Inorg. Chem. 1987, 26, 3860-3863

Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry,
Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada

Outer-Sphere Dithionite Reductions of Metal Complexes

Robert J. Balahura* and Michael D. Johnson

Received July 11, 1986

Kinetics of reduction of a series of Co(III), Fe(III), and Ru(III) complexes by dithionite have been investigated. All the examined reactions using excess dithionite were first order in complex and half order in dithionite; $k_{obsd} = k'[S_2O_4^{2-}]^{1/2}$, where $k' = k_2K_h^{1/2}$ (K_h is the equilibrium constant for dissociation of $S_2O_4^{2-}$ and k_2 represents the rate constant for reduction by SO_2^-). Values for k_2 were 10^2–10^4 L mol^{-1} s^{-1} for Co(III), 10^8–10^9 L mol^{-1} s^{-1} for Fe(III), and 10^8 L mol^{-1} s^{-1} for Ru(III). A Marcus treatment of the cross-reactions gives a consistent self-exchange rate constant of $\sim 10^3$ L mol^{-1} s^{-1} for the SO_2/SO_2^- couple (I = 1.00 mol L^{-1}, T = 25 °C, pH 8.1). In two cases, rate constants were also obtained for reduction by undissociated $S_2O_4^{2-}$, and these are 10^3 times smaller than those for reduction by SO_2^-.

Introduction

Dithionite is an effective reducing agent for inorganic complexes,[1-3] bioinorganic compounds,[4,5] and certain organic species.[6] In most cases the dominant reducing agent is the SO_2^- radical, which results from the dissociation of $S_2O_4^{2-}$. The SO_2^- radical is thought to react mainly by simple outer-sphere electron transfer although adduct formation with ligands and organic species has also been postulated. Adduct formation, however, is difficult to establish unambiguously since the adducts have not been detected. This type of mechanism has been proposed for complexes involving pyridine,[4] imidazole,[4] nitroimidazoles,[4] and azide[3] and is based on relative-rate arguments. Furthermore, for a metal complex oxidant, reaction could take place by substitution of SO_2^- on the metal followed by inner-sphere electron transfer. The latter path is relatively easy to assess on the basis of the metal substitution rates.[7,8]

In systems where simple outer-sphere electron transfer prevails, it is of interest to obtain a value for the intrinsic self-exchange rate constant for the SO_2/SO_2^- couple ($E°$ = −0.26 V).[9] In principle, this parameter can be extracted by application of the Marcus cross relation[10] to the reactions of SO_2^- with different oxidants. However, to date, several different estimates of the self-exchange rate constant have been calculated: 340 L mol^{-1} s^{-1} from reduction of $[Co(EDTA)]^-$ and $[Co(C_2O_4)_3]$,[3-9] approximately 10^7 L mol^{-1} s^{-1} from comparison of SO_2^- reductions to those of O_2^-,[11] and approximately 10^8–10^9 L mol^{-1} s^{-1} from reduction of viologens.[6] The present study is an attempt to further probe the reactivity of dithionite toward a large variety of different metal complexes and to resolve the value of the self-exchange rate constant for the SO_2/SO_2^- couple.

Experimental Section

The following metal complexes were prepared according to literature procedures: $[Fe(CN)_5L]^{2-}$ where L = pyrazine (pyz),[12] 4,4′-bipyridine (4,4′-bpy),[12] imidazole (imid),[13] or pyridine (py);[4] $[Co(NH_3)_5L]^{3+}$ where L = NH_3[14] or 4-cyanopyridine (4-CN-py);[15] $[Ru(NH_3)_5L]^{3+}$ where L = pyz[16] or imid;[17] $[Co(bpy)_3]^{3+}$;[18] *trans*-$[Co(cyclam)(NH_3)_2]^{3+}$;[19] *trans*-$[Co(cyclam)Cl_2]^+$;[19] $[Co(sep)]^{3+}$;[20] $[Co(diamsar)]^{3+}$.[21] For $[Co(NH_3)_5L]^{3+}$ where L = pyz, 4,4′-bpy, imid, or 4-NO_2-imid, the following procedure was followed. A 10-fold excess of ligand was combined with 0.5 g of $[(NH_3)_5Co(trif)](trif)_2$[22] in 50 mL of warm anhydrous sulfolane. The mixture was stirred for 24 h at 25 °C, and the complex was precipitated from solution by using large volumes of diethyl ether. The resulting material was purified by ion-exchange chromatography on CM-Sephadex. Complexes were characterized by comparison of their UV–vis spectra with published data where appropriate. In a number of cases, NMR spectra provided confirmation that the desired complexes had been prepared. Solutions of the iron and ruthenium complexes were shielded from light, since they are extremely photosensitive.

