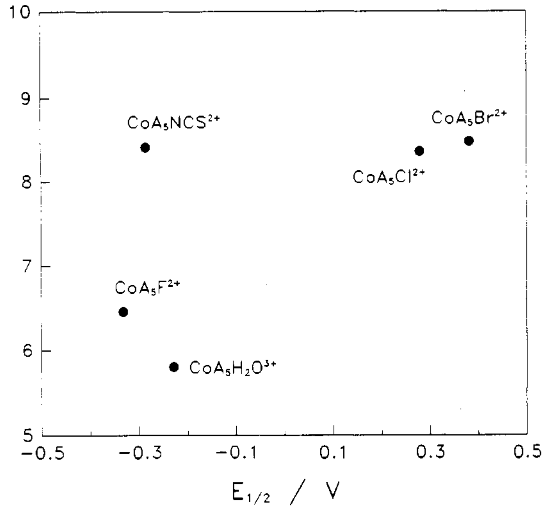

Figure 2. Reaction of $Rh(dmgH)_2PPh_3$ with cobalt(III) complexes, illustrated by plot of the logarithms of the measured second-order rate constants versus half-wave reduction potentials of cobalt(III) complexes.

is 5 times greater than it is for $Ru(NH_3)_6^{2+}$. The ratio $k_{Co(NH_3)_5N_3}/k_{Co(NH_3)_5Br}$ is 10^3 times greater for $Rh(dmgH)_2PPh_3$ than for $Ru(NH_3)_6^{2+}$. This is clearly a significant deviation from the Marcus theory, suggesting that the $Rh(dmgH)_2PPh_3$ reaction is not outer-sphere.

In a previous study[5] of the reaction of $Rh(dmgH)_2PPh_3$ with alkyl halides, an approximately linear correlation was observed between the second-order rate constant and the half-wave reduction potentials of the alkyl halides, which we take as an approximate measure of $E°$. Half-wave reduction potentials are available[16] for some of the cobalt(III) complexes used in the present study, enabling a plot to be made of the second-order rate constant versus $E_{1/2}$. This plot is shown in Figure 2. No correlation is observed. We take this as further evidence against an outer-sphere mechanism. Some caution is in order, however, in that true reduction potentials (for alkyl halides and for cobalt(III) complexes) are not available. The use of $E_{1/2}$ values for irreversible couples is risky, in that voltages associated with irreversible electrode processes cannot be directly taken as $E°$ for a redox couple.

The UV/visible spectrum of the product of the reaction of $Rh(dmgH)_2PPh_3$ with $Co(NH_3)_5Cl^{2+}$ suggests that the chlororhodium complex, $ClRh(dmgH)_2PPh_3$, is the only significant product. As rhodium(III) complexes are substitution inert, this demonstrates that the reaction is inner-sphere. An outer-sphere reaction would yield an aquo–rhodium product.

The observed reactivity order for $Co(NH_3)_5X^{2+}$, $Br^- > Cl^- > F^-$, can be rationalized in terms of a reaction between a soft metal center (Rh^{II}) and a hard metal center (Co^{III}). If the reaction occurs by an inner-sphere mechanism with a rate-determining electron-transfer step, the second-order rate constant is given by the product of the equilibrium constant for the formation of the precursor complex, K_{eq}, and the rate constant for intramolecular electron transfer in the precursor complex, k_{et}. Since a hard metal forms a more stable fluoride complex and a soft metal forms a more stable bromide complex, in the present case one would expect K_{eq} to decrease in the order $Br^- > Cl^- > F^-$. The overall reactivity order is also determined by k_{et}. Since Br^- has a higher electron permeability than F^-, one would also predict a decrease in k_{et} in the order $Br^- > Cl^- > F^-$. The two effects combined to give the normal reactivity order.

