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Photochemistry of rhodium(III) complexes. Ligand field excitation of hexaaminerhodium(III) and characteristics of nonradiative deactivation paths

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On the other hand, characteristics of the  $F_2$ - $UO_2$  reaction are as follows: (i) heating is necessary for its initiation, and (ii) the rate increases remarkably with increasing temperature. Similar characteristics are also observed in other reactions of fluorine: the  $F_2$ - $MoO_3$  and the  $F_2$ - $UF_4$  reaction proceed at temperature above 250 and 220°, respectively,<sup>6,7</sup> and the apparent activation energy is 36.8 kcal/mol for the former and in the range 15.5–19.9 kcal/mol for the latter reaction.

The facts described above indicate that the  $F_2$ - $UO_2$  reaction involves the activated and dissociative adsorption of fluorine. The heating, necessary for the initiation of this reaction, may be attributed to the energy of stretching the interatomic distance of fluorine molecules so as to match the distances between uranium sites on the surfaces.<sup>21,25</sup>

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## Photochemistry of Rhodium(III) Complexes. Ligand Field Excitation of Hexaamminerhodium(III) and Characteristics of Nonradiative Deactivation Paths<sup>1</sup>

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Ligand field excitation of hexaamminerhodium(III),  $Rh(NH_3)_6^{3+}$ , in aqueous solution results in the photoaquation of one coordinated  $NH_3$ . The measured quantum yields at 23° are 0.075 mol/einstein for 313-nm excitation of the  $^1A_{1g} \rightarrow ^1T_{1g}$  transition and 0.07 for 254-nm excitation of the  $^1A_{1g} \rightarrow ^1T_{2g}$  transition, suggesting efficient interconversion of the higher energy state to a common reactive excited state. Under similar conditions, the quantum yield for the perdeuterated complex  $Rh(ND_3)_6^{3+}$  is about twice as large (0.14 in  $H_2O$ , 0.15 in  $D_2O$ , 313-nm excitation). However, the temperature dependence of the photoaquation quantum yields is measurably greater for the perprotio complex than for the perdeuterio complex. To explain these results, it is proposed that temperature-independent weak coupling and temperature-dependent strong coupling mechanisms are competitive in the nonradiative deactivation of the reactive excited state of  $Rh(NH_3)_6^{3+}$ .

### Introduction

In the past several years, interest<sup>3,4</sup> in the photoreactivities of  $d^6$  metal ion complexes has been extended to quantitative studies of the ammine complexes of ruthenium(II)<sup>5</sup> and rhodium(III).<sup>6–10</sup> The rhodium(III)-ammine complexes whose photochemistry reported to date have

been halide complexes such as  $Rh(NH_3)_5X^{2+}$  or  $Rh(en)_2X_2^+$  ( $X = Cl^-$ ,  $Br^-$ , or  $I^-$ ), for which perturbations of the ligand field involve the stereochemistry of the bis(ethylenediamine) complexes or the identity of the halide ion. In order to consider more subtle differences, we have been examining the photochemistry<sup>1,11</sup> and lumines-

cence spectroscopy<sup>12</sup> of complexes of the type  $\text{Rh}(\text{NH}_3)_5\text{L}^{3+}$ , where L is one of a series of uncharged nitrogen bases such as  $\text{NH}_3$ , a substituted pyridine py-X, or an organonitrile RCN. During these studies the dramatic effects<sup>3,3,14</sup> that perdeuteration of the coordinated amines has on the luminescent lifetimes at 77°K of the complex ions  $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$  and  $\text{Rh}(\text{NH}_3)_6^{3+}$  came to our attention. These deuteration effects provide insight into the nonradiative deactivation mechanisms of the emitting states<sup>14</sup> and, conceivably, studies of similar effects under photochemically significant conditions might improve our understanding of processes deactivating chemically reactive excited states. Since  $\text{Rh}(\text{NH}_3)_6^{3+}$ , a member of the  $\text{Rh}(\text{NH}_3)_5\text{L}^{3+}$  series, displays the greatest effect of deuteration on its phosphorescence lifetime,<sup>14</sup> it was decided to examine in some detail the photoreactions of this ion and its perdeuterated analog in aqueous solution. Kelly and Endicott<sup>7</sup> have studied the photoaquation of the ions  $\text{Rh}(\text{ND}_3)_5\text{X}^{2+}$  and found that quantum yields were identical with those of the perprotio analogs for  $\text{X}^- = \text{Br}^-$  or  $\text{I}^-$ , but for  $\text{X}^- = \text{Cl}^-$  perdeuteration led to a small enhancement (~40%) of the quantum yield. A larger effect is seen for the hexaammine complexes whose photochemistry is presented here.

