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Photochemistry of Rhodium(III) Complexes. Aquo Ligand Exchange and Anation Reactions of Aquopentaamminerhodium(III), $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$

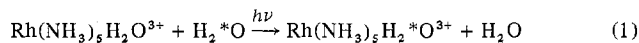
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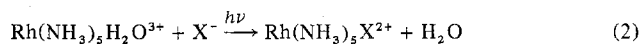
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Ligand field excitation of aqueous $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ leads to photoexchange of solvent and coordinated water with a quantum yield of 0.43 (20°) but very little NH_3 aquation ($\Phi_{\text{NH}_3} \approx 0.001$). Similar excitation in the presence of added chloride or bromide results in photoanation to form the halopentaammine complexes ($\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$) with quantum yields dependent on the concentration of added halide. For these experiments, the direct photolysis of ion pairs (e.g., $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}, \text{Cl}^-$) appears to be an important contributor to the photoanation quantum yields at all concentrations of anion. In contrast, ligand field excitation of the hydroxo complex $\text{Rh}(\text{NH}_3)_5\text{OH}^{2+}$ leads to very little photoexchange ($\Phi_{\text{ex}} < 0.01$) or photoanation. These results are discussed in the context of previous predictions of photoreactivity and in the terms of a mechanistic framework for the various photoreactions.

Studies in these laboratories have been concerned with the photochemistry of pentaammine complexes, $\text{M}(\text{NH}_3)_5\text{L}^{n+}$, of rhodium(III)^{2,3} and ruthenium(II)⁴ where the sixth ligand L is an uncharged nitrogen base. In the course of studies with aqueous rhodium(III) complexes, we have observed that ligand field excitation leads principally to photoaquation of L (when L is NH_3 , a substituted pyridine, acetonitrile, or benzonitrile) to give the photoproduct $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$. Under the experimental conditions, $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ has the appearance of being essentially photolysis insensitive, since little spectral change results when this complex is irradiated with 313- or 254-nm light (wavelengths corresponding to excitation of ligand field bands with maxima at 316 and 263 nm). However, the appearance of photochemical insensitivity does not exclude the possibility of photolabilization of the coordinated H_2O . Such labilization might lead to exchange with solvent water (eq 1)



or to other substitution processes in the presence of added nucleophiles (e.g., eq 2). The photolysis of other coordination



compounds in aqueous solution often results in the formation of aquo complexes which similarly may be photoreactive. To our knowledge the only previously reported quantitative study⁵ of the photoexchange reactions between coordinated and solvent water involved $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. Studies⁶⁻⁸ of aquo complex photoanations have also been limited but include investigations of reactions of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, and $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}$. Reported here are quantitative studies of the photoexchange and photoanation reactions of $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ depicted in eq 1 and 2 as well as a brief study of the hydroxo analog $\text{Rh}(\text{NH}_3)_5\text{OH}^{2+}$.

Experimental Section

Materials. The pentaamminerhodium(III) complexes $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$,⁹ $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$,¹⁰ and $[\text{Rh}(\text{NH}_3)_5\text{N}_3](\text{ClO}_4)_2$ ¹¹ were prepared by published procedures and recrystallized from water. The oxygen-18-enriched water (Miles Laboratories) used in photoexchange studies contained approximately 1.6% oxygen-18 and 0.076% oxygen-17.

Photoanation Studies. Solutions used in photoanation studies varied from 0.05 to 2.0 M Cl^- . These were prepared by gravimetric methods from reagent NaCl or by volumetric dilution of NaCl stock solutions. Anhydrous sodium perchlorate (G. F. Smith) was used for the gravimetric preparation of solutions for photolyses at constant ionic strength. Perchloric acid was used to adjust solutions to pH 2-4. Weighed amounts of $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ were dissolved in the photolysis stock solutions, but because of some difficulty in dissolution, it was found desirable to filter the resulting solution and determine $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ concentration spectrophotometrically at 316 nm (ϵ 105 $M^{-1} \text{cm}^{-1}$).

The apparatus used for photolyses at 313 and 254 nm have been described previously.² Solutions were photolyzed in a 2-cm cylindrical spectrometer cell thermostated at 25°. Solution optical densities ranged from 0.5 to 1.5 ($[\text{Rh}(\text{III})] \approx 0.0025\text{--}0.0075 \text{ M}$). Irradiation beam intensities averaged 3×10^{-6} einstein/(l. sec) at 313 nm and 2.3×10^{-7} einstein/(l. sec) at 254 nm as determined by ferrioxalate actinometry.

