

$F_2 \cdot CrF_4O$ exhibits the smallest frequency separation, suggesting that the covalency of the $KrF_2 \cdot XF_4O$ adducts increases on going from $X = W$ to $X = Cr$.

^{19}F NMR Spectra. The increase in covalency for $KrF_2 \cdot CrF_4O$ was further supported by ^{19}F NMR spectroscopy. Whereas $KrF_2 \cdot XF_4O$ ($X = Mo, W$) show unequivocal NMR evidence for a fluorine-bridged adduct in SO_2ClF solution,²³ the corresponding $KrF_2 \cdot CrF_4O$ adduct in SO_2ClF showed in the temperature range -120 to -10 °C only two sharp signals due to CrF_4O and KrF_2 without any sign of coupling. The chemical shift of the CrF_4O resonance exhibited relatively little temperature dependence and occurred in the range 482–486 ppm. However, the chemical shift of KrF_2 showed a very pronounced temperature dependence varying from about 63 ppm at -118 °C to about 82 ppm at -10 °C. A similarly pronounced temperature dependence of the chemical shift of KrF_2 has previously been observed for BrF_5 solutions (68 ppm at -150 °C and 78 ppm at 27 °C) and was attributed to solvation effects.²⁵

Conclusion. The structure and physical and chemical properties of CrF_4O resemble those of WF_4O and MoF_4O . Thus, CrF_4O

is also a strong Lewis acid and forms a stable $NO^+CrF_5O^-$ salt. With KrF_2 it forms an unstable, highly covalent 1:1 adduct which in SO_2ClF solution, contrary to those of WF_4O and MoF_4O , is completely dissociated to KrF_2 and CrF_4O . The major difference between CrF_4O and MoF_4O and WF_4O is the strong increase in oxidizing power from WF_4O to CrF_4O with the latter being capable of oxidizing O_2 to O_2^+ and NF_3 to NF_4^+ .²⁷

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Registry No. CrF_4O , 23276-90-6; CrO_2F_2 , 7788-96-7; HF, 7664-39-3; $NO^+CrF_5O^-$, 102110-04-3; AsF_5 , 7784-36-3; CrF_3O , 43997-25-7; $KrF_2 \cdot CrF_4O$, 102110-05-4.

(27) Christe, K. O.; Wilson, W. W., unpublished data.

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Kinetics and Mechanism of Electron Transfer to Transition-Metal Complexes by Photochemically Produced Tris(bipyridyl)ruthenium(1+) Ion¹

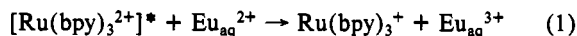
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Rate constants were determined for the one-electron reduction of $Cr(H_2O)_6^{3+}$, several organochromium cations of the family $(H_2O)_5CrR^{2+}$, several substituted pyridine complexes in the series $(H_2O)_5CrNC_5H_4X^{3+}$, cobalt(III) amine complexes, and miscellaneous species including Yb_{aq}^{3+} and $(1R,4R,8S,11S)-Ni(tmc)^{2+}$ (where $tmc = 1,4,8,11$ -tetramethyl-1,4,8,11-tetraazacyclotetradecane). The results are considered in light of the Marcus equation. The data for the pyridine complexes are correlated by the Hammett equation; the reaction constant in comparison with those of other complexes indicates that electron transfer occurs directly to the metal and not, as in certain other instances, by initial reduction of the pyridine ligand bound to chromium. The qualitative differences in rates can be rationalized by a simple MO scheme.

Introduction

The photochemistry of $Ru(bpy)_3^{2+}$ and the excited-state reactivity of $[Ru(bpy)_3^{2+}]^*$ have received much attention during the past decade.²⁻⁷ The electronic structure of the excited state can be approximated most closely as a charge-separated $Ru(III)$ metal center (a strong oxidant) and a ligand radical anion (a strong reductant).³ Our interest here concerns the chemical reactivity of $Ru(bpy)_3^+$, the species that results from quenching the excited state with an electron donor, such as Eu_{aq}^{2+} (most frequently used here; see eq 1), $Ru(NH_3)_6^{2+}$, or $Hasc^-$ (ascorbate ion).



The monovalent ruthenium cation so formed contains the metal in the 2+ oxidation state and a ligand radical anion, $bpy^{\cdot-}$.³ The use of laser flash photolysis techniques makes $Ru(bpy)_3^+$ conveniently accessible. It is an exceptionally strong reducing agent

($E^\circ_{2+/+} = -1.28$ V)³ and thus a particularly useful probe for complexes that are very weak electron acceptors. Their reactions with $Ru(bpy)_3^+$ have, therefore, a very large driving force and are nearly irreversible. The general reaction with such acceptors (A) is



The complexes investigated are very weak oxidizing agents except for a few cobalt(III) complexes that provided useful calibrations. The following classes of complexes have been investigated: (a) hydrated metal ions and other relatively simple complexes that are poor electron acceptors with well-characterized one-electron-reduced forms, including $Yb(aq)^{3+}$, $Sm(aq)^{3+}$, $Cr(H_2O)_6^{3+}$, and $Ni(tmc)^{2+}$;⁸ (b) organometallic complexes, particularly in the series of $(H_2O)_5CrR^{2+}$ cations, where no previous examination has been made of their abilities to undergo one-electron reduction; (c) chromium(III) pyridine complexes, such as $(H_2O)_5CrNC_5H_5^{3+}$ and substituted analogues.^{9,10} In the last

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(8) tmc (= "tetramethylcyclam" or $Me_4N[14]aneN_4$) = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane. [Note the corrected (compared to usage in some of the literature) chirality designators for this nickel complex, often referred to as the "trans III" isomer (Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 713).] Under the reaction conditions the nickel(II) complex is a mixture of aquo and hydroxo species ($pK_a = 11.93$; Herron, N.; Moore, P. *Inorg. Chim. Acta* **1979**, *36*, 89).

series we have tried to ascertain the extent of participation of the pyridine π system through measurements of the kinetic effects of ring substituents. The last series also concerns the issue of whether the initial site of electron transfer is the pyridine or directly the metal center.

Experimental Procedures

Laser Flash Photolysis. The system was based on a flash-lamp-pumped dye laser (Phase-R Model DL-1100), which has a pulse width of ca. 0.6 μ s. The single-shot laser pulse impinges on the sample contained in a fluorescence cell of 1-cm optical path. The transmittance of the sample was monitored with a 50-W quartz-halogen analyzing lamp and a Hamamatsu R928 photomultiplier tube. The voltage-time data were collected, digitized, and displayed on a Nicolet Model 2090-3A digitizing oscilloscope. These arrangements are much like those described in the literature.¹¹ Coumarin-460 (1.5×10^{-4} M in methanol), which emits at 460 nm, was used for the generation of $[\text{Ru}(\text{bpy})_3^{2+}]^*$.

