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Pressure Effects on Photoisomerization/Photosubstitution Reactions of the Rhodium(III) Complexes *cis*- and *trans*-$Rh(NH_3)_4XY^{n+}$ (X = Cl, Br; Y = X, H_2O)

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The effect of pressure up to 200 MPa was studied on the photoisomerization and/or photoaquation reactions of a series of tetraamminerhodium(III) complexes, viz., *cis*- and *trans*-$Rh(NH_3)_4X_2^+$, *cis*-$Rh(NH_3)_4(H_2O)X^{2+}$ (X = Cl, Br), and *trans*-$Rh(NH_3)_4(OH)Cl^+$. The volumes of activation were found to range between −8.8 and +9.3 $cm^3\ mol^{-1}$ for the different reactions, but most systems displayed relatively small absolute values. Partial molar volumes were measured for almost all reactant and product species in their ground state, and from these, reaction volume profiles were calculated. These data are discussed in terms of proposed mechanisms for the excited-state substitution reactions, and it is concluded that the activation volumes observed are consistent with a dissociative pathway for ligand labilization.

Introduction

The cis/trans photoisomerization reactions of transition-metal complexes in general, and those of rhodium(III) in particular, have received significant attention during recent years.[2-7] Several closely related theoretical models[6,8-10] have been proposed to account for the stereochemical rearrangements observed when hexacoordinate d^6 complexes are subjected to ligand field (LF) excitation. The key premise of these models is that ligand dissociation from the hexacoordinate excited state occurs prior to stereorearrangement. The product stereochemistries are then principally interpreted in terms of the comparative energies of the resulting square-pyramidal (SPY), five-coordinate apical and basal intermediates (A* and B*) as shown in Scheme I. These intermediates were proposed to be triplet excited states capable of isomerization on a time scale competitive with deactivation followed by trapping of a solvent molecule.

An important aspect of these models is that the stronger σ-donor ligand should show a strong site preference for the basal position in the SPY intermediate. In this way, various cis to trans as well as trans to cis photoisomerization processes could be predicted.[7,11] In addition, recent observations[12] on the photoisomerization of *cis*- to *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ indicate that water exchange occurs with the same quantum yield as the isomerization, consistent with the model's requirement that ligand photolabilization precede isomerization of the coordination sphere. The success of these models provides strong circumstantial evidence in support of a limiting dissociative mechanism for the LF photosubstitution reactions of d^6 complexes. Notably, the dissociative model postulates a common intermediate, viz., the five-coordinate apical $Rh(NH_3)_4X^{2+}$ excited-state species for each of the photoreactions (1)-(3) (X = Cl, Br).

$$trans\text{-}Rh(NH_3)_4X_2^+ + H_2O \xrightarrow{h\nu} trans\text{-}Rh(NH_3)_4(H_2O)X^{2+} + X^- \quad (1)$$

$$cis\text{-}Rh(NH_3)_4X_2^+ + H_2O \xrightarrow{h\nu} trans\text{-}Rh(NH_3)_4(H_2O)X^{2+} + X^- \quad (2)$$

$$cis\text{-}Rh(NH_3)_4(H_2O)X^{2+} \xrightarrow{h\nu} trans\text{-}Rh(NH_3)_4(H_2O)X^{2+} \quad (3)$$

Recent studies on the effect of pressure on some typical photosubstitution reactions of Cr(III),[13-15] Rh(III),[16] and Co(III)[17] complexes have provided some interesting mechanistic insight. In this context the present article is concerned with the effect of pressure on some typical photoisomerization/photoaquation reactions of disubstituted tetraamminerhodium(III) complexes in an effort to determine the volumes of activation for such processes. In addition, a series of partial molar volumes were measured to enable the construction of reaction volume profiles[18] for model limiting reaction mechanisms. Although the expansion of the reactant molecules during excitation[19,20] complicates the interpretation of the volumes of activation in terms of these volume profiles, the data do provide guidelines as to how volume changes should be related to the nature of the intimate reaction mechanism.

Experimental Section

Materials. The tetraamminerhodium(III) complexes *cis*-$[Rh(NH_3)_4Cl_2]Cl\cdot{}^1/_2H_2O$,[21] *cis*-$[Rh(NH_3)_4Br_2]Br\cdot{}^1/_2H_2O$,[21] *trans*-$[Rh(NH_3)_4Cl_2]Cl$,[22] *trans*-$[Rh(NH_3)_4Br_2]Br$,[22] *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)Cl]S_2O_6$,[6] *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)Br]S_2O_6$,[6] and *cis*-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$[23] were all prepared and recrystallized according to published procedures. UV-visible spectra were in agreement with earlier published data. All other chemicals were of analytical reagent grade, and doubly distilled water was used throughout the investigation.

