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Contribution from the Department of Chemistry,
Kansas State University, Manhattan, Kansas 66506

Stereochemistry and Quantum Yields for the Ligand Field Photolysis of Rhodium(III) Complexes. 2.[1] *cis*- and *trans*-$Rh(en)_2XBr^{n+}$

STEPHEN F. CLARK and JOHN D. PETERSEN*

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Ligand field excitations of *cis*- and *trans*-$Rh(en)_2XBr^{n+}$ complexes (X = Br, H_2O, NH_3), in all cases but one, lead exclusively to the formation of *trans*-$Rh(en)_2(H_2O)Br^{2+}$ as the photoproduct. The exception is the *cis*-$Rh(en)_2(NH_3)Br^{2+}$ complex, where irradiation leads to the formation of both *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ and *trans*-$Rh(en)_2(H_2O)Br^{2+}$. The stereochemistry of all of the photochemical products has been examined in relation to the Vanquickenborne–Ceulemans mechanism, where thermal equilibrium takes place between triplet, five-coordinate, square-based-pyramid isomers generated by loss of a ligand from the six-coordinate ligand field excited state. Experimentally, the rearrangement of the $[Rh(en)_2Y]^*$ fragments depends on the nature of Y. For Y = Br, an energetic preference for Y in the apical position leads solely to trans products. For Y = NH_3, the absence of rearrangement is interpreted as a barrier for isomerization which is too large to compete with nonradiative deactivation of the triplet, five-coordinate fragment. The three separate reaction channels observed for the photolysis of the spectroscopically similar *trans*- and *cis*-$Rh(en)_2(NH_3)Br^{2+}$ complex ions (loss of NH_3 trans to Br^- for the former and loss of Br^- or the NH_3 cis to Br^- for the latter) have been interpreted as a strong preference for the Rh(III) metal center not to break a Rh(III)–en bond in a ligand field excited state.

Introduction

Ligand field photolysis of rhodium(III) amine complexes in aqueous solution customarily leads to the photoaquation of one ligand from the complex,[2] resulting in a monoaquo complex as the photolysis product. Subsequent ligand photosubstitution reactions are not observed spectroscopically since further reactions are usually limited to aquo ligand exchange.[3]

The thermal substitution reactions[4] of cis and trans tetraamine complexes in aqueous solution are stereoretentive, as are the photosubstitution reactions of the trans tetraamine complexes (eq 1). However, the photoaquation of cis tetraamine–Rh(III) complexes does lead, in some instances, to trans-substituted products (eq 2).

$$trans\text{-}RhA_4XY^{n+} \xrightarrow[H_2O]{h\nu,\ LF} trans\text{-}RhA_4(H_2O)X^{(n-1)+} + Y^- \tag{1}$$

X = Y = Cl; $A_4 = (NH_3)_4$,[5,6] $(en)_2$,[1,5,6] (cyclam)[5]

X = Y = Br; $A_4 = (NH_3)_4$,[7] $(en)_2$[6]

X = Y = I; $A_4 = (NH_3)_4$,[8] $(en)_2$[6]

X = NH_3; Y = Cl; $A_4 = (NH_3)_4$,[6,8] $(en)_2$[1]

The geometric difference

$$cis\text{-}RhA_4XY^{n+} \xrightarrow[H_2O]{h\nu,\ LF} trans\text{-}RhA_4(H_2O)X^{m+} + Y^{(m-n)-} \tag{2}$$

X = Y = Cl; $A_4 = (NH_3)_4$,[9] $(en)_2$[1,6]

X = Cl; Y = H_2O; $A_4 = (NH_3)_4$,[9] $(en)_2$[10]

$A_4 = (NH_3)_4$; (X = Y = H_2O),[9] (X = Y = Br),[7] (X = Br, Y = H_2O)[7]

in products obtained from the thermal and photochemical aquation reactions of the cis tetraamine complexes suggests that the photoaquation process occurs from an electronic excited state, rather than a highly excited vibrational level in the ground electronic state. In fact, Ford and co-workers[11] have proven conclusively that aquation does occur from the ligand field excited state in halopentaamminerhodium(III) complexes.

Vanquickenborne and Ceulemans[12] have used an "additive point ligand model" to explain the stereochemical changes

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Table I. Electronic Spectra of *cis*- and *trans*-$[Rh(en)_2XBr]^{n+}$

compd	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	ref
trans-$[Rh(en)_2Br_2]ClO_4$[a]	429 (425)	120 (120)	*b* (15)
	276 (276)	3000 (3000)	
trans-$[Rh(en)_2(H_2O)Br](ClO_4)_2$	470	32	16
	405	55	
	280	520	
	235	5260	
trans-$[Rh(en)_2(NH_3)Br](NO_3)_2$	357	116	*b*
cis-$[Rh(en)_2Br_2]ClO_4$[a]	367 (362)	258 (210)	*b* (14)
	(276 sh)	(900)	
cis-$[Rh(en)_2(H_2O)Br](ClO_4)_2$	358	133	*b*
cis-$[Rh(en)_2(NH_3)Br](NO_3)_2$	357	175	*b*

[a] Two sets of values are given. The values from this work appear first, with previous values and their reference in parentheses. [b] This work.