Formation of the photoproduct $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ was monitored spectroscopically on a Cary 14 spectrophotometer by following the increase in solution optical density at 345 nm (λ_{max} for aqueous $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$). Quantum yields were calculated from optical density changes given the difference in the extinction coefficients (44 $M^{-1} \text{cm}^{-1}$) between $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ at 345 nm. Quantum yield values obtained for successive photolysis intervals were plotted vs. percent reaction. Extrapolation back to zero percent reaction gives the quantum yield for the primary photoreaction exclusive of the secondary involvement of photoproduct.^{2,4} Dark reactions were run parallel to each photolysis experiment; however, no observable changes were detected in their spectra during the time span of irradiation (0.5-2.0 hr). Photolyses of deaerated solutions gave quantum yields indistinguishable from those obtained with air-saturated solutions, so most reactions were carried out under the latter conditions.

Photoexchange Studies. Reaction solutions were prepared by dissolving accurately weighed $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ (90-120 mg) in 5.5 ml of the oxygen-18-enriched water. The solution was thermostated at 20° to minimize nonphotochemical exchange between complex and solvent H_2O .¹² For photoexchange runs at an alkaline pH, solutions were prepared with $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$, 5.4 ml of oxygen-18-enriched water, and 0.15 ml of 2.0 M NaOH (delivered from a micrometer buret).

The photolysis apparatus was similar to that used with the photoanation studies; however, the source was a 250-W medium-pressure mercury lamp and the photolysis beam was filtered successively by 10 cm of water (quartz cell), a 7-54 Corning filter, and an Oriel 313-nm interference filter. Beam intensities averaged 6×10^{-6} einstein/(l. sec). Photolyses were carried out in a 2-cm cylindrical spectrometer cell thermostated at 20°. Reactions were interrupted periodically (approximately every 3 min during photolysis runs of 40-70 min), and the reaction cell was agitated vigorously to maintain solution homogeneity. Total time elapsed from preparation of solution to final quenching (vide infra) was monitored in order to make corrections for thermal-exchange reactions.

Exchange (photo and thermal) of the Rh(III)-coordinated H_2O with solvent was determined by a procedure similar to that of Monacelli and Viel.¹² At the conclusion of a photolysis (or dark) run, a 5-ml aliquot of the reaction solution was mixed with an equal volume of ice-cold, concentrated hydrobromic acid. Within seconds a fine precipitate of the faintly yellow $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Br}_3$ formed. This salt was isolated by filtration, washed with reagent methanol, and air-dried for ~30 min. The product (~70 mg) was vacuum-dried (<0.01 Torr) overnight; then the coordinated H_2O was liberated by heating the tube at 80° for a period exceeding 12 hr. The water released was then condensed into a break-seal tube containing approximately 100 mg of an equimolar mixture of $\text{Hg}(\text{CN})_2$ and HgCl_2 . This tube was sealed and dried overnight at 400°. The CO_2 thus

Table I. Quantum Yields for the Photoexchange (313-nm Photolysis) of the Coordinated Water of Rh(NH₃)₅H₂O³⁺ with Oxygen-18-Enriched Solvent Water^a

Run	Mol of Rh(III) × 10 ⁻⁴	Light absorbed, einsteins × 10 ⁻⁴	Time elapsed, ^b sec × 10 ³	% exchange ^c	Φ _{ex} , ^c mol/einstein
1	2.25	1.91	6.9	32.5	0.417
2	2.45	1.10	4.4	30.6	0.457
3	2.15	1.42	5.9	26.6	0.417
					Av 0.43 ± 0.03
H-1 ^d	1.99	1.47	5.7	0.0	<0.01 ^e
H-2 ^d	1.73	1.86	7.2	0.96	0.009
C-1	2.15	0.00	4.2	2.37	[5.7 × 10 ⁻⁶ sec ⁻¹ f]

^a At 20.3°, [Rh(III)] ≈ 0.04 M, μ ≈ 0.24 M, and pH ~ 4, except where noted. ^b Total time from solution preparation until quenching. ^c See text for calculation. ^d pH ~ 12.3. ^e Calculation of upper limit based on a conservative estimate of the sensitivity in observation of exchange for this experiment. ^f Rate constant for thermal exchange.

formed was then transferred via distillation and VPC procedures¹³ to a Urey tube from which the purified CO₂ was analyzed by means of an Atlas MS-86 mass spectrometer.

Oxygen-18 enrichment in the solvent was sampled by distilling the water from a 0.5-ml aliquot of the photolysis solution. This was equilibrated with CO₂ (~0.1 mmol) by heating at 80° for about 12 hr. The CO₂ was then transferred to a Urey tube, and the mass spectrum analyzed.

