Volume 19
Number 1
January 1980

Inorganic Chemistry

Contribution from the Department of Chemistry, The City University of New York,
Queens College, Flushing, New York 11367

Measurement of the Rates of the Electron-Transfer Reactions between $Ru(bpy)_3{}^{3+}$ and $Co(phen)_3{}^{2+}$ or $Co(bpy)_3{}^{2+}$ by Flash Photolysis Techniques

RUSSELL BERKOFF, KEVIN KRIST, and HARRY D. GAFNEY*

Received November 1, 1977

Flash photolysis of solutions containing $Ru(bpy)_3{}^{2+}$ and $Co(phen)_3{}^{3+}$ or $Co(bpy)_3{}^{3+}$ induces a photochemical reaction which produces the corresponding Ru(III) and Co(II) complexes in relatively high yield. The photochemical reaction is then followed by a rapid exothermic, $\Delta G \approx -0.8$ eV, thermal reaction yielding an overall reaction scheme of $Ru(bpy)_3{}^{2+} + CoL_3{}^{3+} \underset{k_t}{\overset{h\nu}{\rightleftharpoons}} Ru(bpy)_3{}^{3+} + CoL_3{}^{2+}$, where L denotes bipyridine or phenanthroline. The quenching reaction is relatively exothermic, $\Delta G \approx -1.2$ eV, but no spectral evidence for a Co(II) intermediate which has a coordinated radical anion intermediate was obtained. The quenching rate constants, k_q, are essentially diffusion controlled, ca. 2×10^9 M^{-1} s^{-1}. The reaction parameters suggest that nuclear tunneling effects may contribute to the observed electron-transfer quenching rate constant. The thermal back-reactions, $k_t \approx 2 \times 10^8$ M^{-1} s^{-1}, are about an order of magnitude smaller than the diffusion-corrected rate constants obtained from the Marcus equations, $\sim 2 \times 10^9$ M^{-1} s^{-1}. For much slower thermal reactions involving these cobalt complexes, the Marcus theory is generally successful in predicting rate constants between 2+ and 3+ charged reactions to within a factor of 25. Although these reactions are faster, the order of magnitude difference found between k_{calcd} and k_{obsd} suggests that the nonadiabaticities associated with the spin multiplicities or a mixed d–π^* pathway for electron transfer have only a slight retarding effect on the rate of these reactions.

Introduction

Generally considered to be outer-sphere electron-transfer reagents, the substitution-inert 2,2′-bipyridine, bpy, and 1,10-phenanthroline, phen, complexes of the low-spin iron-triad metals have been extensively used to test various aspects of the Marcus–Hush theory.[1] The oxidation potentials of the trivalent-metal complexes are large, however, and with easily oxidizable species favor reaction rates which are often too rapid to be studied by conventional techniques.

Recent luminescence quenching and flash photolysis studies have shown that the luminescent charge-transfer state of $Ru(bpy)_3{}^{2+}$, designated $*Ru(bpy)_3{}^{2+}$, is a strong reductant.[2] In aqueous solution, the oxidation potential of $*Ru(bpy)_3{}^{2+}$ is calculated to be +0.84 V vs. the NHE.[2f] If this state is rapidly "turned on" in the presence of an appropriate quencher, quenching occurs rapidly, and relatively high concentrations of electron-transfer products can be generated. As pointed out by Meyer and co-workers,[3] the formation of the electron-transfer products during the flash duration allows the use of the flash photolysis technique as a relaxation technique in which very rapid electron-transfer reactions can be studied.

For example, the driving forces for the reactions

$$Ru(bpy)_3{}^{3+} + Co(phen)_3{}^{2+} \xrightarrow{\Delta G = -0.82 \text{ eV}} Ru(bpy)_3{}^{2+} + Co(phen)_3{}^{3+} \quad (1)$$

$$Ru(bpy)_3{}^{3+} + Co(bpy)_3{}^{2+} \xrightarrow{\Delta G = -0.87 \text{ eV}} Ru(bpy)_3{}^{2+} + Co(bpy)_3{}^{3+} \quad (2)$$

are large and favorable and yield reaction rates beyond the range of conventional stopped-flow techniques.[4] The cross reaction is interesting, however, in that it offers a test of Marcus–Hush theory[5] under conditions where the driving force is unusually high and the vagaries associated with unfavorable hydrophobic–hydrophilic interactions are a minimum.

We have found that $Co(phen)_3{}^{3+}$ and $Co(bpy)_3{}^{3+}$ quench $*Ru(bpy)_3{}^{2+}$ at essentially a diffusion-controlled rate and lead to electron-transfer products in relatively high yield. The quenching reaction leading to $Ru(bpy)_3{}^{3+}$ and $Co(phen)_3{}^{2+}$ or $Co(bpy)_3{}^{2+}$ occurs within the flash duration, and the back-reactions, eq 1 or 2, can be easily monitored at the absorption maximum of $Ru(bpy)_3{}^{3+}$. We report here the results of a flash photolysis study in which the rates of reactions between $Ru(bpy)_3{}^{3+}$ and $Co(phen)_3{}^{2+}$ or $Co(bpy)_3{}^{2+}$ have been measured. The rate constants for the quenching reactions are diffusion controlled, and the reaction parameters suggest that nuclear tunneling contributes to the quenching rate. The rate constants for the back-reactions, reactions 1 and 2, are about an order of magnitude slower than the diffusion-corrected rate constants calculated from the Marcus–Hush theory.

---

(1) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, Chapter 6; (b) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer", Ronald Press, New York, 1966.

(2) (a) H. D. Gafney and A. W. Adamson, *J. Am. Chem. Soc.*, **94**, 9238 (1972); (b) C. R. Bock, T. J. Meyer, and D. G. Whitten, *ibid.*, **96**, 4710 (1974); (c) R. C. Young, T. J. Meyer, and D. G. Whitten, *ibid.*, **97**, 4781 (1975); (d) G. Navon and N. Sutin, *Inorg. Chem.*, **13**, 2159 (1974); (e) G. S. Lawrence and V. Balzani, *ibid.*, **13**, 2976 (1974); (f) C. T. Lin and N. Sutin, *J. Phys. Chem.*, **80**, 97 (1976).

(3) R. C. Young, F. Richard Keene, and T. J. Meyer, *J. Am. Chem. Soc.*, **99**, 2468 (1977).

(4) M. Chow, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **99**, 5615 (1977).

(5) R. A. Marcus and N. Sutin, *Inorg. Chem.*, **14**, 213 (1975), and references therein.