Solutions to be used in reactions were rigorously deaerated with argon. Typically, 0.1 M $\text{Eu}_{\text{aq}}^{2+}$ and 30–40 μ M $\text{Ru}(\text{bpy})_3^{2+}$, both as chlorides, were present. The solutions contained hydrochloric acid, usually 0.25 M, and sodium chloride as needed to maintain ionic strength constant at 1.00 M. Shortly prior to the laser pulse, the complex was injected into the solution, which was protected from light throughout and mixed by a stream of argon. High transient concentrations of $\text{Ru}(\text{bpy})_3^+$ were produced by a single laser pulse. Typically, a 200–300-mV change in transmittance was measured, corresponding to $[\text{Ru}(\text{bpy})_3^+]_0 = 20\text{--}30 \mu\text{M}$. The reactions were monitored at the 510-nm absorption maximum of $\text{Ru}(\text{bpy})_3^+$, where $\Delta\epsilon = 1.25 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.^{12–15}

Reagents. Europium trichloride was prepared by dissolving the oxide in an excess of hydrochloric acid, yielding a 0.4 M solution of EuCl_3 in 0.25 M HCl. Solutions of $\text{Eu}_{\text{aq}}^{2+}$ were prepared by the reduction of EuCl_3 over zinc amalgam under argon. The solution of $\text{Eu}_{\text{aq}}^{2+}$ was kept on the amalgam, protected from light, for at least 2 h before it was used. (Strict avoidance of $\text{Eu}_{\text{aq}}^{3+}$ in the reactions is essential for reliable results, as discussed below.) Commercial samples of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ were recrystallized from warm water, vacuum-dried, and stored in the dark. Hydrated chromium(III) perchlorate, prepared from the reaction of chromium trioxide with hydrogen peroxide, was twice recrystallized from dilute perchloric acid.

The organochromium complexes were prepared from $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ and the appropriate organic reagents (RCl, RBr, or $\text{H}_2\text{O}_2/\text{RH}$ reactions) by literature procedures¹⁶ and separated and purified by cation-exchange chromatography on Sephadex SP C-25, usually with acidified sodium chloride as the eluting electrolyte. The spectra of these complexes¹⁷ agreed well with literature values.¹⁶

The chromium(III) pyridine complexes *cis*-(H_2O)₄ $\text{Cr}(\text{py})_2^{3+}$,^{18,19} and (H_2O)₅ $\text{Cr}(\text{py})^{2+}$ ²⁰ were prepared by the referenced literature procedures. Substituted pyridines were used to prepare (H_2O)₅ $\text{CrNC}_5\text{H}_4\text{X}^{3+}$ (X = 4-CH₃, 3-Cl, 3-CN) by modifications of the literature preparations.^{21–23} These complexes were characterized by their UV-visible absorption spectra.²⁴ Other complexes, including $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{en})_3]\text{Cl}_3$,

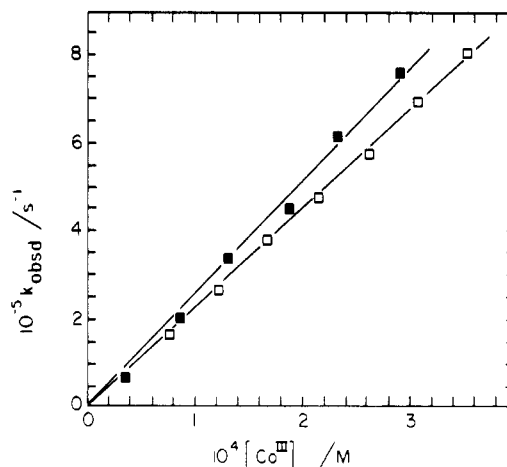


Figure 1. Kinetics of the reaction of $\text{Ru}(\text{bpy})_3^+$ with $\text{Co}(\text{III})$ complexes, as represented by plots of the pseudo-first-order rate constant vs. $[\text{Co}(\text{III})]$. Data are shown for $\text{Co}(\text{NH}_3)_6^{3+}$ (filled squares) and $\text{Co}(\text{en})_3^{3+}$ (open squares). Conditions: ionic strength 1.00 M (HCl/NaCl medium); $T = 23 \pm 1^\circ\text{C}$.

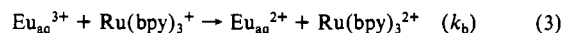
Table I. Rate Constants for Reactions of $\text{Ru}(\text{bpy})_3^+$ with Cobalt(III) Complexes^a

complex A	$[\text{Co}(\text{III})]$ range/M $\times 10^{-4}$	$10^{-9}k_2/\text{M}^{-1} \text{ s}^{-1}$
$\text{Co}(\text{NH}_3)_6^{3+}$	0.36–2.92	2.70 ± 0.08
$\text{Co}(\text{en})_3^{3+}$	0.77–3.54	2.29 ± 0.03
$\text{CH}_3\text{Co}(\text{dmg})\text{BF}_2\text{OH}_2^b$	0.14–0.97	3.2 ± 0.1
$\text{Co}(\text{sep})^{3+}$	0.85–2.85	$>2^c$

^a At $23 \pm 1^\circ\text{C}$, 1.0 M ionic strength, in chloride medium (HCl/NaCl), with $\text{Ru}(\text{bpy})_3^+$ formed with 0.1 M Eu^{2+} as quencher except as noted. ^b Quencher is 0.12 M Hasc⁻. ^c Lower limit, owing to the reaction of Eu^{2+} with $\text{Co}(\text{sep})^{3+}$ (see text).

$[\text{Co}(\text{sep})]\text{Cl}_3$, and $[\text{Ni}(\text{tmc})](\text{ClO}_4)_2$, as well as solutions of Yb^{3+} and Sm^{3+} in perchloric acid, were available from earlier work.^{25–28}

Photochemistry and Kinetics. The charge-transfer excited state $[\text{Ru}(\text{bpy})_3^{2+}]^*$ is produced by irradiating the broad absorption band of $\text{Ru}(\text{bpy})_3^{2+}$ centered at 452 nm. Reductive quenching yields $\text{Ru}(\text{bpy})_3^+$, as in eq 1. For the most part $\text{Eu}_{\text{aq}}^{2+}$ was used as quencher, because it is suitable for use in the strongly acidic solutions required by many of the reactants used, including all of the aquochromium cations. If no acceptor A is present in the system, the oxidized form of the quencher (e.g., $\text{Eu}_{\text{aq}}^{3+}$) and $\text{Ru}(\text{bpy})_3^+$ react by back-electron-transfer (eq 3). Such data



follow pseudo-second-order kinetics, since the starting concentrations of the two are equal, provided no additional $\text{Eu}_{\text{aq}}^{3+}$ has been introduced.