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Reactions of Sulfur Dioxide with Photochemically Generated Polypyridyl Complexes of Chromium(II). Calculation of the $SO_2/SO_2^{\bullet-}$ Self-Exchange Rate Constant[1]

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Three reactions occur when $Cr(NN)_3^{3+}$ ions (NN = bpy, phen, and substituted analogues) are subjected to visible light from a laser pulse in solutions containing SO_2 in 1.0 M H_2SO_4. The quenching reaction produces $Cr(NN)_3^{2+}$ quantitatively. The $Cr(NN)_3^{2+}$ so produced undergoes back electron transfer, but in the presence of millimolar concentrations of SO_2 the predominant reaction is electron transfer between $Cr(NN)_3^{2+}$ and SO_2, yielding the transient $SO_2^{\bullet-}$. The rate constants for both back electron transfer and SO_2 reduction are correlated by the Marcus cross-relation. The calculated value of the $SO_2/SO_2^{\bullet-}$ self-exchange rate constant covers the range (1–18) × 10^4 L mol^{-1} s^{-1} at 25 °C in 1.0 M H_2SO_4.

Introduction

Self-exchange reactions between small molecules and their one-electron-reduced partners continue to be of interest. In a recent study involving the $O_2/O_2^{\bullet-}$ pair, it was noted that the reactions fell into two distinct categories, depending on the direction in which kinetic data were determined.[2] Consider the transformation $O_2 + D \rightleftarrows O_2^{\bullet-} + D^+$. The autoxidation reactions yielded kinetic data that were correlated by the Marcus cross-relation[3-6] and gave consistent values for k_{11}, the $O_2/O_2^{\bullet-}$ self-exchange rate constant. On the other hand, widely scattered values of k_{11} were obtained when data for the reductions by the superoxide radical ion were examined.[2]

The $SO_2/SO_2^{\bullet-}$ couple has been examined only in reactions starting with $SO_2^{\bullet-}$.[7] The reported self-exchange rate constants, k_{ex}, span a large range of values, from 10^2 to 10^9 M^{-1} s^{-1}.[8-11] The values significantly different from ~10^3 M^{-1} s^{-1} have recently been discarded as unreliable,[11] either because there is uncertainty in the parameters needed in the calculations or because the mechanism has not been established with certainty. This left no reliable estimate of k_{ex} for the $SO_2/SO_2^{\bullet-}$ couple based on oxidations by

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SO_2. We found it of interest therefore to examine outer-sphere reactions of aqueous sulfur dioxide and compare the values of k_{ex} obtained from both types of redox reactions of $SO_2/SO_2^{\bullet-}$. The reaction partners we selected are tris(polypyridine)chromium(II) ions, $Cr(NN)_3^{2+}$, where NN = bpy, phen, and their substituted analogues. This choice was governed by their being outer-sphere reagents and by the availability of ancillary data such as Cr(III)/Cr(II) reduction potentials and self-exchange rate constants.[12-17] They offer the further advantage in that the reactions with SO_2 have a small driving force and are thus amenable to correlation by the Marcus cross-relation.

To ensure that only SO_2 and not HSO_3^- is involved (pK_a = 1.86),[18] it was necessary to carry out the kinetic measurements in strongly acidic solutions. Since $Cr(NN)_3^{2+}$ complexes readily dissociate in strong acid, the system is a compatible one only in a scheme where $Cr(NN)_3^{2+}$ is generated in situ by some rapid pulse method, such as flash photolysis, in strongly acidic solutions containing SO_2.

The photophysics and photochemistry of $Cr(NN)_3^{3+}$ complexes have been thoroughly investigated.[12-17] We chose as a quencher $Co^{II}([14]aneN_4)^{2+}$,[19] because it seemed to have the requisite features. Quenching of $^*Cr(NN)_3^{3+}$ by $Co([14]aneN_4)^{2+}$ proved to be rapid, and the quencher did not react with SO_2 or other components of the mixture. Also, the back electron transfer was slow enough not to interfere with the SO_2 reactions in most cases.

The complete investigation entailed a study of the quenching (eq 1), back electron transfer (eq 2), and sulfur dioxide reactions (eq 3).

$$^*Cr(NN)_3^{3+} + Co([14]aneN_4)^{2+} \xrightarrow{k_q} Cr(NN)_3^{2+} + Co([14]aneN_4)^{3+} \quad (1)$$

$$Cr(NN)_3^{2+} + Co([14]aneN_4)^{3+} \xrightarrow{k_{bet}} Cr(NN)_3^{3+} + Co([14]aneN_4)^{2+} \quad (2)$$

$$Cr(NN)_3^{2+} + SO_2 \xrightarrow{k_S} Cr(NN)_3^{3+} + SO_2^{\bullet-} \quad (3)$$

