6×10^7 $M^{-1}\,s^{-1}$ and that SO_3^- and SO_3^{2-} have radii of 3.0 Å. The lines are drawn for $k_{11} = 10^6$, 10^4, 10^2, 10^0, and 10^{-2} $M^{-1}\,s^{-1}$ from the upper to lower curves respectively.

Marcus Theory. With a value of E_f for the SO_3^-/SO_3^{2-} couple in hand it is now possible to conduct an analysis of the rates of oxidation of SO_3^{2-} by outer-sphere oxidants. The relevant data are presented in Table VII. Excluded from this table are the data for oxidation of SO_3^{2-} by $Fe(CN)_6^{3-}$, $Mo(CN)_8^{3-}$, and $W(CN)_8^{3-}$. These reactions have been reported to conform to a LFER consistent with the Marcus theory,[10] but because the rate laws are first order in cation concentration, they are not strictly comparable with the reactions under consideration. The cross-relationship of the Marcus theory is a basis for understanding the data in Table VII. For the present purposes the following equations are used:[47]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \tag{25}$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln (k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT]} \tag{26}$$

$$W_{12} = \exp[(-w_{12} - w_{21} + w_{11} + w_{22})/2RT] \tag{27}$$

$$w_{ij} = (4.23 \times 10^{-8}Z_iZ_j)/(a(1 + 3.28 \times 10^7a(\mu^{1/2}))) \tag{28}$$

In these equations k_{12} represents the rate constant for electron transfer from SO_3^{2-} to the oxidant, k_{11} is the self-exchange rate constant for the SO_3^-/SO_3^{2-} couple, k_{22} is the self-exchange rate constant for the various complexes, and K_{12} is the equilibrium constant for the various electron-transfer reactions. Z in eq 26 is the collision rate, for which a value of 1×10^{12} $M^{-1}\,s^{-1}$ has been used. Z_i and Z_j in eq 28 are the ionic charges of the respective species, and R is the gas constant (kcal mol^{-1} K^{-1}). a is the center-to-center distance (cm) when the species are touching. It is necessary to include the f factor and the work terms in the present calculations because of the wide range of driving forces and various charge-types in the reactions considered.

Equation 25 can be rearranged as follows:

$$\log (k_{12}/W_{12}) - {}^1\!/_2 \log k_{22} = {}^1\!/_2 \log K_{12} + {}^1\!/_2 \log (k_{11}f_{12}) \tag{29}$$

Accordingly, Figure 6 is a plot of log $(k_{12}/W_{12}) - {}^1/_2 \log k_{22}$ as a function of log K_{12}. For the work term calculations it has been assumed that SO_3^- and SO_3^{2-} have radii of 3 Å. It is expected that the points will fall on a curve that reflects the value of k_{11} and the fact that f_{12} changes smoothly as a function of K_{12}. f_{12} is also a function of k_{22}, but, with the exception of MnO_4^-, these values change much less than do the values for K_{12}, and so the effect can be largely ignored. A series of curves has been overlaid in Figure 6; these curves show the theoretical dependence of equation 29 for selected values of k_{11} under the approximation that k_{22} is 6×10^7 $M^{-1}\,s^{-1}$ in the calculation of f_{12}. Inspection

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of Figure 6 shows that the data conform rather well to the theoretical curve for a value of log $k_{11} \approx 0$, with two exceptions. One exception is the reaction of MnO_4^-; this reaction is much faster than predicted, and correction for k_{22} would make the discrepancy even worse. Apparently the reaction of MnO_4^- proceeds by a mechanism more efficient than outer-sphere electron transfer, perhaps by formation of a transient bond between MnO_4^- and SO_3^{2-}. The other outlier is the reaction of $[Os(bpy)_3]^{3+}$. The rate constant for this reaction was extracted from a footnote of a prior report, and it may require confirmation. A more detailed analysis is presented in Table VII, in which values of log k_{11} have been calculated for each of the reactions. The average of these values is log $k_{11} = 0.59$ (excluding those for MnO_4^- and $[Os(bpy)_3]^{3+}$, for the reasons described above, and excluding that for $[Fe(phen)_3]^{3+}$ because it was studied at $\mu = 1.0$ M). This is 5 orders of magnitude less than previously reported.[7] However, the prior report was obtained with a reduction potential for the sulfite radical that differs from the present value by 0.09 V, and it was obtained from reactions with organic redox partners that often yield results discordant with estimates from substitution-inert coordination complexes.