The oxygen-18 fraction (*F*) in a particular sample was calculated (eq 3) from the ratio *R* between mass spectra intensities of masses

$$F = \frac{^{18}\text{O}}{^{18}\text{O} + ^{16}\text{O}} = \frac{R}{2(1 + R)} \quad (3)$$

46 and 44 (i.e., *R* = (intensity of C¹⁶O¹⁸O)/(intensity of C¹⁶O₂). The ratio of exchanged complex (*C_{ex}*) to the total concentration of the complex in solution (*C_i*) was calculated from

$$\frac{C_{\text{ex}}}{C_{\text{i}}} = \frac{F_{\text{sample}} - F_{\text{std}}}{F_{\text{sol}} - F_{\text{std}}} \quad (4)$$

where *F_{std}* is the isotopic fraction for a sample of normal CO₂ whose mass spectrum was obtained with each photolysis or control experiment as a check of the internal consistency of the analytical procedure. For every experiment, *F_{std}* fell in the range 0.00201–0.00205 close to the published value of 0.00204.¹⁴

Competition Experiments. A 63.2-mg sample of [Rh(NH₃)₅N₃](ClO₄)₂ (0.145 mmol) was dissolved in 18 ml of 1.0 M hydrochloric acid at 25°. To this solution was added solid NaNO₂ (20 mg, 0.29 mmol) with stirring. The yellow color of the solution bleached immediately with simultaneous bubble formation. After about a 5-min reaction, the sample was diluted to approximately 50 ml, put on an ion-exchange resin column (Dowex AG-50W-X2), and eluted with successively more concentrated NaClO₄ solution (pH ~ 2). UV-vis spectra were recorded for all aliquots, and aliquots containing Rh(NH₃)₅Cl²⁺ or Rh(NH₃)₅H₂O³⁺ were evaluated for molar content from absorbances at 345 and 316 nm, respectively.

Results

Photoexchange Studies. Photolysis of Rh(NH₃)₅H₂O³⁺ (3 × 10⁻³ M) in pH 4 water leads to little change in the absorption spectrum. This is true both for 254- and for 313-nm irradiation. However, small changes in solution pH were observed, and on this basis the quantum yield of ammonia aquation (Φ_{NH₃}) can be estimated as ~0.001 mol/einstein for 313-nm photolysis and an upper limit of 0.005 can be estimated for Φ_{NH₃} at 254-nm photolysis. The higher value in the latter case may be due to the greater experimental uncertainties derived from lower light intensities at 254 nm.

Exchange of coordinated and solvent water (eq 1) does occur during 313-nm photolysis and the photoexchange results are summarized in Table I. A control solution treated in a manner comparable to the photolysis solutions but not exposed to light displayed relatively little exchange and allowed calculation of the rate constant (*k_{ex}*) for the thermal exchange under the photolysis conditions (20.3°, μ = 0.24) as 5.7 × 10⁻⁶ sec⁻¹. A more extensive study by Monacelli and Viel¹² gave a value of 5.4 × 10⁻⁶ sec⁻¹ for *k_{ex}* at 20.3° and μ = 0.31.

During the photolysis experiment both photoexchange and

thermal exchange processes are occurring, and the instantaneous rate of exchange is equal to

$$-\frac{dC}{dt} = \Phi_{\text{ex}}I_{\text{a}}' + k_{\text{ex}}C \quad (5)$$

where *C* is the concentration of the aquo complex which has not yet undergone exchange with solvent (i.e., *C_i* - *C_{ex}*), *I_a'* is the intensity of light being absorbed by *C*, and Φ_{ex} is the quantum yield for photoexchange. Since the extinction coefficients of product and reactant are identical, *I_a'* = *I_a* (*C*/*C_i*), where *I_a* is the measured intensity of light being absorbed by the reaction solution; therefore

$$-\frac{dC}{dt} = \Phi_{\text{ex}}I_{\text{a}}\left(\frac{C}{C_{\text{i}}}\right) + k_{\text{ex}}C \quad (6)$$

which can be integrated and rearranged to give

$$\ln\left(\frac{C_{\text{i}}}{C}\right) = \frac{\Phi_{\text{ex}}I_{\text{a}}t_{\text{photo}}}{C_{\text{i}}} + k_{\text{ex}}t_{\text{thermal}} \quad (7)$$

$$\Phi_{\text{ex}} = \frac{C_{\text{i}}\left[\ln\left(\frac{C_{\text{i}}}{C}\right) - k_{\text{ex}}t_{\text{thermal}}\right]}{I_{\text{a}}t_{\text{photo}}} \quad (8)$$

where *t_{photo}* is the time for which the sample has been irradiated and *t_{thermal}* is the full lifetime of the solution from preparation to quenching. Of course, this treatment is not completely valid unless *t_{photo}* and *t_{thermal}* are identical. However, since thermal exchange is a relatively minor perturbation on the photoexchange observed, eq 6 can be used to calculate a value for Φ_{ex} with a reasonably good, though approximate, correction for thermal exchange. A quantum yield of Φ_{ex} = 0.43 ± 0.03 mol/einstein (Table I) was thus obtained for the photoexchange reaction (eq 1) at 20.3°.

