Electron Transfer versus Energy Transfer in the Reactions of ^{2}E Cr(bpy)$_3$$^{3+}$ with Organochromium and Organocobalt Complexes

Andreja Bakac* and James H. Espenson*

Contribution from the Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received June 15, 1987*

Abstract: The pentaaquoorganochromium complexes, $(H_2O)_5CrR^{2+}$, and a series of organocobalt complexes, $(H_2O)([14]\text{aneN}_4)CoR^{2+}$ ($[14]\text{aneN}_4$ = 1,4,8,11-tetraazacyclotetradecane), quench the luminescence of ^{2}E $Cr(bpy)_3^{3+}$. The kinetic trend in the reactions of $(H_2O)_5CrR^{2+}$ at 25 °C (R, $10^{-7}k_{Cr}/M^{-1}\ s^{-1}$: CH_3, ~0.15; C_2H_5, 1.9; 2-C_3H_7, 32; $CH_2C_6H_5$, 157; CH_2OCH_3, 8.5; CH_2Cl, ~0.1) is that expected for outer-sphere electron transfer to ^{2}E $Cr(bpy)_3^{3+}$. The organocobalt complexes are generally more reactive, but the reactivity pattern (R, $10^{-7}k_{Co}/M^{-1}\ s^{-1}$: CH_3, 9.4; C_2H_5, 13; 1-C_3H_7, 2.7; CH_2OCH_3, 5.2; CH_2Cl, 22; CH_2Br, 35) is clearly distinct from that observed in the organochromium series. The oxidation of the organocobalt complexes by $Ru(bpy)_3^{3+}$ shows a pattern that is typical of outer-sphere electron transfer (R, k/M^{-1}: CH_3, 16.0; 1-C_3H_7, 442; CH_2OCH_3, 649; CH_2Cl, <0.04; CH_2Br, <0.4). The unusual reactivity trend in the reactions of the organocobalt complexes with $Cr(bpy)_3^{3+}$ thus signals a major change in mechanism. It is proposed that the cobalt complexes react by energy transfer to yield $^*(H_2O)Co([14]\text{aneN}_4)R^{2+}$ and $Cr(bpy)_3^{3+}$. The relaxation of $^*(H_2O)Co([14]\text{aneN}_4)R^{2+}$ to the ground state takes place in competition with the unimolecular homolysis to yield $Co([14]\text{aneN}_4)(H_2O)_n^{2+}$ and $R^\bullet$. The semiquantitatively measured yields of $Cr(bpy)_3^{2+}$ are consistent with these assignments, as are literature data that show efficient energy transfer quenching of $^*Cr(bpy)_3^{3+}$ by inorganic cobalt(III) macrocycles but not by $(H_2O)_5Cr^{III}X$ complexes.

Electron-transfer and energy-transfer reactions of excited states are currently an area of intense research. Both types of quenching are of great theoretical and practical interest, especially as regards the conversion and storage of solar energy. In addition to the clear-cut cases of direct energy or electron transfer,[1,2] an indirect, electron transfer induced energy transfer[3] has also been indentified and well documented in the literature.

The ^{2}E excited state of $Cr(bpy)_3^{3+}$, denoted $^*Cr(bpy)_3^{3+}$, is a strong oxidant and an efficient energy donor, eq 1 and 2, with a lifetime of ~70 μs in aqueous solutions.[1,4–6] Owing to the relatively low $E°$ value for the ground-state couple,[7,8] eq 3, the

$$^*Cr(bpy)_3^{3+} + e^- \rightarrow Cr(bpy)_3^{2+} \qquad E°_{*3+/2+} = +1.46\ \text{V} \tag{1}$$

$$^*Cr(bpy)_3^{3+} \rightarrow Cr(bpy)_3^{3+} \qquad E_{00} = 1.7\ \text{eV} \tag{2}$$

initial products of electron-transfer quenching, eq 4, undergo secondary electron transfer, eq 5, to regenerate the ground-state reactants. This sequence has been observed in the electron-transfer reactions of $^*Cr(bpy)_3^{3+}$ with electron donors (D) such as Fe^{2+},[8–11] organic amines and methoxybenzenes,[12,13] reduced transition-metal polypyridine complexes,[8,14] and I^-.[9b] In fact, the initial products of the reaction with I^-, $I^\bullet$, and $Cr(bpy)_3^{2+}$ have not been detected owing to the extremely efficient secondary step of eq 5.[9b]

$$Cr(bpy)_3^{3+} + e^- \rightarrow Cr(bpy)_3^{2+} \qquad E° = -0.25\ \text{V} \tag{3}$$

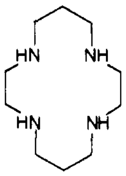
$$^*Cr(bpy)_3^{3+} + D \rightarrow Cr(bpy)_3^{2+} + D^+ \tag{4}$$

$$Cr(bpy)_3^{2+} + D^+ \rightarrow Cr(bpy)_3^{3+} + D \tag{5}$$

The ^{2}E states of $Cr(bpy)_3^{3+}$ and other polypyridine complexes of Cr(III) react with a number of inorganic complexes by energy transfer,[6,15–19] eq 6. A double exchange mechanism has been proposed for these reactions.[17]

$$^*CrL_3^{3+} + Co^{III} \rightarrow CrL_3^{3+} + {}^*Co^{III} \tag{6}$$

This paper reports our findings on the reactions of $^*Cr(bpy)_3^{3+}$ with two series of organometallic complexes, $(H_2O)_5CrR^{2+}$ and $(H_2O)([14]\text{aneN}_4)CoR^{2+}$ ($[14]\text{aneN}_4$ = 1,4,8,11-tetraazacyclotetradecane). The oxidation of the organocobalt series by another



