Photochemical Reduction of Some Carboxylatopentaamminecobalt(III) Complexes by Tris(bipyridine)ruthenium(II). Evidence for Cage Recombination Reactions[1]

Wolfhart Bottcher and Albert Haim*

Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11794. *Received May 18, 1979*

Abstract: The quenching of the luminescent, excited state of $Ru(bpy)_3{}^{2+}$ by pentaamminecobalt(III) complexes of *p*-nitrobenzoate, *o*-nitrobenzoate, benzoate, and acetate has been studied at 25 °C, pH 5.8, and ionic strength 0.10 M as a function of the concentration of the cobalt complex. Linear Stern–Volmer plots were obtained from which the following quenching rate constants have been calculated: $(2.4 \pm 0.2) \times 10^9$, $(1.3 \pm 0.1) \times 10^9$, $(1.5 \pm 0.1) \times 10^8$, and $(2.1 \pm 0.2) \times 10^8$ $M^{-1}\,s^{-1}$. Limiting quantum yields for cobalt(II) production are 0.011 ± 0.001, 0.051 ± 0.001, and 0.45 ± 0.15 for *p*-nitrobenzoato-, *o*-nitrobenzoato-, and benzoatopentaamminecobalt(III), respectively. On the basis of these results and of calculations of diffusion-controlled rate constants, it is suggested that the quenching of $^*Ru(bpy)_3{}^{2+}$ by the cobalt complexes can result in the transfer of an electron from the excited-state donor to the unique ligand of the quencher (for the nitrobenzoate complexes) or to the cobalt center of the quencher (for the benzoate and acetate complexes) to produce ligand-centered or cobalt-centered successor complexes in a solvent cage. For the latter complexes, cage dissociation leading to the production of cobalt(II) and cage recombination resulting in the regeneration of the reactants are competitive, and therefore substantial yields of cobalt(II) are observed. For the ligand-centered complexes, cage recombination predominates and therefore the quantum yields of cobalt(II) are very low.

Introduction

It is well known that electron-transfer reactions between transition-metal complexes can proceed via a resonance exchange or a chemical mechanism.[2] In the chemical mechanism, the electron, initially in an orbital localized in the reducing agent, is transferred to an orbital centered on a ligand bound to the oxidizing metal center. The intermediate produced in this manner undergoes internal electron transfer in a subsequent step, the electron ultimately residing in an orbital localized in the reduced form of the oxidizing metal center. The bulk of the experimental evidence for the operation of the chemical mechanism rests on rate comparisons.[3-6] However, there is direct evidence for the intermediacy of ligand radicals bound to an oxidizing metal center in radiation chemical studies of nitrobenzoatopentaamminecobalt(III) complexes.[7]

In our previous work,[8] we attempted to probe the chemical mechanism by studying the reactions of the excited, luminescent state $^*Ru(bpy)_3{}^{2+}$ with pentaamminecobalt(III) complexes of 4,4′-bipyridine and some of its derivatives. Although radical ions derived from 4,4′-bipyridine are quite stable[9] and can be generated by utilizing $^*Ru(bpy)_3{}^{2+}$,[8,10] we were unable[8] to detect 4,4′-bipyridine radicals bound to the $Co(NH_3)_5{}^{3+}$ moiety. One possible explanation which was advanced[8] for the failure was a very rapid ($>4 \times 10^6\ s^{-1}$) rate of intramolecular electron transfer from the bound radical ion to the cobalt(III) center in a postulated $Co^{III}(NH_3)_5(4,4'\text{-}bpy^-)^{2+}$ intermediate. In view of the relatively slow ($2.6 \times 10^3\ s^{-1}$) rate of internal electron transfer from *p*-nitrobenzoate radical to $Co(NH_3)_5{}^{3+}$,[7] we decided to investigate the photochemical reactions of nitrobenzoatopentaamminecobalt(III) complexes with tris(bipyridine)ruthenium(II), eq 1, where L = *p*- and *o*-nitrobenzoate (PNBz and ONBz). For comparison purposes, we also studied the corresponding reactions of benzoate (Bz) and acetate (Ac). Quenching rate constants and quantum yields for Co(II) production have been measured, and the results provide important information about the mechanism of electron transfer and the question of cage recombination reactions.

$$^*Ru(bpy)_3{}^{2+} + Co(NH_3)_5L^{2+} \rightarrow Ru(bpy)_3{}^{3+} + Co(NH_3)_5L^{+} \quad (1)$$

Experimental Section

Materials. The benzoato and nitrobenzoato complexes were prepared by the method of Gould and Taube,[3] except that four extractions with ether were carried out to remove the excess parent acid. Acetatopentaamminecobalt(III) perchlorate was prepared by the method of Sebera and Taube.[11] The sample of pyridinepentaamminecobalt(III) perchlorate was the same as used in previous work.[12] The purification of the argon, of the water, and of the lithium perchlorate was described previously.[12] All other chemicals were reagent grade and were used as received.

Luminescence Quenching Measurements. A series of solutions of constant $Ru(bpy)_3{}^{2+}$ concentration (2×10^{-6} M) and variable quencher concentration (5×10^{-4} to 5×10^{-3} M) containing also the desired amounts of buffer and of $LiClO_4$ was prepared. These solutions were deaerated for approximately 1 h in 1-cm^2 serum-capped fluorescence cells and then thermostated at 25.0 °C in the cell compartment of a Perkin-Elmer MPF-44A fluorescence spectrophotometer. Emission intensity measurements were carried out at 615 nm with an excitation wavelength of 450 nm.