0020-1669/80/1319-0001$01.00/0

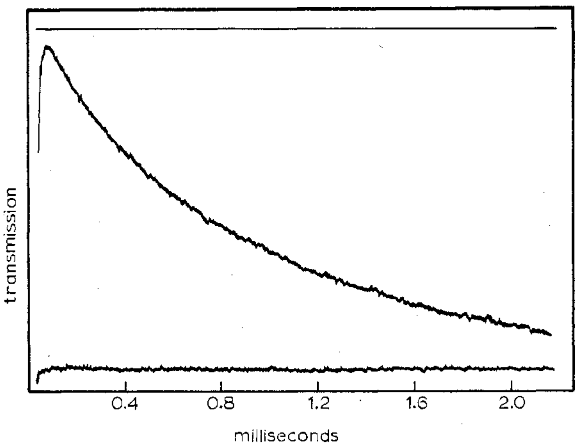


Figure 1. Oscilloscope trace following 250-J flash photolysis of a solution containing 7.5 × 10^{-5} M $Ru(bpy)^{2+}$ and 10^{-3} M $Co(phen)_3^{3+}$, monitored at 675 nm; $T = 25$ °C; $\mu = 1.0$ M.

Experimental Section

Materials. $[Ru(bpy)_3]Cl_2{\cdot}3H_3O$ was purchased from G. Fredrick Smith or J. T. Baker and recrystallized from distilled water prior to use. $[Ru(bpy)_3](ClO_4)_3$ was prepared by Cl_2 oxidation of the Ru(II) complex as described by Creutz and Sutin.[6] This complex was twice recrystallized from cool, ca. 10 °C, distilled water by the addition of $HClO_4$ and/or $NaClO_4$. The extent of hydration of the complex was not known, however, so the extinction coefficients were determined by quantitatively reducing $Ru(bpy)_3^{3+}$ to $Ru(bpy)_3^{2+}$. After the spectrum of a known weight of the Ru(III) complex dissolved in water was recorded, an aliquot of 1 M $NaNO_2$ was added to the solution. Reduction occurred immediately, and on the basis of the amount of $Ru(bpy)_3^{2+}$ formed, the extinction coefficient of $Ru(bpy)_3^{3+}$ at 675 nm was calculated to be 436 M^{-1} cm^{-1}.

$[Co(phen)_3](ClO_4)_3{\cdot}3H_2O$ and $[Co(bpy)_3](ClO_4)_3{\cdot}3H_2O$ were prepared by procedures described in the literature,[7] but we, like others,[7b,c] have found it difficult to obtain pure samples of $Co(phen)_3^{3+}$. Because of the relatively low solubilities of these complexes and the similarity of the absorption spectra of these Co(II) and Co(III) complexes,[8] it was difficult to spectrally characterize the oxidation state of the complex. In one preparation of $Co(phen)_3^{3+}$, 1.2 g of $CoCl_2{\cdot}6H_2O$ and 3.0 g of 1,10-phenanthroline were dissolved in warm (ca. 60 °C) water and the solution was treated with 30% H_2O_2. Following the vigorous effervesence, 60% $HClO_4$ was added, and on cooling of the mixture, a pale yellow precipitate formed. Although the sample was twice recrystallized from distilled water, the transient observed on flash photolysis of this sample in the presence of $Ru(bpy)_3^{2+}$ decayed very rapidly (ca. 60–80 μs) with first-order kinetics. Close examination of the absorption spectrum of the sample in the 410–480-nm region, however, indicated the presence of $Co(phen)_3^{2+}$, and analysis of the sample by the thiocyanate procedure[10] confirmed that the sample contained 25% $Co(phen)_3^{2+}$. A fraction of this sample was redissolved in water, treated with 30% H_2O_2, and precipitated by the addition of 60% $HClO_4$. Thiocyanate analysis of this recrystallized sample indicated that the amount of $Co(phen)_3^{2+}$ had been reduced to <2%. When this sample was used in the flash experiment, the decay was much slower (see Figure 1) and second order. To ensure the H_2O_2 was simply oxidizing the metal ion, we oxidized a second fraction of the above preparation with Cl_2 and precipitated it with $HClO_4$. Again the flash experiment showed that the decay was slower and second order. The rate constant, however, was ca. 1.5 times larger than that obtained with H_2O_2 oxidized samples. The electronic and IR spectra of the two samples were identical, and, at present, the cause of the difference is not known.

Table I. Quantum Yields for Aquation and Reduction and Stern–Volmer Quenching Constants[a,c]

complex	$10^3\phi_{aq}$[b]	$10^3\phi_{Co^{2+}}$[b,e]	$10^{-3}K_{sv}$,[d] M^{-1}	$10^{-9}k_q$,[e] M^{-1} s^{-1}
$Co(bpy)_3^{3+}$	1.58 ± 0.08	0.52 ± 0.02	1.36 ± 0.02	2.27 ± 0.15
$Co(phen)_3^{3+}$	4.4 ± 1.0	1.1 ± 0.3	1.31 ± 0.03	2.18 ± 0.15

[a] $\mu = 1.0$ M; $T = 25$ °C. [b] Determined in solutions containing 1.5 × 10^{-4} M $Ru(bpy)_3^{2+}$ and 10^{-3} M Co(III) complex; λ_{ex} 350 nm. [c] Samples excited with 452-nm radiation and emission monitored at 588 nm. Corrections for trivial effects made by using standard equations.[2d] [d] Calculated by assuming $\tau_0 = 600 \pm 20$ ns. [e] Calculated by assuming $\phi_{Co^{2+}} < {}^1/_3\phi_{aq}$ (see text).

Thus, the complexes $[Co(phen)_3](ClO_4)_3{\cdot}3H_2O$ and $[Co(bpy)_3](ClO_4)_3{\cdot}3H_2O$ used in these experiments were prepared by procedures described in the literature[7a] but were twice crystallized from distilled water which contained 30% H_2O_2. The absorption spectra of the complexes were in good agreement with the spectral data reported in the literature.[8a] $Co(phen)_3^{2+}$ and $Co(bpy)_3^{2+}$ were prepared in situ. An aqueous solution containing a 10-fold excess of the ligand[9] was degassed by repeated freeze–thaw cycles and then mixed under the same conditions with a known weight of $CoCl_2{\cdot}6H_2O$. The absorption spectra of these cobalt complexes were in excellent agreement with published spectra.[8a] Other chemicals used in these experiments were reagent grade, and solutions were prepared with water distilled in a Corning distillation apparatus. Unless otherwise specified, experiments were carried out in solutions deaerated by N_2 bubbling and at an ionic strength of 1.0 M (0.333 M Na_2SO_4 and 0.01 M H_2SO_4).

Photolysis Procedures. The steady-state photolysis equipment used in these experiments has been previously described.[11] The basic flash apparatus used in these experiments has also been previously described[11] but was slightly modified for these experiments. A Bausch and Lomb Model 33-86-08 grating monochromator was used to spectrally resolve the analyzing beam, and the intensity of the beam was monitored with a Hamamatsu R818 red-sensitive photomultiplier. To prevent a direct ultraviolet photolysis of these Co(III) complexes by the analyzing beam, a Plexiglas filter, which transmitted λ >350 nm, or a red filter, which transmitted λ >600 nm, was placed between the analyzing lamp and flash cell.

