Photophysical and Photochemical Properties of Rhodium(III) Halopentaammine Complexes in Aqueous Solution. Reaction Kinetics of Ligand Field Excited States[1]

Michael A. Bergkamp,[2a] James Brannon,[2b] Doug Magde,[2b] Richard J. Watts,*[2a] and Peter C. Ford*[2a]

Contribution from the Departments of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106, and University of California, San Diego, La Jolla, California 92093. *Received December 8, 1978*

Abstract: Reported are the photoluminescence spectra, lifetimes and quantum yields, and ligand photosubstitution reaction quantum yields for the rhodium(III) complexes $Rh(NH_3)_5Cl^{2+}$ and $Rh(NH_3)_5Br^{2+}$ and their perdeuterated analogues in ambient temperature aqueous solution. When combined with the conclusions based on earlier sensitization studies that intersystem crossing/internal conversion to the lowest energy ligand field states occurs with approximately unitary efficiency, these results allow calculation for the first time of the individual rate constants for the radiative, nonradiative, and reactive deactivation pathways from these excited states for a d^6 complex under photochemically relevant conditions. The perdeuterio complexes demonstrated higher quantum yields for both photosubstitution and photoemission than their perprotio analogues, a result which can be attributed to reduction of the nonradiative deactivation rate constants in the former cases. The correspondence between deuteration effects on excited-state lifetimes and on photoreaction quantum yields indicates that chemical reaction is directly competitive with the other deactivation pathways of the ligand field excited state. Lastly, comparison of the excited state ligand substitution rate constants with those of analogous thermal reactions indicates the excited state reactions to be the faster by 14–15 orders of magnitude.

Recent years have witnessed a surge of interest in the photochemical reactions of transition-metal complexes in fluid solutions.[3] This interest stems from a number of factors, a major one being the basic question of how changes in chemical reactivity resulting from light absorption can be correlated with the differences in the orbital parentages of ground and excited states.[3-5] Ligand field (LF), i.e., d-d, excited states (es) have long been a subject of major photochemical attention, especially for complex ions having the d^3 and low-spin d^6 ground-state (gs) configurations. Among the fundamental reactions a metal complex may undergo is replacement of one ligand by another, e.g., a solvent molecule, and photosubstitution reactions are often the result of the population of LF es. For complexes with the d^6 configuration a wealth of information has accrued concerning the LF photochemistry of numerous transition-metal ions, and these data have stimulated several generalized theoretical interpretations.[5-8]

A major problem in interpreting the photosubstitution induced by LF excitation of d^6 complexes is that most of the available quantitative data is principally concerned with the identity of ligands labilized, reaction product stereochemistry and net quantum yields as functions of various perturbations (ligand fields, solution environment, irradiation energy, etc.). Quantum yields even in their simplest forms are products of several terms, each potentially influenced by systemic perturbations.[3,9,10] Thus there is a clear need for the direct measurement of excited-state properties and dynamics to provide a more fundamental experimental data set for evaluating current theory and for stimulating new or improved treatments. The relatively recent activity in quantitative photophysical measurements[10-16] of transition-metal complexes has introduced valuable new information regarding the nature of the lower energy excited states of photochemically active complex ions. However, correlation of photophysical properties with the photochemistry resulting from LF es of d^6 complexes has been hampered by marked contrasts between the conditions normally employed for photophysical spectral and es lifetime measurements (low-temperature glasses or solids) and for photochemical studies (ambient temperature, fluid solutions). It has recently been documented[15] that such differences in conditions can lead to differences in the identity of the emitting states, hence a possible misinterpretation of energy and nature of the reactive es.

For a limited number of cases there have been reported studies of both the photoluminescence and photochemistry of metal complexes under identical conditions or measurements of es lifetimes by direct observation, but these studies largely involve systems for which a charge transfer or intraligand state is the lowest energy es[17-23] or Cr(III) complexes.[24-26] Here we report studies of the photochemical and photophysical properties under identical sets of conditions of the $4d^6$ complexes $Rh(NH_3)_5Cl^{2+}$ and $Rh(NH_3)_5Br^{2+}$ and the perdeuterio analogues by pulse laser and continuous photolysis techniques. These results allow us to extract the rate constants for radiative, nonradiative, and reactive deactivation of the lowest energy es of these species in ambient aqueous solution. To our knowledge this has not been done previously for a d^6 complex displaying only LF emission.