Experimental Section

Materials. The $[Cr(NN)_3](ClO_4)_3$[12] complexes were prepared by the literature method in which the chromium(II) complex, formed from the free ligand (G. F. Smith) and Cr_{aq}^{2+}, was oxidized by bromine. The resulting material was then extracted repeatedly with chloroform to remove excess ligand. The complexes were identified from their UV/visible spectra[17,20] and the lifetimes of their lowest energy excited states.[12,17] These ranged from 71 μs for $^*Cr(bpy)_3^{3+}$ to 683 μs for $^*Cr(4,7\text{-}Me_2phen)_3^{3+}$. All the compounds were stored in the dark.

The Co(II) complex $(H_2O)_2Co([14]aneN_4)^{2+}$ was made in aqueous solution by mixing anaerobically stoichiometric amounts of $Co(ClO_4)_2$ and $[14]aneN_4$.[21] The mixture was stirred under argon until the blue precipitate had redissolved to form an orange solution, at which time sulfuric acid was added to give ca. 0.033 M H_2SO_4. The cobalt(II) complex was kept at 0 °C, under argon, in the dark; the solutions were used only for 3 h. The Co(II) complex is characterized by an absorption maximum at 465 nm (ϵ 22 L mol^{-1} cm^{-1}) and a minimum at 435 nm.

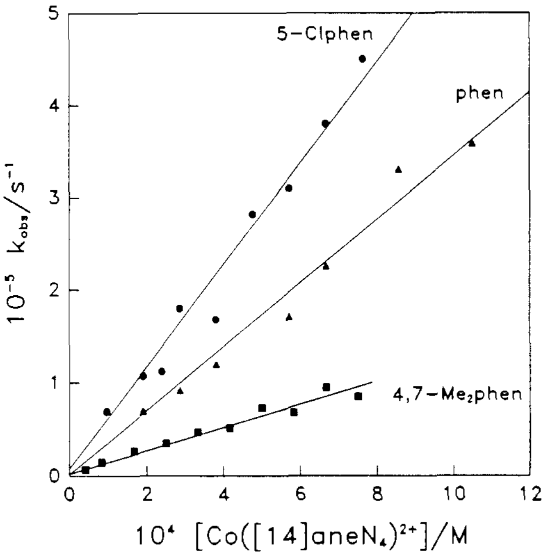

Figure 1. Plots showing the linear variation of k_{obsd} with the concentration of the Co(II) quencher for the reaction of $^*Cr(NN)_3^{3+}$ and Co-$[14]aneN_4^{2+}$.

The Co(III) complex was obtained first as the chloride salt by bubbling O_2 through a methanolic solution of $CoCl_2 \cdot 6H_2O$ and $[14]aneN_4$. After 1 h, concentrated HCl was added to precipitate a green solid.[22] This was purified[23] by passing it through Dowex 1-X8 anion-exchange resin in the hydroxide form from which $[(H_2O)_2Co([14]aneN_4)](ClO_4)_3$ was precipitated with perchloric acid. The complex had absorption maxima at 560 nm (ϵ 28 L mol^{-1} cm^{-1}) and 430 nm (ϵ 46 L mol^{-1} cm^{-1}). The crystals were stable if stored in the mother liquor in a refrigerator and harvested only when needed.

Solutions of sulfur dioxide were prepared by bubbling the anhydrous gas into 1.0 M H_2SO_4. The concentration of SO_2 was determined spectrophotometrically at λ 276 nm (ϵ 388 L mol^{-1} cm^{-1}).[24] On occasion the SO_2 concentration was verified iodometrically.

Solutions of all the reagents were made with Millipore-purified water. The reactions were conducted under an argon atmosphere. The medium was 1.0 M H_2SO_4 unless otherwise noted.

Kinetics by Laser Flash Photolysis. Both emission and absorption experiments were carried out with the apparatus previously described.[25] The laser dye was LD423 (Exciton, 2×10^{-4} M in methanol), and the pulse width was ~0.6 μs. A single pulse was used. The kinetic data for the decay of the excited state itself and for its quenching reaction (eq 1) were collected at 727 nm, an emission maximum of $^*Cr(NN)_3^{3+}$.