Solutions of dithionite were prepared by using solid $Na_2S_2O_4$ (Sigma, ~83%). Weighed samples were placed in a serum-capped vial and a stream of argon gas passed over the solid for 10–15 min. To this solid a known volume of deoxygenated salt/buffer stock solution was added by using gastight Hamilton syringes. All solutions were used immediately after preparation. Standardization of dithionite solutions was performed spectrophotometrically with ferricyanide as a standard.[23] Constant pH was maintained using Tris or MES buffers except in the iron and ruthenium systems, where sodium monohydrogen phosphate was employed. All solutions were deoxygenated with argon just prior to use. Concentrations of dithionite used varied between 5 and 100 mM for $[Co(NH_3)_5L]^{3+}$ where L = pyz, 4,4′-bpy, 4-CN-py, or 4-NO_2-imid, *trans*-$[Co(cyclam)(NH_3)_2]^{3+}$, and *trans*-$[Co(cyclam)Cl_2]^+$; the complexes were 0.5–1 mM. For $[Co(sep)]^{3+}$, $[Co(diamsar)]^{3+}$, and $[Co(NH_3)_5imid]^{3+}$ the dithionite concentrations were between 0.01 and 0.2 M with the complex concentrations at 1 mM. In the more reactive iron and ruthenium systems, dithionite concentrations were 0.1–5 mM and complex concentrations 10–50 μM. To measure $S_2O_4^{2-}$ reduction rates, the oxidant was used in excess. Typical $S_2O_4^{2-}$ concentrations were ~50 μM, and oxidant concentrations ranged between 0.5 and 10 mM. Buffers were 50 mM throughout.

Kinetic measurements of rapid reactions were performed on a Dionex D-110 stopped-flow spectrophotometer interfaced with a DASAR digital storage unit. For the slower reactions a Beckman Acta CIII spectrophotometer was used and ln ΔA versus time was plotted. In all systems studied, pseudo-first-order conditions were maintained with the $S_2O_4^{2-}$ (or the complex) in at least 10-fold excess. Observed rate constants were obtained from the DASAR by matching exponential traces with a calibrated curve generator.

Constant ionic strength was maintained by using stock solutions of $LiClO_4$, $NaClO_4$, or NaCl. Standardization of these solutions was performed by conventional ion-exchange procedures. The cobalt studies were performed with a 3-fold excess of histidine present to prevent CoS precipitation. It has been previously demonstrated that histidine does not interfere with the reduction process.[3]

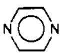
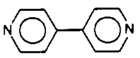
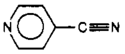
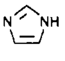
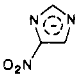
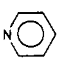
Measurement of the equilibrium constant for the dissociation of $S_2O_4^{2-}$ into SO_2^- was performed on a Bruker ER 2000-5RC EPR/ENDOR spectrometer. The concentration of SO_2^- in a standardized solution was

---

(1) Mehrotra, R. N.; Wilkins, R. G. *Inorg. Chem.* **1980**, *19*, 2177.
(2) Scaife, C. W. J.; Wilkins, R. G. *Inorg. Chem.* **1980**, *19*, 3245.
(3) Pinnell, D.; Jordan, R. B. *Inorg. Chem.* **1979**, *18*, 3191.
(4) (a) Olivas, E.; De Waal, D. J. A.; Wilkins, R. G. *J. Biol. Chem.* **1977**, *252*, 4038. (b) Eaton, D. R.; Wilkins, R. G. *J. Biol. Chem.* **1978**, *253*, 908.
(5) (a) Balahura, R. J.; Wilkins, R. G. *Biochim. Biophys. Acta* **1983**, *724*, 465. (b) Jones, G. D.; Jones, M. G.; Wilson, M. T.; Brunori, M.; Colosimo, A.; Sarti, P. *Biochem. J.* **1983**, *209*, 175. (c) Cassatt, J. C.; Kukmuzineka, M.; Bender, J. W. *Inorg. Chem.* **1977**, *16*, 3371.
(6) Tsukahara, K.; Wilkins, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2632.
(7) Creutz, C.; Sutin, N. *J. Biol. Chem.* **1974**, *249*, 6788.
(8) Itzkowitz, M.; Haim, A. *Bioinorg. Chem.* **1978**, *9*, 323.
(9) Stanbury, D. M.; Lednicky, L. A. *J. Am. Chem. Soc.* **1984**, *106*, 2847.
(10) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.
(11) Bradić, Z.; Wilkins, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 2236.
(12) Malin, J. M.; Toma, H. E. *Inorg. Chem.* **1973**, *12*, 1039.
(13) Shepard, R. E. *J. Am. Chem. Soc.* **1976**, *98*, 3329.
(14) Bjerrum, J., McReynolds, J. P. *Inorg. Synth.* **1946**, *12*, 216.
(15) Balahura, R. J. *Can. J. Chem.* **1974**, *52*, 1762.
(16) Ford, P.; Rudd, D. F. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.
(17) Sundberg, R. J.; Bryan, R. F.; Taylor, I. F.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381.
(18) Burstall, F. H.; Nyholm, R. S. *J. Chem. Soc.* **1952**, 3570.
(19) Bosnich, B.; Pook, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.
(20) Creaser, I. J.; Harrowfield, J.; Herlt, A. J.; Sargeson, A. M.; Springborg, J.; Geue, R. J.; Snow, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 3181.
(21) Geue, R. J.; Hambley, T. W.; Harrowfield, J. M.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5478.
(22) Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrence, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470.
(23) Lambeth, D. O.; Palmer, G. *J. Biol. Chem.* **1973**, *248*, 6095.
(24) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21.
(25) Dunitz, J. D. *Acta Crystallogr.* **1956**, *9*, 579.
(26) (a) Lucchise, R. L.; Haber, K.; Schaefer, H. F. *J. Am. Chem. Soc.* **1976**, *98*, 7617. (b) Kosower, E. M.; Bauer, S. W. *J. Am. Chem. Soc.* **1960**, *82*, 2191.

