Contribution from the Department of Chemistry,
State University of New York, Stony Brook, New York 11794

Quenching of the Luminescent Excited State of Tris(2,2'-bipyridine)ruthenium(II) by Complexes of Pentaamminecobalt(III) with Pyridine, 4,4'-Bipyridine, and Derivatives of 4,4'-Bipyridine

KENNETH R. LEOPOLD[1] and ALBERT HAIM*

Received February 9, 1978

The quenching of the luminescent excited state of tris(2,2'-bipyridine)ruthenium(II) by the complexes $Co(NH_3)_5L^{n+}$ (L = pyridine (py), 1,2-bis(4-pyridyl)ethane ($NC_5-CH_2CH_2-C_5N$), 4,4'-bipyridine (NC_5-C_5N), 1-methyl-4,4'-bipyridyl ($NC_5-C_5NCH_3^+$), 1,2-bis(4-pyridyl)ethene ($NC_5-CH{=}CH-C_5N$)) has been studied at 25 °C, pH 5.6, and ionic strength 0.10 M ($LiClO_4$). The quenching constants in the order given above are $(1.72 \pm 0.21) \times 10^8$, $(2.02 \pm 0.25) \times 10^8$, $(5.67 \pm 0.60) \times 10^8$, $(1.09 \pm 0.01) \times 10^9$, and $(1.15 \pm 0.08) \times 10^9$ $M^{-1}\,s^{-1}$, respectively. A parallel series of quenching measurements has been conducted for the free ligands but only $NC_5-C_5NH^+$, $HNC_5-C_5NH^{2+}$, $NC_5-C_5NCH_3^+$, $HNC_5-C_5NCH_3^{2+}$, and the protonated forms of $NC_5-CH{=}CH-C_5N$ are effective quenchers, the rate constants, in the order given above, being $(5.41 \pm 0.41) \times 10^8$, $(1.65 \pm 0.29) \times 10^9$, $(7.92 \pm 0.12) \times 10^8$, and $(2.51 \pm 0.02) \times 10^9$, for the first four ligands. Flash photolysis experiments with $Ru(bpy)_3^{2+}$ show the formation of radicals derived by one-electron reduction of $NC_5-C_5NH^+$, $HNC_5-C_5NH^{2+}$, and $NC_5-C_5NCH_3^+$ and their subsequent disappearance by reaction with $Ru(bpy)_3^{3+}$. Flash-photolysis experiments with $Ru(bpy)_3^{2+}$ in the presence of the cobalt(III) complexes failed to reveal the existence of analogous radical intermediates. Quantum yield measurements for the production of Co^{2+} in the $Ru(bpy)_3^{2+}-Co(NH_3)_5NC_5-C_5N^{3+}$ and $-Co(NH_3)_5NC_5-C_5NCH_3^{4+}$ systems show that a Co^{2+} ion is produced for every quenching event. The results are interpreted in terms of a quenching mechanism involving electron transfer from the excited state $^*Ru(bpy)_3^{2+}$ to the cobalt(III) complex. For the complexes with 4,4'-bipyridine, 1-methyl-4,4'-bipyridyl, and 1,2-bis(4-pyridyl)ethene the detailed electron-transfer quenching is postulated to proceed via a chemical mechanism, whereby the electron is transferred to the pyridine ligand and, in a subsequent step, from the bound radical to the cobalt(III) center.

Electron-transfer reactions between metal ions can proceed via an inner-sphere or an outer-sphere mechanism.[2] Regardless of the geometric features of the transition state, the detailed path of the electron transferred may involve temporary binding of the electron in an orbital of a ligand in the coordination sphere of one of the metal ions. This is referred to as the chemical or radical mechanism.[2] In contrast, in the resonance or exchange mechanism, the electron is at no time bound in an orbital of a ligand, and transfer proceeds via orbital overlap, the ligand orbitals serving only to mediate the electron transfer.[2]

Most of the available evidence to distinguish between the chemical and the resonance mechanism is indirect, being based on rate comparisons.[3,4] Direct evidence for the intermediacy of radical ions bound to metal centers has been obtained in the chromium(II)[5] reduction of (pyrazinecarboxylato)pentaamminecobalt(III) and in pulse radiolytic studies of (nitrobenzoato)pentaamminecobalt(III) complexes.[6]

