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Photochemistry of Iodoammine Complexes of Rhodium(III). A Case for Inefficient Internal Conversion between Charge-Transfer and d–d Excited States[1]

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Abstract: The ultraviolet irradiation of both $Rh(NH_3)_5I^{2+}$ and *trans*-$Rh(NH_3)_4I_2^+$ leads to formation of *trans*-$Rh(NH_3)_4OH_2I^{2+}$ as a primary product. Product yields are *lower* for irradiation of charge transfer to metal bands than for irradiation of metal ion centered absorption bands. In the case of $Rh(NH_3)_5I^{2+}$, primary aquation yields vary from 0.2 at 254 nm to 0.9 at 470 nm. Charge-transfer excitation of this complex does lead to oxidation of coordinated I^- and the formation of a transient $Rh(NH_3)_4^{2+}$ species. Flash photolysis and ^{131}I tracer studies indicate that the redox yield is $\sim$0.2 at 254 nm. These studies show that internal conversion from charge-transfer to d–d excited-state manifolds is relatively inefficient, compared to product formation and deexcitation. It furthermore appears that the d–d excited state is five-coordinate, pyramidal with I^- apical.

Photochemical studies of nd^6 transition metal complexes have provided a rich variety of reactions,[2] some formidably complex behavior,[3] and difficult and controversial problems of mechanism.[2–4] Of course, the bulk of these studies of nd^6 systems involve complexes of cobalt(III),[2–4] while few quantitative studies have been made of the complexes of heavier metals.[2,4–6]

The pattern for cobalt(III) complexes is of relatively high product yields ($\phi_{\text{redox}} \sim 0.2$)[7,8] following charge transfer to metal (CTTM) excitation, but nearly no products ($\phi_{\text{d-d}} \lesssim 10^{-3}$) resulting from excitation in the lower energy d–d spectral bands. Very recent energy-transfer studies with triplet donor molecules are consistent with a model which suggests that the photochemically active state is a charge-transfer triplet whose energy is near that of the higher energy d–d ($^1T_{2g} \leftarrow {}^1A_{1g}$) absorption band.[9–11]

It is a frequent observation[2,12] that the higher excited states are rapidly deactivated through internal conversion processes to the lowest energy state of a particular spin multiplicity. Thus, one might expect the photochemical reactivity and any luminescence of the compounds to be associated with lowest energy states (*e.g.*, $^1T_1$ or $^3T_1$ in terms of the excited states represented in Figure 1). For example in the $Rh^{III}(NH_3)_5X$ complexes, which are spin-paired $4d^6$ and quite analogous to the cobalt(III) systems, wavelength-independent luminescence is observed apparently from the $^3T_1$ energy level in each case.[13] Thus the great difference in the photochemical behavior which follows d–d and CTTM excitation of cobalt(III) complexes is a funda-

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[1] Partial support of this research by the National Science Foundation is gratefully acknowledged.

[2] For a useful and comprehensive review, see V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970.

[3] For example, see (a) J. F. Endicott, M. Z. Hoffman, and L. S. Beres, *J. Phys. Chem.*, **74**, 1021 (1970); (b) G. Caspari, R. G. Hughes, J. F. Endicott, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **92**, 6801 (1970).

[4] A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

[5] T. L. Kelly and John F. Endicott, *J. Amer. Chem. Soc.*, **92**, 5733 (1970).

[6] L. Moggi, *Gazz. Chim. Ital.*, **97**, 1089 (1967).

[7] For example, irradiation of the charge-transfer absorption bands in $Co^{III}(NH_3)_5X$ complexes leads to $\phi_{Co^{2+}} \simeq 0.2$ for the cases that X = NH_3, OH_2, Cl^-, Br^-, N_3^-, $^-O_2CCH_3$, $C_2O_4H^-$, etc.[2,3,8] Somewhat higher redox yields have been observed for $Co(NH_3)_5I^{2+}$ and $Co(C_2O_4)_3^{3-}$, but these cases are complicated by the peculiar reactivity patterns of radicals and other intermediate species.[2,8] Lower yields have frequently been observed for complexes containing polydentate chelates.[2]

[8] A. F. Vaudo, M. Z. Hoffman, E. Papaconstantinou, and J. F. Endicott, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971, INOR 23.

[9] A. Vogler and A. W. Adamson, *J. Amer. Chem. Soc.*, **90**, 5943 (1968).

[10] M. A. Scandola and F. Scandola, *ibid.*, **92**, 7278 (1970).

[11] It is to be observed that a quantitative relationship between direct and sensitized photolysis of $Co(NH_3)_6^{3+}$ has only been established for the biphenyl sensitization.[10]

[12] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1967.

[13] T. R. Thomas and G. A. Crosby, *J. Mol. Spectrosc.*, **38**, 118 (1971).

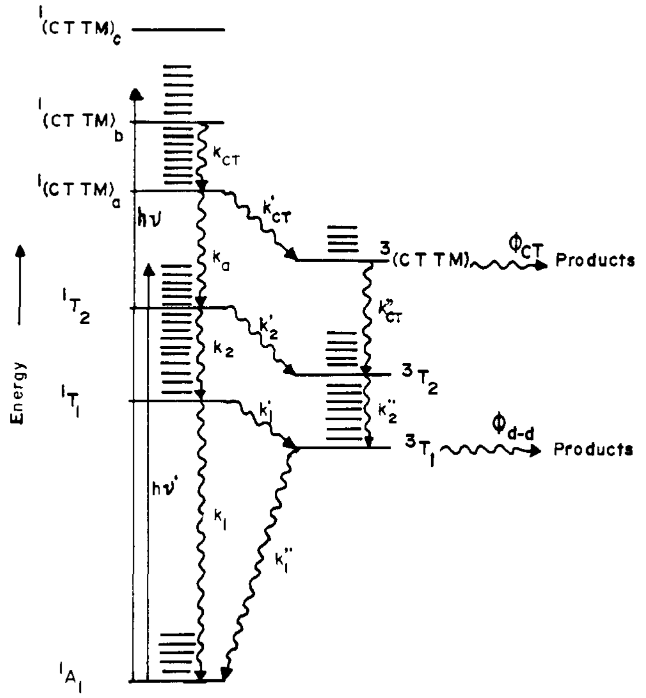

Figure 1. Hypothetical energy level scheme for a low-spin d^6 complex of O_h symmetry. Solid lines indicate typical initial excitations into CTTM or ligand-field (d–d) excited-state manifolds. The triplet CTTM state, ^{3}(CTTM), is intended to be representative. Wavy lines indicate the various, competitive radiationless decay modes of the thermally equilibrated excited states.

