

Figure 4. Potential energy profile for hydrogen motion in FHCN^- . Total F—C distance is fixed at 2.63 Å and $\text{C}\equiv\text{N}$ distance at 1.16 Å.

pense, the total F—C and $\text{C}\equiv\text{N}$ distances were held fixed at their optimized values of 2.63 and 1.16 Å, respectively, while the hydrogen position was varied. This appears to be a reasonable approximation since in the FHCl^- case the total F—Cl distance remained reasonably constant over a wide range of hydrogen positions. The results for FHCN^- , shown in Figure 4, are very different than those for FHCl^- . Although a true double minimum potential well is not observed, a second

"plateau" is seen corresponding roughly to $\text{F}^-\cdots\text{HCN}$ in addition to the true minimum corresponding roughly to $\text{FH}\cdots\text{CN}^-$. This result is quite reasonable in view of the more similar basicities of F^- and CN^- relative to those of the FHCl^- case.

Although the ab initio results for these systems do not show double minimum potential wells, this does not preclude the possibility that such a situation does in fact exist in the species observed under argon matrix isolation conditions. In that medium a strongly polarizing alkali-metal cation is present which may dramatically alter the potential surface, giving rise to a double minimum potential well. The fact that two different types of anions are not reported for FHCN^- may then simply be a result of a very low barrier between the minima produced.

Conclusion

Hydrogen bond strengths in five bihalide ions have been accurately established from ion cyclotron resonance halide-exchange equilibria. In addition, a proposed correlation between hydrogen bond strength and frequency shift of the hydrogen bond stretching motion relative to that in the free halogen acid has allowed prediction of a further four hydrogen bond strengths. With use of these data and empirical correlations, an additional three bihalide ion hydrogen bond strengths are proposed. These values allow us to suggest future directions for the synthesis of new bihalide ion species by using the argon matrix isolation salt-molecule technique. Lastly, ab initio calculations on the geometry and energetics of bihalide species have provided some insight into the nature of the potential energy surface for hydrogen bond motion.

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Pressure Effects on the Photophysical and Photochemical Properties of the Rhodium(III) Ion $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ in Nonaqueous Solvents

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The effect of pressure was studied for the photosolvolytic reactions of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ in formamide, dimethylformamide, and dimethyl sulfoxide. The apparent volumes of activation for the chloride substitution quantum yields are -4.6 ± 0.7 and $-7.8 \pm 1.8 \text{ cm}^3 \text{ mol}^{-1}$ in FMA and Me_2SO , respectively. The corresponding values for the ammonia substitution quantum yields are $+4.2 \pm 0.9$, $+4.4 \pm 0.9$, and $+6.3 \pm 0.9 \text{ cm}^3 \text{ mol}^{-1}$ in FMA, Me_2SO , and DMF, respectively. The pressure dependence of the luminescence lifetimes was studied under comparable conditions, and the volumes of activation for τ^{-1} are -0.3 ± 0.4 , -1 ± 1 , and $+1.3 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$ in FMA, Me_2SO , and DMF, respectively. These data enable the estimate of the volumes of activation for the individual ligand field excited-state deactivation processes, Cl^- labilization, NH_3 labilization, and nonradiative deactivation, from which the effect of the solvent can be deduced. Partial molar volume measurements and volume profile diagrams are used to discuss the intimate nature of the photosolvolytic processes.

Introduction

A recent article from these laboratories³ reported the effects of pressure on the photochemical and photophysical properties

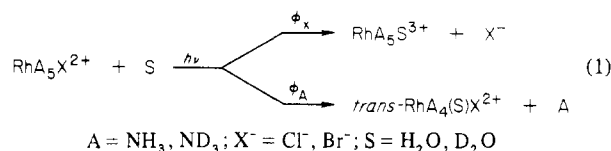
of the rhodium(III) complexes $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ and $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ and the perdeuterio analogues in aqueous solution. Analysis of the pressure effects on the luminescence lifetimes and the photoreaction quantum yields allowed the estimation of the volumes of activation (ΔV^\ddagger) for the individual deactivation processes of the lowest energy ligand field excited states (LEES). The ΔV^\ddagger values for the ligand labilization pathways from the LEES, when interpreted in terms of hypothetical

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reaction volume profiles, were concluded to be consistent with a dissociative mechanism for the photoaquation reactions indicated in eq 1.



In an earlier article from one of these laboratories,⁴ dramatic solvent effects on the relative importance of the two photolabilization pathways (eq 1) for the LF irradiation of the Rh(NH₃)₅Cl²⁺ ion were reported. For example, in aqueous (H₂O) or formamide (FMA) solutions, the major photo-reaction pathway is chloride labilization while in methanol, dimethyl sulfoxide (Me₂SO), or dimethylformamide (DMF) solutions, NH₃ labilization predominates. The quantum yields (ϕ_X , ϕ_A) for these reactions were determined as were the excited-state lifetimes (τ) under the same conditions, and these data were analyzed to give the rate constants for the chloride and the ammine labilization (k_{Cl} and k_{NH_3}) from the LEES as well as for nonradiative deactivation k_n . While all of these rates are solvent dependent, the parameter most sensitive to the medium is k_{Cl} , which changes by several orders of magnitude. In some cases k_{Cl} is much larger than k_{NH_3} (thus making Cl⁻ photosubstitution predominant), but in other cases it is much smaller than k_{NH_3} . In the present investigation the pressure effects on both the photolabilization quantum yields and the photoluminescence lifetimes are examined in the solvents FMA, DMF, and Me₂SO. Comparison of the ΔV^\ddagger values obtained is made to those found in aqueous solution.