0020-1669/87/1326-3860$01.50/0

Table I. Rate Constants for Reduction of Metal Complexes by Dithionite[a]

L	$[Co^{III}(NH_3)_5L]^{n+}$	$[Fe^{III}(CN)_5L]^{n-}$	$[Ru^{III}(NH_3)_5L]^{n+}$
	$(1.1 \pm 0.1) \times 10^5$	$>6 \times 10^2$ $\sim 5 \times 10^8$[d]	$>3 \times 10^8$
	$(7.2 \pm 0.2) \times 10^3$ $(6.1 \times 0.1) \times 10^3$[b]	$>6 \times 10^8$ $\sim 4 \times 10^8$[d] $[(1.8 \pm 0.2) \times 10^5]$	
	$(4.7 \pm 0.2) \times 10^4$		
	188 ± 1[b,e] 188 ± 1[b] 188 ± 3[c]	$(1.6 \pm 0.03) \times 10^8$	$(1.1 \pm 0.2) \times 10^8$ $[(1.1 \pm 0.1) \times 10^5]$
	$(2.3 \pm 0.2) \times 10^4$		
	2.4×10^3[h] $(2.4 \pm 0.02) \times 10^3$[e]	$(1.2 \pm 1.0) \times 10^8$	
NH_3	117 ± 1[e,g]		
CN^-		1.2×10^8[f]	

[a] Units of L mol^{-1} s^{-1}, 25 °C, $I = 1.0$ mol L^{-1} ($LiClO_4$), and pH 8.1, except where noted. Rate constants are for reduction by the SO_2^- radical, obtained from the slope of a plot of k_{obs} vs $[S_2O_4^{2-}]^{1/2}$ according to eq 4. The corresponding intercepts are either statistically zero or very small (1%) with respect to the slope. Due to some scatter in the rate data, no real significance can be assigned to the intercepts. Rate constants in square brackets are for $S_2O_4^{2-}$ as reductant. [b] $I = 0.10$ mol^{-1} L^{-1} ($NaClO_4$). [c] $I = 1.0$ mol L^{-1} ($LiClO_4$), 0.050 mol L^{-1} HPO_4^{2-}, and pH 10.5. [d] $I = 0.050$ mol L^{-1} ($LiClO_4$). [e] pH 6.1. [f] Reference 2; $I = 0.50$ mol L^{-1} (Na_2SO_4) and pH 7.0. [g] $I = 1.0$ mol L^{-1} (NaCl). [h] Reference 3.

determined by double integration of the radical ion signal and comparison with a standardized solution of Fremy's salt, $K_4N_2O_2(SO_3)_4$, in saturated HCO_3^-. The same cell was used to record the spectra of the dithionite and Fremy's salt solutions.

Results and Discussion

Reduction of the iron(III) and ruthenium(III) complexes was established by spectral methods. After the reaction between $S_2O_4^{2-}$ and the complex was complete, the product spectrum corresponded to that of the iron(II) or ruthenium(II) species. For cobalt ammine complexes, cobalt(II) was determined as the blue $[CoCl_4]^{2-}$ species. The overall reaction may be written as in eq 1. Reduction rates

$$2M_{ox} + S_2O_4^{2-} \rightarrow 2M_{red} + S(IV) \qquad (1)$$

were monitored spectrophotometrically at the cobalt(III) or iron(II) and ruthenium(II) peaks.

