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# Photophysical and Photochemical Properties of Rhodium(III) Halopentaammine Complexes in Aqueous Solution. Reaction Kinetics of Ligand Field Excited States<sup>1</sup>

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**Abstract:** Reported are the photoluminescence spectra, lifetimes and quantum yields, and ligand photosubstitution reaction quantum yields for the rhodium(III) complexes  $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$  and  $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$  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.<sup>3</sup> 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.<sup>3–5</sup> 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.<sup>5–8</sup>

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.<sup>3,9,10</sup> 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<sup>10–16</sup> 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<sup>15</sup> 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<sup>17–23</sup> or Cr(III) complexes.<sup>24–26</sup> Here we report studies of the photochemical and photophysical properties under identical sets of conditions of the  $d^6$  complexes  $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$  and  $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$  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  $[\text{Rh}(\text{NH}_3)_5\text{X}](\text{ClO}_4)_2$  ( $\text{X} = \text{Cl}^-$  or  $\text{Br}^-$ ) were synthesized according to procedures described elsewhere.<sup>27</sup> The perdeuterio complexes  $[\text{Rh}(\text{ND}_3)_5\text{X}](\text{ClO}_4)_2$  ( $\text{X} = \text{Cl}^-$  or  $\text{Br}^-$ ) were prepared by repeated recrystallization from  $\text{D}_2\text{O}$  according to a previously published procedure.<sup>28</sup> The purity and isotopic composition after recrystallization were determined by comparison of the electronic and infrared absorption spectra with published data.<sup>29</sup>

**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<sup>28</sup> composed of a PEK 200-W high-pressure mercury short arc lamp as a light source, an IR filter, a 366-nm interference filter (Oriol) for wavelength selection, and a thermostated cell holder ( $\pm 0.5^\circ\text{C}$ ). The solutions were stirred magnetically during the photolysis. Light intensities were determined by ferrioxalate actinometry.<sup>30</sup> 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)<sup>31</sup> of the photolysis solution ( $\sim 3$  for  $\text{X} = \text{Br}^-$ ,  $\sim 4$  for  $\text{X} = \text{Cl}^-$ ) and the pH (pD) measured after irradiation. The release of 1 equiv of  $\text{NH}_3$  ( $\text{ND}_3$ )

**Table I.** Luminescence Data for  $\text{RhA}_5\text{X}^{2+}$  ( $\text{A} = \text{NH}_3$  or  $\text{ND}_3$ ;  $\text{X} = \text{Cl}^-$  or  $\text{Br}^-$ ) in Aqueous Solution

complex	$T$ , K	$\tau$ , <sup>a</sup> ns	$\nu_{\text{max}}$ , <sup>b</sup> $\times 10^3 \text{ cm}^{-1}$	$\nu_{1/2}$ , $\times 10^3 \text{ cm}^{-1}$	$\Phi_{\text{em}}$ <sup>c</sup> ( $\times 10^5$ )
$\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$	298 <sup>d</sup>	$14.2 \pm 1.0$ (4)	14.2	3.8	$3.2 \pm 0.5$ (6)
	278 <sup>d</sup>	$21.9 \pm 1.5$ (19)			
	298 <sup>e</sup>	$17.6 \pm 1.0$ (3)			
$\text{Rh}(\text{ND}_3)_5\text{Cl}^{2+}$	298 <sup>e</sup>	$34.8 \pm 4.2$ (18)	14.3	4.0	$6.6 \pm 0.7$ (3)
	278 <sup>e</sup>	$51.0 \pm 3.2$ (8)			
	298 <sup>d</sup>	$27.3 \pm 1.4$ (4)			
$\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$	298 <sup>d</sup>	$12.4 \pm 1.2$ (5)	14.2	3.9	$1.5 \pm 0.1$ (4)
	278 <sup>d</sup>	$23.6 \pm 0.8$ (6)			
	298 <sup>e</sup>	$14.7 \pm 0.5$ (3)			
$\text{Rh}(\text{ND}_3)_5\text{Br}^{2+}$	298 <sup>e</sup>	$25.7 \pm 1.6$ (10)	14.3	4.8	$3.6 \pm 0.2$ (3)
	278 <sup>e</sup>	$48.9 \pm 1.2$ (8)			
	298 <sup>d</sup>	$24.6 \pm 0.5$ (4)			