Experimental Section

Materials. The complexes [Rh(NH₃)₅Cl](ClO₄)₂,⁵ [Rh(NH₃)₅S](ClO₄)₃ (S = FMA, DMF, Me₂SO),^{4,6} and *trans*-[Rh(NH₃)₄(S)Cl](ClO₄)₂ (S = DMF, Me₂SO)⁴ were all prepared and recrystallized according to published procedures. Chemical analyses⁷ and UV-visible absorption spectra were within experimental error limits of the theoretically expected values and those reported elsewhere,^{4,6} respectively. The preparation of the complex *trans*-[Rh(NH₃)₄(FMA)Cl](ClO₄)₂ had not been described before, and this compound was synthesized as follows: A 0.341-g (1.0 mmol) portion of *trans*-[Rh(NH₃)₄Cl₂](ClO₄)₂ was dissolved in 1 mL of FMA and a 0.22-g (1.05 mmol) quantity of AgClO₄ was added. The mixture was heated at 70 °C for 2 h during which time a gray precipitate formed, mainly consisting of AgCl. The solution was filtered, the yellow filtrate solution was diluted with ca. 5 mL of H₂O and 3 mL of EtOH, and the resultant mixture was then cooled in ice. The perchlorate salt of the complex was precipitated via the slow addition of HClO₄ to the ice-cooled solution to avoid the hydrolysis of the coordinated FMA. The solution was allowed to stand in ice for 4 h after which the light yellow precipitate was filtered off and then washed with EtOH and ether. The product was recrystallized twice from FMA in the same manner as described above. The UV-visible spectrum in FMA exhibited a maximum at 386 nm ($\epsilon = 69.3 \text{ M}^{-1} \text{ cm}^{-1}$). The elemental analyses for C, H, N, and Cl were in agreement with those theoretically expected.

The solvents FMA and DMF, both of analytical grade, were used without further purification. Me₂SO (reagent grade) was further purified by passing through an alumina column or by vacuum distillation.

Instrumentation. The photochemical measurements were performed at the University of Frankfurt, employing a high-pressure photolysis unit described in detail elsewhere.⁸ Light at 366 nm was selected

from a high-pressure mercury lamp (Osram HBO 100/2) using Oriol interference filters. UV-visible spectra were recorded on a Perkin-Elmer 555 spectrophotometer. The concentration of liberated Cl⁻ during photolysis was measured with a Cl⁻-sensitive electrode (Ingold) connected to a WTW pMX 500 digital ion meter. Partial molar volumes were determined from density measurements on a PAR DMA 02/C digital precision density apparatus at 25.000 ± 0.002 °C.

Photophysical measurements were carried out at the University of California, Santa Barbara, with use of an apparatus modified from one described previously.³ The modified apparatus utilized a Quanta Ray Model DCR-1A Nd-YAG pulse laser to excite the solution samples in a high-pressure cell. A Pellam Brocca prism was used to ensure optical purity of the exciting light, and a quartz lens was used to focus the laser beam down to the size of the high-pressure cell windows. The emission was monitored by collecting light from the sample at a cell window perpendicular to the exciting beam. The emitted light was focused onto the entrance slit of a SPEX Model 1672 Doublemate monochromator driven by a SPEX Compudrive. For lifetime measurements on the Rh(NH₃)₅Cl²⁺ solutions, the output from the monochromator was set at 700 nm. The output was recorded by a fast-response-time EMI 9816a photomultiplier tube, and the signal was terminated through a 50-Ω resistor into a Tektronix Model 7912Ad transient recorder (Tektronix WP2110 transient digitizer system) and displayed as emission intensity vs. time on a Tektronix 624 monitor. The data array was transferred to a Tektronix 4052 microcomputer and analyzed by a least-squares fit of ln (intensity) vs. time. The high-pressure cell was a modified Novaswiss Model 545.0040 (four sapphire windows, quartz light guides internally mounted, maximum working pressure 400 MPa). The pressure was generated by an Enerpac hand pump, measured at the primary stage with a Heise 47053 pressure gauge, and transmitted to the high-pressure cell by means of a pressure multiplier. The multiplier was connected through flexible tubing to the cell, where it was attached at a modified window seat. The high-pressure cell contains a fluid separator that prevents mixing of the transmitting fluid and the solution in the cell. The quartz light guides allow an excellent cross-beam arrangement whereby the maximum amount of emitted light is collected. A typical τ vs. P run involved multiple measurements of τ at pressure intervals of 25 or 50 MPa increasing in pressure from 0.1 to 300 MPa and then repeat multiple measurements at the same pressures as P is decreased from the maximum value. For Me₂SO the maximum pressure attained was 100 MPa owing to the tendency of the solvent to freeze at higher pressures.

