

Thermal and Photochemical Reactions of Dibromo(β, β', β'' -triaminotriethylamine)rhodium(III) and α - and β -Aquobromo(β, β', β'' -triaminotriethylamine)rhodium(III) Cations in Acidic Aqueous Solution: Evidence for an Innocent-Ligand Effect

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Ligand-field photolysis of $[\text{Rh}(\text{tren})\text{Br}_2]^+$ in acidic aqueous solution causes efficient Br^- release ($\phi_{\text{Br}^-} = 0.22 \pm 0.03$) and the formation of $[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$. This photoproduct ion differs from $[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$ generated upon thermal aquation of acidic aqueous solutions of $[\text{Rh}(\text{tren})\text{Br}_2]^+$. The thermally produced ion is assigned the α structure, while photoproduct $[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$ is assigned the β structure; the bases for these assignments are discussed. The β aquo bromo ion is photochemically inert but releases bromide when heated in acidic aqueous solutions. Solutions of the α isomer also release Br^- when heated, but photolysis cleanly generates the β aquo bromo isomer ($\phi_{\text{isom}} = 0.19 \pm 0.02$). Temperature-dependent kinetic studies of the thermally induced aquations reveal that the activation parameters for the α isomer contrast sharply with the parameters determined for the β aquo bromo and dibromo ions, suggesting a distinct aquation path for the α ion. Possible mechanisms for the unique $\alpha \rightarrow \beta$ photoisomerization of $[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$ are discussed.

Introduction

Metal complexes containing the tetradentate amine "tren" (β, β', β'' -triaminotriethylamine, $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$) have some unusual and attractive features, and they have been studied for years.¹⁻³ Unlike that of its linear isomer, trien, other linear tetradentates (2,3,2-tet, 3,2,3-tet, etc.), or the cyclic tetradentates (cyclam, cyclen, etc.), the tripodal geometry of tren forces six-coordinate tren complexes into a cis geometry, as isomerization to a trans geometry, or to a second cis geometry (possible for linear tetraamines), is not possible. Many of the studies have concentrated on the tendency of tren to form complexes with a trigonal-bipyramidal (TBP) geometry;^{4,5} numerous stable five-coordinate tren complexes, $[\text{M}(\text{tren})\text{X}]^{n+}$, with approximate C_{3v} symmetry have been reported.⁶⁻⁸ In addition, six-coordinate complexes containing tren have been cited as models for dissociative aquations,^{2,9-11} with the dissociation step presumably driven by the stability of the proposed five-coordinate intermediate.

We have drawn attention to another interesting aspect of the tren ligand; in six-coordinate complexes, the tren ligand puts the two remaining coordination sites in different chemical environments.^{12,13} The site trans to the tertiary amine (site Y in Figure 1), surrounded by six amine-bonded hydrogens, should interact strongly with the primary solvent shell and be hydrophilic. In contrast, a ligand at X, cis to the tertiary amine, abuts the carbon-bonded hydrogen atoms of tren, making this site more hydrophobic than Y. These differences, induced by the unreactive and presumably innocent tren ligand, have been explored in thermal and photochemical studies of $[\text{Rh}(\text{tren})\text{Cl}(\text{X})]^{n+}$ ($\text{X} = \text{Cl}, \text{H}_2\text{O}$).^{12,13} The model that emerged from those studies suggests that the hydrophilic site (Y) is prone to associative

nucleophilic attack, while the recognized propensity of tren for the TBP geometry makes the hydrophobic site (X) susceptible to dissociative labilization.

Rh(III)-tren complexes are excellent subjects for such studies; they are generally photosensitive, while the thermal reactions are slow enough not to interfere with the photochemical studies but fast enough to be conveniently monitored. In addition, thermal and photochemical substitutions of rhodium(III) amines are thought to proceed by contrasting mechanisms. While discussion continues, the thermal aquations (in acidic solution) are generally considered to proceed through an interchange process,^{14,15} with significant Rh-OH₂ bond formation in the transition state; photoinduced substitutions at Rh(III) are presumed to be dissociative.¹⁶⁻¹⁹ These differences were used to account for the observed differences in the sites of chloride labilization in the thermal and photochemical substitutions of $[\text{Rh}(\text{tren})\text{Cl}(\text{X})]^{n+}$ ($\text{X} = \text{Cl}, \text{H}_2\text{O}$).¹² In contrast to the case for Rh(III), ligand-field photolysis and thermally induced aquations of $[\text{Co}(\text{tren})\text{Cl}_2]^+$ (in acidic solutions) generate indistinguishable $[\text{Co}(\text{tren})(\text{H}_2\text{O})\text{Cl}]^{2+}$ ions.²⁰ This is consistent with the observation that thermal substitutions at Co(III) are generally recognized to be dissociative,²¹ so that labilization of the same chloride released photochemically would be expected (and is observed).

To test and/or extend this nascent model, we have pursued studies of related tren-containing complexes; we report here on the thermal and photochemical reactions of $[\text{Rh}(\text{tren})\text{Br}_2]^+$ and the two geometric isomers of $[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$.²²

Experimental Section

Preparation of Compounds. Dibromo(β, β', β'' -triaminotriethylamine)rhodium(III) bromide. This method of Saliby et al.¹³ was used to prepare $[\text{Rh}(\text{tren})\text{Br}_2]\text{Br}$; it involved the base hydrolysis and subse-

- (1) Initial results presented by C. Arpey, W. Bosch, and P. S. Sheridan, 184th National Meeting of the American Chemical Society, Kansas City, MO, 1982.
- (2) Gaudin, M. J.; Clark, C. R.; Buckingham, D. A. *Inorg. Chem.* **1986**, *25*, 2569 and references therein.
- (3) Zipp, S. G.; Madan, S. K.; Zipp, A. P. *J. Indian Chem. Soc.* **1977**, *54*, 149.
- (4) Ciampolini, M.; Paoletti, P. *Inorg. Chem.* **1967**, *6*, 1261.
- (5) Paoletti, P.; Fabbrizzi, L. *Coord. Chem. Rev.* **1975**, *15*, 435.
- (6) Jain, P. C.; Lingafelter, E. C. *J. Am. Chem. Soc.* **1967**, *89*, 724.
- (7) diVaira, M.; Oriolo, P. L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 595.
- (8) diVaira, M.; Oriolo, P. L. *Inorg. Chem.* **1967**, *6*, 490.
- (9) Buckingham, D. A.; Clark, C. R.; Webley, W. S. *Aust. J. Chem.* **1980**, *33*, 263.
- (10) Buckingham, D. A.; Cresswell, P. J.; Sargeson, A. M. *Inorg. Chem.* **1975**, *14*, 1485.
- (11) Buckingham, D. A.; Edwards, J. D.; McLaughlin, G. M. *Inorg. Chem.* **1982**, *21*, 2770.
- (12) Martins, E.; Sheridan, P. S. *Inorg. Chem.* **1978**, *17*, 2822.
- (13) Saliby, M. J.; Kaplan, E. B.; Sheridan, P. S.; Madan, S. K. *Inorg. Chem.* **1981**, *20*, 728.