By comparison with other small-molecule self-exchange rates,[48] it is evident that the calculated self-exchange rate constant for the SO_3^-/SO_3^{2-} system indicates a significant barrier due to structural reorganization of the molecule. An estimate of this barrier can be obtained by the usual model of the transition state as the minimum-energy configuration in which the system is isoenergetic when the hopping electron resides on either molecule. The activation free energy can be derived from this model by using a simple valence force field and assuming that the transition state is symmetric. The result in the case of a pyramidal molecule is

$$\Delta G^*_{is} = {}^3\!/_2\{(r_{ox} - r_{red})^2 k_{1,red}k_{1,ox}/(k_{1,red} + k_{1,ox}) + (\alpha_{ox} - \alpha_{red})^2 k_{\delta,ox}k_{\delta,red}/(k_{\delta,ox} + k_{\delta,red})\} \quad (30)$$

where r_{ox} and r_{red} are the S–O bond lengths, α_{ox} and α_{red} are the O–S–O bond angles, $k_{1,red}$ and $k_{1,ox}$ are the bond stretching force constants, and $k_{\delta,ox}$ and $k_{\delta,red}$ are the bond-bending force constants. Equation 30 resembles the analogous equation for triatomic molecules,[3] but differs in the factor of $^3/_2$. The force constants can be calculated by using the simple valence force field[49] with the vibrational fundamentals of SO_3^{2-} and SO_3^-.[9,25] The values so obtained are $k_{1,ox} = 4.0 \times 10^5$ and $k_{1,red} = 4.5 \times 10^5$ dyn/cm, and $k_{\delta,ox}/r_{ox}^2 = 1.6 \times 10^5$ and $k_{\delta,red}/r_{red}^2 = 1.2 \times 10^5$ dyn/cm. Structural parameters are $r_{red} = 1.504$ Å and $\alpha_{red} = 105.7°$,[50] and $r_{ox} = 1.48$ Å and $\alpha_{ox} = 113.8°$.[9] Note that the structural parameters for SO_3^- were obtained by an ab initio calculation. The outcome of these calculations is a value of 36.8 kJ/mol for ΔG^*_{is}. Approximately 97% of this barrier is due to the bond-bending term in eq 30.

A direct comparison of the calculated value for ΔG^* with the effective self-exchange rate constant can be made by use of the equations

$$k_{11} = Z \exp(-\Delta G^*/RT) \quad (31)$$

and

$$\Delta G^* = \Delta G^*_{is} + \Delta G^*_{os} + w \quad (32)$$

Here, as in eq 26, Z is the collision rate constant, with a value of 1×10^{12} M^{-1} s^{-1}. A value of 68.5 kJ/mol for ΔG^* is derived from eq 31 and our value of k_{11}. The work term, w, has a value of 3.6 kJ/mol, so eq 32 leads to a value of 28 kJ/mol for ΔG^*_{os}, the solvent reorganizational energy. This last result is about 8 kJ/mol less than was previously obtained for triatomics such as the ClO_2/ClO_2^- system.[3] A smaller value of ΔG^*_{os} can be expected because of the larger size of the SO_3^-/SO_3^{2-} system. However, exact agreement cannot be expected for various reasons. Two of these reasons are that eq 31 neglects the contributions of nuclear tunnelling and that eq 30 neglects off-diagonal elements in the force field. In any event, these calculations do support the notion that the reactivity of the SO_3^-/SO_3^{2-} redox couple is substantially influenced by the requirement to bend the molecule in the "umbrella" mode in order to achieve electron transfer.

Scheme II

$$SO_3^- + H^+ \rightleftarrows HSO_3 \qquad K_s \qquad (33)$$

$$[Ru(NH_3)_4(phen)]^{3+} + HSO_3 \rightarrow [Ru(NH_3)_4(phen)]^{2+} + H^+ + SO_3 \qquad k_6 \qquad (34)$$

$$[Ru(NH_3)_4(phen)]^{3+} + HSO_3 \rightarrow [Ru(NH_3)_4(phen\text{-}SO_3)]^+ + 2H^+ \qquad k_7 \qquad (35)$$

Mechanism of Sulfonation. Addition of allyl alcohol, a known scavenger of SO_3^-, has no effect on the kinetics of the reaction, although it does prevent the sulfonation of the complex. Thus, it is clear that sulfonation must occur after the rate-limiting step in the overall reaction. Because of this, our understanding of the mechanism of sulfonation is necessarily limited. Two possible mechanisms are suggested. Both of them include the steps already discussed in Scheme I. The first sulfonation mechanism includes the additional steps in Scheme II. Protonation of SO_3^- in reaction 33 is assumed to occur in a rapid equilibrium, and redox reactions 34 and 35 are required to explain the product yields. These latter reactions occur after the rate-limiting steps k_1 and k_d, and they lead to a product distribution that changes with pH in a region where only the first term is effective in the rate law. The product distribution in eq 3 can also be derived from the above mechanism with the following identities: $A = k_2/(K_s k_6)$ and $B = k_7/k_6 = 2.9$. Knowing k_2 leads to $K_s k_6 = 7.0 \times 10^{14}$ M^{-2} s^{-1}.