Table II. Proton-Decoupled ^{13}C Chemical Shifts of *cis*- and *trans*-$[Rh(en)_2XBr]^{n+}$ and Related Compounds

compd	$\delta(^{13}C)$[a]
trans-$Rh(en)_2Br_2^+$	46.01 (45.2)[b]
trans-$Rh(en)_2(H_2O)Br^{2+}$	45.86
trans-$Rh(en)_2(NH_3)Br^{2+}$	45.78
trans-$Rh(en)_2(NH_3)(H_2O)^{3+}$	45.69[c]
trans-$Rh(en)_2(H_2O)_2^{3+}$	45.68
cis-$Rh(en)_2Br_2^+$	46.96, 46.84 (46.0)[b,d]
cis-$Rh(en)_2(H_2O)Br^{2+}$	48.14, 46.81, 45.65, 45.40
cis-$Rh(en)_2(NH_3)Br^{2+}$	46.76, 46.58, 46.46, 46.26
cis-$Rh(en)_2(NH_3)(H_2O)^{3+}$	47.68, 46.39, 45.99, 45.03[c]

[a] Chemical shifts reported vs. TMS with dioxane (67.40 ppm) as an internal reference. [b] Values reported in ref 17 with dioxane assumed to lie at 66.5 ppm vs. TMS. [c] Reference 10. [d] The two peaks were not resolved in ref 17.

during photosubstitution around d^6 metal centers, and their conclusion is that rearrangement can occur for the five-coordinate fragment which results from ligand dissociation in the lowest, ligand-field, excited state of the complex. They suggest that the stereochemistry of the product is dictated, in the cases of $[ML_4X]^q$ (L = amine, CN^-; X = acido ligand), by a thermodynamic preference for X axial in the square-pyramidal structure of the intermediate.

In this work, we report the results of the ligand field photochemistry of *cis*- and *trans*-$Rh(en)_2XBr^{n+}$ complexes. Besides using the ligand field analysis of Vanquickenborne and Ceulemans[12] to discuss the stereochemistry of the photolysis products, we will also use the complexes where X = NH_3 as models for the corresponding pentaammine $Rh(NH_3)_5Br^{2+}$. A recent article by Kirk and co-workers[13] indicates that ethylenediamine is spectroscopically similar to, but does not possess the same photochemical reactivity as, the ammine ligand in Cr(III) complexes. However, the *cis*- and *trans*-$Rh(en)_2(NH_3)Br^{2+}$ complexes do provide a spectroscopic handle for determining which ammine ligand is lost in the predominant photoaquation reaction[8] of $Rh(NH_3)_5Br^{2+}$ (eq 3). The

$$Rh(NH_3)_5Br^{2+} \xrightarrow[\text{predominant reaction}]{h\nu,\ \text{LF}} trans\text{-}Rh(NH_3)_4(H_2O)Br^{2+} + NH_3 \quad (3)$$

ligand field treatment of Vanquickenborne and Ceulemans[12] suggests that trans products would be observed, in eq 3, regardless of whether cis or trans ammine is lost photochemically. In addition, the minor product observed in the photolysis of $Rh(NH_3)_5Br^{2+}$ is $Rh(NH_3)_5H_2O^{3+}$.[8,11] The analogous reaction for the $Rh(en)_2(NH_3)Br^{2+}$ complexes would form the $[Rh(en)_2(NH_3)^{3+}]^*$ intermediate, which has been shown to result in product stereoretention for the photolysis of *cis*- and *trans*-$Rh(en)_2(NH_3)Cl^{2+}$.[1]

Experimental Section

Synthesis of Metal Complexes. The electronic absorption spectral data and the ^{13}C NMR spectral data for all complexes reported here are listed in Tables I and II, respectively. Elemental analyses were performed by Industrial Testing Laboratories.

trans-**$[Rh(en)_2Br_2]ClO_4$.** This compound was prepared by modification of the procedures of Johnson and Basolo[14] and Bott and Poë.[15] A 380-mg sample of *trans*-$[Rh(en)_2Cl_2]NO_3$ and a 10-fold excess of NaBr (~2.2 g) were dissolved in 30 mL of water containing 1 drop of HBr. The solution was heated at reflux for 4 h followed by the addition of 10 mL of HNO_3. After the solution cooled to room temperature, the nitrate salt of the desired compound was collected. The nitrate salt was placed in a coarse, sintered-glass filter, dissolved in a minimum amount of hot water, and filtered into methanol which had been saturated with $NaClO_4$. After the mixture was cooled overnight at 5 °C, the product was collected, washed with ethanol and then ether, and dried under vacuum: yield 398 mg (77%).

cis-**$[Rh(en)_2Br_2]ClO_4$.** The procedure of Gillard et al.[18] for the preparation of the *cis*-dihalo complexes was used. A 0.2-g sample of $[Rh(en)_2(oxalato)]ClO_4 \cdot 0.5H_2O$ was dissolved in a solution containing 40 mL of water and 10 mL of HBr. After the mixture was heated at reflux for 4 min and cooled overnight, the bromide salt of the product was collected. The bromide salt was converted into the perchlorate salt by the procedure described above for the *trans*-dibromo complex: yield 123 mg (54%).

trans-[16] and *cis*-**$[Rh(en)_2(H_2O)Br](ClO_4)_2$.** The aquobromo complexes were prepared directly from the corresponding dibromo complexes. A 193-mg (0.40 mmol) sample of the corresponding $[Rh(en)_2Br_2]ClO_4$ salt was dissolved in 4 mL of 0.1 M $AgClO_4$ (0.40 mmol), and the solution was heated at reflux for 15 min. The AgBr was removed by filtration, and the remaining solution was cooled and evaporated to near-dryness under vacuum. The resulting precipitate was collected, washed with ethanol and then ether, and dried under vacuum: yield for trans isomer 98 mg (47%), yield for cis isomer 114 mg (55%).