- (14) Swaddle, T. W.; Stranks, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 8357.
- (15) Pavelich, M. L.; Maxey, S. M.; Pfaff, P. C. *Inorg. Chem.* **1978**, *17*, 5640.
- (16) Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1978**, *17*, 2730.
- (17) Monsted, L.; Skibsted, L. H. *Acta Chem. Scand., Ser. A* **1984**, *A38*, 535.
- (18) Skibsted, L. H.; Monsted, L. *Acta Chem. Scand., Ser. A* **1983**, *A37*, 663.
- (19) Weber, W.; DiBenedetto, J.; Offen, H.; van Eldik, R.; Ford, P. C. *Inorg. Chem.* **1984**, *23*, 2033.
- (20) Sheridan, P. S.; Adamson, A. W. *Inorg. Chem.* **1974**, *13*, 2482.
- (21) Swaddle, T. W.; Mak, M. K. S. *Can. J. Chem.* **1983**, *61*, 832.
- (22) There are several methods currently used to distinguish between geometric isomers of $[\text{M}(\text{tren})\text{XY}]$ complexes. For the $[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$ ions discussed here, we use the α and β nomenclature described earlier.¹² For the hypothetical molecule represented in Figure 1, the α isomer has $\text{X} = \text{Br}^-$ and $\text{Y} = \text{H}_2\text{O}$, while the β isomer has $\text{X} = \text{H}_2\text{O}$ and $\text{Y} = \text{Br}^-$. The IUPAC nomenclature has X and Y in the b and f sites, respectively, while Buckingham²³ refers to them as the p and t sites—trans to the primary and tertiary amines, respectively.

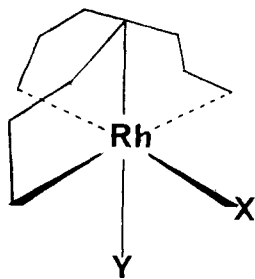


Figure 1. Molecular framework of the $[\text{Rh}(\text{tren})\text{XY}]^{2+}$ ion.

quent bromide anation of the $[\text{Rh}(\text{tren})\text{Cl}_2]^+$ ion.¹² Purity was routinely checked by comparison of electronic spectra with the published spectrum and by decomposition of the complex and determination of Br^- with a calibrated Br^- -sensitive electrode. To ensure the removal of minor amounts of aquated ions, solutions of $[\text{Rh}(\text{tren})\text{Br}_2]^+$ were eluted from an SP Sephadex (C-25) cation-exchange column just before photochemical or thermal reaction studies.

The Aquobromo(β,β',β'' -triaminotriethylamine)rhodium(III) Cation—Thermally Prepared Isomer. Solutions of $[\text{Rh}(\text{tren})\text{Br}_2]\text{Br}$ in 0.1 M H_2SO_4 or HClO_4 were heated at 50–55 °C for 2–3 h, until isosbestic points in the electronic spectral changes were lost. The resulting aquo bromo ion was easily separated from any dibromo and/or diaquo cations by elution (using dilute 0.1 N sulfuric or perchloric acid) from an SP Sephadex (C-25) cation-exchange column in the H^+ form.

The Aquobromo(β,β',β'' -triaminotriethylamine)rhodium(III) Cation—Photochemically Prepared Isomer. Methods analogous to those used for the generation of β - $[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Cl}]^{2+}$ were used for the bromo analogue. Dilute (0.1 M) sulfuric acid solutions of $[\text{Rh}(\text{tren})\text{Br}_2]^+$ were photolyzed by using a broad-band UV cutoff filter until spectral changes ceased. The resulting solution was eluted from a SP Sephadex (C-25) cation-exchange column in the H^+ form just before use.

Photolysis. Irradiation was effected with a vertically mounted 200-W (Illumination Industries, Inc.) or a horizontally mounted 100-W (Photochemical Research Associates) Hg short-arc lamp. For bulk photolyses, a broad-band UV cutoff filter was used; quantum yield determinations were performed by using an interference filter with a maximum transmittance at 355 nm (fwhh 40 nm). In both situations the radiation was passed through a hot mirror (Illumination Industries, Inc.) or 10 cm of cooled water to keep IR radiation from the sample. Light intensities were measured with ferrioxalate actinometry.

Instrumentation. Electronic spectra were recorded on a Beckman Acta MIV or a Varian 219 spectrophotometer. A Beckman Research pH meter with a combined electrode (Beckman) was used for pH measurements, and an Orion Br^- -selective electrode with a bridge-junction reference (Beckman) was used for $[\text{Br}^-]$ determination. The Br^- electrode was calibrated with a range of NaBr solutions. Kinetic studies were performed with the five-cell turret accessory of the Varian 219 spectrophotometer. Solution temperatures were monitored with the built-in thermocouple, which was periodically checked with a standard thermometer.

Product Analyses and Quantum Yields. Methods described earlier for the chloro analogues were used in this study.¹²

Kinetic Studies. Spectral changes at several wavelengths were monitored for at least 3 half-lives for each sample. Reported rate constants are derived from spectral changes observed at 380 nm (reaction 1), 290 nm (reaction 2), and 360 nm (reaction 3). Rate constants were determined by using experimentally observed A_{inf} values; for slow reactions, when accurate determination of A_{inf} was unreliable, the method of Guggenheim²³ was employed. In at least eight cases, internal consistency between these two methods was confirmed. Each rate constant is the arithmetic average of at least three kinetic runs. Experimental data points were closely (correlation coefficients of 0.99 or greater) modeled by a first-order kinetic expression, and linear-least-squares graphical methods were used to determine both rate constants and activation parameters.

The activation energy, E_a , was determined from the Arrhenius relationship, $k_r = A \exp(-E_a/RT)$, while $k_t = (kT/h) \exp(-\Delta G^*/RT)$ (where $\Delta G^* = \Delta H^* - T\Delta S^*$ and $T = 333 \text{ K}$) was used to determine ΔH^* and ΔS^* .

Results

Reactions of $[\text{Rh}(\text{tren})\text{Br}_2]^+$. Thermal Reactivity. At 50 °C, 0.1 M H_2SO_4 solutions of $[\text{Rh}(\text{tren})\text{Br}_2]^+$ undergo the spectral

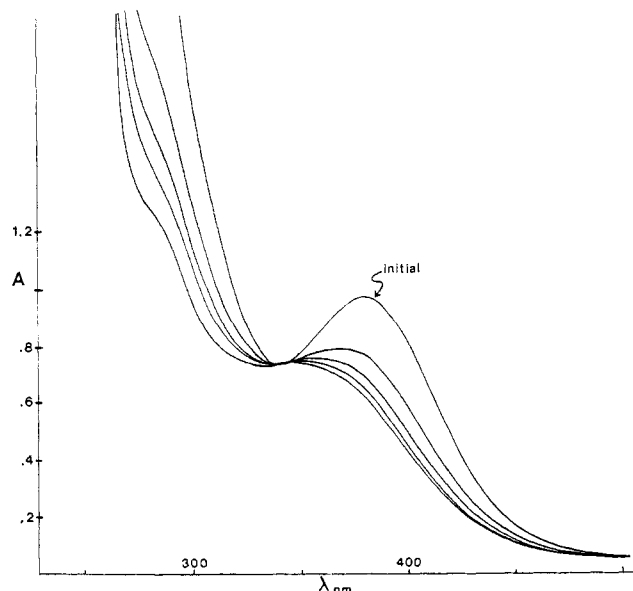
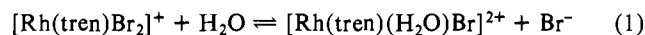


Figure 2. Spectral changes induced upon aquation of $[\text{Rh}(\text{tren})\text{Br}_2]^+$ ($2.66 \times 10^{-3} \text{ M}$, 50 °C, 0.1 M H_2SO_4). Spectra were recorded 600, 1200, 1800, and 3000 s after the initial spectrum. The final spectrum corresponds to the spectrum of $[\text{Rh}(\text{tren})(\text{H}_2\text{O})_2]^{3+}$.

changes shown in Figure 2. The intensity of the initial ligand-field (LF) transition at 382 nm decreases and is replaced by a peak at 345 nm and a shoulder near 288 nm; the steep rise of the charge-transfer (CT) band shifts to shorter wavelengths. Indistinguishable spectral changes occur in HClO_4 solutions.