The *pK_a* of the aquo complex has been reported¹⁵ to be 6.8; therefore, in alkaline solution the predominant rhodium species would be the hydroxo complex Rh(NH₃)₅OH²⁺. Irradiation of this complex in pH 12.3 solution leads to very little photoexchange with solvent (Table I, Φ_{ex} < 0.01). The small amount of incorporation of solvent water into the isolated complex could represent one or all of these possibilities: exchange of coordinated hydroxide with solvent, photoaquation of NH₃ to give complexes such as Rh(NH₃)₄(H₂O)OH²⁺, or experimental uncertainty in the analysis procedure. Regardless, the yield is small. Monacelli¹² has shown that the hydroxo complex is very unreactive toward thermal exchange with solvent (*k_{ex}* < 1.2 × 10⁻⁶ at 60°).

Photoanation Studies. Irradiation at 313 nm of Rh(NH₃)₅H₂O³⁺ in aqueous NaCl solution leads to the formation of Rh(NH₃)₅Cl²⁺ (eq 2) with quantum yields (Φ_{Cl}) which are chloride concentration dependent (Table II). These are also rather dependent on ionic strength, and the higher ionic strength solutions display lower Φ_{Cl} values for a particular chloride concentration. Photolyses carried out with high

Table II. Quantum Yields for the Photoanation of $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ in Aqueous NaCl Solution at Various Ionic Strengths^a

[Cl ⁻], <i>M</i>	Φ_{Cl}^b		
	$\mu \cong [\text{Cl}^-]^c$	$\mu = 1.0$	$\mu = 2.0$
2.00	0.28 ± 0.02 (6)		0.28 ± 0.02 (6)
1.00	0.20 ± 0.02 (8)	0.20 ± 0.02 (8)	~0.15 (2)
		0.18 ± 0.01 (2) ^d	
		0.24 ± 0.04 (4) ^e	
0.50	0.14 ± 0.01 (4)	0.109 ± 0.004 (4)	0.094
0.20	0.100 ± 0.006 (4)	0.044 ± 0.004 (4)	0.03 (2)
0.15	0.080 ± 0.005 (2)		
0.10	0.052 ± 0.001 (2)	0.022 ± 0.001 (2)	~0.01 (2)
0.05	0.043 (1)		

^a At 25°, pH 2.2–2.7, $[\text{Rh}(\text{III})] = (2.4\text{--}6.1) \times 10^{-3} \text{ M}$, and λ_{irr} 313 nm, unless noted otherwise. ^b Quantum yields and standard deviations for formation of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$; ionic strength in excess of $[\text{NaCl}]$ maintained with NaClO_4 . Number of runs shown in parentheses. ^c $\mu = [\text{NaCl}] + 6[\text{Rh}(\text{III})]$ or in most cases $[\text{NaCl}] + 0.03$. ^d At 20°. ^e λ_{irr} 254 nm.

sodium perchlorate concentrations (to maintain ionic strength) suffered from the complication that, once the photolysis had proceeded more than 5–10% toward completion, $[\text{Rh}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ began to precipitate thus making analysis by spectrophotometric techniques impossible.

Ammonia photoaquation (as monitored by pH changes in the reaction solution) was at most a minor pathway for 313-nm photolyses. Because of the relative insensitivity of the analytical technique and the low conversions allowed in the higher ionic strength solutions, a relatively high upper limit value of ≤ 0.015 mol/einstein was established for Φ_{NH_3} . However, given that ammonia aquation in the photolyses of aqueous $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ is very low (< 0.001),¹⁶ it appears unlikely that NH_3 aquation is greatly stimulated by the presence of chloride in solution.

Reaction solutions not subjected to irradiation showed no spectral or pH changes, indicating that the thermal reaction is very slow under the photolysis conditions.

Photolysis at 254 nm gave quantum yields comparable to those at 313 nm (Table II). In 1.0 M NaCl, the Φ_{Cl} value was ~20% higher for the lower wavelength but the experimental uncertainty for this case makes the values essentially indistinguishable. Photolysis at 313 nm of 1.0 M Cl⁻ solution thermostated at 20° gave slightly lower Φ_{Cl} values than at 25°; however, again the values are virtually indistinguishable.