Systems containing an electron acceptor A show an accelerated loss of $\text{Ru}(\text{bpy})_3^+$ (eq 2). Both processes were monitored simultaneously by recording the absorbance decrease at 510 nm.¹² In general the method presents considerable difficulty in evaluating the desired rate constants k_2 if the acceptor is not sufficiently reactive or not present at a sufficiently high concentration. In that case, back-electron-transfer will predominate (e.g., $\text{Eu}_{\text{aq}}^{3+}$, $k_b = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$),²⁹ obscuring the reaction of interest. The problem becomes more severe if any $\text{Eu}_{\text{aq}}^{3+}$ is inadvertently introduced, which is the principal reason for the strict working conditions and also the principal limitation in the generality of this method. The less

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- (17) The various organochromium complexes had the following UV-visible spectra, λ_{max} , nm (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$): (H_2O)₅ $\text{CrCH}_2(4\text{-C}_6\text{H}_4\text{NH})^{3+}$, 550 (92), 308 (1.56×10^4), 225 (6.75×10^3); (H_2O)₅ $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$, 356 (2.2×10^3), 297 (6.97×10^3); (H_2O)₅ $\text{CrCH}_2\text{OCH}_3^{2+}$, 530 (15.3), 385 (4.02×10^2); (H_2O)₅ CrCHCl_2^{2+} , 490 (43.2), 380 (77.6); (H_2O)₅ CrCF_3^{2+} , 514 (38.7), 396 (1.57×10^2), 266 (4.29×10^3).
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Table II. Summary of Rate Constants for Reactions of Ru(bpy)₃⁺ with Transition-Metal Complexes^a

complex	concn range/M	$k/M^{-1} s^{-1}$
Eu _{aq} ³⁺		2.7×10^7 ^b
Yb _{aq} ³⁺ ^c	0.01–0.05	$(1.2 \pm 0.2) \times 10^5$
Sm _{aq} ³⁺ ^c	0.07–0.14	$< 2 \times 10^4$ ^d
Ni(tmc) ²⁺ ^e	$(1.05-4.04) \times 10^{-4}$	$(5.1 \pm 0.1) \times 10^8$
Cr(H ₂ O) ₆ ³⁺	0.0028–0.045	$(4.59 \pm 0.09) \times 10^6$

^aAt 23 ± 1 °C, 1.0 M ionic strength (at the highest [Sm³⁺] it increased, reaching μ = 1.58 M), in chloride medium (HCl/NaCl), with Ru(bpy)₃⁺ formed with 0.1 M Eu²⁺ as quencher except as noted. ^bReference 29. ^cM³⁺ added as perchlorate salt. ^dSee text and ref 31. ^eQuencher is 0.12 M Hasc⁻ at pH 11.1.

reactive a complex, the more it is affected by the back-reaction; the very slowest may be immeasurable for that reason.

The rate constant for a given reaction was obtained by a standard pseudo-first-order analysis of the absorbance decrease at 510 nm accompanying decay of Ru(bpy)₃⁺. This usually gave a highly precise fit to at least 4 half-lives. In a few instances [Ru(bpy)₃⁺]₀ was varied by changing the intensity of the laser flash. No effect on the apparent rate constant was observed, confirming the first-order dependence of reaction rate on [Ru(bpy)₃⁺]. The rate constants evaluated by such measurements were found to vary linearly with the concentration of a given acceptor, as illustrated subsequently for specific cases. For less reactive systems the plot of k_{obsd} vs. [A] often showed a small but appreciable intercept, indicative of a perceptible contribution from back-electron-transfer.

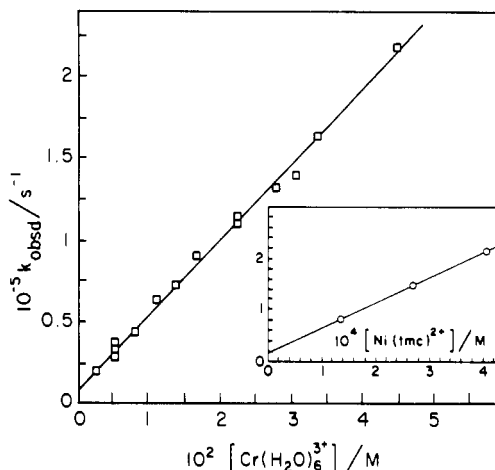
Results

Reduction of Cobalt(III) Complexes. Three complexes in the series Co(am)₆³⁺ and one organocobaloxime were studied. The pseudo-first-order rate constants for these reactions were directly proportional to the concentration of cobalt(III), which was present in substantial excess in each experiment. Data for the reactions with Co(NH₃)₆³⁺ and Co(en)₃³⁺ are shown in Figure 1. The slope of each plot is the second-order rate constant. The three complexes studied gave values only slightly below the diffusion-controlled limit, as summarized in Table I.

The complex Co(sep)³⁺, unlike the others, gave kinetic data that extrapolated to a negative intercept in the plot of k_{obsd} vs. [Co(sep)³⁺]. The reaction of the Eu²⁺ quencher with Co(sep)³⁺, with $k = 0.12 M^{-1} s^{-1}$,³⁰ is rapid enough to cause a decrease in [Co(sep)³⁺], partially replacing it with the less reactive Eu_{aq}³⁺ before the laser pulse. Despite that, it was possible to evaluate data for Co(sep)³⁺; the approximate limit is $k > \sim 2 \times 10^9 M^{-1} s^{-1}$. One experiment was done in the absence of Eu²⁺ with Co(sep)²⁺ itself as a quencher. Little if any Ru(bpy)₃⁺ was detected, however, suggesting this cobalt(II) complex quenches the excited state by energy transfer rather than electron transfer.

Reduction of Other Inorganic Complexes. Studies have been carried out for Eu_{aq}³⁺, Sm_{aq}³⁺, Yb_{aq}³⁺, Cr(H₂O)₆³⁺, and Ni(tmc)²⁺. Kinetic data are summarized in Table II; the features of the individual systems are as follows. The reaction between Ru(bpy)₃⁺ and Eu³⁺ had been characterized previously,²⁹ but other Ln³⁺ ions had not been investigated. The Yb³⁺ reaction, although slower, proceeds analogously. The loss of Ru(bpy)₃⁺ in the presence of Sm³⁺, even at quite substantial concentrations of the latter, is not perceptibly faster than back-electron-transfer.³¹ The latter in effect sets a limit of $\sim 2 \times 10^4 M^{-1} s^{-1}$ on the rate constants for reaction 2 that can be measured under our experimental conditions. The more readily reduced ion Yb³⁺ ($E^\circ = -1.15 V$) reacts with Ru(bpy)₃⁺ with $k_{Yb} = 1.2 \pm 0.2 \times 10^5 M^{-1} s^{-1}$. Although this rate constant is barely large enough to be discerned over back-electron-transfer, we believe that it is reliable within the indicated precision.