Other conceivable mechanisms might include sulfonation occurring through a nonradical mechanism. For example, sulfonation of *p*-benzoquinone by sulfite is believed to occur by simple addition.[51] In the present case, the fact that the degree of sulfonation shows a pH dependence in a region where the rate law shows only one term requires that sulfonation occur through an intermediate after the rate-limiting step. The experiments with allyl alcohol show that this intermediate can be scavenged by allyl alcohol, and it has previously been shown that allyl alcohol is a good scavenger of the sulfite radical.[30] Apparently, the radical adduct undergoes rapid oxidation by Ru(III), because the kinetics is unperturbed by the presence of allyl alcohol. Yet another observation that supports the free-radical nature of the sulfonation is that the position of sulfonation (the 4-position) is inconsistent with an electrophilic mechanism; e.g., sulfonation of free phanthroline by hot ammonium acid sulfate occurs at the 3- and 5-positions.[52]

It is already known that the sulfite radical adds to various olefinic compounds such as allyl alcohol, unsaturated fatty acids,[53] and other olefinic acids.[54] The present system differs because the product, $[Ru(NH_3)_4(phen\text{-}SO_3)]^+$, is not a radical. In a sense the present system is a radical–radical coupling reaction, because the Ru(III) reactant is also paramagnetic. Rollick and Kochi have extensively documented the occurrence of such coupling reactions for alkylation of coordinated phenanthroline.[55,56] In these cases substitution also occurs at the 4-position. A related reaction has also been demonstrated for the sulfite radical, in which it adds to $Fe(CN)_6^{3-}$; the adduct, however, is unstable, and it decomposes to form $Fe(CN)_4^{4-}$ and SO_4^{2-}. Rollick and Kochi have noted that the relative degree of alkylation vs electron transfer is a function of the ionization potential of the radical:[55] increasing I_D leads to lower rates of electron transfer, whereas alkylation shows the

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opposite trend. If this generalization applies to sulfonation, then it would be expected that HSO_3 would be more likely to sulfonate than SO_3^-, as observed.

Another facet of the mechanism in Scheme II is the major role played by the protonation of SO_3^-. Prior to this study there was little evidence in support of HSO_3. The species has been identified by IR spectroscopy in an argon matrix at 11 K.[57] In aqueous solution, however, the kinetics of self-reaction of SO_3^- (or HSO_3) shows only a small pH dependence.[26] Moreover, the ESR spectrum of the sulfite radical has been shown to be constant over the range of acidity from pH 11.3 to 61.2% $HClO_4$.[58] According to Scheme II, sulfonation of $[Ru(NH_3)_4(phen)]^{3+}$ is unusual in displaying a significant difference between the behavior of SO_3^- and HSO_3. Unfortunately, our experimental data do not lead to a value of K_s, the affinity of SO_3^- for H^+. By the setting of an upper limit of 1×10^{10} M^{-1} s^{-1} for k_6 based on the limit of diffusion control, a lower limit of 7×10^4 M^{-1} can be set for K_s; i.e., Scheme II requires the pK_a of HSO_3 to be greater than 4.8. In view of the weak kinetic inhibition by Ru(II) of the reaction of $[Ru(NH_3)_4(phen)]^{3+}$ with S(IV) in acidic media, it is unlikely that k_6 is much less that 10^8 M^{-1} s^{-1}, and therefore the pK_a of HSO_3 may lie between 4.8 and 6.8. Thus, HSO_3 is somewhat more acidic than HSO_3^-, which is as might be expected. This pK_a seems to be consistent with the pH range in which the self-reaction of the sulfite radical changes its product distribution as well as the range in which the kinetics of the self-reaction changes.[26,27]

There have been several prior reports of oxidation of S(IV) by phenanthroline-containing complexes and related species. These include $[Fe(bpy)_3]^{3+}$,[28] $[Fe(phen)_3]^{3+}$,[32] $[Ru(bpy)_3]^{3+}$, $[Os(bpy)_3]^{3+}$, and $^*[Ru(bpy)_3]^{2+}$ (excited-state Ru(II)).[59] None of these prior reports indicated that aromatic sulfonation had occurred. However, it is unlikely that if it had occurred, it would have been detected, because of the small expected shift in the electronic spectrum. According to Rollick and Kochi, the degree of free-radical alkylation of coordinated phenanthroline relative to electron transfer is a function of the reduction potential of the complex: more powerful oxidants show a lesser degree of alkylation.[55] $[Ru(NH_3)_4(phen)]^{3+}$ is a much weaker oxidant than any of the complexes cited above, and thus, it is expected that sulfonation is not a significant process for the stronger oxidants.

