fraction of the adducts involve only one hydrogen bond per complex ion. Experiments carried out in the presence of $Et_2NH_2^+$ have in fact demonstrated[3b] that the quantum yield of photoaquation for the adducts with only one hydrogen bond is equal to that of "free" $Co(CN)_6^{3-}$.

In conclusion, in acidic solutions the $Co(CN)_6^{3-}$–PEI interaction is very similar to the $Co(CN)_6^{3-}$–cyclic polyimine interaction, so that the two classes of organic compounds practically offer analogous protections against the photoaquation of the complex; unlike cyclic polyimines, however, PEIs offer the same protection in a relatively large pH range (from 1 to 6). Another important property of the branched polymers is the high number of $Co(CN)_6^{3-}$ ions which can be bound to a polymer molecule (about 200 for PEI-400); the local concentration of $Co(CN)_6^{3-}$ in the adducts so obtained is extremely large, since two adjacent complex ions are separated only by a $-CH_2CH_2NH-$ chain. Similar adducts may represent a useful alternative to other types of supramolecular structures like polymer-pendant coordination compounds and micelle aggregates. The importance of similar very large supramolecular compounds in the future development of chemistry and photochemistry was recently demonstrated.[15]

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Registry No. [24]ane-N_8, 297-11-0; [30]ane-N_{10}, 862-28-2; [33]ane-N_{11}, 60464-68-8; [36]ane-N_{12}, 24904-24-3; $Co(CN)_6^{3-}$, 14897-04-2; $(C_2H_5N)_n$, 9002-98-6.

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Activation-Controlled Outer-Sphere Oxidation of Thiosulfate: Reaction with Bis(1,4,7-triazacyclononane)nickel(III)

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Oxidation of $S_2O_3^{2-}$ by $[Ni(tacn)_2]^{3+}$ has been studied in aqueous medium at 25.0 °C and 0.10 M ionic strength. The reaction produces $[Ni(tacn)_2]^{2+}$ and $S_4O_6^{2-}$. It is catalyzed by trace levels of Cu(II), but the catalysis can be eliminated by using $C_2O_4^{2-}$ as a copper scavenger. A stopped-flow kinetic study of the uncatalyzed reaction with excess $[S_2O_3^{2-}]$ showed that the rate law is $-d[Ni(III)]/dt = 2k_1[Ni(III)][S_2O_3^{2-}]$ with $k_1 = 1.40 \times 10^3\ M^{-1}\ s^{-1}$. The reactions of $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, and $[IrBr_6]^{2-}$ with $S_2O_3^{2-}$ are also copper catalyzed. A reinvestigation of these reactions in the presence of copper scavengers shows that the reactions of $[Fe(bpy)_3]^{3+}$ and $[IrCl_6]^{2-}$ have the same rate laws as that of $[Ni(tacn)_2]^{3+}$, with k_1 values of 2.05×10^5 and $1.38 \times 10^2\ M^{-1}\ s^{-1}$. For the reaction of $[IrBr_6]^{2-}$, the rate law is $-d[IrBr_6^{2-}]/dt = (k_0 + 2k_1[S_2O_3^{2-}])[IrBr_6^{2-}]$ with $k_1 = 1.23 \times 10$ and $k_0 = 1.46 \times 10^{-2}\ s^{-1}$. It is inferred that for all four reactions the k_1 term represents a mechanism involving rate-limiting formation of $S_2O_3^-$ and the reduced complex. Analysis of a plot of k_1 vs E_f for oxidations of $S_2O_3^{2-}$ indicates that the reactions of $[Ni(tacn)_2]^{3+}$ and $[Fe(bpy)_3]^{3+}$ are activation controlled, whereas those of $[IrCl_6]^{2-}$ and $[IrBr_6]^{2-}$ are limited by diffusion apart of the products. Values of $E_f = 1.30$ V and k_{11} for the $S_2O_3^-/S_2O_3^{2-}$ redox couple are deduced from this analysis.

Introduction

Over the last several years we have been investigating the rates and mechanisms of electron-transfer reactions of simple main-group compounds in aqueous solution. In many cases the reactions have low rate constants that can be traced to significant internal Franck–Condon barriers. One such example is the reaction of NO_2^- with $[Ni(tacn)_2]^{3+}$, for which the rate-limiting step is formation of NO_2 and $[Ni(tacn)_2]^{2+}$; the change in bond angle between NO_2^- and NO_2 (19°) leads to a major component of the activation barrier.[1] Another example is the oxidation of SO_3^{2-} by $[Os(bpy)_3]^{3+}$, where a significant portion of the barrier arises from the pyramidalization mode that relates SO_3^{2-} and SO_3^{-}.[2] Quite a different problem is presented in reactions where there is insignificant structural reorganization. Oxidations of monatomic species such as I^- are extreme cases, because there is no internal structure, but certain molecular species also possess this property, as exemplified by reactions in which N_3^- is oxidized to N_3.[3] There is virtually no structural difference between N_3^- and N_3, and so the only barrier to their outer-sphere self-exchange reaction is imposed by solvent reorganization. Consistent with this idea is the result that the effective self-exchange rate constant (derived from the Marcus cross relationship) is $4 \times 10^4\ M^{-1}\ s^{-1}$, which is much greater than the value deduced for the NO_2/NO_2^- system ($0.3\ M^{-1}\ s^{-1}$).

An interesting question is whether reactions can be found in which nonlinear main-group molecules undergo outer-sphere electron transfer with no structural reorganization. Reactions of $S_2O_3^{2-}$ are expected to be pertinent to this question, because ESR measurements and MO calculations on $S_2O_3^-$ indicate that the unpaired electron resides in an a_1 orbital localized on the terminal sulfur atom.[4-8] It is therefore expected that the structural differences between $S_2O_3^{2-}$ and $S_2O_3^-$ are minimal.

A preliminary survey of the reactions of $S_2O_3^{2-}$ with $[IrBr_6]^{2-}$, $[IrCl_6]^{2-}$, and $[Fe(bpy)_3]^{3+}$ revealed that electron transfer does occur on a convenient time scale and that the general degree of reactivity is consistent with a small structural barrier.[9] Very recently we reported a detailed study of the oxidation of $S_2O_3^{2-}$ by $[Os(phen)_3]^{3+}$ and related Os(III) species;[10] this paper demonstrated that electron-transfer reactions of $S_2O_3^{2-}$ are generally

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catalyzed by trace levels of Cu^{2+} and that significant problems can arise because of the decomposition of $S_2O_3^{2-}$ in acidic media. An important problem that remained unresolved in this paper was whether the reverse reactions ($S_2O_3^-$ with Os(II)) were diffusion controlled.

The present paper describes an investigation of the oxidation of $S_2O_3^{2-}$ by $[Ni(tacn)_2]^{3+}$ and reinvestigations of the oxidations by $[IrBr_6]^{2-}$, $[IrCl_6]^{2-}$, and $[Fe(bpy)_3]^{3+}$. $[Ni(tacn)_2]^{3+}$ was selected as an oxidant because of our hope that the low self-exchange rate constant for the Ni(III)/Ni(II) couple (6×10^3 M^{-1} s^{-1}) would lead to the reverse reaction being slower than diffusion controlled. The other reactions were studied because of our concerns that copper catalysis and thiosulfate decomposition were not fully avoided in the prior study. Our new results allow us to derive a reliable value of $E°$ for the $S_2O_3^-/S_2O_3^{2-}$ redox couple and to obtain a consistent treatment of the reactions of $S_2O_3^{2-}$ in terms of Marcus' theory.

