

Oxidations of Sulfite by Hexachloroiridate(IV) and Tris(2,2'-bipyridine)osmium(III): Two Reinvestigations

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Oxidations of SO_3^{2-} by IrCl_6^{2-} and $[\text{Os}(\text{bpy})_3]^{3+}$ (bpy = 2,2'-bipyridine) have been reinvestigated in aqueous solution at 25 °C. Contrary to some prior reports, the Ir(IV)-S(IV) reaction has a consumption ratio, $\Delta[\text{Ir}(\text{IV})]/\Delta[\text{S}(\text{IV})]$, of 2.1 ± 0.08 , with the sulfur-containing product being exclusively SO_4^{2-} . This result supports the concept that $\text{S}_2\text{O}_6^{2-}$ is a product of S(IV) oxidation only for inner-sphere reactions. For the oxidation by $[\text{Os}(\text{bpy})_3]^{3+}$, the products are SO_4^{2-} and $[\text{Os}(\text{bpy})_3]^{2+}$. A detailed kinetic study of this reaction showed that the rate law is $-\text{d}[\text{Os}(\text{III})]/\text{d}t = 2k_1[\text{Os}(\text{bpy})_3^{3+}][\text{S}(\text{IV})]/(1 + [\text{H}^+]/K_a)$ with $k_1 = (1.63 \pm 0.03) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, K_a being the acid dissociation constant of HSO_3^- . This value of k_1 is more than 3 orders of magnitude greater than reported previously, and now it is consistent with the cross relationship of Marcus' theory.

Introduction

In a recent report, we described the aqueous reaction of sulfite with $[\text{Ru}(\text{NH}_3)_4(1,10\text{-phenanthroline})]^{3+}$ in great detail.¹ The sulfite radical, SO_3^- , figured prominently in the reaction, and considerable insight into its reactivity was gained, including the values of its reduction potential (0.72 V vs NHE) and its effective self-exchange rate constant ($4 \text{ M}^{-1} \text{ s}^{-1}$). Although values for these two parameters had been reported previously,²⁻⁴ the cited values were major refinements. The study of the sulfite/ $[\text{Ru}(\text{NH}_3)_4(1,10\text{-phenanthroline})]^{3+}$ system also led to the conclusion that SO_3^- had to be a fairly effective *reducing* agent. However, it raised certain questions concerning prior literature reports, and in this paper we present answers to these questions.

One of the questions pertained to the nature of redox reactions of sulfite that yield $\text{S}_2\text{O}_6^{2-}$. It is known that sulfite has an unusual feature of undergoing a net one- or two-electron oxidation, resulting in the formation of $\text{S}_2\text{O}_6^{2-}$ or SO_4^{2-} , respectively.⁵ In an extensive survey of these reactions, consumption ratios, $\Delta[\text{oxidant}]/\Delta[\text{S}(\text{IV})]$, were found to vary between 1 and 2 depending on the nature of the oxidant, and it was inferred that any defect from 2 indicated formation of $\text{S}_2\text{O}_6^{2-}$ and a correspondingly diminished yield of SO_4^{2-} . A correlation was suggested between the stoichiometry of the reaction and the lability of the complex oxidant:⁵ substitution-inert complexes formed sulfate exclusively, while the labile complexes reacted with nonintegral stoichiometries less than 2.0, forming both sulfate and dithionate. Our present understanding of sulfur chemistry affords an explanation for the pattern, because any substitution-inert oxidant that is able to oxidize SO_3^{2-} will oxidize SO_3^- very effectively, and so there will be no pathway for formation of $\text{S}_2\text{O}_6^{2-}$. IrCl_6^{2-} , a substitution-inert complex, oxidizes sulfite, and there have been several reports on the stoichiometry of this reaction.⁶⁻¹⁰ Consumption ratios of both 2.0^{6,8} and less than 2.0^{9,10} have been reported. Since there is no obvious reason for the discrepancy between the reports, and since a consumption ratio less than 2.0 is difficult to reconcile with the outer-sphere character of most reactions of IrCl_6^{2-} , the stoichiometry of this reaction has been reinvestigated.

The other question pertained to the rates of outer-sphere oxidations of SO_3^{2-} . In our previous study, by determining the

reduction potential of the $\text{SO}_3^-/\text{SO}_3^{2-}$ couple it was possible to analyze the rates of oxidation of SO_3^{2-} in terms of Marcus' theory.¹ A plot was constructed relating the rate constants to the driving forces for a series of nine outer-sphere oxidants, with only two points deviating significantly from theory. One was the oxidation by MnO_4^- ; its rate constant was too large, implying that the reaction had an inner-sphere mechanism. The other was the oxidation by $[\text{Os}(\text{bpy})_3]^{3+}$ (bpy = 2,2'-bipyridine), which had a rate constant much less than would be predicted. The experimental rate constant, $0.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, was reported with no supporting data in a footnote of a prior report.¹¹ Since it is difficult to rationalize a deviation of this sort, this reaction has also been reinvestigated.

Experimental Section

Reagents. Distilled deionized water was obtained from a Barnstead Fi-Stream glass still. Sodium sulfite was of Fisher Certified ACS grade. Sodium hexachloroiridate(IV) ($\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$) and osmium tetroxide were from Alfa Products and were used as such. Trifluoromethanesulfonic acid was from 3M Co., and sodium trifluoromethanesulfonate (sodium triflate) was prepared by 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. 2,2'-Bipyridine was from Aldrich Chemical Co. $\text{Br}_2/\text{CH}_3\text{CN}$ solutions used for in situ oxidation of Os(II) to Os(III) were prepared by the method of Callahan et al.¹² Argon for the deaeration of solutions was purified by passage through a Catalyst Q1 column (Dow) and then through a tower containing the solvent. Phthalic acid from Eastman Kodak was recrystallized from hot water. All other materials were of Certified or reagent grade.