### Experimental Section

**Materials and Syntheses.** The hexaammine complex  $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$  was prepared by the procedure of Thomas and Crosby.<sup>13</sup> The perdeuterated hexaammine complex  $[\text{Rh}(\text{ND}_3)_6]\text{Cl}_3$  was prepared by heating the perprotio complex in  $\text{D}_2\text{O}$ . Initially,  $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$  (0.25 g) was dissolved in 5 ml of  $\text{D}_2\text{O}$  (Thompson-Packard, 99.8% D) and heated (in a system isolated from atmospheric water by drying tubes) for a period of 5 hr. The solution was then cooled to ice temperatures and diethyl ether (5 ml) added to form a heterogeneous liquid mixture. To this was added ethanol (10 ml) leading to immediate precipitation of the rhodium salt. This material was collected by filtration, washed with ethanol-ether mixtures, and dried in a vacuum desiccator. An infrared spectrum was taken to determine the approximate amount of deuteration. The procedure was repeated three times to give a highly deuterated hexaammine sample in an overall yield of 68%. Per cent deuteration was examined by a published nmr method<sup>7</sup> on a Varian T-60. According to this analysis, no protons were shown to be present in the perdeuterated hexaammine salt; however, experimental uncertainties established an upper limit of 0.8 protons per rhodium, or, in other words, deuteration was at least 95.5% complete.

**Photolysis Procedures.** Photolyses at 313 nm were carried out on an optical train utilizing a PEK 200-W high-pressure mercury short arc lamp as a light source, an infrared filter and a 313-nm interference filter (Oriel) for wavelength selection, and a thermostated cell holder. Photolyses were carried out in aqueous perchloric acid solutions (pH 2-4) in 2-cm pathlength cylindrical quartz cells (volume = 6.0 ml). Irradiation beam intensities (band pass = 12 nm for the interference filter) averaged  $1 \times 10^{-6}$  einstein/min as determined by ferrioxalate actinometry.<sup>15</sup> Beam intensities were monitored continuously with a YSI-Kettering Model 65A radiometer to ensure stability. Solutions irradiated were relatively optically dense (OD ~ 1.5); however, quantum yields are based on einsteins of quanta absorbed as determined by a computational method. Proceeding reactions were monitored periodically by recording the electronic spectrum on a Cary 14

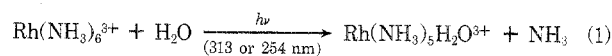
spectrophotometer. Analogous solutions allowed to react in the dark displayed no spectral changes at any of the temperatures studied. On the basis of spectral changes, quantum yields were calculated as moles of reaction per einstein of light absorbed during a particular photolysis interval. As the reaction proceeded, these values dropped off slowly owing to the secondary involvement of the reaction product. For this reason, the interval quantum yields were plotted as a function of per cent reaction, and the resulting plots were extrapolated to zero time to obtain the quantum yield for photolysis of the starting complex. Values obtained in this manner were equivalent within experimental uncertainty to those obtained by plotting overall quantum yield as a function of irradiation time or per cent reaction according to the method of Chaisson, *et al.*<sup>5</sup> Aquation of  $\text{NH}_3$  was also examined by measuring pH changes of the photolysis solution during the course of the reaction. A Sargent-Welch Model NX digital pH meter calibrated against commercial buffers was employed for pH measurements.

Photolyses at 254 nm were carried out on an optical train utilizing a 90-W medium-pressure Philips "spectral" lamp as source, an Oriel 254-nm interference filter to isolate the desired wavelength region, and a thermostated cell compartment. Reactions were carried out in a 2-cm pathlength cylindrical cell. Irradiation beam intensities ( $2 \times 10^{-7}$  einstein/min) were determined by ferrioxalate actinometry and reactions were followed by spectral and pH changes.

**Sensitization.** Sensitization experiments were carried out with two sensitizers, biacetyl (Aldrich, vacuum redistilled) and pyrazine (Aldrich). Solutions were prepared with the appropriate sensitizer and sufficient 1 M  $\text{HClO}_4$  to give the desired pH (~3.1) in redistilled  $\text{H}_2\text{O}$  and were carefully deaerated in all cases using chromous scrubbed argon. Care was taken to ensure that solutions to which  $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$  had been added were entrained for the same period of time as control solutions to which no substrate had been added. Optical densities of the solutions at the excitation wavelength (405 nm for biacetyl, 254 nm for pyrazine) fell in the range 1-2 and direct absorption by  $\text{Rh}(\text{NH}_3)_6^{3+}$  accounted for less than 1% of this for biacetyl sensitization and less than 5% for pyrazine sensitization. Reaction yields for ammonia aquation were determined at the conclusion of photolysis by measuring the pH change on a Radiometer model 26 pH meter. Emission spectra of solutions were obtained in a Perkin-Elmer MPF-3 fluorescence spectrophotometer. Photolyses at 405 nm were carried out using the PEK high-pressure mercury lamp with a 405-nm interference filter (beam intensity ~  $4 \times 10^{-6}$  einstein/min) and at 254 nm using the apparatus described above.