Photolysis of $\text{Rh}(\text{NH}_3)_5\text{OH}^{2+}$ in alkaline solution (pH ~10) of 1 M NaCl did not lead to the formation of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$. The upper limit for Φ_{Cl} is estimated as < 0.0025 for this photolysis experiment.

Photolysis (313 nm) of $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ in 1.0 M aqueous NaBr (25°) was complicated by the low solubility of $[\text{Rh}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ in the reaction medium. The quantum yield for formation of $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$, $\Phi_{\text{Br}} = 0.20 \pm 0.05$, was comparable to Φ_{Cl} under similar conditions but suffered higher experimental uncertainty. Photolysis was also carried out in 0.2 M NaBr ($\mu = 1.0$) and the Φ_{Br} value (0.060 ± 0.005) was 25–30% higher than Φ_{Cl} under comparable conditions.

Competition Experiments. These were initiated to determine the relative abilities of chloride ion and water to capture the reactive intermediate(s) produced by the reactions between nitrous acid and the azido complex, $\text{Rh}(\text{NH}_3)_5\text{N}_3^{2+}$. The general procedure used by Buckingham, Sargeson, and coworkers¹⁷ for competition studies with the cobalt(III) analog was employed. In the present case, reaction in 1 M HCl led to formation of gaseous products (presumably N_2O and N_2) plus $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$. Spectral analysis of the ion exchange aliquots from two independently prepared experiments gave the product molar ratio $[\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}]/[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}]$ equal to 0.24 with a precision of 0.005. However, a more realistic estimate of the

experimental uncertainty of the spectral method in this case would be ± 0.03 . Interestingly the competition ratio obtained is the same as that found for the cobalt(III) analog¹⁷ under similar conditions.

Discussion

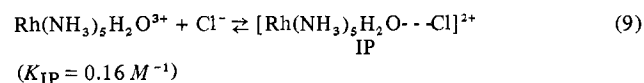
Observation of photoexchange and photoanation clearly demonstrates that aqueous $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ is very reactive when subjected to ligand field excitation. In the absence of added ligand, the principal photoreaction in aqueous perchlorate solution is aquo ligand exchange with solvent although NH_3 aquation may be occurring with a much smaller quantum yield. Comparison of $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ to $\text{Rh}(\text{NH}_3)_6^{3+}$ shows that the aquo complex displays an overall quantum yield of photosubstitution approximately 6 times larger than the hexaammine² but a quantum yield of NH_3 aquation nearly 2 orders of magnitude smaller. The hydroxo complex $\text{Rh}(\text{NH}_3)_5\text{OH}^{2+}$ is substantially less photoreactive than either $\text{Rh}(\text{NH}_3)_6^{3+}$ or $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$.

A recent ligand field theory treatment¹⁸ of rhodium(III) photochemistry has made two predictions for a series such as the pentaammines $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$: (a) “the total labilization will decrease as the ligand field strength of the unique axis approaches that of the other axes” and (b) “the quantum yield of ammine (aquation) will decrease and that of X⁻ will increase as the energy of the donor orbital of X⁻ decreases and approaches that of the ammine”. Prediction (b) appears to be borne out in the present system where $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ (λ_{max} 316, 263 nm) apparently has an average ligand field relatively close to that of $\text{Rh}(\text{NH}_3)_6^{3+}$ (λ_{max} 305, 255 nm), yet the weaker field ligand H_2O is preferentially aquated. This result does not fit Adamson’s empirical rule 2 (the stronger field ligand of the weakest average field axis will be preferentially labilized) proposed originally for the photolyses of Cr(III) complexes¹⁷ but said to be “mildly applicable” to the ligand field photochemistry of cobalt(III) complexes.²⁰ The ligand field theory treatment¹⁸ prediction (a) is not substantiated by the present results. If one takes a series of Rh(III) complexes in order of the increasing ligand field strength of the sixth ligand, $\text{Rh}(\text{NH}_3)_5\text{I}^{2+} < \text{Rh}(\text{NH}_3)_5\text{Br}^{2+} < \text{Rh}(\text{NH}_3)_5\text{Cl}^{2+} < \text{Rh}(\text{NH}_3)_5\text{OH}^{2+} < \text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} < \text{Rh}(\text{NH}_3)_6^{3+}$, the total labilization resulting from excitation of the lowest energy ligand field absorption band does not fall in the same order, $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ (0.85)¹⁶ $>$ $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ (0.43) $>$ $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ (0.19)¹⁶ $>$ $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ (0.16)¹⁶ $>$ $\text{Rh}(\text{NH}_3)_6^{3+}$ (0.07)² $>$ $\text{Rh}(\text{NH}_3)_5\text{OH}^{2+}$ (less than 0.01). Admittedly, the unique ligand does not in each case have the same ionic charge, but this breakdown of the predicted order illustrates that such a perturbation may indeed have significant consequences on the quantitative photochemistry of analogous complexes.