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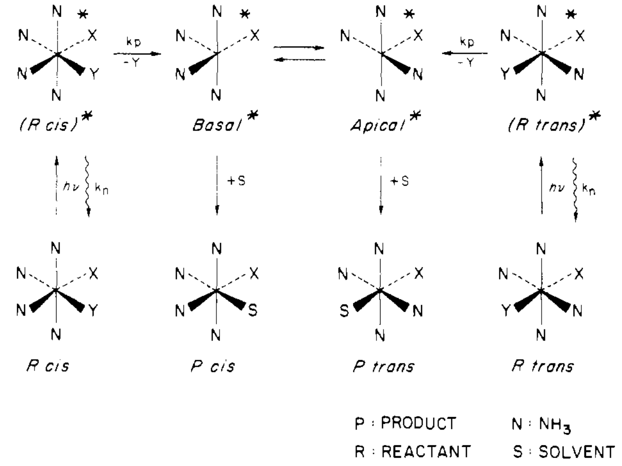
Scheme I



Instrumentation. The photolysis was carried out in a thermostated (25.0 ± 0.2 °C) high-pressure cell[24] situated inside a black metal compartment placed on top of a magnetic stirrer. Three-milliliter (determined at ambient pressure) quantities of test solution were irradiated with use of a "pillbox" cell[25] and vigorously stirred during the photolysis with the aid of a 2 × 6 mm Teflon-coated magnetic bar. Light at 366, 405, or 436 nm was selected from a high-pressure mercury lamp (Osram HBO 100/2) using Oriel interference filters. The light beam was focused with the aid of quartz lenses through a pinhole into the high-pressure cell.

A PRA TX7 electronic feedback system, coupled to a PRA M302 lamp power supply, was employed to control the light flux by monitoring a small constant fraction of the light beam split off with a quartz plate. The light transmitted through the photolysis cell was monitored with a calibrated PIN 25 photodiode[26] connected to a dc amplifier and a strip chart recorder.

UV-visible spectra were recorded on a Perkin-Elmer 555 spectrophotometer. pH measurements were performed on a Radiometer Model PHM 64 instrument using a combination glass electrode. Partial molar volumes were determined from density measurements on a Paar DMA 02/C digital precision density apparatus at 25.00 ± 0.002 °C.

Calculation of Quantum Yields. Photolysis experiments were performed at five different pressures (including ambient or very close to ambient, i.e. <1 MPa, conditions). Each of the reactions under consideration was studied in a series of experiments in which the degree of photochemical conversion was kept almost constant while the applied pressure was varied. Such a series always included an experiment under ambient conditions. The degree of conversion was determined from UV-visible spectrophotometric measurements at ambient pressure and from pH measurements for reactions that include the release of ammonia. In general, complex concentrations were in the range 10^{-3}–10^{-2} M, and calculations were performed from photochemical conversions between 5 and 25%. The number of moles converted during photolysis under pressure was expressed relative to the number of moles converted under ambient conditions, after corrections for any difference in the number of einsteins absorbed had been made. The quantum yields for a certain photoreaction at elevated pressure were thus expressed relative to the quantum yield at normal pressure, for which the data have already been measured and published.[6,7,27] This calculation procedure makes inner-filter effect corrections unnecessary.

Results

Two types of data were measured in this study. First, the partial molar volumes for the series of cis and trans isomers of the disubstituted tetraamminerhodium(III) complexes and their photolysis products were determined. Such data reveal the pattern of the influence of various substituents and their stereochemical orientation on the partial molar volumes and enable the calculation of overall reaction volume data. The experimental results are summarized in Table I along with the partial molar volumes of the ionic species calculated according to standard procedures.[28] It is seen that the values for *cis*- and *trans*-$Rh(NH_3)_4(OH_2)Cl^{2+}$ are almost equal and very close to the value of 82.3 ± 0.5 cm³ mol⁻¹ reported[29] for the $Rh(NH_3)_5Cl^{2+}$ species. A similar agreement exists for the corresponding bromo complexes, whose values also agree very well with the value of 91.5 ± 1.6 cm³ mol⁻¹ reported[29] for the $Rh(NH_3)_5Br^{2+}$ species. These tendencies illustrate the consistency of the data in Table I.

Table I. Partial Molar Volume Data for Some Disubstituted Tetraamminerhodium(III) Complexes in Aqueous Solution at 25 °C

complex	partial molar vol, cm³ mol⁻¹	
	complex	cation[a]
cis-$[Rh(NH_3)_4Cl_2]Cl$	108.9 ± 0.3	87.1 ± 0.3[b]
trans-$[Rh(NH_3)_4Cl_2]Cl$	129.4 ± 0.4	107.6 ± 0.4[b]
cis-$[Rh(NH_3)_4(OH_2)Cl]S_2O_6$	149.2 ± 0.4	83.0 ± 1.5[c]
trans-$[Rh(NH_3)_4(OH_2)Cl]S_2O_6$	151.7 ± 1.0	85.5 ± 1.8[c]
cis-$[Rh(NH_3)_4Br_2]Br$	125.5 ± 0.8	96.1 ± 0.8[d]
trans-$[Rh(NH_3)_4Br_2]Br$	142.2 ± 1.0	112.8 ± 1.0[d]
cis-$[Rh(NH_3)_4(OH_2)Br]S_2O_6$	156.8 ± 0.8	90.6 ± 1.7[c]
trans-$[Rh(NH_3)_4(OH_2)Br]S_2O_6$	157.3 ± 0.9	91.1 ± 1.7[c]

