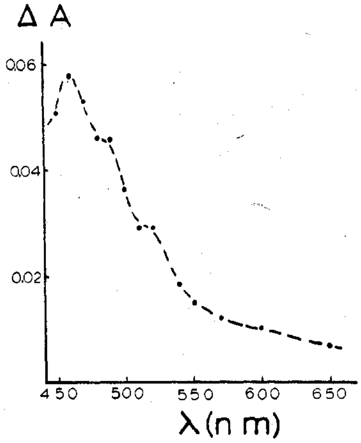
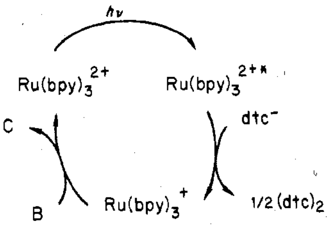


Figure 6. Absorption at different wavelengths after the flash (1 ms) of a solution of $Ru(bpy)_3^{2+}$ (1×10^{-5} M), dtc^- (10^{-3} M), and *o*-dinitrobenzene (5×10^{-4} M) in 0.1 M $CH_3CN-Et_4NClO_4$.

Scheme I



to be of significant importance in our work. This is indicated by the fact that the quantity of $A^{-\cdot}$ produced after the flash is identical with the quantity of $Ru(bpy)_3^+$ obtained under the same conditions without added A, at least within experimental error.

A good agreement is also found for the spectrum of the radical anion of *o*-dinitrobenzene (see the spectrum in Figure 6) obtained after the flash and that published in the literature for the similar compounds nitrobenzene and *p*-nitrotoluene[29] in solution and also with the spectrum of *o*-dinitrobenzene radical anion obtained in a glassy frozen solution.

The experiments described above show that dithio anions like dtc^- can quench $Ru(bpy)_3^{2+*}$ to give $Ru(bpy)_3^+$ and that such systems have potential in photochemical applications for catalysis on the basis of Scheme I. In Scheme I, a compound B is converted into C by an irreversible process which is sufficiently rapid to prevent the oxidation of $Ru(bpy)_3^+$ by the disulfide. In this case (with anthraquinone) the overall scheme is only transient, but in principle it illustrates the ability of such excited-state systems to drive reactions in photochemical or photoelectrochemical applications and to create and observe transients which would otherwise be difficult to observe.

Conclusions

The results of our studies on the system $Ru(bpy)_3^{2+}-dtc^-$ are worth noting in a catalytic sense because we have shown that it is possible in acetonitrile to build up, if transiently, the powerful reductant $Ru(bpy)_3^+$. Unfortunately, the system is limited in any useful sense by the rapidity of the reduction of the disulfide $(dtc)_2$ which was a surprise to us. However, our experiments do demonstrate the potential value of such systems photocatalytically and for the generation of usually unobservable transients. In the future it may be possible to exploit a more appropriate dithio anion or other reductive quencher which will allow the buildup of significant concentrations of Ru^I.

Acknowledgments are made to the National Science Foundation under Grant No. CHE77-03423 and to CNRS France and NATO for support for A.D. and to Dr. Jeffrey Nagle for experimental assistance and valuable conversations.

Registry No. I, 392-74-5; II, 28563-38-4; III, 71141-39-4; IV, 40898-92-8; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(bpy)_3^+$, 56977-24-3; $Ru(bpy)_2(CN)_2^-$, 73746-84-6; $Ru(4,4'-[(CH_3)_2CHOOC]_2bpy)_3^+$, 73746-85-7; $Ru(bpy)_2(4,4'\text{-}bpyMe)_2^{3+}$, 73746-86-8; $(dtc)_2$, 97-77-8.

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Stereochemistry and Quantum Yields for the Ligand Field Photolysis of Rhodium(III) Complexes. 3.[1,2] *cis*- and *trans*-$Rh(en)_2XI^{n+}$

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Ligand field excitations of *cis*- and *trans*-$Rh(en)_2XI^{n+}$ complexes (X = I, NH_3, H_2O), in all cases but one, lead exclusively to the formation of *trans*-$Rh(en)_2(H_2O)I^{2+}$ as the photoproduct. The exception is the *cis*-$Rh(en)_2(NH_3)I^{2+}$ complex, where irradiation leads to the formation of both *trans*-$Rh(en)_2(H_2O)I^{2+}$ and *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$. The stereochemistry of all of the photochemical products is consistent with ligand labilization from the lowest electronic excited state and rearrangement of the triplet, five-coordinate, square-pyramidal fragments as originally proposed by Vanquickenborne and Ceulemans. The three separate reaction channels observed for the photolysis of the spectroscopically similar *trans*- and *cis*-$Rh(en)_2(NH_3)I^{2+}$ complex ions 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. For the series of *cis*- and *trans*-$Rh(en)_2XY^{n+}$ (X = Cl, Br, I; Y = X, NH_3), qualitative series for ease of halogen labilization (Cl > Br > I) and trans-labilizing ability (I ≫ Br > Cl) have been proposed.