Approximately 15–20% reaction was induced by exposure of the samples to 250–350-J flashes. This is an appreciable amount of conversion, but the extinction coefficient of $Ru(bpy)_3^{3+}$ is not large at the analyzing wavelength of 675 nm. For improvement of the signal, the photomultiplier current was dropped across a 150 K resistor. Although this increased the RC time constant to 3.2 μs, this time was short in comparison to the time duration of the signal (see Figure 1).

The solutions were contained in the 1.2 cm diameter × 17 cm inner annulus of the flash cell. Distilled water from a Haake FK2 constant-temperature bath was pumped through the 3.0 cm diameter × 20 cm outer annulus of the cell to thermostat the solutions to a given temperature. Kinetics measurements, carried out in a spectrophotometer, and steady-state photolysis experiments were made with solutions thermostated to 25 ± 0.1 °C.

The photolyte from the steady-state and flash photolysis experiments were analyzed for Co(II) by the thiocyanate method,[10] but the reliability of the measurement is questionable. The principal difficulty, at least for these and other systems we have studied,[12] arises from a precipitation of the supporting electrolyte when acetone is added to develop the Co^{II}–SCN^- color. The precipitate appears to carry down with itself varying amounts of Co(II). Because of this uncertainty, the upper limits of the yields of Co(II), $\phi_{Co(II)}$, reported in this paper were taken as one-third of the yield of the free ligand. The latter species were analyzed by the $CHCl_3$ extraction method described by Moggi and co-workers.[13]

---

(6) C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2858 (1975).

(7) (a) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3577 (1952); (b) P. Ellis, R. G. Wilkins, and M. J. G. Williams, *ibid.*, 4456 (1957); (c) B. R. Baker, F. Basolo, and H. M. Neumann, *J. Phys. Chem.*, **63**, 371 (1959); (d) R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 341 (1962).

(8) (a) R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966); (b) T. J. Przystas and N. Sutin, *J. Am. Chem. Soc.*, **95**, 5545 (1973).

(9) G. Anderegg, *Helv. Chim. Acta*, **46**, 2397 (1963).

(10) E. Kitson, *Anal. Chem.*, **22**, 664 (1950). In applying this scheme to determine the amount of $Co(phen)_3^{2+}$ present in a sample of $Co(phen)_3^{3+}$, we have found it necessary to run the analysis in 2 M acid (HCl or $HClO_4$). Apparently, the acid is necessary to ensure a complete dissociation of $Co(phen)_3^{2+}$; otherwise the amount of Co^{2+} detected in samples containing known amounts of $Co(phen)_3^{2+}$ was 40–60% less than that expected.

(11) M. Katz and H. D. Gafney, *Inorg. Chem.*, **17**, 93 (1978).

(12) P. Fisher, E. Finkenberg, S. M. Huang, and H. D. Gafney, *J. Phys. Chem.*, **82**, 526 (1978).

Physical Measurements. Electronic absorption spectra were recorded on a Cary 14 or Techtron 635 spectrophotometer. The latter instrument was equipped with thermostated cell holders and was used to make kinetic measurements. Emission spectra were recorded on a Perkin-Elmer MPF-2A emission spectrophotometer. Infrared spectra of the complexes were recorded on a Perkin-Elmer 237B spectrophotometer calibrated against polystyrene.

Results

The luminescent charge-transfer state of $Ru(bpy)_3^{2+}$ is efficiently quenched by $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$.[2f] The Stern–Volmer constants, K_{sv}, and bimolecular rate constants, k_q, which describe the dynamics of these quenching reactions are listed in Table I. The bimolecular rate constants are calculated from the relation $K_{sv} = k_q\tau_0$ where τ_0, the radiative lifetime of $*Ru(bpy)_3^{2+}$, is taken to be 600 ± 20 ns.[2d] Comparing the calculated values of k_q with the theoretical diffusion limit, $\sim 6 \times 10^9$ M^{-1} s^{-1},[14] indicates that quenching occurs rapidly and occurs with relatively high efficiency.

Steady-state photolysis experiments, however, indicate that the quenching process induces only a slight net reaction in these Co(III) substrates. Solutions containing 1.5×10^{-4} M $Ru(bpy)_3^{2+}$ and either 10^{-3} M $Co(phen)_3^{3+}$ or 10^{-3} M $Co(bpy)_3^{3+}$ were exposed to 350-nm radiation in a Rayonet reactor (95% of the light is absorbed by the Ru(II) complex). The visible spectra of the solutions, recorded before and after extensive photolysis, were identical. The ultraviolet spectra of chloroform extracts of the photolyte, however, showed that a small amount of the free ligand was formed in the respective photolyses. The quantum yields for these aquation processes are listed in Table I. The photolytes were also analyzed for Co(II) by the thiocyanate procedure, but the results of these tests were inconclusive (see Experimental Section). Thus, the upper limits of $\phi_{Co(II)}$ reported in Table I are taken to be one-third of the yields of the ligands.

If the experiment is repeated in a flash photolysis apparatus, however, the transient absorbance shown in Figure 1 is detected at 675 nm. In these flash photolysis experiments, the concentrations of the Co(III) substrates were the same as that used in the steady-state experiments, but the concentration of $Ru(bpy)_3^{2+}$ was decreased to 7.5×10^{-5} M to obtain a more uniform cross-sectional absorbance. The redox properties of $*Ru(bpy)_3^{2+}$ are well established,[2] yet we were concerned that the transient being observed might be due to a reaction other than that between $*Ru(bpy)_3^{2+}$ and these Co(III) complexes. The experimental data, however, negate such a possibility. The amount of transient formed in the flash, determined by extrapolation of the decays to $t = 0$, was proportional to the initial concentration of the Co(III) complex. Also, flash photolysis of either the individual Co(III) and Ru(II) complexes or solutions containing 7.5×10^{-5} M $Ru(bpy)_3^{2+}$ and 10^{-3} M bpy or phen did not produce any transient absorbance in the 550–800-nm region.

The spectrum of the transient, shown in Figure 2, was obtained by exposing solutions which contained 7.5×10^{-5} M $Ru(bpy)_3^{2+}$ and 10^{-3} M Co(III) substrate to 245-J flashes. Following the flash, the solutions were analyzed at various wavelengths from 560 to 850 nm. The absorbance of the transient, A_0, was obtained by extrapolating to $t = 0$ plots of $1/A$ vs. time. At each wavelength, the plots were linear and yielded rate constants which were identical within experimental error. The values of A_0 determined at the various wavelengths relative to that determined at 675 nm differed by less than 3% from similar ratios calculated from the extinction coefficients of $Ru(bpy)_3^{3+}$. As indicated by Figure 2, the spectrum of the transient is in excellent agreement with the spectrum of $Ru(bpy)_3^{3+}$ and established $Ru(bpy)_3^{3+}$ as a product of the photochemical reaction.