$[14]\text{aneN}_4$

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potent oxidant, $Ru(bpy)_3^{3+}$ ($E° = 1.28$ V), was also briefly examined to "calibrate" the electron-transfer behavior of this new series of complexes. The oxidation of the organochromium complexes by $Ru(bpy)_3^{3+}$, eq 7, has been reported recently.[20] The oxidized organochromium complex $(H_2O)_5CrR^{3+}$ decomposes by

$$Ru(bpy)_3^{3+} + (H_2O)_5CrR^{2+} \xrightarrow{k_{Ru-CrR}} Ru(bpy)_3^{2+} + (H_2O)_5CrR^{3+} \quad (7)$$

either homolytic cleavage or intramolecular electron transfer, depending on R. The high reduction potential of the $^*Cr(bpy)_3^{3+/2+}$ couple, 1.46 V, and the ready accessibility and long lifetime of the excited state present us with an opportunity to explore further the oxidizability of the $(H_2O)_5CrR^{2+}$ and $(H_2O)([14]aneN_4)CoR^{2+}$ complexes.

Several mechanistic possibilities must be considered in the reactions of the organocobalt complexes with $^*Cr(bpy)_3^{3+}$. Electron transfer (eq 8, L = [14]aneN$_4$) would prevail only if the electron-donating properties of the alkyl groups sufficiently lower the reduction potential of the $(H_2O)([14]aneN_4)CoR^{3+/2+}$ couple relative to the inorganic analogues, $(H_2O)(14]aneN_4)CoX^{n/n-1}$ ($X = Cl^-, Br^-, H_2O$). If the change in $E°$ is too small to have a major mechanistic impact, the reactions might take place by energy transfer, eq 9, possibly followed by electron transfer between the primary products, eq 10, or unimolecular homolysis of the excited state organocobalt, eq 11. Since reaction 8, the sequence 9–10, and the follow-up reactions of both fragments formed

$$(H_2O)LCoR^{2+} + {}^*Cr(bpy)_3^{3+} \rightarrow (H_2O)LCoR^{3+} + Cr(bpy)_3^{2+} \quad (8)$$

$$(H_2O)LCoR^{2+} + {}^*Cr(bpy)_3^{3+} \rightarrow {}^*(H_2O)LCoR^{2+} + Cr(bpy)_3^{3+} \quad (9)$$

$$^*(H_2O)LCoR^{2+} + Cr(bpy)_3^{3+} \rightarrow (H_2O)LCoR^{3+} + Cr(bpy)_3^{2+} \quad (10)$$

$$^*(H_2O)LCoR^{2+} \rightarrow (H_2O)LCo^{2+} + R^\bullet \quad (11)$$

in eq 11 all produce $Cr(bpy)_3^{2+}$, the formation of this species alone does not provide sufficient evidence for electron transfer as the primary step.

The results of the kinetic and product studies indicate direct electron transfer in the reactions of $(H_2O)_5CrR^{2+}$ with $^*Cr(bpy)_3^{3+}$, whereas the organocobalt complexes react by energy transfer.

Experimental Section

Tris(bipyridine)chromium(III) perchlorate was prepared according to the published procedure,[8] and the purity was checked by comparison with the reported UV–visible spectrum.[21] The organochromium complexes[22] and $(H_2O)_5CrBr^{2+}$ [23] were prepared as reported earlier and purified by ion exchange on Sephadex SP-C25. The organocobalt complexes[24] $(H_2O)([14]aneN_4)CoR^{2+}$ (R = primary alkyl) were prepared by photolysis of the organocobaloximes, $RCo(dmgH)_2B$ ($B = H_2O$ or pyridine), in the presence of $Co([14]aneN_4)(H_2O)_n^{2+}$ (n = 1 or 2).[25] The 2-propyl complex was too unstable to isolate, and the benzyl homolyzed too rapidly to be used in the quenching studies. Solutions of $Ru(bpy)_3^{3+}$ were prepared in a quartz cell by irradiating $Ru(bpy)_3^{2+}$ (7–43 μM) in the presence of a quencher (0.1–3.0 mM $Co(NH_3)_5Br^{2+}$, $Co(NH_3)_5Cl^{2+}$, or $Co(NH_3)_5H_2O^{3+}$) for 10–20 s by use of a sun lamp. The conversion of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ is quantitative under these conditions. Solutions of $Ru(bpy)_3^{3+}$ were used immediately after preparation.

The kinetics of the quenching reactions were studied by use of the laser flash photolysis system described earlier.[20] The excitation of $Cr(bpy)_3^{3+}$ was provided by a 600-ns pulse from a Phase-R Model DL-1100 dye laser. The absorbance of $Cr(bpy)_3^{3+}$ at the excitation wavelengths (460 and 423 nm in experiments with $(H_2O)_5CrR^{2+}$ and $(H_2O)([14]aneN_4)CoR^{2+}$, respectively) exceeded that of the organometallic complexes by a factor of >10.