Experimental Section

Reagents. Na_2IrCl_6 was from Alfa Products, and K_2IrBr_6 from Pfaltz & Bauer was purified by the procedure of Melvin and Haim.[11] The ligand 2,2′-bipyridine was from Aldrich Chemical Co. Purification of the following reagents was as described previously:[10] water, sodium thiosulfate, sodium acetate, trifluoromethanesulfonic acid (HCF_3SO_3), sodium trifluoromethanesulfoante (sodium triflate, $NaCF_3SO_3$), tetra-*n*-propylammonium bromide, and potassium tetrathionate. All other materials were of certified or reagent grade.

Syntheses. $[Fe(bpy)_3](CF_3SO_3)_2$ was prepared by a modification of the synthesis of the corresponding phenanthroline complex.[12] A 0.5-g sample of $FeSO_4{\cdot}7H_2O$ was dissolved in 5 mL of water, and to this was added 0.88 g of 2,2′-bipyridine with stirring. The solution turned red immediately, and the solid dissolved slowly. To this was added dropwise a saturated solution of sodium triflate until no further precipitation occurred. Refrigeration of this mixture yielded a mass of reddish brown crystals, which were washed with ether and dried under vacuum. Yield: 0.26 g (88%).

$[Ni(tacn)_2](ClO_4)_2$ and $[Ni(tacn)_2](ClO_4)_3$ were available from a prior study.[1] Solutions of $[Ni(tacn)_2]^{3+}$ were found to be 67% pure, with the balance being $[Ni(tacn)_2]^{2+}$. This result was obtained by a spectrophotometric titration of 0.138 mM $[Ni(tacn)_2]^{3+}$ with a 80.0 μM solution of $KMnO_4$. The titration curve and measurements were similar to those described previously.[1]

Preparation of Solutions. Solutions of $[IrCl_6]^{2-}$ and $[IrBr_6]^{2-}$ were prepared in dilute triflic acid ($pH \approx 3$), while those of $[Ni(tacn)_2]^{3+}$ were made in 0.1 M HCl. Fe(III) solutions were generated in situ by oxidation of the corresponding Fe(II) solutions in dilute HCl (0.1 M) with PbO_2. Solutions of $S_2O_3^{2-}$ were prepared in water and were standarized by iodometry.[13]

Analytical Methods. All UV-vis, NMR, pH, cyclic voltammetry (CV), and Osteryoung square-wave voltammetry (OSWV) data were obtained as described previously.[10]

Ion chromatography experiments for analysis of polythionates were conducted on a Wescan Instruments ion analyzer by ion-pair chromatography as described earlier.[14] The mobile phase was composed of 5 mM tetrapropylammonium bromide in 8% acetonitrile, with a flow rate of 1.9 mL/min.

Spectrophotometric titrations of $[Ni(tacn)_2]^{2+}$ with $KMnO_4$ were conducted as described previously.[1]

Kinetic data were collected and analyzed by use of a Hi-Tech SF-51 stopped-flow spectrophotometer equipped with a SU-40 spectrophotometer unit and C-400 circulating water bath maintained at 25.0 ± 0.1 °C. Reactions were conducted at 0.10 M ionic strength (NaCl) and were monitored by following the absorbance of $[IrCl_6]^{2-}$, $[IrBr_6]^{2-}$, $[Fe(bpy)_3]^{2+}$, and $[Ni(tacn)_2]^{3+}$ at 488, 584, 522, and 312 nm, respectively, with a 10-mm path length. Reactions were conducted by mixing equal volumes of oxidant and $S_2O_3^{2-}$/buffer/electrolyte/(phen, bpy, or $C_2O_4^{2-}$) solutions. When tests of the catalytic effect of Cu^{2+} were conducted, a $Cu^{2+}/S_2O_3^{2-}$ solution was prepared, which was then mixed with the oxidant solution in the stopped-flow apparatus. The output from the SU-40 unit was collected by an On-line Instrument (OLIS) Model 4300S data acquisition system based on a Zenith 248/12 computer. Pseudo-first-order rate constants from the exponential fits were evaluated by OLIS subroutines.

The Los Alamos nonlinear-least-squares computer program was used to fit the rate law to the values of k_{obs}.[15] 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 spectra of $[IrBr_6]^{2-}$, $[IrCl_6]^{2-}$, and $[Fe(bpy)_3]^{2+}$ exhibited absorption maxima (ϵ_{max}, M^{-1} cm^{-1}) of 3.71×10^3, 3.80×10^3, and 8.67×10^3 at wavelengths of 584, 488, and 522 nm, respectively. These values are in good agreement with the published values (ϵ_{max}, M^{-1} cm^{-1}, (λ_{max}, nm)) of 3.87×10^3 (585) for $[IrBr_6]^{2-}$,[11] 3.7×10^3 (487) and 4.0×10^3 (488) for $[IrCl_6]^{2-}$,[9,16] and 8.65×10^3 (522) for $[Fe(bpy)_3]^{2+}$.[17] We have previously reported spectral parameters of $\epsilon_{max} = 8.80 \times 10^3$ M^{-1} cm^{-1} and $\lambda_{max} = 312$ nm for $[Ni(tacn)_2]^{3+}$;[1] this value of ϵ_{max} is intermediate between the two prior published values of 1.01×10^4 and 7.20×10^3 M^{-1} cm^{-1}.[18,19]

From the reversible cyclic voltammogram of the Fe(III)/Fe(II) couple (1 mM $[Fe(bpy)_3]^{2+}$ in 0.1 M HCl) the formal potential, E_f, and peak-to-peak potential difference, $\Delta E_{p/p}$, were measured to be 1.050 ± 0.003 V and 59.3 ± 1.0 mV, respectively. This value of E_f is in good agreement with the published value of 1.06 V.[20] A description of the electrochemistry and stability of $[Ni(tacn)_2]^{3+}$ has been reported previously.[1]

The ^1H NMR spectrum of $[Fe(bpy)_3]^{2+}$ comprised two doublets and two triplets. δ: H-3, 7.52 (d, 5.5 Hz); H-4, 7.37 (t, 6.6 Hz); H-5, 8.11 (t, 7.8 Hz); H-6, 8.57 (d, 8.1 Hz). This spectrum is similar to those of $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$.[2]

Stoichiometry. The stoichiometry of the reaction between $[Ni(tacn)_2]^{3+}$ and $S_2O_3^{2-}$ in aqueous solution was investigated by UV-visible spectroscopy and ion-pair chromatography.

With initial concentrations of 0.174 mM $[Ni(tacn)_2]^{3+}$ and 0.180 mM $S_2O_3^{2-}$, UV-visible spectroscopy showed complete consumption of Ni(III). The yield of $[Ni(tacn)_2]^{2+}$ was determined by spectrophotometric titration of the acidified solution (0.01 M HCl). After correction for the $[Ni(tacn)_2]^{2+}$ present as impurity in the starting solution of $[Ni(tacn)_2]^{3+}$, the yield of $[Ni(tacn)_2]^{2+}$ was 0.179 ± 0.005 mM. These results clearly indicate that $[Ni(tacn)_2]^{2+}$ is the only nickel-containing product of the reaction.