With dithionite in excess, all the complexes studied showed a square root dependence on dithionite concentration and a zero y intercept. The experimental rate law is given by eq 2, where

$$\text{rate} = \frac{-d[\text{complex}]}{dt} = k_{obsd}[\text{complex}] \qquad (2)$$

$k_{obsd} = k'[S_2O_4^{2-}]^{1/2}$. No difference in the rates at pH 6.1 and 8.1 was observed.

The above rate law has been found for many dithionite reductions[1-5] and is interpreted to arise from the homolysis of $S_2O_4^{2-}$ into SO_2^- radicals and subsequent rate-determining reduction of the complex by SO_2^- (eq 3a and 3b). For this scheme, (2) can

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^- \quad K_h \qquad (3a)$$

$$SO_2^- + M_{ox} \rightarrow S(IV) + M_{red} \quad k_2 \qquad (3b)$$

be rewritten as (4). Evaluation of k_2 is possible by using K_h =

$$\text{rate} = k_2K_h^{1/2}[\text{complex}][S_2O_4^{2-}]^{1/2} \qquad (4)$$

1.4×10^{-9} mol L^{-1} ($I = 0.25$ M (NaCl), pH 8), as determined by Lambeth and Palmer using ESR.[23] This equilibrium constant was also determined in this study under our reaction conditions: $I = 1.0$ mol L^{-1} ($LiClO_4$), pH 8.1 (phosphate buffer). The value of 3.8×10^{-9} mol L^{-1} obtained in this work is consistent with the Lambeth and Palmer determination at lower ionic strength. The rate constants, k_2, reported in Tables I and II were calculated by using our value for K_h.

Table II. Rate Constants for Reduction of Metal Complexes by Dithionite[a]

complex	k_2, L mol^{-1} s^{-1}
$[Co(bpy)_3]^{3+}$	$(2.1 \pm 0.1) \times 10^7$[b]
trans-$[Co(cyclam)(NH_3)_2]^{3+}$	918 ± 130
trans-$[Co(cyclam)(Cl)_2]^+$	$(6.25 \pm 0.01) \times 10^5$
$[Co(sepulchrate)]^{3+}$[d]	71 ± 18[b] 69 ± 4[b,c]
$[Co(diamsar)]^{3+}$	26 ± 0.5[b]

[a] $I = 1.0$ mol L^{-1} ($LiClO_4$), 25 °C, and pH 8.1, except where noted. Rate constants are for reduction by the SO_2^- radical, obtained from the slope of a plot of k_{obsd} vs $[S_2O_4^{2-}]^{1/2}$ according to eq 4. The corresponding intercepts are either statistically zero or very small (1%) with respect to the slope. Due to some scatter in the rate data, no real significance can be assigned to the intercepts. [b] Supporting electrolyte was $NaClO_4$. [c] pH 6.1. [d] At the high dithionite concentrations used in this study, $(Co(sep))^{3+}$ is reduced, in contrast to a previous report.[31]

For the very rapid reductions studied, a breakdown in the steady-state approximation is expected; i.e., $S_2O_4^{2-}$ dissociation becomes rate determining. However, only exponential traces were observed; therefore, steady-state conditions must be in operation. The absorbance changes measured were much less than those determined by conventional spectrophotometry, thereby indicating that only the end of the reduction was observed where steady-state requirements are achieved.[23] Similar "violations" occur in dithionite studies by Wilkins[6] and Cassatt,[5c] and in each case normal kinetics were observed. It should be emphasized that the rate constants determined for these very fast reactions ($k \geq 10^8$ L mol^{-1} s^{-1}) represent approximations rather than precise evaluations. For the purpose of this study, these approximate values of k are adequate.

One of the goals of this study was to obtain a reliable estimate of the SO_2/SO_2^- self-exchange rate constant. In this context, it is first necessary to establish that the reductions are occurring via a genuine outer-sphere pathway. Three mechanistic pathways are possible: (1) a simple outer-sphere reaction, (2) some type of bridging pathway involving the ligands, and (3) substitution of SO_2^- on the metal and inner-sphere electron transfer. The last mechanism is unlikely due to the nature of the substitutional properties of the oxidants in this study, and no evidence for substitution was observed.