Introduction

The ligand field photolysis of rhodium(III) amine complexes has been extensively studied over the past 8 years.[1-11] This activity is due, in part, to the substitutional inertness and stereoretention of the thermal substitution reactions[12] and the

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lack of secondary photolysis processes (photoaquation of one ligand site is usually followed solely by aquo ligand exchange[7]).

In general, the photosubstitution reactions of the *trans*-tetraamine complexes are stereoretentive as are the thermal substitution reactions (eq 1). However, the photoaquation

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

$X = Y = Cl$; $A_4 = (NH_3)_4$,[4,5] $(en)_2$,[1,4,5] cyclam[4]

$X = Y = Br$; $A_4 = (NH_3)_4$,[11] $(en)_2$[2,5]

$X = Y = I$; $A_4 = (NH_3)_4$,[3] $(en)_2$[5]

$X = NH_3$, $Y = Cl$; $A_4 = (NH_3)_4$,[3,5] $(en)_2$[1]

of *cis*-tetraaminerhodium(III) complexes does lead, in some instances, to trans-substituted products (eq 2). The geometric

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

$X = Y = Cl$; $A_4 = (NH_3)_4$,[9] $(en)_2$[1,5]

$X = Cl$, $Y = H_2O$; $A_4 = (NH_3)_4$,[9] $(en)_2$[13]

$A_4 = (NH_3)_4$; $X = Y = H_2O$,[9] $X = Y = Br$,[11]
$X = Br$ and $Y = H_2O$[11]

$X = Y = Br$; $A_4 = (en)_2$[2]

difference 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 coworkers[10] have illustrated that photoaquation does occur from the ligand field excited state in halopentaamminerhodium(III) complexes.

Vanquickenborne and Ceulemans[14] have used an "additive point ligand model" to explain the stereochemical changes 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-pyramid structure of the intermediate.

The photochemically induced stereochemistry of the pentaamine complexes of Rh(III) is difficult to study experimentally. For example, the predominant photochemical reaction of bromo- and iodopentaamminerhodium(III) is loss of ammine[3] (eq 3). The ligand field treatment of Vanquickenborne and Ceulemans[14] suggests that trans products would be observed, in eq 3, regardless of whether cis or trans ammine is lost photochemically. Recently, we reported[2] a study on the ligand field photolysis of *cis*- and *trans*-$Rh(en)_2(NH_3)Br^{2+}$ in which the spectroscopically similar ethylenediamine was substituted for ammine in order to determine which ammine is lost in the predominant photoaquation of $Rh(NH_3)_5Br^{2+}$ (eq 3). The results of this study showed that ethylenediamine does not follow the same photochemical behavior as ammine. The reactions outlined in eq 4 and 5, which are consistent with the proposed stereochemical control,[14,15] indicate a channel mechanism in which three different sites are labilized: ammine trans to Br (eq 4), ammine cis to Br (eq 5a), and Br^- (eq 5b). The preferential aquation of ammine rather than ethylenediamine in these systems is directly opposite to the results obtained by Kirk and co-workers[15] for mixed ammine/ethylenediamine complexes of Cr(III).

$$Rh(NH_3)_5X^{2+} \xrightarrow[\text{predominant reaction}]{h\nu,\ LF} trans\text{-}Rh(NH_3)_4(H_2O)X^{2+} + NH_3 \qquad (3)$$

