to that of water (AN = 54.8) than to those of ethanol (AN = 37.1) and methanol (AN = 41.3),[24] the molar absorption coefficients for aqueous solutions (slightly alkaline and acid) were substituted for those of B and BH^+OAc^- of pyridine bases in the calculation of K_i, assuming that the degree of hydrogen bonding in acetic acid is similar to that in water.

As is seen from Figure 6, the ionization constant thus determined increases smoothly with the protonation constant of a base in aqueous solution. Bruckenstein et al. have estimated $K_i = 5.37$ for pyridine on the assumption that $\epsilon_0 = 0$,[25] but the nonionized species B absorbs evidently to a certain degree.

Pyridine in carbon tetrachloride absorbs very strongly at 1585 cm^{-1} (IR spectrum A), but this peak becomes rather weak, and new ones appear at about 1600 and 1630 cm^{-1}, on addition of acetic acid (10%, IR spectrum B). The former peak has been assigned to $\nu_{C=N}$ and said to shift to 1630–1640 cm^{-1} on protonation ($\nu_{C=N^+}$).[26,27] In spectrum B, a rather strong peak newly appeared at 1760 cm^{-1} (monomeric carboxyl group), which indicates the formation of monomeric acetic acid resulting from partial cleavage of the dimeric structure of the solvent.[28] Thus, comparison of IR spectra supports the ion-pair formation, i.e. the charge separation.

Now that ionization constants are available, the formation constant K_1° in a proper sense can be calculated

$$M(OAc)_2 + B \rightleftharpoons M(OAc)_2B \quad K_1^\circ \tag{19}$$

where B stands for only the nonionized base. Then

$$K_1 = [M(OAc)_2B]/[M(OAc)_2][B] = (1 + K_i)K_1 \tag{20}$$

As is evident from Table I, the values of K_1° increase monotonically with increasing pK_a, as is ordinarily the case in aqueous solution chemistry. Thus, the aforementioned paradox is now clearly resolved. Acetic acid is not an exceptional solvent with respect to coordination chemistry; only some correction should be made for the ionization of solutes for quantitative interpretation of chemical reactions in this solvent.

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Registry No. Co, 7440-48-4; Ni, 7440-02-0; LiOAc, 546-89-4; 2,4-lutidine, 108-47-4; 3,4-lutidine, 583-58-4; 3-chloropyridine, 626-60-8; pyridine, 110-86-1; 2-chloropyridine, 109-09-1.

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Quenching of the ^2E Excited State of Tris(polypyridine)chromium(III) Ions with Titanium(III)

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The kinetics of the quenching of the ^2E excited state of chromium polypyridine complexes by Ti(III) were investigated at 25 °C in 1.0 M LiCl/HCl. The dependence of the rate on hydrogen ion concentration indicates that both $Ti(H_2O)_6^{3+}$ and $(H_2O)_5Ti(OH)^{2+}$ quench. The quenching rate constants for Ti^{3+} are in the range $(0.26–3.7) \times 10^7\ M^{-1}\ s^{-1}$ and those for $TiOH^{2+}$ are in the range $(0.81–9.7) \times 10^8\ M^{-1}\ s^{-1}$ when a value $K_a = 4.6 \times 10^{-3}$ M is used. The formation of a stable Cr(II) product was observed spectrophotometrically, indicating back electron transfer occurs too slowly to measure. This is explained by the instability of TiO^+, the immediate product of back electron transfer. Plots of log k_q vs ΔE° are linear for the quenching by both Ti^{3+} and $TiOH^{2+}$.

Introduction

Electron-transfer reactions of Ti(III) have been widely studied in recent years. Many studies have been carried out with complexes of Ru(III)[1] and of Co(III)[2] as oxidants. Other oxidants include iodine,[3] 1-hydroxy-1-methylethyl radicals,[4] V(IV),[5] V(V),[6] and complexes of Ni(III)[7] and Os(III).[8] Often a rate law term with an inverse dependence on $[H^+]$ is found, indicating $TiOH^{2+}$ is an active reductant.[8-11] Since the Ti(IV) product is TiO^{2+}, it might be expected that a species with a shorter Ti–O bond, as in $TiOH^{2+}$, would be more reactive.

