however, that the alternative pathway cannot be completely ruled out. If k_1 is assigned to reaction 1b, $k_{1b} = 2.8 \times 10^3$ M^{-1} s^{-1}.

Conclusions

The results presented in this paper and in our previous report[6] confirm the formation of relatively weak chlorito complexes with the two most common transition-metal ions. In the absence of specific effects, similar complexes are formed between Cu^{2+} or Fe^{3+} and simple monodentate ligands such as NO_3^-, Cl^-, and Br^- (cf. ref 8). Also, the rate constants obtained for the formation of $FeClO_2^{2+}$ are in good correlation with literature data for ligand substitution reactions of Fe(III). Providing that the results are typical for the chlorite ion, these findings suggest that no special interactions between the metal ion and ClO_2^- need be considered for the interpretation of the coordination chemistry of this ligand. Furthermore, both $CuClO_2^+$ and $FeClO_2^{2+}$ can be regarded as models for chlorito complexes with di- and trivalent metal ions, respectively.

In the presence of Fe^{3+}, fast catalytic decomposition of the chlorite ion was observed. This reaction is kinetically coupled with the complex formation and must be included in the interpretation of the experimental data. The results also provide some evidence that the $FeClO_2^{2+}$ complex is the precursor in the decomposition reaction. However, the exact kinetic role of this species is not known. Further studies in this system should focus on the intrinsic mechanism of the iron(III)-catalyzed decomposition of ClO_2^-.

Contribution from the Department of Chemistry,
Auburn University, Auburn, Alabama 36849

Oxidation of Thiosulfate by $[Os(phenanthroline)_3]^{3+}$ and Related Complexes

Rajeshuni Sarala, Steven B. Rabin,[†] and David M. Stanbury*

Received May 8, 1991

The kinetics of oxidation of thiosulfate by $[Os(phen)_3]^{3+}$ (phen = phenanthroline) in aqueous media at 25.0 °C and 0.10 M ionic strength has been investigated by stopped-flow spectrophotometry. With excess thiosulfate, the reaction has the stoichiometry $2[Os(phen)_3]^{3+} + 2S_2O_3^{2-} \rightarrow 2[Os(phen)_3]^{2+} + S_4O_6^{2-}$, and the rate law is $-d[Os(III)]/dt = 2k_1[Os(III)][S_2O_3^{2-}] + 2k_2[Os(III)][S_2O_3^{2-}]^2$. Oxidations by $[Os(4,7\text{-}Me_2phen)_3]^{3+}$, $[Os(5,6\text{-}Me_2phen)_3]^{3+}$, and $[Os(5\text{-}Cl\text{-}phen)_3]^{3+}$, having reduction potentials that span a range of 0.65 to 0.94 V, show similar rate laws. Both the k_1 and k_2 rate constants increase as the reduction potential of the oxidant increases. An outer-sphere electron-transfer mechanism is inferred for both terms, with $S_2O_3^-$ and $S_4O_6^{3-}$ as the primary intermediates.

Introduction

Thiosulfate is one of the most industrially and biologically important sulfur oxyanions. Unlike sulfate, thiosulfate has an extensive redox chemistry. Although there have been numerous mechanistic studies of these reactions, much remains to be learned regarding the sulfur-containing intermediates. It is clear that in many cases, oxidation of thiosulfate by coordination complexes occurs via an inner-sphere mechanism.[1-3] The body of literature on outer-sphere mechanisms is much smaller, but such processes are of interest because of the implied free-radical intermediates. The only data available pertain to the oxidations by $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, $[IrBr_6]^{2-}$, $[Mo(CN)_8]^{3-}$, and $[CoW_{12}O_{40}]^{5-}$.[4-6] The reaction of $[CoW_{12}O_{40}]^{5-}$ is difficult to interpret because of the extreme electrostatic problems associated with the 5–/2– charge product.[6] Related problems are found for the reaction of $[Mo(CN)_8]^{3-}$, which is catalyzed by alkali-metal cations.[5] Difficulties also arise in comparing the reactions of $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, and $[IrBr_6]^{2-}$ because of the differing properties of these oxidants.[4]

The objective of this paper is to study a homologous series of reactions, in which thiosulfate is oxidized in an outer-sphere mechanism. Criteria for selection of the oxidants are that they be substitution inert so as to ensure an outer-sphere mechanism and cationic so as to avoid alkali-metal cation catalysis and have smoothly varying reduction potentials so as to facilitate construction of LFERs (linear free energy relationships). $[Os(phen)_3]^{3+}$ (phen = phenanthroline) and its relatives constitute such a series. An advantage of these oxidants is that they are weaker oxidants than the corresponding Fe(III) and Ru(III) series. This weakly oxidizing power allows us to explore the transition from outer-sphere electron transfer to the alternative mechanisms exhibited by very weak oxidants such as $[Fe(CN)_6]^{3-}$. There have been a few reports in the literature in which these Os(III) complexes acted as outer-sphere electron-transfer oxidants.[7,8] These reports demonstrated the applicability of Marcus's theory to reactions of these oxidants. In the present paper we report on the reactions of $S_2O_3^{2-}$ with $[Os(phen)_3]^{3+}$ and three of its relatives.

Experimental Section

Reagents. Distilled deionized water was obtained from a Barnstead Fi-Streem glass still. Sodium thiosulfate and sodium acetate were recrystallized from hot water. Osmium tetroxide was from Alfa Products, and the ligands 1,10-phenanthroline (phen), 4,7-dimethylphenanthroline (4,7-Me_2phen), 5,6-dimethylphenanthroline (5,6-Me_2phen), and 5-chlorophenanthroline (5-Cl-phen) were purchased from Aldrich Chemical Co. Trifluoromethanesulfonic acid (HCF_3SO_3) was from 3M, 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. Br_2/CH_3CN solutions used for in situ oxidation of Os(II) to Os(III) were prepared by the method of Callahan et al.[9] Tetra-*n*-propylammonium bromide was recrystallized from ethanol by addition of ethyl ether. Potassium salts of the polythionates were prepared and purified by literature methods.[10] Trithionate was made from the reaction of SO_2 with an aqueous solution of $K_2S_2O_3$. Tetrathionate was prepared by the oxidation of thiosulfate by iodine, and pentathionate, by the reaction of thiosulfate with HCl in the presence of arsenious acid. All other materials were of certified or reagent grade.

[†] Preliminary investigations conducted at Rice University, Houston, TX, as reported in the Ph.D. dissertation (1987) of S.B.R.

(1) Nord, G.; Skibsted, L. H.; Halonin, A. S. *Acta Chem. Scand. A* **1975**, *29*, 505–512.
(2) Panda, R. K.; Neogi, G.; Ramaswamy, D. *Int. J. Chem. Kinet.* **1981**, *13*, 1001–1010.
(3) Byerley, J. J.; Fouda, S. A.; Rempel, G. L. *J. Chem. Soc., Dalton Trans.* **1973**, 889–893.
(4) Wilmarth, W. K.; Stanbury, D. M.; Byrd, J. E.; Po, H. N.; Chua, C.-P. *Coord. Chem. Rev.* **1983**, *51*, 155–179.
(5) Lamprecht, G. J.; Leipoldt, J. G.; Dennis, C. R.; Basson, S. S. *React. Kinet. Catal. Lett.* **1980**, *13*, 269–275.
(6) Ali, M.; Saha, S. K.; Banerjee, P. *Indian J. Chem.* **1990**, *29A*, 528–530.
(7) Brunschwig, B. S.; Sutin, N. *Inorg. Chem.* **1979**, *18*, 1731–1736.
(8) Nord, G.; Pedersen, B.; Farver, O. *Inorg. Chem.* **1978**, *17*, 2233–2238.
(9) Callahan, R. W.; Brown, G. M.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1443–1453.
(10) Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic Press: New York, 1963; Vol. 1; pp 393–403.

0020-1669/91/1330-3999$02.50/0 © 1991 American Chemical Society

Synthesis of Osmium Complexes. $K_2[OsCl_6]$ was prepared by the method of Dwyer and Hogarth, except KCl was used to precipitate the complex.[11] $[Os(phen)_2Cl_2]Cl$ was prepared from $K_2[OsCl_6]$ by the method of Buckingham et al.[12] Bis complexes of 5,6-Me_2phen and 5-Cl-phen were prepared similarly to that of $[Os(phen)_2Cl_2]Cl$, but the refluxing time was increased from 1 to 2 h.

$[Os(phen)_3]Cl_2 \cdot 3H_2O$ was prepared by a modified procedure of Constable et al.[13] A 12.5-mL volume of $MeOCH_2CH_2OH$ was added to 0.198 g of 1,10-phenanthroline and 0.346 g of $[Os(phen)_2Cl_2]Cl$ in a 100-mL round-bottom flask fitted with an air condenser. The mixture was heated to reflux in an oil bath for 40 h with continuous stirring. The dark green solution was cooled, diluted to 70 mL with water, and then loaded onto a cation-exchange column of Sephadex SP C-25 (40–120-μm bead size) in the H^+ form (28 × 2.5 cm). The column was eluted with water and then with 0.1 M HCl. A faint yellow band of $[Os(phen)_2Cl_2]Cl$ moved down the column. A 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 with diethyl ether. The precipitate was collected, washed with ether, and dried in a vacuum desiccator. Yield: 0.24 g (55%). Anal. Calcd for $[Os(phen)_3]Cl_2 \cdot 3H_2O$: C, 50.5; H, 3.53; N, 9.82. Found: C, 50.2; H, 3.50; N, 9.59.

$[Os(5,6\text{-}Me_2phen)_3]Cl_2$. This compound was synthesized by analogy to $[Os(phen)_3]Cl_2$. To 0.058 g of 5,6-Me_2phen and 0.100 g of $[Os(5,6\text{-}Me_2phen)_2Cl_2]Cl$ in a 100-mL round-bottom flask was added 3.0 mL of $MeOCH_2CH_2OH$. The flask was fitted with an air condenser, and the mixture was heated to reflux in an oil bath for 26 h while it was stirred magnetically. After cooling, the solvent was evaporated and the residue was dissolved in water and extracted with toluene to remove the excess phenanthroline ligand. The aqueous layer was evaporated to dryness. To this, a minimum amount of methanol was added, and the solution was loaded onto a gel filtration column of Sephadex LH-20-100 (bead size 40–120 μm; 30 × 2.5 cm) and was eluted with methanol. Three main bands separated: red, green, and a tailing pale yellow band. The green band was collected, concentrated, and loaded onto a longer column (58 × 1.5 cm) in two batches. A major green and a minor red band separated. The green band was evaporated to dryness, the solid was dissolved in a minimum amount of ethanol, the solution was filtered, and the solid was precipitated by addition of diethyl ether. The precipitate was collected, washed with ether, and dried in a vacuum desiccator. Yield: 0.10 g (53%). Anal. Calcd for $[Os(5,6\text{-}Me_2phen)_3]Cl_2 \cdot 3H_2O$: C, 53.6; H, 4.50; N, 8.94. Found: C, 53.7; H, 4.52; N, 9.00.