Experimental Section

Materials and Syntheses. The compounds $[Rh(NH_3)_5X](ClO_4)_2$ ($X = Cl^-$ or Br^-) were synthesized according to procedures described elsewhere.[27] The perdeuterio complexes $[Rh(ND_3)_5X](ClO_4)_2$ ($X = Cl^-$ or Br^-) were prepared by repeated recrystallization from D_2O according to a previously published procedure.[28] The purity and isotopic composition after recrystallization were determined by comparison of the electronic and infrared absorption spectra with published data.[29]

Photolysis Procedures. Photolyses were carried out in aqueous perchloric acid solutions (pH 2-4) in 2-cm path length cylindrical quartz cells (volume 6.0 mL). Samples were irradiated at 366 nm on an optical train[28] composed of a PEK 200-W high-pressure mercury short arc lamp as a light source, an IR filter, a 366-nm interference filter (Oriel) for wavelength selection, and a thermostated cell holder (± 0.5 °C). The solutions were stirred magnetically during the photolysis. Light intensities were determined by ferrioxalate actinometry.[30] Photolytic and thermal induced spectral changes were monitored by the periodic recording of the electronic spectra on a Cary 118C spectrophotometer. Labilization of coordinated ammonia was also determined from the differences between initial pH (or pD)[31] of the photolysis solution (~3 for $X = Br^-$, ~4 for $X = Cl^-$) and the pH (pD) measured after irradiation. The release of 1 equiv of NH_3 (ND_3)

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Table I. Luminescence Data for RhA_5X^{2+} ($A = NH_3$ or ND_3; $X = Cl^-$ or Br^-) in Aqueous Solution

complex	T, K	τ,[a] ns	ν_{max},[b] $\times 10^3\ cm^{-1}$	$\nu_{1/2}$, $\times 10^3\ cm^{-1}$	Φ_{em}[c] ($\times 10^5$)
$Rh(NH_3)_5Cl^{2+}$	298[d]	14.2 ± 1.0 (4)	14.2	3.8	3.2 ± 0.5 (6)
	278[d]	21.9 ± 1.5 (19)			
	298[e]	17.6 ± 1.0 (3)			
$Rh(ND_3)_5Cl^{2+}$	298[e]	34.8 ± 4.2 (18)	14.3	4.0	6.6 ± 0.7 (3)
	278[e]	51.0 ± 3.2 (8)			
	298[d]	27.3 ± 1.4 (4)			
$Rh(NH_3)_5Br^{2+}$	298[d]	12.4 ± 1.2 (5)	14.2	3.9	1.5 ± 0.1 (4)
	278[d]	23.6 ± 0.8 (6)			
	298[e]	14.7 ± 0.5 (3)			
$Rh(ND_3)_5Br^{2+}$	298[e]	25.7 ± 1.6 (10)	14.3	4.8	3.6 ± 0.2 (3)
	278[e]	48.9 ± 1.2 (8)			
	298[d]	24.6 ± 0.5 (4)			

[a] Measured lifetimes in nanoseconds; mean value and average deviation with number of determinations in parentheses. [b] Energy of emission intensity maximum (corrected) ($10^3\ cm^{-1}$). [c] Emission quantum yield; calculated as described in text. [d] In 10^{-3} M $HClO_4/H_2O$. [e] In 10^{-3} M $DClO_4/D_2O$.

neutralized 1 equiv of acid, and the resulting pH (pD) can be used to evaluate the extent of this reaction.[10,28] Notably, dark reactions monitored under conditions identical with the photolysis experiments displayed no pH or spectral changes.

Since for each of the complexes studied here a single photoaquation pathway is dominant, spectral techniques can be used to evaluate accurate quantum yields. The fraction of light absorbed by the solution was determined by monitoring solution optical densities at 366 nm. The RhA_5X^{2+} concentrations ($A = NH_3$ or ND_3) at the start of the reaction and after intervals of irradiation were determined by monitoring the absorbance of the solution at the λ_{max} of the starting complex. The difference in initial and final concentrations and the amount of light absorbed allow the calculation of total ($t = 0 \rightarrow t = n$) quantum yields and incremental ($t = n - 1 \rightarrow t = n$) quantum yields. The quantum yields thus calculated were plotted against percent reaction and extrapolated back to 0% reaction to eliminate any inner filter effects.[28] The two methods of calculation (total vs. incremental) gave the same quantum yield values.

