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# Deuterium Isotope Effects on the Ligand Field Excited-State Kinetics of Hexaamminerhodium(III)

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Reported is an investigation of the ligand field (LF) excited-state reaction dynamics of the rhodium(III) complexes $Rh(NH_3)_6^{3+}$ in $H_2O$ and $Rh(ND_3)_6^{3+}$ in $D_2O$ as probed by nanosecond pulse laser techniques. These studies confirm an earlier proposal from this laboratory that deuterium isotope effects on rates of nonradiative deactivation from the reactive excited states are responsible for the greater quantum yields for ligand photoaquation in the perdeuterio system. Hydroxide (deuterioxide) ion quenching both of emission from the LF excited state and of ligand photosubstitution was observed for both complexes, and the quenching constants $k_q^H$ ($k_q^D$) were determined, giving an empirical deuterium isotope effect $k_q^H/k_q^D = 1.5$. These observations provide further evidence for a proton-transfer quenching mechanism for the lowest energy LF excited state(s).

## Introduction

Examination of the excited-state reaction dynamics of $d^6$ complexes in ambient-temperature solutions has led to a better understanding of the intimate details of photosubstitution mechanisms resulting from the excitation of ligand field (LF) absorptions.[1,2] From such studies on rhodium(III) complexes,[2a–c] it has been argued that the observed photochemistry and luminescence, as well as nonradiative deactivation to the ground state, occur largely as competitive processes from the lowest energy excited state (or those states in thermal equilibrium with it). This excited state has been assigned as a LF triplet state, formed by rapid, efficient internal conversion/intersystem crossing from the ligand field states populated upon initial excitation (Figure 1).[3] An earlier study[4] from this laboratory demonstrated that perdeuteration of the hexaamminerhodium(III) ion led to a significant enhancement of the photosubstitution quantum yields for eq 1.

$$\begin{gathered} RhA_6^{3+} + S \xrightarrow{h\nu} RhA_5S^{3+} + A \\ A = NH_3 \text{ or } ND_3;\ S = H_2O \text{ or } D_2O \end{gathered} \qquad (1)$$

and provided strong circumstantial evidence for competitive ligand labilization and nonradiative deactivation as the principal pathways exiting from the LF triplet.[2] This interpretation was based in part on the expectation that at least a fraction of the enormous suppression of nonradiative deactivation rates noted for the perdeuterio complexes in low-temperature emission studies ($k_n^H/k_n^D = 62$ in 77 K 4/1 $MeOH/H_2O$ glasses)[5] would carry over to ambient-temperature (298 K) fluid-solution conditions. In subsequent studies using pulse laser techniques to probe the LF excited-state lifetimes of the halopentaammine complexes, this type of behavior was confirmed.[2a,b] Ammine deuteration was shown to enhance photosubstitution quantum yields $\phi_S$, and these larger $\phi_S$ values could be correlated with larger LF excited-state lifetimes owing to smaller $k_n$ values for the deuterated systems. This paper extends these pulse laser studies to the original hexaammine systems.

Another property of the halopentaamminerhodium(III) complexes is that Brønsted bases quench the room-temperature emission and ammine photoaquation pathways without fully quenching the halide photosubstitutions.[2e,6–9] Various explanations have been offered for this phenomenon; however, recent studies with the iodo complex $Rh(NH_3)_5I^{2+}$ strongly suggest that excited-state quenching by hydroxide ion is "noninnocent", i.e., occurs via a chemical process that can also lead to halide substitution.[6] The suggested pathway is proton transfer from coordinated ammine to the Brønsted base. In this context, the deuterium isotope effect on the previously unreported base quenching of the hexaammine complexes was also investigated in order to evaluate this proposed proton-transfer mechanism.