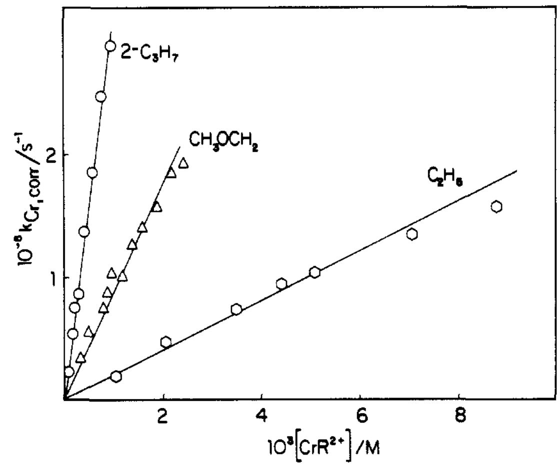

Figure 1. Plot of the corrected pseudo-first-order rate constant for the reactions of $^*Cr(bpy)_3^{3+}$ with $(H_2O)_5CrR^{2+}$ against the concentration of $(H_2O)_5CrR^{2+}$. The reactions were run under air-free conditions in the presence of (4–10) mM Fe^{3+}.

The ionic strength was kept constant at 0.1 and 1.0 M by addition of $LiClO_4$ and $HClO_4$. The variation of $[H^+]$ in the range 0.02–0.1 M had no effect on the kinetics that were monitored at the emission (λ 727 nm) and absorption (λ 443 nm) maxima of $^*Cr(bpy)_3^{3+}$. Identical kinetic results were obtained at the two wavelengths. All the kinetic experiments were run under pseudo-first-order conditions by use of a large excess of the organometallic complexes over $^*Cr(bpy)_3^{3+}$. The concentration of the latter was usually 5–30 μM, as determined from the absorbance change at λ 443 nm ($\epsilon_{*3+} - \epsilon_{3+} = 4.35 \times 10^3$ M^{-1} cm^{-1}).[11] The kinetic data were analyzed by standard methods. All the experimental rate constants were corrected for the intrinsic lifetime of $^*Cr(bpy)_3^{3+}$, $k = 1.2 \times 10^4$ s^{-1} ($\tau_0 = 83.3$ μs) and 2.0×10^4 s^{-1} ($\tau_0 = 50$ μs) in solutions saturated with argon and air, respectively.

The yields of $Cr(bpy)_3^{2+}$ were determined from the absorbance changes at 560 nm, $\epsilon = 4.85 \times 10^3$ M^{-1} cm^{-1}.[21] The gaseous organic products were analyzed by use of Hewlett-Packard 5790 gas chromatograph and commercially available columns.

The kinetics of the oxidation of $(H_2O)([14]aneN_4)CoR^{2+}$ by $Ru(bpy)_3^{3+}$ were determined by use of a Cary 219 spectrophotometer. The ionic strength was kept constant at 1.0 M ($HClO_4 + LiClO_4$). All the experiments were monitored at an absorption maximum for $Ru(bpy)_3^{2+}$ at 452 nm.[26]

Results

Kinetics of the Quenching Reactions. The two families of organometallic complexes, $(H_2O)_5CrR^{2+}$ and $(H_2O)([14]aneN_4)CoR^{2+}$, react readily with $^*Cr(bpy)_3^{3+}$. In argon-saturated solutions in the presence of a large excess of R–M (M = $(H_2O)_5Cr^{2+}$ and $(H_2O)([14]ane)Co^{2+}$) the kinetics are first order. The plots of the corrected pseudo-first-order rate constants, k_{corr} (see Experimental Section), against the concentration of the excess reagent are, however, nonlinear such that the apparent second-order rate constant decreases with concentration. The extent of the curvature and the actual values of k_{corr} are a complicated function of the concentrations of all the species involved ($Cr(bpy)_3^{3+}$, $^*Cr(bpy)_3^{3+}$, and R–M), the identity of R and M, and the actual second-order rate constant. This effect is caused by the fast side reaction between $^*Cr(bpy)_3^{3+}$ and the $Cr(bpy)_3^{2+}$ formed in the reduction of the excited state by R–M, eq 12 and 13, $k_{13} = 5 \times 10^9$ M^{-1} s^{-1}.[11] Even small concentrations of $Cr(bpy)_3^{2+}$ can have a large effect owing to the catalytic nature of the quenching reaction shown in eq 13. Subsequent experiments

$$^*Cr(bpy)_3^{3+} + R\text{–}M^{2+} \rightarrow Cr(bpy)_3^{2+} + R\text{–}M^{3+} \quad (12)$$

$$Cr(bpy)_3^{2+} + {}^*Cr(bpy)_3^{3+} \rightarrow Cr(bpy)_3^{3+} + Cr(bpy)_3^{2+} \quad (13)$$

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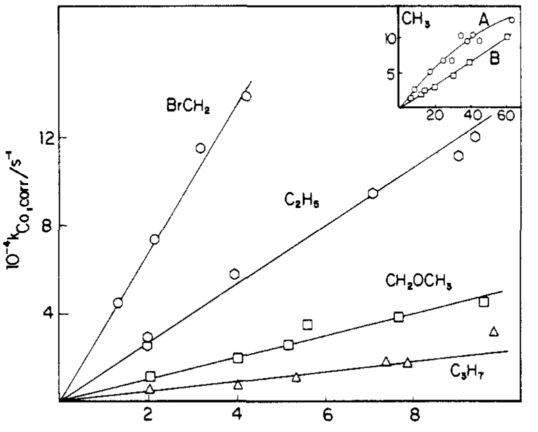
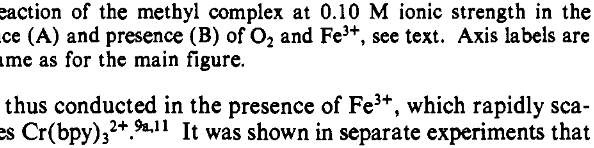


