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Ligand Control of the Photostereochemistry of Rhodium(III) Tetraammine Complexes, $Rh(NH_3)_4XY^{n+}$. Cis to Trans and Trans to Cis Photoisomerization and Photostationary States

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Ligand field excitation of the hydroxo tetraammine complexes *trans*-$Rh(NH_3)_4(OH)Y^{n+}$ leads to photoisomerization concomitant with ligand labilization to give *cis*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$ for Y = Cl^- or Br^-. Photoisomerization to the same product is found for Y = H_2O. These results can be interpreted in terms of Y dissociation from a LF excited state to give a stereochemically labile, square-pyramidal intermediate $Rh(NH_3)_4OH^{2+}$ remaining in an electronic excited state. Earlier calculations have shown that the more stable pentacoordinate isomer will be that with the strong σ-donor OH^- ligand in the basal site. Deactivation and capture by H_2O of this isomer would lead to the observed cis product. The diaqua species $Rh(NH_3)_4(H_2O)_2^{3+}$ form a photostationary state with the quantum yield for cis → trans photoisomerization (0.072 mol/einstein) 6 times that for trans → cis isomerization (0.012 mol/einstein). In contrast both *cis*- and *trans*-$Rh(NH_3)_4(OH)_2^+$ are essentially inert toward photoisomerization, a property attributed to the very small photolability of coordinated hydroxide. The photoreaction behaviors of the (aqua/hydroxo) complexes as a function of pH follow the acid/base properties of these complexes in the ground state, an observation rationalized on the basis that the excited states and intermediates are too short-lived to reach acid/base equilibration with the solution.

Introduction

Ligand field (LF) excitation of rhodium(III) amine complexes leads to ligand labilization in solution.[2] For the disubstituted complexes RhA_4XY^{n+} (A is a saturated amine) this labilization has been shown in some cases to be accompanied by stereoisomerization of the coordination sphere.[3-8] Such studies from this laboratory have focused on the tetraammine complexes (A = NH_3), since the stereomobility of these will not be subject to the constraints favoring or inhibiting isomerization inherent to chelating ligands. In this context, we reported[4,8] earlier the isomerization of *cis*-$Rh(NH_3)_4Cl_2^+$ concomitant with Cl^- photoaquation (eq 1) and the similar photoisomerization of the aqua–chloro analogue (eq 2). In contrast the trans analogues do not photoisomerize[9] (eq 3).

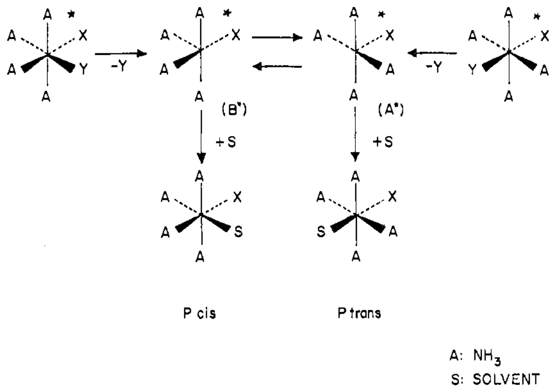
$$cis\text{-}Rh(NH_3)_4Cl_2^+ + H_2O \xrightarrow{h\nu\ (365\ nm)} trans\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} + Cl^- \quad (1)$$

$$cis\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} \xrightarrow{h\nu\ (365\ nm)} trans\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} \quad (2)$$

$$trans\text{-}Rh(NH_3)_4Cl_2^+ + H_2O \xrightarrow{h\nu\ (407\ nm)} trans\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} + Cl^- \quad (3)$$

Several theoretical models of these and similar photoreactions[8,10,11] interpret the product stereochemistries principally on the comparative energies of square-pyramidal (SPY), five-coordinate intermediates of ligand dissociation (A* and B*, Scheme I). Notably, these intermediates were proposed to be triplet excited states capable of isomerizing on a time scale competitive with deactivation to the lower energy singlets followed by solvent trapping. A key feature of these models is that, for the triplet SPY intermediate, the stronger σ-donor ligand will show a strong site preference for the basal position. Hence, for the earlier reported cases where X = Cl^- or another halogen and L is a saturated amine,[3-8] the lower energy SPY triplet is A* with the weaker σ-donor halogen in the apical site, and cis to trans photoisomerization (eq 1 and 2) would be favored in the absence of other constraints. The reverse (trans to cis) is predicted for a ligand X having a greater σ-donor strength than L. This prediction was confirmed in a preliminary communication from this laboratory,[12] where it was demonstrated that the presence of the strong σ-donor OH^- in the coordination sphere is sufficient to favor trans to cis photoisomerization (eq 4) in alkaline solution.

Scheme I



$$trans\text{-}Rh(NH_3)_4(OH)Cl^+ + OH^- \xrightarrow{h\nu(365\ nm)} cis\text{-}Rh(NH_3)_4(OH)_2^+ + Cl^- \quad (4)$$

Here are described in detail the photoreactions of the hydroxo complexes *cis*- and *trans*-$Rh(NH_3)_4(OH)X^+$ (X = Cl^- or Br^-) and their conjugate acids as functions of solution pH in aqueous solution. In addition are described the photoreaction properties of the diaqua complexes *cis*- and *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$ and their conjugate bases over a wide pH range.

Experimental Section

Materials. The tetraamminerhodium(III) complexes *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)Cl]S_2O_6$,[8] *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)$-

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$Br]S_2O_6$,[8] *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$,[13] and the pentaammine complex $[Rh(NH_3)_5(H_2O)](ClO_4)_3$[14] were all prepared and purified by published procedures. Other chemicals were of either reagent or analytical grade, and doubly distilled water was used throughout.

Photolyses. Photolyses were carried out by the same methods and by using the photolysis apparatus previously described.[15] Temperature control was better than ±1 °C. Light intensities were determined by ferrioxalate actinometry. Electronic spectra used in monitoring the photolysis were recorded on a Cary Model 118C spectrophotometer.

pH Measurements. The investigations reported were all done in a 1.0 M perchlorate medium. The definition pH = $-\log [H^+]$ was employed throughout, by using solutions of standardized perchloric acid in sodium perchlorate as pH standards. A Sargent-Welch pH meter, Model NX, with a combination glass electrode modified to contain 1.0 M NaCl in the reference part was used for the pH measurements.

Ion Exchange. Bio-Rad AG50W-X4, 200–400 mesh, hydrogen ion form, ion-exchange resin was used for ion-exchange separation according to the procedure previously described.[8]

Calculations of Quantum Yield. The calculations of quantum yields were based on spectral changes by one of the following methods.

Method A. Quantum yields were calculated as moles of reaction per einstein absorbed in a given time interval. These incremental quantum yields were plotted as a function of percent reaction and extrapolated back to zero time. Similar plots of overall quantum yields were also made, and zero-time incremental and overall quantum yields were found to agree within experimental uncertainties. This method, which was used for photolyses not followed to completion, is essentially identical with those previously described.[15]

Method B. This method, which includes a more rigorous inner filter correction, was used in photolyses where reverse photoreaction was suspected or demonstrated. These photolyses were all followed to completion (i.e., until a constant spectrum was obtained).