$Rh(NH_3)_5Cl^{2+}$. The quantum yield for Cl^- aquation was independent of whether the complex concentration was monitored at 347 nm ($\Delta\epsilon = -55$), the λ_{max} of $Rh(NH_3)_5Cl^{2+}$, or 315 nm ($\Delta\epsilon = +24$), the λ_{max} of the principal photoproduct $Rh(NH_3)_5H_2O^{3+}$. The values for $\Delta\epsilon$ at the monitoring wavelengths were determined from the spectra of authentic samples of $Rh(NH_3)_5Cl^{2+}$ and $Rh(NH_3)_5H_2O^{3+}$. Based on the small values for Φ_{NH_3} determined from pH measurements, calculations of Φ_{Cl^-} based on spectral changes assumed $Rh(NH_3)_5H_2O^{3+}$ as the sole photoproduct. The minor NH_3 aquation pathway would give *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ regardless of which NH_3 is labilized[32] and, if one takes the spectrum of this species into account, the Φ_{Cl^-} values based on the above assumption represent an upper limit for Cl^- loss at 315 nm and a lower limit at 347 nm. The quantum yields calculated at the two wavelengths are indistinguishable as would be expected given the small Φ_A values found by pH changes (see Results). The spectral properties of $Rh(ND_3)_5Cl^{2+}$ are identical with those of the perprotio analogue and the same procedures for quantum yield calculation were employed.

$Rh(NH_3)_5Br^{2+}$ and $Rh(NH_3)_5Br^{2+}$. For these complexes the principal photoreaction is ammine aquation to give *trans*-$RhA_4(H_2O)Br^{2+}$ (see below) and the independence of the spectra from deuteration effects allowed identical spectral techniques to be employed for both systems. Ammine aquation yields, Φ_A, were determined both from spectral changes and from solution pH changes (in H_2O) and gave identical values. The monitoring wavelength was 466 nm ($\Delta\epsilon = +32$), a low-energy absorption band for *trans*-$RhA_4(H_2O)Br^{2+}$ and a region where RhA_5Br^{2+} and $RhA_5H_2O^{3+}$ have no appreciable absorption. Approximate quantum yields for the very minor Br^- photoaquations were determined by photolyzing a reaction solution exhaustively until no further spectral changes occurred. The overall extinction coefficient changes at 359 nm (λ_{max} for *trans*-$RhA_4(H_2O)Br^{2+}$) are −83 and +23 $M^{-1}\ cm^{-1}$, respectively, compared to values of −85 and +26 $M^{-1}\ cm^{-1}$ expected if *trans*-$RhA_4(H_2O)Br^{2+}$ were indeed the only photoproduct. If the small differences are attributed to small yields of $RhA_5H_2O^{3+}$, numerical analysis at both wavelengths give Φ_{Br^-}/Φ_A ratios of <0.11 from which Φ_{Br^-} can be determined approximately from the experimentally measured Φ_A values.

Luminescence Procedures. Luminescence measurements were carried out in dilute acid aqueous solution at ambient temperature. Lifetime measurements were made on two different instruments. The first employed an Apollo mode-locked frequency doubled picosecond ruby laser, and the second used an Avco C-950 pulsed nitrogen laser as the excitation source. In both cases the emission was detected by a red sensitive photolultiplier (RCA C31034 and Amperex 56TVP, respectively) and the decay curves were photographed from oscilloscope traces. Each apparatus has been described in detail previously.[1b,33] Corrected emission spectra from 450 to 1000 nm were obtained by excitation of samples at 365 nm through a Bausch and Lomb grating monochromator blazed at 300 nm with a 1000-W Hanovia 977B-1 Hg-Xe lamp. A 7-cm $CuSO_4$ (150 g/L) solution filter and a Corning 7-60 glass filter were placed in the exciting beam to further improve the spectral purity of the exciting light, which was then passed through a PAR Model 191 chopper modulated at 318 Hz. Emission at right angles to the excitation was passed through a Perkin-Elmer Model 98 monochromator equipped with a dense flint prism and detected with a dry ice cooled RCA 7102 photomultiplier whose output was amplified by a PAR Model 124 lock-in amplifier with a Model 184 preamplifier. Emission spectra were recorded with a RDK Model B161 strip-chart recorder, and corrected for the wavelength sensitivity of the instrument by calibration against an NBS standard tungsten iodine lamp. Luminescence quantum yields were also measured on this apparatus by a modified Parker-Rees method,[35,36] using a 5-nm excitation bandwidth centered at 435 nm. A 7-cm $CuSO_4$ (150 g/L) solution filter and a Corning 5-58 glass filter were used to assure the spectral purity of the exciting light. Fluorescein (less than 6×10^{-7} M) in 0.1 N NaOH at 25 °C was used as the standard with a yield of 0.90.[34,35,37,38] The samples were optically dilute (abs ≤ 0.05/cm) and solvent blanks run in identical unblackened cuvettes were recorded in each case. The working equation is

$$Q_x = Q_r \left(\frac{n_x}{n_r}\right)^2 \left(\frac{E_x}{E_r}\right) \left(\frac{D_x}{D_r}\right) \left(\frac{A_r}{A_x}\right) \qquad (1)$$

where Q is the absolute quantum yield, n is the solvent refractive index, E is the excitation intensity, D is the integrated area under the corrected emission spectrum, and A is the absorbance per centimeter at the exciting wavelength. The subscripts x and r refer to the unknown and known, respectively. The technique described by Parker and Rees was employed for estimating D under the actual quantum-yield conditions.[35] In their method D is inferred from the emission intensity measured at a single wavelength and from a corrected emission spectrum run in a separate experiment. The yield and emission experiments were not carried out on the same samples.