[a] Single-ion volumes calculated on the basis that $\overline{V}(H^+) = -4.5$ cm³ mol⁻¹.[28] [b] $\overline{V}(Cl^-) = 21.8$ cm³ mol⁻¹.[28] [c] $\overline{V}(S_2O_6^{2-}) = 66.2 \pm 1.5$ cm³ mol⁻¹, determined in this study. [d] $\overline{V}(Br^-) = 29.4$ cm³ mol⁻¹.[28]

Second, the pressure dependencies of the photochemical quantum yields for a series of ligand substitution processes, of which some are stereoretentive and others stereomobile, were determined, and the results are summarized in Table II. In addition, the effect of pressure on the course of the photochemical reactions under consideration was also studied, and the findings can be summarized as follows.

***cis*- and *trans*-$Rh(NH_3)_4Cl_2^+$ and *cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$.** Ligand field photolyses of these three complex ions in dilute acidic aqueous solution at ambient pressure are known to give the common principal product *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$.[6,27] Photolysis at elevated pressure was performed under experimental conditions similar to those described before.[6] A solution initially *cis*-$Rh(NH_3)_4Cl_2^+$ in 10^{-2} M $HClO_4$ exhibited, after extensive irradiation under 200 MPa pressure, an electronic spectrum with λ_{max} (ϵ) at 389 (54.5) and 284 nm (112.3 M⁻¹ cm⁻¹), which is within experimental uncertainties identical with that reported[6] for *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$, viz., λ_{max} (ϵ) = 389 (55) and 284 nm (114 M⁻¹ cm⁻¹). A similar result was obtained for the photolysis of *trans*-$Rh(NH_3)_4Cl_2^+$ and *cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$, indicating that the product stereochemistry is not influenced by the applied pressure. During extensive irradiation of *cis*-$Rh(NH_3)_4Cl_2^+$ under 200 MPa, it was also observed that the isosbestic points at 268 and 292 nm were maintained throughout, again in good agreement with the behavior found[6] at ambient pressure. These observations indicate that no intermediates or any secondary thermal or photochemical reactions are induced by the elevated pressure.

cis-$Rh(NH_3)_4Cl_2^+$ is the thermally most reactive species of the three complexes mentioned. However, even for this complex the very minor dark thermal reaction is insignificant at elevated pressures. Very small spectral changes were observed for solutions of *cis*-$Rh(NH_3)_4Cl_2^+$ in diluted $HClO_4$ kept under 100 MPa in the dark for up to 4 h.

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Table II. Pressure Dependence of the Photochemical Quantum Yield for the Ligand Field Photolysis of Some Disubstituted Tetraamminerhodium(III) Complexes in Aqueous Solution at 25 °C

complex	principal product	λ_{irr}, nm	press., MPa	no. of expts	quantum yield, mol/einstein
cis-$Rh(NH_3)_4Cl_2^+$ [a]	*trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$	366	1		0.34[e]
			50	5	0.37 ± 0.01
			100	6	0.38 ± 0.02
			150	8	0.38 ± 0.01
			200	9	0.42 ± 0.01
cis-$Rh(NH_3)_4(H_2O)Cl^{2+}$ [b]	*trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$	366	1		0.46[e]
			50	4	0.45 ± 0.02
			100	3	0.47 ± 0.02
			150	3	0.46 ± 0.02
			200	4	0.46 ± 0.02
cis-$Rh(NH_3)_4Br_2^+$ [b]	*trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$	366	1		0.24[e]
			50	4	0.25 ± 0.01
			100	5	0.26 ± 0.01
			150	4	0.26 ± 0.01
			200	5	0.28 ± 0.01
cis-$Rh(NH_3)_4Br_2^+$ [b]	"$Rh(NH_3)_3(H_2O)Br_2^+$"[d]	366	1		0.064[e]
			50	4	0.053 ± 0.002
			100	5	0.044 ± 0.004
			150	4	0.033 ± 0.004
			200	5	0.033 ± 0.004
cis-$Rh(NH_3)_4(H_2O)Br^{2+}$ [b]	*trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$	366	1		0.50[e]
			50	4	0.51 ± 0.02
			100	3	0.51 ± 0.02
			150	3	0.52 ± 0.02
			200	5	0.52 ± 0.02
trans-$Rh(NH_3)_4Cl_2^+$ [b]	*trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$	405	1		0.13[f]
			50	3	0.13 ± 0.01
			100	4	0.12 ± 0.01
			150	4	0.11 ± 0.01
			200	4	0.11 ± 0.01
trans-$Rh(NH_3)_4Br_2^+$ [b]	*trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$	436	1		0.10[e]
			50	3	0.10 ± 0.01
			100	4	0.085 ± 0.02
			150	3	0.085 ± 0.01
			200	3	0.077 ± 0.02
trans-$Rh(NH_3)_4(OH)Cl^+$ [c]	*cis*-$Rh(NH_3)_4(OH)_2^+$	366	1		0.21[g]
			50	3	0.25 ± 0.02
			100	3	0.27 ± 0.02
			150	3	0.33 ± 0.02
			200	4	0.35 ± 0.02

[a] Reaction medium is 10^{-2}–10^{-3} M $HClO_4$. [b] Reaction medium is 10^{-3} M $HClO_4$. [c] Reaction medium is 10^{-1} M NaOH. [d] Exact configuration is unknown.[6] [e] Taken from ref 6—see Experimental Section. [f] Taken from ref 27—see Experimental Section. [g] Taken from ref 7—see Experimental Section.