The reaction of Ni(tmc)²⁺ with Ru(bpy)₃⁺ is much faster; because of that, this situation is less equivocal, and the rate constant can be evaluated readily. The plot of k_{obsd} vs. [Ni(tmc)²⁺]

**Figure 2.** Pseudo-first-order rate constants for the reaction of Ru(bpy)₃⁺ with Cr(H₂O)₆³⁺ (squares) varied linearly with [Cr(H₂O)₆³⁺]. Conditions: $T = 23 \pm 1$ °C; 1.0 M ionic strength at variable [H⁺], [Cl⁻], and [ClO₄⁻]. Also shown are data for Ni(tmc)²⁺ (circles) at pH 11.1.**Table III.** Rate Constants for Reduction of the Organochromium Cations (H₂O)₅CrR²⁺ by Ru(bpy)₃⁺^a

complex	concn range/M × 10 ³	10 ⁻⁷ $k/M^{-1} s^{-1}$
(H ₂ O) ₅ CrCF ₃ ²⁺	2.2–11.3	<0.05
(H ₂ O) ₅ CrCH ₂ OCH ₃ ²⁺	1.56–7.80	0.22 ± 0.12
(H ₂ O) ₅ CrCHCl ₂ ²⁺	0.90–3.89	2.12 ± 0.07
(H ₂ O) ₅ CrCH ₂ C ₆ H ₅ ²⁺	0.18–2.14	3.2 ± 0.4
4-[(H ₂ O) ₅ CrCH ₂]C ₅ H ₄ NH ³⁺	0.076–0.398	139.0 ± 2

^aAt 23 ± 1 °C, 1.0 M ionic strength, in chloride medium (HCl/NaCl), with Ru(bpy)₃⁺ formed with 0.1 M Eu²⁺ as quencher.

is linear, as shown in Figure 2. Its slope defines the second-order rate constant as $(5.1 \pm 0.1) \times 10^8 M^{-1} s^{-1}$ at pH 11.1. The possibility that Ni(tmc)²⁺ forms a complex with ascorbate (used as a quencher in these experiments at a single concentration of 0.12 M) was not explored.

The reaction of Ru(bpy)₃⁺ with Cr(H₂O)₆³⁺ was investigated over a wide range of concentrations. The rate constant varied linearly with [Cr(H₂O)₆³⁺] over the entire concentration range examined, 2.8×10^{-3} – 4.5×10^{-2} M, and was also independent of [H⁺], 0.068–0.35 M, [Cl⁻], 0.53–0.70 M, and [ClO₄⁻], 0.13–0.45 M. The plot of k_{obsd} vs. [Cr³⁺] is also displayed in Figure 2. The intercept, again quite small, represents the unavoidable contribution from back-electron-transfer. From the slope the rate constant for Cr(H₂O)₆³⁺ was determined to be $(4.59 \pm 0.09) \times 10^6 M^{-1} s^{-1}$.

Experiments were done to confirm that the reaction occurring is, indeed, the reduction of Cr(H₂O)₆³⁺ by Ru(bpy)₃⁺ (eq 4). The Ru(bpy)₃⁺ + Cr(H₂O)₆³⁺ → Ru(bpy)₃²⁺ + Cr(H₂O)₆²⁺ (4)

Cr²⁺ produced was detected in the expected yield by its weak but distinct peak at 710 nm ($\epsilon 5 M^{-1} cm^{-1}$) after 1 h of irradiation with a 250-W sun lamp. All other components have a negligible absorbance at this wavelength.

Reduction of Organochromium Cations, (H₂O)₅CrR²⁺. These reactions, like the others, followed a second-order rate law (eq 5). Every member of this series was, like Cr(H₂O)₆³⁺, relatively $-d[(H_2O)_5CrR^{2+}]/dt = k[(H_2O)_5CrR^{2+}][Ru(bpy)_3^+]$ (5)

unreactive, with rate constants of the order of $10^6 M^{-1} s^{-1}$. (An exception is the pyridiniumylmethyl complex, R = 4-CH₂C₅H₄NH⁺, with $k = 1.4 \times 10^9 M^{-1} s^{-1}$, considered further in the next section.) Since, in general, these ions were not available at concentrations as high as that of Cr(H₂O)₆³⁺, the back-electron-transfer reaction is of somewhat greater importance and the rate constants are not known to comparable precision. Their values are summarized in Table III.

Reaction products were examined gas chromatographically for (H₂O)₅CrCHCl₂²⁺ and (H₂O)₅CrCH₂Ph²⁺, with the expectation

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

(31) The value of k_{Sm} must be $\leq 10^{5.3} M^{-1} s^{-1}$, given the equilibrium constant for the system ($E^\circ(Sm^{3+}/2+) = -1.55 V$), since the reaction of Sm²⁺ and Ru(bpy)₃²⁺ necessarily has $k \leq 10^{10} M^{-1} s^{-1}$.

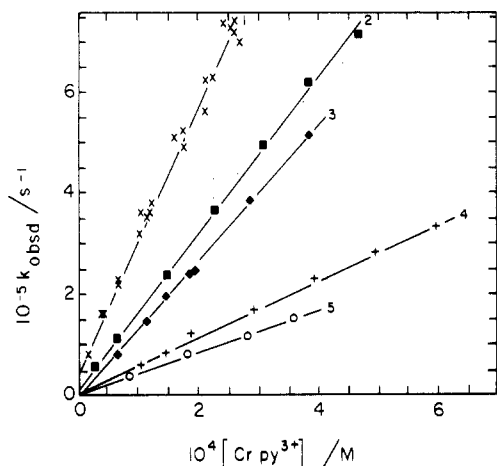


Figure 3. Plots of k_{obsd} vs. $[(\text{H}_2\text{O})_5\text{CrNC}_5\text{H}_4\text{X}^{3+}]$ for the following complexes: (1) X = 3-CN; (4) X = H; (5) X = 4- CH_3 . Values for X = 3-Cl are shown as dots without a line or other identifying symbol. The other data refer to (2) *cis*- $(\text{H}_2\text{O})_4\text{Cr}(\text{py})_2^{3+}$ and (3) $(\text{H}_2\text{O})_5\text{Cr}(4\text{-CH}_2\text{C}_5\text{H}_4\text{NH})^{3+}$.

Table IV. Rate Constants for Reduction of the Chromium Pyridine Cations $(\text{H}_2\text{O})_5\text{CrNC}_5\text{H}_4\text{X}^{3+}$ by $\text{Ru}(\text{bpy})_3^{2+}$ ^a

complex	concn range/M $\times 10^4$	$10^{-9}k/\text{M}^{-1} \text{ s}^{-1}$
$(\text{H}_2\text{O})_5\text{CrNC}_5\text{H}_4\text{-4-CH}_3^{3+}$	0.97–3.69	0.42 ± 0.01
$(\text{H}_2\text{O})_5\text{CrNC}_5\text{H}_5^{3+}$	1.22–6.12	0.55 ± 0.01
$(\text{H}_2\text{O})_5\text{CrNC}_5\text{H}_4\text{-3-Cl}^{3+}$	1.02–4.50	1.29 ± 0.04
$(\text{H}_2\text{O})_5\text{CrNC}_5\text{H}_4\text{-3-CN}^{3+}$	0.73–2.70	2.64 ± 0.07
<i>cis</i> - $(\text{H}_2\text{O})_4\text{Cr}(\text{py})_2^{3+}$	0.40–4.48	1.54 ± 0.03
$(\text{H}_2\text{O})_4\text{Cr}(\text{bpy})_3^{3+}$	1.12–4.49	1.8 ± 0.1

^aAt 23 ± 1 °C, 1.0 M ionic strength, in chloride medium (HCl/NaCl), with $\text{Ru}(\text{bpy})_3^{2+}$ formed with 0.1 M Eu^{2+} as quencher.

that RH products (i.e., CH_2Cl_2 and PhCH_3 , respectively) would be formed by decomposition of the reduced product, CrR^+ . No organic products were detected by GC in the former case, and none other than a trace amount of toluene in the latter. The most probable interpretation³² is that the reduced CrR^+ complex is reoxidized by Eu^{3+} .³³

Chromium–Pyridine Complexes, $(\text{H}_2\text{O})_5\text{CrNC}_5\text{H}_4\text{X}^{3+}$. These complexes are considerably more reactive than others and consequently yield data of higher precision since back-electron-transfer contributes less. Plots of k_{obsd} vs. concentration are shown for several of the complexes in Figure 3. The linearity of these plots over the concentration ranges used establishes the validity of the rate law given in eq 5.³⁴ Numerical data for these reactions are given in Table IV.