<sup>a</sup> Measured lifetimes in nanoseconds; mean value and average deviation with number of determinations in parentheses. <sup>b</sup> Energy of emission intensity maximum (corrected) ( $10^3 \text{ cm}^{-1}$ ). <sup>c</sup> Emission quantum yield; calculated as described in text. <sup>d</sup> In  $10^{-3} \text{ M HClO}_4/\text{H}_2\text{O}$ . <sup>e</sup> In  $10^{-3} \text{ M DClO}_4/\text{D}_2\text{O}$ .

neutralized 1 equiv of acid, and the resulting pH (pD) can be used to evaluate the extent of this reaction.<sup>10,28</sup> 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  $\text{RhA}_5\text{X}^{2+}$  concentrations ( $\text{A} = \text{NH}_3$  or  $\text{ND}_3$ ) at the start of the reaction and after intervals of irradiation were determined by monitoring the absorbance of the solution at the  $\lambda_{\text{max}}$  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.<sup>28</sup> The two methods of calculation (total vs. incremental) gave the same quantum yield values.

**$\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ .** The quantum yield for  $\text{Cl}^-$  aquation was independent of whether the complex concentration was monitored at 347 nm ( $\Delta\epsilon = -55$ ), the  $\lambda_{\text{max}}$  of  $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ , or 315 nm ( $\Delta\epsilon = +24$ ), the  $\lambda_{\text{max}}$  of the principal photoproduct  $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ . The values for  $\Delta\epsilon$  at the monitoring wavelengths were determined from the spectra of authentic samples of  $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$  and  $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ . Based on the small values for  $\Phi_{\text{NH}_3}$  determined from pH measurements, calculations of  $\Phi_{\text{Cl}^-}$  based on spectral changes assumed  $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$  as the sole photoproduct. The minor  $\text{NH}_3$  aquation pathway would give *trans*- $\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$  regardless of which  $\text{NH}_3$  is labilized<sup>32</sup> and, if one takes the spectrum of this species into account, the  $\Phi_{\text{Cl}^-}$  values based on the above assumption represent an upper limit for  $\text{Cl}^-$  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  $\Phi_{\text{A}}$  values found by pH changes (see Results). The spectral properties of  $\text{Rh}(\text{ND}_3)_5\text{Cl}^{2+}$  are identical with those of the perprotio analogue and the same procedures for quantum yield calculation were employed.

