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Oxidation of a Series of Tris(polypyridyl)chromium(II) Ions by Several Cobalt(III) Complexes
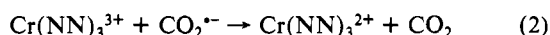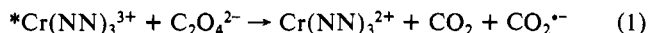
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The kinetics of the outer-sphere oxidation of $Cr(NN)_3^{2+}$ ions (NN = 2,2'-bipyridine, 1,10-phenanthroline, and their substituted derivatives) by tris(chelating ligand) complexes of Co(III) were studied. The second-order rate constants increase with the driving force of the reaction. The rate constants for $Co(en)_3^{3+}$ at 23 ± 2 °C increase from 2.2 (±0.3) × 10^3 M^{-1} s^{-1} for $Cr(bpy)_3^{2+}$ to 1.1 (±0.2) × 10^5 M^{-1} s^{-1} for $Cr(4,7\text{-}Me_2\text{-phen})_3^{2+}$ and agree very well with the values calculated by the Marcus cross relation. For $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$, on the other hand, the experimental rate constants are lower than the calculated values. It is suggested that the reactions of these two species are mildly nonadiabatic, the extent of nonadiabaticity increasing with an increase in the standard free energy of the reaction.

Introduction

Both $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$ complexes have been used to investigate the electron-transfer reactivity of metalloproteins[1-4] and thus to estimate the self-exchange rates of the metalloprotein redox partners. It has recently been reported, however, that reactions of $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$ are nonadiabatic.[5] Consequently, the self-exchange rate constants of metalloenzymes estimated on the basis of the indicated cross-reactions must be viewed with some reservation. The assessment[5] of the nonadiabaticity of the cross-reactions of $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$ ions was achieved by using Weaver's approach[6,7] to the known reactions of these redox couples with mononuclear and binuclear ruthenium(III) amines.

We recently reported[8,9] a laser flash photolysis method for the irreversible quenching of the ^2E excited states of $Cr(NN)_3^{3+}$ to generate the unstable $Cr(NN)_3^{2+}$ ions, where NN = 2,2'-bipyridine, 1,10-phenanthroline, and their substituted derivatives. This method consists of using H_2edta^{2-} or oxalate ions as the quencher; these reagents react by electron transfer that results in the formation of $Cr(NN)_3^{2+}$ with a quantum yield of 2. The quenching is irreversible, and no back electron transfer occurs. The sequence of reactions is shown for oxalate in eq 1 and 2.

$$*Cr(NN)_3^{3+} + C_2O_4^{2-} \rightarrow Cr(NN)_3^{2+} + CO_2 + CO_2^{\cdot-} \quad (1)$$

$$Cr(NN)_3^{3+} + CO_2^{\cdot-} \rightarrow Cr(NN)_3^{2+} + CO_2 \quad (2)$$

We have now employed this method to study the kinetics of the reductions of $Co(en)_3^{3+}$, $Co(bpy)_3^{3+}$, and $Co(phen)_3^{3+}$ by a series of $Cr(NN)_3^{2+}$ complexes. Both sets of reaction partners are inert to substitution, requiring that the reaction proceed through an outer-sphere mechanism. A comparison of the observed rate constants with those calculated by the use of the Marcus theory is possible because all of the parameters such as self-exchange rate constants and standard free energy changes are known.

Experimental Section

Materials. Tris(polypyridine)chromium(III) complexes were prepared according to published procedures, and purities were checked by comparison with the published UV–vis spectra, emission spectra, and lifetimes τ^0.[10,11] The tris(1,10-phenanthroline)cobalt(III) ion was prepared[11b] as the perchlorate salt, $[Co(phen)_3](ClO_4)_3 \cdot 2H_2O$, and recrystallized from

water by adding 5 M $HClO_4$. The UV–vis peak positions and molar absorptivities were 450 nm (sh, 100 M^{-1} cm^{-1}), 350 (3580), and 330 (4650).