Figure 2. Plot of the corrected pseudo-first-order rate constants, obtained at 22 ± 2 °C in air-saturated solutions containing (4–10) mM Fe^{3+}, for the reactions of $^*Cr(bpy)_3^{3+}$ with $(H_2O)([14]aneN_4)CoR^{2+}$ against the concentration of $(H_2O)([14]aneN_4)CoR^{2+}$. The inset shows the data for the reaction of the methyl complex at 0.10 M ionic strength in the absence (A) and presence (B) of O_2 and Fe^{3+}, see text. Axis labels are the same as for the main figure.

were thus conducted in the presence of Fe^{3+}, which rapidly scavenges $Cr(bpy)_3^{2+}$.[9a,11] It was shown in separate experiments that Fe^{3+} does not react with other species in the reaction solutions in the short times involved. The plots of k_{corr} obtained in the presence of Fe^{3+} versus [R–M] are linear (Figures 1 and 2). The values of k_{corr} are independent of $[Fe^{3+}]$ (4–10 mM), confirming that its role is limited to the scavenging of $Cr(bpy)_3^{2+}$.

Once Fe^{3+} has been added to the reaction solutions, the kinetics of the reactions of $(H_2O)([14]aneN_4)CoR^{2+}$ at 1.0 M ionic strength show little sensitivity to oxygen. The difference in the rate constants between argon-saturated and air-saturated solutions, respectively, is <20%. At 0.1 M ionic strength the rate constants in argon-saturated solutions are higher by up to a factor of 2. The effect of oxygen is most likely caused by the scavenging[27] of the carbon-centered radicals which under air-free conditions react with $^*Cr(bpy)_3^{3+}$, eq 14. The analogous reaction with the ground-state



$$^*Cr(bpy)_3^{3+} + R^\bullet \longrightarrow \begin{cases} Cr(bpy)_3^{2+} + \text{“}R^+\text{”} \\ Cr(bpy)_2(bpyR)^{2+} + H^+ \end{cases} \quad (14)$$

complex has been observed.[28] Thus the disappearance of $^*Cr(bpy)_3^{3+}$ in air-saturated solutions containing Fe^{3+} corresponds cleanly to the reaction with $(H_2O)([14]aneN_4)CoR^{2+}$.

All kinetic measurements with $(H_2O)_5CrR^{2+}$ complexes were done at 1.0 M ionic strength under air-free conditions owing to the oxygen sensitivity of some of the complexes.[22] All the kinetic data for the reactions of $^*Cr(bpy)_3^{3+}$ with $(H_2O)_5CrR^{2+}$ and $(H_2O)([14]aneN_4)CoR^{2+}$ are summarized in Tables I and II.

The quenching of $^*Cr(bpy)_3^{3+}$ by the inorganic complexes $(H_2O)_5CrBr^{2+}$ and $Cr(H_2O)_6^{3+}$ is quite inefficient. The former reacts with a rate constant of 4.9×10^6 M^{-1} s^{-1}, whereas the latter shows no reactivity at concentrations of up to 0.016 M ($k < 10^5$ M^{-1} s^{-1}).

Table I. Summary of the Kinetic Data for the Reactions of $(H_2O)_5CrR^{2+}$ with $Ru(bpy)_3^{3+}$ and $^*Cr(bpy)_3^{3+}$ at 25 °C and 1.0 M Ionic Strength

R	$10^{-7}k_{Cr}/M^{-1}$ s^{-1} [a]	$10^{-7}k_{Ru-CrR}/M^{-1}$ s^{-1} [b]
CH_3	~0.15[c]	<0.0001
C_2H_5	1.9	0.020
$2\text{-}C_3H_7$	32	4.2
CH_2OCH_3	8.5	1.0
CH_2Cl	~0.1[c]	
$CH_2C_6H_5$	157	53

[a] Measured in the presence of 4–10 mM Fe^{3+} under air-free conditions. [b] From ref 20. [c] Too slow for accurate determination.

Table II. Summary of the Kinetic Data for the Reactions of $(H_2O)Co([14]aneN_4)R^{2+}$ with $Ru(bpy)_3^{3+}$ and $^*Cr(bpy)_3^{3+}$ at 25 °C and 1.0 M Ionic Strength

R	$10^{-7}k_{Co}/M^{-1}$ s^{-1} [a]	k_{Ru-CoR}/M^{-1} s^{-1}
CH_3	9.4 (1.2)	16.0
C_2H_5	13 (1.6)	
$1\text{-}C_3H_7$	2.7 (≤1)[b]	442
CH_2OCH_3	5.2 (≤1)[b]	649
CH_2Cl	22 (3.2)	≤0.04[b]
CH_2Br	35 (6.4)	≤0.4[b]

[a] Measured in the presence of 5–10 mM Fe^{3+} in air-saturated solutions. The values at 0.10 M ionic strength are given in parentheses. [b] Too low for accurate determination.

Products of the Quenching Reactions. The determination of $[Cr(bpy)_3^{2+}]$ produced in the reactions of $^*Cr(bpy)_3^{3+}$ with $(H_2O)_5CrR^{2+}$ and $(H_2O)([14]aneN_4)CoR^{2+}$ requires air-free conditions and the absence of Fe^{3+}. Under these circumstances reaction 13 interferes signficantly in all the systems that produce $Cr(bpy)_3^{2+}$. Only semiquantitative estimates of the yields could thus be made. The reactions of $(H_2O)_5CrR^{2+}$ produce substantial amounts of $Cr(bpy)_3^{2+}$ for R = C_2H_5, $2\text{-}C_3H_7$, and CH_2OCH_3, and only a trace amount for R = $CH_2C_6H_5$. The other two complexes in Table I, R = CH_3 and CH_2Cl, react very slowly, such that only a small fraction of the reaction takes place within the lifetime of the excited state. Only small amounts of $Cr(bpy)_3^{2+}$ were observed in these reactions. The inorganic complex $(H_2O)_5CrBr^{2+}$ produces no $Cr(bpy)_3^{2+}$.