$[Os(5\text{-}Cl\text{-}phen)_3]Cl_2$. This compound was synthesized by analogy to $[Os(phen)_3]Cl_2$. A 0.06-g sample of 5-Cl-phen and 0.100 g of $[Os(5\text{-}Cl\text{-}phen)_2Cl_2]Cl$ were added to 3.0 mL of $MeOCH_2CH_2OH$ in a 100-mL round-bottom flask, and the mixture was heated to reflux for 24 h with continuous stirring. The mixture was evaporated to dryness. The residue was dissolved in water and extracted with $CHCl_3$ until the organic layer was colorless. The aqueous layer was evaporated to dryness. The solid was dissolved in a minimum amount of water, and the solution loaded onto a cation-exchange column of CM-Sephadex C-50-120 (bead size 40–120 μm; 28 × 2.5 cm) in the H^+ form. The column was eluted with 5 mM HCl and later with 10 mM HCl. A single green band was obtained. This was collected and evaporated to dryness. It was then dissolved in minimum amount of warm ethanol, the solution was filtered, and the solid was precipitated by addition of ether. The precipitate was collected, washed with ether, and dried in a vacuum desiccator. Yield: 0.080 g (60%). Anal. Calcd for $[Os(5\text{-}Cl\text{-}phen)_3]Cl_2 \cdot 3H_2O$: C, 44.9; H, 3.14; N, 8.73. Found: C, 44.4; H, 2.82; N, 8.52. In principle, the product could be the *fac* or *mer* isomer or a mixture of the two. Our NMR and chromatographic techniques did not reveal the presence of two isomers, but this is not unexpected because the two isomers should have very similar physical and chemical properties. Since there is no experimental information on the isomeric distribution, no further reference is made to it.

$[Os(4,7\text{-}Me_2phen)_3]Cl_2$. This compound was prepared by an adaptation of a literature method for $[Os(phen)_3]Cl_2$.[14] A 0.065-g amount of $K_2[OsCl_6]$ was dissolved with heating in 10 mL of ethylene glycol containing 141 mg of 4,7-Me_2phen. The mixture was heated to reflux. Within 15 min, the solution turned green, and the refluxing was continued for a further 1 h. The reaction mixture was cooled and saturated aqueous KI solution was added slowly, to induce precipitation. The precipitate was collected, washed with ether, and dissolved in minimum amount of methanol. The solution was then loaded onto an anion-exchange column of Dowex 1-X8 (20–50 mesh) in the Cl^- form and eluted with methanol. This converted the iodide salt into chloride salt. This was dissolved in a minimum amount of methanol, and the solution was then loaded in two batches onto a gel filtration column of Sephadex LH-20-100 (bead size 40–120 μm; 30 × 2.5 cm). When eluted with methanol, three main bands separated: red, green, and a tailing pale yellow band. The green band was collected and evaporated to dryness. When the green material was loaded on a column of Sephadex LH-20 (30 × 2.5 cm), this gave a single green band, which was evaporated to dryness. The solid was dissolved in the minimum amount of ethanol, and the solution was filtered. A solid was precipitated by addition of diethyl ether. The precipitate was collected, washed with ether, and dried in a vacuum desiccator. Yield: 0.090 g (75%). Anal. Calcd for $[Os(4,7\text{-}Me_2phen)_3]Cl_2 \cdot 4H_2O$: C, 52.7; H, 4.63; N, 8.77. Found: C, 52.8; H, 4.58; N, 8.82.

Table I. UV–Vis and Electrochemical Properties of the $[OsL_3]^{2+}$ Complexes

ligand	λ_{max}, nm ($10^{-4}\epsilon$, M^{-1} cm^{-1})	E_f, V	method[a]
5-Cl-phen	432 (1.7)	0.937	OSWV[b]
phen	430 (1.9)	0.835	CV[c]
5,6-Me_2phen	434 (1.7)	0.776	OSWV[b]
4,7-Me_2phen	440 (1.7)	0.653	OSWV[b]

[a] CV = cyclic voltammetry; OSWV = Osteryoung square-wave voltammetry. [b] μ = 0.1 M (HCl). [c] μ = 0.1 M ($NaCF_3SO_3$).

Preparation of Solutions. Os(III) solutions of all the complexes were generated in situ by oxidation of the corresponding Os(II) solutions in dilute triflic acid or HCl (pH $\approx$ 3) by addition of 0.01 M Br_2/CH_3CN. The solutions were well protected from light. Solutions of $S_2O_3^{2-}$ were prepared freshly in water and standardized by iodometry.[15]

Analytical Methods. All UV–visible absorbance data were obtained by using an HP 8452A spectrophotometer. The NMR data were obtained on a Bruker AM 400 NMR spectrometer with 5 mg of the sample in 0.5 mL of D_2O and 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 Model 130 pH meter with a Ross combination electrode.

Cyclic voltammograms (CVs) and Osteryoung square-wave voltammograms (OSWVs) were recorded on a BAS 100 electrochemical analyzer. The working and reference electrodes were glassy carbon and Ag/AgCl, respectively. Solutions contained 0.1–1.0 mM Os(II) and 0.1 M supporting electrolyte ($NaCF_3SO_3$ or HCl). They were maintained at 25.0 ± 0.1 °C. E_f values for the Os(III) complexes were taken as $E_{1/2}$ values in CV measurements and E_p values in OSWV experiments. They are reported relative to NHE by using a value of 0.197 V as $E°$ for the Ag/AgCl electrode.

Ion chromatography experiments for analysis of polythionates were conducted on a Wescan Instruments ion analyzer by ion-pair chromatography as described previously.[16] The mobile phase was composed of 5 mM tetrapropylammonium bromide in 8% acetonitrile, and the flow rate was 1.9 mL/min.

Kinetic data were collected and analyzed by use of a Hi-Tech SF-51 stopped-flow spectrophotometer equipped with OLIS data acquisition systems as described earlier.[17,18] With all the solutions well protected from ambient light, reactions were studied by monitoring the Os(II) product absorbance at its absorption maximum with a 10-mm path length. For reactions with higher $[Os(III)]_0$, the 2-mm path length was used. Reactions were conducted by mixing equal volumes of Os(III) and $S_2O_3^{2-}$/buffer/electrolyte solutions. Fits to the time-dependent decays were evaluated on North Star and Zenith computers with OLIS subroutines.

The Los Alamos nonlinear least-squares computer program was used to fit the rate law to the values of k_{obs}.[19] The data were weighted as the inverse square of the dependent variable. Uncertainties are expressed as

---

(11) Dwyer, F. P.; Hogarth, J. *Inorg. Synth.* **1957**, *5*, 207.

(12) Buckingham, D. A.; Dwyer, F. P.; Goodwin, H. A.; Sargeson, A. M. *Aust. J. Chem.* **1964**, *17*, 325–336.

(13) Constable, E. C.; Raithby, P. R.; Smit, D. N. *Polyhedron* **1989**, *8*, 367–369.

(14) Vining, W. J.; Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1985**, *89*, 1095–1099.

(15) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. *Quantitative Chemical Analysis*, 4th ed.; Macmillan: New York, 1969; p 849.

(16) Rabin, S. B.; Stanbury, D. M. *Anal. Chem.* **1985**, *57*, 1130–1132.

(17) Sarala, R.; Stanbury, D. M. *Inorg. Chem.* **1990**, *29*, 3456–3460.

(18) Sarala, R.; Islam, M. S.; Rabin, S. B.; Stanbury, D. M. *Inorg. Chem.* **1990**, *29*, 1133–1142.

(19) Moore, R. H.; Zeigler, R. K. LSTSQR. Los Alamos National Laboratory, 1959.

Table II. ^{1}H NMR Spectral Data for the $[OsL_3]^{2+}$ Complexes[a]

ligand	proton assgnt 2	3	4	5	6	7	8	9
5-Cl-phen	8.17/8.10 (dd) (11.0, 5.5)	7.71/7.64 (m)	8.71 (d) (8.4)		8.47 (s)	8.41 (d) (8.2)	7.64/7.71 (m)	8.10/8.17 (dd) (11.0, 5.5)
phen	8.15 (d) (5.2)	7.65 (dd) (8.0, 5.6)	8.48 (d) (8.0)	8.34 (s)	8.34 (s)	8.48 (d) (8.0)	7.65 (dd) (8.0, 5.6)	8.15 (d) (5.2)
5,6-DMP[b]	8.12 (d) (5.2)	7.66 (dd) (8.4, 5.5)	8.58 (d) (8.5)			8.58 (d) (8.5)	7.66 (dd) (8.4, 5.5)	8.12 (d) (5.2)
4,7-DMP[b]	7.93 (d) (5.4)	7.44 (d) (5.5)		8.41 (s)	8.41 (s)		7.44 (d) (5.5)	7.93 (d) (5.4)

[a] Each value of the proton assignment follows the format δ (ppm) (splitting pattern) (*J*, Hz). The slash (/) in the data for the 5-Cl-phen complex indicates uncertainty in the assignment. [b] DMP is Me_2phen.

Table III. Stoichiometry of $[Os(phen)_3]^{3+}$ Reduction by Thiosulfate[a]

$[Os(phen)_3{}^{3+}]_0$, μM	$[S_2O_3{}^{2-}]_0$, mM	$[S_4O_6{}^{2-}]_{cal}$, μM[b]	$[S_4O_6{}^{2-}]_f$, μM[c]
110	0.450	55.0	52.5 ± 3.9
118	0.415	59.0	61.0 ± 3.5
250	1.00	125	127.0 ± 3.0

[a] Room temperature (≈22 °C). Acetate buffer (pH 5.1). Reaction mixture included 1.0 mM phenanthroline. [b] $[S_4O_6{}^{2-}]_{cal} = [Os(III)]_0/2$. [c] Average of 4–5 runs.