The formation of $Cr(NN)_3^{2+}$ in the quenching reaction was verified in absorption experiments at 560 nm (bpy) or 445 nm (all compounds). The yield of $Cr(NN)_3^{2+}$ produced relative to the amount of $^*Cr(NN)_3^{3+}$ initially generated in the laser pulse was 100 ± 20%. (The uncertainty reflects the uncertainties in the molar absorptivities.) In these experiments the Co(II) quencher was added to the septum-sealed fluorescence cell containing $Cr(NN)_3^{3+}$ in 1.0 M sulfuric acid immediately before the flash. To avoid interference from ground-state quenching[16,26] and from quenching by $Cr(NN)_3^{2+}$ (eq 4, $k_{Cr} = 5 \times 10^9$ L mol^{-1} s^{-1}),[27] the concentration of the ground state was <50 μM in all cases, and the laser power was adjusted to generate only some 2-5 μM $^*Cr(NN)_3^{3+}$.

$$^*Cr(NN)_3^{3+} + Cr(NN)_3^{2+} \xrightarrow{k_{Cr}} Cr(NN)_3^{2+} + Cr(NN)_3^{3+} \quad (4)$$

An excess of the Co(III) complex was added to the solutions for the back electron transfer (eq 2) to maintain pseudo-first-order conditions. The kinetic data were collected at wavelengths corresponding to the absorption maxima of $Cr(NN)_3^{2+}$.

The kinetics of reaction 3 were studied in the presence of high concentrations of $Co([14]aneN_4)^{2+}$ (1-5 mM). This was necessary to ensure the complete quenching of $^*Cr(NN)_3^{3+}$ prior to the reaction of $Cr(NN)_3^{2+}$ with SO_2. Even under these conditions the first 15 ± 5% of the

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Table I. Quenching and Back-Electron-Transfer Rate Constants[a] for the Reaction between $^*Cr(NN)_3^{3+}$ and $Co([14]aneN_4)^{2+}$

compd	quenching: $E°$ (*3+/2+)/V[b]	quenching: $10^{-8}k_q$/L mol^{-1} s^{-1} [c]	back electron transfer: $E°$ (3+/2+)/V[d]	back electron transfer: $10^{-8}k_{bet}$/L mol^{-1} s^{-1} [e]
$Cr(5\text{-}Cl\text{-}phen)_3^{3+}$	1.53	5.2 (2)	−0.17	0.170 (8)
$Cr(bpy)_3^{3+}$	1.44	1.8 (2)[f]	−0.26	0.44 (4)
$Cr(phen)_3^{3+}$	1.42	3.3 (2)	−0.28	1.3 (1)
$Cr(5,6\text{-}Me_2phen)_3^{3+}$	1.40	2.55 (7)	−0.29	1.58 (4)
$Cr(5\text{-}Mephen)_3^{3+}$	1.39	4.04 (9)	−0.30	1.05 (4)
$Cr(4,4'\text{-}Me_2bpy)_3^{3+}$	1.25	0.7 (2)	−0.45	~7
$Cr(4,7\text{-}Me_2phen)_3^{3+}$	1.23	1.28 (5)	−0.45	~7

[a] In 1.0 M H_2SO_4 at 25 ± 1 °C. [b] Versus NHE; ref 16. [c] $[Co[14]aneN_4)(H_2O)_2^{2+}] = (0.5–10) \times 10^{-4}$ M; $[^*Cr(NN)_3^{3+}]_0 = 2–5$ μM. [d] Versus NHE in 1.0 M LiCl; ref 12. [e] $[Co([14]aneN_4)(H_2O)_2^{3+}] = (0.6–8) \times 10^{-4}$ M; $[Cr(NN)_3^{2+}]_0 = (0.8–2.5) \times 10^{-5}$ M. [f] In 1.0 M $LiClO_4$ k_q is 1.5×10^8 L mol^{-1} s^{-1}.

kinetic traces were discarded to avoid overlap of reactions 1 and 3.

Kinetic data were collected by a Nicolet digitizing oscilloscope and transferred to an Apple II computer. The transmittance values were converted to absorbances and then fit to first-order kinetics, as described by the equation $A_t = A_\infty + (A_0 - A_\infty) \exp(-kt)$, with a nonlinear-least-squares program.