The quantum yields for the principal photochemical reactions of the three mentioned chloro complexes were evaluated from spectral measurements at five to six wavelengths and are presented in Table II as a function of pressure.

The aquation of ammonia is an alternative photochemical reaction path for the mentioned complexes. However, pressure was not found to promote this reaction significantly. The photochemical quantum yields for NH_3 labilization, determined from pH measurements, at 200 MPa are $\Phi \sim 0.002$ mol/einstein for *cis*-$Rh(NH_3)_4Cl_2^+$, $\Phi \sim 0.003$ mol/einstein for *cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$, and $\Phi < 0.01$ mol/einstein for *trans*-$Rh(NH_3)_4Cl_2^+$.

***cis*- and *trans*-$Rh(NH_3)_4Br_2^+$ and *cis*-$Rh(NH_3)_4(H_2O)Br^{2+}$.** The photolysis of the bromo complexes was performed under experimental conditions similar to those for the chloro analogues. A 4 × 10^{-3} M *cis*-$Rh(NH_3)_4(H_2O)Br^{2+}$ solution in 10^{-3} M $HClO_4$ was irradiated extensively at 200 MPa giving a product spectrum λ_{max} (ϵ) = 406 (63.6) and λ_{sh} (ϵ) = 466 nm (40.9 M^{-1} cm^{-1}) virtually identical with that reported[6] for the photolysis at ambient pressure. The pH of the solution changed from 2.98 to 3.01 during the irradiation, in agreement with earlier observations.[6] These results once again illustrate that pressure does not change the course of the photolysis process nor does it favor any secondary reactions. The *cis*-$Rh(NH_3)_4Br_2^+$ species undergoes two photoreactions: bromide aquation accompanied by isomerization to produce *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$ and ammonia aquation resulting in the formation of $Rh(NH_3)_3(H_2O)Br_2^+$ of unknown stereochemistry.[6] The quantum yield for the latter process was determined from pH measurements, whereas the quantum yield for the former process was estimated from spectral measurements.[6] *trans*-$Rh(NH_3)_4Br_2^+$ simply undergoes photolabilization of Br^- to give the *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$ product.

***trans*-$Rh(NH_3)_4(OH)Cl^+$.** This species was prepared in solution by dissolving *trans*-$[Rh(NH_3)_4(H_2O)Cl]S_2O_6$ in 0.1 M NaOH. Irradiation of the solution led to the *cis*-$Rh(NH_3)_4(OH)_2^+$ product.[7] The quantum yield of the process was estimated from spectral measurements.

Pressure Dependence of Quantum Yields. The data in Table II summarize the effect of pressure on the measured quantum yields for the seven studied reactions. The photoisomerization quantum yields for *cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ and *cis*-$Rh(NH_3)_4(H_2O)Br^{2+}$ are hardly influenced by pressure over the range studied. The application of pressure, however, significantly decreases the quantum yields for the photoreactions of *trans*-$Rh(NH_3)_4X_2^+$ to give *trans*-$Rh(NH_3)_4(H_2O)X^{2+}$ (X = Cl, Br) and of *cis*-$Rh(NH_3)_4Br_2^+$ to give $Rh(NH_3)_3(H_2O)Br_2^+$. The opposite effect, namely a significant increase in the quantum yields with increasing pressure, is observed for the photoaquation/isomerization reactions of *cis*-$Rh(NH_3)_4Cl_2^+$, *cis*-$Rh(NH_3)_4Br_2^+$, and *trans*-$Rh(NH_3)_4(OH)Cl^+$.

Table III. Volumes of Activation for the Photochemical Reactions of Some Disubstituted Tetraamminerhodium(III) Complexes in Aqueous Solution at 25 °C

complex	principal product	$\Delta V_p^{\ddagger}$,[a] $cm^3\ mol^{-1}$
cis-$Rh(NH_3)_4Cl_2^+$	*trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$	-3.5 ± 0.3
cis-$Rh(NH_3)_4(H_2O)Cl^{2+}$	*trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$	0.0 ± 0.4
cis-$Rh(NH_3)_4Br_2^+$	*trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$	-2.3 ± 0.3
cis-$Rh(NH_3)_4Br_2^+$	"$Rh(NH_3)_3(H_2O)Br_2^+$"	$+9.3 \pm 0.8$
cis-$Rh(NH_3)_4(H_2O)Br^{2+}$	*trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$	-1.0 ± 0.4
trans-$Rh(NH_3)_4Cl_2^+$	*trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$	$+2.8 \pm 0.6$
trans-$Rh(NH_3)_4Br_2^+$	*trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$	$+2.9 \pm 0.7$
trans-$Rh(NH_3)_4(OH)Cl^+$	*cis*-$Rh(NH_3)_4(OH)_2^+$	-8.8 ± 0.7

[a] Standard deviations calculated from least-squares analysis.