Inner-sphere mechanisms have been found to operate in cases where there is an efficient bridging ligand such as oxalate,[10,12] thiocyanate,[13] salicylate,[14] or acetate.[15] In these reactions, substitution on Ti(III) is sometimes the rate-limiting step.[16] The

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ligands Cl^- and SO_4^{2-}, generally considered to be good bridging ligands, are not always efficient for Ti(III) electron-transfer reactions.

Outer-sphere electron-transfer processes involving Ti(III) often show agreement with Marcus' theory.[17] From data for (polypyridine)osmium(III) complexes, Ti(III)–Ti(IV) self-exchange rates have been estimated as $>3 \times 10^{-4}$ L mol^{-1} s^{-1} for $Ti^{4+/3+}$ and $\geq 10^{-2}$ L mol^{-1} s^{-1} for $TiOH^{3+/2+}$.[8] Reactions of Ni(III) complexes with Ti(III) fit a Marcus correlation despite the large driving forces.[7]

The Ti(IV) species formed in solution by these reactions has been the subject of many studies. It is generally accepted to be a dipositive species, $Ti(OH)_2^{2+}$ or TiO^{2+}, on the basis of the effect of ionic strength on kinetics,[5] ion-exchange,[18,19] and potentiometric studies.[8,20] The Cr^{2+} reduction of Ti(IV) shows no evidence for Cl^- complexation, seemingly ruling out $Ti(OH)_2^{2+}$.[21] The first direct evidence for TiO^{2+} was reported when the Ti–O Raman stretch was observed.[22] Since that time it has been reported that TiO^{2+} is in equilibrium with low concentrations of oligomeric species in more concentrated Ti(IV) solutions, >0.1 M.[23]

Oxygen does not react with Ti^{3+}, but it oxidizes $TiOH^{2+}$ in an outer-sphere process ($k = 4.25$ L mol^{-1} s^{-1} in 1 M LiCl at 25 °C).[24] Ti(III) reduces perchlorate ions in a slow reaction that is retarded by Cl^- and accelerated by H^+.[25] To avoid this complication, a LiCl/HCl medium is generally used. The complexation of Ti(III) by Cl^- has a measured stability constant $K_1 = 0.07$–0.2 M^{-1}.[26] Others have suggested that the stability of $TiCl^{2+}$ is small, as no kinetic effect of Cl^- is observed.[27]

The reactivity of Ti(III) with excited states has been little investigated. Ti(III) has been reported[8] to quench the excited-state emission of $*Ru(bpy)_3^{2+}$. This occurs by energy transfer, as indicated by the absence of electron-transfer products and by a rate constant that is much higher than expected for electron transfer.

In the present work we have undertaken to evaluate the quenching rate constants between Ti(III) and the excited state of chromium polypyridine complexes such as $*Cr(bpy)_3^{3+}$, $*Cr(phen)_3^{3+}$, and their substituted-ring derivatives. Experiments were done to evaluate emission lifetimes as a function of the important concentration variables, [Ti(III)] and [H^+]. Furthermore, studies were done in the transient absorption mode to detect $Cr(NN)_3^{2+}$, formed according to the equation

$$*Cr(NN)_3^{3+} + Ti(III) \rightarrow Cr(NN)_3^{2+} + Ti(IV) \qquad (1)$$

Experimental Section

Solvents and Reagents. $Cr(bpy)_3(ClO_4)_3$ was prepared according to the literature method.[28,29] Other polypyridine complexes, prepared analogously, were available from earlier work.[30] The $Cr(NN)_3^{3+}$ complexes were characterized by their UV–vis spectra[29] and by the lifetimes of the lowest energy excited states.[28]

Solutions of titanium(III) chloride were prepared by dissolving the metal sponge (Alfa) in 3.3 M HCl by stirring at 30–40 °C under argon for 36–48 h.[13b] The resulting purple solution was filtered through a 5 μM Metricel membrane filter and stored under argon at 0 °C. The Ti(III) concentration was determined spectrophotometrically at 502 nm ($\epsilon = 3.97$ L mol^{-1} cm^{-1}), and that of Ti(IV), at 302 nm ($\epsilon_{Ti(III)} = 0.3$ L mol^{-1} cm^{-1} and $\epsilon_{Ti(IV)} = 15.2$ L mol^{-1} cm^{-1}).[6a] The acid contents of Ti(III) stock solutions were determined by direct titrations with NaOH, which were carried out slowly with constant stirring to prevent formation of a blue-gray polymer.[9c] No metal syringe needles were used at any time with Ti(III) solutions; glass syringes with Teflon needles were used.