Except for $Cr(bpy)_3^{3+}$, all of the complexes showed the phenomenon of ground-state quenching. Plots of τ^{-1} vs $[Cr(NN)_3^{3+}]$ were linear[28] and in 1.0 M H_2SO_4 yielded the following rate constants, $10^{-7}k_g$/L mol^{-1} s^{-1}, for various NN's: 5-Cl-phen, 6.8; phen, 2.9; 5-Mephen, 3.9; 5,6-Me_2phen, 1.0; 4,4'-Me_2bpy, 0.71; 4,7-Me_2phen, 2.0.

Results

All of the kinetic traces for the quenching of $^*Cr(NN)_3^{3+}$ by $Co([14]aneN_4)^{2+}$ fit first-order kinetics. A plot of k_{obsd} versus $[Co([14]aneN_4)^{2+}]$ yields a line of slope k_q and an intercept representing the contributions of the self-decay (k_0), ground-state quenching (k_g), and quenching by $Cr(NN)_3^{2+}$ (k_{Cr}). Figure 1 shows data for several representative compounds. The small intercepts are consistent with the quenching reaction (1) being the dominant reaction pathway under our experimental conditions. Specifically, the quenching by $Cr(NN)_3^{2+}$, which occurs with a rate constant close to the diffusion-controlled limit, was kept at the minimum by working with low concentrations of $^*Cr(NN)_3^{3+}$ and $Cr(NN)_3^{2+}$. The quenching of $^*Cr(bpy)_3^{3+}$ by $Co([14]aneN_4)^{2+}$ was also monitored in absorption experiments at 560 nm, a wavelength corresponding to an absorption maximum for $Cr(bpy)_3^{2+}$. The rate constants from absorption and emission agreed to within 5%. The yields of $Cr(bpy)_3^{2+}$ and $Cr(5\text{-}Cl\text{-}phen)_3^{2+}$ were ~100% in experiments in which $Cr(NN)_3^{2+}$ and $^*Cr(NN)_3^{3+}$ were both measured. The rate constant for the quenching reaction was independent of $[Cr(NN)_3^{3+}]$ and of $[H^+]$. Values of k_q are summarized in Table I.

Back electron transfer (eq 2) is responsible for the disappearance of $Cr(NN)_3^{2+}$ subsequent to its production in reaction 1. Most determinations of k_{bet} were carried out by adding $Co([14]aneN_4)^{3+}$ to the reaction solution before the laser flash. This addition converts a second-order reaction into a pseudo-first-order one. All traces with added $Co([14]aneN_4)^{3+}$ followed first-order kinetics. The plot of k_{obs} versus the concentration of $Co([14]aneN_4)^{3+}$ is a straight line, whose slope represents k_{bet} for the given $Cr(NN)_3^{2+}$ complex. Values of k_{bet} are listed in Table I. The plots of k_{obsd} vs [Co(III)] have finite intercepts that are not predicted by the reactions considered. These intercepts are small and increase somewhat as the $E°$ value for the $Co(NN)_3^{3+/2+}$ couple decreases. The values of k_{bet} are independent of the monitoring wavelength, $[Co([14]aneN_4)^{2+}]$, $[H^+]$, and $[Cr(NN)_3^{3+}]$. Note that the values of k_{bet} span a wider range than the k_q values. For the 5,6-Me_2phen complex, for example, k_q is only approximately twice as large as k_{bet}. For the complexes of 4,4'-bpy and 4,7-Me_2phen the values of k_{bet} are so large that the pseudo-first-order technique described above is not feasible. In these cases the rate constants k_{bet} were derived from second-order kinetic analyses of reactions in which the only Co(III) present was formed by quenching.