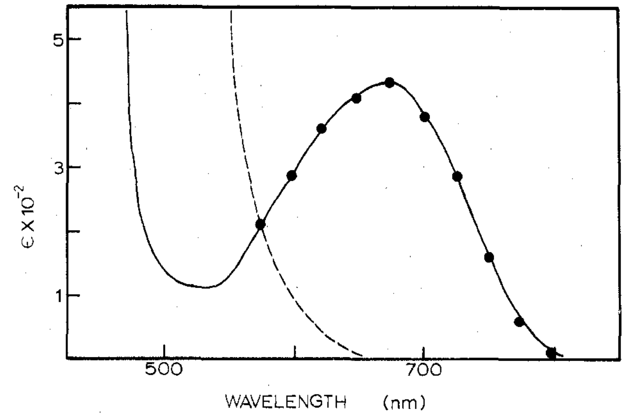


Figure 2. Relative absorbances (●) of the transient observed on 245-J flash photolysis of solutions containing 7.5×10^{-5} M $Ru(bpy)_3^{2+}$ and 10^{-3} M $Co(phen)_3^{3+}$ or $Co(bpy)_3^{3+}$. Spectra of $Ru(bpy)_3^{2+}$ (---) and $Ru(bpy)_3^{2+}$ (—) are shown.

The intense absorptions of Ru(II) and Ru(III) complexes, however, mask the weaker absorptions of $Co(bpy)_3^{2+}$ and $Co(phen)_3^{2+}$ in the visible region. Thus, spectral characterization of the Co(II) product was not possible in these experiments. In the ultraviolet region, however, the high concentration and strong absorptivity make these Co(III) complexes the dominant absorbing species. To ensure that the reaction was not induced by excitation of the Co(III) complex, we filled the outer annulus of the flash cell with 0.0162 M $K_3Fe(ox)_3$ which only transmitted $\lambda > 420$ nm. Under these conditions, flash photolysis of a 7.5×10^{-5} M $Ru(bpy)_3^{2+}$ and 10^{-3} M $Co(phen)_3^{3+}$ solution (95% of the light is absorbed by the Ru(II) complex) led to the transient signal in high yield.

These results, the appearance of $Ru(bpy)_3^{3+}$, and the proportionality of A_0 to the initial concentration of the Co(III) substrate establish the photochemical reaction to be

$$*Ru(bpy)_3^{2+} + CoL_3^{3+} \rightarrow R(bpy)_3^{3+} + CoL_3^{2+} \quad (3)$$

This photochemical reaction is then followed by a rapid reverse reaction, eq 1 or 2.

The differential equations which describe the flash profile, the decay of $*Ru(bpy)_3^{2+}$, the rate of the quenching reaction, and eq 1 or 2 were solved by the Runge–Kutta method.[15] The analysis indicates that quenching and the formation of the redox products occur within the first 15 μs of the flash duration, ca. 30 μs. Thus, the photochemical reaction simply displaces the equilibrium, and the transient absorbance is amenable to analysis of a bimolecular redox reaction. There are, however, potential difficulties in the analysis of these reverse reactions. $Ru(bpy)_3^{3+}$ is thermally unstable and reverts to $Ru(bpy)_3^{2+}$. A number of measurements of the rate made at 25 °C and $\mu = 1.0$ M (0.333 M Na_2SO_4 and 0.01 M H_2SO_4) yielded $k = (6.53 \pm 0.17) \times 10^{-5}$ s^{-1}. The value is in reasonable agreement with previous determinations[6] and establishes that a thermal decay would not be competitive with these electron-transfer reactions.

A potentially more serious difficulty, however, is the possibility of aquation of the Co(II) complexes. For $Co(phen)_3^{2+}$, k_{aq} is 0.174 s^{-1} in a 1 M perchlorate medium.[8b,16] Although the aquation rate may be somewhat different in this sulfate medium, the difference would be small and aquation would

---

(13) L. Moggi, N. Sabbatini, and O. Traverso, *Mol. Photochem.*, 5, 11 (1973).

(14) Calculated from the Smoluchowski equation neglecting electrostatic repulsions: S. W. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill, New York, 1960, p 498.

(15) F. B. Hildebrand, "Introduction to Numerical Analysis", 2nd ed., McGraw-Hill, New York, 1974.

(16) P. Ellis and R. G. Wilkins, *J. Chem. Soc.*, 299 (1959).

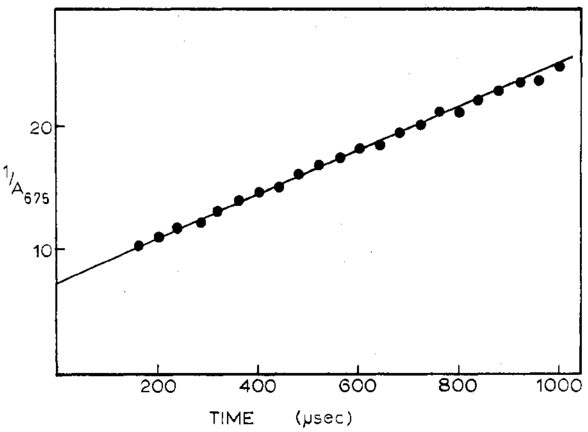


Figure 3. Second-order plot of the decay of the transient monitored at 675 nm. Initial concentrations: [$Ru(bpy)_3^{2+}$] = 7.5 × 10^{-5} M, [$Co(phen)_3^{3+}$] = 1.0 × 10^{-3} M.

Table II. Rate Constants and Activation Energies for the $Ru(bpy)_3^{3+}$ Reactions

$10^3[CoL_3^{3+}]$,[a] M	$10^{-8}k_{av}$,[b] M^{-1} s^{-1}	E_a, kcal/mol
2.00[c]	1.46 ± 0.25 (3)	−1.1 ± 0.9
1.00[c]	1.35 ± 0.26 (7)	
0.75[c]	1.15 ± 0.17 (7)	
0.50[c]	1.71 ± 0.27 (5)	
0.25[c]	1.15 ± 0.09 (3)	
1.00[d]	2.46 ± 0.41 (5)	−2.82 ± 0.41
0.50[d]	2.37 ± 0.24 (3)	

[a] Initial concentrations; [$Ru(bpy)_3^{2+}$] = 7.5 × 10^{-5} M. [b] μ = 1.0 M, T = 25 °C; number in parentheses indicates number of measurements. [c] Measurements with $Co(phen)_3^{3+}$. [d] Measurements with $Co(bpy)_3^{3+}$.

not be competitive with the electron-transfer reaction given by eq 1. With $Co(bpy)_3^{2+}$, aquation is more rapid, k_{aq} = 32 s^{-1} (1 M acid),[17] and ruling out a competitive aquation is somewhat more tenuous. Nevertheless, the assumption that aquation of these Co(II) complexes is negligible is justified by the experimental data. A competitive aquation would require the formation of the free ligand, yet analyses of the flashed solutions were negative. Aquation might also be expected to cause some nonlinearity in the kinetic analysis, but as indicated by Figure 3, plots of $1/A$ vs. time were linear through ca. 80% of the reaction. Furthermore, the decay of the transient was independent of the number of times the sample was exposed to flash; the rate constant obtained after as many as 10 flashes was within experimental error of that obtained after the first flash.