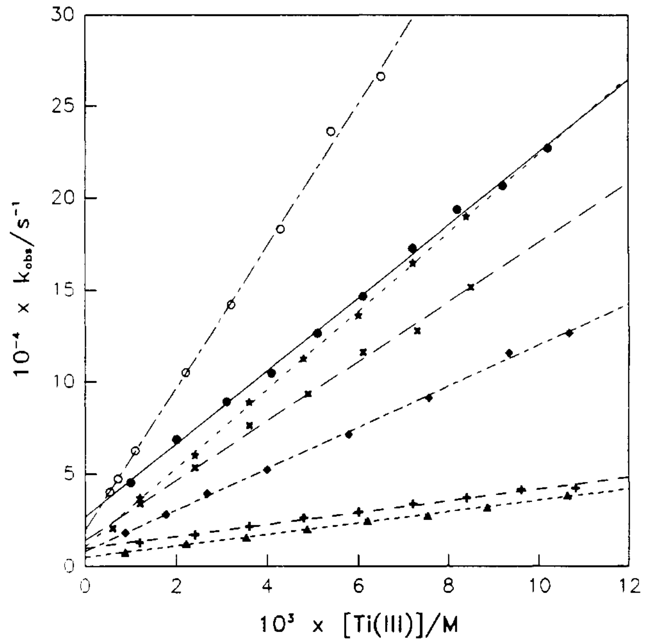

Figure 1. Quenching of $*Cr(NN)_3^{3+}$ by Ti(III) in 1 M HCl. Plots show the linear variation of k_{obs} with $[Ti(III)]_T$. The NN ligands are shown as 5-Cl-phen (open circles), bpy (filled circles), phen (stars), 5-Mephen (×), 5,6-Me_2phen (diamonds), 4,4′-Me_2bpy (+), and 4,7-Me_2phen (triangles).

The laboratory-distilled water was purified by use of a Millipore-Q purification system. Lithium chloride was recrystallized three times. Hydrochloric acid, perchloric acid, and lithium perchlorate (Aldrich) were used as purchased. The complexes $[Co(NH_3)_5Br]Br_2$ and $[Co(NH_3)_5OH_2](ClO_4)_3$ were available from laboratory stock. The $[Co(NH_3)_5Br]Br_2$ complex was converted to the perchlorate by triple recrystallization from dilute perchloric acid in the presence of a large excess of lithium perchlorate.

Kinetics. The reactions were studied by use of the previously described[31,32] laser flash photolysis system. The excitation dyes used were Coumarin 460 and LD-423. Quenching rates were measured by monitoring at 727 nm the emission from the Cr(III) excited-state complex. The data gave excellent fits to first-order kinetics; a nonlinear least-squares program was used to evaluate the rate constants. Observations in the transient-absorption mode were also carried out to measure $Cr(NN)_3^{2+}$ formation at appropriate wavelengths.

Solutions for the kinetic experiments were made up in 1-cm fluorescence cells. The requisite concentrations of LiCl and HCl were added, the cell was deaerated with a flow of argon, and then Ti(III) was added. The $Cr(NN)_3^{3+}$ sensitizer was added just before the flashing. Each solution was generally used for a single laser flash, but on occasion the cell was moved to a different position and flashed a second time.