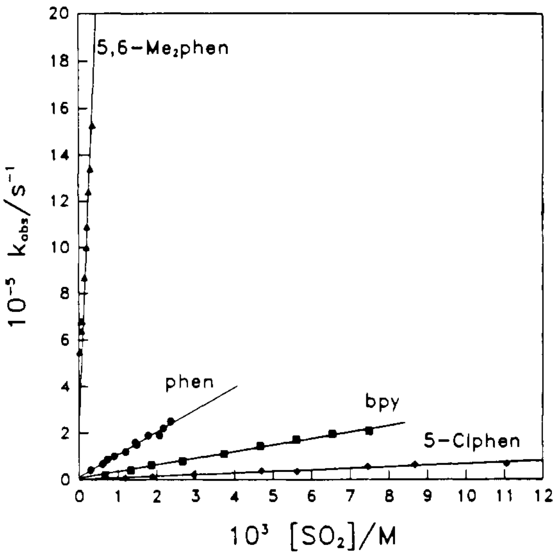

Figure 2. Plots showing the linear variation of k_{obsd} with SO_2 concentration in 1.0 M H_2SO_4 for the reaction of $Cr(NN)_3^{2+}$ with SO_2.

Table II. Kinetic Data[a] for the Reduction of SO_2 by $Cr(NN)_3^{2+}$ Complexes

complex	$10^{-7}k_S$/L mol^{-1} s^{-1}	$\Delta E°$[b]/V
$Cr(5\text{-}Cl\text{-}phen)_3^{2+}$	0.683 (4)	0.0
$Cr(bpy)_3^{2+}$ [c]	2.97 (7)	0.09
$Cr(phen)_3^{2+}$	9.5 (2)	0.11
$Cr(5,6\text{-}Me_2phen)_3^{2+}$	28 (2)	0.12
$Cr(5\text{-}Mephen)_3^{2+}$	17 (1)	0.13

[a] In 1.0 M H_2SO_4 at 25 ± 1 °C. [b] Difference of the standard reduction potentials for the couples $SO_2/SO_2^{\bullet-}$ (−0.17 V) and $Cr(NN)_3^{3+/2+}$, respectively. [c] In 1.0 M $HClO_4$ $k_S = 3.4 \times 10^7$ L mol^{-1} s^{-1}.

The addition of SO_2 resulted in $Cr(NN)_3^{2+}$ being consumed much more rapidly than in its absence. These experiments were conducted with $[SO_2] \gg [Co([14]aneN_4)^{3+}]$ so that the back-electron-transfer reaction would not interfere with the determination of k_S. The kinetic traces followed first-order kinetics. Plots of k_{obsd} versus $[SO_2]$ were linear, with a slope corresponding to k_S (eq 3) and a nearly negligible intercept, which we attribute to the residual back electron transfer that remains at $[SO_2] = 0$. Figure 2 shows the indicated plots. We also did one series of experiments in perchloric acid; the results were the same, and variation of perchloric acid concentration in the range $0.50 < [H^+] < 1.0$ M was without effect on k_S. The values of k_S are given in Table II. It was not possible to obtain valid results for two complexes, $Cr(4,4'\text{-}Me_2bpy)_3^{2+}$ and $Cr(4,7\text{-}Me_2phen)_3^{2+}$, since the values of k_{bet} are so large as to preclude the measurement of additional reactions.

Discussion

Reactions of $Cr(NN)_3^{2+}$. We start with the back-electron-transfer reaction, since it is the best defined in the sense that the necessary parameters for application of the Marcus cross-relation[6,12] are at hand. We take the self-exchange rate constant, k_{CrCr}, for the $Cr(NN)_3^{3+/2+}$ pair at the reported value,[12,29,30] 2×10^9 L mol^{-1} s^{-1}, and assume it is the same for all NN's. The couple $Co([14]aneN_4)^{3+/2+}$ has an $E°$ value of 0.421 V and a self-exchange rate constant, k_{CoCo}, of 8×10^{-4} L mol^{-1} s^{-1}.[19b] This allows us to consider the experimental data in terms of a plot of log k_{bet} versus log K_{12}. The correlation is adequate but not perfect, and the line has a slope of 0.4 ± 0.1 and an intercept of 3 ± 1. The

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(28) For $Cr(phen)_3^{3+}$ and $Cr(5\text{-}Cl\text{-}phen)_3^{3+}$, plots of k_{obsd} vs $[Cr(NN)_3^{3+}]$ are linear only for concentrations below 10^{-4} M. Values of k_g cited in the text refer to the linear region.