A Br^- -sensitive electrode shows the spectral changes parallel an increase in the concentration of free Br^- . Extended heating (80 °C for 60 min) of $[\text{Rh}(\text{tren})\text{Br}_2]\text{Br}$ solutions releases $0.70 + 0.05 \text{ mol of Br}^-/\text{mol of initial } [\text{Rh}(\text{tren})\text{Br}_2]^+$ ion. Under the same conditions, $[\text{Rh}(\text{tren})\text{Br}_2]\text{ClO}_4$ releases $0.90 + 0.05 \text{ mol of Br}^-$ ion. Ion-exchange separation of such solutions leads to a small band of unreacted starting material followed by a more slowly eluting band with a broad plateau centered near 345 nm.

The blue shift in the LF and CT regions of the electronic spectra, the loss of Br^- to solution, and the generation of a more slowly eluting species on a cationic exchange column are all consistent with the simple aquation of the dibromo complex (reaction 1). Based on $[\text{Br}^-]$ in equilibrated solutions (22 °C,



both bromide and perchlorate salts), the equilibrium constant for reaction 1 is $4.5 (\pm 1.5) \times 10^{-3}$.

Kinetic studies of reaction 1 show that it is first order in $[\text{Rh}(\text{tren})\text{Br}_2]^+$ and essentially unaffected by changes in acidity ($0.1 \text{ M} > [\text{H}^+] > 0.001 \text{ M}$) at constant ionic strength. At 60 °C, activation parameters for reaction 1 were determined to be $\Delta H^* = 105 \text{ kJ}$, $\Delta S^* = 19 \text{ J K}^{-1}$, and $A = 1.8 \times 10^{14} \text{ s}^{-1}$.

Photochemical Reactivity. LF photolysis of an acidic aqueous solution of $[\text{Rh}(\text{tren})\text{Br}_2]^+$ at room temperature leads to the spectral changes shown in Figure 3. The initial peak at 382 nm decreases and is replaced by a peak centered at 360 nm; the edge of the CT peaks shifts toward shorter wavelengths, with the eventual appearance of a second LF peak at 290 nm. An isosbestic point occurs at 368 nm. Spectral changes induced upon CT radiation are indistinguishable from those in Figure 3.

Use of a Br^- -sensitive electrode shows that photolysis releases Br^- and that extended photolysis (150 min using broad-band UV cutoff filter) labilizes $0.85 (\pm 0.05)$ equiv of Br^- ion. When passed through cation-exchange columns, photolyzed solutions show an initial band of unreacted starting material and a more slowly eluting band with the spectrum shown for the photoproduct in Figure 3 (λ_{max} at 358 and 290 nm). No other products could be observed on the ion-exchange column.

The similarity of the analytical data for the thermal and photochemical reactions of $[\text{Rh}(\text{tren})\text{Br}_2]^+$ —blue shifts of the

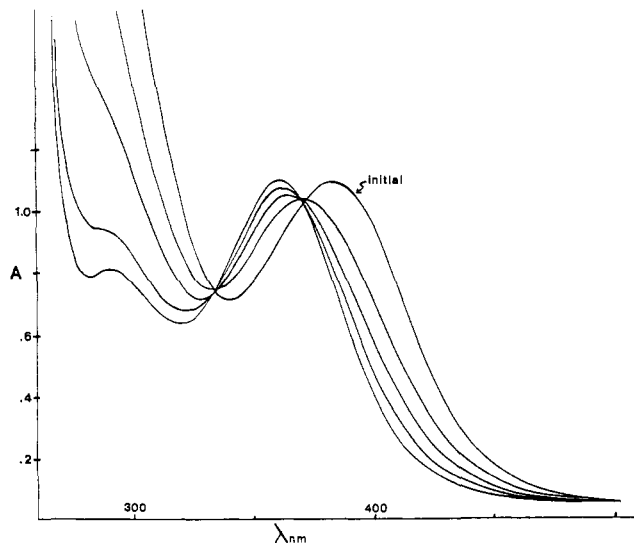


Figure 3. Spectral changes induced upon ligand-field photolysis of [Rh(tren)Br₂]⁺ (2.86 × 10⁻³ M, 20.8 °C, 0.1 M H₂SO₄). Spectra were recorded after 180, 360, 720, and 1350 s of photolysis. The final trace corresponds to the spectrum of the photoproduct [Rh(tren)Br(H₂O)]²⁺ ion.

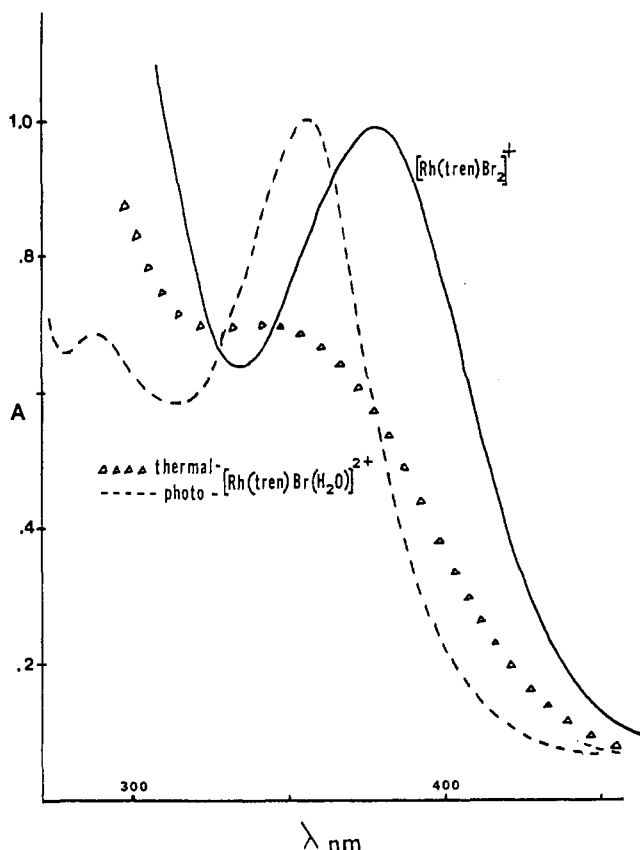


Figure 4. Comparison of the electronic spectra of [Rh(tren)Br₂]⁺ and the two [Rh(tren)(H₂O)Br]²⁺ isomers (2.5 × 10⁻³ M, 22 °C, 0.1 M H₂SO₄).

ligand-field and charge-transfer regions of the electronic spectra, release of slightly less than 1 equiv of Br⁻, and formation of a single, more slowly eluting (more highly charged) aquation product—implies that both processes follow the stoichiometry of reaction 1. The differences in the electronic spectra of the two [Rh(tren)(H₂O)Br]²⁺ ions (Figure 4) imply that the thermal and photochemical reactions lead to different geometric isomers of [Rh(tren)(H₂O)Br]²⁺ or to different mixtures of isomers. In analogy with the [Rh(tren)Cl₂]⁺ system,¹² the ion generated by heating an aqueous solution of [Rh(tren)Br₂]⁺ will be identified as the α isomer, while the photochemically prepared ion will be