Table IV. Kinetics of Reduction of $[OsL_3]^{3+}$ by $[S_2O_3{}^{2-}]$[a]

$[S_2O_3{}^{2-}]_0$, mM	5-Cl-phen[b] k_{obs}, s^{-1}	5-Cl-phen[b] k_{cal}, s^{-1}	phen[c] k_{obs}, s^{-1}	phen[c] k_{cal}, s^{-1}	5,6-Me_2phen[d] k_{obs}, s^{-1}	5,6-Me_2phen[d] k_{cal}, s^{-1}
0.166	4.34	4.09				
0.332	7.85	8.27			0.024	0.021
0.664	18.0	16.9			0.048	0.042
1.00			0.366	0.388		
1.33	32.1	35.2			0.093	0.086
1.90	52.8	52.0				
2.00			0.738	0.795		
2.50	73.5	70.8			0.157	0.163
4.00			1.84	1.66		
5.00					0.299	0.335
8.00			3.92	3.63		
10.0					0.616	0.705
15.0					1.07	1.11
16.0			9.50	8.43		
20.0					1.44	1.55
25.0			14.1	15.3		
26.6					2.38	2.19
30.0					2.89	2.54
32.0			21.2	21.6		

[a] pH = 4.67 (acetate buffer), 25.0 °C, μ = 0.10 M, [phen] = 1.0 mM. [b] $[Os(III)]_0$ = 25.3 μM, background electrolyte = NaCl. [c] $[Os(III)]_0$ = 51.1 μM, background electrolyte = $NaCF_3SO_3$. [d] $[Os(III)]_0$ = 34.7 μM, background electrolyte = NaCl.

one standard deviation. A Macintosh II computer was used for the least-squares optimizations.

Results

Properties of the Compounds. Electrochemical and the UV–vis spectral data of the Os(II) complexes are presented in Table I and are in good agreement with the reported values where available.[8,20–22] The 4,7-Me_2phen complex has been studied to a certain extent,[23] but its electrochemical behavior has not been reported. ^{1}H NMR data of the complexes are presented in Table II and are consistent with the assigned structures.

Stoichiometry. The reaction of $S_2O_3{}^{2-}$ with $[Os(phen)_3]^{3+}$ was examined in detail. With $S_2O_3{}^{2-}$ in excess over $[Os(phen)_3]^{3+}$, the sulfur-containing products were determined by ion-pair chromatography. Tetrathionate was the only product detected, the yields of $S_3O_6{}^{2-}$, $S_5O_6{}^{2-}$, and $S_6O_6{}^{2-}$ being insignificant. Quantitative data for the yield of $S_4O_6{}^{2-}$ are presented in Table III. These data indicate that 1 mol of tetrathionate is formed for every 2 mol of Os(III) consumed.

Cationic products formed in the reaction were separated on a cation-exchange column of Sephadex (SP C-25, 40–120-μm bead size) in the Na^+ form. The product solution from a reaction mixture containing 0.23 mM $[Os(phen)_3]^{3+}$ and 2.3 mM $S_2O_3{}^{2-}$ at pH 4.7 was loaded onto the column. After the column was eluted with water and 0.1 M NaCl, the green band was collected with 0.2 M NaCl. From the UV–vis and ^{1}H NMR data this species was identified as $[Os(phen)_3]^{2+}$, recovered in 98% yield. A minor immobile green band was left at top of the column. This appears to be an artifact of the ion-exchange process with all the Os(II) complexes.[17] However, in view of the high yield of the recovered product, the immobile band can only be a minor product of the reaction. On the basis of these results, the stoichiometry of the reaction is

$$2[Os(phen)_3]^{3+} + 2S_2O_3{}^{2-} \rightarrow 2[Os(phen)_3]^{2+} + S_4O_6{}^{2-} \qquad (1)$$

The reactions of $[Os(5\text{-}Cl\text{-}phen)_3]^{3+}$, $[Os(4,7\text{-}Me_2phen)_3]^{3+}$, and $[Os(5,6\text{-}Me_2phen)_3]^{3+}$ with $S_2O_3{}^{2-}$ were not examined in as great detail, but in all cases the UV–vis spectra of the product solutions had λ_{max} values and absorbances entirely consistent with quantitative yields of the corresponding Os(II) complexes.

Kinetics. Kinetic studies were conducted at 25.0 ± 0.1 °C under pseudo-first-order conditions with $S_2O_3{}^{2-}$ in excess over $[Os(phen)_3]^{3+}$. Strong catalysis by Cu^{2+} was observed when a solution of 3.9 μM $Cu(ClO_4)_2{\cdot}6H_2O$ and 2.0 mM $S_2O_3{}^{2-}$ was mixed with an equal volume of 48 μM Os(III) solution at pH 4.67 (acetate buffer). The rate constant was 5.16 s^{-1}, which may be compared with the value of 0.738 s^{-1} obtained with no added Cu^{2+}. When the reactions were conducted in the presence of 1.0 mM 1,10-phenanthroline the catalysis by Cu^{2+} was eliminated, presumably because Cu^{2+} is converted to a noncatalytic phenanthroline complex. Increasing the concentration of phenanthroline to 10 mM had no further effect on the rates. Thus, it was considered that 1.0 mM phenanthroline was adequate to eliminate catalysis by adventitious Cu^{2+}, and all further studies with $[Os(phen)_3]^{3+}$ and the other oxidants were conducted with this additive. Under these conditions semilog plots were linear over 3 half-lives, and values of k_{obs}, defined by

$$-d[Os(phen)_3{}^{3+}]/dt = k_{obs}[Os(phen)_3{}^{3+}] \qquad (2)$$

were obtained by exponential and semilogarithmic fits to the experimental data.

Pseudo-first-order rate constants were independent of pH over the range from 4.7 to 6.1. Reactions were not investigated in more acidic solutions because of the acid decomposition of $S_2O_3{}^{2-}$, and alkaline conditions were avoided because of the base decomposition of $[Os(phen)_3]^{3+}$. The rates were quite sensitive to the concentration of $S_2O_3{}^{2-}$, and values of k_{obs} obtained from 1.0 to 32 mM $S_2O_3{}^{2-}$ are presented in Table IV. A few experiments were performed to study the kinetic effects of the reaction products. $[Os(phen)_3]^{2+}$ was found to retard the reaction rate mildly. When 0.64 mM $[Os(phen)_3]^{2+}$ was added to a solution of 51 μM Os(III) containing 2 mM $S_2O_3{}^{2-}$, the rate constant decreased from 0.738 to 0.536 s^{-1}. Similarly for a solution with 16 mM thiosulfate the rate constant decreased from 9.5 to 6.2 s^{-1}. On the other hand, addition of 10 mM $S_4O_6{}^{2-}$ increased the rate constant from 0.738

---

(20) Dwyer, F. P.; Gibson, N. A.; Gyarfas, E. C. *J. Proc. R. Soc. N. S. Wales* **1950**, *84*, 80–82.

(21) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309–1319.

(22) Sutin, N.; Creutz, C. In *Inorganic and Organometallic Photochemistry*; Wrighton, M. S., Ed.; American Chemical Society: Washington, DC, 1987; pp 1–27.

(23) Stalnaker, N. D.; Solenberger, J. C.; Wahl, A. C. *J. Phys. Chem.* **1977**, *81*, 601–604.

Table V. Kinetics of Reduction of $[Os(4,7\text{-}Me_2phen)_3]^{3+}$ by $[S_2O_3^{2-}]$[a]

$[S_2O_3^{2-}]_0$, mM	k_{obs}, s^{-1}	k_{cal}, s^{-1}	k'_{obs}, M s^{-1}
2.5	4.90×10^{-3}	5.55×10^{-3}	5.99×10^{-7}
5.0	1.42×10^{-2}	1.22×10^{-2}	7.46×10^{-7}
10.0	3.17×10^{-2}	2.90×10^{-2}	1.26×10^{-6}
20	7.89×10^{-2}	7.60×10^{-2}	2.23×10^{-6}
30	1.31×10^{-1}	1.41×10^{-1}	3.70×10^{-6}

[a] 25.0 °C, $\mu = 0.10$ M (NaCl), [phen] = 1.0 mM, $[Os(III)]_0 = 124$ μM, pH = 6.05 (cacodylate buffer).

to 0.864 s^{-1}. Although the origin of these effects is not fully understood, it is clear that the concentrations of $S_4O_6^{2-}$ and $[Os(phen)_3]^{2+}$ formed as reaction products are so low as to have negligible effects on the kinetics.

The reaction of $[Os(5\text{-}Cl\text{-}phen)_3]^{3+}$ with $S_2O_3^{2-}$ was much faster than that of $[Os(phen)_3]^{3+}$ under similar conditions, as demonstrated in Table IV. Otherwise, the qualitative features of the kinetics were quite similar.

Other oxidants used in the study were $[Os(5,6\text{-}Me_2phen)_3]^{3+}$ and $[Os(4,7\text{-}Me_2phen)_3]^{3+}$, both of which reacted with $S_2O_3^{2-}$ relatively slowly. Semilog plots for these oxidants exhibited curvature, which had the appearance of parallel first- and zero-order kinetics. Tests were performed with both oxidants to determine if this non-first-order behavior was due to insufficient scavenging of Cu(II) by phen: under conditions of 20 mM $S_2O_3^{2-}$, increasing the concentration of phen from 1 to 10 mM and deliberately adding Cu(II) had no effect, and thus, we believe that catalysis by Cu(II) is not a problem. For $[Os(5,6\text{-}Me_2phen)_3]^{3+}$ the curvature appeared in the later part of the third half-life and was not a major problem. In this case tests with various optical filters and monochromator slit widths demonstrated that the non-pseudo-first-order behavior was not due to photolysis by the monitoring light. Likewise, identical behavior was found for solutions saturated in air and for solutions rigorously sparged with argon. Pseudo-first-order rate constants were evaluated over the first half-life to minimize any possible errors introduced by deviations in the latter half-lives. Values of k_{obs} so obtained are presented in Table IV.

More difficulty was encountered with $[Os(4,7\text{-}Me_2phen)_3]^{3+}$, which was the most sluggish of the oxidants. Initial studies of this species were conducted at pH 4.7. Curvature in the semilog plots was detectable immediately after the first half-life; the problem was more severe at the higher concentrations of thiosulfate. On the other hand, the linearity of the semilog plots improved with increasing $[Os(III)]_0$. Concentrations of Os(III) greater than 0.17 mM were not employed because of the high absorbance of the product solutions. With 30 mM $S_2O_3^{2-}$, which is the highest concentration of $S_2O_3^{2-}$ used, rates were found to increase with standing time of the solutions. The effect of standing time could be reduced by decreasing the concentration of $S_2O_3^{2-}$ and by increasing the pH of the reaction from 4.67 to 6.05. This relates to the decomposition of thiosulfate, which occurs with a rate law first order in $[H^+]$ and second-order in $[S_2O_3^{2-}]$.[24] In order to minimize these complications, all further studies were conducted at high (0.17 mM) $[Os(III)]_0$ and at pH 6.05 with freshly prepared solutions. Even under these conditions the exponential plots showed significant deviation from pseudo-first-order behavior, and so the time-dependent decays were analyzed according to the differential rate law

$$-d[Os(4,7\text{-}Me_2phen)_3^{3+}]/dt = k_{obs}[Os(III)] + k'_{obs} \quad (3)$$

for which the integrated rate law is

$$[Os(III)] = ([Os(III)]_0 + k'_{obs}/k_{obs}) \exp(-k_{obs}t) - k'_{obs}/k_{obs} \quad (4)$$

Fits over the entire time course of these decays were very good, and the fitted values of k_{obs} and k'_{obs} are presented in Table V. The pseudo-zero-order (k'_{obs}) term was not investigated in great detail, but it was found to be approximately first order with respect to $[S_2O_3^{2-}]$ and $[Os]_{tot}$ and to be independent of pH.