Synthesis of Osmium Complexes. $[\text{Os}(\text{bpy})_2\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ was prepared by the method of Lay et al.¹³

$[\text{Os}(\text{bpy})_3]\text{Cl}_2$ was prepared by a modified procedure of Constable et al.¹⁴ 12.5 mL of $\text{MeOCH}_2\text{CH}_2\text{OH}$ was added to 0.16 g of 2,2'-bipyridine and 0.3 g of $[\text{Os}(\text{bpy})_2\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ in a 100-mL round-bottom flask fitted with an air condenser. The mixture was heated to reflux in an oil bath for 24 h while it was stirred magnetically. The dark green solution was cooled, diluted to 50 mL with water, and then loaded onto a column of Sephadex SP C-25 (40-120- μm bead size) in the H^+ form. A faint yellow band eluted with water. Upon elution with 0.1 M HCl a red band slowly separated from the green band. From its UV-vis spectrum it was identified as the starting material, $[\text{Os}(\text{bpy})_2\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$. The green band was then eluted with 0.2 M HCl, leaving an immobile dark green band at the top of the column. The green solution was taken to dryness by rotary evaporation, and the solid was dissolved in a minimum volume of warm ethanol and precipitated by dropwise addition of diethyl ether. The precipitate was collected, washed with ether, and dried in a vacuum desiccator. Yield: 0.134 g (34%). Anal. Calcd for $[\text{Os}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$: C, 43.0; H, 4.3; N, 10.0. Found: C,

- (1) Sarala, R.; Islam, M. S.; Rabin, S. B.; Stanbury, D. M. *Inorg. Chem.* **1990**, *29*, 1133-1142.
- (2) Huie, R. E.; Neta, P. *J. Phys. Chem.* **1984**, *88*, 5665-5669.
- (3) Huie, R. E.; Neta, P. *J. Phys. Chem.* **1986**, *90*, 1193-1198.
- (4) Merenyi, G.; Lind, J.; Shen, X. *J. Phys. Chem.* **1988**, *92*, 134-137.
- (5) Veprek-Siska, J.; Wagnerova, D. M.; Eckschlager, K. *Collect. Czech. Chem. Commun.* **1966**, *31*, 1248-1255.
- (6) Sen Gupta, K. K.; Das, S.; Sen, P. K. *Transition Met. Chem. (London)* **1987**, *12*, 33-36.
- (7) Novoselov, R. I.; Muzykantova, Z. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1970**, *15*, 1606-1608.
- (8) Wilmarth, W. K.; Stanbury, D. M.; Byrd, J. E.; Po, H. N.; Chua, C.-P. *Coord. Chem. Rev.* **1983**, *51*, 155-179.
- (9) Stapp, E. L.; Carlyle, D. W. *Inorg. Chem.* **1974**, *13*, 834-837.
- (10) Brown, A.; Higginson, W. C. E. *J. Chem. Soc., Dalton Trans.* **1972**, 166-170.

- (11) Creutz, C.; Sutin, N.; Brunshwig, B. S. *J. Am. Chem. Soc.* **1979**, *101*, 1297-1298.
- (12) Callahan, R. W.; Brown, G. M.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1443-1453.
- (13) Lay, P. A.; Sargeson, A. M.; Taube, H. *Inorg. Synth.* **1986**, *24*, 293-294.
- (14) Constable, E. C.; Raithby, P. R.; Smit, D. N. *Polyhedron* **1989**, *8*, 367-369.

43.5; H, 4.1; N, 9.8. These results are in good agreement with the reported hexahydrate nature of the chloride salt.¹⁵

Preparation of Solutions. $[\text{Os}(\text{bpy})_3]^{3+}$ was generated in situ by oxidation of $\text{Os}(\text{II})$ solutions in triflic acid (pH \approx 3) by a dropwise addition of 0.01 M $\text{Br}_2/\text{CH}_3\text{CN}$. The solutions were prepared under argon and protected from light. Solutions of $\text{S}(\text{IV})$ were prepared by adding sodium sulfite to deaerated water. Prepared thus, these solutions were iodometrically found to be stable over the entire period of their use.¹⁶ All the solutions were freshly prepared and purged with argon prior to use. Gastight syringes with platinum needles and Teflon hubs were used for transfer of solutions.

Analytical Methods. All UV-visible absorbance data were obtained with an HP 8452A spectrophotometer equipped with 10-mm quartz cells; solutions of high optical density were diluted as necessary with water. The NMR data were obtained on a Bruker 400-MHz NMR spectrometer with 5 mg of the sample in 0.5 mL of D_2O with 1.0 mg of DSS (3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt) as an internal reference. pH measurements were made at room temperature on a Corning pH meter, Model 130, with a Ross combination electrode.

Cyclic voltammograms were recorded on a BAS 100 electrochemical analyzer. The working and reference electrodes were glassy carbon and Ag/AgCl respectively. The reference electrode was calibrated against a Ag/AgCl and two calomel electrodes and was found to have a potential of 0.202 V vs NHE. Solutions were thermostated at 25.0 ± 0.1 °C under N_2 . $[\text{Os}(\text{II})]$ solutions were \approx 1 mM with an ionic strength of 0.1 M (NaCF_3SO_3).

Ion chromatography experiments for analysis of SO_4^{2-} and $\text{S}_2\text{O}_6^{2-}$ were conducted as described previously.¹ In order to prevent the column from saturating, sample solutions of high initial concentrations of IrCl_6^{2-} were diluted before injection. Corrections were made for SO_4^{2-} and $\text{S}_2\text{O}_6^{2-}$ contaminants present in the stock $\text{S}(\text{IV})$ solutions.

The kinetic data were collected by the stopped-flow method as described previously,¹ with all the solutions well protected from ambient light. The reactions were studied by monitoring the product absorbance at 480 nm. Since the reactions were fast, the 2-mm path length was used to minimize potential errors due to incomplete mixing. The reactions were conducted by mixing equal volumes of $\text{Os}(\text{III})$ and $\text{S}(\text{IV})$ /buffer solutions. Pseudo-first-order rate constants were evaluated on a North Star computer with OLIS subroutines. k_{obs} values presented are averages of typically 10 shots.