The top four organocobalt complexes in Table II produce small (R = CH_3 and C_2H_5) to moderate (R = $1\text{-}C_3H_7$ and CH_2OCH_3) yields of $Cr(bpy)_3^{2+}$, but none was observed for R = CH_2Cl and CH_2Br.

The only gaseous organic product observed in the reaction of $(H_2O)_5CrC_2H_5^{2+}$ is ethylene. Ethane was also detected, but it is formed by spontaneous acidolysis of the organochromium complex and not in the reaction with $^*Cr(bpy)_3^{3+}$. Similarly, $(H_2O)([14]aneN_4)CoC_2H_5^{2+}$ yielded ethylene as the sole product. No gaseous products were found in the reactions of (methyl)cobalt, (chloromethyl)cobalt, and (2-propyl)chromium complexes with $^*Cr(bpy)_3^{3+}$.

Oxidation of $(H_2O)([14]aneN_4)CoR^{2+}$ by $Ru(bpy)_3^{3+}$ was studied for R = CH_3, $n\text{-}C_3H_7$, CH_2OCH_3, CH_2Cl, and CH_2Br. All of the reactions are much slower than the quenching of $^*Cr(bpy)_3^{3+}$ by the same complexes. When a large excess of the organocobalt complexes was used, a rapid increase in absorbance at 452 nm was observed in mixing time owing to a buildup of $Ru(bpy)_3^{2+}$. This was followed by the slower formation of $Ru(bpy)_3^{2+}$ in the reaction of $Ru(bpy)_3^{3+}$ with $(H_2O)([14]aneN_4)CoR^{2+}$, eq 15. The rapid reaction in the mixing time seems to

$$Ru(bpy)_3^{3+} + (H_2O)([14]aneN_4)CoR^{2+} \xrightarrow{k_{Ru-CoR}} Ru(bpy)_3^{2+} + (H_2O)([14]aneN_4)CoR^{3+} \quad (15)$$

be caused by some reducing impurity present at a low level (~1%) in solutions of the organocobalt complexes. This interpretation is substantiated by the excellent linearity of the pseudo-first-order plot for the reactions of interest, eq 15, and the lack of any correlation between the size of the rapid absorbance change (or the concentration of excess reagent) and the derived second-order rate constants (Table II).

The kinetics of reaction 15 are independent of $[H^+]$ in the range 0.10–1.0 M and the nature and concentration of the quencher used for the preparation of $Ru(bpy)_3^{3+}$.

The reaction of $(H_2O)([14]aneN_4)CoC_3H_7^{2+}$ and $Ru(bpy)_3^{3+}$ in the presence of 3 mM $Co(NH_3)_5Cl^{2+}$ produces propyl chloride in a 100% yield.

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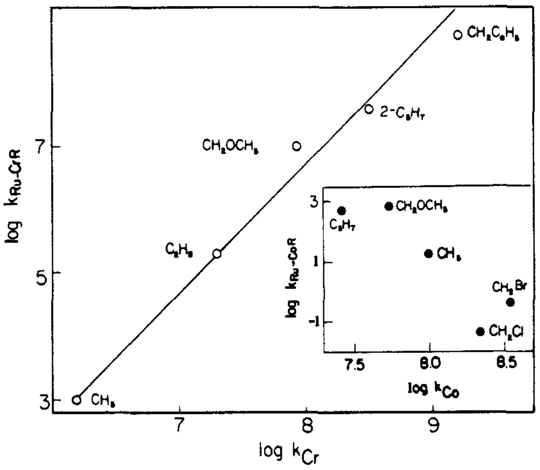
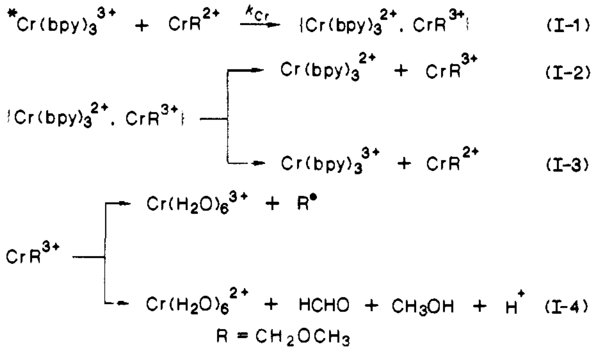


Figure 3. Plot depicting the correlation of the rate constants for the reactions of $(H_2O)_5CrR^{2+}$ with $^*Cr(bpy)_3^{3+}$ and $Ru(bpy)_3^{3+}$. Inset shows the lack of the correlation between the rate constants for the reactions of $(H_2O)([14]aneN_4)CoR^{2+}$ with $^*Cr(bpy)_3^{3+}$ and $Ru(bpy)_3^{3+}$.

Scheme I



Discussion

The organochromium complexes $(H_2O)_5CrR^{2+}$ reduce $^*Cr(bpy)_3^{3+}$ to $Cr(bpy)_3^{2+}$. The latter was observed in all the reactions, although the yields varied somewhat with the group R. There is thus no doubt that electron transfer takes place at some stage of the reaction. The question that remains to be answered is whether electron transfer is the primary step or a secondary one. The evidence available strongly supports the former alternative. The trend in the reactivity parallels almost exactly that observed earlier in the outer-sphere oxidation of the same complexes by $Ru(bpy)_3^{3+}$[20] ($CH_3 < C_2H_5 < 2\text{-}C_3H_7 < CH_2C_6H_5$). This reactivity order reflects the effect of increasing electron donation from the alkyl group on the reduction potential of the organochromium complexes.[20] Figure 3 illustrates the correlation between the rate constants for the two series of reactions.