Results

Luminescence Lifetimes of RhA_5X^{2+} ($A = NH_3$, ND_3). The results of the excited-state emission lifetime studies are listed in Table I. Independent measurements made with two different instruments give identical results. The instrumental limit for lifetime measurements is <10 ns, so that the lifetimes of all complexes are measurable. The perdeuterio complexes have significantly longer lifetimes in each case. The fact that life-

Table II. Quantum Yields for Photoaquation of RhA_5X^{2+} ($A = NH_3$ or ND_3; $X^- = Cl^-$ or Br^-) in Aqueous Solution

complex	T, K	Φ_X[a]	Φ_A[a]
$Rh(NH_3)_5Cl^{2+}$	298[b]	0.18 ± 0.01 (23)	0.02 ± 0.01 (23)
	298[c]	0.17 ± 0.01 (7)	≤0.03 (5)
	338[b]	0.26 ± 0.02 (14)	0.04 ± 0.01 (7)
	278[b]	0.14 ± 0.01 (6)	0.01 ± 0.01 (6)
$Rh(ND_3)_5Cl^{2+}$	298[c]	0.28 ± 0.01 (9)	
	298[b]	0.27 ± 0.01 (6)	≤0.05
	338[c]	0.39 ± 0.02 (9)	
	278[c]	0.26 ± 0.02 (6)	
$Rh(NH_3)_5Br^{2+}$	298[b]		0.18 ± 0.01 (13)
	298[c]	≤0.02	0.18 ± 0.01 (5)
	338[b]		0.26 ± 0.02 (14)
	278[b]		0.09 ± 0.01 (5)
$Rh(ND_3)_5Br^{2+}$	298[c]		0.27 ± 0.01 (9)
	298[b]	≤0.03	0.26 ± 0.02 (7)
	338[c]		0.37 ± 0.03 (9)
	278[c]		0.18 ± 0.02 (3)

[a] λ_{irr} 366 nm; pH 2-4; mol/einstein; mean value and average deviation with the number of determinations in parentheses. [b] In $HClO_4/H_2O$. [c] In $DClO_4/D_2O$.

times measured in $D_2O/DClO_4$ are only marginally larger than those measured for the same complexes in $H_2O/HClO_4$ solution indicates that the "deuterium isotope effect" on the lifetimes is primarily a unimolecular property of the complex rather than a property of the solvent. The lifetimes of the complexes are temperature dependent as evidenced by the measurable increase in the lifetimes when recorded at 278 K. The lifetimes of the chloro complexes increase by 50%, while the bromo complexes show a 90% increase in lifetime when the temperature is lowered from 298 to 278 K. The lifetimes are independent of whether they are measured in neutral or acidic (pH 3) solutions, except in the cases of perprotio complexes in neutral solutions of D_2O or of perdeuterio complexes in neutral H_2O. Under these circumstances the lifetimes of the perprotio complexes increase and those of the perdeuterio complexes decrease. This behavior can be attributed to the increased H/D exchange rate between solvent hydrogens and those of the coordinated ammines owing to the reciprocal hydronium ion dependent term in the exchange rate law.[39] Accordingly, the isotopic compositon of the complexes would not remain constant under these conditions.

Emission Spectra of RhA_5X^{2+} at 298 K. The luminescence spectra of the complexes were measured in acidic (pH 3) aqueous solutions at 298 K. Each complex displayed a broad Gaussian band analogous to those previously assigned as LF emissions.[12] A representative spectrum is shown in Figure 1. The corrected ν_{max} values and the respective bandwidths at half height, $\nu_{1/2}$, are reported in Table I. These results are similar to the low-temperature (77-85 K) emission spectra previously recorded for the complex ions in H_2O-MeOH glasses[12] and of the pure solids.[12,14] The emission spectrum of $Rh(NH_3)_5Br^{2+}$ in aqueous solution exhibits a much broader band than that recorded for the same complex as a pure solid at 77 K, but the energy of the emission maximum is the same. When the solution spectrum (298 K) and low-temperature glass spectrum (77 K) for $Rh(NH_3)_5Br^{2+}$ are compared, a broader band and slightly red-shifted emission maximum are observed under the former conditions. The emission spectrum of $Rh(NH_3)_5Cl^{2+}$ in ambient aqueous solution is also much broader and has an emission maximum at slightly lower energy than the spectrum recorded at low temperatures in glasses or on solid samples. The emission spectrum for $Rh(NH_3)_5Cl^{2+}$ in solution (298 K) agrees very well with a previous emission spectrum reported for a solid sample of $[Rh(NH_3)_5Cl]Cl_2$ at 298 K.[14]