For the photochemical system

$$A \underset{\phi_B}{\overset{\phi_A}{\rightleftarrows}} B$$

the quantum yields for the photoreaction in each direction are defined as $\phi_A = N_A/q_a$ and $\phi_B = N_B/q_b$, respectively, where N_i is the number of moles which have reacted in response to the absorption of q_i einsteins of light by that species. Thus, $\gamma(t)$, the number of moles of net reaction A to B at the time t, is given by eq 5, indicating a linear relation

$$\gamma(t) = \phi_A q_a - \phi_B q_b \qquad (5)$$

between $\gamma(t)/q_a$, the observed net quantum yield, and q_b/q_a, the ratio of light absorbed by the species A and B:

$$\gamma(t)/q_a = \phi_A - \phi_B q_b/q_a \qquad (6)$$

By means of this formula, the quantum yields for the photochemical reactions in both directions were calculated. The moles of net reaction and the intensities of absorbed light were estimated by method 7, where

$$\gamma(t_i) = \frac{[A_M(t_0) - A_M(t_i)]V}{l(\Delta\epsilon_M)} \qquad (7)$$

$A_M(t_i)$ is the absorbance of the reaction solution at the monitoring wavelength at the time t_i, $\Delta\epsilon_M$ is the difference in molar absorptivity of A and B at this same wavelength, l is the cell path length, and V is the volume of solution irradiated. The einsteins of light absorbed from the start of the photolysis until time t_i by B and A were evaluated numerically by summing the light absorbed in small, but finite, time intervals $t_{n+1} - t_n$ (eq 8 and 9), where $\bar{\gamma}$ is the average number of moles

$$q_b(t_i) = \sum_{n=0}^{i} \frac{(\bar{\gamma}/V)\epsilon_B{}^{irr} l}{\bar{A}_{irr}} I_0(1 - 10^{-\bar{A}_{irr}})(t_{n+1} - t_n) \qquad (8)$$

$$q_a(t_i) = \sum_{n=0}^{i} [I_0(1 - 10^{-\bar{A}_{irr}})(t_{n+1} - t_n) - q_b(t_i)] \qquad (9)$$

of net reaction during $t_{n+1} - t_n$, $\bar{A}_{irr}$ is the average absorbance at the wavelength of irradiation (λ_{irr}) during the same time interval, I_0 is the intensity of irradiating light, and $\epsilon_B{}^{irr}$ is the molar absorptivity of B at λ_{irr}.

Table I. pK_a for Aquaamminerhodium(III) Complexes in Aqueous Aqueous 1.0 M NaClO$_4$ at 25 °C[a]

complex	pK_{a1}	pK_{a2}
$Rh(NH_3)_5H_2O^{3+}$	6.93	
cis-$Rh(NH_3)_4(H_2O)_2{}^{3+}$	6.40	8.32
trans-$Rh(NH_3)_4(H_2O)_2{}^{3+}$	4.92	8.26
cis-$Rh(NH_3)_4(H_2O)Cl^{2+}$	7.84	
trans-$Rh(NH_3)_4(H_2O)Cl^{2+}$	6.75	
cis-$Rh(NH_3)_4(H_2O)Br^{2+}$	7.89	
trans-$Rh(NH_3)_4(H_2O)Br^{2+}$	6.87	

[a] K_a's are dissociation constants.[13]

Results

Quantum yields for the LF photolysis in 1.0 M perchlorate solution at 25 °C of *trans*- and *cis*-$Rh(NH_3)_4XY^{n+}$ (X = OH^- or H_2O; Y = X, Cl^-, or Br^-) are listed in Table III. The photoproduct identification, calculation of quantum yields, and evaluation of pH dependence are described here separately for each of the complex ions. The pK_a values[13] and spectral characteristics of the various complexes at 25 °C in 1.0 M aqueous NaClO$_4$ solutions are summarized in Tables I and II, respectively. Thermal reactions during the time span of a photolysis experiment were shown to be insignificant in all cases except for *cis*-$Rh(NH_3)_4(OH)Cl^+$ and *cis*-$Rh(NH_3)_4(OH)Br^+$ which showed slight activity. Consequently dark reaction corrections were incorporated into quantum yield calculations only for the two cis hydroxohalo complexes.

$Rh(NH_3)_5OH^{2+}$. LF photolysis (350 nm) of a solution of $[Rh(NH_3)_5(H_2O)](ClO_4)_3$ in 1.0 M NaClO$_4$ titrated with NaOH to pH ~7 (~pK_a) resulted in very minor spectra changes to give unspecified products. These observations confirm the earlier report[16] that the activities of $Rh(NH_3)_5H_2O^{3+}$ and of its conjugate base $Rh(NH_3)_5OH^{2+}$ toward photoreactions other than oxygen exchange with solvent are very low.

cis- **and** *trans*-**$Rh(NH_3)_4(H_2O)_2{}^{3+}$.** LF photolysis of either of these ions with the same λ_{irr} in acidic aqueous solution (pH 0–2) leads cleanly to product solutions with identical spectral properties. A solution of *cis*-$Rh(NH_3)_4(H_2O)_2{}^{3+}$ in 1.0 M HClO$_4$ exhaustively photolyzed (350 nm, $I_0 \approx 3 \times 10^{18}$ quanta/min, ~7 h of irradiation) had (within experimental uncertainties) spectral characteristics [λ_{max} (ϵ) = 272 nm (93 M^{-1} cm^{-1}), λ (ϵ) = 326 (56.6), λ (ϵ) = 350 (52.3)] identical with those of a solution of *trans*-$Rh(NH_3)_4(H_2O)_2{}^{3+}$ photolyzed under the same condition [λ_{max} (ϵ) = 271 nm (91), λ (ϵ) = 326 (56.1), λ (ϵ) = 350 (52.5)]. Both of these solutions maintained isosbestic points at 308 and 359 nm throughout the photolysis. The spectrum of this common photoproduct is consistent with that expected for a mixture of *cis*- and *trans*-$Rh(NH_3)_4(H_2O)_2{}^{3+}$ only. Thus, each of the two isomers photoisomerize to the other. The product solution is in a photostationary state, which under these conditions (pH 0–2, λ_{irr} = 350 nm, 1.0 M (H,Na)ClO$_4$, 25 °C) corresponds to a cis/trans ratio of 0.12. Evaluation of quantum yields was done from spectral changes at 326 nm, the wavelength of maximum difference between the molar absorptivities of the two isomers. Photolyses of both the cis and the trans complexes were quantitatively followed to completion (i.e., to a constant spectrum) at pH 0–2. Calculation of quantum yields were done by method B (see the Experimental Section), thus revealing values for both ϕ_{cis} and ϕ_{trans} from each experiment. Figure 1 shows the plot of $\gamma(t)/q_c$ vs. q_t/q_c for one such ex-

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Table II. Electronic Spectra of Aquaammine- and Hydroxoamminerhodium(III) Complexes in Aqueous 1.0 M Perchlorate Solution[a]