Energy transfer seems to be ruled out as a dominant reaction pathway not only by the observed reactivity trend but also by the demonstrated slowness of the energy-transfer reactions of the closely related inorganic complexes, $(H_2O)_5CrBr^{2+}$ and $(H_2O)_6Cr^{3+}$. The bromo complex is expected to be among the most efficient energy acceptors in the series.[17] The mechanism we propose for the reaction of the organochromium complexes with $^*Cr(bpy)_3^{3+}$ is shown in Scheme I. The reaction is initiated by electron transfer to form $Cr(bpy)_3^{2+}$ and CrR^{3+} in the solvent cage. The competition between the escape of the initial products from the solvent cage (eq I-2), and the secondary electron transfer to yield the ground-state reactants (eq I-3) is then responsible for the formation of variable amounts of $Cr(bpy)_3^{2+}$ as R is varied. The rate of the cage collapse should be approximately constant throughout the series. The rate constant for the reaction I-3, on the other hand, is expected to show considerable variation and at least some correlation with the reduction potential of the $(H_2O)_5CrR^{3+/2+}$ couple. If this is the case, the complexes that react most slowly in reaction I-1 will be the most reactive ones in the secondary electron-transfer step. Consequently, the yields of $Cr(bpy)_3^{2+}$ should be the lowest for the complexes with the lowest values of k_{Cr} in Table I. This prediction is realized for all the alkyl complexes, but it fails badly for R = benzyl, which yields only a small amount of $Cr(bpy)_3^{2+}$. It seems that the presence of the benzyl group accelerates both the primary and secondary electron-transfer steps beyond the value expected[29] from the electron-donating properties of the benzyl group alone. This is also true for the oxidation of this complex by $Ru(bpy)_3^{3+}$.[20] A special interaction between the aromatic rings of the metal polypyridine complexes and the benzyl group of the organochromium may be involved. This complex may also have a higher self-exchange rate constant than the alkyl analogues. Unfortunately, the Marcus parameters for the organochromium complexes remain unknown.

Reaction I-4 has been discussed in detail earlier.[20] The products are $(H_2O)_6Cr^{3+}$ and the carbon-centered radicals for all the chromium complexes in Table I except $(H_2O)_5CrCH_2OCH_3^{2+}$, which yields $(H_2O)_6Cr^{2+}$, CH_2O, and CH_3OH.

The lack of formation of the gaseous organic products is consistent with the expected ring addition of carbon-centered radicals to $Cr(bpy)_3^{3+}$,[28] eq 14. More surprising is the formation of ethylene from $(H_2O)_5CrC_2H_5^{2+}$, since we have shown[28b] that thermally generated ethyl radicals react with $Cr(bpy)_3^{3+}$ under otherwise identical conditions to yield *no* gaseous products. This suggests that at least some of the radicals in the flash photolysis experiments react with the excited state to yield C_2H_4, eq 16. This interpretation is supported by the fact that the quenching of $^*Cr(bpy)_3^{3+}$ by $(H_2O)([14]aneN_4)CoC_2H_5^{2+}$ also yields C_2H_4. Although it was not anticipated, the formation of the different products in the reactions of ethyl radicals with the ground and

$$^*Cr(bpy)_3^{3+} + {}^{\bullet}C_2H_5 \rightarrow Cr(bpy)_3^{2+} + C_2H_4 + H^+ \quad (16)$$

excited states of $Cr(bpy)_3^{3+}$ is not unreasonable in view of the shift of 1.71 V in the reduction potentials between the two states.

Although the rate constants for the quenching of $^*Cr(bpy)_3^{3+}$ by the methyl and halomethyl complexes are much lower than those for the rest of the series, the values are still much higher than those obtained in the reactions with $Ru(bpy)_3^{3+}$. This may signal a contribution to the overall rate constant from an energy-transfer pathway analogous to that observed with $(H_2O)_5CrBr^{2+}$. The very low yields of $Cr(bpy)_3^{2+}$ obtained in these two reactions seem to reinforce this conclusion.

The reactions of $Ru(bpy)_3^{3+}$ with $(H_2O)([14]aneN_4)CoR^{2+}$ produce $Ru(bpy)_3^{2+}$ and the carbon-centered radicals. The former was observed directly at 452 nm, and the latter was trapped with $Co(NH_3)_5Cl^{2+}$ for R = *n*-Pr. All these data are consistent with the reaction taking place by an initial electron transfer, eq 15, followed by homolysis of the Co–C bond in the oxidized complex, eq 17. The latter process is analogous to that observed in the oxidations of the organochromium complexes by $Ru(bpy)_3^{3+}$ and $^*Cr(bpy)_3^{3+}$.

$$(H_2O)([14]aneN_4)CoR^{3+} \rightarrow (H_2O)([14]aneN_4)Co^{3+} + R^{\bullet} \quad (17)$$

The kinetic pattern (CH_2Cl, $CH_2Br \ll CH_3 < C_3H_7 < CH_2OCH_3$) is also qualitatively the same as that observed in the reactions of the organochromium complexes with $Ru(bpy)_3^{3+}$ and $^*Cr(bpy)_3^{3+}$. All three sets of reactions are quite sensitive to the electronic effects of the alkyl groups so that the rate constants for each series span a range of several orders of magnitude.