$X = Br, I$

$$trans\text{-}Rh(en)_2(NH_3)Br^{2+} \xrightarrow[H_2O]{h\nu} trans\text{-}Rh(en)_2(H_2O)Br^{2+} + NH_3 \qquad (4)$$

$$cis\text{-}Rh(en)_2(NH_3)Br^{2+} \xrightarrow{h\nu,\ H_2O} trans\text{-}Rh(en)_2(H_2O)Br^{2+} + NH_3 \qquad (5a)$$

$$\text{and } cis\text{-}Rh(en)_2(NH_3)(H_2O)^{3+} + Br^- \qquad (5b)$$

Table I. Electronic Spectra of *cis*- and *trans*-$[Rh(en)_2XI]^{n+}$

compd	λ_{max}, nm	ϵ_{max}, $M^{-1}\ cm^{-1}$	ref
trans-$[Rh(en)_2I_2]I$[a]	464 (462) 340 (340) (269) (222)	260 (260) 15 000 (14 300) (31 000) (20 000)	b (16)
trans-$[Rh(en)_2(H_2O)I]$-$(ClO_4)_2$[a]	480 (476)	228 (150)	b (18)
trans-$[Rh(en)_2(NH_3)I]I_2$	413	287	b
cis-$[Rh(en)_2I_2]I$	377	1100	b
cis-$[Rh(en)_2(NH_3)I]I_2$	390	436	b

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

Table II. Proton-Decoupled ^{13}C NMR Chemical Shifts of *cis*- and *trans*-$[Rh(en)_2XI]^{n+}$ and Related Compounds

compd	$\delta(^{13}C)$[a]
trans-$Rh(en)_2I_2^+$	46.78
trans-$Rh(en)_2(H_2O)I^{2+}$	46.12
trans-$Rh(en)_2(NH_3)I^{2+}$	45.87
trans-$Rh(en)_2(NH_3)(H_2O)^{3+}$[b]	45.69
cis-$Rh(en)_2I_2^+$	48.45, 46.51
cis-$Rh(en)_2(NH_3)I^{2+}$	47.76, 46.98, 46.53, 46.02
cis-$Rh(en)_2(NH_3)(H_2O)^{3+}$[b]	47.68, 47.39, 45.99, 45.03

[a] Chemical shifts reported vs. Me_4Si with dioxane (67.40 ppm) as an internal reference. [b] Reference 13.

In this work, we report the results of the ligand field photolysis of *cis*- and *trans*-$Rh(en)_2XI^{n+}$ complexes. For the compounds where X = NH_3, the analogous pentaammine complex photochemically reacts as shown in eq 3. Of specific interest in this work is whether the presence of an iodo ligand in the complex forces the photoaquation of a specific amine site (regardless of whether this amine is en or NH_3) or if the photoinertness of the Rh(III)–en bond leads to photochemical reactivity of the channel type as observed for the bromo complexes[2] discussed above.

Experimental Section

Synthesis of Metal Complexes. The electronic absorption spectral data and the carbon-13 NMR spectral data for all complexes reported here are listed in Tables I and II, respectively. Elemental analyses

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were performed by Industrial Testing Laboratories, St. Louis, MO.

***trans*-[Rh(en)$_2$I$_2$](ClO$_4$).** This compound was prepared by a modification of the procedure of Bott and Poë.[16] One-half gram (1.40 mmol) of *trans*-[Rh(en)$_2$Cl$_2$](NO$_3$) and a 10-fold molar excess of NaI (Mallinckrodt, AR) were dissolved in 40 mL of H_2O, and the mixture was heated at reflux for 3–4 h. The complex precipitated out as the iodide salt almost immediately. After the mixture was allowed to stand overnight in the refrigerator, the iodide salt was collected and converted to the perchlorate salt by dissolution in a minimum amount of hot H_2O, followed by filtering the solution into a beaker containing methanol saturated with $NaClO_4$. After the mixture was cooled, the complex was collected, washed with ethanol and then ether, and dried under vacuum; yield 403 mg (50%).

***cis*-[Rh(en)$_2$I$_2$](ClO$_4$).** A modification of the procedure of Gillard and co-workers[17] for the preparation of the *cis*-dichloro and *cis*-dibromo complexes was used. A 0.3-g sample of [Rh(en)$_2$(oxalato)]-(ClO$_4$)·0.5H$_2$O was dissolved in 60 mL of water. After addition of 18 mL of HI (Fisher ACS, 47%), the solution was heated at reflux for 3–4 min. Cooling overnight in the refrigerator resulted in the crystallization of the iodide salt of the complex. Conversion to the perchlorate salt, collection, and drying were accomplished as described above for the trans isomer; yield 297 mg (72%). Anal. Calcd for the iodide salt *cis*-[Rh(en)$_2$I$_2$]I, $C_4H_{16}I_3N_4Rh$: C, 7.95; H, 2.65; N, 9.27. Found: C, 7.99; H, 2.62; N, 9.31.