The tris(2,2'-bipyridine)cobalt(III) ion was prepared[12] as $[Co(bpy)_3](ClO_4)_3 \cdot 3H_2O$. The UV–vis peak positions and molar absorptivities were 450 nm (sh, 68 M^{-1} cm^{-1}), 316 (30 500), and 305 (33 800).

Kinetic Data. The reactions were initiated and monitored by use of the laser flash photolysis system described earlier.[13] The formation of $*Cr(NN)_3^{3+}$ was achieved by excitation of the $Cr(NN)_3^{3+}$ solution of a 0.6-μs pulse from the dye laser at 452 nm. The quenching of the $*Cr(NN)_3^{3+}$ excited states by oxalate ions (occasionally) or by H_2edta^{2-} (usually) was monitored at the 727-nm maximum in the emission spectrum. The formation and subsequent disappearance of $Cr(NN)_3^{2+}$ were monitored at 440 (NN = 5-Cl-phen), 430 (phen), 480 or 685 (5-Me-phen), 440 (4,7-Me_2-phen), and 560 nm (bpy and 4,4'-Me_2-pby).[14] The kinetic studies were carried out under an oxygen-free atmosphere of argon. Perchlorate salts were used, and ionic strength was maintained at 0.15 M and pH at 5.8. Pseudo-first-order conditions with a 5–10-fold excess of the cobalt(III) complex were used. The absorbance–time data collected in each experiment were analyzed by a nonlinear least-squares fit to the equation $A_t = A_\infty + (A_\infty - A_0) \exp(-kt)$.

Results and Discussion

Kinetics of the Cr(II)–Co(III) Reactions. Under the experimental conditions the formation of $Cr(NN)_3^{2+}$ as in eq 1 and 2 was very rapid. The details of the reductive quenching processes are discussed elsewhere.[8,9] We did blank experiments to learn whether the CoL_3^{3+} complexes function as quenchers for the $*Cr(NN)_3^{3+}$ excited state. Under the experimental conditions no significant quenching by Co(III) was observed, which is not surprising since oxidative quenching is expected to be highly unfavorable, and energy-transfer quenching has been observed[15] and is known to be too slow to interfere.

In the presence of the cobalt(III) complexes, $Cr(NN)_3^{2+}$ disappears rapidly according to eq 3.

$$Cr(NN)_3^{2+} + CoL_3^{3+} \rightarrow Cr(NN)_3^{3+} + CoL_3^{2+} \quad (3)$$
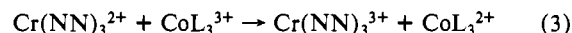
For a given complex the kinetic data were the same regardless of which quencher (oxalate or H_2edta^{2-}) was used in the preparation of $Cr(NN)_3^{2+}$. The rate law for the reaction in eq 3 can be written as

$$-d[Cr(NN)_3^{2+}]/dt = k_{12}[Cr(NN)_3^{2+}][CoL_3^{3+}] \quad (4)$$

$$k_{obsd} = k_{12}[CoL_3^{3+}] \quad (5)$$

Figures 1–3 show the kinetic data for the three CoL_3^{3+} complexes studied. As illustrated in these plots, k_{obsd} increases linearly with the concentration of the CoL_3^{3+} complex. It is evident that the plots in Figures 1–3 pass through the origin; thus, we suggest that eq 3 is the sole pathway for the disappearance of $Cr(NN)_3^{2+}$ and that eq 4 and 5 are applicable.

