

Excited State Processes for Aqueous $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ and $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$

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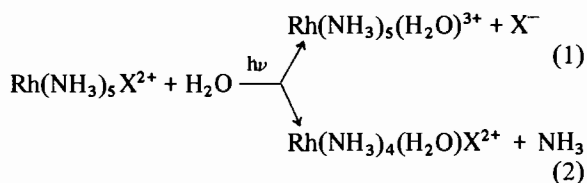
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Emission lifetimes for $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$, A, and $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$, B, are 30.1 ± 0.7 nsec and 24.1 ± 1.2 nsec in aqueous acidified solution at 5°C , respectively, with corresponding apparent activation energies of 5.1 and 5.4 kcal mol⁻¹, again respectively. In both cases the emission maximum is at about 14 kK. There is excited state absorption, which decays with the corresponding emission lifetime, with maxima at 490 nm and 620 nm, for A and B respectively. This second excited state is also photoreactive. The emissions are quenched by hydroxide ion, the bimolecular quenching rate constants being 2.1×10^{10} M⁻¹ sec⁻¹ and 2.7×10^{10} M⁻¹ sec⁻¹ at 5°C , again respectively. Studies with A showed that the other bases such as carbonate and cyanide ions also quench. A undergoes only chloride photoaquation, which is 87% quenched on quenching emission. B is known to show both bromide and ammonia photoaquation; the latter is fully quenched on quenching emission, while the former reaction mode is unaffected. Possible excited state schemes are discussed, one including a reactive quintet state.

Introduction

The ligand field photochemistry of Rh(III) ammine complexes in aqueous solution has been studied by several investigators [1–7]. In the case of $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$, the reactions are of the type



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With $\text{X} = \text{Cl}^-$, only the thermal mode, reaction (1), occurs. The reported room temperature quantum yield ϕ for irradiation wavelength λ in nm, (ϕ, λ) are: (0.11, 254) [5], (0.14, 365) [5], (0.16, 350) [6], and (0.13, 358) [7]. In the case of $\text{X} = \text{Br}^-$, however, both reaction (1) and the antithermal reaction mode (2) occur, the respective room temperature yields being 0.019 and 0.18 for 360 nm irradiation [6, 8]. For the iodo complex, only reaction (2) occurs [6], with a yield of 0.82 at 25°C and 385 nm irradiation. Returning to the case of $\text{X} = \text{Br}^-$, Kelly and Endicott [6, 8] found efficient sensitization by triplet state biacetyl, and concluded that therefore a $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ triplet state, designated “³X” was produced, which underwent reaction (2). In addition, however, ϕ_{NH_3} showed a 2.8 kcal mol⁻¹ temperature dependence, while ϕ_{Br^-} was more nearly temperature independent. This finding called for a second state, “³Y”, which led only to bromide aquation.

Reports that room temperature emission could be observed with aqueous $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ [9, 10] and $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ [10, 11] opened up the possibility of further probing of excited state reactivities. Thus we reported in a preliminary communication that the emission from $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ was quenched by OH^- ion, with concomitant 87% quenching of the photochemistry [11]. The present paper adds detail and extends the investigation to the very interesting case of aqueous $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$.

Experimental

Materials

$[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was obtained from Alpha Inorganics or prepared from RhCl_3 (Alpha Inorganics) by the method of Johnson and Basolo [12]. The compound was recrystallized as the perchlorate salt, and the purity established by comparison of the uv–visible absorption spectrum with that in the literature. The absorption maxima are: $\epsilon_{349} = 105$ (obs), 100 [13], 98 [14]; $\epsilon_{277} = 113$ (obs), 103 [13], 114 [14], where ϵ denotes extinction coefficient in $\text{M}^{-1} \text{cm}^{-1}$ at the indicated wavelength in nm.