Calculations. Photochemical quantum yields were calculated from experiments performed at nine different pressures ranging from 1 to 200 MPa for S = DMF and FMA. For S = Me₂SO, only five different pressures over the range 1–100 MPa were selected. The degree of conversion was determined either by differential spectral measurements and/or by measuring the concentration of the released Cl⁻ with the ion-selective electrode after appropriate dilution of the photolyzed solution with an aqueous NaNO₃ solution to obtain a medium of constant ionic strength. The degree of conversion was always kept under 20% to suppress the inner filter effects caused by absorption of the product species. Under these conditions, the calculated quantum yields were independent of the degree of conversion within the experimental error limits. Complex concentrations were in the range of 5×10^{-3} to 5×10^{-2} M. From the lifetimes, τ , and the quantum yields the corresponding volumes of activation were determined in the usual way³ using a linear fitting routine (see below).

Results

Ligand field excitation of Rh(NH₃)₅Cl²⁺ leads to photosolvolysis competitively of NH₃ or of Cl⁻ (eq 1; X⁻ = Cl⁻; S = FMA, DMF, Me₂SO). No deviations from this scheme were observed as the result of the application of pressure up to 200 MPa. Table I summarizes ϕ_{Cl} and ϕ_{NH_3} measured at different pressures. There are some differences between the values reported here for $P = 0.1$ MPa and those reported earlier⁴ at ambient pressure in Me₂SO and FMA solutions, perhaps the result of more sensitive analytical procedures in use here. However, the trends noted before with regard to the

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Table I. Pressure Dependence of the Photochemical Quantum Yields for the Ligand Field Photolysis of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ in Different Solvents^a

$$\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+} + \text{S} \xrightarrow{h\nu} \begin{cases} \phi_{\text{Cl}} \rightarrow \text{Rh}(\text{NH}_3)_5\text{S}^{3+} + \text{Cl}^- \\ \phi_{\text{NH}_3} \rightarrow \text{trans-Rh}(\text{NH}_3)_4(\text{S})\text{Cl}^{2+} + \text{NH}_3 \end{cases}$$

| solvent | <i>P</i> , MPa | ϕ_{Cl} | ϕ_{NH_3} |
|---------------------------------|----------------|-------------------------|----------------------|
| FMA | 1 | 0.13 ± 0.02 (3) | 0.044 ± 0.004 (4) |
| | 25 | 0.15 ± 0.01 (3) | 0.041 ± 0.002 (3) |
| | 50 | 0.18 ± 0.02 (3) | 0.040 ± 0.002 (3) |
| | 75 | 0.18 ± 0.02 (3) | 0.039 ± 0.003 (3) |
| | 100 | 0.16 ± 0.01 (3) | 0.034 ± 0.003 (3) |
| | 125 | 0.19 ± 0.02 (3) | 0.038 ± 0.003 (3) |
| | 150 | 0.20 ± 0.02 (3) | 0.032 ± 0.004 (4) |
| | 175 | 0.21 ± 0.01 (3) | 0.033 ± 0.003 (3) |
| Me ₂ SO ^b | 1 | 0.024 ± 0.004 (6) | 0.045 ± 0.005 (8) |
| | 25 | 0.026 ± 0.005 (6) | 0.044 ± 0.005 (7) |
| | 50 | 0.027 ± 0.002 (4) | 0.038 ± 0.006 (5) |
| | 75 | 0.030 ± 0.004 (6) | 0.042 ± 0.003 (8) |
| | 100 | 0.032 ± 0.003 (4) | 0.037 ± 0.004 (7) |
| DMF | 1 | <0.004 at all pressures | 0.085 ± 0.007 (3) |
| | 25 | | 0.077 ± 0.008 (3) |
| | 50 | | 0.077 ± 0.008 (3) |
| | 75 | | 0.074 ± 0.006 (3) |
| | 100 | | 0.078 ± 0.004 (3) |
| | 125 | | 0.064 ± 0.005 (3) |
| | 150 | | 0.057 ± 0.004 (3) |
| | 175 | | 0.058 ± 0.004 (3) |
| 200 | | 0.050 ± 0.007 (3) | |

^a $\lambda_{\text{irr}} = 366 \text{ nm}$; $T = 25 \text{ }^\circ\text{C}$ except where noted. Quantum yields in mol einstein⁻¹ reported as mean values with average deviation (number of experimental determinations in parentheses). ^b $T = 30 \text{ }^\circ\text{C}$.

avored photoreaction pathway (Cl^- or NH_3 photosolvolytic) remain valid for the different solvents. Qualitatively, the pressure effects on the quantum yields parallel those seen in aqueous solution.³ The quantum yield for chloride substitution ϕ_{Cl} increases and that for NH_3 substitution decreases as the hydrostatic pressure is raised. Plots of $\ln \phi_i$ vs. P were found to be linear within experimental uncertainties, and the values