**$\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$  and  $\text{Rh}(\text{ND}_3)_5\text{Br}^{2+}$ .** For these complexes the principal photoreaction is ammine aquation to give *trans*- $\text{RhA}_4(\text{H}_2\text{O})\text{Br}^{2+}$  (see below) and the independence of the spectra from deuteration effects allowed identical spectral techniques to be employed for both systems. Ammine aquation yields,  $\Phi_{\text{A}}$ , were determined both from spectral changes and from solution pH changes (in  $\text{H}_2\text{O}$ ) and gave identical values. The monitoring wavelength was 466 nm ( $\Delta\epsilon = +32$ ), a low-energy absorption band for *trans*- $\text{RhA}_4(\text{H}_2\text{O})\text{Br}^{2+}$  and a region where  $\text{RhA}_5\text{Br}^{2+}$  and  $\text{RhA}_5\text{H}_2\text{O}^{3+}$  have no appreciable absorption. Approximate quantum yields for the very minor  $\text{Br}^-$  photoaquations were determined by photolyzing a reaction solution exhaustively until no further spectral changes occurred. The overall extinction coefficient changes at 359 nm ( $\lambda_{\text{max}}$  for *trans*- $\text{RhA}_4(\text{H}_2\text{O})\text{Br}^{2+}$ ) are  $-83$  and  $+23 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively, compared to values of  $-85$  and  $+26 \text{ M}^{-1} \text{ cm}^{-1}$  expected if *trans*- $\text{RhA}_4(\text{H}_2\text{O})\text{Br}^{2+}$  were indeed the only photoproduct. If the small differences are attributed to small yields of  $\text{RhA}_5\text{H}_2\text{O}^{3+}$ , numerical analysis at both wavelengths give  $\Phi_{\text{Br}^-}/\Phi_{\text{A}}$  ratios of  $<0.11$  from which  $\Phi_{\text{Br}^-}$  can be determined approximately from the experimentally measured  $\Phi_{\text{A}}$  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 photomultiplier (RCA C31034 and Amperex 56TYP, respectively) and the decay curves were photographed from oscilloscope traces. Each apparatus has been described in detail previously.<sup>1b,33</sup> 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  $\text{CuSO}_4$  (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,<sup>35,36</sup> using a 5-nm excitation bandwidth centered at 435 nm. A 7-cm  $\text{CuSO}_4$  (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  $6 \times 10^{-7} \text{ M}$ ) in 0.1 N NaOH at 25 °C was used as the standard with a yield of 0.90.<sup>34,35,37,38</sup> The samples were optically dilute ( $\text{abs} \leq 0.05/\text{cm}$ ) and solvent blanks run in identical unblacked cuvettes were recorded in each case. The working equation is

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

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.<sup>35</sup> 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  $\text{RhA}_5\text{X}^{2+}$  ( $\text{A} = \text{NH}_3, \text{ND}_3$ ).** 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  $<10 \text{ ns}$ , 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  $\text{RhA}_5\text{X}^{2+}$  ( $\text{A} = \text{NH}_3$  or  $\text{ND}_3$ ;  $\text{X}^- = \text{Cl}^-$  or  $\text{Br}^-$ ) in Aqueous Solution

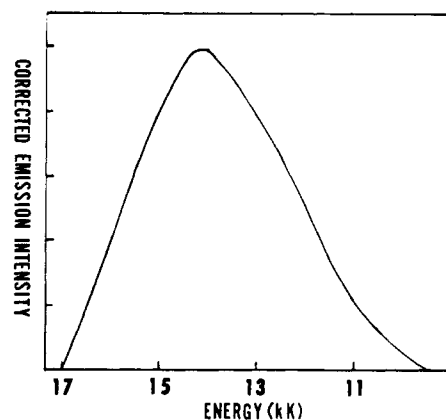
complex	$T$ , K	$\Phi_{\text{X}}^a$	$\Phi_{\text{A}}^a$
$\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$	298 <sup>b</sup>	$0.18 \pm 0.01$ (23)	$0.02 \pm 0.01$ (23)
	298 <sup>c</sup>	$0.17 \pm 0.01$ (7)	$\leq 0.03$ (5)
	338 <sup>b</sup>	$0.26 \pm 0.02$ (14)	$0.04 \pm 0.01$ (7)
	278 <sup>b</sup>	$0.14 \pm 0.01$ (6)	$0.01 \pm 0.01$ (6)
$\text{Rh}(\text{ND}_3)_5\text{Cl}^{2+}$	298 <sup>c</sup>	$0.28 \pm 0.01$ (9)	$\leq 0.05$
	298 <sup>b</sup>	$0.27 \pm 0.01$ (6)	
	338 <sup>c</sup>	$0.39 \pm 0.02$ (9)	
	278 <sup>c</sup>	$0.26 \pm 0.02$ (6)	
$\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$	298 <sup>b</sup>	$\leq 0.02$	$0.18 \pm 0.01$ (13)
	298 <sup>c</sup>		$0.18 \pm 0.01$ (5)
	338 <sup>b</sup>		$0.26 \pm 0.02$ (14)
	278 <sup>b</sup>		$0.09 \pm 0.01$ (5)
$\text{Rh}(\text{ND}_3)_5\text{Br}^{2+}$	298 <sup>c</sup>	$\leq 0.03$	$0.27 \pm 0.01$ (9)
	298 <sup>b</sup>		$0.26 \pm 0.02$ (7)
	338 <sup>c</sup>		$0.37 \pm 0.03$ (9)
	278 <sup>c</sup>		$0.18 \pm 0.02$ (3)