The Los Alamos nonlinear least-squares computer program was used to fit the rate law to the values of k_{obs} . The data were weighted as the inverse square of the dependent variable. Uncertainties are expressed as one standard deviation. A Macintosh II computer was used for the least-squares optimizations.

Results

Properties of the Compounds. The UV-vis spectrum of IrCl_6^{2-} exhibited an absorption maximum at 488 nm with an ϵ_{max} of $3.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. This value is in good agreement with the reported values of $3.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 487 nm⁸ and $4.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 488 nm.⁹

The $[\text{Os}(\text{bpy})_3]^{2+}$ complex showed a λ_{max} at 480 nm with an extinction coefficient of $1.26 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, which is in excellent agreement with the reported value of $1.37 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.¹⁷ From the reversible cyclic voltammogram of the $\text{Os}(\text{III})/\text{Os}(\text{II})$ couple ($\Delta E_{\text{p/p}} = 64 \pm 2 \text{ mV}$), its formal potential, E_f , was $0.839 \pm 0.001 \text{ V}$ vs NHE in 0.1 M NaCF_3SO_3 . This value of E_f is in good agreement with the literature values of 0.855 V in 0.1 M H_2SO_4 ¹⁷ and 0.857 V in 0.1 M NaCl ,¹⁸ but it is higher than the value of 0.79 V (medium unspecified) reported by Creutz et al.¹¹ It is unclear why the E_f value reported by Creutz et al. is discordant, but since it was reported only in a footnote and with no supporting data, the present value is preferred. The ¹H NMR spectrum of the $\text{Os}(\text{II})$ complex comprised two doublets and two triplets: H-3, 7.75 (d, 5.6); H-4, 7.29 (t, 6.8); H-5, 7.87 (t, 8.0); H-6, 8.53 (d, 8.0).¹⁹ This spectrum is similar to that of $[\text{Ru}$

Table I. Oxidation of $\text{S}(\text{IV})$ by IrCl_6^{2-} : Stoichiometry Results^a

| $[\text{Ir}(\text{IV})]_i$, mM | $[\text{S}(\text{IV})]_i$, mM | pH | μ , mM | $\frac{\Delta[\text{Ir}(\text{IV})]}{\Delta[\text{S}(\text{IV})]}$ (UV-vis) | $[\text{SO}_4^{2-}]_f$, mM (ion chromatog) |
|---------------------------------|--------------------------------|-----|------------|---|---|
| 11.5 | 3.64 | 4.9 | 48 | 2.06 | 3.50 ^b |
| 13.4 | 3.00 | 4.1 | 53 | 2.20 | 3.04 ^b |
| 14.3 | 3.00 | 4.9 | 53 | 2.23 | 3.01 ^b |
| 14.6 | 3.00 | 4.8 | 200 | 2.14 | 3.05 ^b |
| 14.7 | 3.00 | 4.9 | 53 | 1.98 | 3.02 ^b |
| 14.7 | 3.00 | 4.9 | 53 | 2.17 | 3.06 ^b |
| 14.6 | 3.00 | 6.2 | 53 | 2.20 | 2.93 ^b |
| 20.9 | 3.00 | 4.9 | 53 | 2.23 | 2.91 ^b |
| 22.1 | 9.00 | 4.9 | 59 | 2.06 | 8.84 ^c |
| 0.262 | 0.050 | 4.3 | 0.55 | 2.02 | 0.0483 ^d |
| 0.262 | 0.050 | 4.8 | 1.00 | 2.06 | 0.0500 ^d |
| 0.260 | 0.050 | 6.4 | 1.00 | 2.15 | 0.0496 ^d |
| 0.317 | 0.050 | 4.3 | 0.55 | 2.12 | 0.0498 ^d |

^a $T \approx 25$ °C. Buffer systems: succinate (pH 4.1 and 4.3); acetate (pH 4.8 and 4.9); cacodylate (pH 6.2 and 6.4). Ionic strength maintained with NaCF_3SO_3 . ^b Yield of $\text{S}_2\text{O}_6^{2-} < 1.2 \times 10^{-4}$ M. ^c Yield of $\text{S}_2\text{O}_6^{2-} < 0.35 \times 10^{-3}$ M. ^d Yield of $\text{S}_2\text{O}_6^{2-} < 2 \times 10^{-6}$ M.

Table II. Oxidation of $\text{S}(\text{IV})$ by $[\text{Os}(\text{bpy})_3]^{3+}$: Sulfate Yield^a

| pH | $[\text{SO}_4^{2-}]_f$, μM | $[\text{SO}_4^{2-}]_{\text{cal}}$, μM^b | μ , mM |
|-----|--|---|------------|
| 3.6 | 48 ± 4 | 49 | 3.0 |
| 5.0 | 48 ± 4 | 49 | 2.0 |

^a $[\text{Os}(\text{III})]_i = 99 \mu\text{M}$; $[\text{SO}_3^{2-}]_i = 1 \text{ mM}$; $T =$ room temperature (≈ 25 °C). Buffer systems: acetate (pH 5.0); phthalate (pH 3.6). ^b $[\text{SO}_4^{2-}]_{\text{cal}} = [\text{Os}(\text{III})]_i/2$.

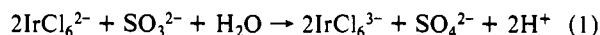
(bpy)₃²⁺: H-3, 7.86 (d, 5.6); H-4, 7.40 (t, 6.8); H-5, 8.08 (t, 8.0); H-6, 8.56 (d, 8.0).