At pH 5.10 and in presence of 1.0 mM oxalate, analysis of the products of a solution initially containing 0.180 mM $[Ni(tacn)_2]^{3+}$ and 0.501 mM $S_2O_3^{2-}$ by ion-pair chromatography indicated the formation of tetrathionate as the only sulfur-containing product, with a quantitative yield of 91.6 ± 1.5 μM. Thus the ratio of Ni(III) consumed to $S_4O_6^{2-}$ produced, $\Delta[Ni(III)]/\Delta[S_4O_6^{2-}]$, is 1.97 ± 0.03.

On the basis of the above results, the reaction is

$$2[Ni(tacn)_2]^{3+} + 2S_2O_3^{2-} \rightleftarrows 2[Ni(tacn)_2]^{2+} + S_4O_6^{2-} \quad (1)$$

with no detectable side reactions. As we have noted previously, stoichiometries other than this can occur in oxidations of thiosulfate.[10] However, formation of tetrathionate is probably the most common, and significantly, it was found in our prior study of oxidations with various Os(III) complexes.[10]

The oxidations by $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, and $[IrBr_6]^{2-}$ with excess $S_2O_3^{2-}$ were verified spectrophotometrically to be consistent with complete formation of $[Fe(bpy)_3]^{2+}$ and complete consumption of Ir(IV). Beyond this, no experiments were performed relevant to the stoichiometries of these reactions. However, the

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Table I. Effect of pH and Background Electrolyte on the Kinetics of Reduction of $[Ni(tacn)_2]^{3+\,a}$

pH	electrolyte	k_{obs}, s^{-1}	pH	electrolyte	k_{obs}, s^{-1}
4.09	$NaCl^b$	3.28	4.65	$NaCF_3SO_3{}^c$	5.42
4.65	$NaCl^c$	4.15	5.70	$NaCH_3COO$	6.59
6.09	$NaCl^d$	6.66	7.14	$Na(CH_3)_2AsO_2$	8.47

[a] μ = 0.10 M, $[Ni(III)]_0$ = 85.2 μM, $[S_2O_3{}^{2-}]$ = 1.67 mM, [oxalate] = 1.0 mM, T = 25 °C. [b] Succinate buffer, 0.01 M. [c] Acetate buffer, 0.01 M. [d] Cacodylate buffer, 0.01 M.

reaction of $[IrCl_6]^{2-}$ has been investigated previously.[9,21] With excess $S_2O_3{}^{2-}$, the product was found to be $[IrCl_6]^{3-}$.[21] With excess $[IrCl_6]^{2-}$, the reported consumption ratio, $\Delta[IrCl_6{}^{2-}]/\Delta[S_2O_3{}^{2-}]$, increased from 3.5 to 6.75 with increasing initial concentrations of $[IrCl_6]^{2-}$, and it was inferred that, with excess $S_2O_3{}^{2-}$, the stoichiometry was analogous to that of reaction 1.[9] It is assumed throughout the rest of this paper that the reactions of $[IrBr_6]^{2-}$ and $[Fe(bpy)_3]^{3+}$ have this stoichiometry also.

Kinetics. Kinetics studies of the oxidation of $S_2O_3{}^{2-}$ by $[Ni(tacn)_2]^{3+}$, $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, and $[IrBr_6]^{2-}$ were conducted in aqueous solution at 25.0 ± 0.1 °C and 0.10 M ionic strength, with $[S_2O_3{}^{2-}]$ in large excess over [oxidant]. Under these conditions, the reactions exhibited pseudo-first-order kinetics, with k_{obs} defined by

$$-d[\text{oxidant}]/dt = k_{obs}[\text{oxidant}] \qquad (2)$$

Reduction of $[Ni(tacn)_2]^{3+}$. The oxidation of $S_2O_3{}^{2-}$ by $[Ni(tacn)_2]^{3+}$ was found to be catalyzed by Cu(II). Thus, a value of 12.6 s^{-1} was obtained for k_{obs} when a solution of 0.170 mM Ni(III) was mixed with an equal volume of 3.34 mM $S_2O_3{}^{2-}$ at pH 4.65 and 0.11 M ionic strength (NaCl). But when the reaction was conducted with 13.3 μM Cu(II), the value of k_{obs} increased to 1.22×10^2 s^{-1}, a factor of 10 greater than without added Cu(II). Such catalysis is strong enough to give significant rate acceleration by Cu(II) present adventitiously.

We reported that the reactions of $S_2O_3{}^{2-}$ with a series of Os(III) complexes showed similar catalysis and that the catalysis could be quenched by adding phenanthroline to scavenge the Cu(II).[10] Unfortunately, this method could not be applied to the reaction of $[Ni(tacn)_2]^{3+}$ because phenanthroline absorbs strongly at the wavelength used to monitor Ni(III). A good substitute for phenanthroline turned out to be oxalate. Thus, when the above reaction was conducted without added Cu(II) but with added oxalate (1 mM), k_{obs} decreased from 12.6 to 3.86 s^{-1} because of scavenging of adventitious Cu(II). A further 10-fold increase in oxalate concentration gave a k_{obs} value of 3.74 s^{-1}, which indicates that 1 mM $C_2O_4{}^{2-}$ is sufficient to eliminate adventitious catalysis. As a further check, when the reaction was conducted with 13.3 μM added Cu(II) the effect of 1.0 mM added oxalate was to decrease the value of k_{obs} from 1.22×10^2 to 9.21 s^{-1}; with 10 mM $C_2O_4{}^{2-}$, k_{obs} dropped to 3.79 s^{-1}. This indicates that 10 mM but not 1.0 mM oxalate is sufficient in the presence of high concentrations of Cu(II). On the other hand, with 1.33 μM added Cu(II) and 1.0 mM oxalate, k_{obs} was 3.99 s^{-1}, which indicates that 1.0 mM $C_2O_4{}^{2-}$ is sufficient for low concentrations of Cu(II). The great effectiveness of oxalate as a copper scavenger in thiosulfate oxidations has also been demonstrated by other workers.[22] For the above reasons, all further studies were conducted in the presence of 1.0 mM $C_2O_4{}^{2-}$.

Under these conditions the stopped-flow traces showed fairly good pseudo-first-order behavior. As encountered in our previous study with the Os(III) oxidants,[10] the semilog plots exhibited slight curvature in the later part of the third half-life, which was not a significant problem; as before, the curvature is attributed to the unavoidable but slight decomposition of $S_2O_3{}^{2-}$ that occurs under these conditions. As shown by the data in Table I, the reaction of Ni(III) and $S_2O_3{}^{2-}$ is virtually independent of the nature of the background electrolyte. The very mild pH dependence demonstrated in Table I is attributed to the decomposition of $S_2O_3{}^{2-}$ in acidic media and the decomposition of $[Ni(tacn)_2]^{3+}$ in media that are not sufficiently acidic. The effect of $[Ni(tacn)_2]^{2+}$ was investigated at pH 4.65 (NaCl/acetate) with 1.67 mM $S_2O_3{}^{2-}$ and 66 μM Ni(III); under these conditions, the addition of 0.66 mM Ni(II) caused k_{obs} to decrease from 4.15 to 3.09 s^{-1}. In view of the small amounts of Ni(II) normally present, the effect of Ni(II) can be safely neglected.