$[\text{Rh}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ was prepared according to a literature procedure [15]. $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was dissolved in a minimum volume of 1 *N* sodium hydroxide and heated for thirty minutes at 90 °C. Bleaching of the solution was observed as $\text{Rh}(\text{NH}_3)_5(\text{OH})^{2+}$ was formed. After cooling to room temperature, hydrobromic acid was added and the white precipitate of $\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})\text{Br}_3$ was collected and dried overnight at 110 °C. The resulting yellow product was recrystallized from water/ HClO_4 to yield $[\text{Rh}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$. The observed and reported absorption maxima are: $\epsilon_{359} = 118$ (obs), 122 [13]; $\epsilon_{424} = 25$ (obs), 25 [13].

$[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{ClO}_4)_3$ was prepared from $[\text{Rh}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ by a published procedure [15]. The absorption maxima are: $\epsilon_{316} = 105$ (obs), 105 [13]; $\epsilon_{263} = 94$ (obs), 89 [13].

$[\text{Rh}(\text{NH}_3)_5(\text{OH})]^{2+}$ was prepared *in situ* by dissolving $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{ClO}_4)_3$ in basic solution. The observed and reported absorption maxima are: $\epsilon_{320} = 135$ (obs), 132 [16]; $\epsilon_{292} = 123$ (obs), 109 [16].

$\text{Rh}(\text{NH}_3)_5(\text{CO}_3)^+$ was prepared *in situ* by dissolving $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{ClO}_4)_3$ in water and adding lithium carbonate until the pH was about 9. After standing overnight, the solution absorption spectrum agreed well with that reported. The absorption maximum is: $\epsilon_{325} = 177$ (obs), 178 [16].

$\text{Rh}(\text{ND}_3)_5\text{Cl}^{2+}$ was prepared *in situ* by dissolving $[\text{Rh}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ in NaOD. Acidified solutions were prepared by the addition of D_2SO_4 (5% in D_2O) until the solution was acidic. Concentrations of OD^- were determined by titration with standard HCl to a bromocresol green endpoint.

Hydroxide ion concentrations were determined by pH measurements. Sodium hydroxide stock solutions were freshly prepared for each experiment to minimize the amount of atmospheric carbon dioxide absorption, and the solutions were prepared from freshly washed sodium hydroxide pellets, again to minimize the amount of adventitious carbonate.

Solutions to be used in pulsed laser experiments were filtered using a 0.22 μm millipore filter, to minimize scattering by suspended particles.

Photolyses

Irradiations were carried out by means of a medium pressure mercury arc lamp, using glass and interference filters to isolate the 366 nm line. Thermostatted cells were used. The degree of chloride aquation was determined spectrophotometrically, from the known spectral change as $\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ is formed in acidic solutions. In the case of photolyses in basic solutions, the relative yields were found by acidifying and again determining the degree of chloride aquation spectrophotometrically.

In the case of $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$, the ammonia aquation yield was found spectrophotometrically,

although a complication was now present. The major photoproduct in basic solution, *trans*- $\text{Rh}(\text{NH}_3)_4(\text{OH})(\text{Br})^+$, is itself photo-labile, yielding *cis*- $\text{Rh}(\text{NH}_3)_4(\text{OH})_2^{3+}$ [17]. Because of this secondary photolysis, the spectral sequences on irradiation of the bromopentaammine complex did not exhibit good isosbestic points, and the following procedure was employed. Acidic aqueous $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ was photolyzed essentially to completion, the solution then consisting of 90% *trans*- $\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}^{2+}$ and 10% $\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$; *trans*- $\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}^{2+}$ is not photosensitive. The solution was made basic, and the photolysis of the *trans*- $\text{Rh}(\text{NH}_3)_4(\text{OH})\text{Br}^+$ now present could be followed. It was determined by this means that 361 nm was an isosbestic point for *trans*- $\text{Rh}(\text{NH}_3)_4(\text{OH})\text{Br}^+$ and *cis*- $\text{Rh}(\text{NH}_3)_4(\text{OH})_2^+$ (the minor amount of $\text{Rh}(\text{NH}_3)_5(\text{OH})^{2+}$ present did not perturb the spectra significantly). The degree of ammonia photoaquation of $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ in alkaline solution would then be determined unambiguously by following the spectral change at 361 nm.