The photochemical quantum yield is the ratio between the primary photochemical reaction step and all processes that deactivate the photoreactive state:

$$\Phi = \frac{k_p}{k_p + k_n + k_r} \sim \frac{k_p}{k_p + k_n} \tag{4}$$

where k_p is the rate constant for the primary photoreaction, k_n is the rate constant for the nonradiative deactivation processes, and k_r is the rate constant for radiative decay, which is known to be orders of magnitude smaller than k_p and k_n for these types of Rh(III) complexes.[30] These relationships are valid if internal conversion and intersystem crossing from states formed by initial excitation to the reactive excited state occur with efficiency near unity and if deactivation processes are slow relative to vibrational relaxation and thermalization of the relevant state. It has been shown for several Rh(III) complexes and assumed for others that initial ligand field excitation is followed by efficient interconversion to the lowest energy excited state, a LF triplet state, from where the photoreaction originates.[3,30]

The volume of activation for a chemical reaction can be estimated from[18]

$$\Delta V^{\ddagger} = -RT\left(\frac{\partial \ln k}{\partial P}\right)_T \tag{5}$$

Equation 4 can be rewritten in the form

$$k_p = k_n\left(\frac{\Phi}{1 - \Phi}\right) \tag{6}$$

which on differentiation with respect to P results in

$$\left(\frac{\partial \ln\left(\frac{\Phi}{1 - \Phi}\right)}{\partial P}\right)_T = \left(\frac{\partial \ln k_p}{\partial P}\right)_T - \left(\frac{\partial \ln k_n}{\partial P}\right)_T \tag{7}$$

It can be assumed (see Discussion) that the pressure dependence of k_n is close to zero, such that eq 7 simplifies to

$$\left(\frac{\partial \ln\left(\frac{\Phi}{1 - \Phi}\right)}{\partial P}\right)_T = \left(\frac{\partial \ln k_p}{\partial P}\right)_T = -\frac{\Delta V_p^{\ddagger}}{RT} \tag{8}$$

which on integration results in

$$\ln\left(\frac{\Phi}{1 - \Phi}\right) = -\frac{(\Delta V_p^{\ddagger})P}{RT} + \text{constant} \tag{9}$$

The data in Table II were plotted according to eq 9, and $\Delta V_p^{\ddagger}$ (Table III) was estimated from the slope of such plots. Within the experimental error limits, no significant curvature could be detected in these plots, suggesting that $\Delta V_p^{\ddagger}$ is independent of pressure up to 200 MPa.

Discussion

Application of pressure to the systems under investigation might have been expected to influence two parameters, the stereochemical course of the reactions and/or the absolute quantum yields. Although some quantum yield variations were indeed seen, reaction stereochemistries were not affected. Thus, since only one photoproduct isomer was detected for the major reaction of each complex studied, the applied pressures did not change the reaction pathway free energies sufficiently to generate measurable concentrations of the alternative isomer. In the context of the reaction model described in Scheme I, product stereochemistries would be determined by the relative energies of the pentacoordinate species A* and B*. These might be expected to have similar partial molar volumes; thus, the equilibrium between them is little affected by pressure.

In the context of the same model, the quantum yields for photoisomerization are determined by the photosubstitution yields Φ, which in turn are dependent on the competition of ligand labilization (k_p) and nonradiative deactivation (k_n) from the LF excited state of the hexacoordinate complexes (eq 4). It follows that the pressure dependencies of k_p and k_n will determine the pressure dependence of Φ. Recent measurements[16,31] of pressure effects on luminescence lifetimes indicate that nonradiative deactivation can be expected to be nearly insensitive to pressure ($\Delta V_n^{\ddagger} = 0 \pm 2$ $cm^3\ mol^{-1}$) for transition-metal complexes of this type. Thus the values for $\Delta V_p^{\ddagger}$ in Table III can be viewed as representing the approximate volumes of activation for ligand labilization from the hexacoordinate triplet state. Notably, $\Delta V_p^{\ddagger}$ falls into a narrow range (−3.5 to +2.9 $cm^3\ mol^{-1}$) for the photoisomerization/aquation of *cis*-$Rh(NH_3)_4X_2^+$, the photoisomerization of *cis*-$Rh(NH_3)_4(H_2O)X^{2+}$, and the photoaquation of *trans*-$Rh(NH_3)_4X_2^+$. However, further discussion of these data needs to be deferred until the reaction volume calculations are considered.