Table II. Volumes of Activation ($\text{cm}^3 \text{ mol}^{-1}$) Calculated from Pressure Effects on the Photoreaction/Photoluminescence Properties of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ in Various Solvents^a

| solvent | $\Delta V^\ddagger_{\phi_{\text{Cl}}}$ | $\Delta V^\ddagger_{\phi_{\text{NH}_3}}$ | $\Delta V^\ddagger_{\tau^{-1}}$ | $\Delta V^\ddagger_{\text{Cl}}$ | $\Delta V^\ddagger_{\text{NH}_3}$ | $\Delta V^\ddagger_{\text{n}}$ | ref. |
|--------------------|--|--|---------------------------------|---------------------------------|-----------------------------------|--------------------------------|-----------|
| H ₂ O | -5.2 ± 0.4 | +12.7 ± 1.2 | (-3.4) ^b | -8.6 ± 1.6 | +9.3 ± 1.9 | (-2.6) ^b | 3 |
| D ₂ O | -4.2 ± 0.5 | +9.5 ± 1.6 | -3.5 ± 1.1 | -7.7 ± 1.6 | +6.0 ± 2.2 | -2.6 ± 1.0 | 3 |
| FMA | -4.6 ± 0.7 | +4.2 ± 0.9 | -0.3 ± 0.4 | -4.9 ± 1.1 | +3.9 ± 1.3 | 0.2 ± 0.5 | this work |
| DMF | | +6.3 ± 0.9 | +1.3 ± 0.2 | | +7.6 ± 1.1 | 0.7 ± 0.3 | this work |
| Me ₂ SO | -7.8 ± 1.8 | +4.4 ± 0.9 | -1 ± 1 | -8.9 ± 2.7 | +3.3 ± 1.8 | -1 ± 1 | this work |

^a ΔV^\ddagger_i 's defined in the text; units $\text{cm}^3 \text{ mol}^{-1}$. ^b Estimated; see ref 3.

Table III. Partial Molar Volumes Measured at 25.0 $^\circ\text{C}$

| solvent | compd | \bar{V} , $\text{cm}^3 \text{ mol}^{-1}$ | | |
|--------------------|--|--|-------------|-------------------|
| | | compd | cation | anion |
| FMA | $[\text{Rh}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ | 197.1 ± 0.5 | 95.7 ± 1.8 | 50.7 ± 1.3 |
| | $[\text{Rh}(\text{NH}_3)_6](\text{ClO}_4)_3$ | 233.1 ± 1.8 | 81.0 ± 2.9 | ... |
| | $[\text{Rh}(\text{NH}_3)_5\text{FMA}](\text{ClO}_4)_3$ | 251.0 ± 2.4 | 98.9 ± 3.3 | ... |
| | $\text{trans-}[\text{Rh}(\text{NH}_3)_4(\text{FMA})\text{Cl}](\text{ClO}_4)_2$ | 223.1 ± 1.3 | 121.7 ± 2.2 | ... |
| | NaClO_4 | 49.5 ± 1.4 | -1.2 ± 1.9 | ... |
| | NaCl | 22.6 ± 1.0 | -1.2 ± 1.9 | 23.8 ± 2.1 |
| | FMA | 39.9 | | |
| | NH_3 | 26.3 ± 0.5 | | |
| DMF | NH_3 | 27.4 ± 1.0 | | |
| | Cl^- | | | 22.0 ^a |
| Me ₂ SO | NH_3 | 25.4 ± 2.7 | | |
| | Cl^- | | | 25.3 ^b |
| H ₂ O | NH_3 | 25.3 ± 0.7 | | |
| | Cl^- | | | 21.8 ^c |

^a Kawaizumi, F.; Zana, R. *J. Phys. Chem.* 1974, 78, 1099. ^b Kale, K. M.; Zana, R. *J. Solution Chem.* 1977, 6, 733. ^c Reference 11.

of $\Delta V^\ddagger_{\phi_i}$ were determined from the slopes according to the relationship³

$$\Delta V^\ddagger_{\phi_i} = -RT \frac{d \ln \phi_i}{dP} \quad (2)$$

These $\Delta V^\ddagger_{\phi_i}$ values are summarized in Table II.

The luminescence lifetimes were determined over a comparable set of conditions. Pressure effects were quite modest and nearly swamped by the uncertainties in the τ values. Nonetheless, the internal self-consistency of individual τ vs. P runs (e.g., Figure 1) was quite good. More important, there were reasonable reproducibility between the slopes of the $\ln(\tau_0/\tau)$ vs. P plots, hence between the calculated apparent volumes of activation $\Delta V^\ddagger_{\tau^{-1}}$ for the individual solvent systems. The average values calculated according to eq 3 are listed in Table II.

$$\Delta V^\ddagger_{\tau^{-1}} = -RT \frac{d \ln(\tau_0/\tau)}{dP} \quad (3)$$

A brief summary of the photophysical experiments is as follows. For DMF a modest and reproducible tendency for τ to increase upon raising the pressure was found. For example, the run illustrated in Figure 1 showed τ to increase from 35.0 ± 0.5 ns at 0.1 MPa to 41 ± 0.2 ns at 300 MPa, an increase of 15%. In FMA, τ appeared to undergo a very small decrease as P was raised; however, the experimental uncertainties were nearly as large as these differences. For example, in a typical run, the τ_0 ($P = 0.1 \text{ MPa}$) value from six measurements was found to be 27.4 ± 0.9 ns (23.1 ± 1 $^\circ\text{C}$) while τ at 300 MPa was 25.6 ± 1.7 ns. In Me₂SO, there was a similar small systematic decrease in τ ($\tau_0 = 62.2 \pm 2 \text{ ns}$ over 52 measurements) with increased P , but the small pressure range available led to larger uncertainty.