## Experimental Section

The perchlorate salt of the hexaammine complex $[Rh(NH_3)_6](ClO_4)_3$ was prepared and recrystallized according to published procedures.[4,10] The perdeuterated compound $[Rh(NH_3)_6](ClO_4)_3$ was prepared from the perprotio analogue by repeated recrystallization from $D_2O$ (99.8%). Isotope purity was evaluated by comparison of infrared spectra for N–H and N–D stretching frequency intensities. All other chemicals used were of analytical reagent grade, and the water used in all preparations was deionized and then distilled. Sodium hydroxide stock solutions were freshly prepared with boiled water to minimize carbonate impurities from atmospheric carbon dioxide. The sodium deuterioxide stock solution was prepared from sodium metal and boiled $D_2O$ and standardized with oxalic acid.

Electronic absorption spectra were recorded on a Cary 118 spectrophotometer equipped with a thermostated cell holder, and infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer.

Continuous photolyses were carried out by the same methods and by using the photolysis apparatus previously described.[2a,4] The complex was irradiated at 313 nm, and quantum yields were evaluated from changes in the electronic absorption spectra. Parallel dark reactions showed no significant spectral changes over the course of the continuous-photolysis measurements (<25% reaction).

Photoluminescence lifetimes were measured by using a Quanta Ray DCR-1A Nd/YAG pulse laser as the excitation source. The optics and detection system have been described previously.[11] An excitation wavelength of 353 nm (third harmonic) was used (pulse width ~10 ns), and emission was monitored at 600 nm with a fast-response-time photomultiplier (EMI 9816A, rise time 1 ns) positioned perpendicular to the excitation beam. Sample solutions were placed in a four-window, 1-cm path length, quartz fluorescence cell mounted in a thermostated (±0.5 °C) cell holder, which permitted lifetime and spectra measurements over the temperature range 278–298 K.

## Results and Discussion

Several earlier investigations have shown that at low temperatures (77 K) salts of hexaamminerhodium(III) display a relatively weak emission with a Gaussian band shape and a maximum at 600 nm. This has been assigned to luminescence from the lowest

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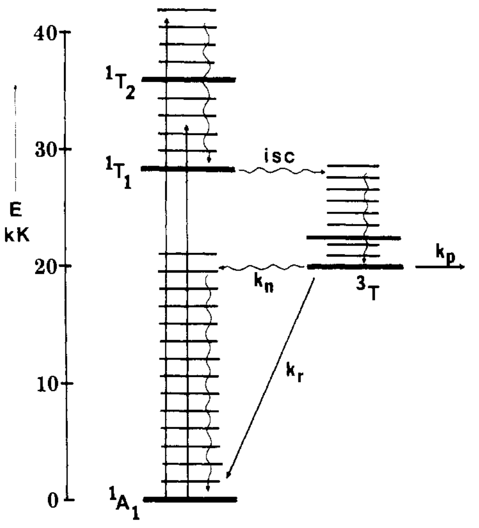

**Figure 1.** Excited-state diagram for $Rh(NH_3)_6^{3+}$.

**Table I.** Properties of $Rh(NH_3)_6^{3+}$ and $Rh(ND_3)_6^{3+}$ in Aqueous Solution

| temp, K | $\phi_p$[b] | $\tau$, ns | $10^{-7} \times k_n$[c] | $10^{-6} \times k_p$[c] | $10^{-10} \times k_q$[d] |
|---|---|---|---|---|---|
| 2 | | | | | |
| | | $Rh(NH_3)_6^{3+}$ | | | |
| 298 | 0.080 ± 0.005 | 21 ± 2 | 4.4 | 3.8 | [e] |
| 282 | 0.065 ± 0.005 | 40 ± 2 | 2.3 | 1.6 | 1.60 |
| | | $Rh(ND_3)_6^{3+}$ | | | |
| 298 | 0.150 ± 0.010 | 45 ± 2 | 1.9 | 3.3 | [e] |
| 282 | 0.135 ± 0.010 | 89 ± 5 | 0.97 | 1.5 | 1.07 |

| temp, K | $\phi_p^H/\phi_p^D$ | $\tau^H/\tau^D$ | $k_n^H/k_n^D$ | $k_p^H/k_p^D$ | $k_q^H/k_q^D$ |
|---|---|---|---|---|---|
| 298 | 0.53 | 0.47 | 2.3 | 1.2 | |
| 282 | 0.48 | 0.45 | 2.4 | 1.1 | 1.5 |