Laser Actinometry. The molar absorptivity of $*Cr(bpy)_3^{3+}$ at 445 nm, ϵ_{3*}, was determined by laser actinometry with $Ru(bpy)_3^{2+}$. Solutions of $Ru(bpy)_3^{2+}$ (1.89×10^{-5} M in D_2O) and $Cr(bpy)_3^{3+}$ (2.78×10^{-4} M in H_2O), both containing 0.10 M $HClO_4$, were prepared. These two solutions have the same absorbance at 445 nm. The $Ru(bpy)_3^{2+}$ solution contained $Co(NH_3)_5Br^{2+}$ (5.0×10^{-3} M) as oxidative quencher, whereas the $Cr(bpy)_3^{3+}$ solution had $Co(NH_3)_5OH_2^{3+}$ added (2.85×10^{-3} M) to serve as an absorbance-matching blank. After the flash, the ruthenium solution showed a permanent (on the millisecond time scale) absorbance loss at 445 nm owing to the conversion of $Ru(bpy)_3^{2+}$ ($\epsilon_{445} = 12\,700$ M^{-1} cm^{-1}) to $Ru(bpy)_3^{3+}$ ($\epsilon_{445} = 1500$ M^{-1} cm^{-1}).[33] After flash irradiation of the $Cr(bpy)_3^{3+}$ solution, the absorbance of $*Cr(bpy)_3^{3+}$ at 445 nm was monitored. The maximum absorbance change was taken as due to the

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Table I. Rate Constants[a] for the Quenching of $^*Cr(NN)_3^{3+}$ by Titanium(III) in 1 M HCl

NN	$10^{-7}k_q$/L mol^{-1} s^{-1}	$10^{-4}k^\circ_{obs}$/s^{-1} [b]
bpy	1.99	2.6
4,4'-Me$_2$bpy	0.334	0.90
phen	2.12	1.1
5-Cl-phen	3.87	1.9
5-Mephen	1.69	1.1
5,6-Me$_2$phen	1.12	0.83
4,7-Me$_2$phen	0.311	0.49

[a] At ~25 °C. [b] From extrapolation of the [Ti(III)] variation to [Ti(III)] = 0.

Table II. Rate Constants[a,b] for the Quenching of $^*Cr(NN)_3^{3+}$ by Ti^{3+} (k_1) and $TiOH^{2+}$ (k_2)

	NN	$E^\circ_{*/2}$ [c]	$10^{-7}k_1$/L mol^{-1} s^{-1}	$10^{-8}k_2$/L mol^{-1} s^{-1}
1	bpy	1.44	1.9	6.0
2	4,4'-Me$_2$bpy	1.25	0.26	1.0
3	phen	1.42	1.6	4.6
4	5-Cl-phen	1.53	3.7	9.7
5	5-Mephen	1.39	1.4	4.7
6	5,6-Me$_2$phen	1.40[d]	1.2	3.0
7	4,7-Me$_2$phen	1.23	0.28	0.81

[a] At μ = 1.00 M (HCl/LiCl). [b] From least-squares fit to eq 3 using the value $K_a = 4.6 \times 10^{-3}$ M. [c] Standard reduction potentials vs NHE for $^*Cr(NN)_3^{3+} + e^- = Cr(NN)_3^{2+}$ as given in ref 28. [d] Reference 39.

loss of the Cr(III) ground-state complex and formation of the excited state. The concentration of $^*Cr(bpy)_3^{3+}$ formed was assumed to be equal to that of $^*Ru(bpy)_3^{2+}$ formed in the parallel experiment in which a calculated 92.6% of the quenching took place by electron transfer to $Co(NH_3)_5Br^{2+}$. Thus, in the chromium system a value of $\Delta\epsilon = \epsilon_{3*} - \epsilon_3$ (and thus ϵ_{3*}) could be calculated.

Results and Discussion

Lifetimes. The lifetime of each excited state was measured in 1 M HCl by monitoring the emission from the ^2E excited state[34] at 727 nm. The lifetimes for most of the $^*Cr(NN)_3^{3+}$ excited states depended on $[Cr(NN)_3^{3+}]$ because of ground-state quenching. In general, the values obtained agreed with previously determined values.[28,35,36]

Upon addition of Ti(III) the emission lifetime was shortened significantly. Quenching rate constants for eq 1 were measured in 1 M HCl by varying the Ti(III) concentration. Plots of k_{obs} vs $[Ti(III)]_T$ (the stoichiometric concentration of Ti(III)) for the different $^*Cr(NN)_3^{3+}$ excited states are linear. These data are depicted in Figure 1. The slope of each line represents the rate constant for quenching of the given $^*Cr(NN)_3^{3+}$ complex by Ti(III) in this medium. Values are listed in Table I. The intercept denoted, k°_{obs}, should represent k° values for $^*Cr(NN)_3^{3+}$ decay and ground-state quenching, but the values (Table I) are in fact somewhat higher than k°'s measured in the absence of Ti(III). This is attributed to the known[37] quenching of $^*Cr(NN)_3^{3+}$ by $Cr(NN)_3^{2+}$, the latter species being the product of the Ti(III) quenching. We shall return to this process later.