Stoichiometry. Reduction of IrCl_6^{2-} . With $[\text{Ir}(\text{IV})]$ in excess over $[\text{S}(\text{IV})]$, consumption ratios, $\Delta[\text{Ir}(\text{IV})]/\Delta[\text{S}(\text{IV})]$, were determined by UV-vis spectrophotometry. The measurements were made with wide variations of $[\text{Ir}(\text{IV})]_i$, $[\text{S}(\text{IV})]_i$, and μ , and with pH varying from 4.1 to 6.4. The results are presented in Table I. The consumption ratios showed no significant dependence on pH or on the concentration of the reactants and had an average value of 2.12 ± 0.08 . Slight deviation of this value from 2.0 might be due to experimental errors in the determination of ϵ_{max} . Unlike those in some of the previous reports,^{9,10} the consumption ratio was never less than 2.0.

Stoichiometric information was also obtained by ion chromatography. Analyses were made for sulfate and dithionate in each of the solutions also analyzed by the consumption ratio method. In all cases the yield of dithionate was below the detection limit, which varied depending on the amount of background $\text{S}_2\text{O}_6^{2-}$ and the dilution factors. The yield of SO_4^{2-} , presented in Table I, was always significant, and the relative yield, $[\text{SO}_4^{2-}]_f/[\text{S}(\text{IV})]_i$, was 0.99 ± 0.02 , where the subscripts f and i designate final and initial concentrations.

To study the effect of oxygen on the stoichiometry, solutions prior to the reaction were deaerated partially; a consumption ratio of 1.2 was obtained. Analyses of these product solutions by ion chromatography showed sulfate as the only product, with no detectable yield of dithionate.

The above results, together with prior reports that IrCl_6^{3-} is the sole iridium-containing product,^{6-8,10} indicate that under anaerobic conditions the stoichiometry is simply



Reduction of $[\text{Os}(\text{bpy})_3]^{3+}$. The yield of sulfate and dithionate under anaerobic conditions with excess $\text{S}(\text{IV})$ at pH 3.6 and 5.0 was determined by ion chromatography. No dithionate was detected, with sulfate being the only oxidation product. The yield of sulfate is presented in Table II, from which it is clear that 1 mole of sulfate is produced for every 2 mol of $\text{Os}(\text{III})$ consumed.

A study of the cationic products was made on the solution generated from a mixture of 1×10^{-3} M $[\text{Os}(\text{bpy})_3]^{3+}$ and 9×10^{-3} M $\text{S}(\text{IV})$ at pH 4.0. This product solution was loaded onto a cation-exchange column (Sephadex SP C-25, 40–120- μm bead

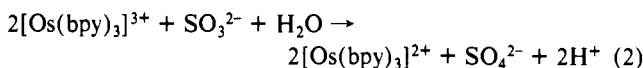
- (15) Burstall, F. H.; Dwyer, F. P.; Gyrfas, E. C. *J. Chem. Soc.* **1950**, 953–955.
 (16) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. *Quantitative Chemical Analysis*, 4th ed.; Macmillan: New York, 1969; p 857.
 (17) Schilt, A. A. *Analytical Applications of 1,10-Phenanthroline and Related Compounds*; Pergamon: New York, 1969; pp 36, 107, 122.
 (18) Nord, G.; Pedersen, B.; Floryan-Løvborg, E.; Pagsberg, P. *Inorg. Chem.* **1982**, *21*, 2327–2330.
 (19) Proton assignment follows the format δ in ppm (splitting pattern, J in Hz).

Table III. Observed and Calculated Rate Constants for Oxidation of S(IV) by Os(III)^a

| [S(IV)], mM | pH | k_{obs} , s ⁻¹ | k_{cal} , s ⁻¹ |
|-------------|------|------------------------------------|------------------------------------|
| 10.0 | 4.07 | 274 | 307 |
| 7.5 | 4.02 | 182 | 205 |
| 5.0 | 3.92 | 116 | 109 |
| 4.0 | 3.89 | 86 | 81 |
| 2.0 | 3.83 | 37.9 | 35.3 |
| 1.0 | 3.79 | 16.5 | 16.1 |
| 1.0 | 3.40 | 6.5 | 6.5 |
| 1.0 | 3.83 | 17.3 | 17.4 |
| 1.0 | 4.10 | 33.9 | 33.0 |
| 1.0 | 4.43 | 71 | 70 |
| 1.0 | 4.77 | 157 | 154 |

^a [Os(III)]_i = 89.0 μM; μ = 0.1 M (NaCF₃SO₃); T = 25.0 ± 0.1 °C. Buffer systems: acetate (pH 4.43 and 4.77); phthalate (pH 3.4); succinate for the others. k_{obs} values reproducible within ±5%.

size, in the Na⁺ form). First, a pale yellowish green band was eluted with 0.1 M NaCl. This monovalent cation had spectral characteristics similar to those of [Os(bpy)₃]²⁺ with a 2-nm shift in all the peaks. By analogy with the chemistry of [Ru(NH₃)₄phen]³⁺,¹ it is assumed that the monovalent species is a ring-sulfonated derivative of [Os(bpy)₃]²⁺, and thus that its ε_{max} is about the same as that of [Os(bpy)₃]²⁺. On this basis, its yield was less than 3.0%. With 0.2 M NaCl, a green band moved down the column. This species was identified as [Os(bpy)₃]²⁺ from its UV-vis spectrum, its yield being 90%. An immobile dark green band remained on the column and could not be eluted even with 1 M NaCl. It is unknown whether this is an artifact of the ion-exchange process or whether it represents an additional reaction product. However, in view of the large yield of [Os(bpy)₃]²⁺, the immobile band cannot be more than a minor product. On the basis of these observations, the major products are consistent with the stoichiometry