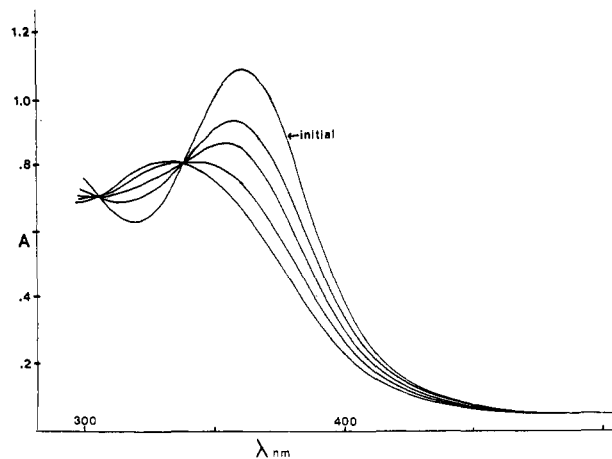
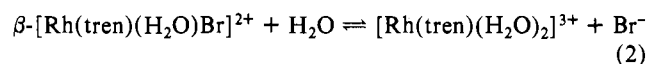


Figure 5. Spectral changes induced upon heating (49 °C) an acidic solution of the photoproduct, β-[Rh(tren)(H₂O)Br]²⁺, generated in the experiment shown in Figure 3 (2.86 × 10⁻³ M, 0.1 M H₂SO₄). Spectra were recorded 1200, 1800, 3600, and 7200 s after the initial spectrum. The 7200-s trace is the infinite time spectrum.

identified as the β form (vide infra).

Based on spectral changes at 390 and 350 nm (Figure 3), the quantum yield for Br⁻ release from [Rh(tren)Br₂]⁺ is 0.22 (±0.03). Photoinduced release and subsequent protonation of an arm of the tren amine could be monitored by pH changes; no photoinduced pH changes could be detected, however, and an upper limit for an amine labilization quantum yield was calculated to be 1 × 10⁻³. Photolyses were studied in 0.10 and 0.001 M H₂SO₄ solutions, and in the presence and in the absence of atmospheric O₂, with no measurable change in the photoinduced reaction.

Reactions of Photochemically Produced β-[Rh(tren)(H₂O)Br]²⁺.
Thermal Reactivity. Acidic aqueous solutions of β-[Rh(tren)(H₂O)Br]²⁺ are thermally reactive, undergoing the spectral changes shown in Figure 5. Isobestics are maintained, Br⁻ ion is released, and the product is tenaciously held to a cation-exchange column, suggesting it is more positively charged than the dicationic starting material. The electronic spectrum of the product is somewhat sensitive to the nature and concentration of anions in solution (presumably due to charge transfer from the anions to the 3+ complex) and is readily recognized as the spectrum of [Rh(tren)(H₂O)₂]³⁺ (reaction 2).



Kinetic studies of reaction 2 show that, as with reaction 1, it is first order in starting Rh complex and essentially unaffected by changes in [H⁺] in acidic solution. The kinetic parameters were determined (at 60 °C) to be ΔH^{*} = 109 kJ, ΔS^{*} = 18 J K⁻¹, and A = 1.6 × 10¹⁴ s⁻¹.

Photochemical Reactivity. Extended ligand-field photolysis of an acidic solution of β-[Rh(tren)(H₂O)Br]²⁺ does not significantly change the electronic spectrum of the starting material nor does it release Br⁻ to the solution; a maximum quantum yield for bromide release of 5 × 10⁻⁴ was determined.

Reactions of Thermally Produced α-[Rh(tren)(H₂O)Br]²⁺.
Thermal Reactivity. Thermally prepared α-[Rh(tren)(H₂O)Br]²⁺ is relatively robust toward further Br⁻ loss, but extended heating does cause spectral changes (Figure 6) consistent with the formation of [Rh(tren)(H₂O)₂]³⁺ (reaction 3). Ion-exchange separation of the heated solutions confirms that the diaquo ion is the primary reaction product.

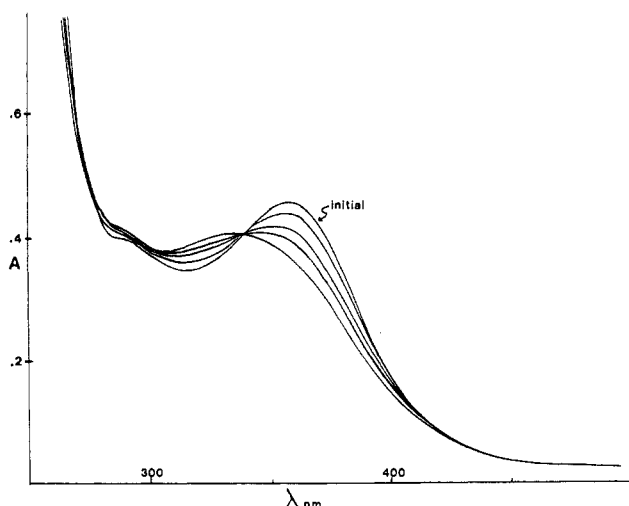
Aquation of the α isomer follows the same first-order rate law observed for the other ions; activation parameters (at 60 °C) are ΔH^{*} = 153 kJ, ΔS^{*} = 133 J K⁻¹, and A = 1.7 × 10²⁰ s⁻¹. Kinetic results for the aquations of these three ions are summarized in Table I.

Table I. Kinetic Data for the Aquation of $[\text{Rh}(\text{tren})(\text{X})\text{Br}]^{n+}$ ($\text{X} = \text{Br}, \text{H}_2\text{O}$) in HClO_4 Solutions (T in $^\circ\text{C}$, k in s^{-1})

(A) Effect of Temperature (in 0.10 M HClO_4)							
$[\text{Rh}(\text{tren})\text{Br}_2]^+$				$\beta\text{-}[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$		$\alpha\text{-}[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$	
T	$10^4 k$	T	$10^4 k$	T	$10^4 k$	T	$10^4 k$
42	2.44	58	21.3	50	1.44	55	.334
45	3.84	60	23.7	55	2.70	60.2	.656
48	5.92	61	26.7	60	4.65	65	1.93
51	8.43	65	40.5	68.5	12.7	68	2.97
55	14.6	67	52.6	70	16.9	71	4.70
						75.4	8.33

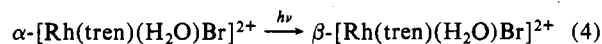
(B) pH Effects (μ Adjusted with NaClO_4)					
$[\text{Rh}(\text{tren})\text{Br}_2]^+$		$\beta\text{-}[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$		$\alpha\text{-}[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$	
$T = 51.5^\circ\text{C}; \mu = 0.10$		$T = 71.0^\circ\text{C}; \mu = 0.12$		$T = 66.7^\circ\text{C}; \mu = 0.12$	
$[\text{H}^+], \text{M}$	$10^4 k$	$[\text{H}^+], \text{M}$	$10^4 k$	$[\text{H}^+], \text{M}$	$10^4 k$
0.10	8.5	0.12	17.8	0.12	2.7
0.05	7.6	0.06	17.1	0.06	2.5
0.02	7.5	0.03	17.9	0.03	2.1

(C) Ionic Strength Effects $[(\text{Na}^+/\text{H}^+)\text{ClO}_4^-]$ Solutions; T as in Part B							
$[\text{Rh}(\text{tren})\text{Br}_2]^+$				$\beta\text{-}[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$		$\alpha\text{-}[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$	
$[\text{H}^+] = 0.02 \text{ M}$		$[\text{H}^+] = 0.05 \text{ M}$		$[\text{H}^+] = 0.03 \text{ M}$		$[\text{H}^+] = 0.06 \text{ M}$	
μ	$10^4 k$	μ	$10^4 k$	μ	$10^4 k$	μ	$10^4 k$
0.10	7.2	0.10	7.6	0.12	18.0	0.12	2.1
0.06	8.3	0.05	8.0	0.07	17.3	0.06	2.4
0.02	8.1			0.03	16.3	0.03	2.1

**Figure 6.** Spectral changes induced upon heating thermally prepared $\alpha\text{-}[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$ (reaction 3, 51°C , $1.3 \times 10^{-3} \text{ M}$). Spectra were recorded 600, 1500, 2400, and 4800 s after the initial spectrum. An infinite-time trace was not recorded in this experiment, but the last trace corresponds to a solution that is 85% ($\pm 5\%$) $[\text{Rh}(\text{tren})(\text{H}_2\text{O})_2]^{3+}$.