Hydrogen Ion and Chloride Dependences. For each chromium(III) complex the H^+ concentration was varied in the range $0.100 < [H^+] < 1.00$ M, LiCl used to maintain ionic strength at 1.0 M. The values of the rate constants get systematically larger as $[H^+]$ decreases. We attribute this to quenching paths by both Ti^{3+} and $TiOH^{2+}$ and thus write the following expression

$$k_{obs} = k^\circ_{obs} + (k_1[Ti^{3+}] + k_2[TiOH^{2+}])[^*Cr(NN)_3^{3+}] \qquad (2)$$

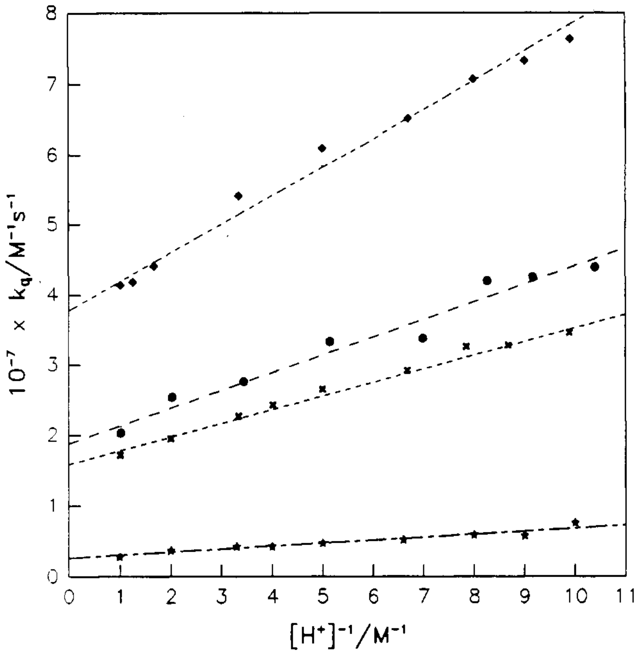

Figure 2. Effect of $[H^+]$ on the quenching of $^*Cr(NN)_3^{3+}$ by Ti(III). Plots show the variation of k_q with $[H^+]$, as in a simplified form of eq 3. The different NN ligands are 5-Cl-phen (diamonds), bpy (circles), phen (×), and 4,4'-Me$_2$bpy (stars).

When the acid ionization equilibrium between $Ti(H_2O)_6^{3+}$ and $(H_2O)_5TiOH^{2+}$ is allowed for, the quenching rate can be expressed as a function of $[H^+]$ by the equation

$$k_q = \frac{k_{obs} - k^\circ_{obs}}{[Ti(III)]_T} = \frac{k_1[H^+] + k_2K_a}{K_a + [H^+]} \qquad (3)$$

A value for K_a of 4.6×10^{-3} M, determined by kinetic fitting, has been reported[38] at 1 M ionic strength in an HCl/LiCl medium. The data were fit to eq 3 by use of a nonlinear least-squares program. Values for k_1 and k_2 are given in Table II, along with the excited-state reduction potentials.[39] Since $K_a \ll [H^+]$, eq 3 can be approximated as $k_q = k_1 + k_2K_a/[H^+]$. Figure 2 displays data for four of the systems studied; the lines shown are those from the least-squares fitting procedure. An alternative value for K_a is 2.3×10^{-3} M, determined spectrophotometrically in (K,H)Cl solution at μ = 3.0 M.[40] If this value (or any other) is taken for K_a, the values of k_2 in Table II would need to be adjusted accordingly, such that k_2K_a remains constant.

The effect of $[Cl^-]$ on the quenching rate was investigated by using ClO_4^- to maintain 1 M ionic strength. This was done at low $[H^+]$, 0.10 M, to minimize the reduction of ClO_4^- by Ti(III). The average k_{obs} in 1.0 M Cl^- is 2.32×10^5 s^{-1}, compared to 9.8×10^4 in 0.9 M ClO_4^-/0.1 M Cl^-. Complexation of Cl^- by Ti(III) is minimal, and the effect of varying $[Cl^-]$ was not explored further.