Kinetics. Kinetic studies were conducted under pseudo-first-order conditions with [S(IV)] ≫ [Os(bpy)₃]³⁺. Semilog plots were linear over 4 half-lives or more. Pseudo-first order rate constants, k_{obs} , defined by the equation

$$d[\text{Os}(\text{bpy})_3^{2+}]/dt = k_{\text{obs}}[\text{Os}(\text{bpy})_3^{3+}] \quad (3)$$

were obtained from exponential fits of the kinetic data. When the reactions were conducted with S(IV) solutions containing 1.9 × 10⁻⁵ M Cu(ClO₄)₂·6H₂O, the rate constants were similar to those obtained when there was no added Cu(II). Addition of 1 × 10⁻⁴ M 1,10-phenanthroline to either the [Os(bpy)₃]³⁺ or S(IV) solutions had no effect on kinetics. On the other hand, the reactions were highly sensitive to contamination by atmospheric dioxygen as per previous reports of S(IV) oxidation by metal complexes.²⁰⁻²² Such contamination led to apparent induction periods, with the subsequent formation of [Os(bpy)₃]²⁺ occurring at a lower rate. This is attributed to a chain autoxidation of S(IV) induced by the [Os(bpy)₃]³⁺.^{8,23}

The kinetics of the anaerobic oxidation of [S(IV)] by [Os(bpy)₃]³⁺ was studied over the pH range 3.40–4.77 at various S(IV) concentrations; the data are presented in Table III. Since the reactions were accelerated at higher pH and at higher concentrations of S(IV), these two parameters were constrained by the dead time of the instrument. The lower limit on pH was set by our efforts to avoid the regime in which S₂O₅²⁻ becomes a significant reactant, and the lower limit on the S(IV) concentration was set by the requirement of a large excess over [Os(bpy)₃]³⁺. Figure 1 displays the linear dependence of k_{obs} on pH at constant

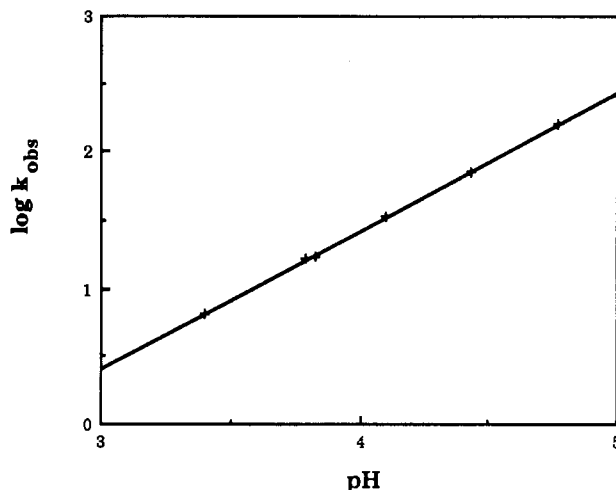


Figure 1. pH dependence of the kinetics of oxidation of S(IV) by [Os(bpy)₃]³⁺ at 1.0 mM S(IV) and 25 ± 0.1 °C. Data are from Table III. The solid line is calculated from the fit to experimental rate constants of eq 4 as explained in the text.

[S(IV)]. Values of k_{obs} for both the pH and the [S(IV)] dependence were fit by the equation

$$k_{\text{obs}} = \frac{2k_1[\text{S(IV)}]_t}{1 + [\text{H}^+]/K_a} \quad (4)$$

where [H⁺] is defined as 10^{-pH}, [S(IV)]_t designates the total S(IV) concentration, and K_a is taken as 8.0 × 10⁻⁸ M.¹ The fit resulted in values of (3.26 ± 0.06) × 10⁷ M⁻¹ s⁻¹ for 2k₁ and the values of k_{cal} presented in Table III. The uncertainty in 2k₁ derives from the scatter in the experimental data; presumably, if systematic errors were included, the uncertainty would be somewhat greater. Our results clearly show that under the present experimental conditions, pathways first-order and second-order in [HSO₃⁻] were not observed.

A few studies were made on the effect of added [Os(bpy)₃]²⁺. Experiments were performed with 88.2 μM [Os(bpy)₃]³⁺ and 1.0 mM S(IV) at pH 3.79. Unfortunately, due to the strong absorption by [Os(bpy)₃]²⁺, studies could only be made in the range of 0.25–1.37 mM [Os(bpy)₃]²⁺. Under these conditions, addition of [Os(bpy)₃]²⁺ had no effect on the reaction rates.

Discussion

Reduction of IrCl₆²⁻. Including the present report, there have been several studies of the oxidation of S(IV) by IrCl₆²⁻.⁶⁻¹⁰ Four of these have included an investigation of the iridium-containing products, with general agreement that IrCl₆³⁻ is the sole product.^{6-8,10} There is less agreement where consumption ratios have been determined. The present paper and papers by Wilmarth et al.⁸ and Sen Gupta et al.⁶ report consumption ratios, Δ[IrCl₆²⁻]/Δ[S(IV)], of 2.0 ± 0.1, whereas the papers of Brown and Higginson¹⁰ and Stapp and Carlyle⁹ report consumption ratios consistently less than 2.0. This is a significant problem, because consumption ratios less than 2.0 require a modification of our present concepts of the mechanisms of oxidation of S(IV).¹ Because the prior studies were conducted under various conditions of pH, ionic strength, and concentrations of the reactants, the reasons for the discrepancies were unclear.

Brown and Higginson, who obtained low consumption ratios, conducted their studies at pH 4.40 and 6.53 with 20 mM concentrations of the reactants.¹⁰ In the work of Wilmarth et al.,⁸ much lower concentrations of the reactants were used, and in the work of Sen Gupta et al.,⁶ the pH was much lower. Thus we have determined consumption ratios under conditions similar to those employed by Brown and Higginson. Our results, however, support a consumption ratio of 2.0 and hence disagree with those of Brown and Higginson. The discrepancy is tentatively attributed to incomplete deoxygenation of the solutions in the prior study.

Stapp and Carlyle,⁹ who also obtained low consumption ratios, conducted their experiments under conditions similar to those of

(20) Westley, F. *NBS Spec. Publ. (U.S.)* **1982**, 630, 1–31.

(21) Hoffmann, M. R.; Boyce, S. D. In *Trace Atmospheric Constituents*; Schwarz, S. E., Ed.; Wiley: New York, 1983; pp 147–189.

(22) Huie, R. E.; Peterson, N. C. In *Trace Atmospheric Constituents*; Schwarz, S. E., Ed.; Wiley: New York, 1983; pp 117–146.