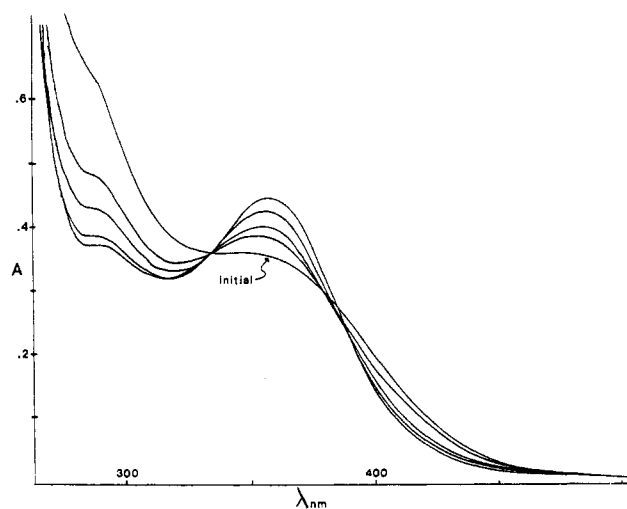
Photochemical Reactivity. LF irradiation of a room-temperature aqueous solution of $\alpha\text{-}[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$ (freshly separated by ion-exchange chromatography) causes the spectral changes (with isosbistics) observed in Figure 7. There is only a marginally detectable increase in $[\text{Br}^-]$; in three separate experiments involving extended photolyses, the maximum amount of released Br^- corresponded to 0.03 equiv. There is no detectable formation of the diaquo ion.

The spectral changes are diagnostic; irradiation of the α isomer causes isomerization to the β isomer (reaction 4). Based on



spectral changes at 356 nm, the isomerization quantum yield is 0.17 (± 0.02); no evidence for photoinduced amine labilization, and subsequent protonation, could be detected by pH changes. Reaction 4 is not significantly affected by the presence or absence of atmospheric O_2 .

Table II summarizes the spectral data, photochemical quantum yields, and kinetic activation parameters for these three ions.

**Figure 7.** Spectral changes induced upon photolysis of an acidic solution of $\alpha\text{-}[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$ ($1.04 \times 10^{-3} \text{ M}$, $0.1 \text{ M H}_2\text{SO}_4$). Spectra were recorded after 180, 360, 960, and 2460 s of photolysis.**Table II.** Spectral, Photochemical, and Kinetic Parameters

	$[\text{Rh}(\text{tren})\text{Br}_2]^+$	$\beta\text{-}[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$	$\alpha\text{-}[\text{Rh}(\text{tren})(\text{H}_2\text{O})\text{Br}]^{2+}$
Electronic Spectra (λ_{max} , nm (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$))			
	382 (400)	358 (390) 290 (280)	345 (290) 288 sh
Photochemistry			
ϕ_{Br}	0.22 ± 0.03	$< 5 \times 10^{-4}$...
ϕ_{isom}	0.17 ± 0.02
Aquation Kinetics			
k , s^{-1} (at 60°C)	2.4×10^{-3}	4.6×10^{-4}	6.6×10^{-5}
ΔH^\ddagger , kJ mol^{-1}	105 ± 2	109 ± 2.5	153 ± 5.5
ΔS^\ddagger , $\text{J mol}^{-1} \text{ K}^{-1}$	19 ± 0.5	18 ± 0.5	133 ± 5
A , s^{-1}	1.9×10^{14}	1.6×10^{14}	1.8×10^{20}

Additional Reactions. Anation of $[\text{Rh}(\text{tren})(\text{H}_2\text{O})_2]^{3+}$. When acidic aqueous solutions of $[\text{Rh}(\text{tren})(\text{H}_2\text{O})_2]^{3+}$ containing a 10-fold excess of Br^- are heated (50°C), spectral changes occur that are the reverse of those shown in Figure 5. Isosbistics are maintained throughout the reaction, which is the Br^- anation of

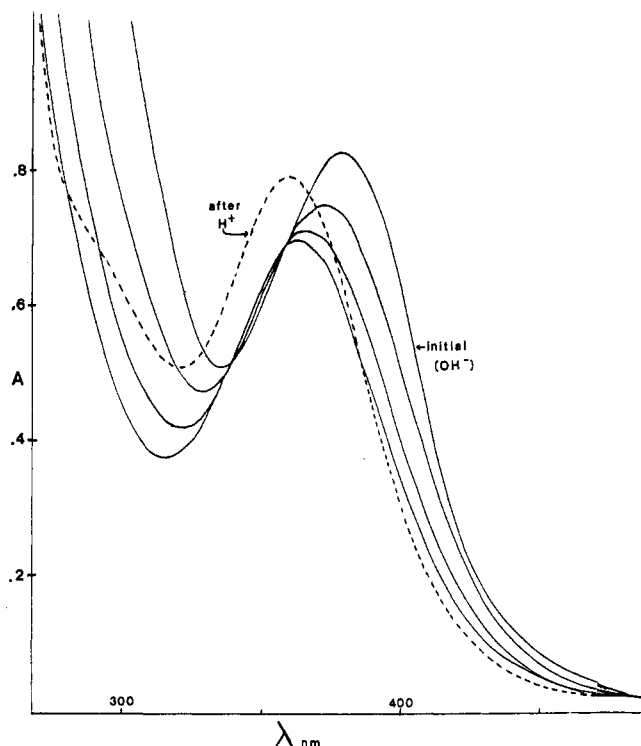


Figure 8. Spectral changes (solid curves) induced upon the base hydrolysis of [Rh(tren)Br₂]⁺ (1.95 × 10⁻³ M, 0.01 M OH⁻, 20 °C). Addition of 1 drop of concentrated H₂SO₄ to the final solution immediately generates a solution that gives the dashed-line spectrum.

[Rh(tren)(H₂O)₂]³⁺, generating β-[Rh(tren)(H₂O)Br]²⁺. This is the same species generated upon photolysis of [Rh(tren)Br₂]⁺, and the reaction is simply the reverse of reaction 2.

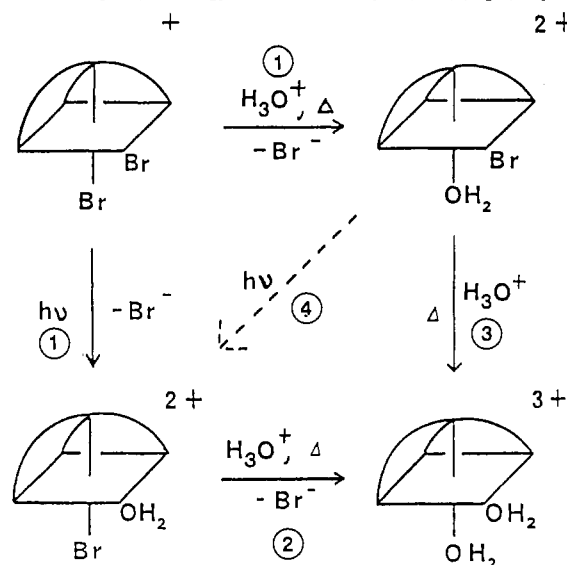
Base Hydrolysis of [Rh(tren)Br₂]⁺. When held at room temperature, basic solutions of [Rh(tren)Br₂]⁺ undergo the spectral changes shown in Figure 8. This reaction was not studied in detail but is assumed to involve hydroxide substitution of a bromide ligand. After formation of [Rh(tren)(OH)Br]⁺, indicated by an electronic spectrum that is unchanged over a 15-min period, addition of one drop of concentrated H₂SO₄ (to protonate the coordinated hydroxide) causes an immediate spectral change to the dashed-line spectrum shown in Figure 8. The resulting spectrum (λ_{max} 358 nm, ε 388 M⁻¹ cm⁻¹) is readily recognized as that of β-[Rh(tren)(H₂O)Br]²⁺.