Polaroid photographs of the oscilloscope traces, one of which is shown in Figure 1, were analyzed according to second-order kinetics for equimolar concentrations of the Ru(III) and Co(II) complexes. As indicated by Figure 3, the plots of $1/A$ vs. time were linear, and the rate constants obtained from these plots are summarized in Table II. A number of kinetic measurements were also carried out under pseudo-first-order conditions. Solutions containing 7.5 × 10^{-5} M $Ru(bpy)_3^{2+}$, 7.5 × 10^{-4} M $Co(phen)_3^{3+}$, and 1.0 × 10^{-4} M $Co(phen)_3^{2+}$ were exposed to a 245-J flash and monitored at 675 nm. The transient is short-lived and was monitored on a 20 μs/division scan rate. At these scan rates, however, light scattered during the flash, ca. 30 μs, introduces an uncertainty in the analysis of the transient decay. Plots of ln (A_0/A) vs. time had a slight upward curvature during the first 30 μs of the decay but were linear for longer times. From the linear portion of the plots, a series of five experiments yielded an average rate constant of (1.4 ± 0.9) × 10^4 s^{-1}. The second-order rate constant is obtained by dividing these first-order rate constants by the concentration of $Co(phen)_3^{2+}$ present in the flash solution; i.e., the $Co(phen)_3^{2+}$ formed in the flash and calculated from A_0 plus the amount added initially, 1.0 × 10^{-4} M, is (1.4 ± 0.9) × 10^8 M^{-1} s^{-1}. In view of uncertainty associated with the tail in the flash and aquation of the Co(II) complex, the value is in reasonable agreement with the rate constants listed in Table II.

The activation parameters for reactions 1 and 2 were determined by 245-J flash photolysis of 7.5 × 10^{-5} M $Ru(bpy)_3^{2+}$ and 10^{-3} M $Co(phen)_3^{3+}$ or $Co(bpy)_3^{3+}$ solution. These solutions were thermostated to 5, 10, 15, 25, 35, and 45 °C, but at the two higher temperatures plots of $1/A$ vs. time showed a distinct upward curvature. Because of this nonlinearity, the activation parameters listed in Table II were determined from data obtained at the lower temperatures.

It has been suggested, but as yet not experimentally detected, that an intermediate in the redox reactions of these Co(III) complexes is an excited state of the Co(II) complex which has a coordinated ligand radical anion.[18] Thus, in a number of flash photolysis experiments, detection of this possible reaction intermediate was sought. In these experiments, the samples were analyzed at the isosbestic point in the spectra of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$. At this wavelength, 568 nm, the extinction coefficients of the Co(II) and Co(III) complexes, $\epsilon \leq 10$ M^{-1} cm^{-1}, are insufficient to induce a measurable change in optical density, and, of course, no change would be induced by the ruthenium complexes. On the other hand, pulse radiolysis studies, principally done with $Co(bpy)_3^{3+}$, have shown that the intermediate having a coordinated ligand radical anion absorbs at 568 nm, $\epsilon \sim$300–600 M^{-1} cm^{-1}, and decays at a relatively slow rate, $k \approx 10^4$–10^5 s^{-1}. Since bipyridine and phenanthroline are similar ligands, both $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$ were used in these flash experiments. Solutions containing 7.5 × 10^{-5} M $Ru(bpy)_3^{2+}$ and 10^{-3} or 5 × 10^{-4} M Co(III) complex were exposed to a 300-J flash and monitored at 568 nm. We were unable to detect, however, any indication of this intermediate during the flash or any change in absorbance, $\Delta A \leq 0.02$, which persisted for longer than 20 μs.

Discussion

Our interest in the reactions of $*Ru(bpy)_3^{2+}$ with the tris(bipyridine) and -(phenanthroline) complexes of Co(III) was spurred by Waltz and Pearson's report of a transient intermediate in the γ radiolysis of aqueous solutions of $(bpy)_3^{3+}$.[19] The transient, whose spectral and kinetic parameters are listed above, was attributed to a low-spin $Co(bpy)_3^{2+}$ species. These findings were subsequently confirmed by Baxendale and Fiti,[18] but they present convincing evidence that the transient absorbance is due to an excited state of $Co(bpy)_3^{2+}$ which has a coordinated bipyridine radical anion. This coordinated radical anion species has been proposed as an intermediate in the thermal redox reactions of these Co(III) complexes, but some question remains, however, as to whether these thermal redox reactions are sufficiently exothermic to produce a radical anion intermediate.[8b] Since the quenching of $*Ru(bpy)_3^{2+}$ by these Co(III) substrates proceeds with a high exothermicity, $\Delta G \approx -1.2$ eV, detection of this possible reaction intermediate was sought in a number of flash photolysis experiments. In these experiments, the solutions were monitored at 568 nm, the isosbestic point in the spectra of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$. Under identical conditions of concentration and flash energy, analysis at 675 nm indicates that the flash induces 20%

---

(17) R. Farina, R. Hogg, and R. G. Wilkins, *Inorg. Chem.*, 7, 170 (1968).

(18) J. H. Baxendale and M. Fiti, *J. Chem. Soc., Dalton Trans.*, 1995 (1972).

(19) W. L. Waltz and R. G. Pearson, *J. Phys. Chem.*, 73, 1941 (1969).

Table III. Comparison of Observed and Calculated Rate Constants

reactants	$E°$,[a,b] V	k_{ex},[a] $M^{-1}\ s^{-1}$	k_{calcd},[c] $M^{-1}\ s^{-1}$	k_{obsd},[c] $M^{-1}\ s^{-1}$
$*Ru(bpy)_3^{2+}$, $Co(bpy)_3^{3+}$	−0.84,[d] 0.37[f]	2×10^9, 7[f]	2.9×10^9	$(2.27 \pm 0.15) \times 10^9$
$*Ru(bpy)_3^{2+}$, $Co(phen)_3^{3+}$	−0.84,[d] 0.42[f]	2×10^9, 44[g]	2.9×10^9	$(2.18 \pm 0.15) \times 10^9$
$Ru(bpy)_3^{3+}$, $Co(bpy)_3^{2+}$	1.24,[e] −0.37[f]	2×10^9, 7[f]	2.5×10^9	$(2.42 \pm 0.51) \times 10^8$
$Ru(bpy)_3^{3+}$, $Co(phen)_3^{2+}$	1.24,[e] −0.42[f]	2×10^9, 44[g]	2.8×10^9	$(1.36 \pm 0.48) \times 10^8$

[a] Potentials and exchange rates are in the same order as the reactants. [b] Written as $M^{3+} + e^- \rightarrow M^{2+}$ for each reactant. [c] At 25 °C and μ = 1.0 M; corrected for diffusion effects. [d] Reference 2f. [e] F. E. Lytle and D. M. Hercules, *Photochem. Photobiol.*, 13, 123 (1971). [f] Reference 8b. [g] A. Haim and N. Sutin, *Inorg. Chem.*, **15**, 476 (1976).

reaction. On the assumption that each quenching encounter which leads to $Ru(bpy)_3^{3+}$ also forms an equal concentration of the radical anion intermediate, X, the change in absorbance at 568 nm, ΔA, due to X is calculated to be 0.12.[20] Although the calculated ΔA is similar to that observed at 675 nm (Figures 1 and 2), at 568 nm we were unable to detect any indication, $\Delta A \leq 0.02$, of the intermediate X either during the last 10 μs of the flash or immediately after the flash.