(23) Anast, J. M.; Margerum, D. W. *Inorg. Chem.* **1981**, 20, 2319–2326.

Brown and Higginson¹⁰ except the ionic strength was rather high (0.2 M). Our attempts to reproduce these experiments also led to consumption ratios of 2.0. Once again, the low prior values are attributed to inadequate deoxygenation. In both cases, the presence of dioxygen is presumed to lead to an Ir(IV)-induced chain autoxidation of S(IV), as is so often seen.^{1,8,23}

Admittedly, consumption ratios are not a very accurate probe when the yields of dithionate are low. On the other hand, direct determination of dithionate was never performed in the prior studies. The present study has closed this gap by reporting ion chromatographic determinations of dithionate. In all cases, no dithionate was detected, the yield of dithionate, $\Delta[\text{S}_2\text{O}_6^{2-}]/\Delta[\text{SO}_4^{2-}]$, always being less than 4%. And, in all cases, the yield of SO_4^{2-} was appropriate for mass balance. In conclusion, we have no evidence that the stoichiometry is other than as represented by eq 1, despite reports^{9,10} to the contrary.

Mechanisms of Dithionate Production. The question arises as to what situations lead to production of dithionate in oxidations of S(IV) by metal complexes. On the basis of consumption ratios, Veprek-Siska et al. have identified a number of labile complexes that yield dithionate.⁵ More recent studies have shown that oxidations by AuCl_4^- ,²⁴ Fe^{3+} ,²⁵ and Mn^{3+} ²⁶ also yield $\text{S}_2\text{O}_6^{2-}$; all of these reactions were proposed to have inner-sphere mechanisms. In addition, dithionate has been reported as the product of the internal redox decompositions of *trans*- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{SO}_3)]^{+27}$ and *trans*- $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_3)]^{+28}$ although the result for the former has been disputed.²⁹ From these reports it would appear as though access to the metal center is a requirement for formation of dithionate.

There are two reactions that may undermine this generalization, and these are the oxidations by MnO_4^- and Cr(VI). It is claimed in the older literature that dithionate is produced in the oxidation by MnO_4^- .³⁰ In a recent study of this reaction it is reported that the product is SO_4^{2-} ;³¹ apparently, $\text{S}_2\text{O}_6^{2-}$ is produced in this system by the subsequent action of MnO_2 . The case of Cr(VI) is less clear. In a detailed study it was found that at high concentrations of Cr(VI) the yield of $\text{S}_2\text{O}_6^{2-}$ became significant, and therefore the kinetic studies were conducted at low Cr(VI) concentrations, where SO_4^{2-} was the product.³⁰ Thus we have no kinetic data obtained under the conditions where $\text{S}_2\text{O}_6^{2-}$ is formed. It is conceivable that formation of dithionate depends on the concentration of dichromate. In any event, it is possible that a Cr(VI) ester with S(IV) could be an intermediate, and thus that the reaction would proceed through an inner-sphere mechanism.

In summary, now that the disagreement regarding the oxidation of S(IV) by IrCl_6^{2-} has been resolved, the generalization stands that dithionate production requires access to the metal center. In the past, it has been inferred that dithionate production is diagnostic of SO_3^- free radicals as intermediates.^{9,10,25,27,28,30} Now, however, for all cases of oxidation by substitution-inert outer-sphere oxidants, where SO_3^- most likely is an intermediate, it is known that dithionate is not a product. This is a reasonable outcome, because it is now known that SO_3^- is a good *reducing* agent, and hence it will be oxidized to SO_3 before it can dimerize with second-order kinetics.¹ The only known case where $\text{S}_2\text{O}_6^{2-}$ results from the SO_3^- radical is the γ -radiolysis of S(IV) solutions,³² and in this case reaction with another oxidant is not a possibility.

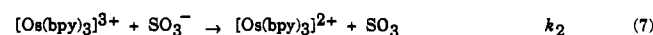
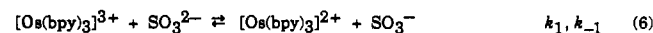
An alternative criterion has been proposed for the production of dithionate vs sulfate: this is that the product ratio depends of

the reduction potential of the oxidant.^{10,26,33} The fact that both Mn^{3+} and Fe^{3+} (strong and weak oxidants, respectively) generate $\text{S}_2\text{O}_6^{2-}$, however, undermines this concept.

A mystery that remains is the exact mechanism by which $\text{S}_2\text{O}_6^{2-}$ is ever formed. The most detailed of such studies to date, those of Mn^{3+} and Fe^{3+} , are not especially revealing.^{25,26} Perhaps the S-S bond is formed by reaction of coordinated sulfite with S(IV) either free or coordinated, but definitive evidence on these ideas is not yet in hand.

Reduction of Os(III) by S(IV). S(IV) is oxidized by $[\text{Os}(\text{bpy})_3]^{3+}$ with a stoichiometry and rate law characteristic of oxidations of S(IV) by substitution-inert oxidants.^{1,8,9,11,34} Our experimental rate constant, k_1 , is $(1.63 \pm 0.03) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, which is much greater than the value of $0.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ reported previously.¹¹ The origin of the discrepancy between these two results is difficult to ascertain, because the prior result was simply reported in a footnote without supporting data. It might be proposed that our greater rate constants are due to metal ion catalysis. However, our experiments showed excellent reproducibility and goodness of fit; moreover, the rate constants were independent of added Cu^{2+} and phenanthroline. For these reasons it is believed that the present results are correct and that the prior result¹¹ is due to some unknown error.