Emission Quantum Yields at 298 K. The emission quantum yields are also listed in Table I. The perdeuterio complexes have larger emission quantum yields than do the perprotio complexes, and the chloro complexes have larger quantum yields than do their bromo analogues. Of particular note, for later discussion, is the small magnitude of the emission quantum yields. In each case Φ_{em} is less than 10^{-4} einsteins emitted per einstein absorbed, over 100 times smaller than the emission quantum yields measured for the same complexes in $MeOH-H_2O$ glasses at 110 K.[13] These results illustrate that the ligand field emissions for these d^6 complexes, while weak, are well within the range of quantitative measurement in fluid aqueous solutions.

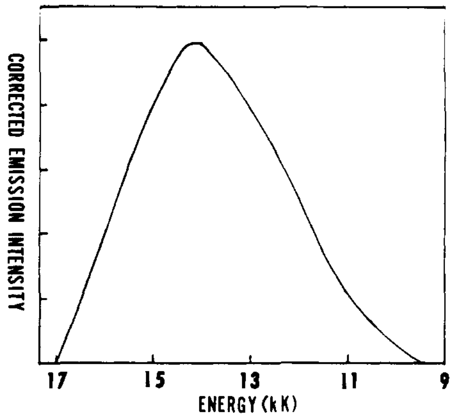

Figure 1. Corrected emission spectrum of $Rh(NH_3)_5Br^{2+}$ measured at 298 K in 10^{-3} M $HClO_4/H_2O$.

Photochemical Quantum Yields of RhA_5X^{2+}. As previously reported,[40,41] irradiation of the lowest energy ligand field band of these halopentaamminerhodium(III) complexes in water results only in ligand substitution reactions (eq 2). When X^-

$$\mathrm{RhA_5X^{2+} + H_2O} \begin{cases} \longrightarrow \mathrm{RhA_5H_2O^{3+} + X^-} & \text{(2a)} \\ \longrightarrow \mathrm{RhA_4(H_2O)X^{2+} + A} & \text{(2b)} \end{cases}$$

is Cl^-, the dominant photoreaction is Cl^- photoaquation; however, small but measurable ammonia aquation is also observed.[42] When X^- is Br^-, the predominant photoreaction is ammonia aquation, but measurable amounts of Br^- photoaquation are also observed. Quantum yields for these reactions are listed in Table II. The perdeuteration of the coordinated ammonias leads to a significant increase in the quantum yields for the photoaquation reactions (Table II). However, there is no significant difference in the photoaquation quantum yields

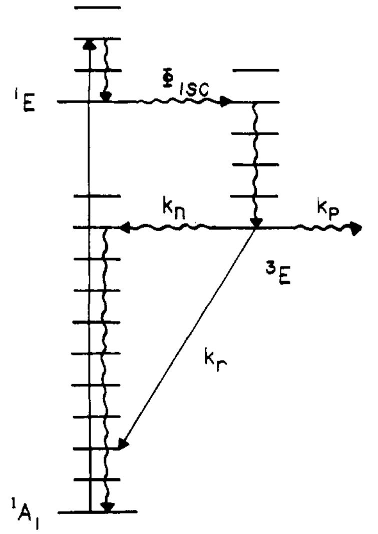

Figure 2. Energy level diagram for RhA_5X^{2+}: k_p represents photoreaction from the excited state, k_n and k_r represent nonradiative and radiative deactivation to the ground state, respectively, and Φ_{isc} represents the efficiency of internal conversion/intersystem crossing from the states initially populated to the lowest energy triplet state.

measured in either H_2O or D_2O indicating that the observed isotope effect on the photosubstitution quantum yield is also a unimolecular property of the complex. The Φ_A values for RhA_5Cl^{2+} complexes were measured by the pH technique (in dilute acidic solution, each equivalent of ammine released neutralized 1 equiv of acid) but instrumental limitations allowed only upper limits to be determined in D_2O solutions. For the RhA_5Br^{2+} complexes Φ_{Br} values were determined by a potentiometric method based on that of Shriner and Smith.[43] Again, only upper limits could be determined in D_2O solutions. A simultaneous determination of Φ_{Br} by a spectral technique also provided only upper limits owing to the small percentage of Br^- photoaquation and the spectral properties of the products.