A remarkable feature of the data in Table I is the marked differences in the partial molar volumes of the *cis*- and *trans*-dihalo isomers, the trans complexes being the larger by 20 and 17 $cm^3\ mol^{-1}$ for X = Cl and Br, respectively. This can be ascribed to differences in the microscopic charge distributions of the two types of structures resulting in stronger specific solvation accompanied by a decrease in volume of the less symmetrical cis isomers. However, this effect is not observed for the aquohalo complexes where the cis and trans species have similar volumes very close to those for the corresponding $Rh(NH_3)_5X^{2+}$ species.[29] The latter tendency confirms the good agreement for analogous complexes of identical charges usually observed in partial molar volume data.[28,32] (The partial molar volume for the $Rh(NH_3)_3(H_2O)Br_2^+$ species could not be determined from density measurements and was assumed to be close to the value for *cis*-$Rh(NH_3)_4Br_2^+$, in line with the above tendencies.) The overall volume change $\Delta\bar{V}$ for the various reactions was calculated from the relationship

$$\Delta\bar{V} = \sum\bar{V}(\text{products}) - \sum\bar{V}(\text{reagents}) \tag{10}$$

In a similar manner the volume changes $\Delta\bar{V}_D$ for the hypothetical dissociation reactions (eq 11 and 12) were calculated

$$MX_2^+ \rightarrow MX^{2+} + X^- \tag{11}$$

$$MX(H_2O)^{2+} \rightarrow MX^{2+} + H_2O \tag{12}$$

$$M = Rh(NH_3)_4$$

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Table IV. Summary of Estimated Volume Changes for Various Photoreactions of Some Disubstituted Tetraamminerhodium(III) Complexes[a] at 25 °C

overall reacn	$\Delta\overline{V}^b$	$\Delta\overline{V}_D{}^c$	$\Delta\overline{V}_p{}^{\ddagger\,d}$
$cis\text{-}MCl_2{}^+ + H_2O \xrightarrow{h\nu} trans\text{-}M(H_2O)Cl^{2+} + Cl^-$	+2.2 ± 1.8	+17.0 ± 0.6[e]	−3.5 ± 0.3
$cis\text{-}MBr_2{}^+ + H_2O \xrightarrow{h\nu} trans\text{-}M(H_2O)Br^{2+} + Br^-$	+6.4 ± 1.9	+24.8 ± 1.8[f]	−2.3 ± 0.3
$\xrightarrow[H^+]{h\nu}$ "$Rh(NH_3)_3(H_2O)Br_2{}^+$" $+ NH_4{}^+$	+0.7[g]	+24.8[h]	+9.3 ± 0.8
$cis\text{-}M(H_2O)Cl^{2+} \xrightarrow{h\nu} trans\text{-}M(H_2O)Cl^{2+}$	+2.5 ± 2.3	+17.3 ± 1.6[e]	0.0 ± 0.4
$cis\text{-}M(H_2O)Br^{2+} \xrightarrow{h\nu} trans\text{-}M(H_2O)Br^{2+}$	+0.5 ± 2.4	+18.9 ± 2.3[f]	−1.0 ± 0.4
$trans\text{-}MCl_2{}^+ + H_2O \xrightarrow{h\nu} trans\text{-}M(H_2O)Cl^{2+} + Cl^-$	−18.3 ± 1.8	−3.5 ± 0.6[e]	+2.8 ± 0.6
$trans\text{-}MBr_2{}^+ + H_2O \xrightarrow{h\nu} trans\text{-}M(H_2O)Br^{2+} + Br^-$	−10.3 ± 2.0	+8.1 ± 1.9[f]	+2.9 ± 0.7

[a] M = $Rh(NH_3)_4$; all volume quantities are quoted as $cm^3\ mol^{-1}$. [b] Overall reaction volume calculated from partial molar volumes of ground-state molecules (data from Table I and ref 28). [c] Estimated volume change for a dissociative reaction mode—see Discussion. [d] Taken from Table III. [e] Assume $\overline{V}(Rh(NH_3)_4Cl^{2+}) = \overline{V}(Rh(NH_3)_5Cl^{2+}) = 82.3 \pm 0.5$.[29] [f] Assume $\overline{V}(Rh(NH_3)_4Br^{2+}) = \overline{V}(Rh(NH_3)_5Br^{2+}) = 91.5 \pm 1.6$.[29] [g] Assume $\overline{V}$("$Rh(NH_3)_3(H_2O)Br_2{}^+$") = $\overline{V}(Rh(NH_3)_4Br_2{}^+)$—see Discussion. $\overline{V}(NH_4{}^+) = 14.2$;[28] $\overline{V}(H^+) = -4.5$.[28] [h] Assume $\overline{V}(Rh(NH_3)_3Br_2{}^+) = \overline{V}(cis\text{-}Rh(NH_3)_4Br_2{}^+)$; it is assumed that NH_3 is not protonated in the transition state of NH_3 labilization, given the absence of an acid dependence of quantum yields.

(Table IV). In this respect it is important to note that certain assumptions[33,34] (which have proved somewhat controversial;[35] see below) have been made regarding the partial molar volumes of the five-coordinate intermediates, namely that $\overline{V}(Rh(NH_3)_4X^{2+}) = \overline{V}(Rh(NH_3)_5X^{2+})$. (An alternative assumption that $\overline{V}$ of the pentacoordinate species is the same as that of the $Rh(NH_3)_4(H_2O)X^{2+}$ ion with the analogous stereochemistry leads to $\Delta\overline{V}_D$ values that are quantitatively different but qualitatively indistinguishable from those listed.) Neither $\Delta\overline{V}_D$ nor $\Delta\overline{V}$ was calculated for the *trans*-$Rh(NH_3)_4(OH)Cl^+$ photoreaction owing to the lack of sufficient partial molar volume data.