The absence of a transient absorbance at 568 nm, however, is not considered conclusive evidence to rule out this intermediate in these quenching reactions. Baxendale and Fiti reported that the coordinated radical anion intermediate is rapidly scavenged by the original Co(III) substrate.[18] Since relatively high concentrations of the Co(III) substrate were used, it is questionable whether the intermediate could be detected in these flash experiments.

It is our opinion, however, that a distinct coordinated radical anion, X, is not an intermediate in these electron-transfer quenching reactions. The rapid rate at which X reduces $Co(bpy)_3^{3+}$ suggests that X is a facile reductant.[18] Since $Ru(bpy)_3^{3+}$ is a strong and facile oxidant, we would expect that the reaction

$$[X,Ru(bpy)_3^{3+}] \rightarrow Ru(bpy)_3^{2+} + Co(bpy)_3^{3+} \qquad (4)$$

would occur prior to the separation of the reaction pair, indicated by the brackets. In other words, quenching would not lead to the reaction products $Co(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$. Yet, quantum yield measurements, which will be detailed elsewhere, indicate that the quantum yield of $Ru(bpy)_3^{3+}$ is >0.50.[21]

This reasoning, which is based on the kinetics of these reactions, is not intended to imply that electron transfer cannot occur through the π system but rather to imply that, if electron transfer does occur through the π system of these ligands, at no time during the course of the reaction does a coordinated radical anion species exist as a separate and distinct intermediate. This conclusion is somewhat analogous to the recent postulation by Sutin and co-workers that the absence of back-bonding should preclude a π–π^* pathway in the self-exchange reactions of $Co(phen)_3^{2+/3+}$.[4]

Spectral characterization of $Ru(bpy)_3^{3+}$ in the photolyte (Figure 2) indicates that quenching occurs by an electron-transfer mechanism. The quenching reaction is followed by a rapid exothermic back-reaction, reaction 1 or 2, which regenerates the original ground-state reactions. The rate constants for these electron-transfer reactions can be compared to the electron-transfer rate constants calculated from the Marcus equations

$$k_{12} = (k_{11}k_{22}fK_{12})^{1/2} \qquad (5)$$

$$\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \qquad (6)$$

where the symbols have there usual significance.[5] Using the parameters listed in Table III, the Marcus equations yield $6.6 \times 10^{10}\ M^{-1}\ s^{-1}$ for the quenching of $*Ru(bpy)_3^{2+}$ by $Co(bpy)_3^{3+}$ and $9.8 \times 10^{10}\ M^{-1}\ s^{-1}$ for the quenching by $Co(phen)_3^{3+}$. On the assumption that these calculated rate constants, which we will designate k_M, represent the rate constants when diffusion is infinitely rapid, corrections for diffusion effects can be made according to

$$1/k_{calcd} = 1/k_D + 1/k_M \qquad (7)$$

where k_D is the rate constant for diffusion.[3,22] The electrostatic repulsions for these cationic reactants are a minimum at an ionic strength of 1.0 M, but the uncertainty in the parameters used in the Smoluchowski equation makes the calculated diffusion limit one of questionable usefulness.[14] Instead, the value of k_D, $3 \times 10^9\ M^{-1}\ s^{-1}$, is taken from recent studies of the quenching of $*Ru(bpy)_3^{2+}$.[3,4] By substitution of this value for k_D and the values calculated from the Marcus equations for k_M, eq 7 yields $k_{calcd} = 2.9 \times 10^9\ M^{-1}\ s^{-1}$ for the reactions of $*Ru(bpy)_3^{2+}$ with $Co(bpy)_3^{2+}$ or $Co(phen)_3^{3+}$.

Using the parameters listed in Table III in a similar manner, eq 5 and 6 yield $k_M = 1.7 \times 10^{10}\ M^{-1}\ s^{-1}$ for reaction 1 and $k_M = 1.4 \times 10^{10}\ M^{-1}\ s^{-1}$ for reaction 2. Unlike the quenching reactions which are photochemically driven, reactions 1 and 2 are chemically activated. In computation of the rate constants for reactions 1 and 2 via eq 5 and 6, the assumption is made that diffusion is infinitely rapid.[3] To correct for diffusion effects through eq 7, we assume that $k_D = 3 \times 10^9\ M^{-1}\ s^{-1}$.[3,4] The assumption appears justified, however, since the overall charge on the reactants, 5+, is identical with that in the quenching reactions, and the sizes of the different oxidation states of the complexes are very similar.[23] Substituting $1.7 \times 10^{10}\ M^{-1}\ s^{-1}$ for k_M and $3 \times 10^9\ M^{-1}\ s^{-1}$ for k_D in eq 8 yields $k_{calcd} = 2.8 \times 10^9\ M^{-1}\ s^{-1}$ for the reaction between $Ru(bpy)_3^{3+}$ and $Co(phen)_3^{2+}$. The same calculation, except that $k_M = 1.4 \times 10^{10}\ M^{-1}\ s^{-1}$, yields $k_{calcd} = 2.5 \times 10^9\ M^{-1}\ s^{-1}$ for the reaction between $Ru(bpy)_3^{3+}$ and $Co(bpy)_3^{2+}$.

The experimental values of the quenching rate constants listed in Table I were obtained from the relation $K_{sv} = k_b\tau_0$ where τ_0 is the radiative lifetime of $*Ru(bpy)_3^{2+}$, 600 ± 20 ns.[2d] When compared to the calculated rate constants, Table III, the agreement is quite good. Yet, to claim that this agreement implies that the nonadiabaticities associated with the reduction of these Co(III) complexes are small or nonexistent is somewhat premature. To make such a claim implies that the electron-transfer reaction occurs by a Marcus path where nuclear tunneling contributions have been neglected. In these rather exothermic quenching reactions, however, $\log K_{12} \simeq 2 \log (Z^2/k_{11}k_{22})$. For example, $\log K_{12}$ for the electron-transfer quenching of $*Ru(bpy)_3^{2+}$ by $Co(phen)_3^{3+}$ is 21.35, while $2 \log (Z^2/k_{11}k_{22})$ is 23.1. Since the values of these

---

[20] The calculated ΔA is the product of the assumed concentration of the coordinated radical anion intermediate, 1.55×10^{-5} M; the path length of the flash cell, 17 cm; and the average of the extinction coefficient reported by Waltz and Pearson, 450 $M^{-1}\ cm^{-1}$. The latter appears to be a conservative estimate, however, in view of the reported spectrum for the 2,2′-bipyridine monoanion: E. Konig and S. Kremer, *Chem. Phys. Lett.*, **5**, 87 (1970).