trans-**$[Rh(en)_2(NH_3)Br](NO_3)_2$.** The procedure of Johnson and Basolo[14] for preparing *trans*-$[Rh(en)_2(NH_3)Cl](NO_3)_2$ was modified for use in this synthesis. A 470-mg sample of *trans*-$[Rh(en)_2Br_2]NO_3$ was dissolved in 22 mL of NH_4OH and heated at reflux for 10 min. The volume of the solution was reduced by evaporation to ~8 mL, and N_2 was bubbled through the solution until no more ammonia odor could be detected (~10 min). After the remaining solution was evaporated to dryness, the solid was redissolved in 4 mL of H_2O, the mixture was filtered into 4 mL of cold HNO_3, and the resulting solution was added to 10 mL of 95% ethanol. After the volume was again reduced to 10 mL and 5 mL of HNO_3 was added, 95% ethanol was added until precipitation started, and then an additional 20 mL of ethanol was added to complete the precipitation. The suspension was cooled overnight at 5 °C, and the product was collected, washed with ethanol and then ether, and dried under vacuum: yield 335 mg (72%). Anal. Calcd for $C_4H_{19}BrN_7O_6Rh$: C, 10.8; H, 4.3; N, 22.1. Found: C, 10.9; H, 4.4; N, 22.6.

cis-**$[Rh(en)_2(NH_3)Br](NO_3)_2$.** A 500-mg sample of *cis*-$[Rh(en)_2Br_2]ClO_4$ was dissolved in 23 mL of NH_4OH and the solution was heated at reflux for 20 min. An additional 6 mL of NH_4OH was added and heating at reflux was continued until the solution changed from orange to a light yellow-green. The volume was reduced to 7 mL and N_2 was bubbled through the solution for 10 min to remove free NH_3. (If after the volume is reduced, the solution color begins to change back to the color of the starting material, 5 mL of NH_4OH can be added, followed by a short period of heating and reconcentration by evaporation.) The solution was evaporated to dryness and the resulting solid dissolved in 4 mL of H_2O and added to 6 mL of cold HNO_3. The solution was placed in an ice bath, and 95% ethanol was added until a precipitate started to form. Complete precipitation was achieved by adding an additional 25 mL of ethanol. After overnight cooling, the product was collected, washed with ethanol and then ether, and dried under vacuum: yield 359 mg (80%). Anal. Calcd for $C_4H_{19}BrN_7O_6Rh$: C, 10.8; H, 4.3; N, 22.1. Found: C, 10.9; H, 4.3; N, 22.2.

Apparatus. Quantum yields were determined with a continuous-beam photolysis apparatus described elsewhere.[19] Usable intensities at irradiation wavelengths of 405 and 365 nm were determined by ferrioxalate actinometry[20] and approximated 1.6 × 10^{16} and 1.0 × 10^{18} quanta/min, respectively.

Table III. Quantum Yields for the Photoaquation for *cis*- and *trans*-$[Rh(en)_2XBr]^{n+}$[a]

complex	λ_{irr}, nm	product	Φ_{Br}[b]	Φ_X[c]	Φ_{isom}[d]
trans-$Rh(en)_2Br_2^+$	405	*trans*-$Rh(en)_2(H_2O)Br^{2+}$	0.062 ± 0.005 (3)		*e*
f	254	*trans*-$Rh(en)_2(H_2O)Br^{2+}$	0.054 ± 0.005		*e*
trans-$Rh(en)_2(H_2O)Br^{2+}$	405	*g*	$<10^{-3}$	*h*	*e*
trans-$Rh(en)_2(NH_3)Br^{2+}$	365	*trans*-$Rh(en)_2(H_2O)Br^{2+}$	$<10^{-3}$	0.16 ± 0.01 (3)	*e*
cis-$Rh(en)_2Br_2^+$	365	*trans*-$Rh(en)_2(H_2O)Br^{2+}$	0.37 ± 0.03 (3)		0.37
cis-$Rh(en)_2(H_2O)Br^{2+}$	365	*trans*-$Rh(en)_2(H_2O)Br^{2+}$	$<10^{-2}$	0.95 ± 0.05 (2)[i]	0.95
cis-$Rh(en)_2(NH_3)Br^{2+}$	365	*cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ and *trans*-$Rh(en)_2(H_2O)Br^{2+}$	~0.054[j]	~0.006[j]	~0.006[j]

[a] Measured in aqueous perchlorate media ($2 \leqslant pH < 5$) at 25 °C. [b] Quantum yield for loss of Br^- (mol/einstein) with average deviation and number of determinations in parentheses. [c] Quantum yield for loss of X (mol/einstein) with average deviation and number of determinations in parentheses (except for X = Br). [d] Quantum yield for geometric isomerization (mol/einstein). [e] None detectable. [f] Reference 6. [g] No photochemical reaction observable. [h] Not determined; aquo ligand exchange with solvent water would not be detected under these conditions. [i] Assuming photoisomerization to trans product proceeds by dissociation of aquo ligand (see text). [j] Quantum yield for decomposition of *cis*-$Rh(en)_2(NH_3)Br^{2+}$ is 0.061 ± 0.005 (4) by absorption spectroscopy; Φ_{Br}, Φ_{NH_3}, and Φ_{isom} were determined by the ratio of products as determined by ^{13}C NMR spectroscopy and ion-exchange chromatography.

All absorption spectra and optical density measurements used to determine quantum yields were recorded on a Cary-14 spectrophotometer. The ^{13}C NMR spectra, which were used to check the purity of the reactants and confirm the geometric configuration of the photochemical products, were recorded on a Varian XL-100-15 NMR spectrometer operating at a frequency of 25.2 MHz and equipped with a Nicolet FT-100 data system. NMR procedures and data treatment have been described previously.[21,22] A Corning Model 5 pH meter, calibrated against commercially available buffer solutions, was used to adjust the pH of the photolysis solutions.