Bromide aquation yields could not be found spectrophotometrically because of the minor contribution of this reaction mode. These yields were therefore determined potentiometrically. Aqueous $[\text{Rh}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ was photolyzed in solutions containing a known amount of added sodium bromide and 0.2 *M* in sodium perchlorate as supporting electrolyte. After each photolysis interval, the potential was measured using an Orion Bromide Ion Electrode. The reference electrode was immersed in 0.2 *M* sodium perchlorate, and connected to the sample compartment by means of a 5% agar-agar salt (0.2 *M* sodium perchlorate) bridge. The difference between the measured potential and that before photolysis, $\Delta\mathcal{E}$, was found, and the data plotted according to the equation

$$\exp[\Delta\mathcal{E}\mathcal{F}/RT] = 1 + [\phi_{\text{Br}}I_{\text{a}}/(\text{Br}^-)_{\text{in}}]t \quad (3)$$

where I_{a} denotes the absorbed light intensity and $(\text{Br}^-)_{\text{in}}$ is the initial Br^- ion concentration. Such plots were linear, and the ratios of slopes for irradiations in various hydroxide ion concentrations, after correction for any variation in I_{a} , gave the ratios of quantum yields for bromide aquation.

In all cases, product concentrations were corrected for the usually small degree of dark or thermal reaction.

Pulsed Laser Experiments

The basic equipment consisted of an amplified, frequency tripled Nd glass laser with emission detection and means for observing transient absorptions as previously described [18]. Emission was followed at 700 nm, using pulses gated to 5 nsec half-intensity

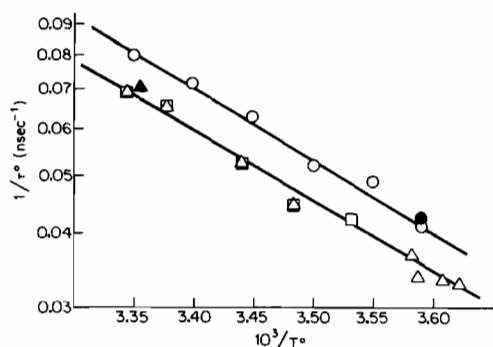


Fig. 1. Arrhenius plots of emission and ESA lifetimes for Rh(NH₃)₅Cl²⁺ and Rh(NH₃)₅Br²⁺. Δ , Rh(NH₃)₅Cl²⁺ emission; \square , Rh(NH₃)₅Cl²⁺ ESA; \circ , Rh(NH₃)₅Br²⁺ emission. Solid points are from Ref. [2].

time, and excited state absorption, using 20 nsec pulses.

Results

Emission and Emission Quenching

As previously reported [11], we find the emission lifetime τ^0 for Rh(NH₃)₅Cl²⁺ to be 30.1 ± 0.7 nsec at 5 °C, and 14.8 nsec at 25 °C, this last value being in good agreement with a reported one of 14.2 nsec [9]. These and other points gave a linear Arrhenius plot corresponding to an apparent activation energy of 5.4 ± 0.3 kcal mol⁻¹. The emission maximum is at 14.2 kK [2], which we confirm. The emission is broad, however, and the energy of the emitting thexi state, as estimated from the short wavelength tail, could be as high as 16–18 kK. Thomas and Crosby [19] estimated the energy of the transition from the ground state to the first triplet (the emitting state) to be 21.8 kK, probably a maximum value. From their sensitization studies, Kelly and Endicott [8] placed the thexi state energy as below 19.6 kK.