Table IV also lists the $\Delta V_p{}^{\ddagger}$ values with those calculated for $\Delta\overline{V}$ and $\Delta\overline{V}_D$ for the purpose of comparison. Before such comparison is made, we will examine the relationship between $\Delta V_p{}^{\ddagger}$ and these parameters in the context of possible models for the photolabilization process. Ligand field excitation followed by intersystem crossing leads to a hexacoordinate triplet state, the species that undergoes deactivation to the ground state with the rate constant $k_n + k_r$ or reaction to products with the rate constant k_p (eq 13–15) (Y = X or H_2O,

$$MXY^{n+} \xrightarrow{h\nu} \rightarrow {}^3[MXY]^* \qquad (13)$$

$$^3[MXY^{n+}]^* \xrightarrow{k_n + k_r} MXY^{n+} \qquad (14)$$

$$H_2O + {}^3[MXY^{n+}]^* \xrightarrow{k_p} I \xrightarrow{\text{fast}} MX(H_2O)^{n+} + Y \qquad (15)$$

and I represents the intermediates of the rate-limiting k_p step). The activation parameter $\Delta V_p{}^{\ddagger}$ represents the differences between the volumes of the reactants, $\overline{V}(H_2O) + \overline{V}(^3[MXY^{n+}]^*)$, and of those species present at the transition state along the reaction coordinate of the k_p step leading to the intermediates I. The excited-state volume cannot be measured with current techniques; however, it was concluded in recent analyses of the vibrational structure of low-temperature electronic absorption and emission spectra of octahedral d^6 complexes, including $Rh(NH_3)_6{}^{3+}$, that the lowest LF triplet state has at least several metal–ligand bonds more than 0.1 Å longer than those of the ground state.[19,20] From this information and the $\overline{V}$ values of the ground-state ions, volume increases by as much as +10 $cm^3\ mol^{-1}$ can be estimated for such triplet excited states by using a simple spherical model.

Such bond lengthening would certainly be consistent with the $(t_{2g})^5(e_g)^1$ electronic configuration of the triplet state given the σ-antibonding character of the e_g orbital. Furthermore, the bond lengthening and corresponding bond weakening would be consistent with a dissociative mechanism for bond photolabilization as suggested in Scheme I. However, the increased bond lengths presumably would also open channels for associative attack of solvent as well. The question of how the excited-state expansion affects $\Delta V_p{}^{\ddagger}$ is difficult to assess. For example reaction might be expected to occur along triplet LF excited-state surfaces in such a way that the transition state of k_p is itself a LF triplet. In such a case, one might argue that similar bond expansion would also be evident at the transition state; thus, the volume changes seen in $\Delta V_p{}^{\ddagger}$ would parallel similar changes for ground-state mechanisms. Under such circumstances, the extent of volume change expected for a transition state where the leaving group is fully dissociated (and both fragments fully solvated) would be estimated by $\Delta\overline{V}_D$. For a limiting associative mechanism, $\Delta\overline{V}_A$ may be estimated as approximately −18 $cm^3\ mol^{-1}$ by making the key assumption that the heptacoordinate intermediate $MXY(H_2O)^{2+}$ would have the same volume as MXY^{n+}.

Further examination suggests that dissociation along a triplet-state reaction coordinate may not necessarily show the same volume changes as the ground-state $\Delta V_D{}^{\ddagger}$. Given that the expansion of the excited-state volume can be attributed to distortion of several bonds, one might expect some contraction of the other metal–ligand bonds as the excitation becomes channeled along the bond undergoing dissociation. This would tend to diminish the contribution of volume change to the free energy of activation especially for an early transition state. Furthermore, for an anionic leaving ligand, negative solvational contributions to $\Delta V_p{}^{\ddagger}$ due to charge creation may outweigh any resultant volume change from the initial contraction/expansion of metal–ligand bonds. The importance of solvation at the transition state has been demonstrated by pulse laser studies of $Rh(NH_3)_5Cl^{2+}$, which measured the marked dependence of the chloride substitution rates from the triplet LF state on the nature of the solvent medium.[36]

The contraction of the other metal–ligand bonds as one coordination site is opened might also suggest that a fully dissociated pentacoordinate intermediate in a LF triplet state, e.g. $^3[Rh(NH_3)_4X^{2+}]$, would have a partial molar volume very similar to that of an analogous hexacoordinate ion of the same