### Results

The spectrum of  $\text{Rh}(\text{NH}_3)_6^{3+}$  in aqueous solution displays two absorption bands at 305 ( $\epsilon$  134  $\text{M}^{-1} \text{cm}^{-1}$ ) and 255 nm ( $\epsilon$  101) (Figure 1) which can be assigned to the  ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$  and  ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$  ligand field transitions, respectively. Continuous photolysis with 313- or 254-nm light, corresponding to excitation of these transitions, results in substitutional behavior as the only observed photochemical reaction of this complex in acidic aqueous solution (eq 1). Reactions were monitored by examining the



spectral changes in the solution after photolysis intervals

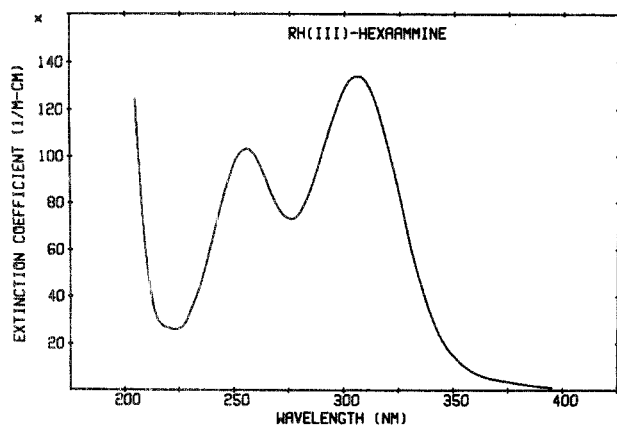


Figure 1. Spectrum of  $\text{Rh}(\text{NH}_3)_6^{3+}$  in aqueous solution.

and by measuring the difference in the solution pH between the initial solution and the product solution at the conclusion of the photolysis experiment (usually carried to approximately 20% reaction as determined by the spectral changes). An increase in pH indicates the photolysis caused release of  $\text{NH}_3$  into the weakly acidic photolysis solution (pH 2-4). Quantum yields determined by the two methods were comparable. Photolysis of  $\text{Rh}(\text{NH}_3)_6^{3+}$  to greater than 90% completion in the acidic perchlorate solutions gave product solutions with  $\lambda_{\text{max}}$  (316 nm) and optical densities essentially identical with those predicted for  $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$  as the sole reaction product. Under these experimental conditions the product  $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$  has the appearance of being essentially photolysis insensitive, and no spectral changes are observed when this complex is photolyzed with 313-nm light.

During each photochemical experiment a parallel dark reaction was carried out with another sample of the same solution under comparable conditions. For all the temperatures used in this study, no reaction was detected by either spectral or pH measurements for solutions not irradiated. Photolysis experiments were carried out both on solutions which had been carefully entrained with deoxygenated argon and on solutions saturated with air. However, no differences in quantum yield measurements were detected, indicating that the photoreactions are not sensitive to the presence of dissolved oxygen. A similar observation was made for the halopentaamminerhodium(III) complexes.<sup>7</sup>

**Quantum Yields.** Table I summarizes the quantum yields for 313-nm photolysis of aqueous  $\text{Rh}(\text{NH}_3)_6^{3+}$  at four temperatures. Considering the values for  $\Phi(\text{NH}_3)$  at 23 and at 68° only, an apparent activation energy,  $E_a$  (apparent), of  $3.6 \pm 0.3$  kcal/mol can be calculated for the  $\text{NH}_3$  photoaquation. Also listed in Table I is the  $\Phi(\text{NH}_3)$  value measured at 23° for 254-nm irradiation. Within experimental uncertainty this quantum yield is indistinguishable from  $\Phi(\text{NH}_3)$  measured for 313-nm photolysis under comparable conditions.

The quantum yields measured for photoaquation of  $\text{Rh}(\text{ND}_3)_6^{3+}$  are also listed in Table I. In each case studied here, photoaquation of  $\text{Rh}(\text{ND}_3)_6^{3+}$  occurred with a higher quantum yield than for the perprotio analog. However, the photoreactivity of the perdeuterio complex is not as temperature sensitive with an  $E_a$  (apparent) value of only  $1.9 \pm 0.4$  kcal/mol between the values measured at 23 and 68°. Plots of  $\ln(\Phi)$  vs.  $T^{-1}$  (Arrhenius type activation plot) are shown in Figure 2 for the perdeuterio hexa-