There are two objections that can be raised to the sulfonation mechanism in Scheme II. One is that it requires that SO_3^- and HSO_3 both react with $[Ru(NH_3)_4(phen)]^{2+}$ at the same rate, because the pulse-radiolysis data show no pH dependence. The other objection comes from the unobservably slow rate of oxidation of HSO_3^- by $[Ru(NH_3)_4(phen)]^{3+}$. In principle the reaction

$$HSO_3^- + [Ru(NH_3)_4(phen)]^{3+} \rightleftarrows HSO_3 + [Ru(NH_3)_4(phen)]^{2+} \quad k_8, k_{-8} \quad (36)$$

can occur. Its equilibrium constant can be calculated by combining the pK_a values for HSO_3^- and HSO_3 and the equilibrium constant for reaction 12. Since the pK_a of HSO_3 must be greater than 4.8, the equilibrium constant for reaction 36 must be greater than 1.8×10^{-6}. From the pulse-radiolysis experiments k_{-8} has a value of 1×10^8 M^{-1} s^{-1} and therefore k_8 must be greater than 1.8×10^2 M^{-1} s^{-1}. However, to be consistent with the kinetics of oxidation of 3 mM S(IV) by $[Ru(NH_3)_4(phen)]^{3+}$ at pH 2.89, k_8 must be less than 5 M^{-1} s^{-1}. It is possible that the accumulated uncertainties in such an involuted argument are large enough that these objections are not entirely compelling.

Scheme III

$$SO_3 + SO_3^{2-} \rightarrow SO_2 + SO_4^{2-} \quad k_9 \quad (37)$$

$$SO_3 + [Ru(NH_3)_4(phen)]^{3+} \rightarrow [Ru(NH_3)_4(phen\text{-}SO_3)]^{2+} + H^+ \quad k_{10} \quad (38)$$

$$[Ru(NH_3)_4(phen)]^{2+} + [Ru(NH_3)_4(phen\text{-}SO_3)]^{2+} \rightarrow [Ru(NH_3)_4(phen)]^{3+} + [Ru(NH_3)_4(phen\text{-}SO_3)]^{+} \quad \text{fast} \quad (39)$$

An alternative mechanism of sulfonation is given in Scheme III, which also includes the steps in Scheme I. This mechanism features SO_3 as a species that undergoes hydrolysis sufficiently slowly that it can participate in other reactions. As discussed above, slow hydrolysis is indeed a distinct possibility. This permits SO_3 to sulfonate $[Ru(NH_3)_4(phen)]^{3+}$ directly and to form SO_4^{2-} by oxygen atom transfer from SO_3^{2-}. Scheme III qualitatively accounts for the pH-dependent stoichiometry, because in acidic media the concentration of SO_3^{2-} is depleted by formation of HSO_3^-. Unfortunately, a quantitative interpretation of the data in terms of Scheme III requires values for three unknown rate constants: k_{hyd}, k_9, and k_{10}. One objection to Scheme III is that it requires sulfonation by SO_3 to occur in the 4-position of the phenanthroline ring, whereas SO_3 usually attacks the 3- and 5-positions. Since the phenanthroline is coordinated to Ru(III), and since the π orbitals of the ring are of the same symmetry as the t_{2g} orbitals containing the unpaired electron on Ru(III), it is possible that the phenanthroline has sufficient radical character to direct sulfonation to the 4-position.

Conclusions. The present research shows that oxidation of SO_3^{2-} by $[Ru(NH_3)_4(phen)]^{3+}$ leads to SO_4^{2-} in nonacidic media and $[Ru(NH_3)_4(phen\text{-}SO_3)]^+$ in acidic media. In both cases, the first step is electron transfer to form SO_3^-. By combination of the kinetics of this reaction with pulse-radiolysis data, a value of 0.72 V has been derived for the reduction potential of SO_3^-. An effective self-exchange rate constant for the SO_3^-/SO_3^{2-} couple of ≈ 4 M^{-1} s^{-1} has been derived from the Marcus cross-relationship. Such a low rate constant is consistent with the barrier imposed by the differing bond angles of the two species. The mechanism of sulfonation is unclear and could either involve attack on Ru(III) by HSO_3 or SO_3.

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