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electrostatic charge, e.g. $Rh(NH_3)_5X^{2+}$, in the ground state. If so, then $\Delta \bar{V}_D$ would overestimate the overall volume change of the step

$$^3[Rh(NH_3)_4XY^{n+}]^* \rightarrow {}^3[Rh(NH_3)_4X^{2+}]^* + Y \quad (16)$$

by the volume difference (i.e., the excitation-induced expansion) between the excited- and ground-state $Rh(NH_3)_4XY^{n+}$. A somewhat different situation might be expected for the case of a limiting associative mechanism. The expanded excited metal complex should be suited to accommodate the added ligand without substantial further expansion; hence, the assumption that $\bar{V}(^3[Rh(NH_3)XY^{n+}]^*) = \bar{V}(^3[Rh(NH_3)_4XY(H_2O)]^*)$ and the conclusion that the volume change should be -18 cm^3 mol^{-1} (i.e., $-\bar{V}(H_2O)$) for eq 17 would appear to be especially legitimate.

$$[Rh(NH_3)_4XY^{n+}]^* + H_2O \rightarrow [Rh(NH_3)_4XY(H_2O)^{n+}]^* \quad (17)$$

Recent pulse laser studies have succeeded in measuring the excited-state lifetimes of a number of the disubstituted tetraamminerhodium(III) ions in ambient aqueous solutions.[37] From these data and the assumption that the predominant photoreactions occur from the thermalized lowest energy LF excited state, values for k_p have been calculated for the ligand labilization from the hexacoordinate excited states. Notably, these values fall into the range $(2.5 \pm 0.7) \times 10^8$ s^{-1} for each of the *cis*-aquohalo and -dihalo complexes studied here. The cis complexes are roughly a factor of 3 more reactive than the *trans*-dihalo and -chlorohydroxo excited states and >1 order of magnitude more reactive than the analogous excited states of the halopentaammine complexes.[30] Such k_p values represent rate accelerations over the analogous ground-state reactions by as much as 14 orders of magnitude. Thus, given such relatively low free energies of activation, an early transition state might be expected along the k_p reaction coordinate regardless of mechanism. The small absolute $\Delta V_p^{\ddagger}$ values for X^- labilization and for H_2O labilization (as indicated in the photoisomerization of the *cis*-$Rh(NH_3)_4X(H_2O)^{2+}$ ions) are consistent with this conclusion.

In the context of an early transition-state hypothesis, the modest negative values for X^- aquation from [*cis*-$Rh(NH_3)_4X^{2+}$]* (X = Cl or Br) might be interpreted in terms of a dissociative mechanism where the solvent reorganization owing to charge creation dominates the volume changes in the early stages of the reaction. An alternative explanation would be that the volume changes reflect the early stages of nucleophilic attack by solvent on the excited-state species in an associative or interchange mechanism. We recognize that the $\Delta V_p^{\ddagger}$ values reported here for these two complexes do not allow one to differentiate between these two possibilities for the *cis*-dihalo or *cis*-aquohalo ions. However, the perponderance of results from excited-state kinetics and stereochemical studies and successful theoretical rationalizations of these point to a general mechanism of considerable dissociative character for the k_p step;[3] thus we favor the former explanation for these $\Delta V_p^{\ddagger}$ values. Notably, the slower (in terms of k_p) aquations of X^- from [*trans*-$Rh(NH_3)_4X_2^+$]* and of NH_3 from [*cis*-$Rh(NH_3)_4Br_2^+$]* each give significantly positive values of $\Delta V_p^{\ddagger}$, which are clearly inconsistent with a limiting associative mechanism regardless of how early the transition state may be. The particularly large positive value for the NH_3 aquation (+9.3 cm^3 mol^{-1}) is indicative of a later transition state than noted for Br^- labilization from the same complex plus the absence of negative volume contributions arising from charge creation.

The last entry in Table III represents the only example of a photochemical trans to cis isomerization that we investigated. A quite negative $\Delta V_p^{\ddagger}$ value was found. However, the interpretation of this result is complicated by the absence of any partial molar volume data, due to our inability to isolate pure samples of the hydroxy species suitable for density measurements. A further complication is that this reaction was studied in a medium of different ionic strength (0.1 M NaOH), which may have a significant influence on the volume data. Meaningful explanation must await obtaining the appropriate partial molar volume determinations.

In summary, while the volume data reported here do not provide a definitive description for the reaction mechanism of ligand substitution from Rh(III), these do indicate that, if a general mechanism is operable, it must be dissociative or dissociative interchange in character. Given other studies pointing to a dissociative mechanism, we conclude that the $\Delta V_p^{\ddagger}$ values reflect volume changes between the reactive excited state and a transition state occurring early along the reaction coordinate. For the *cis*-dihalo and -aquohalo complexes, which are the most reactive according to pulse laser kinetics studies, the transition state must be especially early, given the small $\Delta V_p^{\ddagger}$ values measured. The slower X^- labilization from the *trans*-$Rh(NH_3)_4X_2^+$ excited states and of NH_3 from [*cis*-$Rh(NH_3)_4Br_2^+$]* (a minor reaction pathway from this ion) all show much more positive values of $\Delta V_p^{\ddagger}$ consistent with increasing extent of bond dissociation at the transition state for these reactions. Similar conclusions have been drawn from the volume data for the halopentaammine photoreactions that will be reported elsewhere.[16]

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