Photolysis Measurements. Flash photolysis measurements were carried out with a Xenon Corp. Model 720 apparatus. The experimental details were described recently.[8] The carboxylate complexes are known to undergo redox reactions when irradiated in their ligand to metal charge transfer bands (near-UV). Therefore, in order to prevent the direct photochemical reduction, the outer compartment of the thermostatable photolysis cell was filled with 0.010–0.10 M $Fe(ClO_4)_3$ in 5 M $HClO_4$. This was sufficient to absorb most of the flash light of wavelength shorter than 350 nm. Steady-state photolysis measurements were carried out with a conventional setup consisting of a 450-W Hanovia Xe-Hg lamp mounted in a Schoeffel LH 151 N lamp housing and an optical train with a 0.6-cm glass plate, a 5-cm cell filled with water, a 450-nm interference filter, a lens, a shutter and an iris. The details of the photolysis cell were described previously.[8] Light intensity was determined by tris(oxalato)ferrate(III) actinometry. The cobalt(II) produced was estimated using Kitson's method.[13]

Visible and ultraviolet spectra were recorded in a Cary 17 or 118 spectrophotometer. pH measurements were carried out with an Orion Model 801 or a Radiometer Model 26 pH meter.

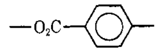
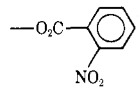
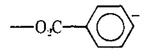
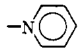
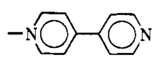
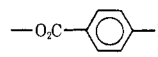
Results

The emission intensities measured in the quenching experiments were treated according to the equation

$$(I_0/I)_{cor} = 1 + K_{sv}[Q] \quad (2)$$

0002-7863/80/1502-1564$01.00/0

Table I. Stern-Volmer Constants K_{sv}, Limiting Quantum Yields Φ_l for Production of Co^{2+}, and Quenching Rate Constants k_q for the Reactions of $*Ru(bpy)_3^{2+}$ with $Co(NH_3)_5L^{n+}$ Complexes[a]

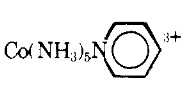
L	$10^{-2}K_{sv}$, M^{-1}	Φ_l	$10^9 k_q$[b], $M^{-1}\ s^{-1}$
	14 ± 1[c]	(1.1 ± 0.1) × 10^{-2}	2.4 ± 0.2,[c] 2.4 ± 0.1
	7.8 ± 0.6	(5.1 ± 0.1) × 10^{-2}	1.3 ± 0.1, 1.2 ± 0.1
	0.90 ± 0.06	0.45 ± 0.15	0.15 ± 0.01, 0.10 ± 0.04
$—O_2C—CH_3^-$	1.3 ± 0.1		0.21 ± 0.02
	1.0 ± 0.06[d]	0.80 ± 0.12	0.17 ± 0.01,[d] 0.21 ± 0.05
	6.45 ± 0.07[d]	0.92 ± 0.10[d]	1.09 ± 0.01[d]
	28 ± 2[c]		4.7 ± 0.3[c]

[a] Measurements at 25 °C, pH 5.8 (phosphate buffer), μ = 0.10 M ($LiClO_4$). [b] The first entry is calculated from K_{sv}/τ_0; see text. The second entry is calculated from eq 13. [c] Measured by K. R. Leopold, B.S. Thesis, State University of New York, Stony Brook, 1977. [d] From ref 8. [e] This entry corresponds to quenching by the free ligand.

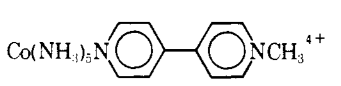
where $(I_0/I)_{cor}$ is the corrected ratio of emission intensities in the absence and presence of quencher, respectively, and K_{sv} is the Stern-Volmer constant. The corrected intensity ratios are related to the observed intensity ratios by the equation

$$(I_0/I)_{cor} = (I_0/I)_{obsd}\frac{1 - 10^{-(A_D+A_Q)}}{1 - 10^{-A_D}}\frac{A_D}{A_D + A_Q} \times \frac{1 - 10^{-A'_Q}}{2.303A'_Q} \quad (3)$$

where A_D and A_Q are the absorbances per centimeter of donor and quencher, respectively, at the excitation wavelength and A'_Q is the absorbance per centimeter of the quencher at the emission wavelength. As shown in Figure 1, the plots of $(I_0/I)_{cor}$ vs. [Q] were linear.[14] Values of K_{sv} for the complexes studied and for the *p*-nitrobenzoate anion were obtained by a least-squares fitting of the data to eq 2 with the requirement that the intercept be 1. From these values of K_{sv}, listed in column 2 of Table I, and the relationship $K_{sv} = k_q\tau_0$, where k_q is the rate constant for reaction 1 and $\tau_0 = 0.60 \pm 0.02\ \mu s$[15] is the lifetime of $*Ru(bpy)_3^{2+}$, values of k_q were calculated and are listed in column 4 of Table I. Included in the table for purposes of comparison are the quenching rate constants[8] for i ($Co(NH_3)_5py^{3+}$) and ii ($Co(NH_3)_5bpy^{4+}$). It will be seen



i



ii

that the nitrobenzoate and *N*-methyl-4,4′-bipyridine complexes react at rates near the diffusion-controlled limit, whereas the benzoate, acetate, and pyridine complexes react at rates one order of magnitude slower. The mechanistic implications of these observations will be discussed below.

In the steady-state photolysis measurements, solutions of constant $[Ru(bpy)_3^{2+}]$ (~2.5 × 10^{-5} M) and variable $[Co(NH_3)_5L^{2+}]$ (2 × 10^{-4} to 7 × 10^{-3} M) were irradiated for a period of time *t*, and then analyzed for Co^{2+}. Quantum yields Φ_m were calculated from the expression $\Phi_m = (V[Co^{2+}]/tI)$ where V is the volume of the solution irradiated, $[Co^{2+}]$ is the concentration of Co^{2+} present after irradiation for a time *t*, and I is the light intensity. Plots of $1/\Phi_m$ vs. $1/[Co(NH_3)_5L^{2+}]$ were linear (see Figure 2) and least-squares treatment of the data yielded values of intercepts and slopes. The inverses of the intercepts are the limiting quantum yields for Co^{2+} production, Φ_l, and are listed in column 3 of Table I. The ratios of intercepts to slopes, as shown below, are equal to K_{sv}. Values of k_q calculated from K_{sv}/τ_0 are listed in column 4 of Table I.