Pyridinium ions would be released after electron transfer to the chromium complex. Experiments were done to detect them directly, based on the UV spectrum of pyH^+ at 256 nm (ϵ $5.29 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). The reaction mixture (1.5 mM $\text{Cr}(\text{py})_3^{3+}$, 0.10 M Eu^{2+} , 36 μM $\text{Ru}(\text{bpy})_3^{2+}$, 0.19 M HCl), was flashed about 100 times with the laser. The solution was passed through a short column of Sephadex ion-exchange resin to remove all metal complexes. Several fractions were collected and their UV spectra determined. An intense spectrum of pyH^+ was detected, corre-

sponding to a substantial yield of pyH^+ . This clearly confirms its formation in the reaction; an identical solution, not irradiated, gave no free pyH^+ .

A search was also conducted for a transient pyridine radical anion coordinated to chromium, which would have to be produced if the initial electron transfer occurs to pyridine. To permit spectrophotometric detection of such a transient, which is expected to absorb between 300 and 360 nm,³⁵ a quencher that absorbs less than Eu^{2+} in that region was needed. The reductive electron-transfer quencher $\text{Ru}(\text{NH}_3)_6^{2+}$ was used. No such short-lived absorption was noted, however, leading us to conclude that its lifetime was too short and/or its absorption too weak^{35b} to be observed or that it was not formed. Other aspects of the chemistry, discussed below, indicate that coordinated pyridine radical anions are not formed in this system.

A few experiments were conducted on the reaction of pyridinium and *N*-methylpyridinium ions with $\text{Ru}(\text{bpy})_3^{2+}$. These reactions all gave kinetic data with badly curved pseudo-first-order plots that were unaffected by the addition of excess $\text{Ru}(\text{bpy})_3^{2+}$. The appearance of the plot is suggestive of a biphasic process (electron-transfer formation of pyridyl radical that undergoes additional reduction by $\text{Ru}(\text{bpy})_3^{2+}$). In any event no further work was performed with these compounds. The complex kinetic pattern contrasts with the situation for the $(\text{H}_2\text{O})_5\text{CrNC}_5\text{H}_4\text{X}^{3+}$ complexes, all of which followed precise first-order kinetics. The existence of this difference also supports our contention, detailed below, that a "chemical" mechanism does not function in this system.

Discussion

Marcus Equation Analysis. For further analysis of these outer-sphere electron-transfer reactions we use the Marcus relation (eq 6–9).³⁶ Here w_{ij} represents the work required to bring ions

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

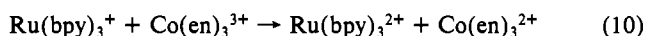
$$W_{12} = \exp[-(w_{11} + w_{22} - w_{12} - w_{21})/2RT] \quad (7)$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln(k_{11}k_{22}/A_{11}A_{22}) + (w_{11} + w_{22})/RT]} \quad (8)$$

$$A_{ii} = [4\pi N\sigma^2\nu_n\delta_r/1000]_{ii} \quad (9)$$

i and j to the separation distance σ (taken as the sum of the radii), ν_n is the nuclear vibration frequency that destroys the activated complex, and δ_r is the thickness of the reaction layer. Other symbols have their usual meaning. A value of A/σ^2 of $3.6 \times 10^{26} \text{ M}^{-1} \text{ cm}^{-2} \text{ s}^{-1}$ was used.

The reaction of $\text{Co}(\text{en})_3^{3+}$ with $\text{Ru}(\text{bpy})_3^{2+}$ (eq 10) is the one most suited for analysis, because the necessary parameters are known most reliably. They are $E^\circ(\text{Co}(\text{en})_3^{3+/2+}) = -0.19 \text{ V}^{30}$



and self-exchange rates of $10^8 \text{ M}^{-1} \text{ s}^{-1}$ (for $\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^{2+}$)^{37,38} and $3.4 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ (for $\text{Co}(\text{en})_3^{3+}/\text{Co}(\text{en})_3^{2+}$).³⁹ The calculated rate constant is $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, in excellent agreement with the experimental value.

The applicability of the Marcus cross relation to the $\text{Eu}_{\text{aq}}^{3+}$ – $\text{Ru}(\text{bpy})_3^{2+}$ reaction has already been noted.²⁹ Experimental and calculated values agree well, 2.7×10^7 and $1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The expressions cannot be used in the same manner for the Yb^{3+}

(32) We discount the possibilities that the CrR^{2+} reactions do not, in fact, occur at all and that the experimental observations are artifacts of back-electron-transfer, because (a) the data follow pseudo-first-order (not second-order) kinetics, (b) the data proved reproducible on different occasions with fresh and independent reagents, and (c) it was shown independently that CrR^{2+} ions do not react with Eu^{2+} over times long compared to those of the experiments.

(33) In effect, then, the organochromium cation serves as a catalyst for back-electron-transfer, albeit one whose low efficiency is manifest only because of the concentration imbalance $[\text{CrR}^{2+}] \gg [\text{Eu}^{3+}]$.

(34) It should be noted, as shown in Figure 3, that the plots for the 3-Cl- and 3-CN-py complexes, but not the others, had substantial intercepts that are not readily explained. This observation persisted for these two even in several repetitions using independent reagents. The observed rate constants remained independent of $[\text{Ru}(\text{bpy})_3^{2+}]_0$, from 18 to 72 μM .

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(36) (a) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (b) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1985**, *24*, 3403.

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(38) Lin, C.-T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536.