A mechanism for this reaction that is consistent with the stoichiometry and rate law and is analogous to that previously proposed^{1,9,23,34} is as follows:



This mechanism leads to the observed rate law under the conditions that the equilibrium K_a is established rapidly and that the k_2 step competes efficiently with back electron transfer through k_{-1} . It is quite reasonable to expect that an acid/base reaction such as for K_a will be established rapidly. That the second electron transfer, k_2 , competes effectively with back electron transfer is demonstrated by the fact that $[\text{Os}(\text{bpy})_3]^{2+}$ did not inhibit the kinetics. This is as expected on the basis of the oxidation of S(IV) by $[\text{Ru}(\text{NH}_3)_4(\text{phen})]^{3+}$, because in the latter case inhibition by $[\text{Ru}(\text{NH}_3)_4(\text{phen})]^{2+}$ was only a weak effect.¹ Since $[\text{Os}(\text{bpy})_3]^{2+}$ is a substantially weaker reducing agent than $[\text{Ru}(\text{NH}_3)_4(\text{phen})]^{2+}$, it should undergo back electron transfer more slowly, and so its inhibitory effect on the oxidation of S(IV) by $[\text{Os}(\text{bpy})_3]^{3+}$ should be even weaker.

Recently it has been suggested that $\text{S}_2\text{O}_7^{2-}$ can be an intermediate in redox reactions of HSO_3^- ³⁵ and that SO_4^{2-} is formed by its hydrolysis. Such a possibility cannot be ruled out in the present system, but if it occurs, it is not expected to have a significant influence on interpretation of the rate law.

As noted above, there are no substantiated reports of dithionate being a product of the oxidation of S(IV) by substitution-inert oxidants. The present study with $[\text{Os}(\text{bpy})_3]^{3+}$ extends that generalization. There is some evidence, however, for formation of minor amounts of another sulfur-containing product. This evidence comes from examination of the *cationic* reaction products. As noted under Results there is a small yield of species tentatively identified as $[\text{Os}(\text{bpy})_2(\text{bpy}-\text{SO}_3)]^+$. Similar behavior was observed in the oxidation of SO_3^{2-} by $[\text{Ru}(\text{NH}_3)_4(\text{phen})]^{3+}$, where $[\text{Ru}(\text{NH}_3)_4(\text{phen}-\text{SO}_3)]^+$ was a significant product.¹ It was proposed that this sulfonation occurred by attack of SO_3^- on $[\text{Ru}(\text{NH}_3)_4(\text{phen})]^{3+}$, in analogy with the free-radical alkylation

(24) Sen Gupta, K. K.; Das, S.; Sen Gupta, S. *Transition Met. Chem. (London)* **1988**, *13*, 261–263.

(25) Kraft, J.; van Eldik, R. *Inorg. Chem.* **1989**, *28*, 2306–2312.

(26) Siskos, P. A.; Peterson, N. C.; Huie, R. E. *Inorg. Chem.* **1984**, *23*, 1134–1137.

(27) Murray, R. S.; Stranks, D. R. *Inorg. Chem.* **1970**, *9*, 1472–1475.

(28) Thacker, M. A.; Scott, K. L.; Simpson, M. E.; Murray, R. S.; Higginson, W. C. E. *J. Chem. Soc., Dalton Trans.* **1974**, 647–651.

(29) El-Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1986**, *25*, 1323–1329.

(30) Haight, G. P., Jr.; Perchonock, E.; Emmenegger, F.; Gordon, G. J. *Am. Chem. Soc.* **1965**, *87*, 3835–3840.

(31) Simandi, L. I.; Jaky, M.; Savage, C. R.; Schelly, Z. A. *J. Am. Chem. Soc.* **1985**, *107*, 4220–4224.

(32) Eriksen, T. E. *Radiochem. Radioanal. Lett.* **1974**, *16*, 147–153.

(33) Sen Gupta, K. K.; Das, S.; Sen Gupta, S. *Transition Met. Chem. (London)* **1987**, *12*, 417–420.

(34) Carlyle, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 4525–4529.

(35) Littlejohn, D.; Hu, K.-Y.; Chang, S.-G. *Ind. Eng. Chem. Res.* **1988**, *27*, 1344–1348.

Table IV. Cross-Exchange Kinetics Data

| oxidant | k_{12} , $M^{-1} s^{-1}$ | E_f , V | k_{22} , M^{-1} s^{-1} | r , Å ^a | log K_{11} calc |
|--|--------------------------------|-------------------|---------------------------------|----------------------|----------------------|
| [Ru(NH ₃) ₄ (phen)] ³⁺ | 3.7×10^4 ^a | 0.52 ^a | 1.2×10^7 ⁱ | 4.4 | 2.15 |
| MnO ₄ ⁻ | 1.3×10^5 ^b | 0.56 ^b | 7.2×10^2 ^m | 3.5 | 10.26 |
| *[Ru(bpy) ₃] ²⁺ | 3.0×10^5 ^c | 0.84 ^d | 1.0×10^8 ⁿ | 6.8 | -0.65 |
| IrBr ₆ ²⁻ | 3.2×10^5 ^d | 0.84 ^h | 2.0×10^8 ^h | 4.5 | 0.70 |
| IrCl ₆ ²⁻ | 5.6×10^4 ^d | 0.89 ⁱ | 2.0×10^5 ^o | 4.4 | 1.39 |
| [Fe(bpy) ₃] ³⁺ | 2.1×10^8 ^d | 1.06 ^j | 5.0×10^8 ^p | 6.8 | 0.20 |
| [Fe(phen) ₃] ³⁺ | 4.6×10^6 ^e | 1.09 ^k | 5.0×10^8 ^q | 6.8 | -2.31 |
| [Ru(bpy) ₃] ³⁺ | 2.2×10^9 ^c | 1.26 ^d | 4.0×10^8 ^q | 6.8 | -0.27 |
| [Os(bpy) ₃] ³⁺ | 1.6×10^7 ^f | 0.84 ^f | 2.0×10^9 ^r | 6.8 | 0.67 |
| [Os(bpy) ₃] ³⁺ | 9.0×10^3 ^c | 0.79 ^c | 2.0×10^9 ^r | 6.8 | -5.04 |

^aReference 1. ^bReference 31. ^cReference 11. ^dReference 8. ^eReference 34. ^fThis work. ^gReference 38. ^hReference 39. ⁱReference 40. ^jReference 17, p 118. ^kReference 17. ^lReference 41. ^mReference 42. ⁿReference 43. ^oReference 44. ^pReference 45. ^qReference 46. ^rReference 47. ^sEstimated.

reactions reported by Rollick and Kochi.^{36,37} These workers reported a correlation between the degree of alkylation and the reduction potential of the metal ion complex, with more powerful oxidants showing a lesser degree of alkylation.^{36,37} If sulfonation follows the same trend, then the low degree of sulfonation in the [Os(bpy)₃]³⁺ system is as expected.