In the present work, we seek additional, direct evidence for a chemically produced bound radical ion intermediate which occurs as a precursor to the reduction of the metal center to which it is bound. For the reducing agent we have chosen the long-lived, luminescent excited state of tris(2,2'-bipyridine)ruthenium(II), $^*Ru(bpy)_3^{2+}$. There is ample[7-9] evidence that this state is a thermodynamically strong and kinetically rapid reducing agent. Especially noteworthy is the reduction of 1,1'-dimethyl-4,4'-bipyridinium (methylviologen or paraquat), $CH_3NC_5-C_5NCH_3^{2+}$ (MV^{2+}) to the stable[10] radical ion MV^+ during flash photolysis of $Ru(bpy)_3^{2+}$.[8] For the oxidizing agents we have chosen a series of pentaamminecobalt(III) complexes, $Co(NH_3)_5L^{n+}$, where L = pyridine (py), 1,2-bis(4-pyridyl)ethane ($NC_5-CH_2CH_2-C_5N$), 4,4'-bipyridine (NC_5-C_5N), 1-methyl-4,4'-bipyridyl ($NC_5-C_5NCH_3^+$), and 1,2-bis(4-pyridyl)ethene ($NC_5-CH{=}CH-C_5N$). The similarity of these ligands to methylviologen suggests that relatively stable, coordinated radical ions could be produced upon quenching of $^*Ru(bpy)_3^{2+}$ by $Co(NH_3)_5L^{n+}$.

Experimental Section

Materials. Lithium perchlorate was prepared and standardized as described elsewhere.[11] 1,2-Bis(4-pyridyl)ethane, *trans*-1,2-bis(4-pyridyl)ethene, and 4,4'-bipyridine were recrystallized repeatedly from water. $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (G. F. Smith Chemical Co.) was recrystallized from water. Potassium tris(oxalato)ferrate(III) trihydrate[12] was recrystallized three times from water. The water and argon were purified as described previously.[13] All other materials were reagent grade and were used as received.

Preparation of Compounds. 1-Methyl-4,4'-bipyridinium perchlorate was prepared by the reaction of 4,4'-bipyridine with methyl iodide.[14] Small portions of a solution of 6 mL of methyl iodide in 30 mL of methanol were added at 10-min intervals to a refluxing solution of 15 g of 4,4'-bipyridine in 120 mL of methanol. When the red-orange dimethylated adduct began to precipitate, the solution was brought to room temperature and the solid was filtered out. Evaporation of the filtrate yielded 20 g of crude 1-methyl-4,4'-bipyridinium iodide. This was converted to the chloride salt by metathesis in the dark with 16 g of freshly prepared silver chloride. The solids were filtered out and the filtrate was evaporated to near dryness. The residue was dissolved in 11 mL of methanol, and $[NC_5-C_5NCH_3]Cl$ was precipitated by addition of 56 mL of acetone. The resulting solid was dissolved in a few milliliters of water and the perchlorate salt was precipitated by addition of a concentrated solution of sodium perchlorate and cooling to 0 °C. The perchlorate was recrystallized three times from water; yield 1.23 g. Anal. Calcd for $C_{11}H_{11}N_2O_4Cl$: C, 48.8; H, 4.10; N, 10.35. Found: C, 49.27, 49.45; H, 4.14, 4.23; N, 10.15, 10.44.

1-Methyl-4,4'-bipyridinium pentaamminecobaltate(III) was prepared by treatment of 1.5 g of $[Co(NH_3)_5OS(CH_3)_2](ClO_4)_3$[15] in 3 mL of dimethyl sulfoxide at 90 °C with 5.2 g of $[NC_5-C_5NCH_3]ClO_4$. After 10 min, 3 mL of dimethyl sulfoxide was added and heating at 90 °C was continued for 35 min. The solution was allowed to cool to room temperature and then was added to 85 mL of 0.1 M hydrochloric acid. The solution was filtered and the filtrate added to a column of Dowex 50W-X2 (200–400 mesh) in the H^+ form. The resin was rinsed with 1 and 2 M HCl, and the desired complex was then eluted with 4 M HCl. The eluate was evaporated to near dryness at 40–45 °C in a rotary evaporator. The residue was dissolved in 20 mL of 0.1 M HCl and the resulting solution was added to a column of Dowex 50W-X2 (200–400 mesh) in the H^+ form. The resin was rinsed with 1, 2, and 3 M HCl, and then the desired complex was eluted with 4 M HCl. The eluate was rotary evaporated to near dryness. The residue was dissolved in a small amount of water (0.5 g/mL) and then 6–8 drops of 72% perchloric acid was added. The solution was kept at 0 °C overnight and the resulting crystals were filtered, washed with ethanol, and then dried to constant weight in a vacuum desiccator; yield 440 mg. Anal. Calcd for [Co-

0020-1669/78/1317-1753$01.00/0 © 1978 American Chemical Society

$(NH_3)_5NC_5{-}C_5NCH_3](ClO_4)_4{\cdot}H_2O$: Co, 8.06; C, 18.07; H, 3.86; N, 13.41. Found: Co, 8.04; C, 17.85, 17.86; H, 3.80, 4.07; N, 13.13, 13.27.