***trans*-[Rh(en)$_2$(H$_2$O)I](ClO$_4$)$_2$.** This compound was prepared by the method of Burgess, Hartley, and Rogers[18] as modified by Jakse.[1] A 267-mg (0.463-mmol) sample of *trans*-[Rh(en)$_2$I$_2$](ClO$_4$) was added to an equimolar amount (0.463 mmol) of $AgClO_4$ solution (prepared by dissolving 53.7 mg of Ag_2O in a minimum amount of $HClO_4$) and enough H_2O to make 5 mL of solution, and the mixture was heated at reflux for 10 min. After the mixture was cooled, the AgI was removed by filtration and the remaining solution evaporated on a rotary evaporator until crystals formed. The crystals were collected, washed with ethanol then ether, and dried under vacuum; yield 100 mg (38%). Anal. Calcd for $C_5H_{18}Cl_2IN_4O_9Rh$: C, 8.47; H, 3.17; N, 9.88. Found: C, 8.67; H, 3.26; N, 9.52. The ^{13}C NMR spectrum of this compound showed a very slight impurity of *trans*-Rh(en)$_2$I$_2$$^+$.

***cis*- and *trans*-[Rh(en)$_2$(NH$_3$)I]I$_2$.** These compounds were prepared by a modification of the Johnson and Basolo[19] synthesis of the chloroammine complexes. A 380-mg sample of the corresponding diiodo complex, *cis*- or *trans*-[Rh(en)$_2$I$_2$]I, was dissolved in 15 mL of concentrated NH_4OH and heated at reflux for 10 min. An additional 5 mL of NH_4OH was added and heating at reflux was continued for 10 min longer. The solution volume was reduced to ~7 mL, nitrogen gas was bubbled through the solution for 20 min, and the solution volume was then reduced to ~3 mL. Addition of 2 mL of HI and cooling in the refrigerator overnight gave the desired product which was collected, washed, and dried as described above. Cis isomer: yield 363 mg (92%). Anal. Calcd for $C_4H_{19}I_3N_5Rh$: C, 7.73; H, 3.06; N, 11.27. Found: C, 7.67; H, 3.20; N, 10.98. Trans isomer: yield 114 mg (29%). Anal. Calcd for $C_4H_{19}I_3N_5Rh{\cdot}H_2O$: C, 7.51; H, 3.29; N, 10.95. Found: C, 7.39; H, 3.26; N, 10.75.

***cis*- and *trans*-[Rh(en)$_2$(NH$_3$)I](S$_2$O$_6$).** (For photolysis reactions, the iodide salts of the iodoammine complexes were converted to the dithionate salt. Photolysis of the iodide salts of these complexes leads to a very rapid iodide anation of the photolysis product. We were unable to find any noncoordinating anions which would result in a pure compound with the result that our best anion, dithionate, still precipitates the complex in the presence of some $Na_2S_2O_6$. Also, addition of a strong acid such as $HClO_4$ or H_2SO_4 leads to decomposition of Rh(en)$_2$(NH$_3$)I^{2+} in solution.)

A 150-mg sample of the iodide salt of the desired isomer was dissolved in 2 mL of H_2O. Following addition of 0.8 g of $Na_2S_2O_6$, the solution volume was reduced until crystals started to appear. The precipitate, which contained the dithionate salt of the complex along with $Na_2S_2O_6$, was washed repeatedly with cold H_2O until the material contained <15% $Na_2S_2O_6$; yield 50 mg (39%).

Photolysis Apparatus. Photosubstitution quantum yields were determined by using a continuous-beam photolysis apparatus described elsewhere.[2] Usable intensities at irradiation wavelengths of 366, 405, and 436 nm were determined by ferrioxalate actinometry[20] and approximated as 8×10^{18}, 1.3×10^{18}, and 1.2×10^{18} quanta/min, respectively.

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 TT-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 except those noted below. 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 spectroscopies from samples photolyzed to completion; however, the product extinction coefficient values were obtained (except for the photolysis of *cis*-Rh(en)$_2$(NH$_3$)I^{2+}) from authentic samples. *cis*-Rh(en)$_2$(NH$_3$)I^{2+} was the only complex in this study which gave more than one photolysis product. A disappearance quantum yield of *cis*-Rh(en)$_2$(NH$_3$)I^{2+} was obtained from electron absorption spectral changes with use of the spectrum of the starting compound and the spectrum of a sample irradiated until no further spectral changes were observed. The ratio of the two photolysis products, *cis*-Rh(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$ and *trans*-Rh(en)$_2$(H$_2$O)I^{2+}, was approximated from a ^{13}C NMR spectrum of the photolysis product and confirmed by ion-exchange chromatography.