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Table III. Calculated Self-Exchange Rate Constants for the $SO_2/SO_2^{\bullet -}$ Couple[a,b]

compd	$k_{ex}^c/10^4$ L mol^{-1} s^{-1}	compd	$k_{ex}^c/10^4$ L mol^{-1} s^{-1}
$Cr(5\text{-}Clphen)_3^{3+}$	0.78	$Cr(5,6\text{-}Me_2phen)_3^{2+}$	18
$Cr(bpy)_3^{2+}$	1.1	$Cr(5\text{-}Mephen)_3^{2+}$	4.7
$Cr(phen)_3^{2+}$	2.8		

[a] In 1.0 M H_2SO_4 at 25 ± 1 °C. [b] Electrostatics-corrected rate constants. The $SO_2/SO_2^{\bullet -}$ potential is −0.17 V vs NHE;[8] the radius of $SO_2/SO_2^{\bullet -}$ is taken as 2.83 Å (Stanbury, D. M.; Lednicky, L. A. *J. Am. Chem. Soc.* **1984**, *106*, 2847), and that of $Cr(NN)_3^{3+}/^{2+}$, as 6.8 Å, about the same as those of Ru(III) and Co(III) analogues (Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883. Cummins, D.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 5158). [c] $k_{CrCr} = 2 \times 10^9$ L mol^{-1} s^{-1}.

calculated values from the Marcus cross-relations shown in eq 5 and 6 are 0.4 ± 0.1 (= 0.5(1 + α))[12] and 3.1, respectively. The

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \qquad \log f_{12} = \frac{(\log K_{12})^2}{4\log(k_{11}k_{22}/Z^2)} \tag{5}$$

$$\log k_{12} = 0.50 \log (k_{11}k_{22}) + 0.50(1 + \alpha) \log K_{12} \tag{6}$$

$$\alpha = \frac{\log K_{12}}{4 \log (k_{11}k_{22}/Z^2)}$$

agreement between the observed and calculated values implies that the self-exchange rate constant for $Cr(NN)_3^{3+/2+}$ couples was approximately correct and that the $\Delta E°$ values (0.59–0.72 V) were sufficiently low that the Marcus cross-relation was applicable.

The internal consistency apparent in the Marcus treatment of the back-electron-transfer reactions increases our confidence in the values of k_{CrCr} and k_{CoCo} despite the limited data used to estimate these parameters.[12,19b,29,30] It has been suggested earlier that the reactions of $Co([14]aneN_4(H_2O)_2^{3+/2+}$ are nonadiabatic[19b] with $\kappa_{el} = 10^{-3\pm1}$. Our data provide no support for that claim, as the reactions with the chromium polypyridine complexes appear to be adiabatic.

$SO_2/SO_2^{\bullet -}$ Self-Exchange Rate Constant. We again set the self-exchange rate constant of each $Cr(NN)_3^{3+/2+}$ couple at an average value of 2×10^9 L mol^{-1} s^{-1}. The individual complexes then yield an average self-exchange rate constant for the $SO_2/SO_2^{\bullet -}$ couple, k_{ex}, of ~5×10^4 L mol^{-1} s^{-1}, with the individual rate constants scattered between 0.78×10^4 and 18×10^4 L mol^{-1} s^{-1}, as given in Table III. Note that the very small driving force in reaction 3 (0.0–0.13 V), based on $E°(SO_2/SO_2^{\bullet -}) = -0.17$ V at 1 M acid,[31] makes the system particularly amenable to treatment by the simple Marcus cross-relation.

The rate constant k_{ex} for $SO_2/SO_2^{\bullet -}$ can be compared with previous estimates, all of which derive from experiments in which $SO_2^{\bullet -}$ is the reactant. Some data derive from pulse-radiolytically prepared $SO_2^{\bullet -}$; others, from the homolysis of dithionite ions. The reduction of Co(III) and Fe(III) complexes by $SO_2^{\bullet -}$ yields values of k_{ex} between 3×10^2 and 5×10^4 L mol^{-1} s^{-1},[9,11] close to the value obtained in this work. It is especially encouraging to see that there is a reasonable agreement between the values of k_{ex} derived from oxidations by SO_2 and reductions by $SO_2^{\bullet -}$, given the difficulties in the related $O_2/O_2^{\bullet -}$ system. The values obtained from the reaction of $SO_2^{\bullet -}$ with trivalent metalloporphyrins are considerably higher, 5×10^5–3×10^9 L mol^{-1} s^{-1},[8] as are the values calculated from reactions between $SO_2^{\bullet -}$ and methylviologen ions (and related species), 9×10^6–1.4×10^8 L mol^{-1} s^{-1}.[9] These latter reactions we discount since the reverse reactions are at the diffusion-controlled limit. Indeed, these latter reactions have already been discounted[11] owing to the uncertainties in the collision diameters and the self-exchange rate constants for the viologens, as well as the uncertainties about the reaction mechanism. The reactions with the metalloporphyrins[8] might be accelerated by special interactions between $SO_2^{\bullet -}$ and the porphyrin ring. A similar interaction was proposed in the reaction of $SO_2^{\bullet -}$ with the viologens.[11] We also note that the ratio of $k(SO_2/SO_2^{\bullet -})$ to $k(O_2/O_2^{\bullet -})^2$ is ~10^3, consistent with the earlier estimate by Bradić and Wilkins.[10]