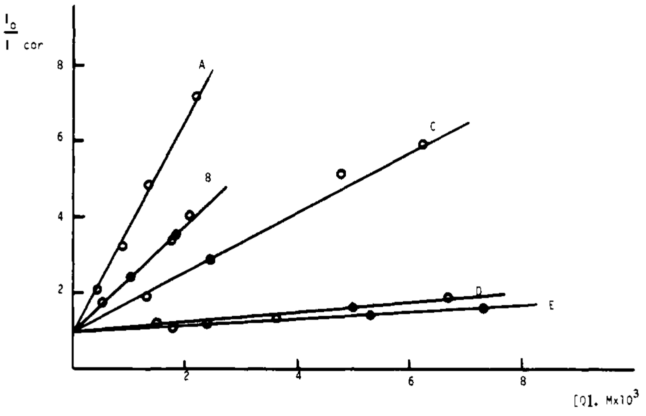


Figure 1. Stern-Volmer plots for the quenching of $*Ru(bpy)_3^{2+}$: A, $PNBz^-$; B, $Co(NH_3)_5PNBz^{2+}$; C, $Co(NH_3)_5ONBz^{2+}$; D, $Co(NH_3)_5Ac^{2+}$; E, $Co(NH_3)_5Bz^{2+}$.

A solution containing ~3 × 10^{-4} M $Co(NH_3)_5PNBz^{2+}$ and ~1 × 10^{-5} M $Ru(bpy)_3^{2+}$ at pH 5.8 was subjected to flash photolysis. No transients could be seen at 330 or 420 nm, the reported[7] wavelengths for the maxima of $Co^{III}(NH_3)_5(PNBz^{2-})^+$.

Discussion

The results of the quenching measurements are interpreted on the basis of the equations

$$Ru(bpy)_3^{2+} \underset{1/\tau_0}{\overset{h\nu}{\rightleftharpoons}} *Ru(bpy)_3^{2+} \quad (4)$$

$$*Ru(bpy)_3^{2+} + Q \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} *Ru(bpy)_3^{2+}\text{---}Q \quad (5)$$

$$*Ru(bpy)_3^{2+}\text{---}Q \xrightarrow{k_{et}} Ru(bpy)_3^{3+}\text{---}Q^- \quad (6)$$

The forward and reverse reactions in eq 4 represent the excitation of $Ru(bpy)_3^{2+}$ by absorption of light and the first-order radiative and nonradiative decays of $*Ru(bpy)_3^{2+}$, respectively. The forward reaction in eq 5 represents the diffusion-controlled approach of the excited state ($*Ru(bpy)_3^{2+}$) and

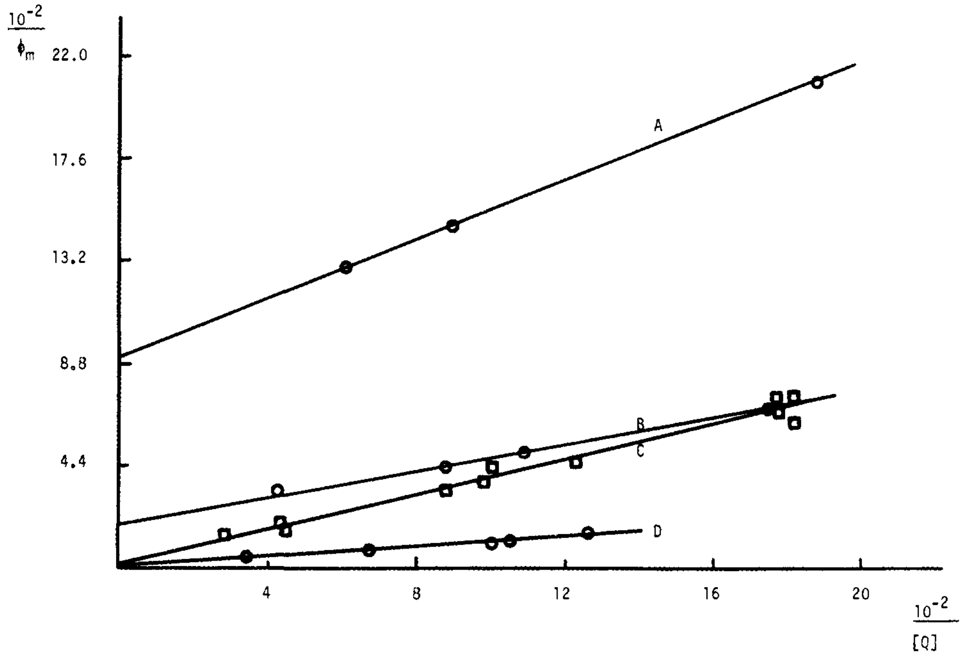
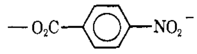
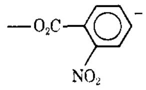
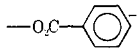
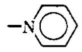
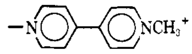
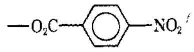
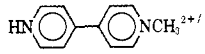


Figure 2. Quantum yields for Co^{2+} production: A, $Co(NH_3)_5PNBz^{2+}$; B, $Co(NH_3)_5ONBz^{2+}$; C, $Co(NH_3)_5Bz^{2+}$; D, $Co(NH_3)_5py^{3+}$.