Photolysis Procedures. All photolyses were carried out at 25 °C in acidic solutions (pH 2–5, $HClO_4$) in 2-cm, quartz, cylindrical cells. Quantum yields were calculated from changes in the electronic spectra as a function of irradiation time. Photolysis products were identified by ^{13}C NMR and electronic absorption spectroscopy from samples photolyzed to ~100%; however, the product extinction coefficient values used for quantum yield calculations were obtained (except for photolysis of *cis*-$Rh(en)_2(NH_3)Br^{2+}$) from independent syntheses. *cis*-$Rh(en)_2(NH_3)Br^{2+}$ was the only system in this study which gave more than one photolysis product. A disappearance quantum yield for *cis*-$Rh(en)_2(NH_3)Br^{2+}$ was obtained from electronic absorption spectral data by using the spectrum of the starting compound and the spectrum of a sample photolyzed until no further spectral changes occurred. The ratio of the two photolysis products, *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ and *trans*-$Rh(en)_2(H_2O)Br^{2+}$, was approximated from a ^{13}C NMR spectrum and ion-exchange chromatography of a sample photolyzed to ~100% reaction.

Ion-Exchange Separation. An extensively photolyzed sample of *cis*-$Rh(en)_2(NH_3)Br^{2+}$ was separated into component parts by ion-exchange chromatography. The column, 10 cm of Dowex 50W X-4, 200–400 mesh (originally H^+ form), was prepared by extensive washings with 1 M $NaClO_4$. The photolysis sample was reduced in volume from 6 to 1 mL by rotoevaporation to aid effective separation. After the photolysis solution was placed onto the column, elutions with increasing concentrations of $NaClO_4$ were carried out. Each fraction (~10 mL of eluant) was monitored by electronic spectroscopy. At 5 M $NaClO_4$, all compounds had been separated and removed from the column.

Results

The quantum yields for the photolysis of *cis*- and *trans*-$Rh(en)_2XBr^{n+}$ complexes in acidic aqueous solution appear in Table III. The quantum yields are calculated on the basis of electronic absorption spectral changes, while the exact nature of the products are deduced from the ^{13}C NMR spectrum of extensively photolyzed samples. Only one of the complexes irradiated in this study, *cis*-$Rh(en)_2(NH_3)Br^{2+}$, gave more than one photolysis product, and the product composition was determined by ion-exchange chromatography techniques. Irradiation wavelengths of 365 and 405 nm correspond to population of the lowest, spin-allowed, ligand field excited state derived from the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition in octahedral geometry. Photolysis of all complexes in this work leads to the net photosubstitution at one coordination site by solvent water and formation of a monoaquo product. There is no evidence for secondary photochemical reactions other than aquo ligand exchange, since isosbestic points are maintained throughout entire photolysis reactions.

trans-**$Rh(en)_2XBr^{n+}$.** For the trans complexes, where X is Br, NH_3, or H_2O, photoaquation of X occurs as the only detectable photochemical reaction. For X = Br, irradiation at 405 nm leads to loss of Br^- to form *trans*-$Rh(en)_2(H_2O)Br^{2+}$ with a quantum yield of 0.062 mol/einstein. Subsequent irradiation of the *trans*-bromoaquo photolysis product, or photolysis of a pure sample of *trans*-$Rh(en)_2(H_2O)Br^{2+}$, leads to no spectral or pH changes. This limits any photochemical reaction of the *trans*-bromoaquo complex to aquo ligand exchange, which would be nonobservable under the reaction conditions. For X = NH_3, irradiation at 365 nm leads to loss of NH_3 with a quantum yield of 0.16 mol/einstein as the only detectable photolysis product. The ^{13}C NMR spectrum of an extensively photolyzed sample of the *trans*-bromoammine complex is identical with that of an authentic sample of the *trans*-bromoaquo complex, with the signal-to-noise ratio indicating >95% isomeric purity.

cis-**$Rh(en)_2Br_2^+$.** The 365-nm irradiation of the *cis*-dibromo complex leads to formation of *trans*-$Rh(en)_2(H_2O)Br^{2+}$ with a quantum yield of 0.37 mol/einstein. The stereochemistry of the product was confirmed by ^{13}C NMR spectroscopy at >95% isomeric purity. The change in the electronic spectrum during photolysis was monotonic, indicating that the loss of Br^- and the cis/trans isomerization processes were concomitant.

cis-**$Rh(en)_2(H_2O)Br^{2+}$.** The 365-nm irradiation of the *cis*-bromoaquo complex leads to formation of the *trans*-bromoaquo complex with a quantum yield approaching unity (0.95 mol/einstein). There is no detectable change in solution pH or any free Br^- in solution as the photolysis progresses, and the ^{13}C NMR spectrum of the product indicates >97% isomeric purity for the trans product.

cis-**$Rh(en)_2(NH_3)Br^{2+}$.** Irradiation of the *cis*-bromoammine complex at 365 nm leads to the formation of two products, *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ and *trans*-$Rh(en)_2(H_2O)Br^{2+}$ (eq 4). The quantum yield for the disappearance of starting

$$\textit{cis}\text{-}Rh(en)_2(NH_3)Br^{2+} \xrightarrow[-Br,\ +H_2O]{h\nu\ (365\ nm)} \textit{cis}\text{-}Rh(en)_2(NH_3)(H_2O)^{3+} \quad (4a)$$

$$\xrightarrow[-NH_3,\ +H_2O]{h\nu\ (365\ nm)} \textit{trans}\text{-}Rh(en)_2(H_2O)Br^{2+} \quad (4b)$$

material is ~0.06 mol/einstein. The ^{13}C NMR spectrum of an extensively irradiated sample gave five peaks, four of which were attributable to *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ and a fifth which had a chemical shift typical of *trans*-$Rh(en)_2XY^{n+}$ complexes (Table II) and was suspected to be derived from *trans*-$Rh(en)_2(H_2O)Br^{2+}$. The exact identity of the trans compound was confirmed by electronic spectroscopy and ion-exchange chromatography.