The oxidation of the organocobalt complexes by $Ru(bpy)_3^{3+}$ is much slower than the oxidation of the organochromium series. It is reasonable to expect a similar relative reactivity toward other oxidants as well, regardless of which parameter(s) (reduction potential, self-exchange rate constant, or the electronic transmission coefficient κ) in the Marcus equation makes the organocobalt complexes less reactive toward $Ru(bpy)_3^{3+}$.

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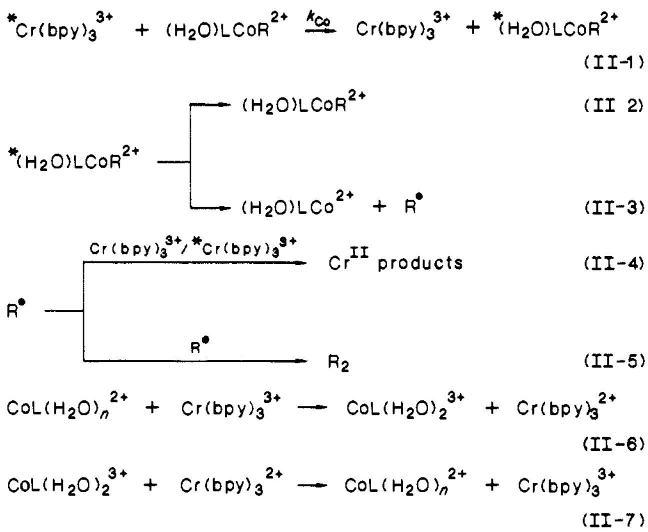
(29) The reactivity order $k_{2\text{-}C_3H_7} > k_{CH_2C_6H_5}$ has been observed in the oxidation of organocobaloximes by $IrCl_6^{2-}$ (Halpern, J.; Chan, M. S.; Tom, G. M. *Acta Chem. Scand.* **1979**, *33A*, 141).

Scheme II



Quenching of $*Cr(bpy)_3^{3+}$ by the Organocobalt Complexes. It may not be too surprising that the reactions of the top four complexes in Table II (R = CH_3, C_2H_5, C_3H_7, and CH_2OCH_3) result in the net reduction of $*Cr(bpy)_3^{3+}$, whereas those of the halo-substituted alkyls do not. This finding might be easily explained by the trend in the reducing power within the series. Surprisingly, however, the reactivity order is quite different from that observed in the electron-transfer reactions with $Ru(bpy)_3^{3+}$, such that the two halomethyl complexes react faster than the electron-rich alkyls. The pattern for the unsubstituted alkyls ($CH_3 \sim C_2H_5 > C_3H_7$) is also different from that observed in the reactions with $Ru(bpy)_3^{3+}$ ($CH_3 < C_3H_7$), as shown in the inset of Figure 3. The observed rate constants span a strikingly narrow range ($(2.7–35) \times 10^7$ M^{-1} s^{-1}), and the absolute values are many orders of magnitude higher than those for the reactions with $Ru(bpy)_3^{3+}$, despite the relatively small differences in the reduction potentials and self-exchange rate constants for the two oxidants.[30] In fact the observed rate constants are even higher than those for the reactions of $*Cr(bpy)_3^{3+}$ with the organochromium complexes, contrary to all the expectations for outer-sphere reactions, see the preceding paragraph.

All the data suggest that the organocobalt complexes react with $*Cr(bpy)_3^{3+}$ by a mechanism that is different from an outer-sphere electron transfer but that still produces some $Cr(bpy)_3^{2+}$ for R = CH_3, C_2H_5, C_3H_7, and CH_2OCH_3.

Energy transfer from $*Cr(bpy)_3^{3+}$ to the inorganic complexes $(H_2O)([14]aneN_4)CoX^{n+}$ is very efficient.[19] The rate constants increase in the series X = H_2O ($k = 7 \times 10^5$ M^{-1} s^{-1}) < Cl^- (2.2×10^7 M^{-1} s^{-1}) < Br^- ($\sim 10^8$).[31] The chemical identity and spectral features of the organocobalt complexes indicate that they might also react with $*Cr(bpy)_3^{3+}$ by energy transfer. The ready photohomolysis of these organocobalt complexes induced by visible light[32] establishes that low-lying excited state(s) are available. We thus propose the mechanism in Scheme II for the reactions of $*Cr(bpy)_3^{3+}$ with $(H_2O)Co([14]aneN_4)R^{2+}$.

The energy-transfer step of eq II-1 produces an excited-state complex, $*(H_2O)Co([14]aneN_4)R^{2+}$, which can either relax to the ground state, eq II-2, or homolyze to yield $Co([14]aneN_4)H_2O^{2+}$ and a carbon-centered radical, eq II-3. The amount of energy transferred in eq II-1, ~40 kcal/mol, matches or exceeds the energies of the Co–C bonds of the organocobalt complexes. The bond dissociation energies (BDE) of the methyl[33] and benzyl[34] complexes have been estimated as ~40 and ~23 kcal/mol, respectively. The BDE's of the complexes with R = C_2H_5, C_3H_7, and CH_2OCH_3 are expected to lie between the two limits. The values for the halomethyl complexes are not expected to differ significantly from that for the methyl. The reaction of eq II-3 thus appears feasible, at least for the complexes with R = C_2H_5, C_3H_7, and CH_2OCH_3. Indeed, these complexes produced the highest, although not quantitative, amounts of $Cr(bpy)_3^{2+}$.

The similarity in the rate constants for energy transfer, k_{Co}, between the inorganic and alkyl complexes of $Co([14]aneN_4)(H_2O)^{3+}$ is consistent with their spectral similarity and provides additional support for the proposed mechanism.