Table II. Diffusion-Controlled Rate Constants and Quenching Efficiencies for the Reactions of $^*Ru(bpy)_3{}^{2+}$ with $Co(NH_3)_5L^{n+}$ Complexes

L	$10^8(r_A + r_B)$, cm[a]	$10^{-9}k_d$, M^{-1} s^{-1} [b]	f_q[c]	$10^{-9}k_{-d}$, s^{-1} [d]	$10^{-10}k_{et}$, s^{-1} [e]
	10.3	3.0	0.80	4.2	1.7
	10.1	2.9	0.45	4.4	0.4
	10.1	2.9	0.05	4.4	0.02
$—O_2C—CH_3{}^-$	9.7	2.8	0.08	5.3	0.06
	9.8	1.8	0.09	6.8	0.07
	10.4	1.4	0.78	6.8	2.5
	8.8	4.8	0.98	1.2	5.6
	9.1	2.6	0.96	6.8	17

[a] Calculated from $r_A = 6.8 \times 10^{-8}$ cm for $Ru(bpy)_3{}^{2+}$ and values of r_B estimated as described in the text. [b] From eq 7 and 8. [c] Calculated from k_q/k_d. [d] Calculated from k_d and K_0, eq 10. [e] Calculated from $f_qk_d/(1-f_q)$. [f] This entry corresponds to the free ligand.

the cobalt(III) complex (Q) to produce an encounter or precursor complex. The precursor complex can dissociate to yield the reactants (reverse of eq 5) or undergo the well-established[10,15] electron transfer quenching reaction (eq 6). The reduced quencher in eq 6 is represented by Q^-. It will be seen later that two alternative formulations are possible for Q^-.

Applying the steady-state approximation to the excited state $^*Ru(bpy)_3{}^{2+}$ and to its encounter complex with Q, it can be shown that $(I_0/I)_{cor} = 1 + \tau_0k_q[Q]$, where $k_q = k_dk_{et}/(k_{-d} + k_{et})$. Of major interest in the present work are the nature and the reactions of the species $^*Ru(bpy)_3{}^{3+}$---Q^- produced in the primary quenching process. However, before discussing this point, it is instructive to examine the values of k_q for various cobalt(III) complexes (column 4 of Table I). It must be recognized that k_q is a measure of the fraction of encounters between $^*Ru(bpy)_3{}^{2+}$ and Q which result in the deactivation of the excited state. In order to assess the quenching efficiency of the encounters, it is necessary to have values of k_d, the diffusion-controlled rate constants for the reactions of $^*Ru(bpy)_3{}^{2+}$ with the Co(III) complexes. Values of $k_d{}^0$ at infinite dilution were estimated using the Debye equation[16] corrected for the hydrodynamic effect:[17,18]

$$k_d{}^0 = \frac{4\pi(D_A + D_B)N_0}{1000}(r_A + r_B)\Big/\int_0^1 \frac{\exp(ax)}{1 - bx} \qquad (7)$$

D_A and D_B are the diffusion coefficients of the two reactants (taken to be 5×10^{-6} cm² s⁻¹). N_0 is Avogadro's number. r_A and r_B are the effective radii of the reactants. For water at 25 °C, a is $7.131 \times 10^{-8}z_Az_B/(r_A + r_B)$, where z_A and z_B are the charges of the reactants. $b = 3r_Ar_B/(r_A + r_B)^2$. Values of k_d at ionic strength 0.10 M were calculated from the infinite dilution values $k_d{}^0$ and the Debye-Brønsted equation:[19]

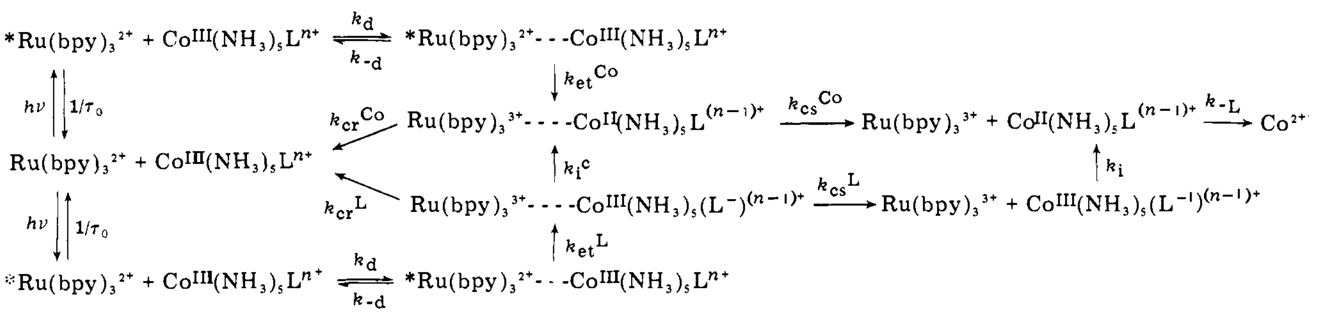
$$\log k_d = \log k_d{}^0 + 2z_Az_B\alpha\mu/[1 + \beta(r_A + r_B)\sqrt{\mu}] \qquad (8)$$

μ is the ionic strength. α and β are 0.509 and 3.29×10^7 for water at 25 °C, respectively. Equations 7 and 8 are applicable to spherical reactants. For $Ru(bpy)_3{}^{2+}$, which is spherical, we take $r_A = 6.8 \times 10^{-8}$ cm.[20] However, the cobalt complexes are not spherical and therefore we have calculated the radii equivalent to the sphere of equal volume from the equation[20]

$$r_B = \tfrac{1}{2}(d_1d_2d_3)^{1/3} \qquad (9)$$

d_1, d_2, and d_3, the diameters along the three principal axes, have been estimated from bond distances and geometric considerations. Values of $r_A + r_B$, k_d, and f_q, the fraction of encounters between $^*Ru(bpy)_3{}^{2+}$ and the quencher (k_q/k_d) that result in deactivation, are listed in Table II. It will be seen that for the PNBz, ONBz, and bpy complexes, the measured values of k_q approach calculated values of k_d and, therefore, nearly every encounter (or every other encounter for $Co(NH_3)_5ONBz^{2+}$) result in electron transfer. In contrast, the values of k_q for the benzoate, acetate, and pyridine complexes are at least one order of magnitude smaller than the diffusion-controlled limits ($f_q < 0.1$) and, therefore, less than 10% of the encounters result in deactivation. An alternate and instructive approach to view this data is to calculate the values