The ion-exchange column separated the extensively photolyzed sample of *cis*-$Rh(en)_2(NH_3)Br^{2+}$ into four components. First off the column (2 M $NaClO_4$) was a small amount of *trans*-$Rh(en)_2Br_2^+$. This compound is not detected in the final photolysis spectrum and presumably arises during the sample concentration process from bromide anation (Br^- comes from the major photochemical reaction, eq 4a) of *trans*-$Rh(en)_2(H_2O)Br^{2+}$. The second compound (3 M $NaClO_4$) was *trans*-$Rh(en)_2(H_2O)Br^{2+}$. Shortly following the *trans*-bromoaquo complex, a small amount of *cis*-$Rh(en)_2(NH_3)Br^{2+}$, which could have been the unreacted starting material or arisen from anation of *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$, was eluted. The last compound off the column (5 M $NaClO_4$) was the major photolysis product, *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$. The relative amounts of *cis*-aquoammine complex vs. the combined *trans*-bromoaquo and *trans*-dibromo compounds (determined by comparison to the spectra of authentic samples) were used to calculate the relative quantum yields for loss of Br^- vs. NH_3, respectively. The ratio 90% Br^- loss/10% NH_3 loss was consistent with both ^{13}C NMR product analysis and the final absorption spectrum of extensively photolyzed *cis*-$Rh(en)_2(NH_3)Br^{2+}$. The values for Φ_{Br} and Φ_X (Φ_{NH_3}) for *cis*-$Rh(en)_2(NH_3)Br^{2+}$ in Table III correspond to 90 and 10%, respectively, of the overall disappearance quantum yield (~0.06 mol/einstein), as determined by electronic spectroscopy.

Discussion

The ligand field photochemistry of *cis*- and *trans*-$Rh(en)_2XBr^{2+}$ complexes (X = Br, H_2O, NH_3) proceed in aqueous solution to the monoaquo products from either loss of X or Br^-. The salient features that will be discussed from this work are the stereochemical control of the product geometry, the effects on the reactivity of using ethylenediamine as a ligand in place of ammine, and the implications of the magnitude of the substitutional quantum yields for the various compounds studied in this work.

The product geometries obtained from the photochemistry of the complexes in this work are consistent with a single theoretical model[12,23] which describes the photostereochemistry. This model is illustrated in Figure 1 for the photochemical loss of X from *cis*- and *trans*-$Rh(en)_2XBr^{n+}$. (The only complex in this study for which a reaction is observed that is not wholly represented in Figure 1 is *cis*-$Rh(en)_2(NH_3)Br^{2+}$. This complex shows two reaction channels, loss of NH_3 (X) to form $[Rh(en)_2Br^{2+}]^*$ which is described by Figure 1 and loss of Br^- to form $[Rh(en)_2(NH_3)^{3+}]^*$ which results in stereoretention in the product.) The calculations performed by Vanquickenborne and Ceulemans[12] to explain the stereochemistry of the photoaquation of *cis*- and *trans*-$Rh(NH_3)_4Cl_2^+$ [9] (both give *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ product) suggest that the stereomobility is occurring from a triplet, five-coordinate fragment $[Rh(NH_3)_4Cl^{2+}]^*$ which shows a strong thermodynamic preference for Cl to appear in the axial position of a square-based pyramid. They also derive a general zero-order relation (for heteroligands other than Cl^-) which suggests that the heteroligand must be a weaker σ donor than the amine for the trans structure to be preferred. This calculated axial preference for the ligand with the smaller e_σ value exists for the lowest energy, triplet, ligand field state ($^3SP_{ax}{}^*$ and $^3SP_{eq}{}^*$ in Figure 1) while very little or no calculated site preference exists when the electronic configuration is $(d_{xy})^2(d_{xz})^2(d_{yz})^2$ ($^1SP_{ax}$ and $^1SP_{eq}$ in Figure 1).

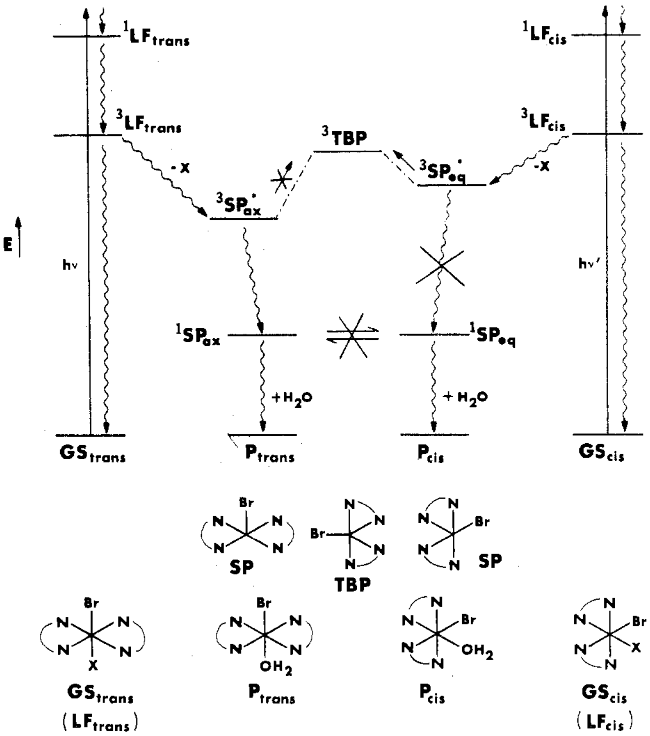


Figure 1. Photostereochemistry for loss of X from *cis*- and *trans*-$Rh(en)_2XBr^{n+}$. The terms GS, ^1LF, ^3LF, and P refer to six-coordinate complexes which represent the ground electronic state of the starting material, the lowest energy singlet and triplet ligand field excited states, and the photolysis product, respectively. The terms $^3SP_{ax}{}^*$, $^3SP_{eq}{}^*$, and ^3TBP correspond to the lowest energy, triplet, five-coordinate fragments with electronic configurations $(t_{2g})^5(e_g)^1$ in octahedral notation. The terms $^1SP_{ax}$ and $^1SP_{eq}$ are five-coordinate fragments with $(t_{2g})^6$ electronic configurations in octahedral notation. Idealized geometries for the species appear on the figure.