<sup>a</sup>  $\lambda_{\text{irr}}$  366 nm; pH 2–4; mol/einstein; mean value and average deviation with the number of determinations in parentheses. <sup>b</sup> In  $\text{HClO}_4/\text{H}_2\text{O}$ . <sup>c</sup> In  $\text{DClO}_4/\text{D}_2\text{O}$ .

times measured in  $\text{D}_2\text{O}/\text{DClO}_4$  are only marginally larger than those measured for the same complexes in  $\text{H}_2\text{O}/\text{HClO}_4$  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  $\text{D}_2\text{O}$  or of perdeuterio complexes in neutral  $\text{H}_2\text{O}$ . 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 amines owing to the reciprocal hydronium ion dependent term in the exchange rate law.<sup>39</sup> Accordingly, the isotopic composition of the complexes would not remain constant under these conditions.

**Emission Spectra of  $\text{RhA}_5\text{X}^{2+}$  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.<sup>12</sup> A representative spectrum is shown in Figure 1. The corrected  $\nu_{\text{max}}$  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  $\text{H}_2\text{O}$ – $\text{MeOH}$  glasses<sup>12</sup> and of the pure solids.<sup>12,14</sup> The emission spectrum of  $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$  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  $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$  are compared, a broader band and slightly red-shifted emission maximum are observed under the former conditions. The emission spectrum of  $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$  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  $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$  in solution (298 K) agrees very well with a previous emission spectrum reported for a solid sample of  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  at 298 K.<sup>14</sup>

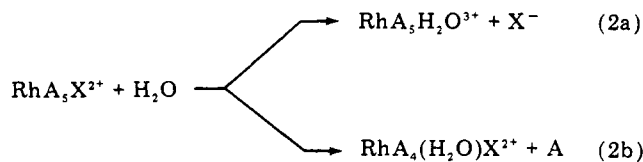
**Emission Quantum Yields at 298 K.** The emission quantum yields are also listed in Table I. The perdeuterio complexes have larger emission quantum yields than do the perprotio



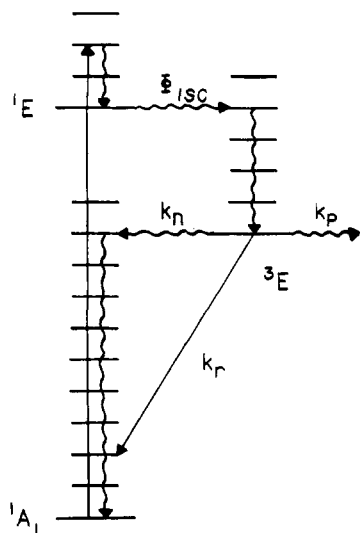
**Figure 1.** Corrected emission spectrum of  $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$  measured at 298 K in  $10^{-3}$  M  $\text{HClO}_4/\text{H}_2\text{O}$ .

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  $\Phi_{\text{em}}$  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  $\text{MeOH}$ – $\text{H}_2\text{O}$  glasses at 110 K.<sup>13</sup> 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.