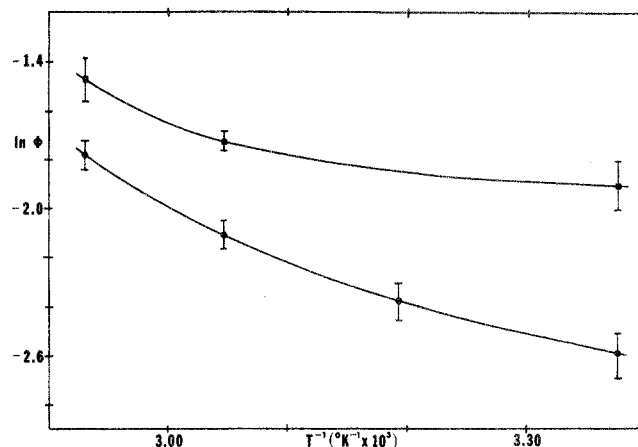


Figure 2. "Activation energy" plots of the temperature-dependent quantum yield for photoaquation of hexaamminerhodium(III) in aqueous solution: upper curve shows data for  $\text{Rh}(\text{ND}_3)_6^{3+}$  in  $\text{D}_2\text{O}$ ; lower curve data for  $\text{Rh}(\text{NH}_3)_6^{3+}$  in  $\text{H}_2\text{O}$ .

TABLE I: Quantum Yields for the Photoaquation of Hexaamminerhodium(III)

Complex	$T$ , °C	$\lambda_{\text{irr}}$ , nm	$\Phi^a$	$\Phi(\text{ND}_3)/\Phi(\text{NH}_3)^b$
$\text{Rh}(\text{NH}_3)_6^{3+}$	23	313 <sup>c</sup>	$0.075 \pm 0.007$ (19) <sup>d</sup>	
		313	$0.07 \pm 0.01$ (2) <sup>e</sup>	
		254 <sup>c</sup>	$0.07 \pm 0.02$ (4) <sup>d</sup>	
	40	313	$0.093 \pm 0.007$ (6) <sup>d</sup>	
		55	313	$0.122 \pm 0.007$ (6) <sup>d</sup>
$\text{Rh}(\text{ND}_3)_6^{3+}$	23	313	$0.169 \pm 0.010$ (4) <sup>d</sup>	2.00
		313	$0.14 \pm 0.02$ (6) <sup>d</sup>	1.87
	55	313	$0.179 \pm 0.007$ (3) <sup>e</sup>	1.47
		68	313	$0.23 \pm 0.02$ (3) <sup>e</sup>

<sup>a</sup> Quantum yield (initial) for  $\text{NH}_3$  or  $\text{ND}_3$  aquation, mean value and average deviation reported with number of determinations in parentheses.

<sup>b</sup> Ratio of quantum yields for perdeuterio vs. perprotio systems. <sup>c</sup> 313-nm irradiation corresponds to  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$  excitation, 254-nm irradiation to  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$  excitation. <sup>d</sup> In  $\text{H}_2\text{O}$  solution,  $\text{HClO}_4 \sim 10^{-3} M$ . <sup>e</sup> In  $\text{D}_2\text{O}$  solution,  $\text{D}_2\text{SO}_4 \sim 10^{-3} M$ .

amine complex and for the perprotio complex. Neither plot appears to be linear, but it is evident that over the range the perprotio system is the more temperature sensitive.

Quantum yields for photoaquation of  $\text{Rh}(\text{ND}_3)_6^{3+}$  were determined both in  $\text{D}_2\text{O}$  solution and in  $\text{H}_2\text{O}$  solution (Table I). A slightly higher quantum yield was found for the deuterated solvent, although the differences fall into the ranges of experimental uncertainty. Similarly, photolysis of  $\text{Rh}(\text{NH}_3)_6^{3+}$  in  $\text{D}_2\text{O}$  solution gives quantum yields essentially indistinguishable from those values measured in  $\text{H}_2\text{O}$  solution (Table I).

**Sensitization Studies.** No net photochemical reaction was observed when deaerated solutions of biacetyl ( $\sim 0.2 M$ ) and  $2 \times 10^{-3} M$   $\text{Rh}(\text{NH}_3)_6^{3+}$  in pH 3.1 water were photolyzed extensively at 405 nm. Similarly a solution with  $1.2 \times 10^{-2} M$   $\text{Rh}(\text{NH}_3)_6^{3+}$  gave a small pH change on irradiation, but this could be attributed entirely to direct photolysis of the rhodium(III) substrate. Thus, it appears that no biacetyl sensitization of  $\text{Rh}(\text{NH}_3)_6^{3+}$  photochemistry occurs. Emission studies demonstrated that the failure to see sensitized photochemistry was not the result of impurity quenching of biacetyl. Solutions containing  $\text{Rh}(\text{NH}_3)_6^{3+}$  and control solutions without  $\text{Rh}(\text{III})$  both displayed the biacetyl phosphorescence and fluorescence

emission bands at 510 and 465 nm, respectively, with peak height ratios ranging from  $\sim 5:1$  to  $\sim 10:1$ . Rh(III) and control solutions prepared identically (including deaeration procedures, etc.) have similar phosphorescence/fluorescence ratios, but for each pair the solution containing Rh(III) showed a smaller ratio by about 10–20%. Greater variations were observed between different pairs of solutions indicating that impurity quenching (presumably  $O_2$  quenching of phosphorescence) was playing some role.