In addition to the photolysis reactions of *cis*-Rh(en)$_2$(NH$_3$)I^{2+} run as the dithionate salt, certain photolysis runs were taken on the iodide salt ([complex] = $\sim 1 \times 10^{-3}$ M), in the presence of added iodide ion ([I$^-$] = 10^{-2} M) or in the presence of added perchlorate ion ([ClO$_4$$^-$] = 10^{-2} M). In the presence of excess iodide ion, the ultimate product observed for extensive photolysis was *trans*-Rh(en)$_2$I$_2$$^+$.

Ion-Exchange Separation. An extensively irradiated sample of *cis*-Rh(en)$_2$(NH$_3$)I^{2+} was separated into component parts by ion-exchange chromatography. The column, 10 cm of Dowex 50W-X4 200–400 mesh (originally H$^+$ form), was prepared by extensive washings with 1 M $NaClO_4$. A sample, which had been irradiated to near completion, was reduced in volume from 6 mL to 1 mL and eluted with increasing concentrations of $NaClO_4$ solution. Each fraction (~10 mL of eluant) was monitored by electronic spectroscopy. At eluant concentrations of 5 M $NaClO_4$, all compounds had been removed from the column.

Results

The quantum yields for the photolysis of *cis*- and *trans*-Rh(en)$_2$XI^{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 is deduced from the carbon-13 NMR spectra of extensively irradiated samples. Only one of the complexes irradiated in this study, *cis*-Rh(en)$_2$(NH$_3$)I^{2+}, gave more than one photolysis product, and the product composition was determined by ion-exchange chromatography techniques. Irradiation wavelengths of 366, 405, and 436 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 (except in the case where small amounts of excess I$^-$ are present), since isosbestic points are maintained

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Table III. Quantum Yields for the Photoaquation for *cis*- and *trans*-$[Rh(en)_2XI]^{n+}$[a]

complex	λ_{irr}, nm	product	ϕ_{I^-}[b]	ϕ_X[c]	ϕ_{isom}[d]
trans-$Rh(en)_2I_2^+$	436	*trans*-$Rh(en)_2(H_2O)I^{2+}$	0.33 ± 0.02 (5)	$X = I^-$	[e]
[f]	254	*trans*-$Rh(en)_2(H_2O)I^{2+}$	0.23	$X = I^-$	[e]
trans-$Rh(en)_2(H_2O)I^{2+}$	436	[g]	$<10^{-3}$	[h]	[e]
trans-$Rh(en)_2(NH_3)I^{2+}$	405	*trans*-$Rh(en)_2(H_2O)I^{2+}$	$<10^{-3}$	0.60 ± 0.02 (3)	[e]
cis-$Rh(en)_2I_2^+$	366	*trans*-$Rh(en)_2(H_2O)I^{2+}$	0.040 ± 0.03 (4)	$X = I^-$	0.040
cis-$Rh(en)_2(NH_3)I^{2+}$	405	*trans*-$Rh(en)_2(H_2O)I^{2+}$		~0.034[i]	~0.034[i]
		cis-$Rh(en)_2(NH_3)(H_2O)^{3+}$	~0.006[i]		[e]

[a] Measured in aqueous perchlorate media ($2 \leqslant pH \leqslant 5$) at 25 °C. [b] Quantum yield for loss of I^- (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 = I). [d] Quantum yield for geometric isomerization (mol/einstein). [e] None detectable. [f] Reference 5. [g] No photochemical reactions observable. [h] Not determined; aquo ligand exchange with solvent water would not be detected under these conditions. [i] Quantum yield for decomposition of *cis*-$Rh(en)_2(NH_3)I^{2+}$ is ~0.040 by absorption spectroscopy. ϕ_X and ϕ_{isom} were determined by formation of *trans*-$Rh(en)_2I_2^+$ in excess iodide ion (see text).

throughout entire photolysis reactions.