Another complication in the prediction of photoreaction quantum yields concerns the role of nonradiative deactivation pathways. For a photoreaction quantum yield less than 0.5, more than half the excited states must be depleted by such pathways. Yet, apparently by necessity, quantitative treatments of transition metal complex photoreactions have assumed that for an analogous series of complexes nonradiative deactivation pathways are approximately invariant. Given recent results of luminescence studies of rhodium(III)–ammine complexes²¹ and the photochemistry² of perprotio- and perdeuteriohexaamminerhodium(III), it is unlikely that such an assumption can be very accurate. Interestingly, a previous attempt²² to examine the luminescence of $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ in a $\text{H}_2\text{O}\text{--}\text{CH}_3\text{OH}$ glass at 77°K proved unsuccessful, and it was suggested that hydrogen bonding couples the solvent to the aquo ligand and provides an especially efficient nonradiative deactivation pathway. If such an explanation is valid, it certainly does not apply to the photo-

chemical conditions (298°K) where ligand labilization occurs with a quantum yield of 0.43. (Such an explanation may apply to the hydroxo complex, however.) In this laboratory, the luminescent emission from [Rh(NH₃)₅H₂O](ClO₄)₃ has been observed²³ for the solid salt at 77°K, and the measured lifetime is substantially shorter than that of the hexaammine complex.²¹ This may indicate that indeed the coordinated H₂O does provide a pathway for fast nonradiative deactivation in protic solvent. However, given the high photoreactivity of the aquo complex, one might speculate that there is some relation between the labilization pathway at 298°K and the deactivation path at 77°K.

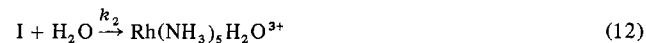
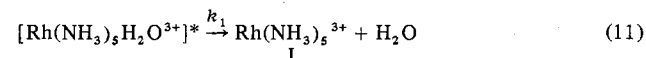
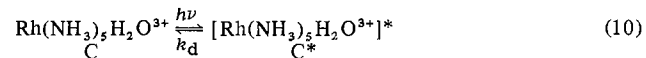
The character of solutions containing Cl⁻ and Rh-(NH₃)₅H₂O³⁺ have been examined by Monacelli,²⁴ who has determined the ion-pairing equilibrium constant for eq 9 (25°, μ = 4 M Na(Cl, ClO₄)). If one assumes that a comparable



K_{IP} value is applicable for ionic strength 1.0 or 2.0 M, it is clear that a significant fraction of the Rh(NH₃)₅H₂O³⁺ is in the ion-paired form at the higher concentrations of Cl⁻. Since at 313 nm (λ_{irr} for most photolyses) the extinction coefficient for Rh(NH₃)₅H₂O³⁺ and IP are identical,²⁴ the photoanation studies must involve the photolysis of both components.

Photoexchange with solvent and photoanation with chloride conceivably may occur by either a dissociative or an associative mechanism. The associative mechanism has been discounted by Schläfer²⁵ for hexacoordinate d⁶ complexes on the basis of crystal field activation energy (CFAE) arguments; however, he considered only a pentagonal-bipyramidal configuration for the transition state of the substitution pathway. The octahedral wedge geometry gives a more favorable CFAE value²⁶ for the t_{2g}⁵e_g¹ electronic configuration. Intuitively, the σ* character of the e_g orbital of an octahedral (or near octahedral) complex prejudices one's thinking toward dissociative mechanisms for photolabilization. For this reason the subsequent discussion will focus on a proposed dissociative mechanism for photo-reaction, although the present data cannot distinguish these alternative mechanisms. Interestingly, the photoanation quantum yields in bromide solution are not dramatically different from those in chloride solution, an observation which would appear to be more consistent with the dissociative mechanism.