Discussion

Isomer Assignment. Isomer assignment for the aquo bromo ions is based on the mechanistic and spectral arguments used for the chloro analogues.¹² Thermally induced, stereoretentive aquation at the hydrophilic site trans to the tertiary amine (site Y in Figure 1) would be expected to lead to the α isomer; photoinduced loss of the ligand in the hydrophobic site (X in Figure 1), accompanied by collapse of tren toward a TBP geometry, would eventually lead to the β isomer. Results for [Rh(tren)Br(X)]²⁺ (X = Br, H₂O) generally support this model, although the photochemistry of α-[Rh(tren)(H₂O)Br]²⁺ may not be consistent with a model in which the identity of the photolabilized ligand is determined by its geometric relationship to the tren in the ground-state complex. The reactions observed are summarized in Scheme I.

While the mechanistic arguments make chemical sense, a single-crystal X-ray structure would allow a more definitive (and satisfying) assignment. Unfortunately, we have not been able to obtain crystalline samples of either aquo bromo (or aquo chloro) isomer, although work on this problem is continuing. An X-ray structure could also shed light on the importance of steric blockage at either of the coordination sites. Qualitative work with space-filling molecular models does not indicate any steric problems for either of the non-amine sites for the chloro or bromo (or the aquo halo) complexes. Despite this limitation, further support for the proposed isomer assignment comes from the

Scheme I. Summary of the Thermally and Photochemically Induced Reactions of [Rh(tren)Br₂]⁺ and α- and β-[Rh(tren)(H₂O)Br]²⁺^a



^a The circled numbers refer to the reactions numbered under Results.

electronic spectra of the aquo bromo ions.

The intensity of symmetry-forbidden LF transitions is often used as a qualitative measure of the distortion from holohedral *O_h* symmetry. Of the two aquo bromo isomers, the β isomer has the water molecule coordinated in the hydrophobic site and should be the more distorted complex. As with the chloro analogues, the lowest energy ligand-field transition (an unresolved combination of (¹A', ¹A'', ¹A'') ← ¹A₁ in *C_s* site symmetry, descended from T₁ ← ¹A₁ in *O_h* symmetry) of the photoproduct aquo bromo ion is the more intense (Table II), consistent with the assignment of the photoproduct as the β isomer.

In addition, water coordinated at X (in the β isomer) would experience atypical hydrophobic repulsions from portions of the tren and could not be expected to induce as marked a d-orbital splitting as an H₂O coordinated in the hydrophilic site. It follows that the lowest energy ligand-field transition in the β isomer should also occur at an energy lower than that observed for the α isomer, consistent with proposed assignment.

The electronic spectra of a series of α and β isomers of [Co(tren)(NH₃X)]²⁺ (X = Cl⁻, H₂O, N₃⁻, NCS⁻, SCN⁻) show the trends predicted by these spectral arguments. For the isomer with the ammonia in the hydrophobic site cis to the tertiary amine (the t isomer in the Buckingham nomenclature^{2,9,22}), the lowest energy ligand-field band occurs with longer wavelength and greater intensity than those of the corresponding band in the other (the p) isomer.²

As with the chloro analogues,¹² the second ligand-field bands ((¹A', ¹A'', ¹A'') ← ¹A₁, descended from T₂ ← ¹A₁ in *O_h* symmetry) occur at about the same wavelength for the α and β isomers.

An important question concerns whether solutions of the α or β aquo bromo ions are isomerically pure or whether mixtures of isomers are generated. We attempted to chromatographically separate prepared mixtures of the α- and β-ion solutions but were only able to effect partial separations. Given this limitation, no evidence for the second isomer could be found when either the thermally or the photochemically generated aquo bromo ion solutions were passed down cation-exchange columns. Evidence of the β isomer in the thermally generated α aquo bromo solutions would have appeared during kinetic studies of the bromide aquation of the latter; as little as 5% of the more rapidly aquating β isomer would have appeared as a more steeply slanted portion in the initial portions of the log (A - A_{inf}) vs time graphs used in the kinetic analysis. No such deviation from linearity was ever observed. Base hydrolysis of [Rh(tren)Br₂]⁺, followed by acidification, leads to a solution with an electronic absorption spectrum that is indistinguishable from the spectrum of the ion generated upon photolysis of the dibromo complex. It is unlikely that these

two processes would generate the same mixture of α and β isomers, unless both processes are regioselective.

The presence of the more slowly aquating α ion in solutions of β -[Rh(tren)(H₂O)Br]²⁺ would not be detectable in the kinetic studies. The spectra of β -[Rh(tren)(H₂O)Br]²⁺ generated upon Br⁻ anation of [Rh(tren)(H₂O)₂]³⁺ are indistinguishable (peaks, valleys, and position of the isobestics) from the spectra observed upon photolysis of [Rh(tren)Br₂]⁺. Unless these two very different processes fortuitously generate the same isomeric mixture, it is reasonable to conclude that both of these reactions are regioselective, with the β isomer as the dominant product.

Thermal Reactivity. All three ions lose Br⁻ when heated in acidic aqueous solution; the observed rate constant and estimated equilibrium constant for reaction 1 is in the range observed for other monocationic dihalo amine complexes of Rh(III).²⁴ Comparison of absolute aquation rates would not be productive, as the effects of charge, and the resulting changes in ion pairing, on the rates of (associative) interchanges are not straightforward. In contrast to those of Co(III) analogues (where I_d processes dominate), the aquation rates of rhodium(III) halo amine complexes (or pseudohalo amines) are not sensitive to the overall charge on the complex.²⁵ Site X is trans to primary amine, while Y is trans to a tertiary amine; it is not known whether this difference would change the kinetic trans-labilizing effect²⁶ at those sites. It is clear that both aquo bromo ions are less reactive than the starting dibromo ion and that the coordination site of the labilized bromide affects the substitution rate.

Aquation of [Rh(tren)Br₂]⁺ and β -[Rh(tren)(H₂O)Br]²⁺ labilizes a bromide coordinated in the hydrophilic site (Y), while the bromide released upon aquation of α -[Rh(tren)(H₂O)Br]²⁺ sits in the hydrophobic site (X) cis to the tertiary amine. As discussed above, interchange with a solvent water should be more facile at the hydrophilic site, making the dibromo and β aquo bromo ions more susceptible to such ligand interchange. The activation parameters observed for aquation of the dibromo and β aquo bromo ions are similar to parameters found for aquations and anations of scores of amine,²⁷ ethylenediamine,^{24,26,28,29} and polydentate amine³⁰ complexes of Rh(III), suggesting that a ligand interchange is also the dominant reaction path for the dibromo and β aquo bromo tren complexes.