Table III lists some partial molar volume data measured for NH_3 in the various solvents and for the key ionic species in formamide solution. It is notable that, for an uncharged species such as NH_3 , the partial molar volume $\bar{V}(\text{NH}_3)$ is essentially independent of the solvent and is in close agreement with the value of 24.8 $\text{cm}^3 \text{ mol}^{-1}$ reported for water.⁹ In

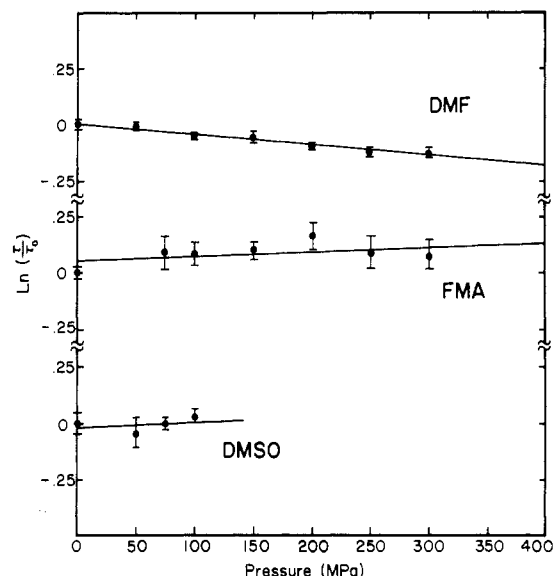


Figure 1. Examples of typical $\ln(\tau/\tau_0)$ vs. P plots for the pressure dependence of the emission lifetime of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ in DMF, FMA, and Me_2SO . For the plots illustrated, the respective ΔV_{τ}^* values for the three solvents were +1.2, -0.6, and -0.5 $\text{cm}^3 \text{mol}^{-1}$, respectively, as compared to the reported averaged values of $+1.3 \pm 0.2$, -0.3 ± 0.4 , and $-1 \pm 1 \text{ cm}^3 \text{mol}^{-1}$ (see text).

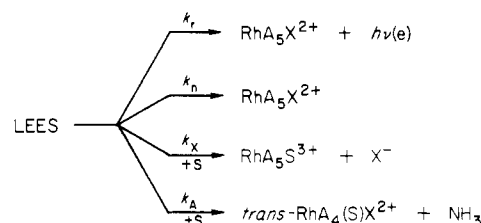
contrast the cationic species $\text{Rh}(\text{NH}_3)_6^{3+}$ and $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ display \bar{V} values 12.4 and 17.8 $\text{cm}^3 \text{mol}^{-1}$, respectively, larger than those found in aqueous solution. For ionic species an arbitrary reference species is usually chosen since uncertainties still remain in the determination of absolute ionic molar volumes in nonaqueous solvents.¹⁰ In the present case $\bar{V}(\text{ClO}_4^-)$ was assumed to be independent of solvent and to have the value $50.7 \pm 1.3 \text{ cm}^3 \text{mol}^{-1}$ measured previously in water.¹¹ Although the partial molar volumes for the ionic species were calculated given this assumption (Table III), it should be noted that this approximation did not influence the subsequent conclusions since the only partial molar volume data relevant to the discussion were drawn from volume differences.³ Table III also includes the literature values for $\bar{V}(\text{Cl}^-)$, and it is notable that the partial molar volume of this anion is relatively insensitive to the differences between these solvents.

Discussion

The preponderance of data for the ligand field photochemistry of the rhodium(III) halopentaammine complexes is consistent with an excited-state reaction model for which initial LF excitation is followed by rapid and efficient internal conversion/intersystem crossing ($\phi_{ic} \approx 1$) to the lowest energy excited state (LEES).^{12,13} From this state, reactive, radiative, and nonradiative deactivation occur competitively (Scheme I), where k_r , k_n , k_x , and k_A are the rate constants for emission, nonradiative deactivation, solvolysis of halide, or solvolysis of ammine, respectively, from the LEES or those states in thermal equilibrium with the LEES. It has been shown¹² previously that the k_i values can be calculated from eq 4. Thus, volumes

$$k_i = \phi_i \tau^{-1} \quad (4)$$

Scheme I



of activation for a specific process from the LEES ΔV_i^* can be calculated from eq 5.³ Accordingly, values of ΔV_{Cl}^* and

$$\Delta V_{\tau}^* = \Delta V_{\phi_i}^* + \Delta V_{\tau}^* \quad (5)$$

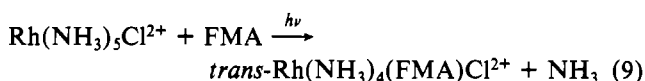
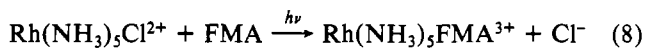
ΔV_A^* (activation volumes for the two solvolysis reactions) were calculated and summarized in Table II. These parallel the respective $\Delta V_{\phi_i}^*$ values owing to the small ΔV_{τ}^* values. Given that $k_r \ll k_n$, k_A , or k_x ,¹² ΔV_n^* (the apparent activation volume for nonradiative deactivation)¹⁴ can be calculated from eq 6.

$$\Delta V_n^* = \Delta V_{\tau}^* - \frac{\phi_{\text{Cl}} \Delta V_{\phi_{\text{Cl}}}^* + \phi_A \Delta V_{\phi_A}^*}{1 - \phi_A - \phi_{\text{Cl}}} \quad (6)$$

For the nonaqueous solvents these ΔV_n^* 's all have small absolute values (Table II) in agreement with the previous assumptions¹⁵ that the rate of nonradiative deactivation should be relatively pressure insensitive.