We should also consider the fate of the $SO_2^{\bullet -}$ formed as a product of the reaction represented by eq 3. There are two plausible reactions by which $SO_2^{\bullet -}$ is consumed. One is the oxidation of $SO_2^{\bullet -}$ by the Co(III) complex and the other is the combination of two $SO_2^{\bullet -}$ to yield dithionite ions (eq 7 and 8).

$$SO_2^{\bullet -} + Co([14]aneN_4)^{3+} \xrightarrow{k_7} SO_2 + Co([14]aneN_4)^{2+} \tag{7}$$

$$2SO_2^{\bullet -} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} S_2O_4^{2-} \tag{8}$$

The value of k_7 is unknown, but it may be estimated from the data in the literature for the reaction between $SO_2^{\bullet -}$ and $Co([14]aneN_4)(NH_3)_2^{3+}$ ($k = 9.2 \times 10^2$ L mol^{-1} s^{-1}) and $Co([14]aneN_4)Cl_2^{+}$ (6.3×10^5 L mol^{-1} s^{-1}).[11] Also, reductions of $Co(edta)Cl^{2-}$ and $Co(edta)^-$ by $SO_2^{\bullet -}$ show the chloro is reduced ~200 times faster than the aquo species; for $Co^{III}(medta)L$ complexes (medta = *N*-methylethylenediamine-*N*,*N′*,*N″*-triacetate), the bromo is reduced about 400 times faster than the aquo complex.[9] For the sake of argument, a value of $k_7 = 10^4$ L mol^{-1} s^{-1} seems like a generous upper limit for reduction of $Co([14]aneN_4)(H_2O)^{3+}$. The value of k_8 is 1.8×10^9 L mol^{-1} s^{-1}.[31] Given the relative rates and concentrations of the various reactants, the dimerization of $SO_2^{\bullet -}$ will predominate over reactions with $Co([14]aneN_4)^{3+}$, and the latter species will build up in solution.

Quenching of $*Cr(NN)_3^{3+}$ by $Co([14]aneN_4)^{2+}$. Quenching of $*Cr(bpy)_3^{3+}$ and of $*Cr(5\text{-}Cl\text{-}phen)_3^{3+}$ has been shown to yield quantitatively the chromium(II) complex. This indicates that quenching occurs entirely by electron transfer.

In one sense it is possible to claim that the electron-transfer quenching reaction of eq 1 is well-understood in that the value of k_q for each $*Cr(NN)_3^{3+}$ complex is within a factor of 5 of that calculated by use of the Marcus theory. The larger picture is less clear, however, since the overall variation of k_q with $\Delta E°$ is a factor of 8, whereas it should theoretically span a factor of 20. Put another way, the plot of log k_q versus log K_{12} has a slope of 0.15 ± 0.04, whereas the Marcus cross-relation predicts from eq 6 a value of ~0.38.

A similarly low sensitivity of the rate constants to the driving force has been observed earlier in the quenching of $*Cr(NN)_3^{3+}$ by $Ru(NN)_3^{3+}$,[12] as well as in the quenching of $*Ru(NN)_3^{2+}$ by Cu^{2+} [25b] and in several other reactions.[30] It has been suggested[25b] that the theoretical equations tend to overestimate the rate constants for reactions with large driving forces. It would thus seem that the results on the quenching reaction of eq 1 are consistent with outer-sphere electron transfer despite the relatively small spread in values of k_q.

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