From Vanquickenborne and Ceulemans'[12] calculations for the $Rh(NH_3)_4Cl_2^+$ system, the lowest energy triplet fragment is analogous to $^3SP_{ax}{}^*$ in Figure 1, which is separated from another minimum at $^3SP_{eq}{}^*$ by a barrier of ~0.28 μm^{-1} at ^3TBP. The barrier in going from $^3SP_{eq}{}^*$ to ^3TBP is only ~0.11 μm^{-1}. This interpretation[12] of the chlorotetraammine rearrangement should also apply to the similar bromobis(ethylenediamine) complexes in that (with reference to $[RhA_4X^{2+}]^*$, X = Cl) Br is a more weakly σ-bonding group than A = NH_3 or en.

As previously mentioned, the only complex that does not entirely follow the reaction scheme outlined in Figure 1 is *cis*-$Rh(en)_2(NH_3)Br^{2+}$. For this complex, photochemical loss of *both* NH_3 and Br^- is observed. When NH_3 is lost, the scheme in Figure 1 *is* followed with isomerization to give the product, *trans*-$Rh(en)_2(H_2O)Br^{2+}$ ($\Phi_{NH_3} \simeq 0.006$). However, the predominant photochemical pathway for *cis*-$Rh(en)_2(NH_3)Br^{2+}$ is loss of Br^-, *with stereoretention of configuration*, to give *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ as the photolysis product ($\Phi_{Br} \simeq 0.054$). The result can be consistent with the mechanism described in Figure 1 if the triplet, five-coordinate fragment generated, $^3SP_{eq}{}^*$ $[Rh(en)_2(NH_3)]^*$ instead of $[Rh(en)_2Br]^*$, experiences a large barrier to isomerization to $^3SP_{ax}{}^*$. In terms of the Vanquickenborne–Ceulemans model, the similar e_σ values for NH_3 and en should be reflected as showing no thermodynamic difference between $^3SP_{ax}{}^*$ and $^3SP_{eq}{}^*$. Since only stereoretentive photoaquation reactions are observed, the ^3TBP barrier connecting $^3SP_{ax}{}^*$ and $^3SP_{eq}{}^*$ must be too large to be accessible within the intersystem crossing lifetimes of the triplet, five-coordinate fragments. The same intermediate, $[Rh(en)_2(NH_3)]^*$, can be generated either in the $^3SP_{eq}{}^*$ or $^3SP_{ax}{}^*$ form by photochemical dissociation of Cl^- from *cis*- and *trans*-$Rh(en)_2(NH_3)Cl^{2+}$,[1] respectively. In both chloroammine complexes,[1] as well as the *cis*-bromoammine complex reported here, photochemical loss of halogen, giving $^3SP_{ax}{}^*$ or $^3SP_{eq}{}^*$ $[Rh(en)_2(NH_3)]^*$, results in *no* isomerization products. Calculations to support this interpretation will be published separately.[23]

The mechanism outlined in Figure 1 assumes that ligand loss precedes any rearrangement that may occur. This assumption is borne out by the results obtained for the photolysis of *cis*-Rh(en)$_2$(NH$_3$)Br^{2+}. If cis to trans rearrangement was occurring prior to loss of NH$_3$ or Br$^-$, the geometries of the two products arising from photolysis of *cis*-Rh(en)$_2$(NH$_3$)Br^{2+} would be the same, i.e., trans. The fact that loss of NH$_3$ leads to stereoisomerization while loss of Br$^-$ gives stereoretention indicates that rearrangement occurs following ligand labilization. These data and the data for the thermal substitution reactions[4] of Rh(III) amine complexes (where only stereoretentive products are observed) strongly suggest that the stereomobility of the photosubstitution reactions is associated with five-coordinate fragments which, after loss of ligand, maintain the electronic configuration of the six-coordinate ligand field excited state.

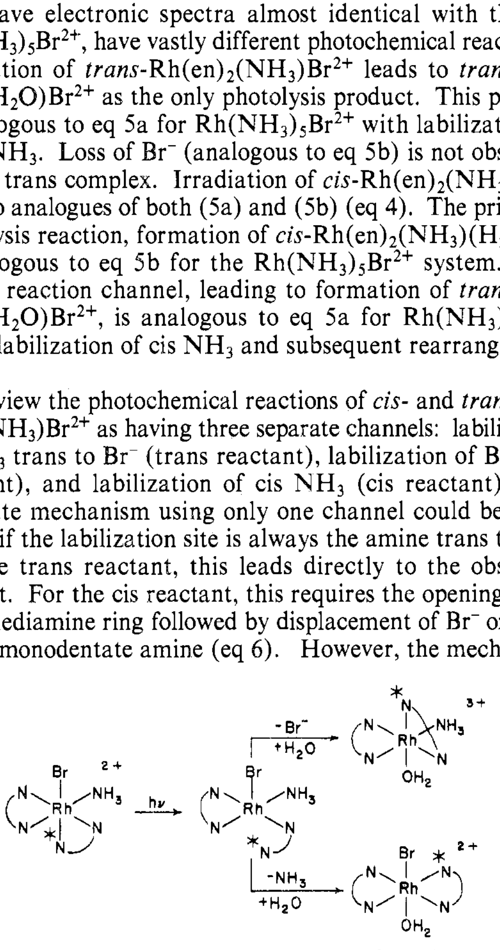
One of our initial reasons for studying the photochemical reactions of the Rh(en)$_2$XBr^{n+} complexes was to use the cis and trans complexes, where X = NH$_3$, as a model for determining which ammine is labilized in the photochemical reaction of Rh(NH$_3$)$_5$Br^{2+}.[8,11] The predominant photochemical process is loss of ammine (eq 5a) to give *trans*-Rh(NH$_3$)$_4$(H$_2$O)Br^{2+}.