Unlike biacetyl, pyrazine appears to sensitize the photochemistry of  $Rh(NH_3)_6^{3+}$ . Solutions containing  $\sim 2 \times 10^{-4} M$  pyrazine and  $7.0 \times 10^{-4} M$   $Rh(NH_3)_6^{3+}$  displayed pH changes sufficient to give an overall quantum yield of 0.012 based on the total light absorbed by the solution. A maximum upper limit of 40–45% of this reaction can be attributed to direct photolysis of the complex, thus the quantum yield for sensitized photolysis is about 0.006 to 0.007 mol per einstein absorbed by pyrazine. A lower concentration of Rh(III) ( $4.7 \times 10^{-4} M$ ) led to a smaller sensitized photolysis quantum yield ( $\sim 0.004$ ). Pyrazine does not display a phosphorescence band in its room temperature emission spectrum, so quenching efficiency cannot be compared to sensitized photolysis yields. However, the presence of Rh(III) does not affect the fluorescence intensity of pyrazine at 342 nm, so the photochemistry observed apparently is not due to energy transfer to the singlet state of  $Rh(NH_3)_6^{3+}$  but to energy transfer from the pyrazine triplet. Intersystem crossing for pyrazine occurs with less than unitary efficiency ( $\Phi_{ISC} = 0.33$  in hexane),<sup>16</sup> thus the observed quantum yields of sensitized photochemistry (not under limiting concentration) are in fact closer to the direct photolysis value of 0.075 than immediately obvious.

## Discussion

Aquation of  $NH_3$  (eq 1) is the sole photoreaction observed for aqueous  $Rh(NH_3)_6^{3+}$  when ligand field transitions  $^1A_{1g} \rightarrow ^1T_{1g}$  or  $^1A_{1g} \rightarrow ^1T_{2g}$  are excited in acidic aqueous solution. The quantum yields are independent of the ligand field state initially populated by irradiation, suggesting that the higher state undergoes efficient interconversion to a reactive state common to that reached by excitation directly into the lower state.

The failure to see biacetyl triplet sensitization of  $Rh(NH_3)_6^{3+}$  photoaquation contrasts to the behavior of the halopentaammine complexes<sup>7</sup> but is not surprising. The energy of the biacetyl triplet is 19.2 kK<sup>17</sup> compared to the estimated  $Rh(NH_3)_6^{3+}$  triplet energy of 20.3 kK;<sup>13</sup> thus, energy transfer in this case would be endothermic. The modest quenching (10–20%) of biacetyl phosphorescence in the presence of  $Rh(NH_3)_6^{3+}$  does not appear significant and may be due to impurities, most likely  $O_2$ . However, such quenching conceivably may result from significant perturbation of biacetyl nonradiative deactivation pathways owing to "exiplex" formation with the Rh(III) in solution. Energy transfer from the pyrazine lowest triplet (26.2 kK)<sup>16</sup> to  $Rh(NH_3)_6^{3+}$  would be significantly exothermic. Energy transfer from the pyrazine singlet (30.1 kK)<sup>16</sup> to give the  $Rh(NH_3)_6^{3+}$   $^1T_{1g}$  state (29.3 kK, estimated from spectral data of ref 13) also would be exothermic but may be slow owing to Franck-Condon effects. The failure to detect any Rh(III) quenching of pyrazine fluorescence indicates that neither direct energy transfer nor "trivial" sensitization (absorption by Rh(III) of emitted radiation) is an important process under the experimental conditions. Thus, observation of photoreac-

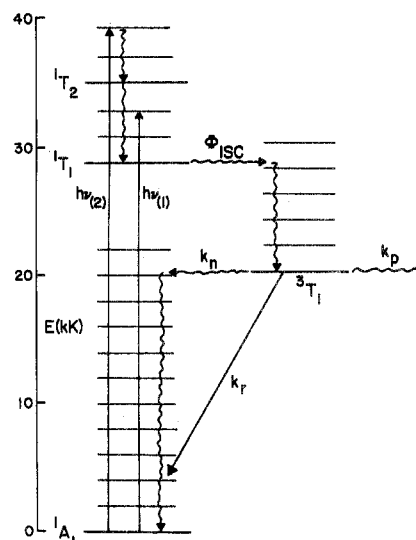


Figure 3. Energy level diagram for photoreaction of  $Rh(NH_3)_6^{3+}$ :  $h\nu(1)$  and  $h\nu(2)$  represent excitation into the  $^1T_1$  and  $^1T_2$  states, respectively,  $k_p$  is aquation of excited state  $^3T_1$  to give photoproducts, and  $k_n$  and  $k_r$  represent nonradiative and radiative deactivation to ground state, respectively.

tion exceeding the small direct photolysis suggests triplet sensitization of  $Rh(NH_3)_6^{3+}$ .