Marcus' Theory. In our recent study of the application of Marcus' theory to outer-sphere oxidations of SO₃²⁻, it was found that a good correlation existed for most of the reactions.¹ However, one outlier was the oxidation by [Os(bpy)₃]³⁺. The present results show that both the E° for this oxidant and the electron-transfer rate constant pertaining to its reaction were in error. In interpreting the present revised results, we use the same Marcus theory expressions as before,¹ which are classical equations including the substantial effects of electrostatics. The data are presented in Table IV and in Figure 2 as a plot of $\log(k_{12}/W_{12}) - 1/2 \log k_{22}$ as a function of $\log K_{12}$, where k_{12} is the forward electron-transfer rate constant, W_{12} is the electrostatic work term, and k_{22} is the

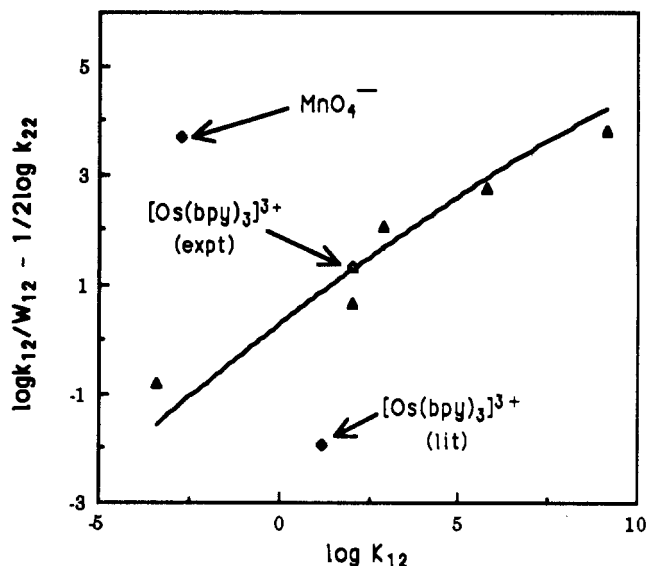


Figure 2. Plot of $\log(k_{12}/W_{12}) - 1/2 \log k_{22}$ as a function of $\log K_{12}$ for various electron-transfer reactions with data as in Table IV. The solid line is drawn for a k_{11} value of 3.9 under the approximation that SO₃⁻ and SO₃²⁻ have radii of 3 Å.

self-exchange rate constant for the metal complex. The solid line in Figure 2 is the theoretical function when the value of k_{11} (the self-exchange rate constant for the SO₃⁻/SO₃²⁻ system) is taken as $4 M^{-1} s^{-1}$, k_{22} is given an average value of $6 \times 10^7 M^{-1} s^{-1}$ in the calculation of f , and 3 Å is taken as the radius of SO₃²⁻ and SO₃⁻. The theoretical line is a curve because of the quadratic nature of the Marcus cross relationship. It is clearly apparent that the revised data lead to an excellent correlation with Marcus' theory. Since the erroneous prior data were not used in the prior determination of k_{11} , there is no need to revise our estimate of $4 M^{-1} s^{-1}$ for the value of this parameter.¹ The positive deviation of MnO₄⁻ from the line in Figure 2 remains a significant problem, but perhaps it represents formation of an intermediate complex.

Conclusions. The stoichiometry of the oxidation of S(IV) by IrCl₆²⁻ has been reinvestigated. Contrary to some prior reports, SO₄²⁻ is the exclusive sulfur-containing product of this reaction. This result leads to the generalization that oxidation of S(IV) to S₂O₆²⁻ by metal complexes occurs only through inner-sphere mechanisms. The kinetics of the oxidation of S(IV) by [Os(bpy)₃]³⁺ has been reinvestigated. The correct rate constant is more than 3 orders of magnitude greater than reported previously. Analysis of this rate constant in terms of Marcus' theory shows that it is quite consistent with rate constants for oxidations of SO₃²⁻ by most other outer-sphere oxidants.

Acknowledgment. This research was supported by the National Science Foundation.

- (36) Rollick, K. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 1319-1330.
 (37) Rollick, K. L.; Kochi, J. K. *J. Org. Chem.* **1982**, *47*, 435-444.
 (38) *Standard Potentials in Aqueous Solution*; Bard, A. J., Parsons, R., Jordan, J., Eds.; Marcel Dekker, Inc.: New York, 1985; p 437.
 (39) Stanbury, D. M.; Wilmarth, W. K.; Khalaf, S.; Po, H. N.; Byrd, J. E. *Inorg. Chem.* **1980**, *19*, 2715-2722.
 (40) Margerum, D. W.; Chellappa, K. L.; Bossu, F. P.; Burce, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 6894-6896.
 (41) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883-892.
 (42) Spiccia, L.; Swaddle, T. W. *Inorg. Chem.* **1987**, *26*, 2265-2271.
 (43) Sutin, N.; Creutz, C. In *Inorganic and Organometallic Photochemistry*; Wrighton, M. S., Ed.; American Chemical Society: Washington, DC, 1978; pp 1-27.
 (44) Hurwitz, P.; Kustin, K. *Trans. Faraday Soc.* **1966**, *62*, 427-432.
 (45) Ruff, I.; Zimonyi, M. *Electrochim. Acta* **1973**, *18*, 515.
 (46) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113-127.
 (47) Nord, G.; Pedersen, B.; Farver, O. *Inorg. Chem.* **1978**, *17*, 2233-2238.