Theoretically, the oxidants $[Co(NH_3)_6]^{3+}$, $[Co(sep)]^{3+}$, and $[Co(diamsar)]^{3+}$ must react by an outer-sphere process. Furthermore, it is reasonable that $[Co(bpy)_3]^{3+}$ and $[Co(NH_3)_5py]^{3+}$ also must react by an outer-sphere mechanism. However, for the latter complexes, it is possible that reduction is determined by the rate of nucleophilic attack on the ligand as first postulated by Eaton and Wilkins.[4b] The remaining oxidants can in principle react by any of the three possibilities. Mechanism 2 is difficult to discount because no physical evidence for bridge formation has been found. However, we do not favor this possibility for the following reasons. First, the $[Co(NH_3)_5py]^{3+}$ complex does not show increased reactivity with SO_2^- as might be expected.[3] Also, the $[Co(NH_3)_5]^{3+}$ complexes with pyrazine, bipyridine, 4-cyanopyridine, imidazole, and nitroimidazole show a similar reactivity with SO_2^-. Second, the reductions of 1-methylimidazole, imidazole, and 2-methylimidazole adducts of metmyoglobin by SO_2^- and $[Fe(EDTA)]^{2-}$ follow the same rate order.[4b] Since $[Fe(EDTA)]^{2-}$ reacts at the periphery of the protein by an outer-sphere path, the observed rate order may simply be a reflection of a change in redox potential of the protein adducts as opposed to any special effect due to SO_2^-. Bridge formation has also been postulated in the reduction of $[Co(NH_3)_5N_3]^{2+}$ by SO_2^-, presumably via interaction with the lone pairs on the azido ligand. The suggestion is based on charge-corrected rate ratios of re-

Table III. Calculated Self-Exchange Rate Constants for the SO_2/SO_2^- Couple

complex	$E°$, V	K_{12}	r, Å	W_{12}	k_{22}, L mol^{-1} s^{-1}	k_{11}, L mol^{-1} s^{-1}
$[Co(sep)]^{3+}$	-0.30[a]	2.3×10^{-1}	4.5[b]	3.3	11.5[a]	3.6×10^2
$[Co(NH_3)_6]^{3+}$	$+0.06$[c]	2.8×10^5	3.3[b]	6.6	10^{-7}[a]	5.5×10^4
$[Co(bpy)_3]^{3+}$	$+0.37$[d]	4.8×10^{10}	6.8[b]	2.0	17[a]	1.9×10^4
$[Fe(CN)_6]^{3-}$	$+0.41$[e]	2.3×10^{11}	4.0[b]	2.2	2×10^3[e]	5×10^3
$[Fe(CN)_5py]^{2-}$	$+0.55$[f]	5.3×10^{13}	4.0[g]	0.81	3.4×10^5[h]	3.3×10^2
$[Fe(CN)_5(4,4'\text{-bpy})]^{2-}$	$+0.46$[i]	1.1×10^{12}	4.0[e]	0.81	7×10^5[i]	2×10^3
$[Ru(NH_3)_5imid]^{2+}$	$+0.11$[j]	1.9×10^6	3.4[b]	6.1	4×10^5[c]	8×10^3
$[Co(diamsar)]^{3+}$	-0.30[a]	2.3×10^{-1}	4.5[k]	3.3	0.5[a]	1×10^3
$[Co(edta)]^-$	$+0.38$[l]	6.5×10^{10}	4.0[k]	0.75	4×10^{-7}[l]	1×10^3[m]
$[Co(ox)_3]^{3-}$	$+0.57$[l]	1.1×10^{14}	4.0[k]	1.1	2×10^{-7}[l]	2×10^3[m]
$[Mn(cydta)]^-$	$+0.82$[l]	1.8×10^{18}	4.5[k]	0.78	1[l]	2×10^2
$[Fe(edta)]^-$	$+0.12$[l]	2.9×10^6	4.0[e]	0.75	3×10^4[l]	5×10^2

[a] Creaser, I. I.; Sargeson, A. M.; Zanella, A. W. *Inorg. Chem.* **1983**, *22*, 4022. [b] Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1983**, *74*. [c] Bond, A. M.; Lawrence, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 2010. [d] Paglia, E.; Sironi, C. *Gazz. Chim. Ital.* **1957**, *87*, 1125. [e] Wherland, S.; Gray, H. B. In *Biological Aspects of Inorganic Chemistry*; Addison, A. W., Cullen, W. R., Dolphin, D., James, B. R., Eds.; Wiley: New York, 1977; p 323. [f] Hrepic, N. V.; Malin, J. M. *Inorg. Chem.* **1979**, *18*, 409. [g] Radius assumed equal to $(Fe(CN)^6)^{3-}$ radius. [h] Johnson, M. D.; Wilkins, R. G., unpublished data. [i] Haim, A.; Phillips, S. *Inorg. Chem.* **1980**, *19*, 1616. [j] Sundberg, R. J.; Bryon, R. F.; Taylor, I. F.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381. [k] Assumed value. [l] Reference 1. [m] Reference 9.