(39) Dwyer, F. P.; Sargeson, A. M. *J. Phys. Chem.* **1961**, *65*, 1892.

reaction unless a value is assumed for self-exchange rate of the Yb^{3+/2+} couple. One option is to use the value calculated^{40,41} from data for the reactions between the divalent lanthanide ions and Co(en)₃³⁺, $k_{YbYb} = 1.6 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ (revised slightly from our earlier estimate⁴⁰). On that basis the expected value for k_{YbRu} is $1.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, some 10² times smaller than observed. Perhaps values calculated for lanthanide ions should not be taken too seriously, however, whether they agree or not, since their reactions are notorious for problems arising from nonadiabaticity.^{29,42}

There is, however, an interesting question that emerges: *What really is the self-exchange rate constant for the Yb^{3+/2+} couple?* To our knowledge, this has not been answered experimentally. It is possible to use for the reactions of Ln³⁺ with Ru(bpy)₃⁺ the same approach taken⁴⁰ for Co(en)₃³⁺. This is expressed by

$$\frac{k_{YbRu}}{k_{EuRu}} = \left(\frac{k_{YbYb}}{k_{EuEu}} \right)^{1/2} \left(\frac{K_{YbRu}}{K_{EuRu}} \right)^{1/2} \left(\frac{f_{YbRu}}{f_{EuRu}} \right)^{1/2} \quad (11)$$

All of the values in the equation other than k_{YbYb} are known by direct experimental measurement. From it we calculate $k_{YbYb} = 2.5 \text{ M}^{-1} \text{ s}^{-1}$. This is *much* larger ($\times 10^5 \text{ M}^{-1} \text{ s}^{-1}$!) than the value of the same parameter calculated⁴⁰ from the data for Co(en)₃³⁺. There is no convincing way to reconcile the discrepancy; to some extent these arguments are circular, because if the Marcus equation is not applicable to the reactions of lanthanide ions, then none of the values is necessarily valid. In that event even the magnitude of the Yb^{3+/2+} self-exchange rate constant remains unknown.

The rate constant for the Cr³⁺ reaction from Marcus theory is $k \leq 1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, compared to the observed value $4.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. This calculation was based on a self-exchange rate constant $< 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ and $K_{12} = 5.2 \times 10^{14}$.

The rate constant predicted for Ni(tmc)²⁺ on the basis of Marcus theory is $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ from the reported reduction potential and calculated self-exchange rate at pH ~7.⁴³ This is $> 10^2$ times lower than observed at pH 11.1. At this stage of development, at least, we consider the disagreement to be not too alarming, since Ni(tmc)²⁺ participates in acid-base and coordination equilibria with $pK_a = 11.9$.⁴⁴

Rate Effects and Reaction Mechanism for Cr(III) Complexes.

The reactions of the chromium complexes fall into two distinct groups, those with a pyridine coordinated to chromium, through carbon or nitrogen, and all others. The former react some 3 orders of magnitude more rapidly, although they clearly fall below the diffusion-controlled limit, and can be analyzed in terms of chemical activation processes. The σ -alkyl complexes are not remarkably more reactive than the simple hydrated Cr³⁺ ion; indeed, some are less reactive.

Our consideration of their reactivity is not based on the Marcus treatment, since neither reduction potentials nor self-exchange rates are known. Rather, we consider the data from the point of view of the orbitals utilized (here) and the effects of substituents (next section). The LUMO of the Cr(III) complexes is formed from the 3d_{x²-y²} orbital of chromium (i.e., an e_g* orbital in O_h). (Note that the electron must occupy that orbital and not one of the singly occupied HOMO set, else an excited state of Cr²⁺ would be formed.) In neither point group does the LUMO have the proper symmetry to mix with the p_z orbital on the ligand. Because of that, the energy of the LUMO, and thus the reaction rate, is largely independent of the ligand set. The complex CrCF₃²⁺ is remarkably less reactive than Cr³⁺ or other CrR²⁺ complexes. This

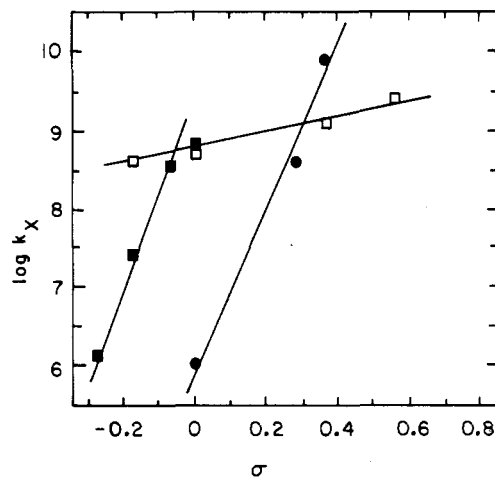


Figure 4. Plots of $\log(k_X)$ vs. the Hammett substituent parameter σ for Ru(bpy)₃⁺ with chromium pyridine complexes (H₂O)₅CrNC₅H₄X³⁺ (open squares), [[Ir(COD)(μ-pz)]₂]^{*} with CH₃NC₅(2,6-Me₂)H₂X⁺ (filled squares),⁴⁹ and [Ru(bpy)₂(CN)₂]^{*} with CH₃NC₅H₄X⁺ (filled circles).

is particularly striking, because the incorporation of three highly electronegative groups would have been expected to enhance its electron acceptor ability by the inductive effect. Other characteristics of this complex are, in contrast, quite as expected. For example, unlike other CrR²⁺ cations,¹⁶ CrCF₃²⁺ is remarkably resistant to solvolysis of the Cr-C bond⁴⁵ and less reactive than CrCH₃²⁺ (by $\geq 10^{13}$ -fold)⁴⁶ to electrophilic cleavage by Hg²⁺. We can suggest two factors that contribute to the slowness of electron transfer from Ru(bpy)₃⁺ to CrCF₃²⁺. First, CrCF₃²⁺ would be expected to be more strongly hydrogen-bonded to the solvent than others, thus inhibiting the encounters with Ru(bpy)₃⁺ at distances sufficiently close to allow efficient electron transfer. Second, the demonstrated strength of the Cr-C bond will increase the inner-shell reorganizational energy, also tending to lower the rate.

The accelerated rates for the (H₂O)₅Cr(py)³⁺ complexes are probably related to the known π -accepting properties of pyridine. In this case additional mixing of appropriate MO levels can occur, as evidenced also in the aquation rates of these complexes.^{18b} The orbitals of appropriate symmetry are the vacant π^* orbitals of pyridine, the half-filled, triply degenerate, (roughly) nonbonding metal-centered orbitals, and the lowest σ^* level of the complex, which is the LUMO into which the electron transfer will occur. The mixing of these levels lowers the energy of the LUMO sufficiently to enhance the rate.

In this model, the LUMO still remains an MO centered on chromium, not on pyridine. That is, electron transfer occurs to produce Cr²⁺ directly and not a pyridyl radical anion. This view is supported by the arguments based on the substituent effects, as discussed presently.

Substituent Effects. LFER Analysis. The rate constants for the substituted pyridine complexes vary in a systematic way with the nature of the substituent. It is clear from the results summarized in Table IV that electron-releasing substituents lower the rate and electron-attracting substituents raise it. This is what would be expected on the basis of inductive effects for a reaction in which the chromium pyridine complex acts as an electron acceptor.

This influence can be expressed quantitatively in terms of the Hammett equation with the established values of the substituent constants (σ). The expression is given in eq 12, in which k_0 refers

$$\log k_X = \log k_0 + \rho \sigma \quad (12)$$

to the parent pyridine complex, k_X refers to a substituted analogue, and ρ is the reaction constant, a measure of the sensitivity of this particular reaction to inductive effects.