The atypical activation parameters for α -[Rh(tren)(H₂O)Br]²⁺ suggest a different aquation path for this ion. Given the propensity of complexes with such tripodal ligands for the five-coordinate TBP geometry, a dissociative process is an obvious possibility. Ligand dissociation from site X would allow simultaneous distortion of the tren ligand and collapse of the entire complex toward a TBP geometry; bromide occupies site X in α -[Rh(tren)(H₂O)Br]²⁺. Associative interchange of water would be inhibited at this relatively hydrophobic region, allowing the dissociative path to operate. The abnormally positive entropy of activation (Table II) for the aquation of α -[Rh(tren)(H₂O)Br]²⁺ supports this suggestion.

Dissociative processes are not thought common for rhodium(III) amines, but Robb, Harris, and co-workers³¹ have proposed dissociative substitutions for the [Rh(H₂O)_xCl_{6-x}]^{(x-3)+} series. For anations of aquo chloro complexes in which the labilized ligand is trans to a coordinated H₂O (with a trans-labilizing effect comparable to that for amines), the activation parameters—

especially the entropies of activation—are similar to those observed for the aquation of α -[Rh(tren)(H₂O)Br]²⁺.^{31a} The atypically large entropy of activation ($\Delta S^* = 95.6 \text{ J K}^{-1} \text{ mol}^{-1}$) for bromide anation of *trans*-[Rh(en)₂(H₂O)₂]³⁺ led Harris^{31c} to propose a dissociative process; in contrast, the ΔS^* values for chloride or bromide anation of *trans*-[Rh(en)₂(H₂O)L]²⁺ (L = Cl, Br, I) varied from -5.9 to +21.8 J K⁻¹ mol⁻¹.

While it may be futile to draw sharp distinctions between reaction mechanisms occurring in aqueous solution,³² these results do imply that aquation of α -[Rh(tren)(H₂O)Br]²⁺ involves a path different from that taken by the dibromo and β aquo bromo ions. Activation parameters for the latter two ions are analogous to parameters observed for substitutions at most Rh(III)-amine complexes, suggesting a normal interchange path. The geometry of the α isomer and the large ΔS^* for its aquation suggest a more dissociative aquation path. The kinetic results further support the notion that the tren ligand significantly alters the chemical reactivity of two adjacent coordination sites at the same metal center.

Photochemical Reactivity. Photoreaction of [Rh(tren)Br₂]⁺ to yield the thermally inaccessible aquo halo isomer rules out a hot-ground-state process and is analogous to the photochemistry of [Rh(tren)Cl₂]⁺.¹² The efficiency of bromide loss ($\phi_{\text{Br}} = 0.22 \pm 0.03$) is within the range observed for Br⁻ loss from similar Rh(III) complexes.³³ The photoinertness of β -[Rh(tren)(H₂O)Br]²⁺ also mimics its chloro analogue. As discussed previously,¹² this pattern of photosensitivity and photoinertness does not follow the patterns predicted by the various d⁶ photolysis models,³⁴ suggesting that the photochemical reaction path is being guided by the tren ligand.

Again, we suggest that the ligand-field excitation of [Rh(tren)XBr]ⁿ⁺ (X = H₂O, Br) results in an excited state that undergoes two concerted processes: (a) lengthening of the Rh-X bond and (b) collapse of the remaining five ligands toward a TBP geometry. Water attack along any edge of the resulting C_{3v} species would result in aquation at the site cis to the tertiary amine. This is consistent with the photosensitivity of [Rh(tren)Br₂]⁺ and the photoinertness of the β aquo bromo ion. (As with the chloro analogues, photolysis of β -[Rh(tren)(H₂O)Br]²⁺ would presumably induce exchange between coordinated and solvent H₂O molecules, but we have no evidence to support or refute this supposition.)

Support for the proposal that dissociative substitution of [Rh(tren)Br₂]⁺ leads to the β aquo bromo isomer comes from the base hydrolysis of [Rh(tren)Br₂]⁺. Base hydrolysis of rhodium(III) amines has been proposed^{25,35} to involve a dissociative rate-determining step, consistent with the formation of the β isomer. As shown in Figure 8, protonation of the bromo hydroxo base-hydrolysis product clearly leads to β -[Rh(tren)(H₂O)Br]²⁺.

This reaction model also implies that α -[Rh(tren)(H₂O)Br]²⁺ would undergo photoinduced halide loss to generate the diaquo ion; this is not observed. Only minor bromide loss occurs upon photolysis of α -[Rh(tren)(H₂O)Br]²⁺; the amount was variable and difficult to quantify, and it is assumed to be due to minor impurities of the dibromo ion. The photoinduced spectral changes (Figure 7) are clean and unequivocal; the product is the β aquo bromo isomer. Confirmation that this photoproduct is the same β -[Rh(tren)(H₂O)Br]²⁺ produced upon photolysis of [Rh(tren)Br₂]⁺ came from its subsequent reactivity. Heating solutions of β -[Rh(tren)(H₂O)Br]²⁺ produced upon photolysis of the α isomer also generates the diaquo ion (reaction 2) with spectral changes indistinguishable from those induced by heating the β aquo bromo ion generated upon photolysis of the dibromo complex.

Photoinduced isomerizations of Rh(III)-amine complexes are common,^{33,36-39} but the rigid constraints of tren force a cis ge-

(24) Bott, H. L.; Poe, A. J. *J. Chem. Soc. A* **1967**, 205.

(25) Johnson, S. A.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 1741.

(26) (a) Bounsall, E. J.; Poe, A. J. *J. Chem. Soc. A* **1966**, 286. (b) Poe, A. J.; Shaw, K. *Chem. Commun.* **1967**, 52.

(27) (a) van Eldik, R. *Inorg. Chim. Acta* **1980**, *42*, 49. (b) Poe, A. J.; Shaw, K.; Wendt, M. J. *Inorg. Chim. Acta* **1967**, *1*, 371. (c) Chan, S. C. *Aust. J. Chem.* **1967**, *20*, 61. (d) Bott, H. L.; Poe, A. J.; Shaw, K. *J. Chem. Soc. A* **1970**, 1745.

(28) Poe, A. J.; Shaw, K. *Chem. Commun.* **1970**, 393.

(29) Poe, A. J.; Vuik, C. P. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2250.

(30) Martins, E.; Kaplan, E. B.; Sheridan, P. S. *Inorg. Chem.* **1979**, *18*, 2195.

(31) (a) Palmer, D. A.; Harris, G. M. *Inorg. Chem.* **1975**, *14*, 1316. (b) Robb, W.; Steyn, M. M. de V. *Inorg. Chem.* **1967**, *6*, 616. (c) Swaminathan, K.; Harris, G. M. *J. Am. Chem. Soc.* **1966**, *88*, 4411. (d) Buchacek, R. J.; Harris, G. M. *Inorg. Chem.* **1976**, *15*, 926.

(32) van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 1520.

(33) (a) Petersen, J. D.; Jakse, F. P. *Inorg. Chem.* **1979**, *18*, 1818. (b) Clark, S. F.; Petersen, J. D. *Inorg. Chem.* **1979**, *18*, 3394.

(34) Vanquickenborne, L. G.; Ceulemans, A. J. *Am. Chem. Soc.* **1977**, *99*, 2208.

(35) Poe, A.; Vuik, C. *Can. J. Chem.* **1975**, *53*, 1842.

(36) (a) Skibsted, L. H.; Ford, P. C. *Inorg. Chem.* **1983**, *22*, 2749. (b) Skibsted, L. H.; Strauss, D.; Ford, P. C. *Inorg. Chem.* **1979**, *18*, 3171.

ometry. The observed $\alpha \rightarrow \beta$ photoisomerization seems to require that the two non-tren ligands (Br and H₂O) simply exchange positions (Scheme I). Intramolecular exchange seems unlikely, but the mechanism for this photoisomerization is not known.