The following reactions provide a general mechanism for photoexchange and photoanation of Rh(NH₃)₅H₂O³⁺ assuming a dissociative pathway



In the absence of added chloride only eq 10–12 are relevant, and according to the mechanism the quantum yield of exchange Φ_{ex} would be equal to $k_1/(k_1 + k_d)$ since formation of Rh-(NH₃)₅³⁺ leads directly to exchange with solvent. In the presence of chloride, I can be trapped either by H₂O to give starting complex or by chloride to give Rh(NH₃)₅Cl²⁺, while IP is converted to Rh(NH₃)₅Cl²⁺ with a quantum yield $\Phi_{\text{IP}} = k_4/(k_4 + k_d')$. Taking into account the ion-pair formation (eq 9), one can write expression 15 for Φ_{Cl} based upon this

$$\Phi_{\text{Cl}} = \Phi_{\text{ex}} \left(\frac{k_3[\text{Cl}^-]}{k_2 + k_3[\text{Cl}^-]} \right) \left(\frac{1}{1 + K_{\text{IP}}[\text{Cl}^-]} \right) + \Phi_{\text{IP}} \left(\frac{K_{\text{IP}}[\text{Cl}^-]}{1 + K_{\text{IP}}[\text{Cl}^-]} \right) \quad (15)$$

mechanism. The two terms represent the contributions to Φ_{Cl} from irradiation of C and IP respectively. (Note that the same expression for Φ_{Cl} would result if k_2 and k_3 represented the respective associative attack of solvent H₂O or Cl⁻ on the excited state C* instead of attack on the dissociated intermediate I.)

Although there are some differences of temperature and ionic strength, the values of Φ_{ex} (0.43 mol/einstein) and K_{IP} (0.16 M⁻¹) probably represent a fair approximation of these values under conditions of the photoanation experiments. Also useful may be the competition ratio obtained (0.24) for the nitrous acid decomposition of Rh(NH₃)₅N₃²⁺ in 1.0 M HCl. It has been suggested¹⁷ for the cobalt analog that this reaction proceeds by attack of NO⁺ on the coordinated azide to give N₂O plus the dinitrogen complex Co(NH₃)₅N₂³⁺. The latter because of its instability presumably decomposes by a dissociative pathway to the pentacoordinate intermediate Co-(NH₃)₅³⁺ and N₂. If the Rh(III) analog reacts in this manner, then the ratio of chloro and aquo products represents the ratio $k_3[\text{Cl}^-]/k_2$ in 1 M HCl. Thus k_3/k_2 would equal 0.24 M⁻¹. This is an oversimplification, as it is likely that even if limiting dissociative intermediates are produced in the photochemical reaction and in the azido complex decomposition, the different modes of formation may give different pentacoordinate intermediates. An additional complication is that the role of ion-paired species in these competition studies has not been fully elucidated.

Despite these reservations, it is instructive to use eq 15 and the values of Φ_{ex} , K_{IP} , and k_3/k_2 to calculate a value for Φ_{IP} and to examine the contributions of the ion-paired and free complex to the photochemistry according to this mechanism. The value of $\Phi_{\text{IP}} = 0.89$ is derived from eq 15 and Φ_{Cl} (0.109) at 0.5 M Cl⁻ (μ = 1.0), and Table III shows the contributions to Φ_{Cl} according to eq 15 using this value for Φ_{IP} . A reasonable fit of $\Phi_{\text{Cl}}(\text{calcd})$ and $\Phi_{\text{Cl}}(\text{exptl})$ is obtained. However, the more important consideration is the magnitude of the contribution to Φ_{Cl} from photolysis of the ion-paired complex. Approximately 60% of the product is produced from photolysis of the ion pair at 1.0 M Cl⁻ according to eq 15, and the fraction of the product originating from the ion-paired species is nearly invariant over a range in chloride concentration (0.1–1.0 M) where the fraction of complex in the ion-paired form ranges from 1.6 to 14%.

As a test of the sensitivity of $\Phi_{\text{Cl}}(\text{calcd})$ to the Φ_{IP} used, a Φ_{IP} value of 0.5 was used to recalculate Φ_{Cl} according to eq 15. At chloride concentrations of 1.0, 0.5, 0.2, and 0.1 M, $\Phi_{\text{Cl}}(\text{calcd})$ equals 0.14, 0.080, 0.036, and 0.018, respectively, values which do not fit well with $\Phi_{\text{Cl}}(\text{exptl})$. If it is assumed that ion-paired species are not present in the reaction medium (that is, $K_{\text{IP}} = 0$), then application of eq 15 would require a k_3/k_2 ratio equalling ~0.7–0.8 to give the Φ_{Cl} values observed for [Cl⁻] = 0.5 or 1.0 M. This ratio is much larger than that found for the thermal competition studies thus leading to two possible conclusions: either I or C* is much more efficiently scavenged by Cl⁻ than is the intermediate produced in the nitrous acid reaction with Rh(NH₃)₅N₃²⁺ (the thermally produced analog of I?) or Φ_{Cl} includes contributions from direct photolysis of IP. In fact, if an alternative limit is assumed, that is, $k_3/k_2 \approx 0$, an excellent fit of Φ_{Cl} to eq 15 is obtained with the values $K_{\text{IP}} = 0.25 M^{-1}$ and $\Phi_{\text{IP}} = 1.0$. Therefore it is at least equally reasonable that most or all photoanation occurs via photolysis of the ion pair rather than