(1) Holwerda, R. A.; Knaff, D. B.; Gray, H. B.; Clemmer, J. D.; Crowley, R.; Smith, J. M.; Mauk, A. G. *J. Am. Chem. Soc.* **1980**, *102*, 1142.
(2) Wherland, S.; Gray, H. B. In *Biological Aspects of Inorganic Chemistry*; Addison, A. N., Gulley, W., Dolphin, D., James, B. R., Eds.; Wiley: New York, 1977; p 285.
(3) Segal, M.-G.; Sykes, A. G. *J. Am. Chem. Soc.* **1978**, *100*, 4585.
(4) Wherland, S.; Gray, H. B. *Proc. Nat. Acad. Sci. U.S.A.* **1976**, *73*, 2950.
(5) Fürholz, U.; Haim, A. *J. Phys. Chem.* **1986**, *90*, 3686.
(6) (a) Hupp, T. J.; Weaver, M. J. *Inorg. Chem.* **1983**, *22*, 2557. (b) Weaver, M. J.; Hupp, T. J. *ACS Symp. Ser.* **1982**, *No. 198*, 181.
(7) Endicott, J. F.; Burnham, B.; Kumar, K. *Inorg. Chem.* **1982**, *21*, 2437.
(8) Zahir, K.; Espenson, J. H.; Bakac, A. *J. Am. Chem. Soc.*, in press.
(9) Steffan, C. R.; Espenson, J. H.; Bakac, A., unpublished results.
(10) Brunschwig, B.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 7568.
(11) (a) Konig, E.; Herzog, S. J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 585. (b) Przystas, T. J.; Sutin, N. *J. Am. Chem. Soc.* **1973**, *95*, 5545.

(12) Burstall, F. H.; Nyholm, R. S. *J. Chem. Soc.* **1952**, 3570.
(13) Melton, J. D.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986**, *25*, 6104.
(14) Serpone, W.; Jamieson, M. A.; Emmi, S. S.; Fuochi, P. G.; Mulazzani, Q. G.; Hoffman, M. Z. *J. Am. Chem. Soc.* **1981**, *103*, 1091.
(15) Gandolfi, M. T.; Maestri, M.; Sandrini, D.; Balzani, V. *Inorg. Chem.* **1983**, *22*, 3435.

Table I. Summary of the Experimental and Calculated Rate Constants (M^{-1} s^{-1}) for the Reduction of CoL_3^{3+} Complexes by $Cr(NN)_3^{2+}$ and Estimation of Nonadiabaticity of the Reaction[a]

NN	$Co(en)_3^{3+}$				$Co(bpy)_3^{3+}$				$Co(phen)_3^{3+}$			
	$\Delta E°/V$	$10^{-3}k_{exptl}$	$10^{-3}k_{calcd}$	κ_{12}	$\Delta E°/V$	$10^{-8}k_{exptl}$	$10^{-8}k_{calcd}$	κ_{12}	$\Delta E°/V$	$10^{-8}k_{exptl}$	$10^{-8}k_{calcd}$	κ_{12}
5-Cl-phen					0.49	1.2 ± 0.2	4	0.3	0.54	1.6 ± 0.2	10	0.16
bpy	0.10	2.2 ± 0.2[b]	2	1.0	0.58	1.1 ± 0.2	8	0.14	0.63	1.3 ± 0.2	17	0.08
phen					0.60	2.0 ± 0.3	14	0.14	0.65	2.0 ± 0.3	30	0.07
5-Me-phen	0.15	16 ± 3	9	1.0								
4,4'-Me₂-bpy	0.29	66 ± 4	60	1.0	0.77	2.8 ± 0.4	40	0.07	0.82	3.6 ± 0.4	80	0.05
4,7-Me₂-phen	0.29	110 ± 15	85	1.0	0.77	3.5 ± 0.6	55	0.06	0.82	4.1 ± 0.6	110	0.04