Thiosulfate was found to have a strong effect on the kinetics. The dependence was investigated over a $[S_2O_3{}^{2-}]$ range of 0.333–2.5 mM (Table II). These data show a clear first-order dependence on the concentration of $S_2O_3{}^{2-}$. k_{obs} values were fit with the simple rate law

$$k_{obs} = 2k_1[S_2O_3{}^{2-}] \qquad (3)$$

to obtain $k_1 = (1.43 \pm 0.02) \times 10^3$ M^{-1} s^{-1}. As is shown by the k_{cal} values given in Table II, rate law 3 fits the data quite accurately. Because of the potential complications of pH effects and Cu catalysis, systematic errors could lead to an uncertainty somewhat larger than the statistical standard deviation cited.

Reduction of $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, and $[IrBr_6]^{2-}$. The reaction of $[Fe(bpy)_3]^{3+}$ with $S_2O_3{}^{2-}$ showed mild catalysis by Cu(II). With added Cu(II) (0.133 mM) in a reaction with $[Fe(III)]_0$ = 46.1 μM and 0.167 mM $S_2O_3{}^{2-}$ at pH 6.95 and 0.11 M ionic strength ($NaAsO_2(CH_3)_2$), k_{obs} increased from 1.44×10^2 to 2.02×10^2 s^{-1}. This is not a large effect when compared to that found in the Ni(III) reaction. Nevertheless, all subsequent studies were conducted in the presence of 1.0 mM 2,2′-bipyridine in order to eliminate the possible effects of adventitious copper catalysis. As is shown in Table III, the rates showed a mild pH dependence similar to that in the Ni(III) reaction and attributable to minor complications from $S_2O_3{}^{2-}$ decomposition; the apparent mild effect of background electrolyte is likely due to the accompanying changes in pH. All further studies were conducted at pH 4.67 with NaCl as the background electrolyte in order to facilitate comparison with our prior report on the Os(III) reactions. Rate constants were measured over a $[S_2O_3{}^{2-}]$ range of 41.6 μM to 0.334 mM; the data are presented in Table II, and there is a good first-order dependence on $[S_2O_3{}^{2-}]$. A fit of eq 3 gave a value for k_1 of $(2.05 \pm 0.05) \times 10^5$ M^{-1} s^{-1}.

The reaction of $[IrCl_6]^{2-}$ with $S_2O_3{}^{2-}$ is also catalyzed by Cu(II). Thus, with $[IrCl_6{}^{2-}]_0$ and $[S_2O_3{}^{2-}]$ being 0.176 mM and 2.5 mM respectively (pH 4.70 and μ = 0.1 M ($NaCF_3SO_3$)), k_{obs} increased from 0.73 to 1.73 s^{-1} with addition of 13.3 μM Cu(II). Subsequent experiments were conducted with 1 mM phen added as a sequestrant for Cu(II). As with the reactions of Ni(III) and Fe(III), the reaction of $IrCl_6{}^{2-}$ exhibited a mild pH dependence; for example, when the pH was varied from 4.70 (acetate buffer) to 6.10 (cacodylate buffer) at 2.5 mM $S_2O_3{}^{2-}$, k_{obs} changed from 0.734 to 1.17 s^{-1}. As is shown in Table II, the reaction showed a good first-order dependence on $[S_2O_3{}^{2-}]$. A fit of the data with rate law 3 gave a value of $(1.38 \pm 0.03) \times 10^2$ M^{-1} s^{-1} for k_1.

Quite strong copper catalysis was observed in the reaction of $[IrBr_6]^{2-}$ with $S_2O_3{}^{2-}$. For example, upon addition of 13.3 μM Cu(II), the rate constant increased from 0.150 to 4.11 s^{-1} for a reaction of 91.6 μM $[IrBr_6]^{2-}$ with 5.0 mM $S_2O_3{}^{2-}$ at pH 4.70 and 0.1 M ionic strength ($NaCF_3SO_3$). Thus, all further experiments were conducted with 1 mM phen to scavenge Cu(II). Under these conditions, the semilog plots exhibited slight curvature in the later part of the third half-life. Similar behavior was reported for the slowest of the Os(III) reactions and was attributed to problems with decomposition of $S_2O_3{}^{2-}$.[10] The $IrBr_6{}^{2-}$ reaction is the slowest in the present report, and the same explanation for the deviations is proposed. Since the deviations occurred only in the last half-lives, pseudo-first-order rate constants were obtained by fitting only the early half-lives, and these are the data presented in Table II. Plots of k_{obs} as a function of $[S_2O_3{}^{2-}]$ revealed a significant intercept, and thus rate law 3 was deemed inappropriate. A good fit of the data with the two-term rate law

$$k_{obs} = k_0 + 2k_1[S_2O_3{}^{2-}] \qquad (4)$$

led to values for k_0 and k_1 of $(1.5 \pm 0.2) \times 10^{-2}$ s^{-1} and 12.3 ±

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(22) Kimura, M.; Ishibashi, M. *Inorg. Chim. Acta* **1987**, *129*, 69–74.

Table II. Effect of $[S_2O_3^{2-}]$ on Reduction of $[Ni(tacn)_2]^{3+}$, $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, and $[IrBr_6]^{2-}$ [a]

$[S_2O_3^{2-}]_0$, mM	oxidant							
	$[Ni(tacn)_2]^{3+}$ [b]		$[Fe(bpy)_3]^{3+}$ [c]		$[IrCl_6]^{2-}$ [d]		$[IrBr_6]^{2-}$ [e]	
	k_{obs}, s^{-1}	k_{cal}, s^{-1}	k_{obs}, s^{-1}	k_{cal}, s^{-1}	k_{obs}, s^{-1}	k_{cal}, s^{-1}	k_{obs}, s^{-1}	k_{cal}, s^{-1}
0.042			16.8	17.0				
0.083			35.8	34.1				
0.125			50.3	51.2				
0.167			64.3	68.4				
0.250			100	102				
0.332	0.917	0.930						
0.333			149	136				
0.664	1.94	1.86					0.029	0.031
0.835	2.53	2.34						
1.33	3.75	3.72			0.368	0.366	0.050	0.047
1.67	4.15	4.68						
2.50	7.32	7.00			0.734	0.689	0.079	0.076
2.70							0.088	0.081
5.00					1.42	1.38	0.148	0.137
10.0					2.68	2.75	0.239	0.260
15.0					3.92	4.13	0.363	0.383

[a] $\mu = 0.10$ M, 25.0 °C. Values of k_{cal} obtained from the fit of eq 3, except for the reaction of $[IrBr_6]^{2-}$, where eq 4 was used. [b] $[Ni(III)]_0 = 65.9$ μM, pH = 4.65 (acetate buffer), background electrolyte = NaCl, [oxalate] = 1.0 mM. [c] $[Fe(III)]_0 = 10.4$ μM, pH = 4.67 (acetate buffer), background electrolyte = NaCl, [bpy] = 1.0 mM. [d] $[IrCl_6^{2-}]_0 = 197$ μM, pH = 4.70 (acetate buffer), background electrolyte = $NaCF_3SO_3$, [phen] = 1.0 mM. [e] $[IrBr_6^{2-}]_0 = 91.6$ μM, pH = 4.70 (acetate buffer), background electrolyte = $NaCF_3SO_3$, [phen] = 1.0 mM.