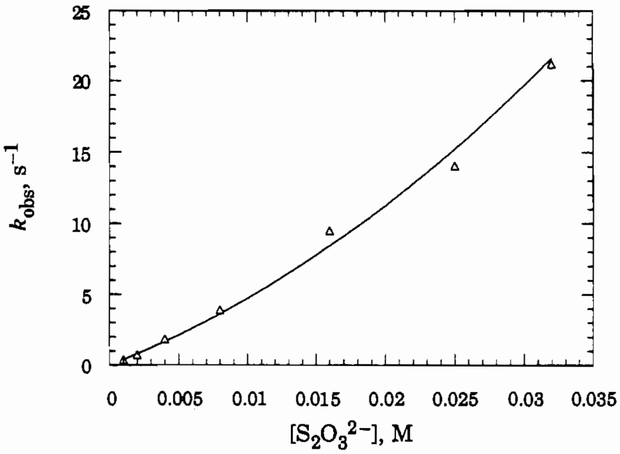

Figure 1. Effect of $[S_2O_3^{2-}]$ on the reduction of $[Os(phen)_3]^{3+}$ at μ = 0.10 M and 25.0 °C. Data are as in Table IV. The solid line is calculated from the fit of experimental rate constants by rate law (5).

Table VI. Rate Constants for Reduction of $[OsL_3]^{3+}$ by Thiosulfate[a]

ligand	k_1, M^{-1} s^{-1}	k_2, M^{-2} s^{-1}
4,7-Me_2phen	(1.00 ± 0.12)	$(4.52 \pm 0.99) \times 10^1$
5,6-Me_2phen	$(3.17 \pm 0.18) \times 10^1$	$(3.55 \pm 1.3) \times 10^2$
phen	$(1.90 \pm 0.11) \times 10^2$	$(4.61 \pm 0.85) \times 10^3$
5-Cl-phen	$(1.22 \pm 0.064) \times 10^4$	$(7.80 \pm 4.8) \times 10^5$

[a] 25.0 °C, $\mu = 0.10$ M.

For all four oxidants the dependence of the pseudo-first-order (k_{obs}) term on $[S_2O_3^{2-}]$ is greater than first order, as shown for $[Os(phen)_3]^{3+}$ in Figure 1. A good fit with the rate law

$$k_{obs} = 2k_1[S_2O_3^{2-}] + 2k_2[S_2O_3^{2-}]^2 \quad (5)$$

was obtained, with the values of k_{cal} given in Table IV and k_1 and k_2 as indicated in Table VI. As shown by the values of k_{cal} in Table IV, the fit for $[Os(5\text{-}Cl\text{-}phen)_3]^{3+}$ is quite good, but as shown by the standard deviations in Table VI, the value of k_2 is not very well defined. For $[Os(5,6\text{-}Me_2phen)_3]^{3+}$ and $[Os(4,7\text{-}Me_2phen)_3]^{3+}$ the fits with rate law 5 were good, with values of k_{cal} given in Tables IV and V, respectively. In the case of $[Os(4,7\text{-}Me_2phen)_3]^{3+}$ the actual uncertainty for k_1 is probably greater than the statistical value cited in Table VI because k_1 is defined by the values of k_{obs} at low $[S_2O_3^{2-}]$, and under these conditions the zero-order (k'_{obs}) term is dominant.

Discussion

The objective of this research was to determine rate constants for electron transfer between thiosulfate and a graded series of substitution-inert oxidants. We believe this objective has been achieved, but only after surmounting several complications. In the following discussion the complications are described first, then the general features of the intrinsic reaction mechanism are presented, and then the specific features of the two different electron-transfer pathways are discussed.

Potential Complications. The Os(II) complexes, although reported in the literature, were rather difficult to obtain in a pure state in high yield. Retrospectively, the most effective general method would be that described in the preparation of $[Os(4,7\text{-}Me_2phen)_3]Cl_2$. Interestingly, we found that ^1H NMR spectroscopy was not an adequate measure of purity because the method is insensitive to paramagnetic Os(III) contaminants, notably the osmium(III) bis(phenanthroline) complexes. These impurities were detected by CV and OSWV methods, and they were removed by column chromatography.

Copper(II) was found to be an excellent catalyst for the oxidation of $S_2O_3^{2-}$ by Os(III). Similar results have been reported for other oxidants.[4,25] In the present case this catalysis was so

---

[24] Dennis, C. R.; Leipoldt, J. G.; Basson, S. S.; Lamprecht, G. J. *Polyhedron* **1985**, *4*, 1621–1624.

effective that reproducible results could only be obtained by masking adventitious Cu(II) with phenanthroline. Traditional masking agents such as EDTA could not be used because of their susceptibility to oxidation by Os(III). We did not study the catalytic pathway in sufficient detail to comment on its rate law or mechanism, but we note that a kinetic study of the rapid oxidation of $S_2O_3^{2-}$ by ammoniacal Cu(II) has been reported.[3]

The most serious difficulty affecting the kinetic studies was the decomposition of thiosulfate solutions. Thiosulfate is widely known to undergo such decomposition: the spontaneous rate is first order in acid and second order in thiosulfate.[26] Under our conditions this decomposition was not a problem for the faster reactions, but for $[Os(4,7\text{-}Me_2phen)_3]^{3+}$, the most sluggish oxidant of the series, decomposition of thiosulfate during the kinetic runs led to non-pseudo-first-order behavior. This is believed to arise because Os(III) is consumed by reacting with a decomposition product, which can lead to pseudo-zero-order kinetics. Similar results have been reported for the oxidations of $S_2O_3^{2-}$ by $Fe(CN)_6^{3-}$ and $W(CN)_8^{3-}$, except for these weaker oxidants the rates were strictly zero order with respect to [oxdiant].[24,27,28] Good agreement was reported between the spontaneous decomposition kinetics and the kinetics of oxidation by $Fe(CN)_6^{3-}$ and $W(CN)_8^{3-}$,[24,28] but a completely different rate law was reported in a subsequent study of the oxidation by $Fe(CN)_6^{3-}$ at higher pH.[27] Moreover, an additional pathway catalytic in cations was reported in the earlier study of the $Fe(CN)_6^{3-}$ reaction.[28] In the present case we see apparent decomposition rates that are much greater than would have been predicted by these prior studies. Our tentative suggestion is that the cationic osmium complexes have a dual role, acting both as catalysts for decomposition of $S_2O_3^{2-}$ and as oxidants (in the Os(III) state) for the decomposition products.

In summary, we believe that the reactants have been prepared in adequate purity and that the Cu^{2+} catalysis pathway has been eliminated. Effects due to $S_2O_3^{2-}$ decomposition can be neglected for the oxidations by $[Os(5\text{-}Cl\text{-}phen)_3]^{3+}$, $[Os(phen)_3]^{3+}$, and $[Os(5,6\text{-}Me_2phen)_3]^{3+}$. However, in the case of $[Os(4,7\text{-}Me_2phen)_3]^{3+}$ the effects of $S_2O_3^{2-}$ decomposition are sufficient to give some uncertainty in the rate constants for direct oxidation of $S_2O_3^{2-}$.

General Mechanism. The direct reaction of $S_2O_3^{2-}$ with Os(III) forms $S_4O_6^{2-}$ and the corresponding Os(II) complex as indicated in reaction 1. Note that unlike the reaction of $[Ru(NH_3)_4phen]^{3+}$ with SO_3^{2-},[18] the phenanthroline ring system is not altered. Tetrathionate is commonly but not invariably the product in oxidations of thiosulfate. For example, sulfur and sulfate were reported as products in the oxidation by $Fe(CN)_6^{3-}$,[27] sulfate alone can be obtained with a large excess of $[IrCl_6]^{2-}$,[4] and oxidation of coordinated $S_2O_3^{2-}$ can lead to coordinated $S_2O_5^{2-}$.[29] However, formation of $S_4O_6^{2-}$ is not sufficient to specify the mechanism, since it is formed in the oxidation by $[W(CN)_8]^{3-}$ (which has rate-limiting decomposition of $S_2O_3^{2-}$), by $[Au(NH_3)_4]^{3+}$ (which reacts via an inner-sphere mechanism), and by $[Mo(CN)_8]^{3-}$ (which has an outer-sphere mechanism).[1,5,24]

If the $S_2O_3^{2-}$ decomposition effects are neglected, the direct oxidation by Os(III) has the rate law

$$-d[Os(III)]/dt = (2k_1[S_2O_3^{2-}] + 2k_2[S_2O_3^{2-}]^2)[Os(III)] \quad (6)$$

Similar two-term rate laws have been reported for oxidations of I^- and SCN^-,[8,30] for example, but this is the first report of such a rate law in $S_2O_3^{2-}$ chemistry. It is the k_2 term that is unique. A mechanism for the reaction of $S_2O_3^{2-}$ with the various Os(III) complexes that is consistent with the observed stoichiometry and rate law is presented in Scheme I.

Scheme I

$$[Os(III)] + S_2O_3^{2-} \rightleftarrows [Os(II)] + S_2O_3^- \quad k_1, k_{-1}, K_1 \quad (7)$$

$$[Os(III)] + 2S_2O_3^{2-} \rightleftarrows [Os(II)] + S_4O_6^{3-} \quad k_2, k_{-2}, K_2 \quad (8)$$

$$S_2O_3^- + S_2O_3^{2-} \rightleftarrows S_4O_6^{3-} \quad K_3 \quad (9)$$

$$S_4O_6^{3-} + [Os(III)] \rightarrow [Os(II)] + S_4O_6^{2-} \quad k_4 \quad (10)$$

The existence of the proposed intermediates, aqueous thiosulfate and tetrathionate radicals, is well supported in the literature.[31] Schoneshofer reported values of 8×10^8 M^{-1} s^{-1} and $<8.0 \times 10^2$ s^{-1} for the forward and reverse reactions of equilibrium 9.[32] In contrast to this, Mehnert and co-workers measured the reverse rate constant to be 2.5×10^6 s^{-1}.[31,33] According to Mehnert et al., the work of Schoneshofer was in error because the spectra of $S_2O_3OH^{2-}$ and $S_2O_3^-$ were incorrectly assigned to $S_2O_3^-$ and $S_4O_6^{3-}$. Thus, there is reason to doubt the accuracy of Schoneshofer's value for the forward rate constant. On the other hand, the forward rate constant is expected to be close to the diffusion-controlled limit, as it is for the analogous reactions forming I_2^-, $(SCN)_2^-$, and related species.[34] Under the present conditions, equilibrium 9 would be established rapidly relative to the k_{-1} and k_{-2} steps, and it would lead to comparable concentrations of the two radicals. As is discussed below, tetrathionate radical is a good reducing agent, and so the k_4 step is expected to be fast. These ideas are supported by the observation that Os(II) inhibits the kinetics only weakly. With these assumptions the proposed mechanism leads to the observed rate law; the measured rate constant k_1 thus refers to the second-order electron-transfer process between Os(III) and $S_2O_3^{2-}$, and k_2 reflects the overall third-order process in which electron transfer to Os(III) and formation of the S–S bond in $S_4O_6^{3-}$ occur simultaneously. Since both the Os(III) and Os(II) complexes are substitution inert, the k_1 and k_2 pathways must be formally outer-sphere processes.