ductions by SO_2^- as compared to those of reductions by the outer-sphere reagent $[Ru(NH_3)_6]^{2+}$. This is approximately constant for the $[Co(NH_3)_5]^{3+}$ complexes with Cl^-, SO_4^{2-}, pyridine, and NH_3 but is about 5 times larger for the azido complex. The implication is that the former complexes react by an outer-sphere reaction and that the azido complex has a bridging component. However, if the same analysis is carried out with vanadium(II) as the comparative reductant, the azido complex is predicted to react by an outer-sphere process whereas the chloro and sulfato complexes should involve bridging paths. Since this correction is an oversimplification, it may be more appropriate to correct for the charge of the reactants by calculating the work terms associated with the reaction. The corrected rate constant is then the observed rate constant divided by W_{12} (defined later). Ratios obtained by using work term corrected rate constants vary by a factor of 20 for SO_2^- compared to $[Ru(NH_3)]_6^{2+}$[27] and by a factor of 300 for SO_2^- compared to $[V(OH_2)_6]^{2+}$.[27] Furthermore, the ratios show no discrimination between the azido and the remaining complexes. Thus, it seems reasonable that all of the reactions occur by a simple outer-sphere process and that the work term corrected ratios represent a more realistic test of the predictive value of the Marcus theory. Finally, the fact that the rate constant for reduction of the imidazole complex does not change appreciably as the uncoordinated nitrogen is deprotonated indicates that a bridging interaction involving the lone pair on nitrogen is unimportant.

Thus it appears reasonable to apply the Marcus theory to calculate the self-exchange rate constant for the SO_2/SO_2^- couple. The relevant equations are

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \qquad (5)$$

$$\ln f_{12} = \left(\ln K_{12} + \frac{w_{12} - w_{21}}{RT}\right)^2 \Big/ 4\left(\ln\left(\frac{k_{11}k_{22}}{Z^2}\right) + \frac{w_{11} + w_{22}}{RT}\right) \qquad (6)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \qquad (7)$$

$$w_{ij}(r) = Z_1Z_2e^2/D_sr(1 + \beta r\mu^{1/2}) \qquad (8)$$

$$\beta = (8\pi Ne^2/1000D_skT)^{1/2} \qquad (9)$$

k_{12}, k_{11}, and k_{22} are the rate constants for the cross-reaction and the respective self-exchange reactions for the reagents while K_{12} is the equilibrium constant for the cross-reaction; Z is the collision frequency, usually assumed equal to 10^{11} L mol^{-1} s^{-1}; the w_{ij} terms denote the work required to assemble the species; Z_1 and Z_2 are the charges on the ions; D_s is the static dielectric constant for the medium; r is the collision diameter usually assumed equal to the ionic radii; μ is the ionic strength. These equations or abbreviated versions have been widely used to estimate self-exchange rate constants, sometimes inappropriately. A few obvious comments to this end are in order. For reactions of like-charged ions at high ionic strength and a collision diameter of about 5 Å or greater, the work term correction W_{12} approaches unity. However, for reactions of ions with opposite charge, the work terms become substantial especially where one of the reactants is a small ion as in the case of SO_2^-. The dominant factor in the work term calculation is the collision diameter, which for small molecules is difficult to estimate accurately. Table III summarizes the calculations for the complexes in this study. The relatively consistent value of $\sim 10^3$ L mol^{-1} s^{-1} for the self-exchange rate constant for SO_2/SO_2^- supports the previous assignment of an outer-sphere mechanism to these reactions. Considering the errors introduced by using reduction potentials and self-exchange rate constants determined under varying conditions, any greater agreement would probably be fortuitous. The value obtained in this study for a wide variety of complex types (both positively and negatively charged) agrees well with that obtained by Stanbury and Lednicky.[9] The changes in molecular parameters for the SO_2/SO_2^- couple are similar to those for the ClO_2/ClO_2^- couple, and the derived self-exchange rate constants are similar. Furthermore, much larger molecular changes occur for the NO_2/NO_2^- couple and the corresponding self-exchange rate constant is several orders of magnitude less. Thus the results obtained in this study appear consistent with those obtained for other triatomic couples.[9]

Two other estimates of the self-exchange rate constant for the SO_2/SO_2^- couple have been reported. One of these is based on a Marcus treatment of SO_2^-–viologen cross-reactions.[6] In this calculation the work term correction, W_{12}, was assumed to be negligible. However, our calculations indicate that this term cannot be ignored and can affect the calculated exchange value substantially. Furthermore, for the viologen–SO_2^- system, the final calculated value of k_{22} is highly dependent on the choice of the collision diameter, r, and the self-exchange rate constant of the oxidant, k_{22}. Unfortunately, both of these terms must be estimated. If a π-cloud interaction between SO_2^- and the viologens is assumed, a value of r = 3.2 Å is obtained by using the S–O bond length in $S_2O_4^{2-}$,[25] 1.5 Å, and half the thickness of a benzene ring, 1.7 Å. This latter value has been used by Meyer et al.[28] for methylviologen. Furthermore, it is reasonable to assume that some sort of charge-transfer "complex" is formed between SO_2^- and the viologens, and a calculation of the collision diameter appropriate to this situation gives an r value of 2.8 Å. With these considerations, we have chosen r = 3.0 Å as a realistic estimate for our calculations. Use of this value gives a self-exchange rate