The other cobalt(III) complexes were taken from our laboratory stock and had been prepared by A. J. Miralles ($[Co(NH_3)_5py](ClO_4)_3$ and $[Co(NH_3)_5NC_5{-}C_5NH](ClO_4)_4{\cdot}H_2O$) and by J. J. Jwo ($[Co(NH_3)_5NC_5{-}CH{=}CH{-}C_5NH](ClO_4)_4{\cdot}H_2O$ and $[Co(NH_3)_5NC_5{-}CH_2CH_2{-}C_5NH]ClO_4{\cdot}H_2O$).

C, H and N analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Luminescence Quenching Measurements. A series of solutions of constant $Ru(bpy)_3^{2+}$ concentration and variable-quencher concentration (0 to maximum) containing the desired amounts of buffer, perchloric acid, or sulfuric acid were prepared. The samples were deaerated for at least 1 h in 1-cm² serum-capped fluorescence cells. Emission-intensity measurements were made on a Ferrand Mark I or a Perkin-Elmer MPF-44A fluorescence spectrophotometer. The excitation wavelength was 450 nm and the emission was monitored at 590 or 610 nm. When the intensity was seen to decrease with time (irreversible oxidation of Ru(II) by Co(III) complexes), extrapolation to zero time yielded the desired intensity.

Photolysis Measurements. Flash-photolysis measurements were carried out with a Xenon Corp. Model 720 apparatus. The output of the photomultiplier tube was monitored through a 10-kΩ load resistor with a Biomation Model 805 waveform recorder connected to a Tektronix 602 display unit.

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 with a focusing lens, an iris, a 0.6-cm glass plate, a 5-cm cell filled with water, a 450-nm interference filter (Corion Corp.), a lens, a shutter, and an iris. The photolysis cell was an ordinary 10-cm spectrophotometric cell modified by blowing a small well in the bottom to accommodate a magnetic stirring bar.[16] The cell was placed in a thermostated cell holder with a hole drilled in the bottom.[16] A magnetic stirrer drove the magnet in the well, stirring the solution during photolysis. Light intensity was determined by tris(oxalato)ferrate(III) actinometry.[12] The cobalt(II) produced by photolysis was analyzed by Kitson's method.[17]

Electronic spectra were recorded in a Cary 17 or 118 spectrophotometer. pH measurements were carried out with an Orion Model 801 pH meter.

Results

The emission intensities measured in the quenching experiments were treated according to eq 1, where $(I_0/I)_{cor}$ is

$$(I_0/I)_{cor} = 1 + K_{SV}[Q] \tag{1}$$

the corrected ratio of the 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 means of eq 2, where

$$(I_0/I)_{cor} = (I_0/I)_{obsd}\,\frac{1 - 10^{-(A_D + A_Q)}}{1 - 10^{-A_D}}\,\frac{A_D}{A_D + A_Q} \times \frac{1 - 10^{-A'_Q}}{2.303A'_Q} \tag{2}$$

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. Plots of $(I_0/I)_{cor} - 1$ vs. [Q] were linear, and values of K_{SV} were obtained by least-squares treatment of the data. The values of K_{SV} for the quenchers examined in the present work are given in column 4 of Table I.

The entries for the free ligands in Table I call for special comment since, depending on the pH, protonated and/or unprotonated species are present in solution. The pK_a of pyridine is 5.2,[18] and therefore, at pH 5.6, substantial amounts of protonated and unprotonated forms are present. Since no quenching is observed under these conditions, it is concluded that $K_{SV} \leq 20$ for both py and pyH^+. The conclusion is strengthened by the observation that 1.89×10^{-3} M $pyCH_3^+$ at pH 5.6 produces no observable quenching. The pK_1 and pK_2 values of $HNC_5{-}C_5N^{2+}$ are 3.2 and 4.9, respectively.[19] At 0.0944 M $HClO_4$, all the ligand is present in the diprotonated form, and application of eq 1 with [Q] equal to the total concentration of 4,4′-bipyridine gives values of K_{SV} for the diprotonated form. In the pH range of 3.89–4.87, diprotonated, monoprotonated, and unprotonated 4,4′-bipyridine are present in solution. Only the protonated forms are effective quenchers,[20] and, under these conditions, the Stern–Volmer relationship takes the form of eq 3, where K_{SV}^{m}

$$(I_0/I)_{cor} = 1 + K_{SV}^{m}[NC_5{-}C_5NH^+] + K_{SV}^{d}[HNC_5{-}C_5NH^{2+}] \tag{3}$$