[21] R. Berkoff, K. Krist, and H. D. Gafney, manuscript in preparation.

[22] R. M. Noyes, *Prog. React. Kinet.*, **1**, 129 (1961).

[23] Although the sizes of the different oxidation states are very similar, the analogy may not be precisely correct since the effective reaction volume of $*Ru(bpy)_3^{2+}$ may be larger than that of $Ru(bpy)_3^{3+}$. The larger size might be expected since the excited complex has additional electron density in a ligand π^* orbital.

factors are quite similar, we assume that nuclear tunneling effects may contribute to the observed electron-transfer quenching rate constant.

For the reduction of Ru(bpy)$_3^{3+}$ by Co(phen)$_3^{2+}$, on the other hand, log K_{12}, 14.0, is less than 2 log $(Z^2/k_{11}k_{22})$, 23.1. These back-reactions then are not within the nonadiabatic (nuclear tunneling) region. For these chemically activated redox reactions, the rate constants listed in Table III show that the calculated diffusion-corrected rate constants, k_{calcd}, are about an order of magnitude larger than the observed rate constants, k_{obsd}, determined at 25 °C. The difference in the observed and calculated rate constants is not due to the approximation made for k_{D}. A k_{D} of ca. 10^8 M^{-1} s^{-1} would be needed to obtain agreement, but such a slow rate appears unreasonable, however, when k_{q} from the quenching experiments is $\geq 10^9$ M^{-1} s^{-1}.

When the rates measured in these experiments where the reactants are generated in situ are compared to the calculated rates, the obvious concern is that the reaction being monitored corresponds to that proposed, i.e., reactions 1 and 2. It might be assumed that the difference in k_{obsd} and k_{calcd} is due to an aquation of the Co(II) complex prior to the reverse reaction. Such an assumption receives, however, little support from the experimental data. The reported rates of aquation of Co(phen)$_3^{2+}$[8b] and Co(bpy)$_3^{2+}$[17] are slow and would not be competitive with the electron-transfer reaction. The rates of aquation, however, were measured in an ionic medium slightly different from that used in these experiments, but the steady-state and flash photolysis experiments indicate that aquation of the Co(II) complex is negligible. The quantum yields of aquation, listed in Table I, indicate that the aquated product would be formed in less than 1% yield in the flash experiments. Furthermore, if aquation did occur, each flash the sample is exposed to would change the composition of the solution and we would expect a change in the rates of reactions 1 and 2. Yet we find that the rate constant obtained from the flash experiments is independent of the number of times, at least through 10 flashes, that the sample is exposed to the flash.

Although the rates indicate that the overall aquation of these Co(II) complexes would not be competitive with reactions 1 and 2, the initial aquation product, a Co(II) complex with a monodentate ligand, would be formed more rapidly.[17] It is feasible then that the back-reactions might involve a partially dissociated Co(II) species. With the bipyridine ligand where a pyridine moiety can rotate about the C–C linkage, a monodentate intermediate is possible. The distortion reduces the symmetry of the Co(II) complex and would be expected to enhance the absorption spectrum of the intermediate, yet the spectrum of the transient, Figure 2, gave no indication of such a species. The phenanthroline ligand is more rigid, however, and would be less likely to undergo the necessary distortion to form a monodentate intermediate. Since the rates found with both Co(II) complexes are similar and no spectral evidence for a monodentate intermediate was found, we discount these possible intermediates.

The difference in the k_{calcd} and k_{obsd} for reactions 1 and 2 is not due to an intervening chemical reaction; rather the difference must lie in the nonadiabaticities associated with the electron-transfer reactions. Previous studies of the rates of oxidation or reduction of these cobalt complexes have suggested that the nonadiabaticity lies in either the hydrophobic–hydrophilic interaction or the spin change which occurs in the cobalt complexes.[8b] The similarity of the coordination shells or Ru(III) and Co(II), however, suggests that the barriers associated with a hydrophobic–hydrophilic interaction must be very slight or nonexistent.

We also find it difficult to attribute the slowness of the observed rate to a spin change in the Co(II) complex. If the high-spin Co(II) complex, which has a $t_{2g}^5e_g^2$ configuration, rearranged to a low-spin $t_{2g}^6e_g^1$ configuration prior to electron transfer, we would expect that the energy of activation would reflect the energy required to form this excited state. By use of the crystal-field parameters reported by Palmer and Piper[8a] for Co(bpy)$_3^{2+}$, an estimate of 15–16 kcal/mol for a $^4T_1(t_{2g}^5e_g^2) \rightarrow {}^2E(t_{2g}^6e_g^1)$ transition is obtained from a Tanabe–Sugano diagram of a d^7 system. Although the experimental error is large, the energies of activation, <2.0 kcal/mol, are too small, in our opinion, to be consistent with a preequilibrium spin change.

Electron transfer prior to a spin change, on the other hand, leaves the Co(III) complex in a $t_{2g}^5e_g^1$ configuration. In a formal sense, the subsequent relaxation, a $t_{2g}^5e_{2g}^1$ to t_{2g}^6 transition, is analogous to a phosphorescent decay. The absence of an emission detected from these Co(III) complexes, however, negates estimating the activation energy for this process. For a series of bis(*N*-R-2,6-pyridinedicarboxaldimine)cobalt(II) complexes, recent measurements have shown that the rate constants for the $^2E \rightarrow {}^4T$ transitions are on the order of 10^7 s^{-1}.[24] The rates are sufficiently slow to be taken as prima facie evidence that spin conversions may have a retarding effect on the overall rate of electron transfer. On the other hand, these complexes differ substantially from the bipyridine and phenanthroline complexes. With the more analogous Co(terpy)$_2^{2+}$, however, spin-relaxation times are ≤30 ns.[24] It would appear then that spin-multiplicity restrictions are not a wholly satisfactory rationale for the generally sluggish electron-transfer rates for these cobalt complexes.[8b]

Perhaps, the difference in k_{obsd} and k_{calcd} can be attributed to a mismatch between detailed path for electron transfer for the cross reaction and that for the self-exchange reactions of the reactants.[4] The absence of back-bonding in the cobalt complexes precludes a π^*–π^* pathway, while the back-bonding in the ruthenium complex could provide for a π^*–π^* pathway. The cross reaction may proceed by a CoL$_3^{2+}$ d–Ru(bpy)$_3^{3+}$ π^* overlap where the overlap may be considerably poorer than that in the individual exchange reactions.