---

(27) For the $[Co(NH_3)_5L]^{n+}$ complexes, where L = SO_4^{2-}, Cl^-, N_3^-, py, NH_3, and imid, work term corrected rate ratios for $[Ru(NH_3)_6]^{2+}$ and SO_2^- reductions ($k_{SO_2^-}/k_{Ru}$) are 2.6, 7.9, 26, 18, 52, and 66, respectively. For the same series of oxidants, rate ratio values for $[V(OH_2)_6]^{2+}$ and SO_2^- reductions ($k_{SO_2^-}/k_V$) are 1.3, 310, 6.8, 44, 140, and 120.

(28) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 3833.

(29) De Oliveire, L. A. A.; Haim, A. *J. Am. Chem. Soc.* **1982**, *104*, 3363.

constant of approximately 10^7 L mol^{-1} s^{-1} for SO_2/SO_2^-. If the collision diameter is lowered to 2.5 Å,[30a] the self-exchange rate constant obtained is $\sim 10^4$ L mol^{-1} s^{-1}. The choice of r at the short contact distances appropriate to these reactions is obviously critical and somewhat arbitrary.[30b]

The choice of a k_{22} value is also troublesome. Almost certainly, each viologen will have a unique value of k_{22} and this value will *not* be constant for the viologens used. In fact, analysis by Tsukahara and Wilkins[4] indicates that the self-exchange rate constant for the BDQ couple is ~20 times less than that for the PDQ couple. However, there does appear to be a reliable estimate for MV^{2+}/MV^+ of 8×10^5 L mol^{-1} s^{-1}.[29] For the reduction of MV^{2+} by Cr^{2+}, V^{2+}, $^*[Ru(bpy)_3]^{2+}$, and $[Ru(bpy)_3]^{2+}$, the value of 8×10^5 M^{-1} s^{-1} gives good agreement between calculated and observed reductant self-exchange rate constants except for the case of $[Ru(bpy)_3]^{2+}$. Use of this exchange value, however, gives SO_2/SO_2^- self-exchange constants at or above the diffusion-controlled limit. Thus, the values obtained must be viewed with caution. In light of the known charge-transfer interactions between SO_2^- and aromatic organic molecules,[26b] it may be that the reactions considered are not simple outer-sphere reactions.

The remaining estimate of the SO_2/SO_2^- rate constant[11] of approximately 10^7 L mol^{-1} s^{-1}, from comparison of the reactions of SO_2^- and O_2^-, suffers from the lack of a reliable k_{11} value for O_2/O_2^-. Estimates for k_{11} obtained from cross-reactions are not constant but in fact vary from 10^{-6} to 10^5 L mol^{-1} s^{-1}.[32]

Finally, by use of the Marcus theory, the rate constant for the self-exchange reaction can be predicted from structural data:[10]

$$k_{ex} = Z \exp[-(w_r + \Delta G^*_{in} + \Delta G^*_{out})/RT]$$

From the values calculated by Stanbury and Lednicky[9] for the activation energies to rearrange the inner, ΔG^*_{in}, and outer, ΔG^*_{out}, "coordination" spheres and work terms, w_r, from eq 8, a value of 1.1×10^3 M^{-1} s^{-1} can be obtained. The excellent agreement between this calculated value and the value derived from the cross-reactions in this study, $\sim 10^3$ M^{-1} s^{-1}, clearly demonstrates the applicability of the Marcus theory to dithionite reductions.

In conclusion, this study has shown that SO_2^- is an effective reducing agent for a wide variety of complexes and reacts by a simple outer-sphere pathway. A reasonable value for the SO_2/SO_2^- exchange rate constant is obtained from the Marcus reactive collision model when applied to these systems. It is also necessary to consider work terms in the calculations when the collision diameter is small. Although most reactions involving dithionite proceed via the SO_2^- radical, under appropriate conditions $S_2O_4^{2-}$ can also be an effective reducing agent. Further work is necessary to characterize the reactivity of undissociated dithionite.

Acknowledgment. We thank Dr. Y. Kotake and Prof. E. Janzen for the ESR measurements and the Natural Sciences and Engineering Research Council for support of this work.