mental puzzle, since it implies that the photochemically most active excited states are generally inaccessible from the lower energy d–d excited-state manifolds.[14–16] In fact, some recent quantitative energy-transfer work[10] strongly suggests that the nonradiative deactivation of the CTTM singlet excited state of $Co(NH_3)_6^{3+}$ is more efficient than, but in competition with, intersystem crossing into the charge-transfer triplet excited-state manifold; *i.e.*, in terms of our oversimplified representation in Figure 1, this work implies that $k_{CT}' \sim {}^1/_5 k_a$.[17] Unfortunately, even the energy-transfer work gives little insight into the factors which govern the relative efficiencies of internal-conversion (between CTTM and d–d excited states) and intersystem-crossing processes. In this regard, it is to be recalled that although formal metal ion electronic configurations ($t_{2g}^6e_g$ and $t_{2g}^5e_g$, respectively) involve similar population of antibonding e_g orbitals, one might expect a larger metal-ligand distortion in the vibrationally equilibrated CTTM excited states, since the charge density on the metal is less in these cases. Furthermore, charge-transfer excitation of $Ru^{III}(NH_3)_5X$ complexes (excited-state formal electronic distribution, t_{2g}^6)[18] does not lead to significant photochemistry, implying that metal ligand distortions which follow population of antibonding e_g orbitals are of fundamental importance in determining excited-state reactivity.[19]

We have undertaken the investigation of the photochemical behavior of $Rh^{III}(NH_3)_5X$ complexes, in part because the relatively high photosensitivity determined[7] or inferred[20] for d–d absorption bands suggested that some of the mechanistic problems which have arisen in photochemical studies of cobalt(III) complexes could be answered relatively definitively for the analogous rhodium(III) complexes. We have found that the photochemistry of $Rh(NH_3)_5I^{2+}$ and related iodoammines is particularly rich in new chemical and mechanistic insights.

Experimental Section

(A) **Preparation of Reagents and Solutions.** Standard literature procedures[21,22] were used to prepared $[Rh(NH_3)_5I](ClO_4)_2$ and $[Rh(NH_3)_5H_2O](ClO_4)_3$. Purity of preparations was determined by comparison of their absorption spectra with published data.[23,24] *trans*-$Rh(NH_3)_4I_2^+$ was prepared by photolysis of a sodium iodide solution containing $Rh(NH_3)_5H_2O^{3+}$. The complex separated from the reaction mixture by ion exchange (Bio-Rad Ag 50 W-X2, H$^+$ form) and eluted with $HClO_4$. The volume of eluent containing $Rh(NH_3)_4I_2^+$ was reduced by evaporation, and the perchlorate salt was crystallized by cooling the concentrated solution in an ice–salt bath. The orange-brown powder was collected and washed with cold dilute $HClO_4$, cold ethanol, and ether, and air dried. The product was recrystallized from dilute $HClO_4$. The absorption spectrum of our preparations of [*trans*-$Rh(NH_3)_4I_2$]-ClO_4 compared well with that of *trans*-$Rh(en)_2I_2^+$ [25,26] (see Table I). *Anal.* Calcd for $RhN_4H_{12}O_4ClI_2$: N, 10.7; I, 48.4. Found: N, 10.7; I, 47.5.

Table I. Absorption Spectra of Some Rh(III)N$_4$XI Complexes

Complex	Absorption maxima[a]	Ref
trans-$Rh(NH_3)_4I_2^+$	470 (333), 340 (1.9 × 10^4), 270 (3.5 × 10^4), 222 (1.8 × 10^4)	*b*
trans-$Rh(NH_3)_4OH_2I^{2+}$	485 (285),[c] 295 (2050), 226 (3.6 × 10^4)	*b*
trans-$Rh(en)_2I_2^+$	462 (260), 341 (10^4), 269 (3 × 10^4), 222 (2 × 10^4)	18
	462 (260), 340 (1.4 × 10^4), 269 (3.1 × 10^4) 222 (2 × 10^4)	19
trans-$Rh(en)_2OH_2I^{2+}$	465 (95), 300 (1000)	19

[a] Wavelength in nm, ϵ in M^{-1} cm^{-1}, given in parentheses. [b] This work. [c] Estimated for a sample prepared *in situ* and concentration determined by conversion to diiodo complex.

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(14) One referee reminded us that Adamson and Sporer[15a] long ago suggested an explanation of this phenomenon. This early explanation involved a radical-pair model which was based on the erroneous[2,3,7,16] assumption that for CTTM excitation, $\phi_{Co^{2+}}$ increased with the "reducibility" of X; furthermore, such a model seems incompatible with the recent sensitization studies.[9,10] A number of important modifications of the radical-pair model have recently been proposed by Vogler and Adamson.[15b] These latter authors have also explicitly discussed the point that "the CT and d–d excited-state systems do not strongly intercommunicate" in cobalt(III) photochemistry. It must be noted, however, that if CTTM excitation leads to $\phi_{Co^{2+}} \sim 0.2$[7] and if d–d excitation leads to nearly no products, then the CTTM excited states *could* be deactivated ~80% of the time by means of internal conversion to the d–d excited states. This is far better "communication" than observed in the present study.

(15) (a) A. W. Adamson and A. H. Sporer, *J. Amer. Chem. Soc.*, **80**, 3865 (1958); (b) A. Vogler and A. W. Adamson, *J. Phys. Chem.*, **74**, 67 (1970).

(16) J. F. Endicott and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **87**, 3348 (1965).

(17) Note that deactivation of ^{1}(CTTM) may proceed by means of a direct return to the ground state without populating any d–d excited states. See the discussion below.

(18) This description of electronic distribution is of course a limiting strong-field description for complexes of O_h symmetry. It does provide a convenient expression of distinctions between nonbonding and antibonding metal-centered orbitals.

(19) W. L. Wells and J. F. Endicott, *J. Phys. Chem.*, **75**, 3075 (1971).

(20) (a) R. A. Bauer and F. Basolo, *J. Amer. Chem. Soc.*, **90**, 2437 (1968); (b) *Inorg. Chem.*, **8**, 2231 (1969).

(21) J. N. Brønsted and K. Valquartz, *Z. Phys. Chem.*, **134**, 103 (1928).

(22) G. W. Bushwell, G. C. Lalor, and E. A. Moelewyn-Hughes, *J. Chem. Soc. A*, 717 (1966).

(23) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 500 (1956).

(24) H. Schmidtke, *Z. Phys. Chem. (Frankfurt am Main)*, **45**, 305 (1965).

(25) S. N. Johnson and F. Basolo, *Inorg. Chem.*, **1**, 925 (1962).

(26) (a) E. J. Bounsall and A. J. Pöe, *J. Chem. Soc. A*, 280 (1966); (b) H. L. Bott and A. J. Pöe, *ibid.*, *A*, 205 (1967).

Solutions were prepared for photolysis using reagent grade salts and water redistilled from alkaline potassium permanganate. All solutions were deaerated, except as noted, by the passing of Cr^{2+}-scrubbed N_2 or argon through them before and during photolysis.