Quantum Yields. The ratio $[Cr(bpy)_3^{2+}]_\infty/[^*Cr(bpy)_3^{3+}]_0$ is taken to define a quantum yield ϕ. Both concentrations can be determined spectrophotometrically. The amount of $Cr(bpy)_3^{2+}$ formed was calculated from the stable final absorbance at 560 nm ($\epsilon = 4.8 \times 10^3$ L mol^{-1} cm^{-1}).[29] The concentration of excited state formed initially in the laser flash was estimated from the absorbance at 445 nm, a maximum for the excited state. The extinction coefficient of $^*Cr(bpy)_3^{3+}$ has been reported as ca. 3×10^3 M^{-1} cm^{-1}.[41] This quantity was confirmed during the course of this work by laser actinometry with $Ru(bpy)_3^{2+}$. Values of ϵ_{3*} obtained in this work are as follows (in parentheses): 445 nm ($\epsilon = 3.0 (\pm 0.2) \times 10^3$ M^{-1} cm^{-1}, max), 385 (5.4×10^3, max), 430

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(34) For simplicity, the excited state is designated as a ^2E state, whereas there are really two emission bands (at 695 and 727 nm) with the same lifetimes; the emitting states are believed to be in thermal equilibrium.

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(2.7×10^3, min), 470 (1.6×10^3), and 500 (8×10^2). Note that these values replace those that we reported earlier.[37]

The quantum yields increase steadily from 0.49 to 0.92 as the titanium(III) concentration increases (1.7–11.3×10^{-3} M). Ideally, the value will approach unity as Ti(III) quenching comes to dominate. Additional sources of quenching must be considered, however, including the quenching by $Cr(bpy)_3^{2+}$, eq 4. The

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

question is how to allow for the contribution of the $k_{Cr}[Cr(bpy)_3^{2+}]$ term in the rate law in that the concentration of the chromium(II) complex is increasing with time throughout each experiment. The expression for the quantum yield is

$$\phi = \frac{k_q[Ti(III)]_T}{k° + k_{Cr}[Cr(bpy)_3^{2+}] + k_q[Ti(III)]_T} \quad (5)$$

in which $[Cr(bpy)_3^{2+}]$ is a time-dependent quantity. To deal with this problem, we performed a number of numerical simulations using the program KINSIM.[42] In the simulation $[^*Cr(bpy)_3^{3+}]_0$ was set at 3.8×10^{-6} M (10% of the ground-state concentration), and all of the rate constants were set at their known values, including $k_{Cr} = 5 \times 10^9$ M^{-1} s^{-1}.[37] The simulations gave for each experiment the final concentration, $[Cr(bpy)_3^{2+}]_\infty$. We then proceeded in two directions. First, we calculated a value of the intercept in the plot of k_{obs} vs $[Ti(III)]_T$ and compared it with $k°$. The difference was taken to be $k_{Cr}[Cr(bpy)_3^{2+}]$. With this term known, one can reconstruct the quantum yield (eq 5). The variations in ϕ so calculated parallel those found experimentally. Also, the plot of log k_{obs} vs $[Ti(III)]_T$ has a calculated value of $k° = 2.2 \times 10^4$ s^{-1}, which is satisfactorily close to the true value, 1.5×10^4 s^{-1}. A second approach is to use $[Cr(bpy)_3^{2+}]_\infty$ from the numerical simulation routine. We simply take half of this value to represent an average value of its concentration during each experiment. This also appears satisfactory in that both the quantum yields and the values of k_{obs} show agreement of measured and calculated quantities to within 10%.

Back Electron Transfer. The possibility of the following reaction was explored:

$$TiO^{2+} + Cr(NN)_3^{2+} + 2H^+ \rightarrow Ti_{aq}^{3+} + Cr(NN)_3^{3+} \quad (6)$$

The formation of $Cr(NN)_3^{2+}$ from the quenching reaction was evident from the transient absorption measurements. For example, formation of $Cr(5\text{-}Cl\text{-}phen)_3^{2+}$ and $Cr(bpy)_3^{2+}$ was evident at 410 and 560 nm directly. Also, the final absorption spectrum in the case of the quenching of $^*Cr(bpy)_3^{3+}$ was taken point-by-point. This spectrum agrees with that reported for $Cr(bpy)_3^{2+}$.[29] The absorbance of $Cr(NN)_3^{2+}$ remains constant for at least 200 ms. This is taken to mean that reaction 6 occurs too slowly to measure and that back electron transfer is unimportant in this system.