[a] Using the following $E°$ and k_{ex} (self-exchange rate constant) for $Co(en)_3^{3+/2+}$, $Co(bpy)_3^{3+/2+}$, and $Co(phen)_3^{3+/2+}$, respectively: 0.16 V,[17] 7.7 × 10^{-5} M^{-1} s^{-1};[18] 0.32 V, 20 M^{-1} s^{-1}; 0.37 V, 40 M^{-1} s^{-1}.[16a] For $Cr(NN)_3^{3+/2+}$ complexes k_{ex} = 1 × 10^9 M^{-1} s^{-1} for NN = bpy or substituted bpy and 2 × 10^9 M^{-1} s^{-1} for NN = phen or substituted phen and $E°_{3/2}$ is −0.17 (5-Cl-phen), −0.26 (bpy), −0.28 (phen), −0.31 (5-Me-phen), −0.45 (4,4'-Me₂-bpy), and −0.45 V (4,7-Me₂-phen).[10] Other parameters used in the calculations are ionic strength = 0.10 M, T = 298K, and r = 7.0 Å for both $Cr(NN)_3^{3+}$ and CoL_3^{3+} and 4.5 Å for $Co(en)_3^{3+}$. [b] Zwickel, A. M.; Taube, H. *Discuss. Faraday Soc.* **1960**, *29*, 42.
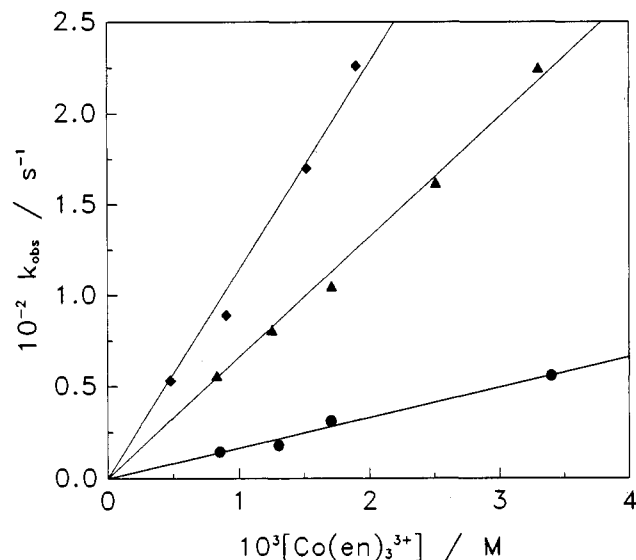
Figure 1. Plot of k_{obsd}, the observed rate constant for the reduction of $Co(en)_3^{3+}$ by $Cr(NN)_3^{2+}$ complexes, versus $[Co(en)_3^{3+}]$ at ambient temperature. The data are shown for L = 5-Me-phen (circles), 4,4'-Me₂-bpy (triangles), and 4,7-Me₂-phen (diamonds).
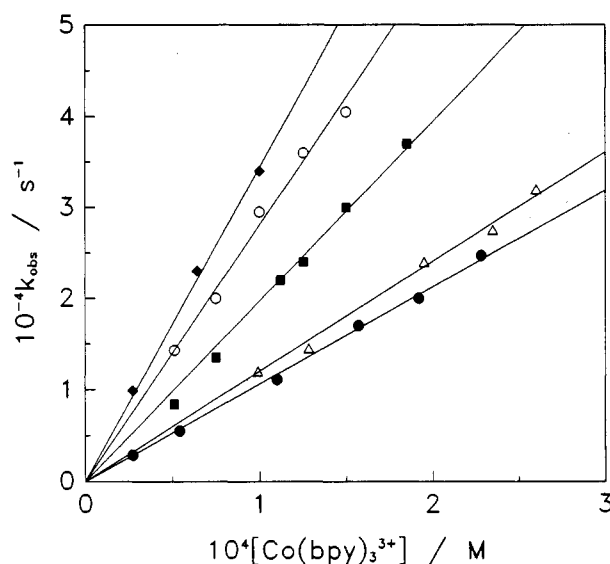
Marcus Theory Analysis. A summary of the cross-reaction rate constants (k_{12}) for reaction 3, along with the $\Delta E°$ value for each reaction, is presented in Table I. It is apparent from these data that k_{12} increases with the standard free energy change of the reaction. For example, the slowest reaction of $Co(en)_3^{3+}$ is that with $Cr(bpy)_3^{2+}$ ($\Delta E°$ = 0.10 V, k = 2.2 × 10^3 M^{-1} s^{-1}), and the fastest is that with $Cr(4,7-Me_2-phen)_3^{2+}$ (0.29 V, 1.1 × 10^5 M^{-1} s^{-1}). Both of the partners in eq 3 are substitutionally inert, and it is thus expected that the reaction will proceed by an outer-sphere electron-transfer mechanism. We noted, however, that the variation of k_{12} with $\Delta E°$ was different for the three complexes. In an effect to understand this phenomenon, we examined the data in light of the Marcus cross relation for electron transfer, as represented by the equations relating the rate constant for electron transfer to the driving force of the reaction and to the self-exchange rate constants. Equations 6–9 were used.[16]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \tag{6}$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln (k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT]} \tag{7}$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \tag{8}$$

$$w_{ij} = \frac{4.25 \times 10^{-8}Z_iZ_j}{r(1 + 3.285 \times 10^7 r\mu^{1/2})} \tag{9}$$