(B) Analytical Procedures. Concentration of NH_3 was determined in two ways, the first being colorimetric. A modification of the method of Bolleter, *et al.*,[27] was used. An aliquot of the photolyte was passed through an anion-exchange resin (Dowex 1-X8, 20–50 mesh, Cl^- form) to remove any I^-. To this solution were added 15 ml of saturated H_3BO_3 solution, 5 ml of chlorine water, and 5 ml of 8% phenol solution. The resulting solution was heated for 3 min in boiling water. It was then removed and cooled in ice water for about 3 min. After cooling, 3 ml of 3 *N* NaOH solution was added and the absorbance at 625 nm measured. The method was checked by determining the NH_4^+ concentration in solution containing known amounts of NH_4^+ and various amounts of I^- and $Rh(NH_3)_5I^{2+}$. The second method was determination of change in pH. An Instrumentation Laboratories Model 145 pH meter was used to measure the pH. For solutions with an initial pH of 3, the difference in $[H^+]$ of photolyte and unphotolyzed solution is a measure of the $[NH_3]$ released due to protonation of NH_3.

Good agreement was obtained between determinations on similar solutions performed by both methods. Because of the greater experimental ease, the change of pH method was more commonly used.

In many cases, and particularly in solutions with pH <3, we have used the rate of formation of tetraamminerhodium(III) product as an equivalent measure of the rate of NH_3 aquation. This method was feasible because *trans*-$Rh(NH_3)_4(OH_2)I^{2+}$ anated very rapidly in 0.5 *M* NaI; this method proved to be the most sensitive measure of NH_3 aquation due to the distinct and intense absorption spectrum of $Rh(NH_3)_4I_2^+$ (see Table I and Figure 2).

The attempted determinations of $[I^-]$ in photolyzed solutions were performed using 0.001 *M* $AgNO_3$ in potentiometric titrations.

The rhodium(III) products of photolysis were identified from their absorption spectra and their chromatographic elution characteristics. Cationic products were separated from the photolyte by placing a measured aliquot on the clean cation-exchange resin (Bio-Rad AG 50W-X2, 200–400 mesh, Na^+ form). Any tetraamminerhodium(III) products were converted to *trans*-$Rh(NH_3)_4I_2^+$ and eluted first with 0.3 *M* NaI as eluent. Then any $Rh(NH_3)_5I^{2+}$ was eluted with 1 *M* $Mg(ClO_4)_2$. Complex ion concentrations in eluent were determined spectrophotometrically.

In a second method, all unphotolyzed $Rh(NH_3)_5I^{2+}$ was precipitated as the diiodide salt from a solution made 1 *M* in NaI. The precipitate was washed, dried, and weighed. Any *trans*-$Rh(NH_3)_4I^+$ remaining in solution was determined spectrophotometrically.

(C) Continuous Photolysis. Apparatus and Procedures. The 254-nm irradiations of I^- solutions and some of the irradiations of $Rh(NH_3)_5I^{2+}$ were performed using an Ultraviolet Products, Inc. low-pressure Hg immersion lamp with a Vycor jacket as described elsewhere.[3] All other irradiations were performed using a Xenon Corp. Model 727 spectral irradiator in the monochromator mode. Half-widths of irradiating bands were found to be approximately 20 nm using a Bausch and Lomb high-intensity monochromator in combination with a microvoltmeter and a RDR-F2 thermopile from Charles M. Reeder and Co., Detroit, Mich.

All light intensities were determined using ferrioxalate actinometry.[28]

For studies using the immersion lamp apparatus, samples were withdrawn after various timed periods of irradiation and analyzed for products. Initial slopes of plots of product concentration *vs.* irradiation times were used to calculate an initial rate of product formation. This initial rate was used along with I_a values to calculate a quantum yield (see ref 3 and 16).

When the spectral irradiator was used, a known volume of solution (*ca.* 3 ml) was pipeted into a rectangular quartz spectrophotometer cell, and Cr^{2+}-scrubbed N_2 was passed through the solution during irradiation. The solution was irradiated for a preset time period, then analyzed for products. An average rate of product formation was calculated using product concentration and irradiation time. This average rate, along with I_a, was used to calculate quantum yield. Various irradiation times were used to ensure that the average rate was not a function of irradiation time. The constancy of the light flux was monitored using the RDR-F2 thermopile (see ref 19).

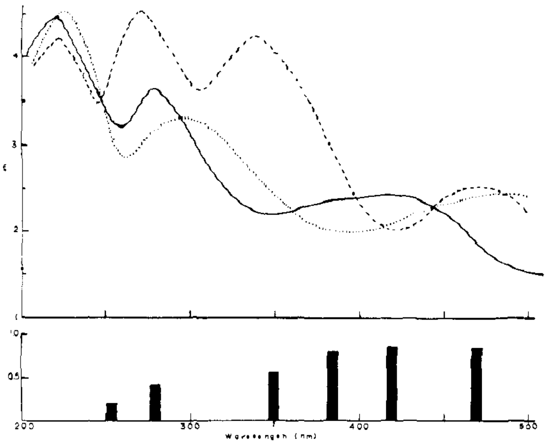

Figure 2. Absorption spectra of iodoammine complexes of rhodium(III) and primary photoaquation yields of $Rh(NH_3)_5I^{2+}$. Spectra: $Rh(NH_3)_5I^{2+}$ (——), *trans*-$Rh(NH_3)_4I_2^+$ (– – –), *trans*-$Rh(NH_3)_4OH_2I^{2+}$ (· · · ·).

In nearly all cases, the absorbance of the solutions was greater than 2 and photolysis was limited to, at most, 15% of reaction.

For irradiation at 214 nm a 25-W Phillips zinc resonance was operated at 27.8 V and 0.9 A. Radiation from the lamp was columnated with a uv-grade quartz lens and fixed slits. A 1-cm quartz spectrophotometer cell filled with redistilled water or an acetic acid filter solution was placed between the lamp and the sample irradiated. Uranyl oxalate actinometry was used. Photolyses (including the actinometric determinations) with the pure water "filter" were compared to those with an acetic acid filter to ensure that spectral lines with wavelength >240 nm did not complicate the observations.

(D) Flash Photolysis. The flash apparatus (Xenon Corp. Model 720) has been described elsewhere.[3b] It was operated in the kinetic spectrophotometric mode. The flash lamps dissipated 250 J at 10 kV with a rise time of 5 μsec, a half-peak duration of 20 μsec, and total duration of about 50 μsec.

Samples to be irradiated were placed in a jacketed 20-cm pathlength quartz cell. Samples were purged with Cr^{2+}-scrubbed N_2 and sealed from atmospheric contact by means of stopcocks before photolysis. Filter solutions were placed in the outer quartz jacket of the sample cells in order to eliminate incident radiation of higher energy than some desired limit.

For those solutions in which I^- was the predominant (>90%) absorbing species, transient decay data were treated as described elsewhere.[3b] Transient decay was followed at 404.7 nm instead of the λ_{max} for I_2^-, 370 nm,[29] because the reaction products have much lower absorptivity at this wavelength.

For solutions containing $Rh(NH_3)_5I^{2+}$ as the principle absorbing species, either in the presence or absence of relatively nonabsorbing amounts of I^-, various filter solutions were introduced into the outer jacket of the flash photolysis cell. Concentrations of absorbing species in filter solutions were adjusted until the absorbance at the desired (cutoff) wavelength was 2.0. The filter solutions (and cutoff wavelengths) used were: 2 *M* NaBr (230 nm), aqueous $Na_2S_2O_3$ (250 nm), $(C_2H_5O)_2O$ (284 nm), and $C_{10}H_{10}$ in ethanol (320 nm).