Scheme I



of k_{et} (eq 6) from the expression $f_q k_{-d}/(1 - f_q)$. In order to perform the calculation, it is necessary to have values of k_{-d}. These were estimated from the expression $k_{-d} = k_d/K_O$ where K_O, the outer-sphere association constant for eq 6, is given by[12]

$$K_O = \frac{4\pi N(r_A + r_B)^3}{3000} \exp\left(-\frac{a}{1 + \beta\mu^{1/2}(r_A + r_B)}\right) \quad (10)$$

It will be seen that the values of k_{-d} are nearly the same for all the Co(III) complexes in Table II, but the values of k_{et} vary considerably, ranging from 2.4×10^8 to 2.5×10^{10} s^{-1}. Evidently, the cobalt complexes of Table II fall into two categories. $Co(NH_3)_5Ac^{2+}$, $Co(NH_3)_5Bz^{2+}$, and $Co(NH_3)_5py^{3+}$, relatively inefficient quenchers, have k_{et} values in the vicinity of 10^8 s^{-1}, whereas the complexes $Co(NH_3)_5ONBz^{2+}$, $Co(NH_3)_5PNBz^{2+}$, and $Co(NH_3)_5bpy^{4+}$, quite efficient quenchers, have k_{et} values near 10^{10} s^{-1}. It is noteworthy that the distinction between the two classes of cobalt(III) complexes is not associated with varying rates of dissociation of the precursor complexes (reverse of eq 5), but with *different rates of intramolecular electron transfer within the precursor complexes*. The difference between the two classes is ascribed to a different detailed mechanism for the electron transfer. For the nitrobenzoate and *N*-methyl-4,4′-bipyridine complexes, it is postulated that the chemical mechanism is operative, the electron being transferred from $^*Ru(bpy)_3^{2+}$ to an orbital localized in the unique ligand L of $Co(NH_3)_5L^{n+}$. For the acetate, benzoate, and pyridine complexes, it is postulated that the acceptor orbital is localized in the cobalt center.

Some additional, albeit indirect, evidence for the proposed mechanism comes from a consideration of the quenching of $^*Ru(bpy)_3^{2+}$ by the free ligands. *N*-Methyl-4,4′-bipyridinium and *p*-nitrobenzoate ions quench $^*Ru(bpy)_3^{2+}$ at diffusion-controlled rates (k_q for bpy^{2+} is 2.5×10^9 M^{-1} s^{-1}), whereas benzoate, acetate, and pyridinium ions are ineffective quenchers ($k_q < 10^7$ M^{-1} s^{-1}). Values of k_{et} for the first two ligands are $\geq 6 \times 10^{10}$ s^{-1} and for the last three $<10^7$ s^{-1}. We suggest that the first two ligands, whether free or bound to a $Co(NH_3)_5^{3+}$ moiety, accept an electron from $^*Ru(bpy)_3^{2+}$ at rates equal to or near the diffusion-controlled limit, e.g., for the bound ligands the chemical mechanism obtains. In contrast, the last three ligands, whether free or bound to $Co(NH_3)_5^{3+}$, do not accept an electron from $^*Ru(bpy)_3^{2+}$, because of their highly negative reduction potentials. Under these circumstances, the chemical mechanism for the bound ligands is precluded, and the alternate, but slower, electron transfer to the cobalt(III) center becomes operative. To be sure,[21] the key difference between the two classes of ligands is that those that promote the chemical mechanism have accessible, long-lived radicals[8,9,22] whereas the remaining ligands do not. In fact, the radical generated from *N*-methyl-4,4′-bipyridinium and $^*Ru(bpy)_3^{2+}$ has been detected and characterized by flash photolysis.[8] Similar attempts to detect the *p*-nitrobenzoate radical formed by quenching of $^*Ru(bpy)_3^{2+}$ have failed. However, there is no concern about this point since the products of the electron-transfer quenching have opposite charges (+3, −2) and, presumably, undergo cage recombination in preference to cage dissociation, as observed previously[23] for the quenching of $^*Ru(bpy)_3^{2+}$ by a variety of nitroaromatic compounds.

Additional details for the postulated mechanisms come from an examination of the fate of the successor complexes $Ru(bpy)_3^{3+}$---Q^-. Two detailed electronic formulations can be ascribed to the successor complexes, I and II. In I the electron added to the Co(III) complex is localized in an orbital centered in the cobalt, whereas in II the electron is in a ligand orbital. In general both formulations can be accessible, and therefore eq 6 must be replaced by eq 11 and 12:

$$Ru(bpy)_3^{3+}\text{---}Co^{II}(NH_3)_5L^{(n-1)+}$$

I

$$Ru(bpy)_3^{3+}\text{---}Co^{III}(NH_3)_5(L^-)^{(n-1)+}$$

II

$$^*Ru(bpy)_3^{2+}\text{---}Co^{III}(NH_3)_5L^{n+} \xrightarrow{k_{et}^{Co}} Ru(bpy)_3^{3+}\text{----}Co^{II}(NH_3)_5L^{(n-1)+} \quad (11)$$

$$^*Ru(bpy)_3^{2+}\text{---}Co^{III}(NH_3)_5L^{(n-1)+} \xrightarrow{k_{et}^{L}} Ru(bpy)_3^{3+}\text{----}Co^{III}(NH_3)_5(L^-)^{(n-1)+} \quad (12)$$