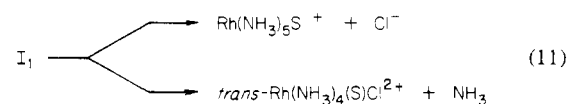
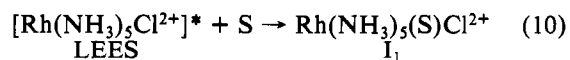
From the partial molar volume data such as in Table III, overall volume changes for reactions can be calculated according to eq 7. For eq 8 and 9 the $\Delta \bar{V}$ values -12.9 and

$$\Delta V = \sum \bar{V}(\text{products}) - \sum \bar{V}(\text{reactants}) \quad (7)$$



+12.4 $\text{cm}^3 \text{mol}^{-1}$ were calculated. The difference of 25.3 $\text{cm}^3 \text{mol}^{-1}$ between these values can be attributed to solvation changes due to the charge creation in the former reaction in which a dipositive ion reacts to give a tripositive cation and a monoanion. A similar difference of 21.7 $\text{cm}^3 \text{mol}^{-1}$ has been calculated for the analogous reactions in aqueous solution.³

In order to evaluate the ΔV^* values for the excited-state substitution pathways, it is necessary to propose some mechanistic models for which reaction volume profiles can be constructed. The problem with such models is the uncertainty in estimating the partial molar volumes of intermediate species. For excited-state reactions an additional complexity is the uncertain volume of the excited state itself. As a first example, consider the mechanism for which the rate-limiting step is associative attack by solvent to give a seven-coordinate intermediate, I_1 , followed by ligand loss to give products (eq 10 and 11). The volume of the transition state (eq 10) would



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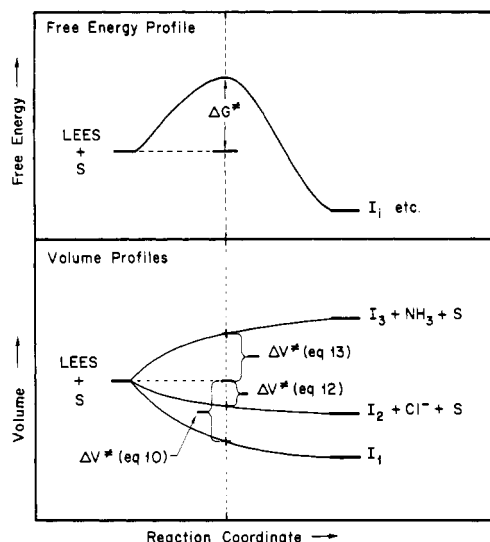
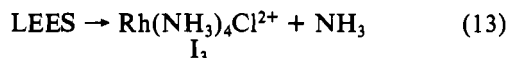
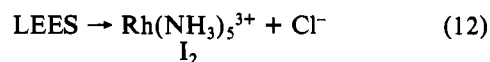


Figure 2. Top: Free energy/reaction coordinate profile for an arbitrary substitution mechanism of the lowest energy ligand field excited state (LEES) of $\text{RhA}_5\text{Cl}^{2+}$ ($A = \text{NH}_3, \text{ND}_3$) in a solvent S . Indicated is the free energy barrier ΔG^\ddagger to achieve the transition state of the progression from the reactants LEES plus S to the intermediate species I of the arbitrary mechanism. Bottom: Illustrative volume profile for the reaction coordinate of the reaction mechanisms eq 13 (dissociative loss of NH_3), eq 12 (dissociative loss of Cl^-), and eq 10 (associative reaction with S to give a seven-coordinate intermediate). ΔV^\ddagger values represent the volume change from reactants to transition state ($I_1 = \text{RhA}_5\text{Cl}^{2+}$, $I_2 = \text{RhA}_5^{3+}$, $I_3 = \text{RhA}_4\text{Cl}^{2+}$).

lie along the volume profile between the volumes of the reactants and of I_1 . The position of the transition state would determine how much of the overall volume change of the step would be reflected in ΔV^\ddagger , an early transition state showing a much smaller change than a late one.^{3,8} This aspect of the ΔV^\ddagger values is illustrated qualitatively in Figure 2 for model limiting associative and dissociative mechanisms (see below).

For the associative mechanism $\Delta \bar{V}(\text{eq 10}) = \bar{V}(I_1) - \bar{V}(\text{LEES}) - \bar{V}(S)$, but both $\bar{V}(I_1)$ and $\bar{V}(\text{LEES})$ are unknown. The $\bar{V}(\text{LEES})$ value can be estimated as being somewhat larger than $\bar{V}(\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+})$ given that Franck-Condon calculations¹⁶ for the LF excited states of such complexes have concluded that metal-ligand bonds for the excited states are larger by as much as 0.1 Å than those for the ground state. A minimum estimate for $\bar{V}(I_1)$ would be equal to $\bar{V}(\text{trans-Rh}(\text{NH}_3)_4(\text{S})\text{Cl}^{2+})$. Thus, one might make the estimate $\Delta \bar{V}(\text{eq 10}) = \bar{V}(\text{trans-Rh}(\text{NH}_3)_4(\text{S})\text{Cl}^{2+}) - \bar{V}(S) - \bar{V}(\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}) = -13.9 \text{ cm}^3 \text{ mol}^{-1}$ in FMA assuming that, while the calculation incorporates low estimates for $\bar{V}(I_1)$ and $\bar{V}(\text{LEES})$, the errors are self-canceling.