The following procedure was used in flash photolysis experiments with solutions containing both $Rh(NH_3)_5I^{2+}$ and I^-. First, the absorption spectrum of the solution after deaeration was determined spectrophotometrically. Second, the solution was flashed and the decay of the transient recorded. Finally, the absorption spectrum of the irradiated solution was measured. The percentage of photocomposition due to the flash irradiation was calculated from these data as follows. The absorbance *vs.* time plot of transient decay was extrapolated to the beginning of the flash ($t = 0$) to obtain a value of A_0 for the transient. The A_0 value,

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[27] W. Bolleter, C. Bushman, and P. Tidwell, *Anal. Chem.*, **33**, 592 (1961).

[28] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. Ser. A*, **235**, 518 (1956).

[29] L. L. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, **61**, 1089 (1957).

along with $\epsilon_{404.7}$ 1.17 ± 0.35 × 10^4 M^{-1} cm^{-1} for I_2^-, was used to calculate the initial $[I_2^-]$. In order to estimate $[I\cdot]$, we used the equilibrium expression[29] $I\cdot + I^- \rightleftarrows I_2^-$, our calculated value of $[I_2^-]_0$, and the known initial $[I^-]$. Thus, assuming that all the I· originated from $Rh(NH_3)_5I^{2+}$, $[I\cdot]_0 = ([I_2^-]_0/([I^-] - [I_2^-])_0)(1/K_{eq})$, where $K_{eq} = 8.4 \times 10^4\ M^{-1}$.[30] Note that the total bulk concentration of iodine atoms produced from $Rh(NH_3)_5I^{2+}$ by the flash photolysis equals concentration of free iodine atom plus concentration of diiodide anions. The amount of $Rh(NH_3)_5I^{2+}$ decomposed in the flash was calculated from the absorbance at 405 nm and the initial concentration of $Rh(NH_3)_5I^{2+}$ by assuming that $Rh(NH_3)_5I^{2+}$ and *trans*-$Rh(NH_3)_4OH_2I^{2+}$ are the only rhodium-containing species present after the flash. The amount of photodecomposition due to irradiation in a particular wavelength region was calculated from the differences in photodecomposition produced from flash photolysis experiments using filter solutions with progressively longer cutoff wavelengths. Percentage reduction is the sum of $[I\cdot]_0$ and $[I_2^-]_0$ produced from $Rh(NH_3)_5^{2+}$ divided by the $[Rh(NH_3)_5I^{2+}]$ photodecomposed. Approximate photoredox quantum yields[31] were calculated from an estimate of the average quantum yield for photoreaction in the particular spectral region (Table IV) and the percentage of the photoredox for that region.

(E) **Iodine-131 Tracer Studies.** A sample of $[Rh(NH_3)_5{}^{131}I](ClO_4)_2$ free of ionic iodide was prepared by using ^{131}I-enriched NaI in the usual preparative procedure.[21] The product $[Rh(NH_3)_5{}^{131}I]{}^{131}I_2$ was dissolved in water and placed on a cation-exchange resin (Dowex 50W-8X Na^+ form, 50 mesh) washed, and eluted with 2 *M* $NaClO_4$. The solution was then concentrated on a steam bath and the yellow crystals were collected. A sample of the crystalline product was used to prepare a stock solution. The samples for photolysis and a $Rh(NH_3)_5{}^{131}I^{2+}$ standard were prepared from this stock solution.

Samples containing the $Rh(NH_3)_5{}^{131}I^{2+}$ along with varying quantities of nonradioactive iodide ion were photolyzed at various wavelengths. The extent of photodecomposition of the substrate never exceeded 10%. The $Rh(NH_3)_5{}^{131}I^{2+}$ was immediately separated from the solution by cation-exchange techniques (Dowex 50W-8X, Na^+ form). The column was rinsed with 3.5 times its volume of water to remove all the I^-. These washings were collected and made to volume, and an aliquot was removed for counting. A well-type scintillation detector was used for counting. The counts for any day were normalized first for differing settings of the counter using a ^{137}Cs standard and then for decay of the ^{131}I ($t_{1/2}$ = 8.04 days) by comparing the ^{131}I standard with the ^{131}I standard for the first day.

Regardless of the mechanism for exchange, the rate of exchange is given by[32]

$$Rh^*I + I^- \rightleftarrows RhI + {}^*I^-$$

$$\text{rate } (M\ \text{min}^{-1}) = \frac{-2.303}{t}\frac{[RhI][I^-]}{[Rh(III)]} + [I^-] \log (1 - F_x) \tag{1}$$

where [RhI] = total concentration of RhI species, $[I^-]$ = total concentration of iodide, and F_x = fraction exchange = (activity after exchange)/(activity at equilibrium). The equilibrium activity was calculated from

$$A_{eq} = \left(\frac{[RhI]}{[RhI] + [I^-]}\right)A_{original} \tag{2}$$

Results

(A) **Continuous Photolysis.** (1) Irradiation of I^- solutions containing nonabsorbing amounts of $Rh(NH_3)_5OH_2{}^{3+}$, at 254 nm, produces no net photooxidation of I^-. The principal Rh(III) containing product of photolysis under these conditions is *trans*-$Rh(NH_3)_4I_2^+$. To facilitate our interpretation of results, we have determined the stability constant of *trans*-$Rh(NH_3)_4I_2^+$ to be (2.2 ± 0.4) × 10^3 M^{-1} (25°, μ = 0.1) with respect to *trans*-$Rh(NH_3)_4OH_2I^{2+}$. We also find that *trans*-$Rh(NH_3)_4OH_2I^{2+}$ anates with a pseudo-first-order specific rate constant (6.5 ± 0.2) × 10^{-3} sec^{-1} in 0.1 *M* I^- (25°, μ = 0.1). Thus, in these photolysis experiments at $[I^-]$ = 0.1 *M*, we were not able to detect *trans*-$Rh(NH_3)_4OH_2I^{2+}$ in the continuous photolysis of I^- solutions containing $Rh(NH_3)_5OH_2{}^{3+}$.