Photolysis of α -[Rh(tren)(H₂O)Br]²⁺ may cause labilization of the coordinated water at site Y; photoinduced water exchanges at Rh(III) centers are known⁴² and have been shown to occur with isomerization.⁴⁰ Loss of H₂O would lead to a square-pyramid {[Rh(tren)Br]³⁺}* excited state, and rapid distortion of this species toward a C_{3v} geometry before attack of solvent water would lead to β -[Rh(tren)(H₂O)Br]²⁺.

Photolabilization of the ligand at site Y conflicts with the tren-directed-photochemistry model proposed earlier, but electronic factors may favor H₂O photolabilization over Br⁻ loss in these complexes. Photolysis of the *cis*-[Rh(N₄)(H₂O)Br]²⁺ ions efficiently generates *trans*-[Rh(N₄)(H₂O)Br]²⁺ for N₄ = (NH₃)₄ (ϕ = 0.50),^{36b,c} (en)₂ (ϕ = 0.95),^{33b} and bis(1,3-diaminopropane) (ϕ = 0.55).³⁷ These reactions presumably involve water exchange, so a photoinduced isomerization of α -[Rh(tren)(H₂O)Br]²⁺ to the β form could also involve a water-exchange step. It is interesting to note that while the *cis*-[Rh(N₄)(H₂O)Cl]²⁺ analogues (N₄ =

(NH₃)₄,^{36b,c} (en)₂,^{33b} bis(1,3-diaminopropane)³⁷) also photoisomerize (presumably via water exchange), photolysis of α -[Rh(tren)(H₂O)Cl]²⁺ causes chloride labilization.¹²

To maintain the tren-directed-photochemistry model, one is forced to propose a reaction path in which photoinduced Br⁻ labilization (generating [Rh(tren)(H₂O)₂]³⁺ and Br⁻) is followed by rapid Br⁻ anation of the nascent diaquo ion. Bromide anation of independently prepared [Rh(tren)(H₂O)₂]³⁺ does lead to β -[Rh(tren)(H₂O)Br]²⁺, but the reaction requires several hours at 50 °C; photoisomerization of α -[Rh(tren)(H₂O)Br]²⁺ proceeds quickly, with isobestics, at room temperature and below. Seeking spectroscopic evidence for a diaquo intermediate, we attempted to slow the anation by photolyzing α -[Rh(tren)(H₂O)Br]²⁺ solutions at 2 °C; apart from the expected narrowing of electronic transitions, the photoinduced spectral changes are indistinguishable from those observed at room temperature. Isobestics are maintained even at 2 °C. If this two-step mechanism is operating, photolabilized Br⁻ would have to remain tightly bonded to the newly formed {[Rh(tren)(H₂O)₂]³⁺}*, presumably as part of an ion pair. Such rapid recombination within a solvent cage have been invoked for radical-pair recombinations^{41,42} and for nonradical processes,^{40,43} but further work would be needed to determine if such a process is important here.

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- (37) Skibsted, L. H.; Hancock, M. P.; Madge, D.; Sexton, D. A. *Inorg. Chem.* **1984**, *23*, 3735.
 (38) Howland, K.; Skibsted, L. H. *Acta Chem. Scand., Ser. A* **1983**, *37*, 647.
 (39) Monsted, L. *Acta Chem. Scand., Ser. A* **1986**, *A40*, 590.
 (40) Ford, P. C.; Petersen, J. D. *Inorg. Chem.* **1975**, *14*, 1404.
 (41) Adamson, A. W.; Sporer, A. H. *J. Am. Chem. Soc.* **1958**, *80*, 3865.
 (42) Adamson, A. W. *Discuss. Faraday Soc.* **1960**, *29*, 163.
 (43) Endicott, J. F. In *Concepts in Inorganic Photochemistry*; Adamson, A. W., Fleishauer, P. D., Eds.; Wiley-Interscience: New York, 1975; pp 126-132.

- (43) (a) Bergkamp, M. A.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1980**, *102*, 2627. (b) Bergkamp, M. A.; Watts, R. J.; Ford, P. C. *J. Chem. Soc., Chem. Commun.* **1979**, 623.

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Thermal and Photochemical Reactions of d⁹ Metal Complexes: The Silver(II) Macrocyclus

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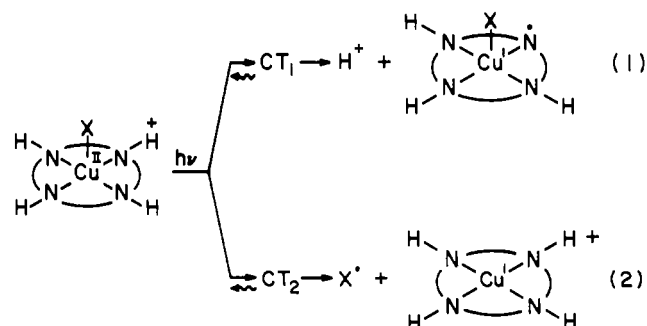
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Rate constants for electron-transfer reactions of d⁹ metal (Cu(II), Ni(I), and Ag(II)) macrocyclic complexes have been determined by pulse radiolysis. The self-exchange rate constants reveal slow exchanges for d^{9/10} couples (values between 10³ and 10⁻² M⁻¹ s⁻¹) and fast ones for d^{8/9} couples (values between 10⁴ and 10⁹ M⁻¹ s⁻¹). The photochemical oxidation of the macrocyclic ligand in Ag([14]aneN₄)²⁺ takes place with larger quantum yields than in the corresponding Cu(II) complex (10⁻¹ vs 10⁻³). No photooxidation of axially coordinated ligands has been detected with Ag(II) complexes. The thermal and photochemical reactivities are discussed in terms of the differences in the electronic levels and nuclear configurations between these d⁹ metal complexes.

Introduction

The thermal and photochemical redox reactivities of amino complexes of copper(II) have been studied in some detail.¹⁻³ The self-exchange electron transfer in Cu(II)/Cu(I) complexes is slow with most of the reported rate constants having values close to 10² M⁻¹ s⁻¹.^{4,5} The self-exchange in d⁸/d⁹ couples, e.g., Cu(III)/Cu(II), has been investigated with a rather limited number of compounds that have rate constants on the order of 10⁶-10⁴ M⁻¹ s⁻¹.^{1,3} From the standpoint of the photochemical reactivity, the Cu(II) complexes of the [14]aneN₄ macrocycle exhibit a meager photochemistry in the UV region (quantum yields below 10⁻² for $\lambda_{\text{exc}} > 230$ nm), which can be described in terms of two primary processes,⁶ i.e. the photooxidations of the macrocycle (eq

1) and the axial ligand (eq 2). Not much is known about the



redox chemistry of complexes with other d⁹ metal ions, in particular Ag(II) and Ni(I), because most of these compounds are regarded as too unstable for these studies.^{7,8} We report here the

- (1) Ferraudi, G.; Muralidharan, S. *Coord. Chem. Rev.* **1981**, *36*, 45.
 (2) Ferraudi, G. *Isr. J. Chem.* **1985**, *25*, 122.
 (3) Endicott, J. F.; Kumar, K.; Ramasami, T.; Rotzinger, F. P. *Prog. Inorg. Chem.* **1983**, *30*, 141.
 (4) Hoselton, M. A.; Lin, C. T.; Schwartz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 2383.
 (5) Agustin, M. A.; Yandall, J. A. *Inorg. Chem.* **1979**, *18*, 577.

- (6) Muralidharan, S.; Ferraudi, G. *Inorg. Chem.* **1981**, *20*, 2306.
 (7) Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1969**, *8*, 1611.