In the absence of quantitative photophysical data for the pyrazine sensitizer in aqueous solution, the limiting quantum yield for reaction of the  $Rh(NH_3)_6^{3+}$  triplet excited state cannot be established from the current data. However, our data indicate that this state is reactive toward aquation. This conclusion is consistent with the holopentaammine complexes<sup>7</sup> where it was concluded using biacetyl as a photosensitizer that intersystem crossing from ligand field singlet states populated by initial excitation to reactive triplet states occurred with unitary efficiency. Highly efficient intersystem crossing from ligand field singlets to triplet emitting states has also been concluded<sup>13,14</sup> from studies of the low-temperature (77°K) emission spectra of rhodium(III)-ammine complexes including  $Rh(NH_3)_6^{3+}$ . Such high rates of intersystem crossing can be in large part attributed<sup>18</sup> to the sizeable spin orbit coupling of the rhodium atom. For these reasons, we will assume for sake of the present discussion that like the halopentaammine complexes, higher energy ligand field excited states of  $Rh(NH_3)_6^{3+}$  undergo very efficient internal conversion/intersystem crossing to a reactive lowest energy triplet state.

An electronic state diagram for  $Rh(NH_3)_6^{3+}$  illustrating relevant photochemical and photophysical processes is shown in Figure 3. Implicit are the assumptions that internal conversion, intersystem crossing, and vibrational relaxation are rapid relative to the processes responsible for deactivation of the reactive triplet state ( $^3T_1$ ) and that the chemically relevant form of this species is thermally equilibrated (a "thexi" state).<sup>4</sup> The processes depleting the reactive state are chemical reactions leading to substitution of  $H_2O$  for  $NH_3$  in the Rh(III) coordination sphere ( $k_p$ ), radiative deactivation (phosphorescence) to ground state ( $k_r$ ), or nonradiative deactivation to ground state ( $k_n$ ). Based on the earlier stated assumptions, the lifetimes ( $\tau$ ) of the reactive state and the quantum yield of the photochemical reaction ( $\Phi_p$ ) can be expressed in terms of the rate constants  $k_p$ ,  $k_n$ , and  $k_r$

$$\tau = (k_p + k_n + k_r)^{-1} \quad (2)$$

$$\Phi_p = k_p / (k_p + k_n + k_r) \quad (3)$$

Attempts to observe luminescence from  $\text{Rh}(\text{NH}_3)_6^{3+}$  at room temperature were unsuccessful<sup>12,13</sup> and under these conditions  $k_r$  is apparently much smaller than  $k_n$  or  $k_p$ . Thus eq 3 can be rewritten as

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

and rearrangement of eq 4 gives the ratio of the rate constants

$$k_n/k_p = (1 - \Phi_p)/\Phi_p \quad (5)$$

The importance of the nonradiative deactivation pathway is illustrated by considering the photoaquation of  $\text{Rh}(\text{NH}_3)_6^{3+}$  at 23° (Table I) where the quantum yield of 0.075 mol/einstein can be translated into a  $k_n/k_p$  ratio of 12.3. Thus it should be clear that any interpretative discussion of photoreaction quantum yields should consider other deactivation pathways as well.

Kelly and Endicott,<sup>7,8</sup> in discussing the photochemistry of the haloammine complexes of rhodium(III), have focused attention on the theories of radiationless deactivation mechanisms proposed by Robinson and Frosch<sup>19</sup> for excited organic compounds and extended by others.<sup>20-23</sup> The low-temperature (77–110°K) luminescence of certain Rh(III) amines has been subject<sup>14,24</sup> to similar theoretical considerations. For large molecules, the nonradiative deactivation rate constant  $k_n$  is primarily determined by intramolecular processes and is the product of vibrational and electronic factors. Vibronic coupling between two states has been analyzed in terms of two limiting cases.<sup>21,22</sup> The *strong coupling limit* is one for which there is large displacement of the potential surface (at least one normal mode) of one state with respect to the other and for which the surfaces are expected to cross not far from the minimum of the higher state. The *weak coupling limit* represents the case where relative displacement of potential energy surfaces is small. For the limiting weak coupling case, it is predicted that  $k_n$  will increase exponentially as the difference in energy between the ground and excited state decreases and that  $k_n$  is dominated by the highest frequency vibrational modes of the molecule.<sup>21</sup> The presence of high frequency modes allows an isoenergetic transition from the thermally equilibrated excited state to an electronic ground state vibrational level of relatively low quantum number thus increasing the probability of such a transition. In the strong coupling limit,  $k_n$  increases exponentially as the energy gap ( $\Delta E'$ ) between the lowest vibrational level of the excited state and the intersection of the ground and excited state surfaces<sup>22</sup> decreases. In this case, the nonradiative deactivation rate depends on the mean vibrational frequency<sup>21</sup> and is relatively insensitive to the highest frequency vibrational modes. In gross simplification, it might be said that in the weak coupling limit for metal-ammine complexes, the radiationless transition from  ${}^3T_1$  to the  ${}^1A_1$  ground state primarily involves activation of the N–H vibrations of the coordinated ammonias<sup>25</sup> (the highest frequency modes) while in the strong coupling limit radiationless deactivation involves major distortion (and activation) of the metal–ligand bond framework as well.