Under the conditions of these experiments, the primary absorption process can be considered to lead to production of e_{eq}^-[33-35]

$$I^- + h\nu \longrightarrow I + e_{aq}^- \qquad (\phi I_a)$$

In the presence of the electron scavengers $Rh(NH_3)_5OH_2{}^{3+}$ and H^+, the e_{aq}^- would be scavenged competitively

$$Rh(III) + e_{aq}^- \longrightarrow Rh(II) \tag{3}$$

$$H^+ + e_{aq}^- \longrightarrow 0.5H_2 \tag{4}$$

followed by complexation

$$I\cdot + I^- \rightleftarrows I_2^- \tag{5}$$

and recombination

$$Rh(NH_3)_4{}^{2+} + I_2^- + H_2O \longrightarrow trans\text{-}Rh(NH_3)_4OH_2I^{2+} + I^- \tag{6}$$

or

$$Rh(NH_3)_4{}^{2+} + I\cdot + H_2O \longrightarrow trans\text{-}Rh(NH_3)_4OH_2I^{2+} \tag{7}$$

or

$$Rh(NH_3)_4{}^{2+} + I_3^- + H_2O \longrightarrow trans\text{-}Rh(NH_3)_4OH_2I^{2+} + 2I^- \tag{8}$$

and finally anation

$$trans\text{-}Rh(NH_3)_4OH_2I^{2+} + I^- \longrightarrow trans\text{-}Rh(NH_3)_4I_2^+ + H_2O \tag{9}$$

For low $[H^+]$ and high $[I^-]$, assuming every rhodium(II) species produced by reaction 3 is reoxidized by some iodine species to Rh(III), the steady-state expression is[36]

$$\phi_{app}I_a = \frac{d[trans\text{-}Rh(NH_3)_4I_2^+]}{dt} \simeq \frac{\phi I_a k_3[Rh(III)]}{k_3[Rh(III)] + k_4[H^+]} \tag{10}$$

where ϕ_{app} is the quantum yield for *trans*-$Rh(NH_3)_4I_2^+$ and I_a is based on radiation absorbed by I^-. Consistent with (10), a plot of ϕ_{app}^{-1} *vs.* $[H^+]/[Rh(III)]$ (at constant $[H^+]$) gives a straight line.[36] The ϕ_{app} value obtained from this intercept (0.26 ± 0.03) corresponds closely to the value of 0.29 obtained by Jortner, Ottolenghi, and Stein[35] for the quantum yield of electrons produced by 2537-Å irradiation of aqueous I^- at 25°.

(2) **Irradiation of $Rh(NH_3)_5I^{2+}$.** The perchlorate salt of $Rh(NH_3)_5I^{2+}$ was irradiated at pH 3 ($HClO_4$) in the spectral region 254–280 nm, where the principal absorption was due to ligand to metal change-transfer (CTTM) transition,[37] or at 385 and 420 nm in the d–d absorption bands.[23,37] The net photochemical products for irradiation of both types of transitions with solutions most rigorously purged of oxygen were principally NH_4^+ and *trans*-$[Rh(NH_3)_4OH_2I^{2+}]$ along with a limited amount of *trans*-$[Rh(NH_3)_4I_2^+]$. Quantum

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(30) J. K. Thomas, *Advan. Radiat. Chem.*, **1**, 103 (1969).

(31) Note that the difference in estimates of ϕ_{redox} in Table IV and similar estimates in the preliminary communication[5] results from a different choice of K_{eq} and thus different estimates of $[I\cdot]_0$.

(32) O. E. Meyers and R. J. Prestwood in "Radioactivity Applied to Chemistry," A. C. Wahl and N. A. Boner, Ed., Wiley, New York, N. Y., 1951.

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Table II. Product Yields from the Photolysis of Iodoammine Complexes of Rhodium(III)

Irradiation wavelength, nm	Absorption band irrad	$10^4 I_a$, einsteins $l.^{-1}$ min^{-1}	Medium[a] conditions	Quantum yields		
				NH_3[b]	*trans*-Rh-$(NH_3)_4I_2^+$[c]	*trans*-$Rh(NH_3)_5OH_2I^{2+}$[b]
(A) For $Rh(NH_3)_5I^{2+}$						
214	CTTM (σ)[d]	0.32		0.41 ± 0.02 (3)	0.02	h
254	CTTM ($\sigma + \pi$)[d]	1.98–0.60[e]		0.43 ± 0.04 (21)	~0.03	0.43 ± 0.03 (6)[f]
			Air[g]	0.47	$<10^{-3}$	h
280	CTTM (π)[d]	3.0		0.52 ± 0.08 (16)	~0.02	0.53 ± 0.04 (5)[f]
			Air[g]	0.54	$<10^{-3}$	h
350	CTTM (π)[d] + d-d	5.8		0.58 ± 0.03 (6)	h	h
385	d-d ($^1A_1 \rightarrow {}^1A_2$)[i]	7.7		0.82 ± 0.08 (10)	~0.01	h
			Air[g]	0.81	$<10^{-3}$	h
420	d-d ($^1A_1 \rightarrow {}^1E$)[i]	8.5		0.87 ± 0.07 (11)	h	0.86 (1)[f]
			Air[g]	0.92	$<10^{-3}$	h
470	d-d ($^1A_1 \rightarrow {}^1E$)[i]	5.6		0.85 ± 0.04 (6)	h	h
(B) For *trans*-$Rh(NH_3)_4I_2^+$						
254	CTTM[k]	2.0–0.6[e]				0.20 ± 0.02 (4)[j]
280	CTTM[k]	3.1–2.0[e]				0.32 ± 0.03 (6)[j]
340	CTTM[k]	6.8–5.8[e]				0.33 ± 0.03 (6)[j]
470	d-d ($^1A_1 \rightarrow {}^1T_1$)[k]	5.4				0.48 ± 0.01 (3)[j]

[a] 25°, $1 \leqslant pH \leqslant 3$ ($HClO_4$), $\mu = 0.10$ ($NaClO_4$); all solutions N_2 scrubbed during and before photolysis. Exceptions noted. [b] Mean values and average deviations indicated. Number of determinations in parentheses. [c] Estimated from increase in absorbance at 340 nm, except as indicated. This is the yield of *trans*-$Rh(NH_3)_4I_2^+$ observed in the photolyte without added I^-. [d] Reference 37. [e] Quantum yields were independent of variations in I_a over this range. [f] Determined as *trans*-$Rh(NH_3)_4I_2^+$ after equilibration in 0.3 *M* NaI. [g] Air bubbled through solution during irradiation. [h] Not specifically determined. [i] Reference 13. [j] Quantum yield estimated from ion-exchange separation of products. [k] Assignment by analogy with *trans*-$Rh(en)_2I_2^+$; ref 25 and 26.

yields for these products are summarized in Table II. Product yields were found to be pH independent in the range $1 \leqslant pH \leqslant 3$. Attempted potentiometric determinations failed to reveal any I^-, indicating that $[I^-] < 2 \times 10^{-5}$ *M* and $\phi_{free\ I^-} \leqslant 10^{-4}$. Either the inadequate exclusion of air or the deliberate bubbling of air in place of N_2 during photolysis resulted in a disappearance of *trans*-$Rh(NH_3)_4I_2^+$ among the products at all wavelengths. The bubbling of air, however, had no effect on the quantum yield for NH_3 aquation (Table II).

Using cation-exchange chromatography, we have been able to separate unchanged substrate from product rhodium(III) complexes to account for all (*i.e.*, within ±2%) the rhodium originally present in solution. No complexes with fewer than four coordinated NH_3 ligands result from either direct irradiation of $Rh(NH_3)_5I^{2+}$ or the reactions 3–8 following I^- irradiation.