**Photochemical Quantum Yields of  $\text{RhA}_5\text{X}^{2+}$ .** As previously reported,<sup>40,41</sup> irradiation of the lowest energy ligand field band of these halopentaamminerhodium(III) complexes in water results only in ligand substitution reactions (eq 2). When  $\text{X}^-$



is  $\text{Cl}^-$ , the dominant photoreaction is  $\text{Cl}^-$  photoaquation; however, small but measurable ammonia aquation is also observed.<sup>42</sup> When  $\text{X}^-$  is  $\text{Br}^-$ , the predominant photoreaction is ammonia aquation, but measurable amounts of  $\text{Br}^-$  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  $\text{RhA}_5\text{X}^{2+}$ ;  $k_p$  represents photoreaction from the excited state,  $k_n$  and  $k_r$  represent nonradiative and radiative deactivation to the ground state, respectively, and  $\Phi_{\text{isc}}$  represents the efficiency of internal conversion/intersystem crossing from the states initially populated to the lowest energy triplet state.

measured in either  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  indicating that the observed isotope effect on the photosubstitution quantum yield is also a unimolecular property of the complex. The  $\Phi_A$  values for  $\text{RhA}_5\text{Cl}^{2+}$  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  $\text{D}_2\text{O}$  solutions. For the  $\text{RhA}_5\text{Br}^{2+}$  complexes  $\Phi_{\text{Br}}$  values were determined by a potentiometric method based on that of Shriver and Smith.<sup>43</sup> Again, only upper limits could be determined in  $\text{D}_2\text{O}$  solutions. A simultaneous determination of  $\Phi_{\text{Br}}$  by a spectral technique also provided only upper limits owing to the small percentage of  $\text{Br}^-$  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  $\tau$  (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  $^3E$ ,<sup>12</sup> and the longer  $\tau$ 's for deuterated analogues can be attributed to decreased rates of nonradiative deactivation.<sup>13</sup> Hence the direct correlation between deuteration-induced lengthening of  $\tau$  and increase of  $\Phi_p$  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<sup>17</sup> 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  $\text{RhA}_5\text{X}^{2+}$  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<sup>41</sup> that internal conversion, intersystem crossing, and vibrational relaxation to give the lowest triplet LF state occur with near unitary efficiency (i.e.,  $\Phi_{\text{isc}} = 1$ ) 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  $k_r$ .

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

$$\Phi_p = k_p / (k_p + k_n + k_r) \quad (4)$$

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

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

$$\Phi_p = k_p \tau \quad (6)$$

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

$$\Phi_{\text{em}} = k_r \tau \quad (7)$$

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

$$k_n = \tau^{-1} - k_p - k_r \quad (8)$$

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  $\text{A}_5\text{RhCl}^{2+}$  or  $\text{A}_5\text{RhBr}^{2+}$  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.<sup>10,13</sup> 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  $\Phi_p$  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<sup>28</sup> regarding the photoaquation reactions of  $\text{RhA}_6^{3+}$  which were based on deuteration-induced changes in the photochemical quantum yields alone. The calculated values of  $k_r$  verify the previous assumptions<sup>9,10,16,28</sup> 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  $\tau_0$  at 298 K of 0.5 ms for  $\text{RhA}_5\text{Cl}^{2+}$  and 0.8 ms for  $\text{RhA}_5\text{Br}^{2+}$  compared to the respective values 6.8 and 1.1 ms at 77 K,<sup>13</sup> 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<sub>5</sub>X<sup>2+</sup> Excited States

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

<sup>a</sup> Rate constant for product formation from reactive excited state. <sup>b</sup> Rate constant for nonradiative deactivation from excited state. <sup>c</sup> Rate constant for radiative deactivation from excited state.

**Table IV.** Apparent Activation Energy Values<sup>c</sup> for the Variation of Photochemical and Photophysical Parameters of RhA<sub>5</sub>X<sup>2+</sup> Ions

complex	$\tau^a$	$\Phi_T^b$	$k_p^a$	$k_n^a$
Rh(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>2+</sup>	4.1 ± 1.4	2.2 ± 0.6	6.0 ± 2.9	3.0 ± 1.4
Rh(ND <sub>3</sub> ) <sub>5</sub> Cl <sup>2+</sup>	3.3 ± 1.2	1.0 ± 0.5	3.7 ± 2.3	2.6 ± 3.5
Rh(NH <sub>3</sub> ) <sub>5</sub> Br <sup>2+</sup>	5.0 ± 1.1	2.7 ± 0.5	10.2 ± 3.3	4.5 ± 1.2
Rh(ND <sub>3</sub> ) <sub>5</sub> Br <sup>2+</sup>	5.8 ± 0.8	1.9 ± 0.6	8.5 ± 3.5	4.3 ± 1.2