	λ, nm (ϵ, L mol^{-1} cm^{-1})		
complex ion	maxima	ϵ_{irr}[b]	ϵ_{mon}[b]
cis-$Rh(NH_3)_4(H_2O)_2^{3+}$	326 (107), 268 (89)	$\epsilon_{313} = 94.6$, $\epsilon_{350} = 71.7$, $\epsilon_{405} = 7.7$	$\epsilon_{326} = 107$
cis-$Rh(NH_3)_4(H_2O)OH^{2+}$ [c]	329 (122), 279 (104)	$\epsilon_{350} = 96.4$	$\epsilon_{326} = 123$[c]
cis-$Rh(NH_3)_4(OH)_2^+$	335 (125), 283 (120)	$\epsilon_{350} = 108$	
trans-$Rh(NH_3)_4(H_2O)_2^{3+}$	353 (52), 273 (94)	$\epsilon_{313} = 64.0$, $\epsilon_{350} = 51.7$, $\epsilon_{405} = 10.6$	$\epsilon_{326} = 51.0$
trans-$Rh(NH_3)_4(H_2O)OH^{2+}$	347 (83), 291 (124)	$\epsilon_{313} = 98.2$, $\epsilon_{350} = 82.6$, $\epsilon_{405} = 17.5$	$\epsilon_{326} = 80.1$
trans-$Rh(NH_3)_4(OH)_2^+$	347 (96), 303 (120)	$\epsilon_{350} = 96.0$	
cis-$Rh(NH_3)_4(H_2O)Cl^{2+}$	348 (111), 283 (94)		
cis-$Rh(NH_3)_4(OH)Cl^+$	350 (121), 287 (98)		
trans-$Rh(NH_3)_4(H_2O)Cl^{2+}$	389 (55), 284 (117)	$\epsilon_{365} = 38.5$, $\epsilon_{405} = 45.7$	
trans-$Rh(NH_3)_4(OH)Cl^+$	372 (102), 289 (110)	$\epsilon_{365} = 99.1$, $\epsilon_{405} = 53.0$	
cis-$Rh(NH_3)_4(H_2O)Br^{2+}$	363 (126)		
cis-$Rh(NH_3)_4(OH)Br^+$	364 (131)		
trans-$Rh(NH_3)_4(H_2O)Br^{2+}$	466 (39),[d] 406 (61)	$\epsilon_{365} = 32.3$, $\epsilon_{405} = 61.6$	
trans-$Rh(NH_3)_4(OH)Br^+$	382 (119), 288 (115)[d]	$\epsilon_{365} = 101$, $\epsilon_{405} = 85.8$	

[a] Partly from ref 13. [b] Values tabulated are those used in calculations in the Results. [c] The spectrum reported is that of a mixture at pH = $^1/_2$(pK_{a_1} + pK_{a_2}), listed if different from λ_{max}, where $\alpha_0 = 0.09$, $\alpha_1 = 0.82$, and $\alpha_2 = 0.09$. ϵ_{326} is corrected for the presence of the diaqua and the hydroxoaqua species. [d] Shoulders.

Table III. Photoreaction Quantum Yields for Aquaammine- and Hydroxoamminerhodium(III) Complexes in Aqueous 1.0 M (Na,H)(ClO_4,OH) at 25 °C

complex	principal product	λ_{irr}[a]	ϕ[b]	pH
$Rh(NH_3)_5OH^{2+}$	*c*	350	*d*	~7
trans-$Rh(NH_3)_4(H_2O)_2^{3+}$	*cis*-$Rh(NH_3)_4(H_2O)_2^{3+}$	350	0.012	0–2
cis-$Rh(NH_3)_4(H_2O)_2^{3+}$	*trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$	350	0.072	0–2
trans-$Rh(NH_3)_4(H_2O)(OH)^{2+}$	*cis*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$	350	0.59	6.5
cis-$Rh(NH_3)_4(H_2O)(OH)^{2+}$	*trans*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$	350	*e*	7.4
trans-$Rh(NH_3)_4(OH)_2^+$	*c*	350	*d*	13
cis-$Rh(NH_3)_4(OH)_2^+$	*c*	350	*d*	13
trans-$Rh(NH_3)_4(H_2O)Cl^{2+}$	*c*	365	~0.02[f]	1
cis-$Rh(NH_3)_4(H_2O)Cl^{2+}$ [g]	*trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$	365	0.46	3–5
trans-$Rh(NH_3)_4(OH)Cl^+$	*cis*-$Rh(NH_3)_4(OH)_2^+$	365	0.21	9–14
cis-$Rh(NH_3)_4(OH)Cl^+$	*c*	365	~0.02[h]	9–13
trans-$Rh(NH_3)_4(H_2O)Br^{2+}$	*c*	365	~0.01[f]	1
cis-$Rh(NH_3)_4(H_2O)Br^{2+}$ [g]	*trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$	365	0.50	3–5
trans-$Rh(NH_3)_4(OH)Br^+$	*cis*-$Rh(NH_3)_4(OH)_2^+$	365	0.33	9–14
cis-$Rh(NH_3)_4(OH)Br^+$	*c*	365	~0.02[h]	9–13

[a] Wavelength of irradiation in nm. [b] Quantum yield for principal photoreaction in mol/einstein. [c] Not determined; only minor photoreaction observed. [d] The quantum yield not estimated as the product of the (very minor) photoreaction was not identified. [e] The photoreaction observed could quantitatively be accounted for by the photoreactivity of the *cis*-$Rh(NH_3)_4(H_2O)_2^{3+}$ present in equilibrium with the *cis*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$. [f] Quantum yield estimated by assuming *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$ as the photoproduct. [g] In dilute aqueous solution.[8] [h] Quantum yield estimated by assuming *cis*-$Rh(NH_3)_4(OH)_2^+$ as the photoproduct.

periment starting with *cis*-$Rh(NH_3)_4(H_2O)_2^{3+}$ and of $\gamma(t)/q_t$ vs. q_c/q_t for an experiment under the same conditions but starting with *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$. The quantum yields calculated are presented in Table IV, together with the C_c^∞/C_t^∞ coefficient calculated directly from the spectrum of the solution in the photostationary state. This coefficient is related to the quantum yields by[17] eq 10 where ϵ_t^{irr} and ϵ_c^{irr} are the molar

$$\frac{C_c^\infty}{C_t^\infty} = \frac{\epsilon_t^{irr}\phi_{trans}}{\epsilon_c^{irr}\phi_{cis}} \qquad (10)$$

absorptivities of the *trans*- and *cis*-diaqua species, respectively, at λ_{irr} (Table II). The values calculated with eq 10 agree well with the value estimated directly from the product spectrum (see Table IV).