A mechanism similar to that in Scheme I, except for replacement of the k_4 step by dimerization of the $S_2O_3^-$ radicals, is considered unlikely. This is because such a process would lead to a high steady-state concentration of $S_2O_3^-$, which would then lead to kinetic inhibition by Os(II). However, Os(II) was shown not to inhibit these reactions. Significant kinetic inhibition is seen in oxidations of N_3^-, but in these systems the N_3 intermediate is not scavenged to form an easily oxidized species.[35]

Yet another variation on Scheme I is to replace the k_2 step by the reactions

$$[Os(III)] + S_2O_3^{2-} \rightleftarrows [Os(III)],S_2O_3^{2-} \quad K_{ip} \quad (11)$$

and

$$[Os(III)],S_2O_3^{2-} + S_2O_3^{2-} \rightleftarrows [Os(II)],S_2O_3^{2-} + S_2O_3^- \quad k_1', k_{-1}' \quad (12)$$

This would lead to the identification of k_2 as $K_{ip}k_1'$. In principle this alternative could be tested, because the substantial anticipated value of K_{ip} would lead to kinetic saturation at high concentrations of $S_2O_3^{2-}$. Unfortunately, the quality of our data do not permit this test to be performed with confidence. One important deficiency of this ion-pair mechanism is that it introduces two additional intermediates; in the pursuit of simplicity we ignore the ion-pair mechanism in the following discussion.

There have been several prior kinetic studies of oxidation of $S_2O_3^{2-}$ by coordination compounds. In the case of $[Co(ox)_3]^{3-}$ only a copper(II)-catalyzed pathway could be detected.[25] Rate-limiting decomposition of $S_2O_3^{2-}$ was found when $[Fe(CN)_6^{3-}]$ and $[W(CN)_8]^{3-}$ were the oxidants.[24,27,28] With $[Ag(OH)_4]^-$, $[Fe(H_2O)_6]^{3+}$, Cr(VI), $[Au(NH_3)_4]^{3+}$, and partially hydrolyzed $[AuCl_4]^-$, coordination of $S_2O_3^{2-}$ precedes the redox

---

(25) Kimura, M.; Ishibashi, M. *Inorg. Chim. Acta* **1987**, *129*, 69–74.
(26) Dinegar, R. H.; Smellie, R. H.; La Mer, V. K. *J. Am. Chem. Soc.* **1951**, *73*, 2050–2054.
(27) Panda, R. K.; Neogi, G.; Ramaswami, D. *Bull. Soc. Chim. Belg.* **1981**, *90*, 1005–1016.
(28) Howlett, K. E.; Wedzicha, B. L. *Inorg. Chim. Acta* **1976**, *18*, 133–138.
(29) Johnson, M. D.; Balahura, R. J. *Inorg. Chem.* **1988**, *27*, 3104–3107.
(30) Stanbury, D. M.; Wilmarth, W. K.; Khalaf, S.; Po, H. N.; Byrd, J. E. *Inorg. Chem.* **1980**, *19*, 2715–2722.
(31) Mehnert, R.; Brede, O. *Radiat. Phys. Chem.* **1984**, *23*, 463–468.
(32) Schoneshofer, M. *Int. J. Radiat. Phys. Chem.* **1973**, *5*, 375–386.
(33) Mehnert, R.; Brede, O.; Janovsky, I. *Radiochem. Radioanal. Lett.* **1982**, *53*, 299–310.
(34) Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027–1284.
(35) Ram, M. S.; Stanbury, D. M. *J. Phys. Chem.* **1986**, *90*, 3691–3696.

Table VII. LFER and Marcus Calculations for the k_1 Pathway

species no.	oxidant	E_f, V	k_1, $M^{-1}\ s^{-1}$	k_{-1}, $M^{-1}\ s^{-1}$[a]	k_{11}(cal), $M^{-1}\ s^{-1}$[j]	k_{22}, $M^{-1}\ s^{-1}$	r[b]
1	$[Os(4,7\text{-}DMP)_3]^{3+}$[c]	0.653	1.00	8.7×10^{10}	2.6×10^2	2×10^9[e]	7.4
2	$[Os(5,6\text{-}DMP)_3]^{3+}$[c]	0.776	3.17×10^1	2.3×10^{10}	2.3×10^2	2×10^9[e]	7.4
3	$[Os(phen)_3]^{3+}$	0.840	1.90×10^2	1.1×10^{10}	1.7×10^2	2×10^9[e]	6.7
4	$[IrBr_6]^{2-}$[d]	0.843	1.75×10^1	9.7×10^8	1.3×10^3	2×10^8[f]	4.5
5	$[IrCl_6]^{2-}$[d]	0.892	1.74×10^2	1.4×10^9	1.3×10^7	2×10^5[g]	4.4
6	$[Os(5\text{-}Cl\text{-}phen)_3]^{3+}$	0.944	1.22×10^4	1.3×10^{10}	6.8×10^3	2×10^9[e]	7.4
7	$[CoW_{12}O_{40}]^{5-}$[h]	1.0	0.39	7.0×10^4			
8	$[Fe(bpy)_3]^{3+}$[d]	1.06	9.50×10^4	1.1×10^9	3.1×10^3	5×10^8[i]	6.8

[a] $k_{-1} = k_1/K_1$ for reaction 7; $E°$ of 1.30 V was used for $S_2O_3^-/S_2O_3^{2-}$. [b] Estimated. [c] DMP is dimethylphenanthroline. [d] Reference 4. [e] Reference 7. [f] Reference 30. [g] Reference 57. [h] Reference 6. [i] Reference 58. [j] Average $k_{11} = 3.2 \times 10^3\ M^{-1}\ s^{-1}$.

process.[1,36-38] Inner-sphere mechanisms of this sort were also inferred for oxidations by $[OsO_4(OH)_2]^{2-}$, $[Co(nta)(H_2O)_2]$, and $[Cu(NH_3)_4]^{2+}$.[2,3,39] $[Mo(CN)_8]^{3-}$, which is a stronger oxidant than $[W(CN)_8]^{3-}$, oxidizes $S_2O_3^{2-}$ directly, but the reaction is catalyzed by alkali-metal ions to the degree that the intrinsic electron-transfer rate constant is unknown.[5] Oxidation by $[PtCl_6]^{2-}$ occurs with a simple second-order rate law and presumably has a mechanism similar to that in Scheme I;[40] unfortunately, the uncertain nature of the Pt(III) intermediates precludes a more detailed examination. A study of the oxidation by $[CoW_{12}O_{40}]^{5-}$ showed that the reaction had an alkali metal ion catalyzed pathway and also an uncatalyzed direct electron-transfer pathway.[6] Direct overall second-order electron-transfer pathways were also observed in the oxidations by $[IrCl_6]^{2-}$, $[IrBr_6]^{2-}$, and $[Fe(bpy)_3]^{3+}$.[4] The results from these last two papers are quite pertinent to the present study and are further discussed below.

Reduction Potential of $S_2O_3^-$. An important test of Scheme I is whether the principle of detailed balancing gives values of k_{-1} that do not exceed the limits of diffusion control. Such a test can be performed by using the measured values of E_f for the Os(III)/Os(II) couples and E_f for the $S_2O_3^-/S_2O_3^{2-}$ couple to calculate K_1. Then, by use of the relationship $K_1 = k_1/k_{-1}$, values of k_{-1} can be obtained from the measured values of k_1. The difficulty in such an approach is that the required value of E_f for the $S_2O_3^-/S_2O_3^{2-}$ couple is not known very accurately.

In a recent critical summary of efforts to determine this potential a value of 1.35 V was selected.[41] This estimate is now known to be slightly in error because of computational errors that have come to light. One of the errors occurred in the original estimate,[4] in which a value of 1.35 V was derived by combining the previously estimated potential for the SCN/SCN⁻ couple ($E°$ = 1.66 V) with pulse-radiolytically determined equilibrium constants for the reactions

$$SCNS_2O_3^{2-} \rightleftarrows SCN^- + S_2O_3^- \tag{13}$$

$$SCN + S_2O_3^{2-} \rightleftarrows SCNS_2O_3^{2-} \tag{14}$$

On the basis of these data, the correct calculation yields 1.40 V for the $S_2O_3^-/S_2O_3^{2-}$ potential. However, a computational error was also committed in determining $E°$ for the SCN/SCN⁻ couple.[30] This potential was estimated by combining $E°$ for the I/I⁻ couple (1.33 V) and pulse-radiolytically determined equilibrium constants for the reactions

$$ISCN^- \rightleftarrows I^- + SCN \tag{15}$$

$$I + SCN^- \rightleftarrows ISCN^- \tag{16}$$

The correct potential for the SCN/SCN⁻ couple should have been 1.60 V, which is in agreement with Martins's result that was based on the same data.[42] Other workers have recommended potentials of 1.62 V for the SCN/SCN⁻ couple.[8,43] On this basis, we presently recommend a value of 1.61 V for the SCN/SCN⁻ couple. When this value is combined with the equilibrium constants for reactions 11 and 12,[44] a value of 1.34 V can be derived for the $S_2O_3^-/S_2O_3^{2-}$ couple.