(40) Christensen, R. J.; Espenson, J. H.; Butcher, A. B. *Inorg. Chem.* **1973**, *12*, 564.

(41) The analysis for Yb^{3+/2+} is confined to the case of Co(en)₃³⁺, where the reduction potential and self-exchange rates are reliably known.^{30,39}

(42) Taube, H. *Adv. Chem. Ser.* **1977**, *No. 162*, 127.

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(44) (a) Herron, A.; Moore, P. *Inorg. Chim. Acta* **1979**, *36*, 89. (b) Moore, P.; Sachinidis, J.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1984**, 1323.

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Table V. Summary of Hammett Reaction Constants for Electron-Transfer Reactions to Pyridinium Ions and Metal Pyridine Complexes

donor	acceptor	ρ	ref
Group I: Electron Transfer to Pyridine			
$\cdot\text{C}(\text{CH}_3)_2\text{OH}$	$\text{X}-\text{C}_5\text{H}_4\text{NH}^+$	8.5	48
$\cdot\text{C}(\text{CH}_3)_2\text{OH}$	$\text{X}-\text{C}_5\text{H}_4\text{NCH}_3^+$	9.0	48
$[\text{Ru}(\text{bpy})_2(\text{CN})_2]^*$	$\text{X}-\text{C}_5\text{H}_4\text{NCH}_3^+$	10.2	47
$[[\text{Ir}(\text{COD})(\mu\text{-pz})_2]^*{}^b$	$\text{X}-2,6\text{-Me}_2\text{C}_5\text{H}_2\text{NCH}_3^+$	10.3	49, 50
Group II: Electron Transfer to Metal			
$\cdot\text{C}(\text{CH}_3)_2\text{OH}$	$(\text{NH}_3)_5\text{Co}(\text{NC}_5\text{H}_4\text{X})^{3+}$	1.1	10
$\text{Ru}(\text{NH}_3)_6^{2+}$	$(\text{NH}_3)_5\text{Co}(\text{NC}_5\text{H}_4\text{X})^{3+}$	1.3	10
$\text{V}(\text{H}_2\text{O})_6^{2+}$	$(\text{NH}_3)_5\text{Co}(\text{NC}_5\text{H}_4\text{X})^{3+}$	1.5	10
$\text{Cr}(\text{H}_2\text{O})_6^{2+}$	$(\text{NH}_3)_5\text{Co}(\text{NC}_5\text{H}_4\text{X})^{3+}$	1.9	52
$\text{V}(\text{H}_2\text{O})_6^{2+}$	$(\text{NH}_3)_5\text{Ru}(\text{NC}_5\text{H}_4\text{X})^{3+}$	1.8	53
$\text{Ru}(\text{bpy})_3^+$	$(\text{H}_2\text{O})_5\text{Cr}(\text{NC}_5\text{H}_4\text{X})^{3+}$	1.1	a

^aThis work. ^bCOD = 1,5-cyclooctadiene; pz = pyrazolyl.

The analysis of the data according to this equation is shown in Figure 4. The data are adequately correlated by this straight-line relationship and give the value $\rho = 1.1$. We interpret these data to suggest that the initial site of electron transfer is the chromium and not the pyridine. The basis for this conclusion has been analyzed in detail previously.¹⁰ In brief, the argument is that those reagents that must react directly at the pyridine itself show great sensitivity to the substituent. These are the reactions⁴⁷⁻⁵¹ in Table V with values of ρ between 8.5 and 10.3. Two of the systems involve electron transfer to a series of *N*-methylpyridinium ions from the excited-state complexes $[\text{Ru}(\text{bpy})_2(\text{CN})_2]^*$ ⁴⁷ and $[[\text{Ir}(\text{COD})(\mu\text{-pz})_2]^*{}^b$ ⁴⁹⁻⁵¹. These systems had not been previously analyzed by the Hammett LFER method, although each had been treated on the basis of the Marcus equation. Provided only those rate constants below the diffusional limit are considered (see further comment below on this point), the Hammett LFER relationship quite successfully correlates the data. (See also Figure 4.)

In contrast to these, however, the members of a second group^{10,52,53} of reactions are all much less sensitive to substituent effects on their pyridine rings. They, too, are correlated by the Hammett equation, but with values of ρ between 1.1 and 1.9. This category includes systems in which electron transfer must be directed to the metal center itself and not to the pyridine (for example, those with weak electron donors, ML_6^{2+} in general, where the driving force is quite inadequate for a chemical mechanism). It also includes situations where this distinction is not clear a priori, including the present system. We postulate that all the members of this group react by a similar mechanism. In summary, then, we interpret that data for the chromium pyridine complexes as supporting a resonance-transfer mechanism and not a chemical mechanism. This interpretation can be expressed in more familiar terms as follows. The value of $\rho \sim 1$ is the reflection of the effects that substitution on the pyridine has on the $\text{M}^{\text{III/II}}$ reduction

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(48) Shimura, M.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 334.

(49) Marshall, J. L.; Stobart, S. R.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 3027.

(50) (a) The extensive series of alkylpyridinium ions studied⁴⁹ did not cover solely monosubstituted alkylpyridinium ions throughout the wide range of potential. This required that a different aromatic residue be taken as the unit on which substitution occurs to do meaningful Hammett correlations; although not identical, they are perfectly comparable in this context. They are $\text{X}-\text{C}_5\text{H}_4\text{NCH}_3^+$ (diffusion-controlled limit, three values) and $\text{X}-2,6\text{-Me}_2\text{C}_5\text{H}_2\text{NMe}^+$ (activation-controlled range, four values). The correlations gave $\rho = 1.8$ and 10.3, respectively. (b) It is, of course, no accident that these two compound classes are grouped by both potential and reactivity. The latter series is the one with low reactivity, smaller driving force, and therefore the greater sensitivity to substituents, and vice versa.

(51) We are grateful to Professor Harry B. Gray for calling the data in ref 49 to our attention and for discussions concerning these effects.

(52) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1162.

(53) Brown, G. M.; Krentzien, H. J.; Abe, M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 3374.

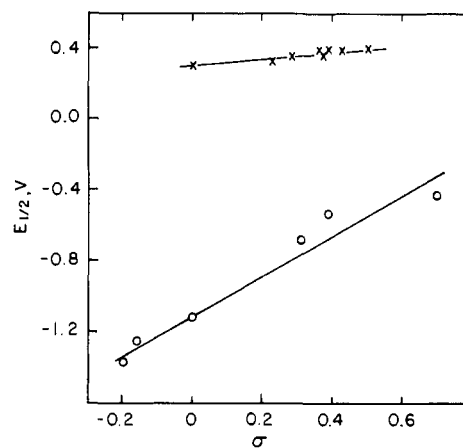


Figure 5. Variation of the reduction potential with the Hammett substituent constant is significantly more pronounced for free *N*-alkylpyridinium ions (circles) than for (substituted pyridine) $\text{Ru}(\text{NH}_3)_5^{3+}$ complexes (crosses). Data are from ref 49 and 65.

potential. The effects on E° for the py/py^- couples are manifest in the value of $\rho \sim 10$. Indeed, a plot of E° vs. σ for a series of substituted pyridines is significantly (~ 5 -fold) steeper than the corresponding plot for the metal pyridine complexes, Figure 5.⁵⁴ The rates of the reduction of free pyridines are thus expected to be much more sensitive to the substituent effects than the corresponding rates for the reduction of metal pyridine complexes, provided, in the latter case, that the reduction takes place at the metal center.