The reaction of $Co([14]aneN_4)(H_2O)_n^{2+}$ with $*C(bpy)_3^{3+}$ takes place with a rate constant of $k_{II-6} = 1.5 \times 10^8$ M^{-1} s^{-1}.[35] Clearly, the amount of $Cr(bpy)_3^{2+}$ formed in reaction II-6 is minimal owing to the similarity of the rate constants k_{Co} and k_{II-6} and the use of a large excess of $(H_2O)Co([14]aneN_4)R^{2+}$ in all the experiments. Even if some $Cr(bpy)_3^{2+}$ is formed in reaction II-6, it will be oxidized to $Cr(bpy)_3^{3+}$ by secondary electron transfer of eq II-7.

The lack of the formation of measurable amounts of $Cr(bpy)_3^{2+}$ in the reactions of the haloalkyl complexes seems to indicate that $k_{II-2} \gg k_{II-3}$. A possibility that the homolysis did take place but no $Cr(bpy)_3^{2+}$ was formed owing to the low value of k_{II-4}[36] relative to k_{II-5} for this radical is inconsistent with the fact that no $ClCH_2CH_2Cl$ was formed either.

The rate constant k_{II-2} is expected to be similar for all the complexes involved, such that the yields of $Cr(bpy)_3^{2+}$ are a measure of the relative rate constants for homolysis of the excited-state complexes: $C_3H_7 \sim CH_2OCH_3 > C_2H_5 > CH_3 \gg CH_2Cl$, CH_2Br.

Several other mechanistic possibilities were considered for the reactions of $*Cr(bpy)_3^{3+}$ with $(H_2O)Co([14]aneN_4)R^{2+}$. In one the products of energy transfer, $*(H_2O)Co([14]aneN_4)R^{2+}$, react exclusively as in eq II-2. The $Cr(bpy)_3^{2+}$ is then formed in a parallel electron-transfer reaction, eq 8. The relative amounts of $Cr(bpy)_3^{2+}$ formed are consistent with the electron-transfer reactivity trend confirmed independently in the reactions with $Ru(bpy)_3^{3+}$. However, the required absolute rate constants for electron transfer, calculated as a fraction of k_{Co} that yields $Cr(bpy)_3^{2+}$, seem unjustifiably high for this mechanism to be valid (CH_2OCH_3, $\gtrsim 10^7$ M^{-1} s^{-1}; C_3H_7, $\gtrsim 10^7$; C_2H_5, $\gtrsim 10^7$; CH_3, $\gtrsim 10^6$).

Another possibility consists of energy transfer of eq II-1 followed by electron transfer from $*(H_2O)Co([14]aneN_4)R^{2+}$ to ground-state $Cr(bpy)_3^{3+}$, eq 10. Unlike the direct electron transfer of eq 8, which entails a transfer of an electron from a t_{2g} orbital of the organocobalt complex is a t_{2g} orbital of $*Cr(bpy)_3^{3+}$, the reaction of eq 10 requires that an electron be transferred from an e_g orbital of $*(H_2O)Co([14]aneN_4)R^{2+}$ to a t_{2g} orbital of $Cr(bpy)_3^{3+}$. The latter possibility should be quite unfavorable.[8,9b] In addition, this mechanism would require a long-lived $*(H_2O)Co([14]aneN_4)R^{2+}$. No experimental evidence for such a species was obtained.

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Registry No. $Cr(bpy)_3^{3+}$, 15276-15-0; $(H_2O)_5Cr(CH_3)^{2+}$, 32108-96-6; $(H_2O)_5Cr(C_2H_5)^{2+}$, 52653-39-1; $(H_2O)_5Cr(2\text{-}C_3H_7)^{2+}$, 60764-48-9; $(H_2O)_5Cr(CH_2OCH_3)^{2+}$, 78402-17-2; $(H_2O)_5Cr(CH_2Cl)^{2+}$, 17477-09-7; $(H_2O)_5Cr(CH_2C_6H_5)^{2+}$, 34788-74-4; $(H_2O)Co([14]aneN_4)(CH_3)^{2+}$, 51240-12-1; $(H_2O)Co([14]aneN_4)(C_2H_5)^{2+}$, 111323-55-8; $(H_2O)Co([14]aneN_4)(i\text{-}C_3H_7)^{2+}$, 111323-58-1; $(H_2O)Co([14]aneN_4)(CH_2OCH_3)^{2+}$, 111323-64-9; $(H_2O)Co([14]aneN_4)(CH_2Cl)^{2+}$, 111323-60-5; $(H_2O)Co([14]aneN_4)(CH_2Br)^{2+}$, 111323-62-7.

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[30] Taking $E°(Cr(bpy)_3^{3+*/2+}) = 1.46$ V, $E°(Ru(bpy)_3^{3+/2+}) = 1.28$ V, and the two self-exchange rate constants $k_{CrCr} = 10^8$ M^{-1} s^{-1}, $k_{RuRu} = 10^9$ M^{-1} s^{-1} (Sutin, N.; Creutz, C. *J. Chem. Educ.* **1983**, *60*, 809), one calculates $k(Ru(bpy)_3^{3+} - RCo([14]aneN_4)H_2O^{2+}) \approx 0.1\ k(*Cr(bpy)_3^{3+} - RCo([14]aneN_4)H_2O^{2+})$. Consistent with this the rate constants for the oxidation of the organochromium complexes by the two oxidants are quite similar, Table I.

[31] Estimated from the data in ref 17 and 19.

[32] (a) Mok, C. Y.; Endicott, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 1276. (b) Mok, C. Y.; Endicott, J. F. *J. Am. Chem. Soc.* **1978**, *100*, 123.

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