Registry No. *trans*-$[Co(cyclam)(NH_3)_2]^{3+}$, 53176-75-3; *trans*-$[Co(cyclam)Cl_2]^+$, 19973-61-6; $[Co(sep)]^{3+}$, 72496-77-6; $[Co(diamsar)]^{3+}$, 85663-96-3; $[Co(bpy)_3]^{3+}$, 19052-39-2; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Co(NH_3)_5(4\text{-}NO_2\text{-}imid)]^{2+}$, 110682-59-2; $[Co(NH_3)_5imid]^{3+}$, 38716-02-8; $[Co(NH_3)_5imid]^{2+}$, 61159-81-7; $[Co(NH_3)_5pyz]^{3+}$, 59389-55-8; $[Co(NH_3)_5(4,4'\text{-}bpy)]^{3+}$, 53879-90-6; $[Co(NH_3)_5py]^{3+}$, 31011-67-3; $[Ru(NH_3)_5pyz]^{3+}$, 38139-16-1; $[Fe(CN)_5py]^{2-}$, 61332-63-6; $[Fe(CN)_5(4,4'\text{-}bpy)]^{2-}$, 84823-86-9; $[Fe(CN)_5imid]^{2-}$, 61332-60-3; $[Fe(CN)_5pyz]^{2-}$, 61332-65-8; $[Ru(NH_3)_5imid]^{3+}$, 80593-52-8; $[Fe(CN)_5bpy]^{2-}$, 73295-95-1; SO_2^-, 12143-17-8; $S_2O_4^{2-}$, 14844-07-6.

Supplementary Material Available: A table of kinetic data for reduction of Co(III), Fe(III), and Ru(III) by dithionite (4 pages). Ordering information is given on any current masthead page.

---

(30) (a) An extreme view with respect to ref 26a and may imply charge-transfer complex formation. (b) Rosseinsky, D. *Comments Inorg. Chem.* **1984**, *3*, 153.

(31) Balahura, R. J.; Ferguson, G., Ruhl, B., Wilkins, R. G. *Inorg. Chem.* **1983**, *22*, 3990.

(32) Espenson, J.; Bakac, A.; McDowell, M. S. *Inorg. Chem.* **1984**, *23*, 2232.

Contribution from the Department of Chemistry,
State University of New York at Stony Brook, Stony Brook, New York 11794-3400

Synthetic and Structural Studies of Phosphine and Phosphite Derivatives of the $[FeCo_3(CO)_{12}]^-$ Anion and Their $[Ph_3PAu]^+$ Adducts

Arthur A. Low and Joseph W. Lauher*

Received February 25, 1987

Synthetic and structural studies of phosphine- and phosphite-substituted derivatives of $[FeCo_3(CO)_{12}]^-$ and $[Ph_3PAuFeCo_3(CO)_{12}]$ are reported. The anion reacts with phosphine or phosphites to yield monosubstituted derivatives of the formula $[FeCo_3(CO)_{11}L]^-$. When L = $P(OMe)_3$ or PMe_2Ph, $[Ph_3PAuNO_3]$ reacts with $[FeCo_3(CO)_{11}L]^-$ to give substituted gold derivatives. For L = $P(OMe)_3$, the isolated product is the disubstituted gold compound $[Ph_3PAuFeCo_3(CO)_{10}\{P(OMe)_3\}_2]$. When L = PPh_3, no reaction is observed with $[Ph_3PAuNO_3]$. Crystal structures of the compounds $[Et_4N][FeCo_3(CO)_{11}PPh_3]$, $[Co(CO)\{P(OMe)_3\}_4][FeCo_3(CO)_{11}P(OMe)_3]$, $[Ph_3PAuFeCo_3(CO)_{11}PMe_2Ph]$, and $[Ph_3PAuFeCo_3(CO)_{10}\{P(OMe)_3\}_2]$ are reported. Significant angular distortions are found in the packing of the carbonyl ligands. In the substituted gold derivatives, the Ph_3PAu moiety is significantly distorted from the symmetrical position observed in $[Ph_3PAuFeCo_3(CO)_{12}]$.

In a preliminary report several years ago we published a structural study of the trigonal-bipyramidal cluster, $[Ph_8PAuFeCo_3(CO)_{12}]$, the first example of a cluster with an Au atom triply bridging three transition-metal atoms.[1] In that report, we noted a close structural relationship between certain hydrido–metal complexes and the corresponding $[Ph_3PAu]^+$ adducts. Our proposed gold–hydride analogy has been further explored by others, and many new gold cation adducts of transition-metal cluster anions have been reported.[2] Most gold derivatives have indeed proved to be structural analogues of the corresponding hydride complexes, but many have not.

The structural relationships between gold phosphine and hydride derivatives have thus proved to be subtle and are not yet defined. Few direct comparisons of the reaction chemistry of hydrides and the corresponding gold complexes have been reported.

---

(1) Lauher, J. W.; Wald, K. *J. Am. Chem. Soc.* **1981**, *103*, 7648.

(2) Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237–326 and references therein.

0020-1669/87/1326-3863$01.50/0