[a] Acidic solutions of $HClO_4/H_2O$ and $DClO_4/D_2O$. [b] Photochemical quantum yield, mol/einstein. [c] Calculated from eq 3 and 4 as described in text, $s^{-1}$. [d] Bimolecular quenching constant, $M^{-1}\ s^{-1}$; in alkaline solution. [e] Not determined.

energy ligand field state ($^3T_{1g} \rightarrow {}^1A_{1g}$).[10,12-15] Previous attempts here to measure lifetimes of the $Rh(NH_3)_6^{3+}$ ion in fluid aqueous solution were unsuccessful; however, with a more powerful laser probe and a more sensitive detection system, the present investigation was indeed successful at detecting a weak emission centered at about 600 nm. The measured lifetime for $Rh(NH_3)_6^{3+}$ was 21 ± 2 ns in 298 K aqueous solution (pH 3). A longer lifetime of 40 ± 2 ns was measured at 282 K with intermediate values found at intermediate temperatures. The perdeuterio complex $Rh(ND_3)_6^{3+}$ in $D_2O$ displayed lifetimes of 45 ± 2 and 89 ± 5 ns at these respective temperatures. Irradiation of either complex in pH 3 aqueous solution with 313-nm light (corresponding to the first spin-allowed LF absorption band, $^1A_{1g} \rightarrow {}^1T_{1g}$) led to spectral and pH changes consistent with the photoaquation of a single ammonia (e.g., eq 2) as described previously.[4] Measured quantum yields at 282 and 298 K are reported in Table I.

$$Rh(NH_3)_6^{3+} + H^+ + H_2O \xrightarrow{h\nu} Rh(NH_3)_5H_2O^{3+} + NH_4^+ \tag{2}$$

Measurement of $\tau$ and of $\phi_p$ under the same conditions allows the evaluation of the rate constants for ammine aquation ($k_p$) and nonradiative deactivation ($k_n$) from the rhodium(III) complexes' LF excited states according to eq 3 and 4.[3] These calculations

$$k_p = \phi_p/\tau \tag{3}$$

$$k_n \approx \tau^{-1} - k_p \tag{4}$$

are based on the conclusions that internal conversion/intersystem crossing, from initially formed higher energy LF states to the lowest energy LF states, occurs rapidly with high efficiency (supported by the results of wavelength dependence and sensitization experiments with Rh(III) ammine complexes)[4,16] and that $k_r \ll k_n$ or $k_p$ (as evidenced by the very weak emission intensities). The resulting values of $k_n$ and $k_p$ for $Rh(NH_3)_6^{3+}$ in $H_2O$ and $Rh(ND_3)_6^{3+}$ in $D_2O$ are summarized in Table I. From these it can be seen that the rates for both deactivation processes are temperature sensitive with $E_a$ for $k_n$ (7 kcal/mol) being slightly less than that for $k_p$ (8–9 kcal/mol). A similar observation was made for the analogous deactivation pathways for the halopentaammine ions $Rh(NH_3)_5X^{2+}$.[2a]

Comparison of the excited-state rate constants for the perprotio and perdeuterio hexaammine systems indicates an important difference. Although the ammine aquation rate $k_p$ is little affected by perdeuteration, the nonradiative deactivation rate ($k_n$) is suppressed by a factor of 2.3 (Table I). Given that, under all the conditions studied here, excited-state decay occurs mostly by nonradiative deactivation (>80%), it is the $k_n$ term which dominates $\tau$. As a consequence, the perdeuterio system displays a lifetime and a photoreaction quantum yield ($\phi_p = k_p\tau$) each about a factor of 2 larger than those in the perprotio hexaammine system. These results confirm the earlier interpretation[4] of the isotope effects on the photoaquation quantum yields for the $RhA_6^{3+}$ ions (eq 1) in terms of perturbation of the nonradiative deactivation rates, presumably because of the sensitivity of a "weak-coupling" component of this photophysical pathway to the nature of the highest frequency vibrational modes of the excited-state species.[17]