It is noteworthy that reactions 11 and 12 are entirely analogous to the reactions postulated to account for the direct formation of Co(II) and of the bound ligand radical in the reaction of $Co(NH_3)_5PNBz^{2+}$ with hydrated electrons.[7] The possible reactions of the successor complexes are depicted in Scheme I (which also includes all the previous steps). The upper and lower sets of reactions in the scheme correspond to the formation of cobalt-centered and ligand-centered quenching product, respectively. The successor complexes are shown to undergo cage recombination reactions, k_{cr}^{Co} and k_{cr}^{L}, to regenerate the reactants. In competition with the cage recombination reactions, the successor complexes undergo cage separation reactions, k_{cs}^{Co} and k_{cs}^{L}, to produce III and IV,

$$Co^{II}(NH_3)_5L^{(n-1)+} \qquad Co^{III}(NH_3)_5(L^-)^{(n-1)+}$$

III IV

respectively. III is known to undergo rapid spin interconversion[24] and/or ligand detachment[25] reactions, k_{-L}, to produce Co^{2+}. The metal-bound ligand radical, whether in the cage, k_i^c, or separated from its geminate partner, k_i, reacts via intramolecular electron transfer to produce the appropriate Co(II) species. Because of the low concentrations of $Ru(bpy)_3^{3+}$, III, and IV, the homogeneous bimolecular recombination reactions of $Ru(bpy)_3^{3+}$ with III or IV are too slow to compete with the first-order reactions of III (k_{-L}) or IV (k_i).[26] On the basis of Scheme I, and applying the steady-state approximations to the precursor and successor complexes and to III and IV, the quantum yield of Co^{2+}, Φ_m, is given by

$$\Phi_m = \frac{k_d[Co(NH_3)_5L^{n+1}]R}{(k_{et}{}^{Co} + k_{et}{}^{L})k_d[Co(NH_3)_5L^{n+}] + (k_{-d} + k_{et}{}^{Co} + k_{et}{}^{L})/\tau_0} \quad (13)$$

$$R = \frac{k_{et}{}^{Co}k_{cs}{}^{Co} + \dfrac{k_{cs}{}^{Co}k_i{}^{c}k_{et}{}^{L}}{k_{cr}{}^{L} + k_{cs}{}^{L} + k_i{}^{c}}}{k_{cs}{}^{Co} + k_{cr}{}^{Co}} + \frac{k_{et}{}^{L}k_{cs}{}^{L}}{k_{cr}{}^{L} + k_{cs}{}^{L} + k_i{}^{c}} \quad (14)$$

From eq 13 it is predicted that a plot of $1/\Phi_m$ vs. $1/[Co(III)]$ should yield a straight line with an intercept equal to $(k_{et}{}^{Co} + k_{et}{}^{L})/R$ and a ratio of intercept to slope equal to $(k_{et}{}^{Co} + k_{et}{}^{L})k_d\tau_0/(k_{-d} + k_{et}) = K_{sv}$. This prediction is borne out by the experimental results (see Figure 2). Values of K_{sv} calculated from the measurements of yields of Co^{2+} are in excellent agreement with values of K_{sv} derived from the emission quenching measurements (compare the two sets of values of $k_q = K_{sv}/\tau_0$ in the last column of Table I).

The values of the limiting quantum yields, $R/(k_{et}{}^{Co} + k_{et}{}^{L})$, provide information about the fates of the successor complexes and additional support for the two proposed reaction pathways ($k_{et}{}^{Co}$ and $k_{et}{}^{L}$) of the precursor complexes. Since the rates of outer-sphere reactions of carboxylatopentaamminecobalt(III) complexes are quite insensitive to the nature of the carboxylate ligand,[27] we would expect that a cobalt-centered successor complex would give limiting yields of Co(II) that are nearly independent of the carboxylate ligand. For a cobalt-centered successor complex, the limiting quantum yield is given by $k_{cs}{}^{Co}/(k_{cs}{}^{Co} + k_{cr}{}^{Co})$. $k_{cs}{}^{Co}$ and $k_{cr}{}^{Co}$ are determined largely by the charge of the cobalt complex and the redox properties of the $Co(NH_3)_5L^{2+/+}$ couple, and thus little variation in Φ_l is expected when L represents a series of related carboxylato complexes. However, this expectation is in marked contrast with the experimental observations. For the PNBz and ONBz complexes the limiting quantum yields for Co^{2+} formation are very small (0.011 and 0.051, respectively), whereas a substantial value of Φ_l (0.45) is found for $Co(NH_3)_5Bz^{2+}$. The difference in behavior between the nitrobenzoate and benzoate complexes can be accommodated nicely within the postulated dual pathway for the disappearance of the precursor complexes and assigning different rates of cage recombination to cobalt-centered and ligand-centered successor complexes. Thus, for the nitrobenzoate complexes, the dominant path for the disappearance of the precursor complexes is via the chemical mechanism with the resulting formation of a bound radical ligand. Since internal electron transfer from nitrobenzoate radicals to the cobalt(III) center to which they are attached is slow (2.6×10^3 and 4.0×10^5 s^{-1} for $Co(NH_3)_5PNBz^{2+}$ and $Co(NH_3)_5ONBz^{2+}$, respectively) compared to cage separation (10^9–10^{10} s^{-1}), the low quantum yields indicate that cage recombination is a highly favored process. This result appears reasonable when it is recognized that the successor complex consists of a 3+ ruthenium product and a cobalt complex with a 2− charge localized on the nitrobenzoate ligand, and it is recalled that free radicals produced by quenching $^*Ru(bpy)_3{}^{2+}$ with nitroaromatic compounds[23] do not escape the cage. From eq 8 and 10, we estimate that the rate constant for cage separation of $Ru(bpy)_3{}^{3+}$---$Co^{III}(NH_3)_5(PNBz^{2-})^+$ is 4×10^9 s^{-1}. If the only source of Co^{2+} is cage separation of the ligand-centered successor complex, the limiting quantum yield of Co^{2+} is given by $k_{cs}{}^{L}/(k_{cs}{}^{L} + k_{cr}{}^{L})$. Using $k_{cs}{}^{L} = 4 \times 10^9$ s^{-1} and Φ_l values of 0.011 and 0.051 we obtain $k_{cr}{}^{L} = 3.6 \times 10^{11}$ and 6.9×10^{10} s^{-1} for $Co(NH_3)_5PNBz^{2+}$ and $Co(NH_3)_5ONBz^{2+}$, respectively. These rate constants are of reasonable magnitude for a reaction with a 1.6-V driving force between two species having self-exchange rate constants of the order of 10^8 M^{-1} s^{-1}.[28-30] However, if the Co^{2+} is produced by the alternate pathway leading to cobalt-centered successor complexes, the values of $k_{cr}{}^{L}$ given above represent lower limits, and, in fact, arguments presented below suggest that this may be the case. For $Co(NH_3)_5Bz^{2+}$, electron transfer to the cobalt(III) center was suggested above as the major pathway for the disappearance of the precursor complex, and the substantial quantum yield observed (0.45) indicates that cage separation competes favorably with cage recombination. If only a cobalt-centered successor complex is formed, the limiting quantum yield is $k_{cs}{}^{Co}/(k_{cs}{}^{Co} + k_{cr}{}^{Co})$. Therefore, $k_{cs}{}^{Co} = 0.82k_{cr}{}^{Co}$ and using $k_{cs}{}^{Co} = 4.3 \times 10^9$ s^{-1} we obtain $k_{cr}{}^{Co} = 5.2 \times 10^9$ s^{-1} to be compared with $k_{cr}{}^{L} > 6.9 \times 10^{10}$ s^{-1}. The smaller rate constant for electron transfer from the cobalt-centered successor complex as compared to the ligand-centered successor complex is consistent with the lower rate of self-exchange and oxidation potential of I vs. II.[31]