The photoaquation quantum yields were measured at three temperatures (278–338 K) and all four complexes exhibited a significant temperature dependence (Table II). The perprotio complexes appear slightly more temperature sensitive over the range studied than are the perdeuterio analogues.

Discussion

The effects of ammine perdeuteration on the luminescence lifetimes τ (Table I) and on the photoaquation quantum yields ($\Phi_p = \Phi_X + \Phi_A$) have important implications with regard to the mechanism(s) for the es deactivation of these Rh(III) complexes. Clearly, there is a direct correlation of these effects. The longer lived perdeuterated analogues also display larger aquation quantum yields as well as larger emission quantum yields. The emission spectra and lifetimes are clearly properties of the LF excited state, previously assigned as the lowest energy triplet state ^3E,[12] and the longer τ's for deuterated analogues can be attributed to decreased rates of nonradiative deactivation.[13] Hence the direct correlation between deuteration-induced lengthening of τ and increase of Φ_p indicates that the chemical reaction(s) leading to photoproducts must be also a process of this electronic excited state (see discussion of individual rate constants below). This conclusion, although implicitly assumed in most theoretical treatments of the LF photochemistry of transition-metal complexes, is not necessarily obvious. It does sharply contradict the proposal[7] that the photosubstitution mechanism involves first the isoenergetic intersystem crossing from the ^3E es to give a vibrationally excited, *ground electronic state* configuration from which rapid deactivation either to starting material or to photoproducts occurs. Notably, this mechanism requires the branching of the deactivation and reaction channels to be *after* the rate-limiting intersystem crossing. Thus, no correspondence between the deuterium isotope effects on the photoreaction quantum yields and on the emission lifetimes is predicted in contrast to our experimental results.

An electronic state diagram for RhA_5X^{2+} illustrating the relevant photochemical and photophysical processes is shown in Figure 2. The processes depleting the excited state are reactions to give photoproducts (k_p), radiative decay to the ground state (k_r), and nonradiative deactivation to the ground state (k_n). It was concluded on the basis of earlier sensitization studies[41] that internal conversion, intersystem crossing, and vibrational relaxation to give the lowest triplet LF state occur with near unitary efficiency (i.e., $\Phi_{isc} = 1$) and are rapid relative to the processes responsible for deactivation of the reactive triplet state. Based on this conclusion the photochemical quantum yield, emission quantum yield, and emission lifetime can be expressed in terms of the rate constants k_p, k_n, and k_r.

$$\tau = (k_p + k_n + k_r)^{-1} \tag{3}$$

$$\Phi_p = k_p/(k_p + k_n + k_r) \tag{4}$$

$$\Phi_{em} = k_r/(k_p + k_n + k_r) \tag{5}$$

Since the photochemical and emission quantum yields and the emission lifetimes were measured under identical conditions, eq 3 and 4 can be combined to give

$$\Phi_p = k_p\tau \tag{6}$$

(where Φ_p is the total quantum yield for photoaquation) and eq 3 and 5 to give

$$\Phi_{em} = k_r\tau \tag{7}$$

Thus, using the experimental quantum yield and lifetime data, k_p and k_r can be calculated. Lastly k_n can be calculated by rearranging eq 3 to give

$$k_n = \tau^{-1} - k_p - k_r \tag{8}$$

which simplifies to $k_n \simeq \tau^{-1} - k_p$ given the very small values of k_r under these conditions.

The values of k_p, k_n, and k_r so calculated (Table III) demonstrate that the major effect of systemic perdeuteration of either A_5RhCl^{2+} or A_5RhBr^{2+} is to decrease the rates of nonradiative deactivation to gs. Decreased k_n under these conditions is consistent with arguments for the important contribution of a "weak coupling mechanism" to the nonradiative deactivation pathways.[10,13] The rate of reactive deactivation (i.e., k_p) is unchanged (within experimental uncertainty) or at most slightly decreased by perdeuteration, and radiative deactivation is an insignificant contributor to overall deactivation. Hence the increased Φ_p values can be directly attributed to the decreased nonradiative deactivation rates allowing a greater percentage of the overall es deactivation to occur via the reaction channel to give photoproducts. These results agree with earlier arguments[28] regarding the photoaquation reactions of $RhA_6{}^{3+}$ which were based on deuteration-induced changes in the photochemical quantum yields alone. The calculated values of k_r verify the previous assumptions[9,10,16,28] that $k_r \ll (k_n + k_p)$, and insensitivity of these to perdeuteration indicates that the enhanced values of the photoreaction and emission quantum yields must be due to decreases in the nonradiative deactivation rates.