Table III. Effect of pH and Background Electrolyte on the Kinetics of Reduction of $[Fe(bpy)_3]^{3+}$

pH	electrolyte [a]	k_{obs}, s^{-1}	pH	electrolyte [a]	k_{obs}, s^{-1}
4.09	NaCl [b]	58.9	4.65	$NaCF_3SO_3$ [c]	59.2
4.67	NaCl [c]	64.3	5.78	$NaCH_3COO$	117
6.09	NaCl [d]	128	7.16	$Na(CH_3)_2AsO_2$	178
4.67	$NaClO_4$ [c]	49.3			

[a] $\mu = 0.10$ M, $[Fe(III)]_0 = 10.4$ μM, $[S_2O_3^{2-}] = 0.167$ mM, [phen] = 1.0 mM, $T = 25.0$ °C. [b] Succinate buffer, 0.01 M. [c] Acetate buffer, 0.01 M. [d] Cacodylate buffer, 0.01 M.

0.6 M^{-1} s^{-1}, respectively. In an effort to understand the origin of the k_0 term, experiments were conducted to examine the effects of light on the kinetics. For this propose, experiments were conducted where the monitoring light intensity was adjusted by use of various optical filters and monochromator slit widths. These experiments had a negligible effect on the rate constant. Likewise, varying the initial concentration of $IrBr_6^{2-}$ from 86.2 to 43.1 μM had a negligible effect on k_{obs}.

Discussion

Experimental results on four reactions of $S_2O_3^{2-}$ are presented in this paper. These reactions are the oxidations by $[Ni(tacn)_2]^{3+}$, $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, and $[IrBr_6]^{2-}$. All four oxidants are substitution inert, all four reactions are believed to have $S_4O_6^{2-}$ and the corresponding reduced metal complex as products (eq 1), and all four reactions have simple mixed second-order terms in their rate laws. A common mechanism that is consistent with these second-order terms is as follows:

$$\mathrm{Ox} + S_2O_3^{2-} \rightleftarrows \mathrm{Red} + S_2O_3^{-} \quad k_1, k_{-1} \tag{5}$$

$$S_2O_3^{2-} + S_2O_3^{-} \rightleftarrows S_4O_6^{3-} \quad K_2 \tag{6}$$

$$\mathrm{Ox} + S_4O_6^{3-} \rightarrow \mathrm{Red} + S_4O_6^{2-} \quad k_3 \tag{7}$$

As we have discussed previously,[10] equilibrium 6 (K_2) should be established rapidly, K_2 is large enough to maintain a substantial fraction of the radicals as $S_4O_6^{3-}$, and k_3 is expected to be quite large. Moreover, there was never any evidence that reverse electron transfer (k_{-1}) occurred to a significant degree. It is thus reasonable to apply the steady-state approximation to the two radicals, ignore k_{-1}, and derive the rate law

$$-d[\mathrm{ox}]/dt = 2k_1[\mathrm{ox}][S_2O_3^{2-}] \tag{8}$$

Thus, the above mechanism is consistent with the observed stoichiometries and rate laws.

The mechanism presented above is the same as was proposed in our prior study of the oxidations by $[Os(phen)_3]^{3+}$ and a series of related Os(III) complexes;[10] it was also proposed in the original study of the oxidations by $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, and $[IrBr_6]^{2-}$.[9]

An alternative mechanism was proposed[23] in a study of the oxidation by $[CoW_{12}O_{40}]^{5-}$, in which the $S_2O_3^{-}$ radical decays by self-reaction as in

$$2S_2O_3^{-} \rightarrow S_4O_6^{2-} \tag{9}$$

A similar mechanism was proposed for the oxidation by $[PtCl_6]^{2-}$.[24] Two objections to this mechanism can be raised. One is that such a mechanism, which involves a second-order decay of the intermediate, would have a relatively high steady-state concentration of the intermediate. Present estimates of $E°$ for the $S_2O_3^{-}/S_2O_3^{2-}$ system (1.3 V)[10] require that the reverse rate constant k_{-1} be very large, and hence such a mechanism should show kinetic inhibition by the reduced complex. However, no such inhibition has ever been reported. The other objection arises because equilibrium 6 (K_2) is known to occur,[10,25-27] and $E°$ for the $S_4O_6^{2-}/S_4O_6^{3-}$ couple is estimated to be −1.08 V.[10] Thus reaction 7 (k_3) has a huge driving force and should be very fast. It is clear that the combination of these two steps provides a much more efficient pathway for decay of the radical intermediates than does reaction 9.

Another feature that is common to all four reactions is copper catalysis. Similar catalysis was previously reported for the oxidations by $[Os(phen)_3]^{3+}$ and related Os(III) complexes[10] and by $[Co(ox)_3]^{3-}$.[22] We have not conducted any experiments directed toward determining the catalytic rate law and hence prefer not to speculate regarding the mechanism. However, such catalysis appears to be a general phenomenon when $S_2O_3^{2-}$ reacts with substitution-inert oxidants. Reports of the oxidations by $[PtCl_6]^{2-}$ and $[CoW_{12}O_{40}]^{5-}$, which do not mention the possibility of Cu^{2+} catalysis, should be viewed with caution.[23,24]

In what follows we first discuss some of the details of the individual reactions and then develop a general theory of the rate constants.

Reaction Specifics. The present paper is the first to report data on the reaction of $S_2O_3^{2-}$ with $[Ni(tacn)_2]^{3+}$. Data have been reported previously on the oxidations by $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, and $[IrBr_6]^{2-}$,[9] but because of various potential difficulties, we have chosen to reinvestigate them.

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Table IV. LFER and Marcus Calculations for the k_1 Pathway[a]

no.	oxidant	E_f, V	k_1, $M^{-1}\,s^{-1}$	k_{-1},[a] $M^{-1}\,s^{-1}$	k_{22}, $M^{-1}\,s^{-1}$	k_{12}(cal),[b] $M^{-1}\,s^{-1}$	k_1(cal),[c] $M^{-1}\,s^{-1}$	r,[d] Å
1	$[Os(4,7\text{-}DMP)_3]^{3+}$[e]	0.653	0.997	8.70×10^{10}	2×10^9[h]	8.88	0.278	7.4
2	$[Os(5,6\text{-}DMP)_3]^{3+}$[e]	0.776	3.17×10	2.30×10^{10}	2×10^9[h]	4.41×10^2	3.23×10	7.4
3	$[Os(phen)_3]^{3+}$[e]	0.840	1.90×10^2	1.14×10^{10}	2×10^9[h]	3.56×10^3	3.73×10^2	6.7
4	$[IrBr_6]^{2-}$	0.843	1.23×10	6.57×10^8	2×10^8[i]	1.59×10^2	5.26×10	4.5
5	$[IrCl_6]^{2-}$	0.892	1.38×10^2	1.09×10^9	2×10^5[j]	2.83×10	2.69×10	4.4
6	$[Os(5\text{-}Cl\text{-}phen)_3]^{3+}$[e]	0.944	1.22×10^4	1.28×10^{10}	2×10^9[h]	5.65×10^4	1.68×10^4	7.4
7	$[Ni(tacn)_2]^{3+}$	0.952	1.40×10^3	1.07×10^9	6×10^3[k]	1.40×10^3	1.34×10^3	3.8
8	$[Fe(bpy)_3]^{3+}$	1.05	2.05×10^5	3.46×10^9	5×10^8[l]	7.25×10^5	5.44×10^5	6.8
9	$[CoW_{12}O_{40}]^{5-}$[f]	1.07[g]	0.39	3.40×10^3				

[a] $k_{-1} = k_1/K_{eq}$ for reaction 5; $E°$ of 1.30 V was used for $S_2O_3^-/S_2O_3^{2-}$. [b] Rate constant with electron transfer as the rate limiting step. Calculated from eq 26 of ref 10. k_{11} of $2.30 \times 10^5\ M^{-1}\,s^{-1}$ was used for the $S_2O_3^-/S_2O_3^{2-}$ couple. [c] Rate constant including effects of diffusion of the products. Calculated from eq 17. [d] Estimated radius of oxidant. [e] DMP is dimethylphenanthroline; ref 10. [f] Reference 23. [g] E_f is extremely medium-dependent: see ref 28. [h] Reference 47. [i] Reference 46. [j] Reference 48. [k] Reference 30. [l] Reference 49.