Table IV. Photoisomerization Quantum Yields and Photostationary State for *cis*- and *trans*-Tetraamminediaquarhodium(III) Ions at 25 °C in Acidic Aqueous 1.0 M Perchlorate Solution[a]

A. Quantum Yields

	cis-$Rh(NH_3)_4$-$(H_2O)_2^{3+}$ [b]		*trans*-$Rh(NH_3)_4$-$(H_2O)_2^{3+}$ [b]		mean values	
pH	ϕ_{cis}	ϕ_{trans}	ϕ_{cis}	ϕ_{trans}	ϕ_{cis}	ϕ_{trans}
0.0	0.069	0.011	0.075	0.009	0.072	0.010
1.0	0.071	0.014	0.065	0.010	0.068	0.012
2.0	0.073	0.015	0.080	0.013	0.077	0.014

B. Photostationary State

pH	C_c^∞/C_t^∞ [c]	$(\phi_{trans}/\phi_{cis})\cdot(\epsilon_{t,350}/\epsilon_{c,350})$	pH	C_c^∞/C_t^∞ [c]	$(\phi_{trans}/\phi_{cis})\cdot(\epsilon_{t,350}/\epsilon_{c,350})$
0.0	0.11	0.10	2.0	0.12	0.13
1.0	0.12	0.13			

[a] Photoisomerization resulting from irradiation at 350 nm. Quantum yields expressed in mol/einstein, calculated by method B; see Results. ϕ_{cis} refers to the photoreaction *cis*-$Rh(NH_3)_4$-$(H_2O)_2^{3+}$ → *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$; ϕ_{trans} refers to the reaction in the opposite direction. [b] Photolysis of the complex mentioned. [c] Coefficient of concentrations of cis and trans isomers in solution photolyzed to completion.

***cis*- and *trans*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$.** The photoreactivity of solutions of *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$ increased dramatically by raising the pH, indicating a different photochemical behavior for *trans*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$. Solutions of *trans*-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$ in aqueous 1.0 M $NaClO_4$ (titrated with 0.04 M NaOH in 1.0 M $NaClO_4$ to pH ~6.6 which corresponds to the average of pK_{a_1} plus pK_{a_2}) were irradiated at 350 nm to give a final solution spectrum equivalent to that of *cis*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$ [λ_{max} (ϵ) = 329 nm (122), λ_{max} (ϵ) = 279 (101) (compare to values in Table II)]. Isosbestic points were maintained at 264, 311, and 358

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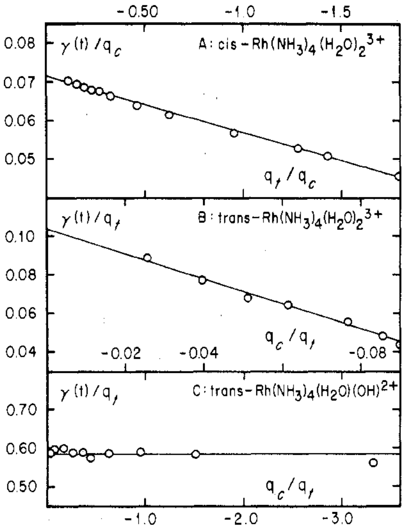


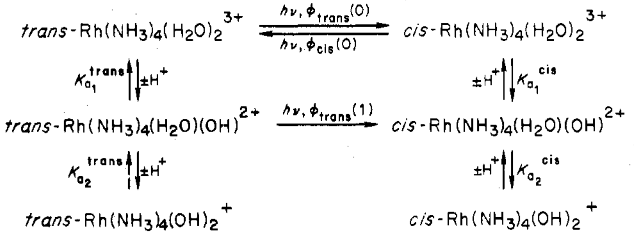
Figure 1. Graphical determination of quantum yields for the diaquatetraamminerhodium(III) ions by method B (see Experimental Section). $\gamma(t)/q$, the observed net quantum yield, is plotted vs. the ratio of light absorbed by product and reactant; λ_{irr} = 350 nm. A: *cis*-$Rh(NH_3)_4(H_2O)_2^{3+}$ in 0.10 M $HClO_4$ and 0.90 M $NaClO_4$. ϕ_{cis} = 0.071 (intercept); the nonzero slope indicates reverse photoreaction, ϕ_{trans} = 0.014 (slope). The last point corresponds to complete photolysis. B: *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$ in 0.10 M $HClO_4$ and 0.90 M $NaClO_4$. ϕ_{trans} = 0.0104 (intercept); the nonzero slope indicates reverse photoreaction, ϕ_{cis} = 0.065 (slope). The last points corresponds to complete photolysis. C: *trans*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$ in 1.0 M $NaClO_4$, pH 6.56. ϕ_{trans} = 0.58 (intercept), with no indication of reverse photoreaction. The last points correspond to ~98% photolysis.

nm throughout the photolysis. For a solution initially at pH 6.53, the final product solution pH was 7.29, equivalent to the expected value of 7.30 based on the assumption that *cis*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$ is the sole photoproduct. Quantum yields were calculated from three exhaustive photolyses by method B; ϕ_{trans} = 0.59 ± 0.01 mol/einstein. The value $\gamma(t)/q_t$ did not depend on q_c/q_t (see Figure 1), indicating that *cis*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$ does not photoisomerize. This latter point was confirmed by direct photolysis of a solution of *cis*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$ in 1.0 M $NaClO_4$ at pH 7.35. The minor pH and spectral changes observed during long-term photolysis corresponded to a cis to trans isomerization quantum yield of 0.007. However, this value can equally be attributed to photoreactions of *cis*-$Rh(NH_3)_2(H_2O)_2^{3+}$ which accounts for 9% of the cis species at pH 7.35 and which photoisomerizes with a quantum yield of 0.072.

***cis*- and *trans*-$Rh(NH_3)_4(OH)_2^+$.** LF photolysis of either tetraamminedihydroxorhodium(III) ion led to but minor photoreaction. When *trans*-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$ was dissolved in 0.04 M NaOH and 1.0 M $NaClO_4$ and photolyzed at 350 nm, spectral changes were uncharacteristic of those expected for photoisomerization. *cis*-$Rh(NH_3)_4(OH)_2^+$ photolyzed under similar conditions also showed very minor spectral changes. For tetraamminedihydroxo ions these spectral changes are likely due to some ammonia aquation.

pH Dependence of the Diaqua Ion Photostationary State. The differences in the photoreactivities of *cis*-$Rh(NH_3)_4(H_2O)_2^{3+}$, *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$, *cis*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$, and *trans*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$ lead to photostationary states, in which the cis/trans composition depends on the pH of the photolysis solution (Scheme II). The cis fraction was determined directly by spectral analysis of exhaustively photolyzed solutions of *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$ in 1.0 M $NaClO_4$ at different pH after irradiation at 313, 350, or 405 nm. When a constant absorption spectrum was obtained, the solution pH was measured, and the distribution between the cis and the trans species was calculated by eq 11–14. ϵ_{exp}^{pH} is the experimental apparent