trans-**$Rh(en)_2XI^{n+}$.** For the trans complexes, where X is I, NH_3, or H_2O, photoaquation of X occurs as the only detectable photochemical reaction. For X = I, irradiation at 436 nm leads to loss of I^- to form *trans*-$Rh(en)_2(H_2O)I^{2+}$ with a quantum yield of 0.33 mol/einstein. Subsequent irradiation of the *trans*-iodoaquo photolysis product, or photolysis of a pure sample of *trans*-$Rh(en)_2(H_2O)I^{2+}$, leads to no spectral or pH changes. This limits any photochemical reaction of the *trans*-iodoaquo complex to aquo ligand exchange, which would be nonobservable under the reaction conditions. For X = NH_3, irradiation at 405 nm leads to loss of NH_3 with a quantum yield of 0.60 mol/einstein as the only detectable photolysis product. The ^{13}C NMR spectrum of an extensively irradiated sample of the *trans*-iodoammine complex is identical with that of an authentic sample of the *trans*-iodoaquo complex with the signal-to-noise ratio indicating >95% isomeric purity. However, if the *trans*-iodoaquo complex is allowed to sit for a period of 2 weeks or longer a new peak in the ^{13}C NMR spectrum grows which is assigned as the slow thermal or low-efficiency secondary photolysis reaction giving *trans*-$Rh(en)_2(H_2O)_2^{3+}$.

cis-**$Rh(en)_2I_2^+$.** The 366-nm irradiation of the *cis*-diiodo complex leads to formation of *trans*-$Rh(en)_2(H_2O)I^{2+}$ with a quantum yield of 0.040 mol/einstein. The stereochemistry of the product was confirmed by ^{13}C NMR spectroscopy to >95% isomeric purity. The change in the electronic spectrum during photolysis was monotonic, indicating that the loss of I^- and the cis/trans isomerization processes were concomitant.

cis-**$Rh(en)_2(NH_3)I^{2+}$.** Irradiation of the *cis*-iodoammine complex at 405 nm leads to the formation of two products, *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ and *trans*-$Rh(en)_2(H_2O)I^{2+}$ (eq 6).

$$cis\text{-}Rh(en)_2(NH_3)I^{2+} \xrightarrow[-I^-,\ +H_2O]{h\nu} cis\text{-}Rh(en)_2(NH_3)(H_2O)^{3+} \tag{6a}$$

$$\xrightarrow[-NH_3,\ +H_2O]{h\nu} trans\text{-}Rh(en)_2(H_2O)I^{2+} \tag{6b}$$

The quantum yield for the disappearance of starting material is ~0.040 mol/einstein. The carbon-13 NMR spectrum of an extensively irradiated sample gave four peaks attributable to *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$, one peak corresponding to *trans*-$Rh(en)_2(H_2O)I^{2+}$ and a small peak characteristic of *trans*-$Rh(en)_2I_2^+$. The presence of the *trans*-diiodo complex arises from a facile anation of *trans*-$Rh(en)_2(H_2O)I^{2+}$ by the I^- produced in eq 6a. This anation process complicates the calculation of the relative importance of pathways 6a and 6b but is not significant in the first 20% of the photolysis process where the disappearance quantum yield is measured. The actual quantum yield for process 6b was obtained by irradiating *cis*-$Rh(en)_2(NH_3)I^{2+}$ in the presence of small amounts (2×10^{-3} M) of I^- and monitoring the formation of *trans*-$Rh(en)_2I_2^+$ (ϕ = ~0.034 mol/einstein). The quantum yield for formation of *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ was approximated from the difference between the disappearance quantum yield and the quantum yield for formation of *trans*-diiodo complex in excess iodide.

The ion-exchange separation of an extensively photolyzed sample of *cis*-$Rh(en)_2(NH_3)I^{2+}$ confirmed the presence of both *trans*-$Rh(en)_2I_2^+$ and *trans*-$Rh(en)_2(H_2O)I^{2+}$ in the photolyte solution. The product which should have been obtained in eq 6a, *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$, was not directly observed in the elution of the photolyte solution. From the approximate product ratios observed in the ^{13}C NMR spectrum and the amount of materials recovered in each ion-exchange fraction, it appears that *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ came off the column at about the same time as *trans*-$Rh(en)_2(H_2O)I^{2+}$ and was masked in the electronic spectrum by a highly intense charge-transfer transition of the latter.

Discussion

The ligand field photochemistry of *cis*- and *trans*-$Rh(en)_2XI^{2+}$ complexes (where X = I, H_2O, or NH_3) proceeds in aqueous solution to the monoaquo products from loss of either X or I^-. 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.