There are several problematic aspects in the prior study[9] of the reaction of $[Fe(bpy)_3]^{3+}$. One is that the reaction was studied mostly at 10 °C because of its great rapidity; at 25 °C, data were collected only at a single concentration of $S_2O_3^{2-}$. Another is that a plot of the data collected at 10 °C supports a two-term rate law as in eq 4, rather than the simple second-order rate law used in the analysis. A third is that there was no mention of copper catalysis. Finally, it is not clear how the reaction was maintained at pH 6; this is worrisome because solutions of $[Fe(bpy)_3]^{3+}$ must be prepared under acidic conditions.

In our reinvestigation we have been able to resolve these uncertainties. Our new stopped-flow mixing system and data acquisition system have allowed us to collect data as a function of $[S_2O_3^{2-}]$ at 25 °C. The data so obtained demonstrate a first-order dependence on $[S_2O_3^{2-}]$, with no evidence of a zero-order term. We have found that the reaction is subject to copper catalysis, and we have also found that the problem can be eliminated by addition of free bpy. The pH problem has been solved by using the stopped-flow system to prepare the buffer in situ (mixing the acidic Fe(III) solution with the alkaline $S_2O_3^{2-}$/buffer solution).

Despite all of these improvements, the rate constant we have obtained ($k_1 = 2.05 \times 10^5\ M^{-1}\,s^{-1}$) is not very different from that reported previously ($9.5 \times 10^4\ M^{-1}\,s^{-1}$).[9]

There was no report of copper catalysis in the prior study of the reaction of $[IrCl_6]^{2-}$.[9] However, our present results clearly show that such catalysis can occur. By conducting our experiments with 1 mM phen as a scavenger of Cu(II), we have obtained a rate constant (k_1) of $1.38 \times 10^2\ M^{-1}\,s^{-1}$, which is somewhat less than the prior value[9] of $1.74 \times 10^2\ M^{-1}\,s^{-1}$.

Copper catalysis was reported in the prior study of the reaction of $[IrBr_6]^{2-}$.[9] However, instead of the addition of Cu(II) scavengers to the reaction system, the data were handled by fitting the rate law

$$-d[IrBr_6^{2-}]/dt = (k_0 + 2k_1[S_2O_3^{2-}] + k_{Cu}[Cu(II)])[IrBr_6^{2-}] \qquad (10)$$

Unfortunately, the individual values of k_{obs} were not reported, and so it is difficult to understand the significance of the k_0 term in this rate law.

In our reinvestigation of this reaction system, with phen added as a Cu(II) scavenger, the k_{Cu} term was insignificant (of course). However, the k_0 term was still significant; our value of k_0 is 0.015 s^{-1}, which is much less than the prior value of 0.07 s^{-1}. The mechanistic significance of the k_0 term is still unclear, but it may reflect impurities in $[IrBr_6]^{2-}$ that are present at lower concentrations than in the prior study. Our value of k_1 is 12.3 $M^{-1}\,s^{-1}$, which is somewhat less than the prior value of 17.5 $M^{-1}\,s^{-1}$. This difference can be attributed to the presence of Cu(II) scavengers in our experiments.

Generalities. With these new data in hand, a more definitive analysis can be made of the general factors controlling the rates of electron-transfer reactions of $S_2O_3^{2-}$. A hint of these factors can be derived by examining Figure 1, which is a plot of log k_1 as a function of E_f for all known reactions where $S_2O_3^{2-}$ is oxidized by a substitution-inert oxidant, where the rate law has a second-order term, and where the single-electron E_f value for the oxidant is known. The values of k_1 and E_f used in constructing this graph are summarized in Table IV; these are the same data used in a previously-published graph of this type,[10] with the exceptions that the $[Ni(tacn)_2]^{3+}$ point is new, the k_1 values for the reactions of $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, and $[IrBr_6]^{2-}$ are our revised values, the E_f value for $[Fe(bpy)_3]^{3+}$ is that determined in the present study, and the E_f value for $[CoW_{12}O_{40}]^{5-}$ is from a recent redetermination.[28] The graph shows that there is a general trend for k_1 to increase with increasing driving force.

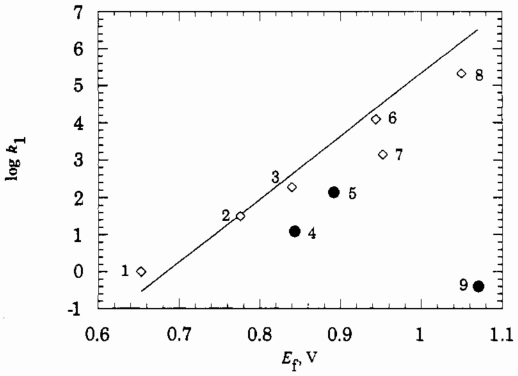

Figure 1. log k_1 for oxidation of $S_2O_3^{2-}$ as a function of E_f for various oxidants. Points are numbered as in Table IV. The solid line is drawn with a slope of 16.91, which corresponds to k_{-1} being a constant.

A serious outlier in Figure 1 is point 9, which represents the reaction of $[CoW_{12}O_{40}]^{5-}$. There are several reasons to disregard this reaction. One is that there was no mention of the possibility of copper catalysis in the original report;[23] correction for this effect could increase the deviation. Another problem is that the value of k_1 was reported to be independent of ionic strength; it is difficult to reconcile this observation with the presumed charges of the reactants. Third, it is unreasonable to expect present theories of medium effects to be able to handle the quantitative aspects of reactions of such high charge type. For these reasons this reaction is excluded from further discussion.

Further insight can be derived from Figure 1 by temporarily excluding points 4 and 5, which represent the reactions of $[IrCl_6]^{2-}$ and $[IrBr_6]^{2-}$. The remaining points (open diamonds) all refer to reactions with oxidants bearing a 3+ charge. The immediate question raised by these points is whether they are limited by reverse reactions (k_{-1}) that are diffusion controlled. If this is the case, then the values of k_{-1} will be essentially the same, and this will lead to a LFER with a slope of 16.9. The solid line drawn in Figure 1 has this slope. Whether the points for the Os(III) reactions are properly described by such a relationship has been discussed previously[10] and is further discussed below, but it is clear that the point for the reaction of $[Ni(tacn)_2]^{3+}$ (point 7) lies below the line. Thus, for the reaction of $[Ni(tacn)_2]^{3+}$ the reverse reaction (k_{-1}) must not be diffusion controlled.