With the above estimates in mind, we examined some potential energy transfer quenchers having excited state energies below 20 kK. The results were negative. Up to 0.6 M MnCl₂ showed no quenching; Mn(II) has a quartet state at 18.9 kK [20]. Concentrated solutions of Co(II) (either as the chloride or the perchlorate salt) showed partial emission intensity quenching, traced to some precipitation of the rhodium complex, but no lifetime quenching. In this case, excited state energies of 8 kK and 12 kK have been estimated for the low lying quartet and doublet states, respectively [20]. Finally, nitrite ion has a triplet state energy of 18.5 kK [21] but, again, there was no detectable quenching, up to 0.04 M NO₂⁻, at 5 °C. from the τ^0 for Rh(NH₃)₅Cl²⁺, k_q ,

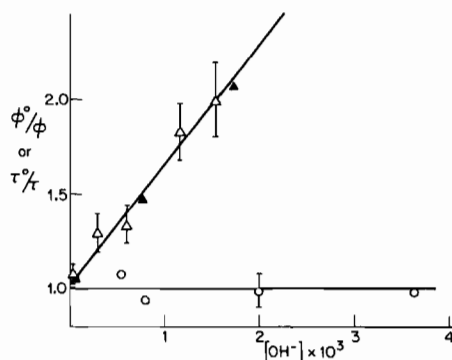


Fig. 2. Stern-Volmer plots of hydroxide ion quenching of excited state processes of aqueous Rh(NH₃)₅Br²⁺ at 5 °C. \blacktriangle , ammonia aequation; Δ , emission; \circ , bromide aequation.

the bimolecular quenching rate constant, must be significantly less than about 10^8 M⁻¹ sec⁻¹. It was impractical to test organic potential energy transfer quenchers because of solubility restrictions.

In view of some observations with Cr(III) complexes [22, 23], the possibility of quenching by hydroxide ion was investigated. This indeed occurred. The results for Rh(NH₃)₅Cl²⁺ have been reported [11]; k_q was found to be 2.1×10^{10} M⁻¹ sec⁻¹ at 5 °C. We further report here that the behavior of Rh(ND₃)₅Cl²⁺ is similar, with $k_q = 8.11 \times 10^9$ M⁻¹ sec⁻¹, again at 5 °C. Other basic anions have been examined. As previously reported [11], carbonate ion quenches, with $k_q = 8.3 \times 10^9$ M⁻¹ sec⁻¹ at 5 °C, cyanide ion showed a weaker quenching, and borate, acetate, formate, and oxalate ions showed none.

The emission lifetimes for Rh(NH₃)₅Br²⁺ are given in Fig. 1; the value of τ^0 at 5 °C is 24.1 nsec, in agreement with a literature value of 23.6 nsec [2]. The temperature dependence corresponds to an apparent activation energy of 5.1 kcal mol⁻¹, in essential agreement with literature [2]. The emission maximum is again at 14.2 kK [2] which we confirm. The emission is quenched by hydroxide ion, as shown in Fig. 2, with $k_q = 2.7 \times 10^{10}$ M⁻¹ sec⁻¹ at 5 °C. Emission yields for both complexes were small *ca.* 10^{-4} – 10^{-5} .

Excited State Absorption, ESA

Transient absorptions were observed for both Rh(NH₃)₅Cl²⁺ and Rh(NH₃)₅Br²⁺ in acidic media, with absorption maxima at 490 nm and 620 nm, respectively, see [10]. In both cases, the absorption decayed with the emission lifetime, and, in the case of Rh(NH₃)₅Cl²⁺, it was further determined that the absorption has the same temperature dependence, as shown in Fig. 1. Further, the absorptions were quenched upon quenching of the emission. We

therefore attribute them to ESA of the emitting state.