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

by factors of about 700 for the two perprotio complexes and of about  $1.5 \times 10^4$  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<sub>5</sub>X<sup>2+</sup> 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  $\Phi_T$  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<sup>-</sup> from Rh(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> in acidic solution displays a first-order rate law with a calculated 298 K rate constant of  $5.4 \times 10^{-8}$  s<sup>-1</sup>.<sup>44</sup> In the excited state  $k_p$  is  $1.4 \times 10^7$  s<sup>-1</sup> indicating that promotion of an electron of the (t<sub>2g</sub>)<sup>6</sup> gs configuration to give the (t<sub>2g</sub>)<sup>5</sup>(e<sub>g</sub>)<sup>1</sup> es leads to aquation rate accelerations by more than 14 orders of magnitude. For Rh(NH<sub>3</sub>)<sub>5</sub>Br<sup>2+</sup> the predominant photoreaction is antithermal (NH<sub>3</sub> vs. Br<sup>-</sup> aquation). However, comparison of  $k_p$  to the thermal Br<sup>-</sup> aquation rate constant of about  $1 \times 10^{-8}$  s<sup>-1</sup><sup>39</sup> at 298 K indicates a  $10^{15}$  acceleration in the overall lability of the complex and about  $10^{14}$  in the Br<sup>-</sup> 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.<sup>12</sup> 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<sub>3</sub>.

A thermal model for the enhanced reactivities of LF excited states might be drawn from the comparative labilities of the 4d<sup>6</sup> Ru(II) in Ru(NH<sub>3</sub>)<sub>5</sub>Cl<sup>+</sup> and the 4d<sup>7</sup> Rh(II) homologue Rh(NH<sub>3</sub>)<sub>5</sub>Cl<sup>+</sup> formed in the pulse radiolysis of aqueous Rh(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup>. The Ru(II) ion undergoes Cl<sup>-</sup> aquation with a rate constant of  $6.3$  s<sup>-1</sup><sup>15</sup> while the Rh(II) analogue equates both Cl<sup>-</sup> and NH<sub>3</sub> so rapidly that the lifetime of the hexacoordinate Rh(II) ion is less than 1 μs.<sup>46</sup> Hence Cl<sup>-</sup> labilization from the Rh(II) center is at least  $10^5$  faster than from the undistorted d<sup>6</sup> Ru(II) center. A more dramatic comparison can

be drawn from the NH<sub>3</sub> aquation rates. In pH 3 or less acidic solution, the amines of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> and the pentaammine analogues are not substitution labile, aquating with rate constants  $< 1 \times 10^{-6}$  s<sup>-1</sup>.<sup>47</sup> 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<sub>2g</sub>)<sup>6</sup>(e<sub>g</sub>)<sup>1</sup> electronic configuration of Rh(II) and the (t<sub>2g</sub>)<sup>5</sup>(e<sub>g</sub>)<sup>1</sup> 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<sub>2g</sub>)<sup>5</sup>(e<sub>g</sub>)<sup>1</sup> configuration is more electrophilic than the (t<sub>2g</sub>)<sup>6</sup>(e<sub>g</sub>)<sup>1</sup> 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<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup>, Rh(NH<sub>3</sub>)<sub>5</sub>Br<sup>2+</sup>, 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

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**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  $1.2 \times 10^5$  in toluene to less than 10 in DMF,  $\text{Me}_2\text{SO}$ , 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.<sup>1-15</sup> Conductivity measurements and infrared spectroscopy have been the primary means of investigation. During our studies of ion-pairing effects upon the NMR pa-

rameters of thallium salts,<sup>16</sup> we examined  $\text{TlCo}(\text{CO})_4$  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  $\text{TlCo}(\text{CO})_4$  ion pair. This unique CT system is similar to the silver ion-