(16) (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265–322. (b) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679, 2654. (c) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275. (d) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

Figure 2. Plot of k_{obsd}, the observed rate constant for the reduction of $Co(bpy)_3^{3+}$ by $Cr(NN)_3^{2+}$ complexes, versus $[Co(bpy)_3^{3+}]$ at ambient temperature. The data are shown for L = bpy (dots), 5-Cl-phen (open triangles), phen (squares), 4,4'-Me₂-bpy (open circles), and 4,7-Me₂-phen (diamonds).
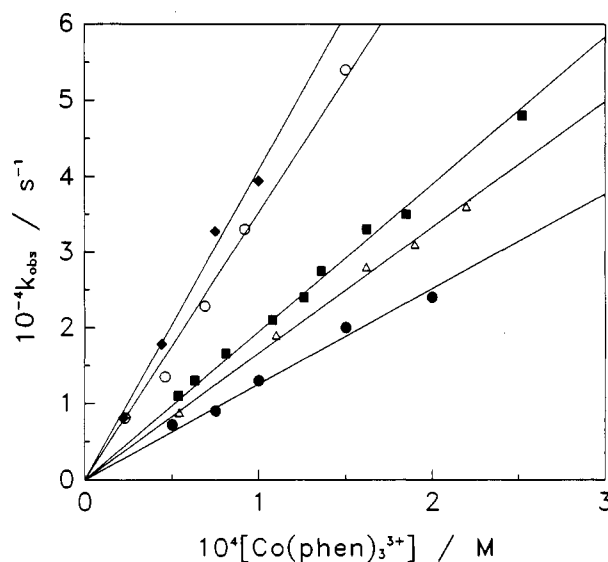
Figure 3. Plot of k_{obsd}, the observed rate constant for the reduction of $Co(phen)_3^{3+}$ by $Cr(NN)_3^{2+}$ complexes, versus $[Co(phen)_3^{3+}]$ at ambient temperature. The data are shown for L = bpy (dots), 5-Cl-phen (open triangles), phen (squares), 4,4'-Me₂-bpy (open circles), and 4,7-Me₂-phen (diamonds).

Table I presents a comparison of the experimental values of k_{12} and those calculated from eq 6–9. It also includes the necessary reduction potentials and self-exchange rate constants.[10,16a,17,18] It
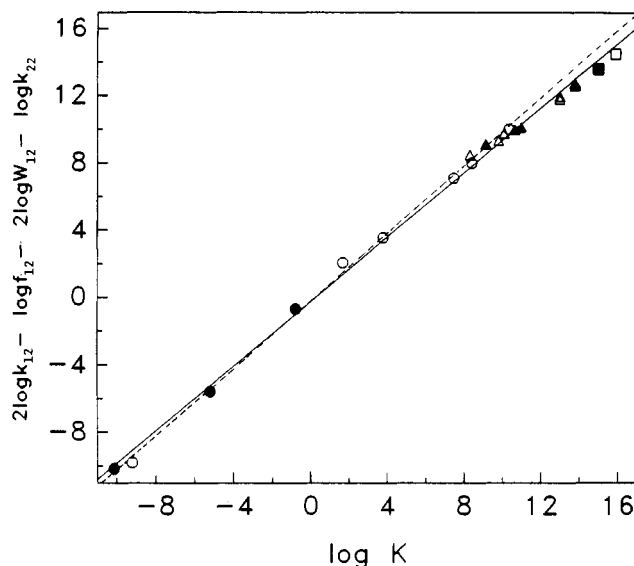
Figure 4. Plot of $2 \log k_{12} - \log f_{12} - 2 \log W_{12} - \log k_{22}$ versus $\log K_{12}$, the logarithm of the equilibrium constants for the reactions of CrL_3^{2+} (triangles), Ru(III) amine complexes (circles), and $Ru(bpy)_3^{3+}$ (squares) with $Co(bpy)_3^{3+/2+}$ (open) and $Co(phen)_3^{3+/2+}$ (filled) redox couples.