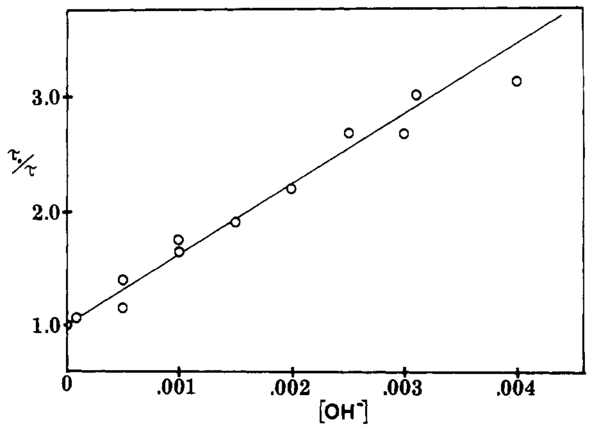

**Figure 2.** Stern–Volmer plot of $\tau_0/\tau$ vs. $[OH^-]$ for $Rh(NH_3)_6^{3+}$ in alkaline solution at 282 K.

The LF luminescence of $Rh(NH_3)_6^{3+}$ in $H_2O$ was also found to undergo dynamic quenching by hydroxide ion in solution. The Stern–Volmer plot of $\tau_0/\tau$ at 9 °C vs. $[OH^-]$ was found to be linear (Figure 2) and gave the Stern–Volmer constant ($K_{SV}^H$) 635 ± 50 $M^{-1}$. Similarly, $OD^-$ quenching of the LF emission from $Rh(ND_3)_6^{3+}$ in $D_2O$ gave a linear Stern–Volmer plot with $K_{SV}^D = 956 \pm 30\ M^{-1}$ at 9 °C. From the lifetime $\tau$ and $K_{SV}$ values, the bimolecular quenching constants $k_q$ were calculated ($k_q = K_{SV}\tau^{-1}$) as $(1.60 \pm 0.17) \times 10^{10}\ M^{-1}\ s^{-1}$ for the perprotio system and $(1.07 \pm 0.05) \times 10^{10}\ M^{-1}\ s^{-1}$ for the perdeuterio system. These give the kinetic isotope effect (KIE) $k_q^H/k_q^D = 1.5 \pm 0.2$ for the quenching process. The photoaquation reaction, as monitored spectrally in continuous-photolysis experiments ($Rh(NH_3)_5OH^{2+}$

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is the photoproduct in this case), also demonstrated hydroxide ion quenching. Stern–Volmer plots of $\phi_p$ values vs. hydroxide concentration were linear, with $K_{SV}$ values that approximated those from the emission experiments; however, experimental uncertainties were much larger owing to the small spectral changes monitored under these conditions ($\Delta\epsilon = -15$ at 305 nm). In strongly basic solutions, the photoreaction under 313-nm irradiation was completely quenched.

The above KIE for the hydroxide quenching of $[RhA_6^{3+}]^*$ and a similar one reported[7] (but not discussed) for the quenching of $[Rh(NH_3)_5Cl^{2+}]^*$ are comparable to the KIE of 1.77 ($k^H = 1.4 \times 10^{11}$ $M^{-1}$ $s^{-1}$) reported[18] for the reaction of $H^+$ ($D^+$) with $OH^-$ ($OD^-$) in $H_2O$ ($D_2O$). This adds credence to the earlier proposal by Adamson and co-workers that such quenching occurs by a proton transfer from the coordinated ammine of the excited complex.[7] That the $k_q$ values approach the diffusion limit (a diffusion limit of $1 \times 10^{11}$ $M^{-1}$ $s^{-1}$ at 25 °C can be estimated for the encounter of a $M(NH_3)_6^{3+}$ ion with $OH^-$ by using 4.4 Å as the distance of closest approach)[19] implies that the ammines of the excited-state complex are significantly more acidic than those of the ground-state complex ($pK_a > 14$).[20] For comparison, the second-order rate constants (25 °C) for the reaction of $OH^-$ with the weak acids $NH_4^+$ ($pK_a = 9.25$)[21] and $Ru(NH_3)_6^{3+}$ ($pK_a = 12.4$)[19] have been reported as $3.4 \times 10^{10}$ and $2 \times 10^9$ $M^{-1}$ $s^{-1}$, respectively. The hexaammineruthenium(III) ion offers as especially interesting comparison, given the analogy between this ion's $(t_{2g})^5$ electronic configuration and the $(t_{2g})^5(e_g)^1$ configuration of the LF state of the hexaamminerhodium(III) ion.