A partially independent estimate of $E°$ for the $S_2O_3^-/S_2O_3^{2-}$ couple can be derived from a recent determination[45] of $E°$ (1.29 ± 0.01 V) for the $(SCN)_2^-/2SCN^-$ couple, which was obtained by measuring the equilibrium constant for the reaction

$$(SCN)_2^- + [Ru(bpy)_3]^{2+} \rightleftarrows 2SCN^- + [Ru(bpy)_3]^{3+} \tag{17}$$

When $E°$ for the $(SCN)_2^-/2SCN^-$ couple is combined with the equilibrium constants[44] for the reactions

$$(SCN)_2^- + S_2O_3^{2-} \rightleftarrows SCN^- + SCNS_2O_3^{2-} \tag{18}$$

$$SCNS_2O_3^{2-} \rightleftarrows SCN^- + S_2O_3^- \tag{19}$$

a value of 1.34 V can be calculated for $E°$ for the $S_2O_3^-/S_2O_3^{2-}$ couple, which is in exact agreement with the value derived above. Note that all the estimates of this reduction potential depend on Schoneshofer's studies of the $S_2O_3^-$ radical. Mehnert et al. have argued that Schoneshofer's data are in error because of some erroneous spectral assignments.[31,33] Consequently there is still considerable uncertainty regarding the value of $E°$ for the $S_2O_3^-/S_2O_3^{2-}$ couple, and the value derived above is used here only as an initial estimate.

From this potential (1.34 V), values of k_{-1} calculated for the reactions of $[Os(4,7\text{-}Me_2phen)_3]^{2+}$, $[Os(5,6\text{-}Me_2phen)_3]^{2+}$, $[Os(phen)_3]^{2+}$, and $[Os(5\text{-}Cl\text{-}phen)_3]^{2+}$ are 4.12×10^{11}, 1.10×10^{11}, 5.44×10^{10}, and $6.09 \times 10^{10}\ M^{-1}\ s^{-1}$, respectively. A reasonable diffusion-controlled upper limit for k_{-1} is $2.5 \times 10^{10}\ M^{-1}\ s^{-1}$. This value is based on the measured rate constants of 2.5×10^{10}, 1.4×10^{10}, 1.1×10^{10}, and $1.0 \times 10^{10}\ M^{-1}\ s^{-1}$ for the reactions of Br_2^- with $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{2+}$, $[Co(sep)]^{2+}$, $[Ni(CR\text{-}2H)]^{2+}$, and $[Ni(CR\text{-}2H)Br]^{2+}$, respectively, and a rate constant of $1.2 \times 10^{10}\ M^{-1}\ s^{-1}$ for reaction of CO_2^- with NiL^{2+},[34] all of which have the same charge type and were measured at 0.10 M ionic strength. This implies that the value of $E°$ for the $S_2O_3^-/S_2O_3^{2-}$ couple (1.34 V) is too high.

If $E°$ is somewhat arbitrarily adjusted to a value of 1.30 V, then the calculated k_{-1} values are 8.7×10^{10}, 2.30×10^{10}, 1.14×10^{10}, and 1.28×10^{10} for $[Os(4,7\text{-}Me_2phen)_3]^{2+}$, $[Os(5,6\text{-}Me_2phen)_3]^{2+}$, $[Os(phen)_3]^{2+}$, and $[Os(5\text{-}Cl\text{-}phen)_3]^{2+}$, respectively. Except for $[Os(4,7\text{-}Me_2phen)_3]^{2+}$ these are all reasonably within the diffusion limits. Because of the various problems encountered in the kinetic study of this last oxidant, further adjustment of $E°$ is unwarranted. In view of the accumulated statistical uncertainties associated with the derived value of 1.34 V and the disagreement between the results of Mehnert et al.[31] and those of Schoneshofer regarding the properties of $S_2O_3^-$,[32] the adjusted value of 1.30 V seems to be the best present estimate, although a lower value cannot be ruled out. With this adjusted potential there is no conflict between the values of k_1, the constraints of diffusion

---

(36) Rush, J. D.; Kirschenbaum, L. J. *Inorg. Chem.* **1985**, *24*, 744–748.
(37) Page, F. M. *Trans. Faraday Soc.* **1960**, *56*, 398–406.
(38) Muirhead, K. A.; Haight, G. P.; Beattie, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 3006–3010.
(39) Thacker, M. A.; Higginson, W. C. E. *J. Chem. Soc., Dalton Trans.* **1975**, 704–711.
(40) Sen Gupta, K. K.; Das, S.; Sen Gupta, S. *Transition Met. Chem.* **1988**, *13*, 155–159.
(41) Stanbury, D. M. *Adv. Inorg. Chem.* **1989**, *33*, 69–138.
(42) Martins, L. J. A. *J. Chem. Soc., Faraday Trans.* **1982**, *78*, 533–543.
(43) Schwarz, H. A.; Bielski, B. H. *J. Phys. Chem.* **1986**, *90*, 1445–1448.
(44) Schoneshofer, M. *Ber. Bunsen-Ges. Phys. Chem.* **1973**, *77*, 257–262.
(45) DeFillipis, M. R.; Faraggi, M.; Klapper, M. H. *J. Phys. Chem.* **1990**, *94*, 2420–2424.

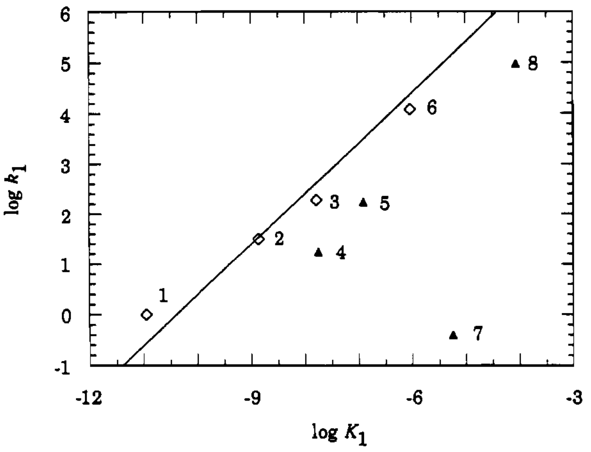

Figure 2. LFER for oxidation of $[S_2O_3^{2-}]$ by the k_1 pathway. Points are numbered as in Table VII, and the Os(III) data are represented by diamonds. The solid line is drawn with a slope of 1.0 and an intercept of 10.4, as explained in the text. K_1 values are estimated from an $E°$ of 1.30 V for the $S_2O_3^-/S_2O_3^{2-}$ couple.

control, and the mechanism of Scheme I.

Details of the k_1 Path. A plot of $\log k_1$ as a function $\log K_1$ is presented in Figure 2, with the data for the Os(III) complexes represented by diamonds. Values of K_1 in this figure were calculated by using the reduction potentials in Table VII and a value of 1.30 V for the reduction potential of the $S_2O_3^-/S_2O_3^{2-}$ couple as discussed above. The four points for Os(III) constitute a good LFER, and a linear least-squares fit to these points has a slope of 0.82. As noted above, there is considerable uncertainty in the k_1 value for $[Os(4,7\text{-}Me_2phen)_3]^{3+}$; if this point is omitted the linear least-squares slope increases to 0.92. Note that these calculated slopes are independent of the value selected for $E°$ for the $S_2O_3^-/S_2O_3^{2-}$ couple. Other points included in Figure 2 are literature values for oxidations by $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, $[IrBr_6]^{2-}$, and $[CoW_{12}O_{40}]^{5-}$.[4,6] It is clear that these points deviate substantially from the LFER defined by the Os(III) data.

In order to understand significance of Figure 2, it is helpful to discuss the k_1 step in terms of Scheme II.

Scheme II

$$[Os(III)] + S_2O_3^{2-} \rightleftarrows [Os(III)],S_2O_3^{2-} \quad K_{1ip} \tag{20}$$

$$[Os(III)],S_2O_3^{2-} \rightleftarrows [Os(II)],S_2O_3^- \quad k_{1et}, k_{-1et} \tag{21}$$

$$[Os(II)],S_2O_3^- \rightleftarrows [Os(II)] + S_2O_3^- \quad k_{1d}, k_{-1d} \tag{22}$$

It is assumed, of course, that ion-pair formation K_{1ip} occurs in a rapid preequilibrium. If the steady-state approximation is applied to the various ion pairs involved, k_1 is related to Scheme II by the equation

$$k_1 = K_{1ip}k_{1et}k_{1d}/(k_{-1et} + k_{1d}) \tag{23}$$

For the limiting case of $k_{-1et} \gg k_{1d}$ we find

$$k_1 = K_{1ip}k_{1et}k_{1d}/k_{-1et} = K_1k_{-1d} \tag{24}$$

i.e., the reaction is diffusion controlled in the sense that it is controlled by the rate of diffusion apart of the products. In the case of $k_{-1et} \ll k_{1d}$ the relation

$$k_1 = K_{1ip}k_{1et} \tag{25}$$

is obtained, which means that the reaction is activation controlled and that electron transfer is rate limiting. In the diffusion-controlled case, for a series of oxidants of the same charge, k_{-1d} is expected to be a constant, and hence, a plot of $\log k_1$ vs $\log K_1$ should be linear with a slope of unity and an intercept of $\log k_{-1d}$. In the activation-controlled case electron transfer is rate limiting, and since the reactions are of the outer-sphere type, it is expected that a plot of $\log k_1$ vs $\log K_1$ will have the characteristics predicted by Marcus theory. In such a case the plot will have a slope less than unity and somewhat greater scatter.

Figure 2 is discussed first in terms of the diffusion-controlled mechanism. For such a mechanism, ideal behavior for the Os(III) complexes is indicated by the solid line, which is drawn with a slope of 1.0 and an intercept of 10.4. The good agreement of the three faster Os(III) oxidants indicates that these reactions could well be diffusion controlled. Points for oxidants $[Os(4,7\text{-}Me_2phen)_3]^{3+}$, $[IrCl_6]^{2-}$, $[IrBr_6]^{2-}$, $[Fe(bpy)_3]^{3+}$, and $[CoW_{12}O_{40}]^{5-}$ deviate substantially from the solid line. The deviation of $[Os(4,7\text{-}Me_2phen)_3]^{3+}$ can be understood because of the considerable uncertainty regarding the value of k_1 for this oxidant. The two points for $[IrCl_6]^{2-}$ and $[IrBr_6]^{2-}$ are expected to deviate because of their ionic charge. There is no well-established diffusion-controlled rate constant for reactions of this charge type at 0.1 M ionic strength, but a value of 7×10^8 M^{-1} s^{-1} can be estimated on the basis of the reaction of CO_2^- with $[Fe(CN)_6]^{3-}$.[34] As shown in Table VII, the values of k_{-1} for the reactions of $[IrCl_6]^{2-}$ and $[IrBr_6]^{2-}$ are in reasonable agreement with this rate constant, and thus these two reactions are consistent with a diffusion-controlled mechanism. Experimental error is tentatively proposed to explain the deviation of the point for $[Fe(bpy)_3]^{3+}$. This reaction is very fast, with rate constants near the limit of the stopped-flow method. Moreover, the reported rate constant was based on a triplicate run at a single thiosulfate concentration, and at low temperature (where the dependence on $[S_2O_3^{2-}]$ was investigated) the k_{obs} data reveal a peculiar term in the rate law that is zero order with respect to $[S_2O_3^{2-}]$. The point of greatest deviation in Figure 2 is that for the reaction of $[CoW_{12}O_{40}]^{5-}$. Such an oxidant poses severe electrostatic problems that could distort the values of k_1 and K_1. Indeed, cation catalysis was reported for this reaction. For these reasons this reaction is excluded from further consideration. In summary, it appears as though the diffusion-controlled mechanism is capable of explaining the behavior in Figure 2.