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These matters can be clarified by considering the individual steps involved in the overall electron-transfer process, as shown by eqs 11–13. It is assumed that these electron-transfer reactions

$$\mathrm{Ox} + \mathrm{S_2O_3}^{2-} \rightleftarrows \mathrm{Ox,S_2O_3}^{2-} \quad K_{1\mathrm{ip}} \qquad (11)$$

$$\mathrm{Ox,S_2O_3}^{2-} \rightleftarrows \mathrm{Red,S_2O_3}^{-} \quad k_{1\mathrm{et}},\ k_{-1\mathrm{et}} \qquad (12)$$

$$\mathrm{Red,S_2O_3}^{-} \rightleftarrows \mathrm{Red} + \mathrm{S_2O_3}^{-} \quad k_{1\mathrm{d}},\ k_{-1\mathrm{d}} \qquad (13)$$

are energetically unfavorable in the direction written, and therefore the first step, $K_{1\mathrm{ip}}$, can be treated as a preequilibrium. If the steady-state approximation is applied to the species Red,$\mathrm{S_2O_3}^-$, then

$$k_1 = K_{1\mathrm{ip}}k_{1\mathrm{et}}k_{1\mathrm{d}}/(k_{-1\mathrm{et}} + k_{1\mathrm{d}}) \qquad (14)$$

which allows for the possibility that both electron transfer ($k_{1\mathrm{et}}$) and diffusion ($k_{1\mathrm{d}}$) can be rate limiting.

If diffusion is rate limiting ($k_{-1\mathrm{et}} \gg k_{1\mathrm{d}}$), then eq 14 simplifies to

$$k_1 = K_{1\mathrm{ip}}K_{1\mathrm{et}}k_{1\mathrm{d}} = K_1k_{-1\mathrm{d}} \qquad (15)$$

and the reaction can be said to be diffusion controlled. This is the situation that would lead to a LFER with a slope of 16.9 in Figure 1.

If electron transfer is rate limiting ($k_{-1\mathrm{et}} \ll k_{1\mathrm{d}}$) then eq 14 simplifies to

$$k_1 = K_{1\mathrm{ip}}k_{1\mathrm{et}} = k_{12} \qquad (16)$$

and the reaction is said to be activation controlled. This is the case for the reaction of $[\mathrm{Ni(tacn)_2}]^{3+}$.

It is to be expected that the cross relationship of Marcus' theory should apply to the reaction of $[\mathrm{Ni(tacn)_2}]^{3+}$ with $\mathrm{S_2O_3}^{2-}$. This is because the reaction is activation controlled; moreover, the Ni(III) complex is substitution inert and provides no lone pairs or π-systems that could bridge to the $\mathrm{S_2O_3}^-$ radical. The form of Marcus' cross relationship that we use is the one we have used previously, which includes the f factor and work terms.[10,29] k_{11} and k_{22} represent the self-exchange rate constants for the $\mathrm{S_2O_3}^-/\mathrm{S_2O_3}^{2-}$ redox couple and the various complexes used in the analysis. k_{12} is as defined in eq 16, and K_{12} is the equilibrium constant for eq 5.

We have previously argued that $E_f = 1.30$ V is a good estimate for the $\mathrm{S_2O_3}^-/\mathrm{S_2O_3}^{2-}$ system.[10] When this potential is combined with that for the $[\mathrm{Ni(tacn)_2}]^{3+}/[\mathrm{Ni(tacn)_2}]^{2+}$ couple, a value of 1.3×10^{-6} is obtained for K_1 ($=K_{12}$). It is therefore possible to use Marcus' cross relationship with this value of K_{12}, our experimental value of k_1 ($=k_{12}$), and the literature value of k_{22} (6×10^3 M^{-1} s^{-1})[30] to calculate a value of 2.3×10^5 M^{-1} s^{-1} for k_{11}, the effective self-exchange rate constant of the $\mathrm{S_2O_3}^-/\mathrm{S_2O_3}^{2-}$ couple. For this calculation, radii of 3.3 Å for $\mathrm{S_2O_3}^{2-}$ and 3.8 Å for $[\mathrm{Ni(tacn)_2}]^{3+}$ are assumed. Note that this calculated value of k_{11} is based on the assumption that E_f is 1.30 V for the $\mathrm{S_2O_3}^-/\mathrm{S_2O_3}^{2-}$ couple, which in turn is based on the assumption that the reactions of Os(III) and Ir(IV) are diffusion controlled. We are now in a position to examine this assumption in greater detail.

If we first propose that all the reactions are activation controlled, and a value of 1.30 V is used for E_f for the $\mathrm{S_2O_3}^-/\mathrm{S_2O_3}^{2-}$ couple, then the Marcus cross relationship can be used to calculate k_{12} values for all the reactions, on the basis of the above-derived value of 2.3×10^5 M^{-1} s^{-1} for k_{11}. The results so obtained are presented in Table IV. As can be seen, the correlation between k_1 and k_{12}(cal) is not very good.

If we next propose that some of the reactions are activation controlled and some are diffusion controlled, we can use the following equation to obtain a general treatment:

$$1/k_1 = 1/(K_{1\mathrm{ip}}K_{1\mathrm{et}}k_{1\mathrm{d}}) + 1/(K_{1\mathrm{ip}}k_{1\mathrm{et}}) = 1/(K_1k_{-1\mathrm{d}}) + 1/k_{12} \qquad (17)$$

This equation can be derived by substitution of eqs 15 and 16 into eq 14. By use of this equation, values of k_1(cal) can be obtained from values of K_1, $k_{-1\mathrm{d}}$, and k_{12}(cal).

In order to apply eq 17, good values of $k_{-1\mathrm{d}}$ are required, and these must be specified for the appropriate charge type and ionic strength (0.1 M). We have selected values for $k_{-1\mathrm{d}}$ by using the largest published experimental rate constants that meet these criteria. Thus, a diffusion-controlled limit of 2.5×10^{10} M^{-1} s^{-1} is taken for $k_{-1\mathrm{d}}$ for the 3+ oxidants. This value is based on the rate constants of 2.5×10^{10} and 1.4×10^{10} M^{-1} s^{-1} for the reactions of $\mathrm{Br_2}^-$ with $[\mathrm{Ir(Hbpy}\text{-}C^3,N')\mathrm{(bpy)_2}]^{2+}$ and $[\mathrm{Co(sep)}]^{2+}$, respectively.[31] $k_{-1\mathrm{d}}$ for the reactions of $[\mathrm{IrBr_6}]^{2-}$ and $[\mathrm{IrCl_6}]^{2-}$ is taken as 7×10^8 M^{-1} s^{-1}, which is estimated on the basis of the reaction of $\mathrm{CO_2}^-$ with $[\mathrm{Fe(CN)_6}]^{3-}$.[31]

Values of k_1(cal) obtained with these values of $k_{-1\mathrm{d}}$ and eq 21 are presented in Table IV. As can be seen, the correlation between k_1 and k_1(cal) is very good, with only two exceptions: the reactions of $[\mathrm{IrCl_6}]^{2-}$ and $[\mathrm{Os(4,7\text{-}DMP)_3}]^{3+}$. We believe that the reaction of $[\mathrm{IrCl_6}]^{2-}$ deviates because it is not properly an outer-sphere reaction. That is, there is probably a bonding interaction between $\mathrm{S_2O_3}^-$ and $[\mathrm{IrCl_6}]^{3-}$ that leads to an accelerated rate. The deviation for the reaction of $[\mathrm{Os(4,7\text{-}DMP)_3}]^{3+}$ probably indicates experimental error; considerable difficulties were encountered in studying this reaction because of its slowness, which allowed the decomposition of $\mathrm{S_2O_3}^{2-}$ to become a major interference.