(3) **Irradiation of *trans*-$Rh(NH_3)_4I_2^+$.** The quantum yields for photodecomposition of *trans*-$Rh(NH_3)_4I_2^+$ as a function of wavelength are given in Table II. Cation-exchange separations and absorption spectra were used to identify *trans*-$Rh(NH_3)_4OH_2I^{2+}$ as the predominant photolysis product. Free I^- could not be determined potentiometrically due to the low concentration and the catalysis of I^- aquation from the starting material by Ag^+.

(B) **Flash Photolysis.** (1) **Iodide Solutions.** Grossweiner and Matheson[29] have shown that the dihalide transient species, I_2^-, obtained on flashing air-free solutions of I^-, has its absorption maximum at 370 nm and that it decays according to pH-independent, second-order kinetics. The rate of the decay increases with decreasing iodide concentration.

Table III gives a summary of the decay kinetics observed from flash photolysis of iodide in solutions containing various additional ions. The addition of other halides has no apparent effect on the second order rate constant for transient decay. The addition of a rhodium(III) substrate, under conditions which should lead to the formation of rhodium(II) through substrate scavenging for e_{aq}^- (eq 3), does decrease the I_2^- lifetime (Table III).

Table III. Second-Order Decay Rate Parameters for I_2^- Generated by Flash Photolysis of I^-[a]

$10^4[I^-]$, *M*	$t_{1/2}$, μsec[b]	$t_{1/2}$, A_0[b]	$10^9 k$, M^{-1} sec^{-1}[c]
(A) In Rhodium-Free Solutions			
1.0	54–84	30 ± 4	5.4 ± 0.5 (5)
	66–76	35 ± 2	4.6 ± 0.3 (4)[d]
	52–72	31 ± 1	5.2 ± 0.2 (4)[e]
10.0	66–72	42 ± 4	3.9 ± 0.6 (4)
	74–80	45 ± 3	3.5 ± 0.2 (4)[d]
	64–70	40 ± 3	4.0 ± 0.4 (4)[e]
(B) In Solutions Containing $Rh(NH_3)_5OH_2^{3+}$			
1.0	50–70	22 ± 5	7.1 ± 1.0 (4)[f]
	46–54	27 ± 2	5.9 ± 0.4 (4)[f]
	40–74	24 ± 2	6.6 ± 0.5 (5)[g]

[a] Temperature = 25°, $\mu = 0.1$ ($NaClO_4$, except as indicated). Monitoring wavelength = 404.7 nm. [b] A_0 calculated from extrapolation of absorbance *vs.* time to $t = 0$. $t_{1/2}$ is time required for A_0 to decrease to $0.5A_0$. [c] Observed second-order rate constant calculated from $k_{obsd} = 0.69l/(t_{1/2}A_0\epsilon_{I_2^-}l)$; $\epsilon_{I_2^-} = 11700 \pm 3500$ M^{-1} cm^{-1} (λ 404.7 nm)[23] and $l = 20$ cm. Mean values and average deviations from the mean are reported. Number of determinations in parentheses. [d] Chloride medium ($\mu = 0.10$). [e] Bromide medium ($\mu = 0.10$). [f] $[Rh(NH_3)_5OH_2^{3+}] = 1.0 \times 10^{-4}$ *M*. [g] $[Rh(NH_3)_5OH_2^{3+}] = 1.0 \times 10^{-3}$ *M*.

(2) **$Rh(NH_3)_5I^{2+}$ Solutions.** Solutions of $Rh(NH_3)_5I^{2+}$ either alone or containing relatively nonabsorbing quantities of I^- were flashed using various cutoff filter solutions. For solutions containing no added I^-, no transient was observed. There was, however, for spectral regions flashed, an immediate (within the lifetime of the flash) decrease in the absorbance of the solution at 404.7 nm along with an increase in absorbance at 485 nm. These spectral changes are consistent with photodecomposition of $Rh(NH_3)_5I^{2+}$ and

Table IV. Transient Yields in the Flash Photolysis of $Rh(NH_3)_5I^{2+}$ as a Function of the Spectral Region Irradiated[a]

Wavelength region irrad,[b] nm	Assignment of band(s) irrad[c]	$[Rh(NH_3)_5I^{2+}]$[d] $\times 10^5$ M	$[I] + [I_2^-]$[e] $\times 10^6$ M	Approx % redox[f]	Approx ϕ_{redox}[g]
230–250	CTTM (σ)	1.0	3.9	30	0.13
250–284	CTTM ($\sigma + \pi$)	1.0	1.0	10	0.05
284–320	CTTM ($\sigma + \pi$)	1.5	0.3	2	0.01
320	d–d CTTM (π)	9.0	0.1	0.1	10^{-3}

[a] $[Rh(NH_3)_5I^{2+}] = 2 \times 10^{-4}$ M, $[I^-] = 1.0 \times 10^{-4}$ or 0.5×10^{-4} M, pH 3, $\mu = 0.1$ ($NaClO_4$), 25°. Single flash experiments only. [b] A white flash was used in combination with cutoff filters. The differences in product yields obtained with successive filters are reported. [c] Reference 37. [d] The amount of $Rh(NH_3)_5I^{2+}$ destroyed was determined from spectral changes at 405 nm. [e] From A_0 of observed I_2^-, ϵ $(1.17 \pm 0.35) \times 10^4$ at 404.7 nm[29] and $K = [I_2^-]/[I][I^-] = 8.4 \times 10^4$.[30] [f] (Value in column 4)/(values in column 3). [g] Average quantum yield for the photodecomposition of $Rh(NH_3)_5I^{2+}$ in the various spectral regions were estimated to be: λ 230–240 nm, $\phi \sim 0.4$; λ 250–284 nm, $\phi \sim 0.5$; λ 284–320 nm, $\phi \sim 0.7$; and $\lambda > 320$ nm, $\phi \sim 0.9$.

Table V. Photocatalyzed Exchange of Coordinated and Solvent Iodide in the Photolysis of $Rh(NH_3)_5I^{2+}$ [a]

Irradiating wavelength,[b] nm	$10^3[I^-]$, M	F_x	$10^5 R_x$, M min^{-1}	$10^4 I_a$, einsteins l.$^{-1}$ min^{-1}	ϕ_x	ϕ_{NH_3}[c]	ϕ_x/ϕ_{NH_3}
254	1.5	0.19–0.10[d]	1.41	0.6	0.23	0.43	0.54
	0.75	0.24	1.28	0.6	0.21	0.43	0.49
280	6	0.088	2.50	1.8	0.14	0.52	0.27
	1.5	0.13	1.90	1.8	0.11	0.52	0.21
420	12	0.013	2.34	7.1	0.03	0.87	0.035

[a] 25°, $[H^+] = 0.01$ M. [b] For spectral band assignments, see Table II. [c] From Table II. [d] For different exposure times.

the production of *trans*-$Rh(NH_3)_4OH_2I^{2+}$ as an immediate (<50 μsec) photolysis product.

By comparing the amount of photodecomposition of $Rh(NH_3)_5I^{2+}$ per flash to the estimated yield of I· and I_2^- per flash, we have been able to show that photoredox is a very important process in the irradiation of the higher energy (σ) $I^- \rightarrow Rh(III)$ CTTM band (Table IV).