The minimum extinction coefficients at the band maxima could be estimated from the energy of the exciting pulse absorbed in the monitoring reaction, and were $>200 M^{-1} \text{ cm}^{-1}$ in both cases. A suggestion is that the ESA might be due to a charge transfer transition [24] presumably charge transfer to metal, CTTM; the shift in the ESA band of 4.1 kK between the chloro and the bromo complex resembles the 5.4 kK shift in the case of the corresponding and perhaps analogous Ru(II) complexes [25]. Consistent with this suggestion, we do observe a shift in the ESA maximum to 510 nm for $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ in dimethylsulfoxide as solvent. Charge transfer but not ligand field transitions are expected to show solvent sensitivity as to band maxima. There was, incidentally, no change in the ESA spectrum in basic solution, under partial quenching conditions.

Quenching of Photochemistry in Basic Solutions

Hydroxide ion quenching of reaction (1) for $\text{X} = \text{Cl}^-$ is 87% efficient, as reported previously [11]. For this same complex there is also quenching of photochemistry, along with emission quenching, in the presence of carbonate ion [11]. In addition, some $\text{Rh}(\text{NH}_3)_5(\text{CO}_3)^+$ is formed in this case, evidenced by large absorbance changes around 320 nm. Photolyzed solutions thus contained three components, unreacted chloro complex, *A*, $\text{Rh}(\text{NH}_3)_5(\text{OH})^{2+}$, *B*, and the carbonate complex, *C*. Their compositions were analyzed spectrophotometrically by means of the triangulation method [26]. One set of results for pH 10.08 carbonate buffer ($6.7 \times 10^{-3} M \text{ CO}_3^{2-}$) at 5 °C was the following, where *t* is the time of 366 nm irradiation in minutes and *F* denotes the fraction of species present, (*t*, F_A , F_B , F_C): (5, 0.935, 0.04, 0.025), (10, 0.88, 0.06, 0.06), (15, 0.82, 0.08, 0.10), (20, 0.76, 0.10, 0.14). The increasing ratio of species *C* to *B* suggests that the carbonate complex was formed by secondary reaction rather than by direct photochemical production. According to Palmer and Harris [16] the reaction $\text{Rh}(\text{NH}_3)_5(\text{OH})^{2+} + \text{CO}_2(\text{aq}) = \text{Rh}(\text{NH}_3)_5(\text{CO}_3)^+ + \text{H}^+$ occurs with a rate constant that would account for our results. We conclude that there was no direct photochemical formation of the carbonate complex.

Turning to $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$, Fig. 2. shows that ammonia aquation is 100% quenchable, with the same Stern–Volmer constant as for emission quenching. Bromide photoaquation, however, is not detectably affected by hydroxide ion concentrations sufficient to greatly reduce the emission lifetime. There is thus selective quenching of one of the two reaction modes, apparently the first such case to be reported for a coordination compound.

Two-Photon Processes

The existence of a fairly strong ESA made the following experiment possible. Acidic aqueous $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ was pulse photolyzed without using the filter which normally eliminates the 530 nm present under frequency tripling conditions, that is, the solution was flashed with simultaneous 353 nm and 530 nm pulses, the latter being several times more energetic. The rationale was that ground state complex, which has only a small absorption at 530 nm, would be excited by the 353 nm component, and the resulting excited state complex would undergo further excitation by the 530 nm component. The higher excited state might well exhibit a different chemistry from that found on 353 nm irradiation.

In order to produce measurable photochemistry several (up to 10) laser pulses were used; the pulses were at one minute intervals and the solution was mixed after each one. The extent of ammonia aquation was determined spectrophotometrically from the change in absorbance at 466 nm, which is sensitive to production of *trans*- $\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}^{2+}$ but not to that of $\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$. The amount of bromide aquation was found potentiometrically, as described under Experimental.

The results were as follows. The combined 353 and 530 nm pulsing led to both reactions (1) and (2), in the ratio 1:0.64, in contrast to the normal photochemical ratio of 1:10. That is, there was a greatly enhanced proportion of bromide relative to ammonia aquation. In addition, however, photolyses using 353 nm only pulses gave the different ratio of 1:2.1. An attempt was made to observe pulsed laser photolysis with 530 nm only pulses, but the extinction coefficient of the complex is small at this wavelength, and sufficient photolysis for a reliable result was not obtained.