$$\mathrm{Rh(NH_3)Br_5}^{2+} \xrightarrow[\Phi\,=\,0.17^{11}]{h\nu,\ \mathrm{LF}} trans\text{-}\mathrm{Rh(NH_3)_4(H_2O)Br^{2+}} \quad (5a)$$

$$\xrightarrow[\Phi\,=\,0.02^{11}]{h\nu,\ \mathrm{LF}} \mathrm{Rh(NH_3)_5H_2O^{3+}} \quad (5b)$$

A mechanism analogous to the one described in Figure 1 would presumably give this trans product regardless of whether cis or trans NH$_3$ was lost photochemically. However, the *cis*- and *trans*-Rh(en)$_2$(NH$_3$)Br^{2+} complexes, which both have electronic spectra almost identical with that of Rh(NH$_3$)$_5$Br^{2+}, have vastly different photochemical reactivity. Irradiation of *trans*-Rh(en)$_2$(NH$_3$)Br^{2+} leads to *trans*-Rh(en)$_2$(H$_2$O)Br^{2+} as the only photolysis product. This process is analogous to eq 5a for Rh(NH$_3$)$_5$Br^{2+} with labilization of trans NH$_3$. Loss of Br$^-$ (analogous to eq 5b) is not observed for the trans complex. Irradiation of *cis*-Rh(en)$_2$(NH$_3$)Br^{2+} leads to analogues of both (5a) and (5b) (eq 4). The principal photolysis reaction, formation of *cis*-Rh(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$, is analogous to eq 5b for the Rh(NH$_3$)$_5$Br^{2+} system. The second reaction channel, leading to formation of *trans*-Rh(en)$_2$(H$_2$O)Br^{2+}, is analogous to eq 5a for Rh(NH$_3$)$_5$Br^{2+} where labilization of cis NH$_3$ and subsequent rearrangement occurs.

We view the photochemical reactions of *cis*- and *trans*-Rh(en)$_2$(NH$_3$)Br^{2+} as having three separate channels: labilization of NH$_3$ trans to Br$^-$ (trans reactant), labilization of Br$^-$ (cis reactant), and labilization of cis NH$_3$ (cis reactant). An alternate mechanism using only one channel could be envisioned if the labilization site is always the amine trans to Br$^-$. For the trans reactant, this leads directly to the observed product. For the cis reactant, this requires the opening of an ethylenediamine ring followed by displacement of Br$^-$ or NH$_3$ by the monodentate amine (eq 6). However, the mechanism in eq 6 does not appear reasonable in light of previous studies[24] where the photolysis of Rh(en)$_3$$^{3+}$ in acidic (HCl) aqueous solution resulted in the formation of *cis*-Rh(en)$_2$(enH)Cl^{3+} with no evidence of ring closure. We have irradiated *cis*-Rh(en)$_2$(NH$_3$)Br^{2+} in 1 M HClO$_4$ and observed *no* monodentate ethylenediamine products.



(6)

The magnitude of the relative *cis*-Rh(en)$_2$(NH$_3$)Br^{2+}/*trans*-Rh(en)$_2$(NH$_3$)Br^{2+} photoaquation quantum yields and the observation of three separate reaction channels for *cis*- and *trans*-Rh(en)$_2$(NH$_3$)Br^{2+} suggest an atypical pattern for initial ligand loss. In all previously reported studies on the photolysis of *cis*- and *trans*-RhA$_4$XY^{n+} (A$_4$ = (NH$_3$)$_4$ or (en)$_2$) complexes,[1,5-7] the quantum yield for ligand loss is 2.5–7 times larger from cis than from trans complexes. Even the *cis*- and *trans*-Rh(en)$_2$(NH$_3$)Cl^{2+} complexes, which have almost identical electronic spectra, show a quantum yield for loss of Cl$^-$ (analogous to the photochemistry of Rh(NH$_3$)$_5$Cl^{2+}) that is 2.5 times greater for the cis isomer.[1] This is not the case for the Rh(en)$_2$(NH$_3$)Br^{2+} isomers in that the quantum yields for the two cis channels *combined* (~0.06) are only approximately one-third the magnitude of the one-channel trans reaction (0.16). We interpret these data as a net photochemical dissimilarity between the spectroscopically similar ammine and ethylenediamine ligands.[25] Apparently, the Rh(III)–NH$_3$ bond is easier to break than the Rh(III)–en bond in the ligand field excited state. For *trans*-Rh(en)$_2$(NH$_3$)Br^{2+}, the preferred channel is labilization of the ligand trans to Br$^-$, and NH$_3$ leaves with a quantum efficiency in the range between other *trans*-RhA$_4$XY^{n+} (A$_4$ = (NH$_3$)$_4$ or (en)$_2$) complexes[1,5,6] which lose halide and loss of NH$_3$ from Rh(NH$_3$)$_5$Br^{2+}.[8,11] For *cis*-Rh(en)$_2$(NH$_3$)Br^{2+}, the site trans to Br$^-$ is occupied by one end of an ethylenediamine ligand. The channel apparently becomes less favorable, and competitive secondary (loss of Br$^-$) and tertiary (loss of NH$_3$ *cis* to Br$^-$) channels are observed. There is some evidence suggesting ammine labilization is easier than ethylenediamine labilization for Rh(III) complexes. The measured lifetime (lowest energy triplet LF excited states) of Rh(en)$_3$$^{3+}$ in a methanol–water glass at 77 K is 19% longer than the lifetime of Rh(NH$_3$)$_6$$^{3+}$.[27] However, the room-temperature photosubstitution (irradiation of the lowest energy LF bands) quantum yield for Rh(NH$_3$)$_6$$^{3+}$[28] is almost twice as large as that of Rh(en)$_3$$^{3+}$.[24] We can also compare the photochemical reactions of various RhA$_4$XY^{n+} complexes. When A$_4$ = (en)$_2$,[1,6] no amine aquation is observed,[26] while for A$_4$ = (NH$_3$)$_4$,[7,9] small quantum yields for loss of NH$_3$ are measured. Differences in ethylenediamine and ammine photoaquation quantum yields have been observed as well for the Cr(III) complexes [Cr(en)$_x$(NH$_3$)$_{6-2x}$]$^{3+}$.[13] However, unlike the Rh(III) system, Cr(III) exhibits a statistical preference for labilization of ethylenediamine over ammine.