The radiative rate constants correspond to radiative lifetimes τ_0 at 298 K of 0.5 ms for RhA_5Cl^{2+} and 0.8 ms for RhA_5Br^{2+} compared to the respective values 6.8 and 1.1 ms at 77 K,[13] hence confirming the relative temperature insensitivity of this quantity previously assumed. In contrast, k_n values increase

Table III. Rate Constants for Deactivation of RhA_5X^{2+} Excited States

complex	T, K	$k_p{}^a$ ($\times 10^{-6}$), s^{-1}	$k_n{}^b$ ($\times 10^{-6}$), s^{-1}	$k_r{}^c$ ($\times 10^{-3}$), s^{-1}
$Rh(NH_3)_5Cl^{2+}$	298	14 ± 3	56 ± 5	2.3 ± 0.5
	278	6.8 ± 1	39 ± 3	
$Rh(ND_3)_5Cl^{2+}$	298	9.5 ± 1	19 ± 4	1.9 ± 0.4
	278	6.1 ± 1	14 ± 3	
$Rh(NH_3)_5Br^{2+}$	298	16 ± 3	65 ± 7	1.2 ± 0.1
	278	4.7 ± 1	38 ± 2	
$Rh(ND_3)_5Br^{2+}$	298	12 ± 2	27 ± 2	1.4 ± 0.2
	278	4.3 ± 1	16 ± 1	

[a] Rate constant for product formation from reactive excited state. [b] Rate constant for nonradiative deactivation from excited state. [c] Rate constant for radiative deactivation from excited state.

Table IV. Apparent Activation Energy Values[c] for the Variation of Photochemical and Photophysical Parameters of RhA_5X^{2+} Ions

complex	τ^a	$\Phi_T{}^b$	$k_p{}^a$	$k_n{}^a$
$Rh(NH_3)_5Cl^{2+}$	4.1 ± 1.4	2.2 ± 0.6	6.0 ± 2.9	3.0 ± 1.4
$Rh(ND_3)_5Cl^{2+}$	3.3 ± 1.2	1.0 ± 0.5	3.7 ± 2.3	2.6 ± 3.5
$Rh(NH_3)_5Br^{2+}$	5.0 ± 1.1	2.7 ± 0.5	10.2 ± 3.3	4.5 ± 1.2
$Rh(ND_3)_5Br^{2+}$	5.8 ± 0.8	1.9 ± 0.6	8.5 ± 3.5	4.3 ± 1.2

[a] Calculated from Arrhenius activation energy plots of temperature dependence using values at 298 and 278 K. [b] Calculated from Arrhenius activation energy plots of temperature dependence using values at 338, 298, and 278 K. [c] kcal/mol.

by factors of about 700 for the two perprotio complexes and of about 1.5×10^4 for the perdeuterio complexes in going from the 77 K methanol/water glasses to 298 K aqueous solution as a medium for observation. Table IV lists apparent activation energies calculated for the photochemical and photophysical parameters over the narrower temperature range studied here. While the experimental uncertainties limit the quantitative interpretations of the E_a values, the following qualitative observations can be made. First, the magnitude of E_a calculated for k_p indicates that the potential well for the reactive excited state of RhA_5X^{2+} is well defined. Second, the apparent activation energy calculated for the photoaquation reactions using k_p values is substantially larger than the value calculated using Φ_p values, as would be expected given the composition of the latter term as a ratio of temperature-dependent parameters (eq 4).

The thermal aquation of Cl^- from $Rh(NH_3)_5Cl^{2+}$ in acidic solution displays a first-order rate law with a calculated 298 K rate constant of 5.4×10^{-8} s^{-1}.[44] In the excited state k_p is 1.4×10^7 s^{-1} indicating that promotion of an electron of the $(t_{2g})^6$ gs configuration to give the $(t_{2g})^5(e_g)^1$ es leads to aquation rate accelerations by more than 14 orders of magnitude. For $Rh(NH_3)_5Br^{2+}$ the predominant photoreaction is antithermal (NH_3 vs. Br^- aquation). However, comparison of k_p to the thermal Br^- aquation rate constant of about 1×10^{-8} s^{-1} [39] at 298 K indicates a 10^{15} acceleration in the overall lability of the complex and about 10^{14} in the Br^- aquation rate in going from the gs to the LF es. Marked increases in lability might be expected given the distortion of the LF es evidenced by the large Stokes shifts between the S → T absorption and T → S emission maxima.[12] The various theoretical treatments of LF photochemistry generally agree that the major part of the distortion will be along the weakest ligand field axis leading to labilization of halide or trans NH_3.