The different from normal reaction ratio using 353 nm only pulses presumably reflects photolysis following ESA at 353 nm. There could certainly be a second excited state absorption band in this wavelength region; we did not look for one because of the difficulty of excluding scatter from the exciting pulse. Two photon processes should show intensity dependent yields. Demonstration of such dependence was not possible in this case, however, because of the need to use near maximum pulse energies in order to obtain measurable amounts of reaction. The absolute yields could not be calculated quantitatively, but, qualitatively, were high.

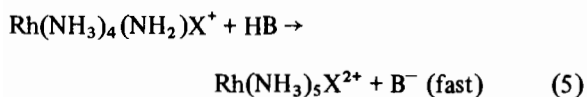
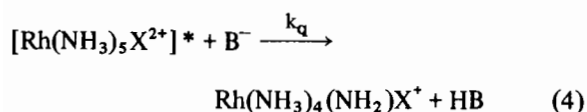
Discussion

We can give an approximate energy bracketing of the emitting state energy for $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ as $14 < E < 18.5$ kK. The lower limit is simply that of the

emission maximum (and is presumably low), and the upper limit is set by the failure of NO₂⁻ ion to quench. The negative results with Mn(II) and Co(II) can be discounted on the basis that charge repulsion between two cations could reduce k_q to a value too small for kinetic quenching to compete with the 30 nsec emission lifetime at attainable quencher concentrations. No electrostatic barrier should exist for NO₂⁻, however, and we attribute lack of observed quenching to the excited state lying below that for NO₂⁻ ion.

The success of hydroxide ion and of other relatively strong inorganic bases as quenchers cannot be attributed to energy transfer as no low lying excited states are known for ions such as OH⁻, nor is a 'heavy atom' effect invocable. Electron transfer quenching is not likely, on energetic grounds. The most likely explanation is one of quenching by excited state proton transfer. Hydroxide ion quenching has been reported before, for Cr(NH₃)₆³⁺ [20], Cr(en)₃³⁺ [21], and *trans*-Cr(en)₂(NCS)₂⁺ [27]. The results in this last case, suggested that the quenching was a reactive one. Also, excited state acid-base processes are known for complex ions. The CT excited state of a Ru(II) bipyridine complex having a carboxylic acid appendage is reported as having a pK of 8.5, as compared to 5.5 in the ground state [28], while that for an Ir(III) aquobipyridine complex is reported to be 3.5 compared to the ground state value of 3.0 [29].

We propose that our observed base quenching is due to the process



The product of reaction (4) could be the excited state species [Rh(NH₃)₄(NH₂)X⁺]^{*}, but in the absence of any indication otherwise, we take the product to be in the ground state, that is, that excitation quenching occurs with proton transfer. Reaction (5) could be fast enough to occur during the period of the reaction (4) encounter complex. A prediction of the proton transfer quenching mechanism is that no quenching would be expected if no acidic protons were present. This prediction was confirmed for the case of Rh(bipy)₂Cl₂⁺, for which we find no quenching by either Co₂²⁻ or OH⁻.

It seems reasonable that k_q should decrease with decreasing basicity of B⁻, as observed, and be negligible for weak bases. If the excited state has acquired additional electron density on the unique or z axis, this could result in stronger equatorial metal-

nitrogen bonding and therefore greater acidity for those ammonia protons. The pK_a would still be relatively large and for k_q to approach the diffusion limit B⁻ would indeed have to be a strong base. The decrease in k_q on deuteration is also expected in terms of the above mechanism. A comparable effect has been reported for an organic system, β-naphthol [30].

We next examine some of the implications of the results on quenching of photochemistry. As noted earlier, Kelly and Endicott [6] could account for their observations by invoking two triplet excited states. The first, ³X, led only to ammonia aqutation and, in the case of Rh(NH₃)₅Br²⁺, lay 2.8 kcal mol⁻¹ above a ³Y state, which led only to bromide aqutation. It was necessary in this explanation that the two states be in steady state equilibrium.