It is obvious from our results that the ethylenediamine complexes *cis*- and *trans*-Rh(en)$_2$(NH$_3$)Br^{2+} do not serve as adequate models for determining the coordination site of labilized ammine in Rh(NH$_3$)$_5$Br^{2+}. The attenuation of the "normal" *cis*-RhA$_4$XY^{n+} (A$_4$ = (NH$_3$)$_4$ or (en)$_2$) quantum yield for *cis*-Rh(en)$_2$(NH$_3$)Br^{2+} may suggest that the loss of trans NH$_3$ in Rh(NH$_3$)$_5$Br^{2+} is favored over loss of cis NH$_3$. However, both pathways may be occurring and experiments such as photolysis of *trans*-Rh(NH$_3$)$_4$(^{15}NH$_3$)Br^{2+} are required before the actual labilization site(s) can be determined.

The photochemical reaction observed for *cis*-Rh(en)$_2$(H$_2$O)Br^{2+} forming *trans*-Rh(en)$_2$(H$_2$O)Br^{2+} could be occurring by two possible mechanisms. Since the nature of the ligands in the first coordination sphere remains unchanged, an excited-state twisting mechanism, involving no bond breaking, is a possibility. However, since isotopic labeling experiments[3] have shown that Rh(NH$_3$)$_5$H$_2$O^{3+} is very photoreactive but only undergoes exchange of coordinated and solvent water, the mechanism in Figure 1, where X = H$_2$O, would be consistent with the observed photochemistry of *cis*-

and *trans*-$Rh(en)_2(H_2O)Br^{2+}$. The photolability of aquo ligand has been demonstrated as well as explained by Ford and coworkers[7] for the tetraammine complexes. Photolysis of *cis*-$Rh(NH_3)_4(H_2O)X^{2+}$ in formamide solution led to the efficient formation of *trans*-$Rh(NH_3)_4(formamide)X^{2+}$ (X = Cl, Br).[7] Assuming an H_2O dissociation mechanism, the intermediates formed by loss of Br^- from *cis*-$Rh(en)_2Br_2^+$ and loss of H_2O from *cis*-$Rh(en)_2(H_2O)Br^{2+}$ are the same, $^3SP_{eq}{}^*$ $[Rh(en)_2Br^{2+}]^*$, as are the subsequent products, *trans*-$Rh(en)_2(H_2O)Br^{2+}$. The quantum yield for H_2O loss from the *cis*-aquobromo complex approaches unity (0.95 mol/einstein) and is over twice the magnitude of the quantum yield for loss of Br^- from *cis*-$Rh(en)_2Br_2^+$ (0.37 mol/einstein). This difference in reactivity, also observed for *cis*-$Rh(NH_3)_4(H_2O)X^{2+}$ vs. *cis*-$Rh(NH_3)_4X_2^+$ (X = Cl, Br),[7] could be due to differences in the lifetimes of the ligand field excited state or reflect the relative excited state thermal reactivities of Rh(III)–OH_2 vs. Rh(III)–Br bond cleavage. In the case of the latter explanation, the ease of bond breaking would parallel the ground-state thermal reactivities where the acid hydrolysis of $Rh(NH_3)_5Br^{2+}$ has a rate constant (25 °C) of $\sim 1 \times 10^{-8}$ s^{-1} for aquation of Br^-,[29] while water exchange for $Rh(NH_3)_5H_2O^{3+}$ has a rate constant of 5.4×10^{-4} s^{-1} (20.3 °C).[30] This apparent ease of Rh(III)–OH_2 bond cleavage from the ligand field excited state would explain why the photoaquation reactions of Rh(III) amine complexes lead solely to monoaquo products with no secondary photolysis reactions occurring other than aquo ligand exchange.

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Registry No. *trans*-$[Rh(en)_2Br_2]ClO_4$, 55683-56-2; *trans*-$[Rh(en)_2(H_2O)Br](ClO_4)_2$, 55683-59-5; *trans*-$[Rh(en)_2(NH_3)Br](NO_3)_2$, 65761-16-2; *cis*-$[Rh(en)_2Br_2]ClO_4$, 53368-53-9; *cis*-$[Rh(en)_2(H_2O)Br](ClO_4)_2$, 71500-68-0; *cis*-$[Rh(en)_2(NH_3)Br](NO_3)_2$, 71605-89-5; *trans*-$[Rh(en)_2Cl_2]NO_3$, 15529-88-1; $[Rh(en)_2(oxalato)]ClO_4$, 52729-89-2; *trans*-$[Rh(en)_2Br_2]NO_3$, 15529-89-2; *trans*-$Rh(en)_2Br_2^+$, 24444-44-8; *trans*-$Rh(en)_2(H_2O)Br^{2+}$, 15337-42-5; *trans*-$Rh(en)_2(NH_3)Br^{2+}$, 61697-85-6; *cis*-$Rh(en)_2Br_2^+$, 53368-52-8; *cis*-$Rh(en)_2(H_2O)Br^{2+}$, 53368-48-2; *cis*-$Rh(en)_2(NH_3)Br^{2+}$, 71563-57-0; *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$, 70223-45-9; *trans*-$Rh(en)_2(H_2O)_2^{3+}$, 21863-10-5.

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