and K_{SV}^{d} are the Stern–Volmer constants for the mono- and diprotonated species, respectively. The concentrations of mono- and diprotonated forms were calculated from the known pK_1 and pK_2 values, and the value of K_{SV}^{m} was obtained from eq 3 using the value of K_{SV}^{d} measured in 0.0944 M perchloric acid. The pK_a value of $HNC_5{-}C_5NCH_3^{2+}$ (measured in the present work) was found to be 3.5 ± 0.1 at 25 °C and ionic strength 0.10 M adjusted with lithium perchlorate. Therefore, the quenching measurements at pH 5.6 and at $[H^+] = 0.0944$ M perchloric acid yield directly Stern–Volmer constants for the unprotonated and protonated forms, respectively. The pK values for $HNC_5{-}CH_2CH_2{-}C_5NH^{2+}$ are not known, but it is reasonable[18] that the pK_2 value be ~5.9. Therefore, at pH 5.6 large amounts of protonated forms are expected to be present. The absence of quenching indicates that protonated and unprotonated forms are unreactive toward $*Ru(bpy)_3^{2+}$. Finally, the pK_1 and pK_2 values of $HNC_5{-}CH{=}CH{-}C_5NH^{2+}$ are 4.4 and 5.9, respectively.[20] At pH 5.6, the di-, mono-, and unprotonated forms are present, and, therefore, the K_{SV} value listed represents a composite quantity that includes pK values and actual K_{SV} values for the species that can quench $*Ru(bpy)_3^{2+}$.

A summary of the results of the steady-state photolysis experiments is given in Table II. Attempts to repeat the experiment with $Co(NH_3)_5NC_5{-}C_5N^{3+}$ in lithium perchlorate resulted in the formation of a precipitate in the photolysis cell, presumably the rather insoluble salt $[Ru(bpy)_3](ClO_4)_2$. Therefore, all subsequent quantum yield measurements were carried out in 0.50 M H_2SO_4.

A summary of the results of the flash-photolysis experiments is given in Table III. Only in the case of $NC_5{-}C_5N$ at pH 4.7 and in 0.0944 M $HClO_4$ and in the case of $NC_5{-}C_5NCH_3^+$ at pH 5.6 were transients observed. Our observations here are entirely similar to those of Bock, Meyer, and Whitten on the analogous $Ru(bpy)_3^{2+} + CH_3NC_5{-}C_5NCH_3^{2+}$ system.[8] Flash photolysis yielded transient species which absorbed at 600 nm and which decayed by reaction with $Ru(bpy)_3^{3+}$. The reaction sequence, exemplified for $NC_5{-}C_5NCH_3^+$ is given by eq 4–6. Rate constants for reaction 6 and for the corresponding reactions of $NC_5{-}C_5NH{\cdot}$ and $HNC_5{-}C_5NH^{2+}$ were all in the vicinity of $\sim 10^9$ M⁻¹ s⁻¹. It is noteworthy that, even with the nanosecond flash apparatus, no transient was observed for $Co(NH_3)_5NC_5{-}C_5N^{3+}$.

$$Ru(bpy)_3^{2+} + h\nu \rightarrow *Ru(bpy)_3^{2+} \tag{4}$$

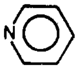
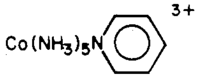
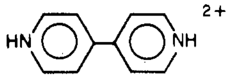
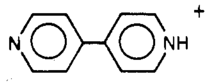
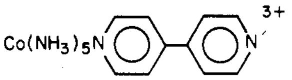
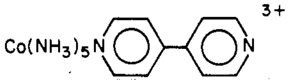
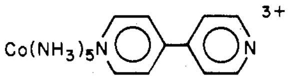
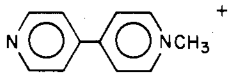
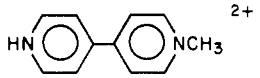
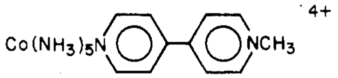
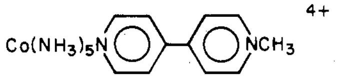
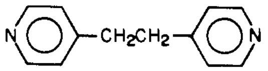
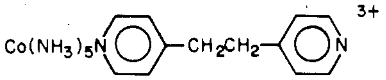
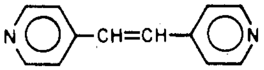
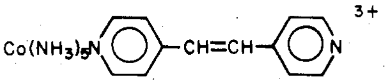
$$*Ru(bpy)_3^{2+} + NC_5{-}C_5NCH_3^+ \rightarrow Ru(bpy)_3^{3+} + NC_5{-}C_5NCH_3{\cdot} \tag{5}$$

$$Ru(bpy)_3^{3+} + NC_5{-}C_5NCH_3{\cdot} \rightarrow Ru(bpy)_3^{2+} + NC_5{-}C_5NCH_3^+ \tag{6}$$