An alternative approach is to treat the data in Figure 2 in terms of Marcus theory. For this purpose the following relationships are used:[46]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \tag{26}$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln (k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT]} \tag{27}$$

$$W_{12} = \exp[(-w_{12} - w_{21} + w_{11} + w_{22})/2RT] \tag{28}$$

$$w_{ij} = (4.23Z_iZ_j)/(a(1 + 0.328a(\mu^{1/2}))) \tag{29}$$

k_{11} and k_{22} represent the self-exchange rate constants for $S_2O_3^-/S_2O_3^{2-}$ and various complexes, respectively. k_{12} is the electron-transfer rate constant (k_1), while K_{12} is the equilibrium constant for k_1 pathway (K_1). Z, the collision rate, is taken as 1×10^{12} M^{-1} s^{-1}. Z_i and Z_j are the ionic charges on the respective species, and a is the center-to-center distance when they are touching. W_{12} is the electrostatic work term. The f factor and work terms are included in order to accommodate the wide range of driving forces and charge types involved in these reactions. It has been assumed that $S_2O_3^{2-}$ and $S_2O_3^-$ have radii of 3.3 Å, and R is taken as 1.98×10^{-3} kcal mol^{-1} K^{-1}. These equations were solved iteratively in order to obtain the values of k_{11} (cal) presented in Table VII. Within the Os(III) series these values range from 1.7×10^2 M^{-1} s^{-1} for $[Os(phen)_3]^{3+}$ to 6.8×10^3 M^{-1} s^{-1} for $[Os(5\text{-}Cl\text{-}phen)_3]^{3+}$. Because of the quadratic dependence of k_{11} (cal) on k_1, this range in k_{11} (cal) is equivalent to a 6-fold range in k_1, which is not unacceptable. On the other hand, the value of k_{11} (cal) derived from the reaction of $[IrCl_6]^{2-}$ is much larger (1.3×10^7 M^{-1} s^{-1}). Although we have no simple explanation for this deviation, it would be unreasonable to reject the activation-controlled mechanism on the basis of this single rate constant.

For the present data it appears as though the above approach is not adequate to distinguish between the two limiting mechanisms of Scheme II. If the reactions are indeed diffusion controlled, then the value of 1.30 V for $E°$ for the $S_2O_3^-/S_2O_3^{2-}$ couple must

---

(46) *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 15, pp 13–47.

Table VIII. k_{-2} and Marcus Calculations for the k_2 Pathway[a]

species no.	oxidant	E_f, V	k_2, $M^{-2}\ s^{-1}$	k_{-2}, $M^{-1}\ s^{-1}$ [b]	k_{11}(cal), $M^{-1}\ s^{-1}$ [c]
1	$[Os(4,7\text{-}Me_2phen)_3]^{3+}$	0.653	4.52×10^1	5.3×10^9	1.5×10^2
2	$[Os(5,6\text{-}Me_2phen)_3]^{3+}$	0.776	3.55×10^2	3.5×10^8	2.2×10^1
3	$[Os(phen)_3]^{3+}$	0.840	4.62×10^3	3.7×10^8	1.1×10^2
4	$[Os(5\text{-}Cl\text{-}phen)_3]^{3+}$	0.944	7.80×10^4	1.1×10^9	6.3×10^2

[a] $k_{-2} = k_2/K_{eq}$ for reaction 8; $E°$ of 1.13 V was used for $S_4O_6^{3-}/2S_2O_3^{2-}$. [b] $k_{22} = 2 \times 10^9$ $M^{-1}\ s^{-1}$; ref 7. [c] Average k_{11} = 39 $M^{-1}\ s^{-1}$.

be fairly accurate (±0.01 V). This situation would require that the values of k_{11} (cal) be lower limits, i.e. that k_{11} be greater than 3×10^3 $M^{-1}\ s^{-1}$ (the geometric mean). Alternatively, if the reactions are activation controlled then $E°$ must be somewhat less than 1.30 V, and k_{11} must be less than 3×10^3 $M^{-1}\ s^{-1}$.

It is becoming evident that the effective self-exchange rate constants for main-group redox couples are well correlated with their structural reorganization. For the $S_2O_3^-/S_2O_3^{2-}$ couple this reorganization is expected to be minimal on the basis of ESR spectra.[47] These spectra show that the spin is localized on the terminal sulfur atom of $S_2O_3^-$, and hence, the molecular structure should be almost identical with that of $S_2O_3^{2-}$. A similar situation is found in the N_3/N_3^- system, for which an effective self-exchange rate constant of 4×10^4 $M^{-1}\ s^{-1}$ has been derived.[35] In the case of the $S_2O_3^-/S_2O_3^{2-}$ system the larger molecular size would be expected to reduce the solvent reorganizational barrier, but the larger charge product would lead to a larger work term. It is likely that the first of these effects would be dominant, which would lead to a predicted value of k_{11} for the $S_2O_3^-/S_2O_3^{2-}$ system that is somewhat larger than 4×10^4 $M^{-1}\ s^{-}$ For the MnO_4^-/MnO_4^{2-} system the self-exchange rate constant is 3×10^3 $M^{-1}\ s^{-1}$, and the inner-sphere reorganizational barrier is a small but significant 1.6 kcal/mol.[48,49] This barrier arises from the 0.042-Å difference in Mn–O bond lengths between the two oxidation states. Since such a barrier should be absent in the $S_2O_3^-/S_2O_3^{2-}$ system, k_{11} is expected to exceed 3×10^3 $M^{-1}\ s^{-1}$. These considerations would support the interpretation that the Os(III) reactions of Figure 2 are diffusion controlled.

Details of the k_2 Path. As noted above, the k_2 pathway, which is second order with respect to $[S_2O_3^{2-}]$, is unique in thiosulfate chemistry. There are several reasons why it has not been observed previously. One reason relates to electrostatics: if the oxidant is anionic, as in the cases of $[IrCl_6]^{2-}$, $[IrBr_6]^{2-}$, and $[CoW_{12}O_{40}]^{5-}$,[4,6] it is to be expected that the k_2 pathway will be disfavored relative to the k_1 pathway. Another reason has to do with the strength of the oxidant: in the one prior case where the k_1 path was observed for a cationic oxidant ($[Fe(bpy)_3]^{3+}$,[4] the rates were so fast that only a very limited range of concentrations of $S_2O_3^{2-}$ were used. Such circumstances make it difficult to detect a k_2 term. For reactions in which I^- and SCN^- are oxidized with substitution-inert complexes such as $[IrCl_6]^{2-}$ and $[Os(bpy)_3]^{3+}$, k_2 paths are seen more commonly.[30,50] Most likely this is due to electrostatics, since the repulsion between two monoanions poses much less of a problem than that between two ions of $S_2O_3^{2-}$.

A more detailed understanding of the k_2 path is dependent on knowledge of $E°$ for the $S_4O_6^{3-}/2S_2O_3^{2-}$ couple. We have previously argued that this reduction potential has a value of 1.18 V,[41] but it is now clear that this value requires minor revision. Our method for estimating $E°$ is to combine the value of $E°$ for the $S_2O_3^-/S_2O_3^{2-}$ couple with the equilibrium constant for the reaction

$$S_4O_6^{3-} \rightleftarrows S_2O_3^- + S_2O_3^{2-} \tag{30}$$

This reaction is reported to have a forward rate constant of 2.5×10^6 s^{-1}.[31,33] If the reverse rate constant is assumed to be diffusion controlled with a value of 2×10^9 $M^{-1}\ s^{-1}$, a value of 1.25×10^{-3} M is obtained for the equilibrium constant. If this is combined with our revised value of 1.30 V for $E°$ for the $S_2O_3^-/S_2O_3^{2-}$ couple, a value of 1.13 V is obtained for $E°$ for the $S_4O_6^{3-}/2S_2O_3^{2-}$ couple. By use of NBS data,[51] the following additional results can be derived: $\Delta_f G°$ = −397 kJ/mol for $S_2O_3^-$, $\Delta_f G°$ = −936 kJ/mol for $S_4O_6^{3-}$, and $E°$ = −1.08 V for the $S_4O_6^{2-}/S_4O_6^{3-}$ couple. If the reverse rate constant (reaction 30) is less than diffusion controlled, then these values must be adjusted accordingly.

Table VIII shows values of k_{-2}, the rate constant for electron transfer from Os(II) to $S_4O_6^{3-}$, that were calculated from the relationship $k_2/k_{-2} = K_2$. These calculations used the measured values of k_2, the known reduction potentials for the Os(III) complexes, and the estimated $E°$ of 1.13 V for the $S_4O_6^{3-}/2S_2O_3^{2-}$ couple. The calculated values of k_{-2} range between 3.5×10^8 and 5.3×10^9 $M^{-1}\ s^{-1}$. An estimate of the diffusion-controlled limit for k_{-2} is that it must lie between 2.5×10^{10} and 2.4×10^{11} $M^{-1}\ s^{-1}$. The lower limit is based on the rate for reactions of the 2+/1− reaction discussed above, and the upper limit is based on the measured rate constant for ion-pair formation between SO_4^{2-} and $[Co(NH_3)_6]^{3+}$ at zero ionic strength.[52] This upper limit is further supported by the Smoluchowski–Debye equation (1.0×10^{11} $M^{-1}\ s^{-1}$ for reactions of this charge type)[52] and an estimated rate constant of 1.2×10^{11} $M^{-1}\ s^{-1}$ for the reaction of MnO_4^{2-} with $[Fe(phen)_3]^{3+}$.[53] It is clear that the tabulated values of k_{-2} are less than the diffusion-controlled limit. To the degree that the reverse rate constant (reaction 30) is less than diffusion controlled, the calculated value of $E°$ for the $S_4O_6^{3-}/2S_2O_3^{2-}$ couple will increase, which will lead to increased calculated values for k_{-2}. This eventuality could lead to calculated k_{-2} values that approach the diffusion-controlled limit. However, the scatter in the k_{-2} values is independent of the value of $E°$ used in the calculations, and the large degree of scatter implies that the rate-limiting step in the k_2 pathway is activation controlled. A similar situation occurs in the oxidations of I^- and SCN^-.[30,50]

A qualitative explanation for this difference between the k_2 and k_1 paths lies in the structural reorganization that accompanies electron transfer. ESR studies show that the species $S_4O_6^{3-}$ is a σ^* radical with the spin on the bond between the two central sulfur atoms.[47] Thus, S–S bond formation accompanies electron transfer in the k_2 pathway, but there is negligible structural reorganization in the k_1 pathway. This is also demonstrated by a related set of examples including reactions showing the reverse process (reductive cleavage);[54] here, the low rate constant for the reaction of Br_2^- with $[W(CN)_8]^{4-}$ (6×10^7 $M^{-1}\ s^{-1}$) is directly attributable to a structural reorganization barrier.