Scheme II



$$C_c^\infty/(C_t^\infty + C_c^\infty) = (\epsilon_{exptl}^{pH} - \epsilon_t^{pH})/(\epsilon_c^{pH} - \epsilon_t^{pH}) \quad (11)$$

$$\epsilon_c^{pH} = \sum_{n=0}^{2}(\epsilon_c(n))(\alpha_c(n)) \quad (12)$$

$$\epsilon_t^{pH} = \sum_{n=0}^{2}(\epsilon_t(n))(\alpha_t(n)) \quad (13)$$

$$\alpha(n) = \frac{\beta_n[H^+]^{-n}}{\sum_{n=0}^{a}\beta_n[H^+]^{-n}} \qquad n = 0, 1, 2 \quad (14)$$

$$\beta_0 = 1 \qquad \beta_1 = K_{a_1} \qquad \beta_2 = K_{a_1}K_{a_2}$$

molar absorptivity found for a solution in the photostationary state at a certain pH, and ϵ_c^{pH} and ϵ_t^{pH} are the molar absorptivities of an equilibrium mixture of the cis species and trans species, respectively, at this same pH. The latter absorptivities are calculated (eq 12 and 13) from the molar absorptivities of each of the complex ions in either of these equilibria, $\epsilon_c(n)$ and $\epsilon_t(n)$, in combination with the distribution coefficients $\alpha_c(n)$ and $\alpha_t(n)$, these latter coefficients being calculated from the pK_a values (eq 14). The monitoring wavelength was 326 nm, and values for the molar absorptivities are found in Table II.

The experimental values for the cis fraction in the photostationary state are tabulated in Table V. A theoretical cis-fraction pH profile for the photostationary state can be calculated from the isomerization quantum yields for *cis*- and *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$ and for *trans*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$ and from the pK_a values for *cis*- and *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$. The photostationary state is characterized by a zero net isomerization rate (eq 15).[17] The Φ's are the

$$\sum_{n=0}^{2}(I_c(n))(\phi_{cis}(n)) - \sum_{n=0}^{2}(I_t(n))(\phi_{trans}(n)) = -V\frac{dC_c}{dt} = V\frac{dC_t}{dt} = 0 \quad (15)$$

quantum yields for the respective ions which have absorbed the light I, n refers to the number of protons dissociated (n = 0, 1, 2), and V is the volume of the solution. By introduction of $\alpha_c(n)$ and $\alpha_t(n)$ calculated by eq 14 and the molar absorptivities for the ions at λ_{irr}, eq 15 can be rearranged to eq 16, where I_0 is the intensity of irradiated light, A is the total

$$I_0(1 - 10^{-A})\frac{l}{A}[C_c\sum_{n=0}^{2}(\epsilon_c(n))(\alpha_c(n))(\phi_{cis}(n)) - C_t\sum_{n=0}^{2}(\epsilon_t(n))(\alpha_t(n))(\phi_{trans}(n))] = 0 \quad (16)$$

absorbance at λ_{irr}, and l is the light path length. The cis fraction in the photostationary state can now be expressed as eq 17. In Table V the cis fractions in the photostationary states found from exhaustive photolysis (eq 11) are compared

$$\frac{C_c^\infty}{C_c^\infty + C_t^\infty} = \frac{\sum_{n=0}^{2} (\epsilon_t(n))(\alpha_t(n))(\phi_{\text{trans}}(n))}{\sum_{n=0}^{2} (\epsilon_t(n))(\alpha_t(n))(\phi_{\text{trans}}(n)) + \sum_{n=0}^{2} (\epsilon_c(n))(\alpha_c(n))(\phi_{\text{cis}}(n))} \quad (17)$$

with the values calculated from eq 17; the agreement is satisfactory.

***trans*-Rh(NH$_3$)$_4$(H$_2$O)Cl^{2+} and *trans*-Rh(NH$_3$)$_4$(OH)Cl$^+$.** Long-term photolysis (365 nm) of *trans*-Rh(NH$_3$)$_4$(H$_2$O)Cl^{2+} in aqueous 0.10 M HClO$_4$ and 0.90 M NaClO$_4$ resulted in only minor spectral changes, thus confirming the previously reported photoinertness of this material.[8] If one assumes the product to be the diaquo species Rh(NH$_3$)$_4$(H$_2$O)$_2^{3+}$ in the expected 1:10 cis/trans photostationary mixture, the quantum yield can be estimated at ~0.02. In contrast to this low photoactivity in acidic solution, LF photolysis of the *trans*-Rh(NH$_3$)$_4$(OH)Cl$^+$ formed in alkaline solution resulted in effective photohydrolysis and photoisomerization (eq 4). Irradiation at 365 nm led to a blue shift of both LF absorption bands to give the product spectrum in 0.10 M NaOH and 0.90 M NaClO$_4$ which matched (after exhaustive photolysis) that of *cis*-Rh(NH$_3$)$_4$(OH)$_2^+$ [$\lambda_{\max}$ (ϵ) = 335 nm (118), 283 (117) (see Table II)]. The small spectral differences were close to the changes observed after direct photolysis of *cis*-Rh(NH$_3$)$_4$(OH)$_2^+$ and can be attributed to minor secondary photolysis of the primary product. Isosbestic points at 359 and 308 nm persisted during the entire photolysis, whereas two other isosbestic points at 292 and 247 nm were observed through the photolysis corresponding to more than 90% overall conversion. The spectrum of the product solution acidified with HClO$_4$ [$\lambda_{\max}$ ($\epsilon_{\max}$) = 326 nm (103), 269 (96)] was very similar to that of *cis*-Rh(NH$_3$)$_4$(H$_2$O)$_2^{3+}$ (Table II). Thermal anation with HCl (boiling for $^1/_2$ h, 1 M HCl) resulted in a solution in which the main product after ion-exchange analysis was identified ($\lambda_{\max}$ = 360, 295 nm[8]) as *cis*-Rh(NH$_3$)$_4$Cl$_2^+$ (~90%). Other rhodium(III) species were not identified, but ion-exchange behavior indicated some uncharged species (presumably Rh(NH$_3$)$_3$Cl$_3$), suggesting some photochemical ammonia aquation. Quantum yields were calculated by method A; $\phi_{\text{Cl}} = \phi_{\text{isom}} = 0.23 \pm 0.02$ independent of pH between 9.5 and 14. The low photoactivities of *trans*-Rh(NH$_3$)$_4$(OH)$_2^+$ and *cis*-Rh(NH$_3$)$_4$(OH)Cl$^+$ (vide infra) exclude both as intermediates in the photolysis of *trans*-Rh(NH$_3$)$_4$(OH)Cl$^+$, demonstrating that the photohydrolysis and photoisomerization are concomitant.

Quantum yields at intermediate pHs, where both *trans*-Rh(NH$_3$)$_4$(H$_2$O)Cl^{2+} and *trans*-Rh(NH$_3$)$_4$(OH)Cl$^+$ absorb significant fractions of the total light absorbed, were determined by photolysis followed to about 15% reaction. Solutions of *trans*-[Rh(NH$_3$)$_4$(H$_2$O)Cl]S$_2$O$_6$ dissolved in 1.0 M NaClO$_4$ were titrated with NaOH to the desired pH and photolyzed. The photoreaction was monitored by pH and absorbance measurements. The difference in acidities between *trans*-Rh(NH$_3$)$_4$(H$_2$O)Cl^{2+} and the photoproduct *cis*-Rh(NH$_3$)$_4$(H$_2$O)$_2^{3+}$ is minor (see Table I), and only small pH changes were observed. In the calculations, pH was assumed constant, and photolyses were stopped when the pH changes exceeded ~0.05 pH units. The quantum yields were calculated by method A from the spectral changes of the numbers of moles reacted as the response to the light absorbed by the photolysis solution.