Discussion

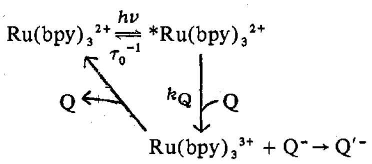
The data from the luminescence quenching experiments were analyzed according to Scheme I, where the excited ruthenium species can disappear by two alternate pathways: (1) unimolecular return to the ground state with a rate constant $\tau_0^{-1} = k_r + k_{nr}$, where k_r and k_{nr} are the first-order rate constants for the natural radiative and nonradiative

Table I. Stern-Volmer and Rate Constants for the Quenching of $^*Ru(bpy)_3^{2+}$ by Pyridines and Pyridine Complexes of $Co(NH_3)_5^{3+}$ [a]

Quencher	Concn × 10^3, M	Medium[b]	K_{SV}, M^{-1}	$10^{-8}k_q$, M^{-1} s^{-1}
	2.48	A	⩽20	⩽0.3[c]
	0.45-1.92	A	103 ± 9	1.72 ± 0.21
	0.42-2.08	B	(1.06 ± 0.03) × 10^3	16.5 ± 0.29
	0.83-2.08, 1.05	C, D	324 ± 13	5.41 ± 0.41
	0.21-1.58	A	340 ± 26	5.67 ± 0.60
	0.20-1.01	B	720 ± 18	12.0 ± 0.7
	0.55-1.55	E	435 ± 25	7.25 ± 0.66
	0.54-1.89	A	475 ± 7	7.92 ± 0.12
	0.60-2.11	B	(1.51 ± 0.01) × 10^3	25.1 ± 0.2
	0.28-2.30	A	645 ± 7	10.9 ± 0.1
	0.45-1.55	E	434 ± 40	7.23 ± 0.21
	1.99	A	⩽25	⩽0.3
	0.50-2.00	A	121 ± 11	2.02 ± 0.25
	1.28-4.88	A	55 ± 5[d]	
	0.13-1.97	A	692 ± 26	11.5 ± 0.8

[a] Measurements in aqueous solution at 25 °C; $[Ru(bpy)_3^{2+}] = (5.08\text{-}6.04) \times 10^{-6}$ M. [b] Medium A = pH 5.6, 0.010 M phosphate buffer, ionic strength 0.10 M adjusted with $LiClO_4$; medium B = 0.0944 M $HClO_4$, ionic strength 0.10 M; medium C = 0.02 M acetate buffer, pH 4.55-4.61, ionic strength 0.10 M adjusted with $LiClO_4$; medium D = added perchloric acid, pH 4.87-3.89, ionic strength 0.10 M adjusted with $LiClO_4$; medium E = 0.50 M H_2SO_4. [c] The limit 1 × 10^7 at pH 4-5, 0.50 M NaCl, is reported in ref 23. [d] This is a composite constant reflecting quenching by the mono- and diprotonated forms present in solution; see text.

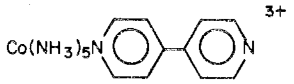
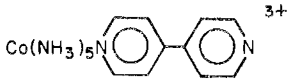
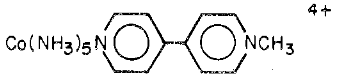
Scheme I



deactivation processes, respectively; (2) bimolecular reaction with the quencher, Q, with a rate constant k_Q. If the excited species is at steady state, emission intensities are given by eq 1, where $K_{SV} = k_Q\tau_0$. Using the previously[21] measured value $\tau_0 = (0.60 \pm 0.02) \times 10^{-6}$ s^{-1} and the values of K_{SV} measured in the present work, values of k_Q were calculated and are presented in Table I.

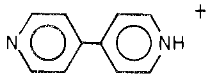
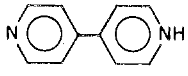
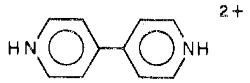
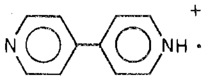
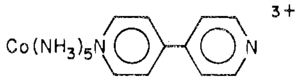
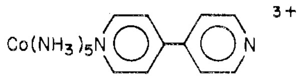
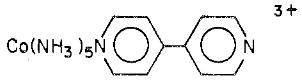
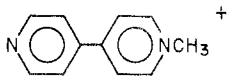
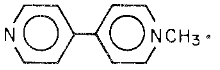
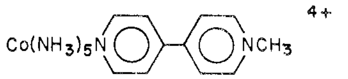
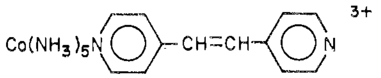
The quenching mechanism for the compounds listed in Table I is taken to be reduction of the quencher by the excited state $^*Ru(bpy)_3^{2+}$ as there is ample evidence[7-9,21] for electron-transfer quenching by compounds of the type studied in the present work. Depending on the nature of Q, the reduced form, Q^-, may react with $Ru(bpy)_3^{3+}$ to regenerate starting materials or may undergo further reaction to form Q'^-. The former case applies to quenching by the protonated forms of 4,4'-bipyridine and its derivatives. The radicals produced by electron-transfer quenching (eq 5) are oxidized by the $Ru(bpy)_3^{3+}$ produced in the quenching step (eq 6). Thus, the starting materials are regenerated, and no net photoinduced reaction takes place. In contrast, there is net photochemistry in the quenching of $^*Ru(bpy)_3^{2+}$ by the cobalt(III) complexes. The one-electron reduction products of the cobalt(III)