Table III. Contributions to Φ_{Cl} from Photolysis of Complex and Ion Pair According to Eq 15

$[\text{Cl}^-], M$	$\Phi_{\text{ex}} \left(\frac{k_3 [\text{Cl}^-]}{k_2 + k_3 [\text{Cl}^-]} \right) \times \left(\frac{1}{1 + K_{\text{IP}} [\text{Cl}^-]} \right)^a$	$\Phi_{\text{IP}} \left(\frac{K_{\text{IP}} [\text{Cl}^-]}{1 + K_{\text{IP}} [\text{Cl}^-]} \right)^a$	$\Phi_{\text{Cl}}(\text{calcd})$	$\Phi_{\text{Cl}}(\text{exptl})^b$
1.0	0.072	0.123	0.195	0.20
0.5	0.043	0.066	0.109	0.109
0.2	0.019	0.028	0.048	0.044
0.1	0.010	0.014	0.024	0.022

^a $\Phi_{\text{IP}} = 0.89$ calculated by solving eq 15 for $[\text{Cl}^-] = 0.5$, $K_{\text{IP}} = 0.16 M^{-1}$,²⁴ $k_3/k_2 = 0.24 M^{-1}$ according to the thermal competition experiments, and $\Phi_{\text{ex}} = 0.43$ mol/einstein. ^b $\mu = 1.0 M$.

simply via competition of I for Cl^- or H_2O free in solution. However, the proposal that $k_3/k_2 \cong 0$ would be inconsistent with the reactivity of $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}$ which cannot undergo significant ion-pair formation with other anions but has been observed to undergo both photoanation⁷ and photoexchange with solvent water.²⁷ Therefore, we favor a mechanism whereby photoanation occurs by reaction of both the free ion $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and the ion pair $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}, \text{Cl}^-$ (e.g., eq 10–14). However, it is clear that the reasonable fit of $\Phi_{\text{Cl}}(\text{calcd})$ and $\Phi_{\text{Cl}}(\text{exptl})$ shown in Table III using eq 15 and the values for Φ_{IP} , k_2/k_3 , Φ_{ex} , and K_{IP} stated does little to substantiate the mechanism proposed but merely indicates that it is consistent with the experimental observations.

An additional complication is the possibility that C^* and IP^* are sufficiently long-lived to be in equilibrium with each other (eq 16). If so, then Φ_{Cl} would be a function of $[\text{Cl}^-]$



(eq 17) similar to eq 15 but considerably less factorable because

$$\Phi_{\text{Cl}} = \left(\frac{k_1 k_3 [\text{Cl}^-]}{k_2 + k_3 [\text{Cl}^-]} + k_4 K^* [\text{Cl}^-] \right) \left(\frac{1}{(k_d + k_1) + (k_d' + k_4) K^* [\text{Cl}^-]} \right) \quad (17)$$

an excited-state species (C^* or IP^*) once produced will have four independent pathways (k_d , k_d' , k_1 , or k_4) available for deactivation.

The effect of solution ionic strength on the values of Φ_{Cl} , especially at low Cl^- concentration is fairly dramatic. Possible explanation may lie in examining the contributing terms to eq 15 (or eq 16). The constants k_3 and K_{IP} in each case involve reactions between a $3+$ ion and a $1-$ ion and therefore should be strongly affected by the ionic atmosphere, presumably increasing at lower ionic strengths. Since at low $[\text{Cl}^-]$, $k_3[\text{Cl}^-] \ll k_2$ and $K_{\text{IP}}[\text{Cl}^-] \ll 1$, increases in k_3 and K_{IP} would lead to increases in Φ_{Cl} under these conditions.

In summary, while we cannot definitively identify a mechanism for photoanation, it is clear that $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ is highly photoreactive. In the absence of added ligands, photoexchange with solvent water is efficient while the presence of ligands such as chloride leads to photoanation. The quantum yields observed and associated data are consistent with the mechanism described in eq 10–14; however, an alternative such as photoanation occurring exclusively via the direct photolysis of ion pairs cannot be excluded. The role of ion-paired complexes is uncertain; however, these appear to play an important role in the photoanation of $\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ at all

concentrations of added chloride.

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