As remarked earlier, the suggested use of the Hammett reaction constant to make the indicated mechanistic distinction requires that the rate constants be in the range of activation control, not diffusion control. In effect, then, this requires the omission of data for any substituent where the diffusional limit is being approached. Without that, an artificially small reaction constant could be taken to suggest direct reaction at the metal center where such is not really the case. Indeed, examination of published data for the reactions of substituted alkylpyridinium ions⁴⁹ with an excited-state binuclear iridium complex *did* give two separate ranges of reactivity,^{50,51} with ρ values of 10.3 and 1.8. The former is as expected (cf. Table V, group I); the latter illustrates the leveling effect at high driving force. Similarly, one rate constant at the diffusion-controlled limit was omitted in the correlation of the data for the ruthenium excited-state reaction.⁴⁷

We are inclined to believe, however, that diffusional leveling has not occurred in the reactions between $\text{Ru}(\text{bpy})_3^+$ and the members examined in the series of $\text{Cr}(\text{py})_3^{3+}$ complexes but cannot back that claim with incontrovertible arguments. The facts bearing on the matter are as follows: (1) The rate constant range is below the diffusion-controlled limit,⁵⁵⁻⁵⁷ albeit not by a large margin. (2) The rate constants are correlated by a single-parameter Hammett equation. Were this, in fact, really a reaction in the high-sensitivity group, then the least reactive of the complexes should have fallen well below the line defining the others. (3) Both series include several reactions of known mechanism having driving forces comparable to, or even larger than, those in this system; note that the E° applicable to $\cdot\text{C}(\text{CH}_3)_2\text{OH}$ is ca. -1.3 V, virtually identical with that of $\text{Ru}(\text{bpy})_3^+$. (4) The fastest reacting members in the high-sensitivity group, in fact, react at rates as high as those in this series. Fast reactions are found in the high-sensitivity group. Given the latter two points especially, we remain inclined to defend the mechanism assigned on the basis

(54) We are grateful to a reviewer for suggesting this plot.

(55) The diffusion-controlled rate constant, k_{diff} , for the reaction between two ions in solution can be calculated by using the Debye-Smolouchowski equation.^{55,56} With $r = 7.1 \text{ \AA}$ ⁵⁶ for $\text{Ru}(\text{bpy})_3^+$ and 6 \AA for $(\text{H}_2\text{O})_5\text{CrNC}_5\text{H}_4\text{X}_3^+$, the calculated k_{diff} at ionic strength 1 M is $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

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of the data available at present.

These points stated, however, we must admit that the argument is not (yet) fully definitive. The Hammett LFER correlation is, as commented earlier, equivalent to the E° approach^{47,49} if only a single reducible center (e.g., a pyridinium ion alone) is present. Its potential value lies in its prospect for addressing suitably constructed cases with two potential acceptor sites, such as the metal pyridine complexes, where a single-site reduction potential will, in general, be unavailable. Since reactions of this type are of some general interest and since the method appears to hold considerable promise for making the indicated assignments, we present it at this stage of its development. Other investigations to establish the limits of its validity are currently in progress.

The question we are addressing as regards the mechanism(s) of reduction of the $(\text{H}_2\text{O})_5\text{Cr}(\text{py})^{3+}$ ions is one that has been considered recently in similar circumstances.^{10,58-60} In the cases cited, there was quite credible evidence that certain systems could, indeed, proceed by either mechanism, resonance-transfer or the

"chemical" mechanism (i.e., ligand reduction).⁶¹⁻⁶⁴ Of course, the latter requires a combination of a donor and a ligand acceptor that together provide a sufficient driving force. In that context, metal pyridine complexes are among the oxidizing substrates that have proved particularly useful in efforts to arrive at general conclusions concerning the controlling factors. The Hammett correlation analysis promises to provide a new tool for assigning mechanisms reliable in such instances.

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Crown Ether-Lanthanide Complexes Studied by CPL and TL. 2. Solution Species in (2*R*,3*R*,11*R*,12*R*)-2,3,11,12-Tetramethyl-18-crown-6-Europium Nitrate and Perchlorate Systems in MeCN, TFE, and HFiP

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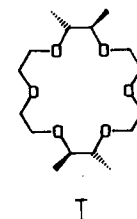
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The solution behavior of complexes of (2*R*,3*R*,11*R*,12*R*)-2,3,11,12-tetramethyl-1,4,7,10,13,16-hexaoxacyclooctadecane ((*all-R*)-2,3,11,12-tetramethyl-18-crown-6, I) with europium(III) nitrate and perchlorate in the solvents acetonitrile (MeCN), trifluoroethanol (TFE), and hexafluoroisopropyl alcohol (HFiP) has been investigated by using the techniques of circularly polarized luminescence (CPL) and total luminescence (TL) spectroscopy, as well as conductivity measurements. The nitrate-crown complex is determined to be $[\text{I-Eu}(\text{NO}_3)_2]^+$, with the europium ten-coordinate, to the hexadentate 18-crown-6 ligand and to the two opposing bidentate nitrate anions. The perchlorate complex, while not as structurally robust as the nitrate, appears to have a similar structure, but with monodentate perchlorate anions. Ligand field splittings of the emission transitions are interpreted in terms of D_2 effective electronic symmetry in the nitrate complex and effective axial symmetry in the perchlorate. Observed changes in the CPL and TL spectra during titrations of $\text{Eu}(\text{NO}_3)_3$ with I in TFE and MeCN indicate the presence of poly(nitrato) anionic species from the nitrate generated by the formation of the crown complex and the excess $\text{Eu}(\text{NO}_3)_3$ present in solution. In MeCN, the formation of the stable $[\text{Eu}(\text{NO}_3)_3]^{2-}$ species limits the formation of additional crown complex, whereas in TFE, the crown complexation goes to completion. In MeCN, the difference in the intensities of the hypersensitive ${}^7F_0 \rightarrow {}^5D_2$ transition used for excitation results in preferential excitation of the pentakis(nitrato) species relative to the crown complex. The data indicate that europium exchange between these two species is slow compared to the lifetime of the europium emission.

Introduction

We have recently been interested in studying the solution interactions of chiral crown ether hosts with cations, through the use of chiroptical techniques.¹ Chiroptical spectroscopy can be quite sensitive to solution complex structure when a normally achiral chromophore gains chirality through association with a chiral ligand. In this study, the solution properties of complexes

of the title tetramethyl-18-crown-6 ether (I) with europium nitrate



I

and perchlorate have been investigated in several solvents by using circularly polarized luminescence (CPL), the differential emission of left and right circularly polarized light. Simultaneously, total luminescence (TL) spectroscopy has been used to probe *all*

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