A quantitative theory for reactions having concerted electron transfer and bond formation has been developed from Marcus theory and applied to the case of reactions forming I_2^- from I^-.[55] The theory is based on the assumption that the Marcus cross relationship can be applied to reactions in which one of the reactants is an ion pair:

$$S_2O_3^{2-},S_2O_3^{2-} + Os(III) \rightleftarrows S_4O_6^{3-} + Os(II) \quad k_{2et},\ k_{-2et},\ K_{2et} \tag{31}$$

---

(47) Symons, M. C. R. *J. Chem. Soc., Dalton Trans.* **1979**, 1468–1472.

(48) Sham, T. K.; Brunschwig, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 1590–1591.

(49) Spiccia, L.; Swaddle, T. W. *Inorg. Chem.* **1987**, *26*, 2265–2271.

(50) Nord, G.; Pedersen, B.; Floryan-Løvborg, E.; Pagsberg, P. *Inorg. Chem.* **1982**, *21*, 2327–2330.

(51) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, *Suppl. No. 2*.

(52) Elder, A.; Petrucci, S. *Inorg. Chem.* **1970**, *9*, 19–22.

(53) Hicks, K. W.; Sutter, J. R. *J. Phys. Chem.* **1971**, *75*, 1107–1113.

(54) Shoute, L. C. T.; Alfassi, Z. B.; Neta, P.; Huie, R. E. *J. Phys. Chem.* **1991**, *95*, 3238–3242.

(55) Stanbury, D. M. *Inorg. Chem.* **1984**, *23*, 2914–2916.

Thus, k_{12} and K_{12} in the Marcus cross relationship (eq 26) refer to k_{2et} and K_{2et} in eq 31. Values of k_{2et} and K_{2et} can be calculated from k_2 and K_2 by dividing these numbers by K_{ip}, which is defined by

$$2S_2O_3^{2-} \rightleftarrows S_2O_3^{2-},S_2O_3^{2-} \quad K_{ip} \qquad (32)$$

In such a treatment the self-exchange rate constants k_{11} and k_{22} are defined for the following reactions:

$$S_2O_3^{2-},S_2O_3^{2-} + {}^*S_4O_6^{3-} \rightarrow S_4O_6^{3-} + {}^*S_2O_3^{2-},{}^*S_2O_3^{2-} \quad k_{11} \qquad (33)$$

$$\text{Os(III)} + {}^*\text{Os(II)} \rightarrow \text{Os(II)} + {}^*\text{Os(III)} \quad k_{22} \qquad (34)$$

Values for k_{11} for this sort of reaction have never been measured directly, and they have only been estimated in the cases of $I_2^-/2I^-$ and $(SCN)_2^-/2SCN^-$ couples.[50,55] The approach used here is to calculate k_{11} by use of the Marcus cross relationship and see whether the result is reasonable.

A value for K_{ip} is required for these calculations. According to Hemmes, the Fuoss equation should be applicable to formation of ion pairs from two like-charged ions.[56] This equation yields a value of 7.06×10^{-4} M^{-1} for K_{ip} at zero ionic strength, and when corrected to 0.1 M ionic strength, K_{ip} is 6.70×10^{-3} M^{-1}. For the work-term calculations the charge and radius of the ion pair $S_2O_3^{2-},S_2O_3^{2-}$ were assumed to be −4 and 6.6 Å, respectively. Similarly $S_4O_6^{3-}$ was assumed to have a radius of 6.6 Å. Calculated values of k_{11} are presented in Table VIII. In view of the significant uncertainty in some of the values of k_2, the scatter in k_{11} is not unacceptable.

The average value of k_{11} calculated for the $S_4O_6^{3-}/2S_2O_3^{2-}$ system is 39 M^{-1} s^{-1}, which may be compared with the value of 3×10^4 M^{-1} s^{-1} that was calculated for the $I_2^-/2I^-$ system.[55] Further interpretation of these numbers is unwarranted because the S–S force constant in $S_4O_6^{3-}$ is unknown.

Conclusions. Oxidation of $S_2O_3^{2-}$ by Os(III) has parallel paths: one with rate-limiting formation of $S_2O_3^-$ and Os(II) and the other with concerted electron transfer and S–S bond formation to yield $S_4O_6^{3-}$ and Os(II). Subsequent steps lead to $S_4O_6^{2-}$. The first path has diffusion apart of the products rather than electron transfer as the rate-limiting step, and this leads to an estimate of $E° = 1.30$ V for the $S_2O_3^-/S_2O_3^{2-}$ redox couple. In the second path electron transfer is rate limiting, which affords an unusual opportunity to apply the Marcus cross relationship to reactions having concerted bond formation.

Acknowledgment. This paper is based upon work supported by the National Science Foundation under Grant No. CHE-8913734.

Registry No. $S_2O_3^{2-}$, 14383-50-7; $[Os(phen)_3]^{3+}$, 47837-53-6; $[Os(4,7\text{-}Me_2phen)_3]^{3+}$, 84259-30-3; $[Os(5,6\text{-}Me_2phen)_3]^{3+}$, 136174-22-6; $[Os(5\text{-}Cl\text{-}phen)_3]^{3+}$, 70101-70-1; $[Os(phen)_3]Cl_2$, 73466-62-3; $[Os(5,6\text{-}Me_2phen)_3]Cl_2$, 136174-23-7; $[Os(5\text{-}Cl\text{-}phen)_3]Cl_2$, 136174-24-8; $[Os(4,7\text{-}Me_2phen)_3]Cl_2$, 136174-25-9.

---

(56) Hemmes, P. *J. Am. Chem. Soc.* **1972**, *94*, 75–76.
(57) Hurwitz, P.; Kustin, K. *Trans. Faraday Soc.* **1966**, *62*, 427–432.
(58) Ruff, I.; Zimonyi, M. *Electrochim. Acta* **1973**, *18*, 515–516.

Contribution from the Dipartimento di Chimica Inorganica e Struttura Molecolare,
Università di Messina, Salita Sperone 31, Vill. S. Agata, 98166 Messina, Italy

A New Reaction Pathway for the Geometrical Isomerization of Monoalkyl Complexes of Platinum(II): Kinetic Behavior of *cis*-$[Pt(PEt_3)_2(\text{neopentyl})Cl]$

Giuseppe Alibrandi, Luigi Monsù Scolaro, and Raffaello Romeo*

Received February 7, 1991

The title complex converts spontaneously into its trans isomer in protic and in some polar aprotic solvents. The process can be easily followed by ^1H and ^{31}P NMR spectroscopy and, in transparent solvents, by conventional spectrophotometric techniques. In 2-propanol there are two reaction pathways. The first is controlled by solvolysis and implies the formation of and the rapid cis-to-trans conversion of a cationic $[Pt(PEt_3)_2(\text{neopentyl})(S)]^+$ (S = 2-propanol) intermediate. At 298.16 K, $k_i = 11.7 \times 10^{-3}$ s^{-1}, $\Delta H^* = 60.7 \pm 0.7$ kJ mol^{-1}, and $\Delta S^* = -78 \pm 3$ J mol^{-1} K^{-1}. By addition of chloride ion, at $[Cl^-] > 0.1$ M, the solvolysis is blocked and a new pathway becomes important with $k_i = 0.76 \times 10^{-3}$ s^{-1} at 298.16 K, $\Delta H^* = 100 \pm 2$ kJ mol^{-1}, and $\Delta S^* = +31 \pm 7$ J mol^{-1} K^{-1}. In dichloromethane at 298.16 K, $k_i = 0.82 \times 10^{-4}$ s^{-1}, $\Delta H^* = 108 \pm 3$ kJ mol^{-1} and $\Delta S^* = +32 \pm 9$ J mol^{-1} K^{-1}. The reaction is thought to proceed through the dissociative loss of a phosphine ligand, presumably that in the trans position to the alkyl group, and the conversion of the uncharged $[Pt(PEt_3)(\text{neopentyl})Cl]$ 14-electron intermediate. The rate of isomerization is strongly accelerated by the presence in solution of very small amounts of the complex *cis*-$[PtMe_2(Me_2SO)_2]$, and it is shown that its catalytic efficiency depends on the extent of formation of a coordinatively unsaturated 14-electron $[PtMe_2(Me_2SO)]$ species. A mechanism for the catalyzed pathway is proposed.

Introduction

There is great chemical interest in understanding the way in which square-planar complexes of d^8 transition metals undergo geometrical isomerization. Indeed, the course of many reactions of these species, such as nucleophilic substitution, electron transfer, oxidative addition, reductive elimination, thermal decomposition, interaction with molecules of biological interest, and so on, is dictated by the geometry in the square-planar configuration.[1-4] Despite the fundamental importance of geometrical isomerization in the chemistry of d^8 metal ion compounds, very few mechanistic studies have been devoted to date to this subject.[5]

---

(1) Lippard, S. J. *Pure Appl. Chem.* **1987**, *59*, 731. Reedijk, J. *Pure Appl. Chem.* **1987**, *59*, 181. Sherman, S. E.; Lippard, S. J. *Chem. Rev.* **1987**, *87*, 1153. Nicolini, M., Ed. *Platinum and Other Metal Coordination Compounds in Cancer Chemiotherapy*; Martinus Nijhoff Publishing: Boston, MA, 1988. Umapathy, P. *Coord. Chem. Rev.* **1989**, *95*, 129.

(2) Loar, M.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174. Moravskiy, A.; Stille, J. K. *Ibid.*, **1981**, *103*, 4182. Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. Ozawa, F.; Ito, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 6457. Ozawa, F.; Yamamoto, A. *Chem. Lett.* **1982**, 865.

(3) Clark, H. C. *J. Organomet. Chem.* **1980**, *200*, 63. Clark, H. C.; Jablonski, C. R. *Inorg. Chem.* **1974**, *13*, 2213. Clark, H. C.; Wong, C. S. *J. Am. Chem. Soc.* **1974**, *96*, 7213. Clark, H. C.; Jablonski, C. R.; Wong, C. S. *Inorg. Chem.* **1975**, *14*, 1332. Clark, H. C.; Wong, C. S. *J. Organomet. Chem.* **1975**, *92*, C31.

(4) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.

(5) Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, *9*, 185.

0020-1669/91/1330-4007$02.50/0 © 1991 American Chemical Society