Table II. Quantum Yield Measurements for the Reactions of $Ru(bpy)_3^{2+}$ with $Co(NH_3)_5NC_5{-}C_5N^{3+}$ and $Co(NH_3)_5NC_5{-}C_5NCH_3^{4+}$ [a]

	10^4[complex], M	I,[b] einstein/s	Δt, 10^3 s[c]	ϕ[d]
	4.73	1.15×10^{-9}	4.89	0.17[e]
	4.68	4.46×10^{-10}	3.22	0.15
	4.15	4.54×10^{-10}	2.74	0.14

[a] At 25 °C with λ 450 nm; $[Ru(bpy)_3^{2+}] = (4.94\text{–}5.00) \times 10^{-5}$ M; $[H_2SO_4] = 0.50$ M. [b] Light intensity arriving at inner wall of the cell; there is essentially complete absorption of all the incident light. [c] Time of photolysis. [d] Quantum yield for production of Co^{2+}. [e] In pH 5.6, 0.010 M phosphate buffer, ionic strength 0.10 M adjusted with $LiClO_4$.

Table III. Summary of Flash-Photolysis Measurements[a]

	10^3[quencher], M	$10^5[Ru(bpy)_3^{2+}]$, M	Observn
	2.07[b]	2.50	 transient
	2.08	2.97	 transient
	2.00–2.19[c]	0.66–2.43	No transient
	1.98	2.41	No transient
	5.0–9.8[d]	1.0–3.0	No transient[e]
	2.00[c]	2.50	 transient
	3.50[d]	21.4	No transient
	1.95[c]	0.59	No transient

[a] Measurements with conventional flash apparatus (80–100 μs flash duration). Observations at 600 nm. At 25 °C, $[HClO_4] = 0.0944$, ionic strength 0.10 M. [b] At pH 4.7; this is the total concentration of 4,4′-bipyridine. [c] pH 5.6. [d] In 0.50 M H_2SO_4. [e] Using 30-ns pulse at 530 nm.

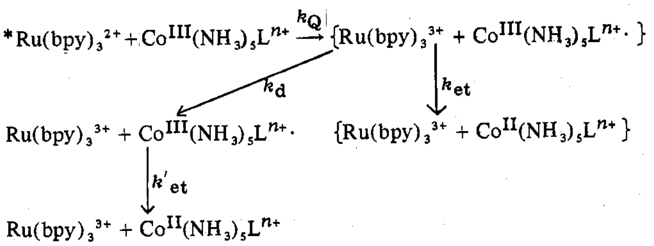
complexes undergo dissociation with formation of Co^{2+}. It is possible to calculate the number of Co^{2+} ions produced per quenching event, N_{Co}, by combining the results of quenching and of quantum yield measurements. The calculation is performed by means of eq 7, where ϕ is the quantum yield

$$N_{Co} = \frac{\phi\{\tau_0^{-1} + k_Q[Co^{III}]\}}{k_Q[Co^{III}]} \qquad (7)$$

for Co^{2+} formation, τ_0 and k_Q are defined in Scheme I, and $[Co^{III}]$ is the average concentration of the cobalt(III) complex in the experiment where the quantum yield was measured. For $Co(NH_3)_5NC_5{-}C_5N^{3+}$ at pH 5.6, $N_{Co} = 1.2 \pm 0.2$. For the same compound in 0.50 M H_2SO_4, we find $N_{Co} = 0.89 \pm 0.2$. For $Co(NH_3)_5NC_5{-}C_5NCH_3^{4+}$ in 0.50 M H_2SO_4, the value of N_{Co} is 0.92 ± 0.10. Thus, we conclude that every quenching event results in the net reduction of cobalt(III) to cobalt(II) and the eventual formation of Co^{2+}, and we rule out the possibility of a cage reaction between the primary one-electron reduction product of the cobalt(III) complex and the $Ru(bpy)_3^{3+}$. Moreover, we rule out any cage reactions between degradation products of the primary cobalt product and $Ru(bpy)_3^{3+}$.