is evident from the data for $Co(en)_3^{3+}$ that the calculated and observed values of k_{12} are in good agreement with each other. In the case of $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$, however, the observed rate constants are always smaller (by a factor of 3–25) than the calculated ones. We attribute this discrepancy to the mildly nonadiabatic behavior of the cross-reactions involving $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$. This suggestion is in accord with the conclusion drawn by Fürholz and Haim[5] regarding the nonadiabaticity of the reactions involving $Co(bpy)_3^{3+}$.

The extent of the nonadiabaticity can be assessed by introducing an electronic factor.[19] With that included, eq 6 becomes

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12}\kappa_{12}/(\kappa_{11}\kappa_{22})^{1/2} \qquad (10)$$

If it is assumed that the self-exchange reactions are adiabatic (i.e., that $\kappa_{11} = \kappa_{22} = 1$), then eq 10 can be rearranged in the following manner:

$$2 \log k_{12} - \log f_{12} - 2 \log W_{12} - \log k_{22} =$$
$$\log (k_{11}\kappa_{12}^2) + \log K_{12} \qquad (11)$$

The assumption, made by us and others,[5] that the self-exchange reactions are adiabatic deserves further comment. Macartney and Sutin[19] reach the same tentative conclusions, as do Endicott et al.[20] The value of k_{exch} for $Co(bpy)_3^{3+/2+}$, calculated[16a] as 18 M^{-1} s^{-1} from an adiabatic model, also agrees well with the experimental value of 20 M^{-1} s^{-1}.

We have also utilized Haim's[5] approach to make a graphical presentation of the phenomenon. Figure 4 depicts a plot of the left-hand side of eq 11 versus $\log K_{12}$ for the cross-reactions measured in the present investigation along with others available in the literature.[5,21,22] According to eq 11, the plot should be linear with a slope of unity and an intercept equal to $\log (k_{11}\kappa_{12}^2)$.

In the treatment of earlier data,[5] the plot has a slope of 1.00 $\pm$ 0.02 and an intercept of -0.11 ± 0.14 (dotted line in Figure 4), which resulted in $\kappa_{12} = 0.16 \pm 0.03$. With the results for $Cr(NN)_3^{2+}$ reactions and $Ru(bpy)_3^{3+}$ reactions included, we obtain (solid line in Figure 4) a slope of 0.98 $\pm$ 0.02 and an intercept of -0.24 ± 0.10. We used an average self-exchange rate constant for $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$ of 30 M^{-1} s^{-1} for the graph only (the individual values were used in the calculations for Table I) and obtained a value of $\kappa_{12} = 0.13 \pm 0.03$, which is in agreement with the previously reported value. The nonadiabaticity may derive from the rigidity of the bipyridine and phenanthroline rings, which precludes the optimal overlap between the orbitals of the two metal centers.

Conclusion

These studies have evaluated the rate constants for a series of outer-sphere reactions between $Cr(NN)_3^{2+}$ and CoL_3^{3+} ions. The cross-reactions of $Co(en)_3^{3+}$ follow the Marcus theory quite well and are thus assessed to be adiabatic. Those for $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$, however, are mildly nonadiabatic, especially the latter. The nonadiabaticity becomes more pronounced as the standard free energy change of the reaction increases.

(17) Creaser, I. I.; Sargeson, A. M; Zanella, A. W. *Inorg. Chem.* **1983**, *22*, 4022.

(18) Geselowitz, D.; Taube, H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 391.

(19) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 3530.

(20) Endicott, J. F.; Ramasani, T.; Gaswick, D. C.; Tamilarasan, R.; Heeg, M. J.; Brubaker, G. R.; Pyle, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 5301.

(21) We have not included reactions with $Fe(OH_2)_6^{3+}$ because the cross-reactions involving $Fe(OH_2)_6^{3+}$ have been suggested to be nonadiabatic.[22]

(22) Fürholz, U.; Haim, A. *Inorg. Chem.* **1985**, *24*, 1966.