In applying the Marcus equations to these electron-transfer reactions, we are impressed not only by their predictive power but also by the uncertainty in the variables used in the equations. Sutin and co-workers have pointed out that, for much slower reactions, $k = 10^4$ M^{-1} s^{-1}, Marcus theory is generally successful in predicting rate constants between 2+ and 3+ charged reactants to within a factor of 25.[4] Although reactions 1 and 2 are considerably faster and involve possible nonadiabatic factors such as spin changes and mismatched reaction pathways, the differences in k_{obsd} and k_{calcd} are within this uncertainty. This suggests then that either the nonadiabatic factors have accidentally canceled each other out or, at least for these reactants, that the factors are much smaller than anticipated by analogy to various thermal redox reactions involving these cobalt complexes. The equations involving the nonadiabatic factors (designated p in eq 11 of ref 5) reduce to the adiabatic equations, eq 6 and 7, when $p_{12} \sim (P_{11}P_{22})^{1/2}$ and log $f \approx 1$; since f for reactions 1 and 2 is ca. 10^{-5}, accidental cancelation seems unlikely. Thus, the rough agreement found between k_{obsd} and k_{calcd} suggests that the nonadiabaticities associated with the spin multiplicities of the cobalt complexes or the mixed d–π^* pathway for electron transfer have only a slight retarding effect on these electron-transfer rates.

Conclusion

Co(phen)$_3^{3+}$ and Co(bpy)$_3^{3+}$ quench *Ru(bpy)$_3^{2+}$ at essentially a diffusion-controlled rate and lead to electron-

---

(24) M. G. Simmons and L. J. Wilson, *Inorg. Chem.* **16**, 126 (1977).

transfer products in relatively high yield. The bimolecular rate constant for quenching is essentially diffusion controlled, and the reaction parameters suggest that nuclear tunneling may be involved in the quenching reaction. The high yield of electron-transfer products observed on flash photolysis suggests that an excited state of the Co(II) complex which has a coordinated radical–anion is not a distinct intermediate in these quenching reactions.

The products of the quenching reaction, the Ru(III) and Co(II) complexes, rapidly revert to the initial reactants, the Ru(II) and Co(III) complexes. The rate constant for the back-reaction is approximately an order of magnitude smaller than the diffusion-corrected calculated rate constant, but within the expected agreement for a reaction between 2+ and 3+ reactants. The agreement suggests that the nonadiabaticities associated with spin multiplicities and mixed d–π^* pathways have only a slight retarding effect on the rate of these redox reactions.

Acknowledgment. We gratefully acknowledge a number of helpful discussions with Professor Albert Haim of The State University of New York at Stony Brook. Financial support of this research from the Research Corp. and The Research Foundation of The City University of New York is gratefully acknowledged.

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Co(bpy)_3^{3+}$, 19052-39-2; $Co(phen)_3^{3+}$, 18581-79-8; $Ru(bpy)_3^{3+}$, 18955-01-6; $Co(bpy)_3^{2+}$, 15878-95-2; $Co(phen)_3^{2+}$, 16788-34-4.

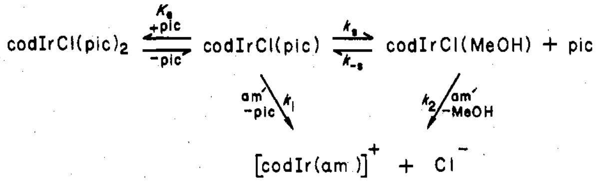
Contribution from the National Chemical Research Laboratory,
South African Council for Scientific and Industrial Research, Pretoria 0001, Republic of South Africa

Kinetics and Mechanism of the Reactions of (1,5-Cyclooctadiene)chloro(picoline)iridium(I) with 2,2′-Bipyridyl and 1,10-Phenanthroline

WYNAND J. LOUW* and CAROL E. HEPNER

Received March 9, 1979

The reactions codIrClY + am′ → codIr(am′)$^+$ + Cl$^-$ + Y {where Y = 2-picoline (pic) or methanol and am′ = 2,2′-bipyridyl (bpy) or 1,10-phenanthroline (phen)} have been studied in methanol spectrophotometrically by a stopped-flow technique. On addition of pic to the reaction solution, it was found that the five-coordinate complex codIrCl(pic)$_2$ was generated. It was also found that the solvo species codIrCl(MeOH) was in a steady state during the reaction. All the data comply with the reaction scheme



from which the rate law

$$k_{obsd} = k_1[am']/(1 + K_e[pic]) + k_s k_2[am']/(k_{-s}[pic] + k_2[am'] + k_2K_e[am'][pic] + k_{-s}K_e[pic]^2)$$

could be derived. When am′ = phen, the contribution of the first term is negligible. Since codIrCl(MeOH) can be generated by dissolving the dimer [codIrCl]$_2$ in methanol, its reaction with am′ could also be studied and thus all the rate and equilibrium constants could be determined.

Introduction

Square-planar substitution reactions of low-spin d^8 metal complexes of the form

$$ML_3X + Y \rightarrow ML_3Y + X \qquad (1)$$

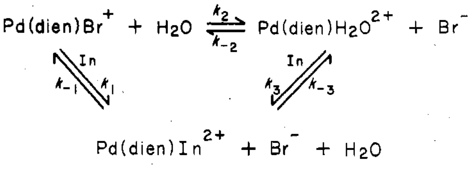
have generally been found[1] to conform to the classic two-term rate law

$$k_{obsd} = k_s + k_y[Y] \qquad (2)$$

where k_s and k_y represent the reactions via a solvent path and direct path, respectively, and [Y] represents the concentration of the incoming nucleophile.

A number of kinetic studies have since shown that the classic rate law 2 could simply be classed as a limiting case of a more general rate law.

The most general case was found for the reaction of Pd(dien)Br$^+$ with inosine[2] in aqueous solution (dien = diethylenetriamine). The proposed mechanism was



giving a rate law of the form

$$k_{obsd} = k_1[In] + k_{-1}[Br^-] + \frac{k_2k_3[In] + k_{-2}k_{-3}[Br^-]}{k_{-2}[Br^-] + k_3[In]} \qquad (3)$$

If the reactions to give the final products are irreversible, i.e., k_{-1} and k_{-3} are zero, and if $k_3[In] \gg k_{-2}[Br^-]$, rate law 3 simplifies to the classical two-term rate law. However, here $k_3[In] \approx k_{-2}[Br^-]$ and the Pd(dien)H$_2$O^{2+} species is in a steady state.

Kennedy, Gosling, and Tobe[3] have recently studied the kinetics of the reaction of $Pt(Me_2S)Cl_3^-$ with a series of amines in methanol to yield $Pt(Me_2S)(am)Cl_2$ + Cl$^-$ and found that

---

[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., Wiley, New York, 1967, Chapter 5.

[2] J. Y. Seguin and M. Zador, *Inorg. Chim. Acta*, **20**, 203 (1976).

[3] B. P. Kennedy, R. Gosling, and M. L. Tobe, *Inorg. Chem.*, **16**, 1745 (1977).