For a limiting dissociative mechanism the key steps are

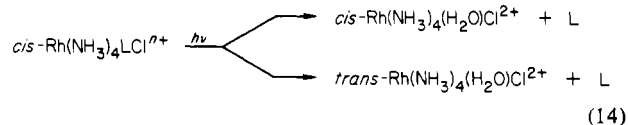


and the volume changes would be $\Delta \bar{V}(\text{eq 12}) = \bar{V}(I_2) + \bar{V}(\text{Cl}^-) - \bar{V}(\text{LEES})$ and $\Delta \bar{V}(\text{eq 13}) = \bar{V}(I_3) + \bar{V}(\text{NH}_3) - \bar{V}(\text{LEES})$. If one estimates the $\Delta \bar{V}$ values using the somewhat controversial¹⁷ approximation that the five-coordinate intermediates have \bar{V} values equal to those of hexacoordinate complexes with the same electrostatic charge, i.e. $\bar{V}(I_2) \approx \bar{V}(\text{Rh}(\text{NH}_3)_6^{3+})$,

$\bar{V}(I_3) \approx \bar{V}(\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+})$, and the assumption that $\bar{V}(\text{LEES}) \approx \bar{V}(\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+})$, then $\Delta \bar{V}(\text{eq 12}) \approx +9.1 \text{ cm}^3 \text{ mol}^{-1}$ and $\Delta \bar{V}(\text{eq 13}) \approx +26.3 \text{ cm}^3 \text{ mol}^{-1}$ in FMA. However, the probable errors in these assumptions are fairly large and are additive, not self-canceling; $\bar{V}(\text{LEES})$ is certainly larger than estimated, perhaps by as much as $10 \text{ cm}^3 \text{ mol}^{-1}$, while $\bar{V}(I_2)$ and $\bar{V}(I_3)$ are undoubtedly smaller than estimated. Hence, both $\Delta \bar{V}$ values should be significantly more negative than the above estimates. However, the errors should be comparable in both sign and magnitude for both, so that the conclusion that NH_3 dissociation should have a $\Delta \bar{V}$ value $\sim 17 \text{ cm}^3 \text{ mol}^{-1}$ more positive than that for Cl^- dissociation in FMA should still be valid.

The observation in FMA that $\Delta V^\ddagger_{\text{Cl}}$ and $\Delta V^\ddagger_{\text{NH}_3}$ differ by $\sim 9 \text{ cm}^3 \text{ mol}^{-1}$, the former being more negative, rules out a common limiting associative mechanism for the two photo-substitution pathways, since in that case the two ΔV^\ddagger values should be nearly identical. The different ΔV^\ddagger values might be explained on the basis of the two reactions proceeding via different mechanisms or, alternately, via very similar pathways involving considerable amounts of ligand dissociation. For the latter alternative, the different ΔV^\ddagger values would reflect the differing amounts of charge creation inherent to Cl^- vs. NH_3 dissociation. The $\Delta V^\ddagger_{\text{NH}_3} - \Delta V^\ddagger_{\text{Cl}}$ value of $+9 \text{ cm}^3 \text{ mol}^{-1}$ would be consistent with a limiting dissociative mechanism for which the transition states of eq 12 and 13 lay midway along the volume profile of the reaction coordinate (Figure 2). The two mechanisms alternatively might involve interchange processes, the Cl^- labilization pathway from the excited state having an associative character and the NH_3 labilization pathway a more dissociative character. However, there is no correlation of the excited-state reaction rates k_{Cl} or k_{NH_3} with the solvent donor numbers proposed by Gutmann.¹⁸

The ΔV^\ddagger values alone cannot differentiate these alternatives. Our prejudice would favor some commonality to the photo-substitution mechanisms. Furthermore, a collection of circumstantial evidence points to a limiting dissociative mechanism for the ligand field photosubstitution reactions of rhodium(III) haloammine complexes in aqueous solution.¹³ An example is the photoaquation/photoisomerization reaction depicted in eq 14 for which the same 5/1 trans/cis ratio is



observed for two different leaving groups $L = \text{Cl}^-$ or H_2^{18}O .¹⁹ This result argues convincingly for a common intermediate, the logical one being the pentacoordinate species $\text{Rh}(\text{NH}_3)_4\text{Cl}^{2+}$, the product of the dissociation of L .