(C) **^{131}I Tracer Studies.** The activity of the cation-exchanged iodide solution was determined after timed exposures, and eq 1 was used to calculate the rate of exchange, R_x. This was used, together with I_a, to calculate a quantum yield for exchange $\phi_x = R_x/I_a$. Data are summarized in Table V.

In no case was the photolyte allowed to stand for more than 20% of one half-life for the anation reaction of $Rh(NH_3)_4OH_2I^{2+}$. Since irradiations were performed to $\leqslant 10\%$ of conversion of $Rh(NH_3)_5I^{2+}$ to products, we have found statistical corrections for the mixing of isotopes to be unimportant even at the lowest $[I^-]$.

Discussion

This study of the photochemistry of $Rh(NH_3)_5I^{2+}$ has provided a large amount of information about the nature and structure of rhodium(II) and the electronic excited states of rhodium(III) and some definitive information about the efficiency of internal conversion processes between different excited state manifolds. The photochemistry of *trans*-$Rh(NH_3)_4I_2^+$ has not been so productive, at least from the point of view of this paper. The work with the latter complex does reinforce the view that the NH_3 ligands coordinated perpendicular to the principal symmetry axis are not very much involved in excited state distortion in the iodo complexes. Flash photolysis of CTTM bands (λ <270 nm) has provided evidence for photoredox processes in these spectral regions. Furthermore, it is evident that secondary photolysis of any *trans*-$Rh(NH_3)_4I_2^+$ generated from $Rh(NH_3)_5I^{2+}$ cannot complicate our work with the pentaammine. The pattern of products and yields for *trans*-$Rh(NH_3)_4I_2^+$ is consistent with the mechanistic model for the photochemistry of $Rh(NH_3)_5I^{2+}$ which is evolved in the following discussion.

(A) **Some Reflections on the Structure and Reactivity of Monomeric Rhodium(II).** From our studies of the irradiation of I^- in weakly acidic solutions of $Rh(NH_3)_5OH_2^{3+}$, we may make several inferences about geometry and reactivity of the rhodium(II) species formed through reaction of the substrate with e_{aq}^-.

First, the correspondence of the limiting yield of *trans*-$Rh(NH_3)_4I_2^+$ under these conditions with the yield of e_{aq}^- from I^- photolysis demonstrates (1) that $Rh(NH_3)_5OH_2^{3+}$ is an efficient electron scavenger, (2) that the resulting rhodium(II) species is labile to the extent that only one coordinated NH_3 exchanges with solvent species during its lifetime; and (3) that all the rhodium(II) produced is rapidly reoxidized by iodine species (recall also that there is no net formation of I_3^-). Since all the final product rhodium(III) complexes, for each reduction event, are of trans geometry, we conclude that rhodium(II) must be a tetragonally distorted six-coordinate or even a four-coordinate planar species.

Our observation that the I_2^- decay lifetime is shortened under conditions that rhodium(II) is present indicates that the I_2^- oxidation of $Rh(NH_3)_4^{2+}$ has about the same magnitude of second-order rate constant as does the redox disproportionation of I_2^- (11); *i.e.*, $k_6 \sim$

$$2I_2^- \longrightarrow I_3^- + I^- \qquad (11)$$

3×10^9 M^{-1} sec^{-1}. Such rapid recombination of $Rh(NH_3)_4^{2+}$ with radical I_2^- is consistent with the hypothesis that low-spin d^7 systems exhibit radical-like properties.[38]

(B) **Charge-Transfer Photochemistry of $Rh(NH_3)_5I^{2+}$.** As we reported in a preliminary communica-

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[38] For other examples, see (a) J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, **86**, 2311 (1964); (b) F. Maspero and H. Taube, *ibid.*, **90**, 7361 (1968); and discussion in J. F. Endicott, *Israel J. Chem.*, **8**, 209 (1970).

tion,[5] irradiation of charge-transfer absorption bands does lead to photoredox processes in rhodium(III) complexes even though net oxidation or reduction is not observed. In the present report we have refined our estimates of redox yields based on flash photolysis. Furthermore, it is evident from the ^{131}I tracer work that the most important path for exchange involves species produced in the irradiation of CTTM bands, that for these excitations the exchange yield, $\phi_x \cong \phi_{redox}$, and in fact exchange must involve reaction 12 followed by 5–8. There also appears to be a minor

$$Rh(NH_3)_5I^{2+} + h\nu\,(CTTM) \xrightarrow{H^+} Rh(NH_3)_4{}^{2+} + NH_4{}^+ + I\cdot \quad (12)$$

exchange path not involving a redox process (about 4% of aquation events lead to exchange through this path).

In view of the imprecision of the values of the extinction coefficient and stability constant of I_2^- as well as the approximations involved in our isolation of spectral bands in the flash photolysis studies, the values of ϕ_{redox} in Table IV are at best only semiquantitative;[31] these yields do show which absorption bands lead to photoredox behavior. The exchange yields, ϕ_x, listed in Table V are certainly our best estimates of redox yields. Clearly our redox yields, 0.2 and 0.1 respectively in σ and π CTTM bands, are comparable in magnitude to the redox yields in cobalt(III) complexes.[7] Redox processes result from CTTM excitation but not from ligand-field excitation, also similar to the case for cobalt(III). The wavelength dependence of product yields may be another characteristic of $t_{2g}{}^6$ systems, but a striking *increase* in photolabilization occurs with decreasing irradiative energy for $Rh(NH_3)_5I^{2+}$ in contrast to the behavior of cobalt(III)-amine complexes.

(C) d–d Photochemistry of $Rh(NH_3)_5I^{2+}$. Irradiation of the two "pure" ligand-field bands of $Rh(NH_3)_5I^{2+}$ gives only ammine aquation with $\phi_{NH_3} = 0.85 \pm 0.06$, independent of band (whether $^1A_2$ or ^1E) or wavelength through a band. This contrasts somewhat to the behavior of $Rh(NH_3)_5Cl^{2+}$.[7,39] The ^{131}I tracer work (Table V) clearly demonstrates that only one coordination position is labilized on d–d excitation of $Rh(NH_3)_5I^{2+}$; the iodide remains coordinated to the metal in the excited state while the ammonia trans to it is dissociated (in nearly every excitation).

Thus, the experimental evidence suggests that this excited state, which leads only to ammonia aquation, is nearly dissociative; *i.e.*, that population of this state leads to molecular dissociation. Since luminescence without photochemical decomposition is observed[13] at liquid nitrogen temperatures, it seems likely that lowest vibrational states are bound and that the photochemical reaction takes place from one of the higher vibrational levels (note that the metal–ligand vibrational frequencies are comparable in magnitude to kT).

The small yield ($\phi \sim 0.01$) of *trans*-$Rh(NH_3)_4I_2{}^+$ reported (Table II) for 385-nm irradiations can be taken as a measure of the yield of iodide aquation under these conditions. The O_2 quenching of the small (but reasonably reproducible) yields of *trans*-$Rh(NH_3)_4I_2{}^+$ remains a puzzle, as the predominant reaction products are unaffected by O_2. This may represent the quenching of some triplet state species (not involved in formation of other products), but we have been unable to verify this.