In summary, a self-consistent treatment of the electron-transfer kinetics of $\mathrm{S_2O_3}^{2-}$ reactions emerges if the rate constants are treated with eq 17 and a reduction potential of 1.30 V is used for the $\mathrm{S_2O_3}^-/\mathrm{S_2O_3}^{2-}$ couple. The key to the success of eq 17 lies in its inclusion of the effects of diffusion control. The degree to which the reactions are limited by diffusion control is best appreciated by examining the values of k_{-1} in Table IV, which were calculated from the relationship $K_1 = k_1/k_{-1}$. These calculations show that the reactions of the osmium complexes are essentially fully limited by diffusion control. This result in turn supports the choice of 1.30 V as the reduction potential for the $\mathrm{S_2O_3}^-/\mathrm{S_2O_3}^{2-}$ couple and the derived value of 2.3×10^5 M^{-1} s^{-1} as the effective self-exchange rate constant of this redox couple. The logic is not circular, because choice of a lower E_f value would lead to k_{-1} values for the osmium reactions that were less than diffusion controlled; therefore the reactions would be activation controlled and the values of k_{12}(cal) would be expected to correlate with k_1 better than the values of k_1(cal), which is not the case.

As noted above, the anomalously high reactivity of $[\mathrm{IrCl_6}]^{2-}$ is ascribed to a bonding interaction between $[\mathrm{IrCl_6}]^{3-}$ and $\mathrm{S_2O_3}^-$. Inner-sphere reactions of $[\mathrm{IrCl_6}]^{2-}$ have been observed previously, for example in the reaction with Cr^{2+},[32] and inner-sphere reactions of $\mathrm{S_2O_3}^{2-}$ have been reported in the cases of $[\mathrm{Cu(NH_3)_4}]^{2+}$, $[\mathrm{OsO_4(OH)_2}]^{2-}$, $[\mathrm{Co(nta)(H_2O)_2}]^{2+}$, $[\mathrm{Au(NH_3)_4}]^{3+}$, Fe^{3+}, and $[\mathrm{Ag(OH)_4}]^-$.[33-38] The distinction between inner-sphere and outer-sphere reactions is not appropriate in the present case because there is no substitution in the metal ion coordination sphere, but the concept of strong overlap is still appropriate. Strong overlap has been detected in other reactions of $[\mathrm{IrCl_6}]^{2-}$.[39,40] Similarly $\mathrm{S_2O_3}^-$ binds with SCN^- to form $\mathrm{SCNS_2O_3}^{2-}$ and with $\mathrm{S_2O_3}^{2-}$ to form $\mathrm{S_4O_6}^{3-}$.[25-27,41] Thus, a strong overlap mechanism is to be expected in the reaction of $[\mathrm{IrCl_6}]^{2-}$ with $\mathrm{S_2O_3}^{2-}$. Strong

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overlap may also be anticipated in the reaction of $[IrBr_6]^{2-}$, except in this case the weak-overlap mechanism gives a rate constant that is already diffusion controlled.

There are two interesting aspects of the conclusion that the reaction of $[Fe(bpy)_3]^{3+}$ is largely activation controlled. One is that the original study of this reaction indicated that the reaction is diffusion controlled.[9] This change in viewpoint is a refinement that has come about primarily because we believe that the correct E_f value for the $S_2O_3^-/S_2O_3^{2-}$ couple is somewhat less than the value used previously. The other aspect is the question of why the reactions of the Os(III) complexes are diffusion controlled whereas that of $[Fe(bpy)_3]^{3+}$ is activation controlled. The explanations are (1) that the reverse process (k_{-1}) for the reaction of $[Fe(bpy)_3]^{3+}$ has the lowest driving force of all the reactions studied and (2) that the Fe(III)/Fe(II) self-exchange rate constant is somewhat lower than in the Os(III)/Os(II) systems.

Some comments regarding the magnitude of k_{11} are also in order. We previously estimated a lower limit of 6.77×10^3 M^{-1} s^{-1} for this parameter, on the basis of the reactions of Os(III).[10] Our present estimate of 2.3×10^5 M^{-1} s^{-1} for k_{11} is entirely consistent with that lower limit. Our value of k_{11} is among the largest to be reported for a main-group system. Other reported values include 4.0×10^4 M^{-1} s^{-1} for the N_3/N_3^- system,[3] 8.5×10^4 M^{-1} s^{-1} for the I_2/I_2^- system,[42,43] 1×10^7 M^{-1} s^{-1} for the SCN/SCN$^-$ system,[44] and values ranging from 1×10^7 to 1×10^9 M^{-1} s^{-1} for the I/I$^-$ system.[44–46] The value of k_{11} reported for the I_2/I_2^- system was based on an $E°$ value for I_2/I_2^- that has been superseded; the revised $E°$ would lead to a substantial reduction of the calculated k_{11} value. The k_{11} values for the I/I$^-$ and SCN/SCN$^-$ systems are probably excessively large, because they were based on reactions that probably have a significant degree of strong overlap. Thus, the results for the N_3/N_3^- system form the strongest basis for comparison with the $S_2O_3^-/S_2O_3^{2-}$ system. As noted in the Introduction, ESR spectral data and molecular orbital calculations imply that the molecular structure of $S_2O_3^-$ is very similar to that of $S_2O_3^{2-}$. This is the case also in the N_3/N_3^- system. For 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. Apparently the first of these two effects dominates, leading to a value larger for the $S_2O_3^-/S_2O_3^{2-}$ system.

Conclusions. The reactions of $S_2O_3^{2-}$ with $[Ni(tacn)_2]^{3+}$, $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, and $[IrBr_6]^{2-}$ all have as a first step (k_1) single-electron oxidation to form $S_2O_3^-$ and the corresponding reduced complex. Consideration of these results together with data previously obtained for oxidation of $S_2O_3^{2-}$ by a series of Os(III) complexes leads to the conclusion that the reactions of $[Ni(tacn)_2]^{3+}$ and $[Fe(bpy)_3]^{3+}$ have the reverse process (k_{-1}) activation controlled, while for the reactions of $[IrCl_6]^{2-}$, $[IrBr_6]^{2-}$, and the Os(III) complexes the reverse process is diffusion controlled. This assignment establishes a formal potential of 1.30 V for the $S_2O_3^-/S_2O_3^{2-}$ couple. Analysis of the reaction of $S_2O_3^{2-}$ with Ni(III) in terms of the cross relationship of Marcus' theory leads to an effective self-exchange rate constant (k_{11}) for the $S_2O_3^-/S_2O_3^{2-}$ couple of 2.3×10^5 M^{-1} s^{-1}. Such a rapid exchange rate constant is consistent with the small expected structural differences between $S_2O_3^{2-}$ and $S_2O_3^-$.

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