A thermal model for the enhanced reactivities of LF excited states might be drawn from the comparative labilities of the $4d^6$ Ru(II) in $Ru(NH_3)_5Cl^+$ and the $4d^7$ Rh(II) homologue $Rh(NH_3)_5Cl^+$ formed in the pulse radiolysis of aqueous $Rh(NH_3)_5Cl^{2+}$. The Ru(II) ion undergoes Cl^- aquation with a rate constant of 6.3 s^{-1} [15] while the Rh(II) analogue equates both Cl^- and NH_3 so rapidly that the lifetime of the hexacoordinate Rh(II) ion is less than 1 μs.[46] Hence Cl^- labilization from the Rh(II) center is at least 10^5 faster than from the undistorted d^6 Ru(II) center. A more dramatic comparison can be drawn from the NH_3 aquation rates. In pH 3 or less acidic solution, the ammines of $Ru(NH_3)_6{}^{2+}$ and the pentaammine analogues are not substitution labile, aquating with rate constants $< 1 \times 10^{-6}$ s^{-1}.[47] Hence the ammine aquated from the Rh(II) homologue is at least 12 orders of magnitude more labile, a rate acceleration comparable to that seen between the ground and excited states. However, the reactivity analogy between the $(t_{2g})^6(e_g)^1$ electronic configuration of Rh(II) and the $(t_{2g})^5(e_g)^1$ LF es configuration should not be overstated given the difference that Rh(II) labilizes two coordination sites, the excited state only one. This difference might be accountable to a mechanism where the triplet state is deactivated simultaneous with aquation of the first ligand. Another possibility is that, since the $(t_{2g})^5(e_g)^1$ configuration is more electrophilic than the $(t_{2g})^6(e_g)^1$ center, the two may undergo different ligand substitution mechanisms, the former perhaps displaying a more associative character. However, confirmation or rejection of these concepts requires considerably more quantitative data on the reaction dynamics of LF excited states, as, for example, might be provided by studies of solvent effects on the k_p for photosolvation.

In summary, the following points are reemphasized. (1) By measuring quantitatively the luminescence and photochemical properties of $Rh(NH_3)_5Cl^{2+}$, $Rh(NH_3)_5Br^{2+}$, and the perdeuterio analogues in aqueous solution, rate constants for the radiative, nonradiative, and reactive deactivation of the lowest energy triplet LF state have been determined. (2) The direct correlation between the deuteration-induced changes in the emission lifetimes, which are clearly a property of the electronic excited state, and the changes in the photoaquation quantum yields demonstrates that the chemical reaction leading to photoproduct formation must also be a competitive process of the electronic excited state. (3) Comparisons of ground and LF excited state rate constants for ligand substitution show the latter to be 14–15 orders of magnitude larger. (4) The temperature sensitivities, as seen through the apparent activation energies of the photochemical and photophysical rate constants, indicate that the potential well for the excited state of these complexes is well defined. The differences in the activation energies for the individual rate constants and the E_a (apparent) values for the photoreaction quantum yields serve to illustrate the inadequacy of using quantum yields only to interpret the excited-state properties of such complexes. Since quantum yields are ratios of individual rate constants, changes in response to systemic modifications (i.e., isotopic composition, temperature, solvent, pressure, etc.) may be the result of perturbations in one or more of the individual rate constants of key excited-state processes. It is evident that a detailed understanding of the photochemical properties of transition-metal complexes requires detailed information regarding excited-state dynamics under photochemically relevant conditions.

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Metal–Metal Charge Transfer in Thallous Tetracarbonylcobaltate Ion Pairs. Spectroscopy and Equilibrium Constants

Charles Schramm and Jeffrey I. Zink*

Contribution from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received November 20, 1978*

Abstract: Ion pairs formed between the thallous cation and the tetracarbonylcobaltate anion exhibit an unusual metal–metal charge transfer electronic absorption band. The energy of the charge-transfer band varies with the solvent. Ion pair association equilibrium constants, calculated using the charge-transfer band, range from 1.2×10^5 in toluene to less than 10 in DMF, Me_2SO, and water. The distance of closest approach of the ion pair, calculated from electrostatic theory, is 3.1 Å. The carbonyl IR spectra support a contact ion pair of C_{3v} symmetry with a direct thallium–cobalt interaction.

Introduction

Recent studies of the association between metal cations and metal carbonyl anions in solution have elucidated both the structure of the ion pairs formed and the reactivity of the solution species.[1-15] Conductivity measurements and infrared spectroscopy have been the primary means of investigation. During our studies of ion-pairing effects upon the NMR parameters of thallium salts,[16] we examined $TlCo(CO)_4$ by a variety of spectroscopic techniques. As expected, infrared measurements demonstrated varying degrees of ion pairing depending upon the solvent. More surprisingly, we observed an intense visible absorption band in certain solvents which results from a metal to metal charge transfer in the $TlCo(CO)_4$ ion pair. This unique CT system is similar to the silver ion–

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