The above scheme encounters difficulties from our results. The emission presumably occurs from either ³X or ³Y, yet if this were so, bromide aqutation would be quenchable along with the emission, contrary to observation. Alternatively put, since the two states are in equilibrium, quenching of ammonia aqutation implies quenching of bromide aqutation, contrary to observation.

An alternative two triplet state scheme is shown in Fig. 3a. Assuming applicability of ligand field theory for tetragonal geometry, excitation leads, after intersystem crossing, to ³E and ³A₂ thexi states. The former should be the lower in energy, and is assumed to give rise both to emission and to ammonia aqutation. The temperature dependence for φ_{NH₃} is not large, and is given no special significance, being the accidental net of the temperature dependencies of non-radiative and chemical reaction rates. The ³A₂ state undergoes bromide aqutation (in competition with conversion to ³E). To accommodate the Kelly and Endicott results, it is also the state populated in biacetyl sensitization.

The orbital population of ³A₂† provides d_{x²-y²} antibonding electron density and should not therefore be particularly labile toward bromide aqutation. However, the geometry of the ³A₂ state could be relatively close to that of the ground state (while ³E is highly distorted, as evidenced by the large Stokes' shift [19]). Relaxation of ³A₂ into the ground state vibrational manifold might therefore produce a hot molecule whose vibrational activation resembled that of the transition state of the thermal reaction, thus leading to bromide aqutation.

†The wave functions for the T_{1g} state, on reduction to tetragonal symmetry are [12, 31]: ^{1,3}E: -(√3/2)[(xy)²-(xz)²(yz)¹(z²)¹] - (1/2)[(xy)²(xz)²(yz)¹(x²-y²)¹]; + (√3/2)[(xy)²(xz)¹(yz)²(z²)¹] - (1/2)[(xy)²(xz)¹(yz)²(x²-y²)¹]. ^{1,3}A₂: [(xy)¹(xz)²(yz)²(x²-y²)¹].

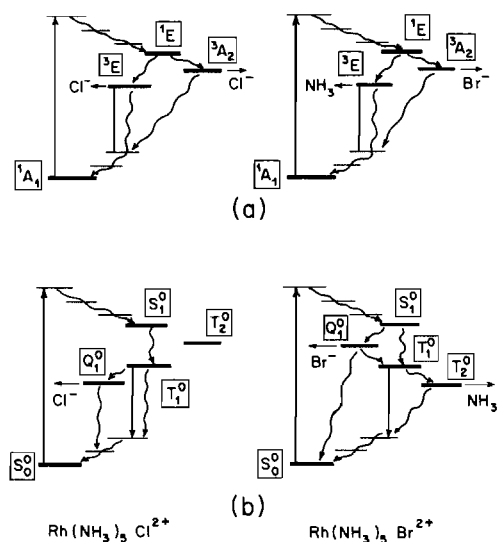


Fig. 3. Energy vs. distortion diagram for $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$. Heavy horizontal lines denote thexi (thermally equilibrated excited) states. Light horizontal lines indicate successive complex-solvent cage energies as a vibrationally excited state relaxes to its thexi state (only a few such lines are shown). Heavy vertical lines denote absorption or emission; wavy lines denote non-radiative processes. (a) Two reactive or emitting states. (b) Three reactive or emitting states.

To explain the results with $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$, the ordering of the triplet levels must now be inverted or, alternatively, the photochemistry of ${}^3\text{E}$ must now be one of chloride aquation. Either requirement seems awkward. The emission from $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ is quite similar to that from $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ in lifetime, temperature dependence, and spectrum. This suggests that the emitting state is of the same species in the two cases, a counterindication of any change in ordering. Possible change in reaction mode has indeed been rationalized qualitatively in terms of ligand field arguments [32], to make the scheme of Fig. 3a acceptable. However, it seems awkward to have to assume that such reactivity change is not accompanied by a comparable degree of change in emission properties.