Product Stereochemistry. The product geometries from the photochemistry of the complexes in this work are consistent with a single, theoretical model[14] which describes the photostereochemistry. This model[14] has been tested on previous systems[1,2] and has been expanded[23] and confirmed[23] for situations not initially studied,[14] so that only the germane points will be discussed here. Briefly, ligand loss occurs from an electronic excited state resulting in a five-coordinate, square-pyramidal fragment which retains a spin-triplet electronic configuration. For the systems described in this work, the five-coordinate, square-pyramidal fragment has the formula $[Rh(en)_2X^{n+}]^*$ (where X = I or NH_3) and X appears apical for trans starting materials and basal for cis starting materials. When X is a weaker σ-bonding ligand than en (i.e., I), there is a thermodynamic preference for X in the apical position. (Note: This is true for the spin-triplet but not the singlet ground state.) In addition, the barrier between $[Rh(en)_2I^{2+}]^*_{basal}$ and $[Rh(en)_2I^{2+}]^*_{apical}$ is low enough in energy that rearrangement (basal → apical) occurs faster than intersystem crossing (triplet → singlet). Thus, the generation of $[Rh(en)_2I^{2+}]^*$ initially in either the basal or apical form leads exclusively to the formation of *trans*-$Rh(en)_2(H_2O)I^{2+}$ in aqueous solution.

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(23) Purcell, K. F.; Clark, S. F.; Petersen, J. D. *Inorg. Chem.* **1980**, *19*, 2183.

For X = NH_3, there is not much difference in the σ-bonding abilities of X and en and therefore there is little thermodynamic preference between apical or basal isomers. However, mixtures of *cis*- and *trans*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ photolysis products are never observed in the photochemistry at 25 °C,[24] and loss of I^- from *cis*- or *trans*-$Rh(en)_2(NH_3)I^{2+}$ results in aquoammine complex with the same stereochemistry as the starting material. The stereoretentive nature of the $[Rh(en)_2(NH_3)^{3+}]^*$ five-coordinate fragment is observed whether the leaving group is Cl^-,[1] Br^-,[2] or I^- or whether the starting compound is cis or trans. This stereoretention has been interpreted[2] as a kinetically controlled phenomenon where basal ↔ apical pseudorotation is slower than triplet → singlet intersystem crossing in the five-coordinate fragment. The fact that two products with different geometries, *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ and *trans*-$Rh(en)_2(H_2O)X^{2+}$ (X = I, Br[2]), are obtained from irradiation of *cis*-$Rh(en)_2(NH_3)X^{2+}$ indicates that ligand loss from the electronic excited state is occurring prior to geometric rearrangement.

None of the complexes in this study, nor the chloro[1] or bromo[2] analogues previously studied, show any evidence for labilization of one or both ends of ethylenediamine. (Monodentate ethylenediamine would have been observed by ^{13}C NMR spectroscopy.[25]) The inability of the lowest excited state to labilize ethylenediamine results in the three separate reaction channels which are observed for the spectroscopically (electronic) similar *cis*- and *trans*-$Rh(en)_2(NH_3)I^{2+}$ complex ions. These three channels are: labilization of NH_3 trans to I^- (trans reactant), labilization of I^- (cis reactant), and labilization of cis NH_3 (cis reactant). The magnitude of the relative *cis*-$Rh(en)_2(NH_3)I^{2+}$/*trans*-$Rh(en)_2(NH_3)I^{2+}$ photoaquation quantum yields and the presence of three channels suggest the same atypical pattern for initial ligand loss as observed for the bromo analogue.[2] Our previous interpretation,[2] which is consistent with these new data, is that the preferred labilization site is that which is trans to the iodo ligand. This is observed for the trans complex with NH_3 loss and $\phi = 0.60$ mol/einstein. However, when this preferred site is occupied by en (i.e., cis complex), the barrier for this process is pushed way up in energy, and secondary (loss of cis NH_3) and tertiary (loss of I^-) processes are observed with much smaller quantum yields (0.034 and 0.006 mol/einstein, respectively). The preference for Rh(III)–NH_3 bond breaking over Rh(III)–en bond breaking has been discussed previously and is exactly opposite to the preference shown in photosubstitution reactions of chromium(III) amines.[15]