Returning to the question of the source of Co^{2+} in the reactions of the nitrobenzoate complexes, if it is assumed that all the Co^{2+} is formed by the reaction of the precursor complex leading to a cobalt-centered successor complex, then the limiting quantum yield of Co^{2+} is given by $k_{cs}{}^{Co}k_{et}{}^{Co}/(k_{cs}{}^{Co} + k_{cr}{}^{Co})(k_{et}{}^{Co} + k_{et}{}^{L})$. Assuming that $k_{cs}{}^{Co}/(k_{cs}{}^{Co} + k_{cr}{}^{Co})$ for the nitrobenzoate complexes is equal to the observed value (0.45) for $Co(NH_3)_5Bz^{2+}$, we obtain[32] $k_q{}^{Co} = 5.9 \times 10^7$ and 1.5×10^8 M^{-1} s^{-1} for $Co(NH_3)_5PNBz^{2+}$ and $Co(NH_3)_5ONBz^{2+}$, respectively, where $k_q{}^{Co}$ is the rate constant for quenching $^*Ru(bpy)_3{}^{2+}$ by the nitrobenzoate complex via the path that produces the cobalt-centered successor complex. The excellent agreement between the calculated values of $k_q{}^{Co}$ for the nitrobenzoate complexes and the measured value of k_q for $Co(NH_3)_5Bz^{2+}$ provides some support for suggesting that the precursor complexes containing $Co(NH_3)_5PNBz^{2+}$ and $Co(NH_3)_5ONBz^{2+}$ react via parallel paths to yield ligand-centered successor complexes which undergo cage recombination and cobalt-centered successor complexes which undergo, in part, cage separation to produce Co^{2+}.

The magnitude of the quenching rate constants for $Co(NH_3)_5py^{3+}$ and $Co(NH_3)_5bpy^{4+}$ led us to suggest different mechanisms for the two systems, namely, electron transfer to cobalt and to the ligand, respectively. However, in contrast with the results for $Co(NH_3)_5PNBz^{2+}$ and $Co(NH_3)_5Bz^{2+}$, where values of k_q and of Φ_l are different for the two mechanisms, both pyridine complexes were found to have values of Φ_l near unity. This result can still be accommodated within the dual mechanistic concept. For $Co(NH_3)_5py^{3+}$, the high quantum yield for Co^{2+} production indicates that the cobalt-centered successor complex undergoes cage separation in preference to cage recombination. Since $\Phi_l = 0.80$, $k_{cs}{}^{Co} = 4k_{cr}{}^{Co}$. From eq 8 and 10 we estimate $k_{cs}{}^{Co} = 6.8 \times 10^9$ s^{-1} and, therefore, $k_{cr}{}^{Co} = 1.7 \times 10^9$ s^{-1}. It is noteworthy that the higher value of Φ_l for $Co(NH_3)_5py^{3+}$ as compared to $Co(NH_3)_5Bz^{2+}$ is associated with a higher rate of cage dissociation as well as a lower rate of intramolecular electron transfer of the successor complex. In the case of $Co(NH_3)_5bpy^{4+}$, one possible interpretation of the high value of Φ_l is that $k_{cr}{}^{L} \ll k_{cs}{}^{L}$. If only a ligand-centered successor complex is formed, then $\Phi_l = k_{cs}{}^{L}/(k_{cs}{}^{L} + k_{cr}{}^{L})$. From the measured value of Φ_l (0.92, Table I) and the calculated value of $k_{cs}{}^{L}$ (6.8×10^9 s^{-1}, Table II) we estimate $k_{cr}{}^{L} = 5.4 \times 10^8$ s^{-1}. This value seems unreasonably small for a reaction with a 1.7-V driving force between two species having self-exchange rate constants of the order of 10^8 M^{-1} s^{-1}.[28,33] Moreover, this calculated value of $k_{cr}{}^{L}$ for $Co(NH_3)_5bpy^{4+}$ is *smaller* than the value $k_{cr}{}^{Co}$ for $Co(NH_3)_5py^{3+}$. Therefore, we suggest that the high quantum yield of Co^{2+} for $Co(NH_3)_5bpy^{4+}$ is associated with the operation of a new pathway (identified by the rate constant k_i^c in Scheme I) for the disappearance of the ligand-centered successor complex, namely, intramolecular electron transfer from the ligand to the cobalt center. Assuming that every k_i^c event leads to formation of cobalt(II), we obtain[34] $k_i^c = 12.5k_{cr}^L - k_{cs}^L$. Since $k_{cs}^L = 6.9 \times 10^9$ s^{-1} (Table II) and $k_{cr}^L \sim 10^{10}$ s^{-1},[35] we estimate $k_i^c \sim 10^{11}$ s^{-1}. In our previous work[8] we had estimated $k_i^c > 10^{11}$ s^{-1} or $> 4 \times 10^6$ s^{-1} depending on whether fast cage recombination or fast intramolecular electron transfer in $Co^{III}(NH_3)_5(bpy)^{3+}$ was responsible for our inability to detect the bound radical in flash photolysis studies. The present, more detailed analysis indicates that fast intramolecular electron transfer is the more likely explanation.