Thus, it appears that TiO^{2+}, once formed, is insufficiently reactive with $Cr(NN)_3^{2+}$ despite a favorable driving force for reaction 6. This experimental fact must be attributed to the stability of the oxo cation in the 4+ oxidation state. Simple outer-sphere reduction will lead to TiO^+. Evidently, this form of titanium(III) is too unstable to be formed in reaction 6.

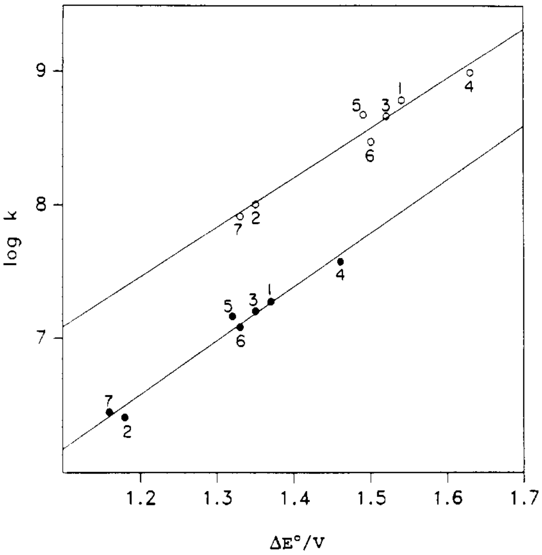

Figure 3. Variation with driving force of second-order rate constants for quenching of $^*Cr(NN)_3^{3+}$ by $TiOH^{2+}$ (open circles) and Ti^{3+} (filled circles).

Linear Free Energy Relationships. The reduction potential for Ti(IV) has been measured in 1 M HCl as −0.016 V. By use of eq 7[8] and the hydrolysis constants of Ti^{4+} ($K_{h1}K_{h2} = 25$ M^2), we

$$E = -0.016 - 0.059 \log \{Ti(III)/[Ti(IV)][H^+]^2\} \quad (7)$$

calculate the potential of the Ti^{4+}/Ti^{3+} couple as ~0.07 V and that for $TiOH^{3+}/TiOH^{2+}$ as ~0.1 V.

Figure 3 considers the kinetic data for Ti^{3+} (k_1) and $TiOH^{2+}$ (k_2) as a function of driving force, $\Delta E°$ for eq 1. The data follow good linear relations. The slope of the line is 4.0 for Ti^{3+} and 3.7 for $TiOH^{2+}$. This compares to a theoretical slope, according to the Marcus cross relation, of 8.4. The discrepancy may arise because these reactions have very large driving forces, of the order 1.2–1.7 V (Figure 3). This range is considerably higher than the values for reactions with ground-state reactants. The rate constants we measure are well below the diffusion-controlled limit, so the difference cannot be attributed to the effect of diffusion in determining rate constants in this system.

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Registry No. $Cr(bpy)_3^{3+}$, 15276-15-0; $Cr(4,4'\text{-}Me_2bpy)_3^{3+}$, 58220-56-7; $Cr(phen)_3^{3+}$, 15276-16-1; $Cr(5\text{-}Cl\text{-}phen)_3^{3+}$, 51194-62-8; $Cr(5\text{-}Mephen)_3^{3+}$, 51194-70-8; $Cr(5,6\text{-}Me_2phen)_3^{3+}$, 51261-67-7; $Cr(4,7\text{-}Me_2phen)_3^{3+}$, 51194-72-0; Ti^{3+}, 22541-75-9; $TiOH^{2+}$, 21029-47-0; Cl^-, 16887-00-6; H^+, 12408-02-5; $Cr(bpy)_3^{2+}$, 17632-84-7.

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[42] Barshop, B. A.; Wrenn, C. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134. We are grateful to Professor Frieden for a copy of this program.