In this context, we must consider the detailed pathway for the electron transfer from $*Ru(bpy)_3^{2+}$ to the cobalt(III) complexes, e.g., the nature of the primary one-electron reduction products of the cobalt(III) complexes. In the chemical mechanism for electron transfer between metal complexes,[2] it is expected that an electron from the reducing agent is added to an orbital of a ligand in the coordination sphere of the oxidant and, subsequently, from the ligand radical to the metal center. In fact, the flash-photolysis measurements were performed anticipating that such radical intermediates could be detected. The excited state $*Ru(bpy)_3^{2+}$ is a powerful and rapid reductant, and 4,4′-bipyridine and its derivatives are known[10] to produce relatively stable radicals by one-electron reduction. Unfortunately, no intermediates could be detected for the reactions of the cobalt(III) complexes, even with the nanosecond flash-photolysis apparatus. Therefore, it must be concluded either that the chemical mechanism does not obtain in these systems or, if the radical intermediate is produced, that the rate constant for intramolecular electron transfer from

Scheme II



the radical to the cobalt(III) center is larger than 4×10^6 s^{-1} or 10^{11} s^{-1}, depending on the details of the mechanism. These limits are obtained by considering Scheme II, where { } denotes a solvent cage, k_d is the rate constant for the separation of the ions from the cage (10^{10}–10^{11} s^{-1}), k_{et} and k'_{et} are the rate constants for intramolecular electron transfer from ligand radical to cobalt(III) center in the solvent cage and in the free ion, respectively, and L· represents the one-electron reduction product of $NC_5–C_5N$ or $NC_5–C_5NCH_3^+$. If intramolecular electron transfer occurs within the solvent cage, then $k_{et} > 10^{11}$ s^{-1}. Alternately, if the ruthenium and cobalt complexes escape the solvent cage, then, assuming that an absorbance of 0.01 would have been detected after 50×10^{-9} s on the laser apparatus, we estimate $k'_{et} > 4 \times 10^6$ s^{-1}.

Although direct evidence for the chemical mechanism has not been obtained, rate comparisons suggest that the ligands $NC_5–C_5N$, $NC_5–C_5NCH_3^+$, and $NC_5–CH{=}CH–C_5N$ are implicated in the electron-transfer pathway. Thus, the rate constants for the outer-sphere reductions within the ion pairs formed between $Fe(CN)_6^{4-}$ and $Co(NH_3)_5py^{3+}$, $Co(NH_3)_5NC_5–CH_2CH_2–C_5N^{3+}$, or $Co(NH_3)_5NC_5–C_5N^{3+}$ are 1.5×10^{-2}, 2.4×10^{-2}, and 1.1×10^{-2} s^{-1}, respectively.[13,22] This narrow range of rate constants has been taken to indicate direct electron transfer from iron to cobalt, without mediation by the pyridine ligands.[13] The rate constants measured in the present work (cf. Table I) for reductions by $*Ru(bpy)_3^{2+}$ cover a wider range than the $Fe(CN)_6^{4-}$ reductions, in spite of the fact that the rate constants are approaching the diffusion-controlled limit. Moreover, the reactivity order toward $*Ru(bpy)_3^{2+}$ for the complexes, $Co(NH_3)_5py^{3+} \sim Co(NH_3)_5NC_5–CH_2CH_2–C_5N^{3+} < Co(NH_3)_5NC_5–C_5N^{3+} < Co(NH_3)_5NC_5–C_5NCH_3^{4+} \sim Co(NH_3)_5NC_5–CH{=}CH–C_5N^{3+}$, is the same as that for ligands, $pyH^+ \sim HNC_5–CH_2CH_2–C_5NH^{2+} \ll HNC_5–C_5NH^{2+} < HNC_5–C_5NCH_3^{2+}$. In fact, the absolute rates of reactions of the pairs $Co(NH_3)_5NC_5–C_5N^{3+}/NC_5–C_5NH^+$ and $Co(NH_3)_5NC_5–C_5NCH_3^{4+}/HNC_5–C_5NCH_3^{2+}$ are very close to each other, and the small differences can be accounted for by the differences in charges. These observations strongly suggest that the ligands L are implicated in the reactions between $*Ru(bpy)_3^{2+}$ and $Co(NH_3)_5L^{n+}$. Moreover, it must be noted that at the higher reactivity end for the free ligands, the flash-photolysis experiments show conclusively the formation of radicals, and, therefore, it is tempting to postulate that the more reactive complexes $Co(NH_3)_5NC_5–C_5N^{3+}$, $Co(NH_3)_5NC_5–C_5NCH_3^{4+}$, and $Co(NH_3)_5NC_5–CH{=}CHC_5N^{3+}$ also react by accepting an electron in an orbital of the pyridine ligand, e.g., that the chemical mechanism obtains. Interestingly, rate comparisons have also been used to support the suggestion[23] that $Fe(CN)_5pyzCH_3^{2-}$ and $Co(CN)_5pyzCOOH^{2-}$ quench $*Ru(bpy)_3^{2+}$ by an electron-transfer mechanism whereby the pyrazine ligands are reduced to the corresponding radicals.