Conclusions

The present investigation provides evidence, as did our previous work,[8] that it is possible to generate bound radicals in the coordination sphere of cobalt(III) complexes by oxidative quenching of $^*Ru(bpy)_3^{2+}$. Complexes of the type $Co(NH_3)_5L^{n+}$, where L is a carboxylate or pyridine ligand, capable of forming a relatively stable free radical, are suitable quenchers in this respect because they accept an electron more readily than the generally slowly reacting cobalt(III) center. A problem in the possible detection of bound radicals and the measurement of intramolecular electron transfer from the radical to the oxidizing metal center to which it is bound lies in the strong oxidizing properties of the $Ru(bpy)_3^{3+}$ generated simultaneously in the solvent cage. The efficient reoxidation of the bound radical by $Ru(bpy)_3^{3+}$ before cage separation limits the use of $^*Ru(bpy)_3^{2+}$ as an electron donor. We have found that isopropyl radicals (generated by photolysis of acetone-2-propanol mixtures[35]) are suitable electron donors. Using this system,[30] we have been able to generate the species $Co^{III}(NH_3)_5(PNBz^{2-})^+$ and measure the rate constant (2.3×10^3 s^{-1}, in excellent agreement with the reported[7] 2.6×10^3 s^{-1} value) for intramolecular electron transfer from bound nitrobenzoate radical to cobalt(III) center.

References and Notes

(1) This work was supported by Grants CHE76-10449 and CHE79-09253 from the National Science Foundation.
(2) Haim, A. *Acc. Chem. Res.* **1975**, *8*, 264–272.
(3) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318–1328.
(4) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1162–1173.
(5) Gaunder, R. G.; Taube, H. *Inorg. Chem.* **1970**, *9*, 2627–2693.
(6) Heh, H. C.-K.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 3138–3142.
(7) Simic, M. G.; Hoffman, M. Z.; Brezniak, N. V. *J. Am. Chem. Soc.* **1977**, *99*, 2166–2172.
(8) Leopold, K. R.; Haim, A. *Inorg. Chem.* **1978**, *17*, 1753–1757.
(9) Kosower, E. M.; Colter, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5524–5527.
(10) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710–4712.
(11) Sebera, D. K.; Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 1785–1791.
(12) Miralles, A. J.; Armstrong, R. E.; Haim, A. *J. Am. Chem. Soc.* **1977**, *99*, 1416–1420.
(13) Kitson, R. E. *Anal. Chem.* **1950**, *22*, 664–667.
(14) A rigorous derivation of eq 3 is given: Leopold, K. R. B.S. Thesis, State University of New York, Stony Brook, N.Y., 1977.
(15) Navon, G.; Sutin, N. *Inorg. Chem.* **1974**, *13*, 2159–2164.
(16) Moelwyn Hughes, E. A. "The Chemical Statics and Kinetics of Solutions"; Academic Press: New York, 1971; p 111.
(17) Friedman, H. L. *J. Phys. Chem.* **1966**, *70*, 3931–3933.
(18) Deutch, J. M.; Felderhof, B. U. *J. Chem. Phys.* **1973**, *59*, 1669–1672.
(19) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism"; Wiley: New York, 1953; p 138.
(20) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883–891.
(21) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318–1328.
(22) Neta, P.; Simic, M. G.; Hoffman, M. Z. *J. Phys. Chem.* **1976**, *80*, 2018–2033.
(23) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 2909–2911.
(24) Simmons, M. G.; Wilson, L. J. *Inorg. Chem.* **1977**, *16*, 126–130.
(25) Lilie, J.; Shinohara, N.; Simic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6516–6520.
(26) Even for the case of $Co^{III}(NH_3)_5(PNBz^-)^+$, where k_i is only 2.6×10^3 s^{-1}, with reactant concentrations at $\sim 10^{-7}$ M and a second-order rate constant of 10^9 M^{-1} s^{-1}, homogeneous recombination would contribute less than 5% to the disappearance of IV.
(27) Fan, F-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647–2651.
(28) Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 241–243.
(29) Neta, P.; Simic, M. G.; Hoffman, M. Z. *J. Phys. Chem.* **1976**, *80*, 2018–2033.
(30) Meisel, D.; Fessenden, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 7505–7510.
(31) But it must be noted that even the value of k_{cr}^{Co} is quite high, perhaps unexpectedly so for a ground-state (high spin) cobalt(II) complex. It is conceivable that k_{cr}^{Co} corresponds to the oxidation of a low-spin cobalt(II) produced as the primary product of the electron transfer within the precursor complex, and that the reaction that competes with cage recombination and leads to Co^{2+} is not cage separation but the conversion of a low-spin to a high-spin cobalt(II) complex: Finkenberg, C.; Fisher, P.; Huang, S-M. Y.; Gafney, H. D. *J. Phys. Chem.* **1978**, *82*, 526–531.
(32) From $k_q k_{et}^{Co}(k_{el}^{Co} + k_{et}^L)$.
(33) Böttcher, W.; Haim, A., unpublished results.
(34) The limiting quantum yield of Co^{2+} is $(k_i^c + k_{cs}^L)/(k_i^c + k_{cs}^L + k_{cr}^L)$.
(35) Estimated from the 0.2–0.4 yield[33] of methyl viologen radical produced upon quenching $^*Ru(bpy)_3^{2+}$