Table V. Cis–Trans Distribution in the Photostationary State at Different pHs in Aqueous 1.0 M Perchlorate Solution for Tetraamminediaquarhodium(III)

pH	λ_{irr}[a]	starting complex	$\epsilon_{\infty,326}$[b]	$\epsilon_{c,326}$[c]	$\epsilon_{t,326}$[c]	$C_c^\infty/(C_c^\infty + C_t^\infty)$ obsd[d]	$C_c^\infty/(C_c^\infty + C_t^\infty)$ calcd[e]
0.0	350	cis	56.6	107.3	51.0	0.10	0.11
0.0	350	trans	56.1	107.3	51.0	0.09	0.11
0.0	313	cis	57.6	107.3	51.0	0.12	0.10
0.0	313	trans	55.9	107.3	51.0	0.09	0.10
1.0	350	cis	57.3	107.3	51.0	0.11	0.11
1.0	350	trans	56.4	107.3	51.0	0.10	0.11
2.0	350	cis	56.4	107.3	51.0	0.10	0.11
2.0	350	trans	57.1	107.3	51.0	0.11	0.11
2.41	350	trans	58.2	107.3	51.1	0.13	0.13
3.31	350	trans	66.2	107.3	51.8	0.26	0.26
3.55	350	trans	70.5	107.3	52.2	0.33	0.33
3.66	350	cis	76.0	107.3	52.5	0.43	0.38
3.69	405	trans	86.0	107.3	52.6	0.61	0.56
3.79	350	cis	81.6	107.3	53.0	0.53	0.43
4.67	405	cis	102.3	107.6	61.5	0.89	0.88
4.97	350	trans	103.6	107.9	66.4	0.90	0.84
6.01	350	trans	108.1	111.9	78.0	0.89	0.92
6.24	405	cis	110.9	113.8	78.9	0.92	0.97
6.38	405	cis	112.8	115.0	79.4	0.94	0.97
6.65	350	trans	118.3	117.3	80.1	1.00	0.96
7.08	350	trans	117.6	120.2	80.9	0.93	0.98
7.25	350	trans	120.5	120.7	81.4	0.99	0.99
7.29	350	trans	118.7	120.9	81.4	0.94	0.99
7.41	350	cis	121.6	121.2	82.0	1.00	0.99

[a] Wavelength of irradiation in nm. [b] Molar absorptivity (in L mol^{-1} cm^{-1}) at 326 nm after irradiation to constant spectrum. [c] Molar absorptivity at 326 nm for the cis and trans complex, respectively, in acid–base equilibrium at a certain pH. [d] Fraction on the cis form in the photostationary state calculated from $\epsilon_{\infty,326}$. [e] Fraction on the cis form in the photostationary state calculated from quantum yields (see Results).

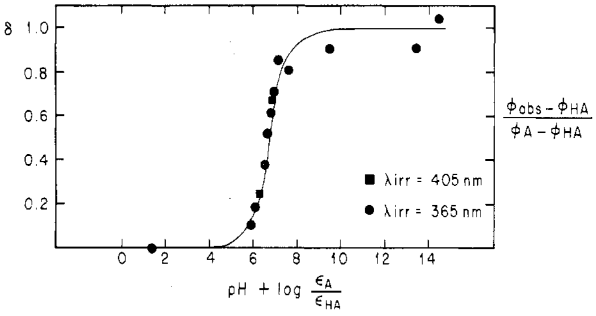


Figure 2. pH dependence of photohydrolysis–photoisomerization of *trans*-Rh(NH$_3$)$_4$(H$_2$O)Cl^{2+}/*trans*-Rh(NH$_3$)$_4$(OH)Cl$^+$: solid line, δ the fraction of light absorbed by the base form of these two trans species predicted from pK_a and molar absorptivities ϵ_{HA} and ϵ_{A} (eq 20); points, experimental values of $(\phi_{\text{obsd}} - \phi_{\text{HA}})/(\phi_{\text{A}} - \phi_{\text{HA}})$ calculated from quantum yields (eq 21).

Consider a photochemical system in an acid–base equilibrium (eq 18) where both the acid and base forms undergo

$$\text{HA} \overset{K_a}{\rightleftarrows} \text{H}^+ + \text{A}^- \quad (18)$$

photoreaction to the same product. The observed quantum yield is a function of the distribution between these two forms as indicated in eq 19, where δ is the fraction of light absorbed

$$\phi_{\text{obsd}} = \delta\phi_{\text{A}} + (1 - \delta)\phi_{\text{HA}} \quad (19)$$

by the base form and ϕ_{A} and ϕ_{HA} are the photoreaction quantum yields for the base and acid forms, respectively. δ is a function of the solution acid concentration and of the molar absorptivities of both forms, ϵ_{A} and ϵ_{HA} at λ_{irr} (eq 20), and

$$\delta = \frac{\epsilon_{\text{A}}[\text{A}^-]}{\epsilon_{\text{A}}[\text{A}^-] + \epsilon_{\text{HA}}[\text{HA}]} = \frac{K_a}{K_a + \frac{\epsilon_{\text{HA}}}{\epsilon_{\text{A}}}[\text{H}^+]} \quad (20)$$

this dependence is shown as a plot of δ vs. pH + log ($\epsilon_{\text{HA}}/\epsilon_{\text{A}^-}$) in Figure 2. Rearrangement of eq 19 gives eq 21, which shows

$$\frac{\phi_{\text{obsd}} - \phi_{\text{HA}}}{\phi_{\text{A}} - \phi_{\text{HA}}} = \delta \qquad (21)$$

that the term on the left should demonstrate the same functionality in pH + log $(\epsilon_{\text{AH}}/\epsilon_{\text{A}})$ as does δ (on the assumption that ϕ_{HA} and ϕ_{A} are independent of λ_{irr} as normally found in the LF photolyses of rhodium(III) ammines).[15] That such is the case is shown also by Figure 2 where there is good agreement between the calculated δ values for *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$/*trans*-$Rh(NH_3)_4(OH)Cl^+$ mixtures and the experimental values of $(\phi_{\text{obsd}} - \phi_{\text{HA}})/(\phi_{\text{A}} - \phi_{\text{HA}})$ for both λ_{irr}'s investigated.

***trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$ and *trans*-$Rh(NH_3)_4(OH)Br^+$.** The photochemical behavior of *trans*-$Rh(NH_3)_4(H_2O)Br^+$ and *trans*-$Rh(NH_3)_4(OH)Br^+$ resembles that of the chloro analogues. Thus, in 0.10 M $HClO_4$ and 0.90 M $NaClO_4$ there was very little photoactivity ($\phi \approx 0.01$), but in alkaline solution, efficient and clean concomitant photohydrolysis–photoisomerization to *cis*-$Rh(NH_3)_4(OH)_2^+$ was seen. An exhaustive photolysis ($\lambda_{\text{irr}} = 365$ nm) of *trans*-$[Rh(NH_3)_4(H_2O)Br]S_2O_6$ in 0.040 M NaOH and 0.96 M $NaClO_4$ led to a solution with a spectrum [$\lambda_{\max}$ (ϵ) = 335 nm (118), 283 (115) (see Table II)] matching that of *cis*-$Rh(NH_3)_4(OH)_2^+$. Isosbestic points at 360 and 309 nm persisted for photolysis corresponding to more than 80% overall photolysis. A solution initally at pH 6.76, photolyzed to completion, had a final pH 6.36, very close to 6.29 predicted if the *cis*-diaqua complex and its conjugated bases are the only photoproducts. In alkaline solution $\phi_{\text{Br}^-} = \phi_{\text{isom}} = 0.33 \pm 0.01$, independent of pH between 9 and 14. As for the chloro analogues, quantum yields were determined in the buffer region. The results of photolysis at 365 and 405 nm are presented in Figure 3, and it is seen that the agreement between the predicted δ and the experimental values is very good.

***cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ and *cis*-$Rh(NH_3)_4(OH)Cl^+$.** *cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ has been shown[8] to display very effective photoisomerization ($\phi_{\text{isom}} = 0.50$). On increasing of the pH, the photoactivity declined. Thus, in 0.10 M NaOH and 0.90 M $NaClO_4$ very little photohydrolysis was observed at $\lambda_{\text{irr}} = 365$ nm. The thermal hydrolysis under these and similar conditions is significant.[13] An estimate for the photoreaction quantum yield assuming *cis*-$Rh(NH_3)_4(OH)_2^+$ as photoproduct is $\phi_{\text{Cl}} \approx 0.02$, correcting for the thermal hydrolysis.

***cis*-$Rh(NH_3)_4(H_2O)Br^{2+}$ and *cis*-$Rh(NH_3)_4(OH)Br^+$.** Again, the bromo complexes resemble their chloro analogues, and only an approximate value for the photohydrolysis quantum yield for *cis*-$Rh(NH_3)_4(OH)Br^+$ could be determined; $\phi_{\text{Br}^-} \approx 0.02$ ($\lambda_{\text{irr}} = 365$ nm, 0.04 M NaOH, 0.96 M $NaClO_4$).

Discussion

The most striking observation described here is the marked change in the photostereochemistry of the disubstituted tetraammine complexes $Rh(NH_3)_4XY^{n+}$ when one of the ligands is hydroxide. When Y = Cl^-, Br^-, or H_2O and X is hydroxide, the LF photolysis product is cis, and trans to cis photoisomerization is concomitant with labilization of Y when this ligand is Cl^- or Br^- (eq 22). For Y = H_2O, eq 22 would be consistent

$$\begin{aligned} \textit{trans}\text{-}Rh(NH_3)_4(OH)Y^{n+} + H_2O &\xrightarrow{h\nu} \\ \textit{cis}\text{-}Rh(NH_3)_4(H_2O)(OH)^{2+} + Y &\rightleftharpoons \\ \textit{cis}\text{-}Rh(NH_3)_4(OH)_2^+ + H^+ &\quad (22) \end{aligned}$$

with the photolability of coordinated H_2O noted in the previous studies.[8,16] However, isotopic labeling is necessary to establish this for certain.

Formation of the cis product in eq 22 can be rationalized in terms of a site preference of the ligand X for the basal or apical coordination sites in the SPY intermediates indicated in Scheme I[8,10,11] (B* or A*, respectively). MO calculations[10,11] suggest the more stable triplet SPY isomer to be that having the weaker σ donor (NH_3 vs. X) in the apical site of $Rh(NH_3)_4X^{n+}$. According to these the major difference between A* and B* lies in the energy of the singularly occupied "d_{z^2}" orbital (approximating the symmetry as C_{4v} for both cases). Qualitatively, the site preference of the weaker donor for the apical position can be understood in terms of this orbital's σ^* character with regard to the metal–ligand apical bond. For X = Cl^- or Br^- the final product is exclusively trans, and for X = H_2O the $Rh(NH_3)_4(H_2O)_2^{3+}$ photostationary state shows the quantum yield for cis → trans isomerization to be about 6 times larger than that for the reverse reaction. Since the ligand order for σ-donor strengths is reportedly[18] $OH^- > NH_3 > H_2O > Cl^- > Br^-$, the models predict A* to be the more stable intermediate for these last three ligands. Notably this order also rationalizes the intermediate behavior for X = H_2O where some trans to cis isomerization is also seen to give a photostationary state. In the case of X = OH^-, the SPY intermediates now would include a stronger σ-donor ligand than NH_3.[19] In this case the basal isomer B* should be the more stable, thus rationalizing the cis products seen regardless of the leaving group (an exception is Y = OH^-; see below).

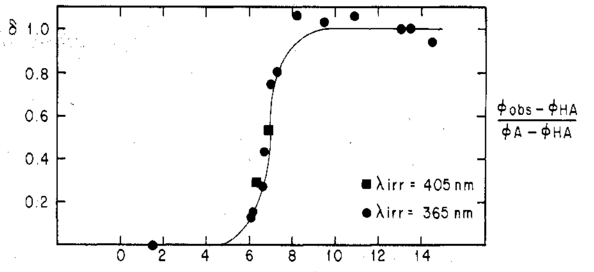


Figure 3. pH dependence of photohydrolysis–photoisomerization of *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$/*trans*-$Rh(NH_3)_4(OH)Br^+$. See Figure 2.

An intriguing aspect of these systems is the markedly different behaviors hydroxide and water show in these photoreactions induced by LF excitation. First, H_2O appears quite photolabile while OH^- appears not to be;[16] second, as the ligand X in Scheme I, H_2O is trans directing while OH^- is cis directing. Thus simple deprotonation of an aqua complex leads to marked differences in photoreaction behavior. Consider for example the *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$ ion. In aqueous solution, this appears nearly photoinert to LF excitation, excluding the very likely photoexchange of solvent and coordinated H_2O. In contrast, its conjugate base *trans*-$Rh(NH_3)_4(OH)Br^+$ undergoes photoreaction analogous to eq 22 with a high quantum yield (0.33 mol/einstein). A similar reversal in behavior is seen in the photochemistry of $Co(CN)_5H_2O^{2-}$ and $Co(CN)_5OH^{3-}$. In the former case, CN^- labilization by LF excitation is very minor,[19] although H_2O exchange with solvent is substantial,[20] while in the latter case CN^- labilization occurs to give *cis*-$Co(CN)_4(OH)_2^{3-}$. However, the stereochemical location of the labilized CN^- in the

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(18) The photoproduct at these intermediate pHs was assumed to be an equilibrium mixture of *cis*-$Rh(NH_3)_4(H_2O)_2^{3+}$ and its conjugate bases. The molar absorptivity of a mixture of these cis species at each pH of photolysis was measured and used in the quantum yield calculation. Ignoring the minor trans fraction which might be a product at the lower pHs introduces only a small error in the quantum yield calculations.