Acknowledgment. This research was supported by the National Science Foundation under Grant CHE 76 10449. The authors are grateful to Drs. Norman Sutin and Carol Creutz for their help with the experiments on the nanosecond flash-photolysis apparatus carried out at Brookhaven National Laboratory.

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; py, 110-86-1; $Co(NH_3)_5NC_5^{3+}$, 31011-67-3; $HNC_5–C_5NH^{2+}$, 46040-54-4; $NC_5–C_5NH^+$, 36221-78-0; $Co(NH_3)_5NC_5–C_5N^{3+}$, 53879-90-6; $NC_5–C_5NCH_3^+$, 22906-73-6; $HNC_5–C_5NCH_3^{2+}$, 66271-18-9; $Co(NH_3)_5NC_5–C_5NCH_3^{4+}$, 66290-41-3; $NC_5–CH_2CH_2–C_5N$, 4916-57-8; $Co(NH_3)_5NC_5–CH_2CH_2–C_5N^{3+}$, 38671-05-5; $NC_5–CH{=}CH–C_5N$, 1135-32-6; $Co(NH_3)_5NC_5–CH{=}CH–C_5N^{3+}$, 38671-06-6; $[Co(NH_3)_5Os(CH_3)_2](ClO_4)_3$, 51667-94-8; $[Co(NH_3)_5NC_5–C_5NCH_3](ClO_4)_4$, 66290-42-4.

References and Notes

(1) From the B.S. thesis of K.R.L., State University of New York, Stony Brook, N.Y., May 1977.
(2) A. Haim, *Acc. Chem. Res.*, **8**, 264 (1975).
(3) F. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, **90**, 1162 (1968).
(4) R. G. Gaunder and H. Taube, *Inorg. Chem.*, **9**, 2627 (1970).
(5) E. S. Gould, *J. Am. Chem. Soc.*, **94**, 4360 (1972).
(6) M. G. Simic, M. Z. Hoffman, and N. V. Brezniak, *J. Am. Chem. Soc.*, **99**, 2166 (1977).
(7) H. D. Gafney and A. W. Adamson, *J. Am. Chem. Soc.*, **94**, 8338 (1972).
(8) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974).
(9) G. Navon and N. Sutin, *Inorg. Chem.*, **13**, 2159 (1974).
(10) E. M. Kosower and J. L. Colter, *J. Am. Chem. Soc.*, **86**, 5524 (1964).
(11) J. R. Ward and A. Haim, *J. Am. Chem. Soc.*, **92**, 475 (1970).
(12) J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, N.Y., 1967, p 784.
(13) A. J. Miralles, R. E. Armstrong, and A. Haim, *J. Am. Chem. Soc.*, **99**, 1416 (1977).
(14) B. Emmert and J. Stawitz, *Ber. Dtsch. Chem. Ges., B*, **56**, 83 (1923).
(15) C. R. Piriz MacColl and L. Beyer, *Inorg. Chem.*, **12**, 7 (1973).
(16) M. Orhanovic and N. Sutin, *Inorg. Chem.*, **16**, 550 (1977).
(17) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).
(18) K. Schofield, "Heteroaromatic Nitrogen Compounds", Plenum Press, New York, N.Y., 1967, p 147.
(19) D. K. Lavallee and E. B. Fleischer, *J. Am. Chem. Soc.*, **94**, 2583 (1972).
(20) Quenching measurements at pH 5.6 with 2×10^{-3} M 4,4′-bipyridine yield a value of $(I_0/I) = 1.08$. The calculated value assuming that only the monoprotonated form (present in 3.3×10^{-4} M concentration under these conditions) is effective in quenching $*Ru(bpy)_3^{2+}$ is 1.11. The reasonable agreement between calculated and experimental values of I_0/I leaves no room for quenching by the nonprotonated form of 4,4′-bipyridine.
(21) C. T. Lin, W. Böttcher, M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **98**, 6536 (1976).
(22) A. J. Miralles, J. J. Jwo, and A. Haim, unpublished observations.
(23) H. E. Toma and C. Creutz, *Inorg. Chem.*, **16**, 545 (1977).