The question remains whether the actual ΔV^\ddagger values measured are consistent with the dissociative mechanism. Examination of Table II shows that the $\Delta V^\ddagger_{\text{Cl}}$ and $\Delta V^\ddagger_{\text{NH}_3}$ values follow similar patterns in all the solvents. Initially we had anticipated more obvious $\Delta V^\ddagger_{\text{Cl}}$ differences because the rates of Cl^- solvolysis from $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ proved markedly solvent dependent. However, given that \bar{V}_{Cl} is relatively solvent invariant, the relative insensitivity of the $\Delta V^\ddagger_{\text{Cl}}$ to the solvent is unsurprising. The same argument can be applied to the $\Delta V^\ddagger_{\text{NH}_3}$ values. The $\Delta V^\ddagger_{\text{NH}_3} - \Delta V^\ddagger_{\text{Cl}}$ difference is smaller in nonaqueous solvents but remains substantial. The negative value of $\Delta V^\ddagger_{\text{Cl}}$ and relatively small value of $\Delta V^\ddagger_{\text{NH}_3}$ relative to the $\Delta \bar{V}(\text{eq 12})$ and $\Delta \bar{V}(\text{eq 13})$ values estimated can probably be attributed to the underestimation of $\bar{V}(\text{LEES})$ and overestimation of \bar{V} for the pentacoordinate intermediate. We

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continue to consider the relatively large $\Delta V_{\text{NH}_3}^* - \Delta V_{\text{Cl}}^*$ differences as evidence for a predominantly dissociative mechanism.

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Registry No. FMA, 75-12-7; DMF, 68-12-2; $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$, 15379-09-6; $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{ClO}_4$, 67573-28-8; $[\text{Rh}(\text{NH}_3)_5\text{FMA}](\text{ClO}_4)_3$, 90246-25-6; *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{FMA})\text{Cl}](\text{ClO}_4)_2$, 90246-26-7; Me_2SO , 67-68-5; Cl^- , 16887-00-6; NH_3 , 7664-41-7.

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Volume Profiles for the Base Hydrolysis of a Series of Pentaamminecobalt(III) Complex Ions in Aqueous Solution¹

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Volumes of activation ($\Delta V_{\text{exptl}}^*$) for the base hydrolysis reactions of the complexes $\text{Co}(\text{NH}_3)_5\text{X}^{(3-n)+}$, where $\text{X}^{n-} = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-, \text{SO}_4^{2-}$, and Me_2SO , were determined from the pressure dependencies of the hydrolysis rate constants and have values between 22 and 40 $\text{cm}^3 \text{mol}^{-1}$. Partial molar volume measurements on all the reactant species, as well as overall reaction volume ($\Delta \bar{V}_0$) determinations by a dilatometric technique, enable the construction of reaction volume profiles for the base hydrolysis reactions. These clearly demonstrate that $\Delta V_{\text{exptl}}^* - \Delta \bar{V}_0$ is fairly constant for almost all the studied systems. Furthermore, these data enable the estimation of the partial molar volume of the five-coordinate species $\text{Co}(\text{NH}_3)_4\text{NH}_2^{2+}$, which turns out to be independent of the nature of X^{n-} . These results underline the validity of the $\text{S}_{\text{N}}1\text{CB}$ mechanism and demonstrate the general applicability of volume equation calculations in obtaining information on the partial molar volumes of intermediate and/or transition-state species.

Introduction

Our general interest in the application of high-pressure kinetic techniques in the elucidation of chemical reaction mechanisms has led us to the study of typical aquation reactions of ammine complexes of cobalt(III), rhodium(III), and chromium(III).³⁻⁹ Volume equation calculations were adopted to demonstrate that the aquation reactions of pentaamminecobalt(III) complexes proceed according to a dissociative reaction mode.³ In these it was assumed that the partial molar volume of the five-coordinate transition state, $\text{Co}(\text{NH}_3)_5^{3+}$, equals that of the hexaammine species on the basis of predictions presented by Stranks.¹⁰ In a later study Swaddle and a co-worker¹¹ criticized this assumption and presented arguments against a common five-coordinate intermediate and in favor of an I_d mechanism. Furthermore, they also ascribed the earlier found consistency in the partial molar volume of the five-coordinate intermediate to errors in the partial molar volumes of some of the studied complexes.

Very recently, Lawrance¹² studied the pressure dependence of the aquation reactions of a series of pentaamminecobalt(III) complexes, all with neutral leaving groups. He finds a good

correlation between the partial molar volume of the complex and that of the neutral sixth ligand. Furthermore, he demonstrates very clearly that the calculated volume of the five-coordinate intermediate in the case of a dissociative mechanism strongly depends on the charge of the complex, i.e. the charge of the sixth ligand—the leaving group during aquation. These and recent theoretical predictions by Swaddle¹³ clearly demonstrate that Stranks' postulate is indeed in error and another approach must be sought.

Along these lines we have studied the volume profiles for a series of base hydrolysis reactions of pentaamminecobalt(III) complexes. These are generally accepted¹⁴⁻¹⁹ to proceed according to a $\text{S}_{\text{N}}1\text{CB}$ mechanism in which a five-coordinate intermediate, $\text{Co}(\text{NH}_3)_4\text{NH}_2^{2+}$, is formed, which rapidly reacts with water or any other competing nucleophile to produce the reaction products. If this is really the case, it should be possible to estimate the volume of this common intermediate from reaction volume and volume of activation measurements. This will add not only to the validity of the suggested mechanism but also to the general understanding of the applicability of volume equation calculations and the construction of reaction volume profiles.²⁰⁻²²

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