There is another possibility, as we have pointed out [33]; this is shown in Fig. 3b. The emitting state is again taken to be a triplet which we now call T_1^\dagger (possibly ${}^3\text{E}$ in tetragonal symmetry), and is

[†] We prefer to use spin rather than orbital symmetry labels, the superscript zero denoting thermally equilibrated. The reason is that while distortion accompanying thermal equilibration could remain within the octahedral framework, e.g. tetragonal, it need not. One or more of the thexi states could, for example, have pentagonal symmetry or be triangularly prismatic. The matter of excited state geometry is as yet a rather obscure one.

unreactive (because of competition from non-radiative processes). T_1° generates one or another reactive state. Ammonia aquation occurs through a second triplet state, T_2° , and halide aquation, through a quintet state, $\text{Q}_1^{\circ\dagger}$. With a nearly uniform d-orbital occupancy, Q_1° should be less distorted from the ground state than the singlet and triplet thexi states, and therefore more apt to resemble the ground state in thermal reactivity (or to relax to a hot ground state showing the thermal mode of reaction).

One accounts for the varying photochemistry and quenching as follows. For $\text{X} = \text{Cl}^-$, T_2° lies above T_1° and Q_1° lies below. Excitation leads only to chloride aquation, which is quenchable, the 13% unquenchable portion being assigned to reactive quenching. For $\text{X} = \text{Br}^-$, T_2° lies below T_1° and Q_1° lies above. Irradiation now leads primarily to ammonia aquation, with an unquenchable component of bromide aquation. For $\text{X} = \text{I}^-$, Q_1° has risen enough in energy not to be populated, and only ammonia aquation occurs. Alternative spin assignments can be rationalized; either T_1° or T_2° might be interchanged with Q_1° , for example.

The results of the two-photon photolyses warrant comment. If the ESA is due to a CTTM transition, the excited state arrived at might be the same as on around 254 nm direct irradiation. While 254 nm photolyses of $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ seem not to have been reported, in the case of $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$, the results of Kelly and Endicott [35, 36] were consistent with a homolytic bond fission leading to $\text{Rh}(\text{NH}_3)_4^+$ and I as primary photoproducts. Subsequent reoxidation then gave $\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$, the principal final photoproduct. Our finding, however, is that bromide aquation is favored, and the mechanism in our case may be analogous to that postulated for $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ (see [37]) in which escaping Br regains an electron from the nascent $\text{Co}(\text{II})$ moiety to yield Br^- and $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ as one set of photoproducts. There is also $\text{Co}(\text{II})$ production, attributed to inefficiency of the back electron transfer process, the $\text{Co}(\text{II})$ then shedding its ligands to become the stable aquo ion. In the case of rhodium, however, such inefficiency would lead to the Kelly and Endicott mechanism and thus to $\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$.

The above explanation accounts for our results using 353 nm only pulses, and can also explain the yet higher relative bromide aquation yield on using the combined 353 + 530 nm pulses. There is now less excess energy given to the escaping Br, and the efficiency of back electron transfer should be higher.

^{††} The quintet state is not necessarily too high in energy to be considered. Qualitatively, while two electrons are promoted, two spin pairing energies are recouped. In fact, possible parameters in tetragonal geometry can place ${}^3\text{T}_2$ between the ${}^3\text{E}$ and ${}^3\text{A}_2$ states of T_{1g} parentage [34].

Alternatively, of course, a completely different excited state, such as a higher ligand field state, might be involved.

Returning to the ordinary photolysis results, our discussion has been limited to the examination of possible assignments of emitting and reactive excited states; it has not dealt with the mechanism of excited state reactions. It has been supposed, for example, that these occur via five-coordinated intermediates [38, 39] although we have preferred to consider concerted processes [26]. Regardless of outcome, the present results will certainly have to be considered in any ligand field rationalization of mechanism.

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