Interpretation of luminescence data for the rhodium(III)–ammine complexes has led to some disagreement.<sup>14,24</sup> For example, it appears that large energy differences be-

tween the estimated maxima of the triplet absorption bands and the phosphorescence bands are the rule.<sup>12-14,24</sup> The estimated Stokes shift for  $\text{Rh}(\text{NH}_3)_6^{3+}$  is 4 kK,<sup>13</sup> and this is easily rationalized in terms of metal–ligand bond lengthening in the  ${}^3T_1$  state (electronic configuration  $(t_{2g})^5(e_g)^1$ ) given that the  $e_g$  orbital is  $\sigma$  antibonding. Nonetheless, comparisons of luminescence lifetimes and quantum yields at 77–110°K for  $\text{Rh}(\text{NH}_3)_6^{3+}$  and the halopentaammine ions and the perdeuterated analogs in methanol–water glasses<sup>14</sup> show that replacing the high-frequency N–H modes with lower frequency N–D modes leads to very large decreases in nonradiative deactivation rate constants. For example,  $k_n$  is 62 times larger for  $\text{Rh}(\text{NH}_3)_6^{3+}$  than for  $\text{Rh}(\text{ND}_3)_6^{3+}$  at 77°K. Such sensitivity to perdeuteration of the high-frequency, nitrogen–hydrogen bonds is considered diagnostic of a dominating weak coupling mechanism for nonradiative deactivation.

Under the conditions of the luminescence experiments (rigid glasses at 77–110°K) no photochemical reactions of the Rh(III) ammine complexes are observed.<sup>13</sup> However, in aqueous solution at ambient temperatures, ligand field excitation of these species results in photosubstitution processes with total quantum yields ranging from the 0.075 for  $\text{Rh}(\text{NH}_3)_6^{3+}$  to near unity<sup>7</sup> for aquation of trans  $\text{NH}_3$  from  $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ . Aquation ( $k_p$ ) is one path for deactivation of the reactive excited state. If this process occurs by unimolecular dissociation of the Rh–L bond, it is clear that the  $k_p$  path would be closely related to a strong coupling process for nonradiative deactivation, and it appears a valid assumption<sup>7</sup> that such a path should be important under photochemically significant conditions. Nonetheless, photoaquation of the hexaammine complex shows a significant deuterium isotope effect (Table I). The effect of carrying out the photolysis in  $\text{D}_2\text{O}$  rather than  $\text{H}_2\text{O}$  is small; hence, the principal isotope effect is a unimolecular property of the hexaammine ion.

Deuterium isotope effects have been studied<sup>26-28</sup> for the thermal aquations of the cobalt(III) complexes  $\text{CoA}_4\text{Cl}_2^+$  (where A = perprotio- or perdeuterioammonia or (ethylenediamine)<sub>1/2</sub>). In each case deuteration of the ammine function led to decreases in the chloride aquation rates. Aquations in  $\text{D}_2\text{O}$  solution also proved to be slower than the analogous reactions in  $\text{H}_2\text{O}$ . These results suggest that ammine perdeuteration would decrease the rate of ligand aquation ( $k_p$ ) from the excited state, if it has any effect at all. However, since  $\Phi_p$  is larger for the perdeuterated hexaammine, the dominant effect of perdeuteration must be to decrease the rate of nonradiative deactivation  $k_n$  instead. If perdeuteration has no effect on  $k_p$ , then the ratio of  $k_n$  for  $\text{Rh}(\text{ND}_3)_6^{3+}$  in  $\text{D}_2\text{O}$  to  $k_n$  for  $\text{Rh}(\text{NH}_3)_6^{3+}$  in  $\text{H}_2\text{O}$  at 23° can be calculated to be 0.46. In other words, perdeuteration reduces the nonradiative deactivation rate by at least a factor of 2 thus indicating that weak coupling is apparently an important mechanism for deactivation of  $\text{Rh}(\text{NH}_3)_6^{3+}$  from  ${}^3T_1$  to the ground state at 23°.