(19) (a) Glerup, J; Mønsted, O.; Schäffer, C. E. *Inorg. Chem.* **1976**, *15*, 1399. (b) Notably, the ligand σ-donor strengths have been calculated for first-row transition elements, and we make the assumption that at least the qualitative order is the same for Rh(III).

(20) Wrighton, M.; Bredesen, D. *Inorg. Chem.* **1973**, *12*, 1707.

(21) Buckingham, D. A.; Ford, P. C., unpublished observations. ϕ exchange was measured as ~0.15 mol/einstein in preliminary experiments carried out at the Research School of Chemistry, The Australian National University.

starting complex was not identified.[19]

Figure 3 shows a photochemical titration, i.e., a quantum yield vs. pH profile for the *trans*-$Rh(NH_3)_4(H_2O/OH)Br^{2+/+}$ conjugate acid/base pair. Notably, the aqua species acts as an inner filter for the photoreaction to give lower apparent quantum yields to the extent it absorbs the incident radiation. Thus once corrections are made for the differences in extinction coefficients (eq 20), it is seen that the photoreaction behavior is that predicted by the ground-state pK_a of this species. Similar conclusions are also reached for *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ and the diaqua ions (Figure 2 and Table V). In a LF excited state, one might expect the complexes to have significantly greater acidity, given the $(t_{2g}{}^5)(e_g{}^1)$ electronic configuration (using O_h labels for simplicity). Thus if the excited complexes underwent acid/base equilibration, the relationship between photoreaction quantum yield and pH should not reflect the ground-state pK_a. Some data is available which allows an estimate of the time required for such equilibration. Rate studies for acid/base equilibration (eq 23)

$$Co(NH_3)_5OH^{2+} + H^+ \underset{k_d}{\overset{k_p}{\rightleftharpoons}} Co(NH_3)_5H_2O^{3+} \qquad (23)$$

of the aquapentaamminecobalt(III) ion (which has a pK_a similar to that of the Rh(III) analogue)[13] report values of k_p as 5.0×10^9 M^{-1} s^{-1} and k_d as 3.6×10^3 s^{-1}.[22] Thus at pH 7 (near the pK_a of the complex), the first-order rate constant to equilibrium is $k_{eq} = (k_d + k_p[H^+]) = 4 \times 10^3$ s^{-1}, corresponding to a relaxation time of ~250 μs. The lifetime of the lowest energy LF excited-state $Rh(NH_3)_5Cl^{2+}$ in ambient aqueous solution has been measured as 14 ns,[23] and it is unlikely that any of the complexes described here have markedly longer lifetimes.[24] Thus, the time domain of the photochemical process is orders of magnitude too short to expect enough Brønsted acid equilibration of excited states to change photoreaction properties from those predicted by the ground-state pK_a's.[25,26]

The data reported here reinforce the observation made earlier in the pentaammine series for $Rh(NH_3)_5OH^{2+}$, namely, the apparent low photoactivity of certain hydroxo complexes. The $Rh(NH_3)_5OH^{2+}$ ion undergoes little or no oxygen photoexchange with solvent in pH 12.3 aqueous solution.[16] Given the inertness of OH^- as a leaving group in thermal substitution reactions,[26] this may not be a surprising result. However, the experiments reported here using and previously[16] using solvent isotopic labeling emphasize that significant NH_3 labilization also does not occur from $Rh(NH_3)_5OH^{2+}$, although this pathway is seen in the photoreactions of the halopentaammines.[23] For other complexes described here, isotope-exchange experiments would be necessary to acertain that OH^- is not undergoing photoexchange with solvent; however, circumstantial evidence suggests that this process is not significant. For example *trans*-$Rh(NH_3)_4(OH)_2{}^+$ does not photoisomerize, although according to the results described in this manuscript, photoisomerization to the cis analogue should be facile if OH^- is labilized. Perhaps more surprising is the relative photoinactivity of *cis*-$Rh(NH_3)_4(OH)Cl^{2+}$ and *cis*-$Rh(NH_3)_4(OH)Br^{2+}$ for which halide labilization might be expected. Certainly the presence of OH^- in the Rh(III) coordination sphere is not in itself sufficient to suppress photoreactivity, given the high quantum yields seen for eq 21 (Table III) which are independent of pH over the range 7–14 for Y = Cl^- or Br^-. We see no ready explanations for these contrasting observations other than to suggest that perhaps for certain hydroxo complexes excited-state lifetimes are too short for significant ligand labilization to occur in competition with anomalously fast nonradiative deactivation to the ground state. This question may be answered by pulse-laser studies now in progress to determine the solution phase excited-state lifetimes.

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Registry No. *cis*-$Rh(NH_3)_4(H_2O)_2{}^{3+}$, 73573-86-1; *cis*-$Rh(NH_3)_4(H_2O)OH^{2+}$, 72901-99-6; *cis*-$Rh(NH_3)_4(OH)_2{}^+$, 73085-23-1; *trans*-$Rh(NH_3)_4(H_2O)_2{}^{3+}$, 61697-83-4; *trans*-$Rh(NH_3)_4(H_2O)OH^{2+}$, 73573-85-0; *trans*-$Rh(NH_3)_4(OH)_2{}^+$, 73573-84-9; *cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$, 71424-38-9; *cis*-$Rh(NH_3)_4(OH)Cl^+$, 73573-83-8; *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$, 38781-25-8; *trans*-$Rh(NH_3)_4(OH)Cl^+$, 73085-22-0; *cis*-$Rh(NH_3)_4(H_2O)Br^{2+}$, 71382-14-4; *cis*-$Rh(NH_3)_4(OH)Br^+$, 73573-82-7; *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$, 71424-39-0; *trans*-$Rh(NH_3)_4(OH)Br^+$, 73085-24-2.

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(24) Low-temperature (77 K) emission studies show the disubstituted complexes to have shorter lifetimes under those conditions than $Rh(NH_3)_5Cl^{2+}$ by an order of magnitude (Bergkamp, M. A.; Skibsted, L. H.; Watts, R. J.; Ford, P. C., unpublished data).

(25) To elaborate on this point, consider the LF excited state of $Rh(NH_3)_5H_2O^{3+}$ to have a p$K_a{}^* = 4.0$ (about 3 pK_a units more acidic than the ground state[13]) and a lifetime in solution of 10 ns. A value of 4.0 is a reasonable estimate given a ground-state pK_a of 4.2 for the d^5 Ru(III) analogue $Ru(NH_3)_5(H_2O)^{3+}$.[26] It is unlikely that k_p would be substantially larger than the 5.0×10^9 M^{-1} s^{-1} measured for eq 23, so we will assume this value for the $Rh(NH_3)_5(H_2O)^{3+}$ excited state. This would give us an estimated value of 5×10^5 s^{-1} for k_d. At pH 7 the first-order rate constant to equilibrium would then be $k_{eq} = (k_d + k_p[H^+] = 5 \times 10^5$ s^{-1} which corresponds to a relaxation time of 2 μs, again far too long for significant equilibration to occur during the lifetime of the excited state.

(26) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", Wiley: New York, 1967; Chapter 3.