Nature of Photosubstituted Ligand. Many useful theoretical treatments have been employed[26-28] to describe and predict which ligand will be lost in the photochemistry of six-coordinate, low-spin, d^6 systems. However, two of these treatments[26,27] do not deal with situations of low enough symmetry as encountered in this work. The third treatment[28] is successful in predicting the ligand which is lost in nine out of twelve of the compounds, *cis*- and *trans*-$Rh(en)_2XY^{n+}$ (X = Cl, Br, I; Y = X, NH_3), but fails for *trans*-$Rh(en)_2(NH_3)Br^{2+}$ and *cis*- and *trans*-$Rh(en)_2(NH_3)I^{2+}$. In examining the mode of labilization and quantum yields from previous work[1,2] and the work reported herein, we feel that some *qualitative* trends and predictions can be made.[29] We would summarize the mode of photoreaction of $Rh(en)_2XY^{n+}$ complexes with two qualitative and competitive series: (1) the ease of halo ligand labilization and (2) the ability of the halo ligand to labilize the ligand trans to itself. The efficiency of halo ligand labilization has been previously discussed by Zink,[27] and we agree with his conclusions. The ease of labilization is largest for the chloro ligand and decreases as Cl > Br > I. This series can be rationalized from two sets of complexes. The *cis*-dihalo complexes, *cis*-$Rh(en)_2X_2^+$, show decreasing quantum yields for X in going from chloro to iodo (X = Cl, $\phi = 0.43$ mol/einstein;[1] X = Br, $\phi = 0.37$ mol/einstein;[2] X = I, $\phi = 0.040$ mol/einstein). The *cis*-haloammine series also shows the same trend for ϕ_X (X = Cl, $\phi = 0.145$ mol/einstein;[1] X = Br, $\phi = 0.054$ mol/einstein;[2] X = I, $\phi = 0.006$ mol/einstein). In both of the series described above, X is trans to en and X occupies the axis populated by σ^*-electron density in the lowest excited state of the molecule.[28]

The ability to labilize the group trans to the halogen follows the opposite trend as described above, i.e., I ≫ Br > Cl. For the series *trans*-$Rh(en)_2X_2^+$, ϕ_X values are 0.061,[1] 0.062,[2] and 0.33 mol/einstein, respectively, for X = Cl, Br, and I. The insignificant difference in ϕ_X in going from X = Cl to X = Br is due to the increase in trans-directing ability of Br coupled with the decrease in lability of Br vs. Cl. The large quantum yield for loss of I^- from *trans*-$Rh(en)_2I_2^+$ indicates that a substantial increase in trans-labilizing ability of I is more than offsetting the reduced lability described above. This trend is again borne out in the haloammine series where loss of NH_3 from *trans*-$R(en)_2(NH_3)X^{2+}$ follows the order X = I ($\phi_{NH_3} = 0.60$ mol/einstein) > X = Br ($\phi_{NH_3} = 0.16$ mol/einstein[2]) > X = Cl ($\phi_{NH_3} < 10^{-3}$ mol/einstein[1]). Once again, as above, the labilized ligand lies on the axis populated by σ^*-electron density in the lowest excited state of the molecule.[29]

The two qualitative trends described above can be arrived at for the bis(ethylenediamine) complexes of Rh(III) mainly because of the photoinertness of the Rh(III)–en bond. If these trends are in fact correct, one prediction can be made. Photolysis of *cis*-$Rh(NH_3)_4I_2^+$ should lead to facile labilization of NH_3. If this prediction is true, this complex would be the only *cis*-$RhA_4X_2^+$ system where the predominant mode of ligand loss was not the halogen.

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Registry No. *trans*-$[Rh(en)_2I_2]I$, 39561-35-8; *trans*-$[Rh(en)_2(H_2O)I](ClO_4)_2$, 55683-60-8; *trans*-$[Rh(en)_2(NH_3)I]I_2$, 65761-15-1; *cis*-$[Rh(en)_2I_2]I$, 53368-51-7; *cis*-$[Rh(en)_2(NH_3)I]I_2$, 74112-69-9; *cis*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$, 70223-45-9; *cis*-$[Rh(en)_2(NH_3)I](S_2O_6)$, 74112-71-3; *trans*-$[Rh(en)_2(NH_3)I](S_2O_6)$, 74081-96-2; *trans*-$[Rh(en)_2I_2](ClO_4)$, 55683-57-3; *cis*-$[Rh(en)_2I_2](ClO_4)$, 74081-97-3; *trans*-$[Rh(en)_2Cl_2](NO_3)$, 15529-88-1; $[Rh(en)_2(oxalato)](ClO_4)$, 52729-89-2.

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(24) At 50 °C, cis/trans mixtures of $Rh(en)_2(NH_3)(H_2O)^{3+}$ are observed for the photolysis of *cis*- or *trans*-$Rh(en)_2(NH_3)H_2O^{3+}$ indicating that the barrier to pseudorotation is accessible within the lifetime of the triplet, five-coordinate fragment: Clark, S. F.; Petersen, J. D., submitted for publication in *Inorg. Chem.*

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(29) We stress the word qualitative since the quantum yields depend upon the rate constant for M–L bond breaking from the excited state as well as the lifetime of the excited state. Lifetime data on the excited states, under photochemically significant conditions, are currently unavailable.