If for a particular case, strong and weak coupling were competitive, independent mechanisms for nonradiative deactivation, we might rewrite  $k_n$  as the sum of the rates of the competitive processes

$$k_n = k_s + k_w \quad (6)$$

where  $k_s$  represents the rate of deactivation by the strong coupling path(s) and  $k_w$  by the weak coupling path(s). Therefore

$$\Phi_p = k_p / (k_p + k_s + k_w) \quad (7)$$

The temperature dependence of the quantum yield  $\Phi_p$  will be a composite of the temperature dependences of the independent terms  $k_p$ ,  $k_s$ , and  $k_w$ . If  $k_p$  is simply a chemical reaction of the thexi state, its temperature dependence might be expected to follow Arrhenius behavior, i.e.,  $k_p = A_p \exp(-E_a/RT)$ . The temperature dependence of the deactivation processes are not so simple; however, strong coupling has been suggested to have an Arrhenius-type behavior and weak coupling to be essentially temperature independent.<sup>23,29</sup> Thus for sake of illustration we might rewrite eq 7 as

$$\Phi_p = \frac{A_p \exp(-E_a/RT)}{A_p \exp(-E_a/RT) + A_s \exp(-\Delta E'/RT) + k_w} \quad (8)$$

where the energy difference  $\Delta E'$  may or may not be closely related to  $E_a$  and where  $k_w$  is independent of temperature. Given this form of the equation for the limiting case where  $k_w$  is much larger at all temperatures than either  $A_p \exp(-E_a/RT)$  or  $A_s \exp(-\Delta E'/RT)$ , then  $\Phi_p$  would follow a simple Arrhenius relationship and  $E_a$  (apparent) would equal  $E_a$  for both the perprotio and perdeuterio cases. On the other extreme, if  $k_w$  were small compared to  $A_s \exp(-\Delta E'/RT)$  at all temperatures studied and if  $\Delta E'$  were comparable to  $E_a$ , then eq 8 would predict  $\Phi_p$  to be essentially temperature independent regardless of its magnitude. Neither limiting behavior is observed for  $\text{Rh}(\text{NH}_3)_6^{3+}$  and  $\text{Rh}(\text{ND}_3)_6^{3+}$  (Figure 2), and it is apparent that  $\Phi_p(\text{D})$  is less temperature sensitive than is  $\Phi_p(\text{H})$ .<sup>30</sup> This observation implies that the temperature independent contribution (e.g.,  $k_w$ ) to  $k_n(\text{H})$  is a smaller fraction of  $k_n(\text{D})$  and, also, that a temperature dependent term not greatly sensitive to perdeuteration (e.g.,  $k_s$ ) is an important contribution to both  $k_n(\text{H})$  and  $k_n(\text{D})$ .

In conclusion, we feel that the data for the hexaammine complex can be explained on the basis of a potential energy surface where the values of  $\Delta E'$  for the strong coupling mechanism and  $E_a$  for ligand aquation are sufficiently large that weak coupling deactivation is the overwhelmingly dominant nonradiative process when  $kT$  is small (e.g., at 77°K). However, at larger values of  $kT$ , the three processes appear to be competitive, at least for  $\text{Rh}(\text{NH}_3)_6^{3+}$  at ambient temperature. Although the relationship between the strong coupling contribution to  $k_n$  and photoaquation is unclear, the observation of an activation energy (apparent) for  $\Phi(\text{NH}_3)$  of about 4 kcal indicates that the potential well for the reactive excited state of  $\text{Rh}(\text{NH}_3)_6^{3+}$  is reasonably defined.

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## References and Notes

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- (a) J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, **92**, 7262 (1970). (b) Note. A recent communication [G. A. Crosby, K. W. Hipps, and W. H. Elfring, Jr., *J. Amer. Chem. Soc.*, **96**, 629 (1974)] has drawn renewed attention to the point that the spin orbit coupling constants of the heavier transition metals are of such a magnitude that spin multiplicity levels may no longer be meaningful for certain excited states of these metals' complexes. For the Rh(III)-ammine complexes, evidence in this paper and ref 7 points to the presence of a reactive, lowest energy excited state which is populated by energy transfer from an excited organic molecule (e.g., biacetyl or pyrazine) in the triplet state but not from the corresponding singlet excited state. Whether this reactive state is in fact a "triplet" does not affect significantly the conclusions of this paper; however, by describing this state as a triplet our discussion has remained consistent with other recent studies (ref 7, 13, 14) of the excited states of these complexes.
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- The term  $k_w$  could show temperature dependence if it represented the composite of several weak coupling deactivation pathways having different rates and occurring from different vibrational states of the electronic excited state. Thus the weak coupling rate could be temperature dependent owing to changes in the Boltzmann distribution between the various vibration states. However, given the criterion that weak coupling mechanisms are largely suppressed by perdeuteration, this possibility alone cannot explain the differing temperature dependences of quantum yields in the perprotio and perdeuterio cases.
- Not only is  $\Phi_p(\text{D})$  less temperature sensitive than  $\Phi_p(\text{H})$  but also the ratio  $k_n/k_p$  is less temperature sensitive for the deuterated complexes. For example, between 23 and 55°,  $k_n/k_p$  falls from 12.3 to 7.2 for the perprotio case and from 5.7 to 4.6 for the perdeuterio case.