In summary, measurement of the excited-state emission lifetimes of $Rh(NH_3)_6^{3+}$ and $Rh(ND_3)_6^{3+}$ in solution supports the conclusion that deuteration effects on photoreaction quantum yields can be attributed to perturbations of the nonradiative deactivation rates. Dynamic quenching of both photoaquation and photoemission by hydroxide further supports the view that both processes originate from the same state or an ensemble of equilibrated states. Lastly, the kinetic isotope effect of 1.5 seen in the $k_q$ values supports the suggestion of reactive quenching by excited-state proton transfer from coordinated ammine.

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**Registry No.** $Rh(NH_3)_6^{3+}$, 16786-63-3; $D_2$, 7782-39-0.

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# Magnetic Dimer Excitations in $Cs_3Cr_2Cl_9$ Studied by Neutron Scattering

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The energy dispersion of the singlet–triplet dimer excitation in $Cs_3Cr_2Cl_9$ has been studied by inelastic neutron scattering (INS) at temperatures down to 1.3 K. The results can be accounted for by using a completely isotropic Heisenberg Hamiltonian in the random phase approximation (RPA). Only nearest-neighbor interactions need to be considered. From the excellent fit, three exchange parameters were obtained: $J = -1.75$ meV (intradimer), $J_p = -0.032$ meV (interdimer, intrasublattice) and $J_c = -0.031$ meV (interdimer, intersublattice). These values indicate that $Cs_3Cr_2Cl_9$ is far from ordering magnetically. The systematic variation of the exchange parameters on substitution of Cl by Br and I is discussed.

## Introduction

$Cs_3Cr_2Cl_9$ exemplifies a family of compounds in which the magnetic ions occur as dimeric complexes, $Cr_2Cl_9^{3-}$. The space group is hexagonal, $P6_3/mmc$, and there are two dimers per unit cell forming two sublattices.[1] A schematic structure is shown in Figure 1, indicating the two sublattices and the three exchange parameters. The Cr–Cr separation is 3.2 Å within the dimers and 7.2 Å (intrasublattice) and 7.1 Å (intersublattice) between nearest-neighbor dimers. There are Cr–Cl···Cl–Cr contacts between the dimers, providing pathways for weak interdimer interaction. The low-temperature magnetic and spectroscopic properties have so far been interpreted as resulting from isolated antiferromagnetically coupled dimers.[2-4] EPR spectra at elevated temperatures, where the first excited dimer level becomes populated, showed some evidence for interdimer exchange.[5] Previous inelastic neutron scattering (INS) experiments on $Cs_3Cr_2Cl_9$ indicated some interdimer interactions even at 1.8 K, where the dimer triplet population is negligible.[6] But the data in ref 6 were ambiguous due to the bad quality of the crystal. Here we report INS results on a high-quality crystal.

The antiferromagnetic intradimer exchange leads to a Landé splitting pattern with the singlet dimer state as ground state and the triplet as first excited state. Much effort has been devoted to the question of under what conditions a singlet ground-state system can order magnetically.[7-9] The present study was motivated by the interest in magnetic dimers and in singlet ground-state magnets. The closely related $Cs_3Cr_2Br_9$ has recently been studied by INS.[8,9] The singlet–triplet excitation was found to exhibit pronounced dispersion. It could be accounted for by using three exchange parameters corresponding to the interactions shown in Figure 1, the intradimer exchange $J$ and the interdimer exchange between nearest neighbors $J_p$ (intrasublattice) and $J_c$

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