(D) Some Mechanistic Considerations. The photochemistry of $Rh(NH_3)_5I^{2+}$ is unique in the number of definitive mechanistic statements which are required by the observations. The structural inferences about rhodium(II) and ligand-field excited-state species have been described. An additional point of considerable significance is that the product yield is much higher when the lower energy ligand-field bands are irradiated than when the CTTM bands are irradiated. In fact when one corrects, as in Figure 2, for the redox yields, there is a fourfold difference in the photoaquation yields which follow from CTTM and d–d excitation. This must mean that internal conversion between CTTM and ligand-field excited-state manifolds[40] is inefficient (relative yield $\leqslant 0.25$) compared to some sort of direct deexcitation (relative yield ~ 0.5) of the CTTM excited state back to the ground state.

The above observations are qualitatively consistent with some of the current thinking on the factors governing the rates of radiationless deactivation processes.[41–44] Thus, while the rate of internal conversion between two electronic states is thought to decrease as the energy gap between the two states increases, it also should depend strongly on a Franck–Condon factor, F, which is a function of the nuclear configurations of the two states. It is the Franck–Condon factor which seems qualitatively useful in the present discussion. On the assumption that the metal center in the CTTM excited state strongly resembles rhodium(II), we would expect considerable lengthening of two (trans) metal–ligand bonds in any CTTM excited state. From our observations concerning the ligand-field photochemistry of $Rh(NH_3)_5I^{2+}$, we have inferred that one metal–ligand bond is greatly lengthened in the thermally equilibrated excited state. Thus, we may visualize the qualitative energy level scheme of Figure 3, in which both the *d–d and *CTTM excited states are distorted, the distortions being greater for the latter. Owing to the relative magnitudes of these distortions and the consequently different values of F, it seems plausible that one should find $\alpha_d > \phi_d'$ and $\phi_d > \phi_{ic}$. That is, the most highly distorted state is most easily deactivated to the ground state. An inference to be drawn from this model is that the *CTTM excited state must have a very short lifetime. Thus we have, within the context of this model, the interesting paradox that those very nuclear distortions which must be necessary for

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[39] That is, the yield of products from $Rh(NH_3)_5Cl^{2+}$ is largely independent of the wavelength of ligand-field excitation. The nature of the products of ligand-field irradiation of $Rh(NH_3)_5Cl^{2+}$ and $Rh(NH_3)_5I^{2+}$ does differ and will be discussed in detail elsewhere.

[40] It is not important to this argument whether the excited states under consideration be triplets or singlets. In fact, some studies in these laboratories, using biacetyl as a triplet donor, have indicated that the photochemical products which result from ligand-field excitation of rhodium pentaammines come from a triplet excited state.

[41] (a) G. W. Robinson, *J. Mol. Spectrosc.*, **6**, 58 (1961); (b) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, 37, 1962 (1962); (c) *ibid.*, **38**, 1187 (1963).

[42] J. P. Byrne, E. F. McCoy, and I. G. Ross, *Aust. J. Chem.*, **18**, 1589 (1965).

[43] J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Advan. Photochem.*, 7, 149 (1969).

[44] An important distinction between our model and those specifically treated for deactivation of organic molecules is that we are proposing deactivation through metal–ligand vibrational modes. This distinction will be discussed in detail elsewhere: T. L. Kelly and J. F. Endicott, manuscript in preparation.

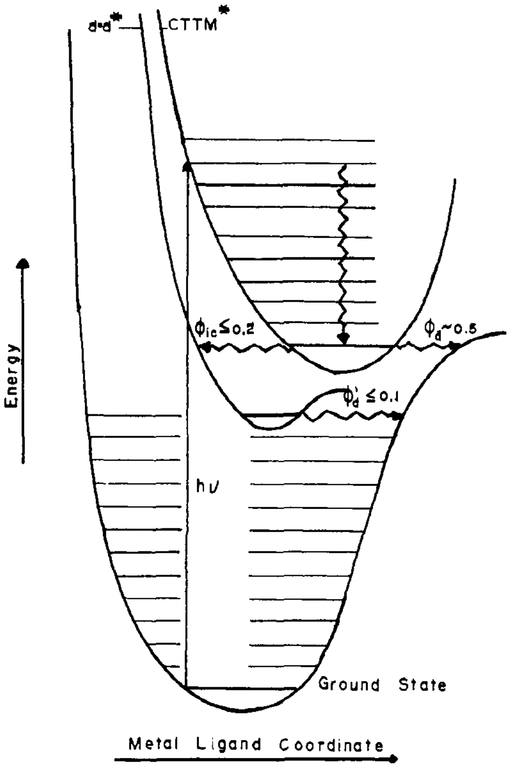

Figure 3. Hypothetical potential energy manifolds for an nd^6 complex. For simplicity, all states have been assumed to have the same spin multiplicity. Relative yields are indicated for the various internal conversion processes inferred from the photochemistry of $Rh(NH_3)_5I^{2+}$.

the formation of photochemical products also are the distortions which shorten the excited-state lifetime sufficiently that the rate of product formation cannot dominate the rate of nonradiative deactivation of the *CTTM state to the ground state.

It is of interest to reexamine some aspects of the photochemistry of cobalt(III) in the context of ideas developed above. First of all, the *d-d and *CTTM excited-state energy manifolds are expected to lie at lower energy for the cobalt(III) than for the rhodium(III) complexes (*e.g.*, emission from the lowest triplet state of $Co(NH_3)_5I^{2+}$ would be expected at about 10^4 cm^{-1} compared to 1.9×10^4 cm^{-1} for the rhodium analog). The smaller energy gap between *d-d excited states and the ground state would favor deactivation of these excited states in cobalt(III).[45] Since these *d-d excited states must be distorted, lowering the energy gap also would be expected to have the effect of enhancing the Franck-Condon factor. Thus the *d-d excited states in cobalt(III) complexes should be more efficiently deactivated through internal-conversion processes than are their rhodium(III) analogs.

On the other hand, the observation of Scandola and Scandola[9] that biphenyl-sensitized photolysis of $Co(NH_3)_6^{3+}$ leads to redox yields approaching 1, in contrast to yields of about 0.2 resulting from direct CTTM excitation, suggests that intersystem crossing (*i.e.*, ^{1}CTTM → ^{3}CTTM) does not compete effectively with nonradiative deactivation of the CTTM singlet excited state directly to the ground state owing to a very large Franck-Condon factor, such as we have inferred for the case of $Rh(NH_3)_5I^{2+}$. In fact, the redox yield from CTTM excitation of the rhodium complex is similar in magnitude to photoredox yields from cobalt pentaammines.[7] It may be typical of nd^6 complexes that a major factor limiting redox product yields is the very efficient nonradiative deactivation of the highly distorted singlet CTTM excited states. It seems clear that geometrical differences (which can often be related to formal electronic configurations) between excited states and/or ground-state species are often the factors determining photochemical reactivity of transition metal complexes.

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(45) See also ref 2, pp 191-196, 230-240, and references cited therein.