tions is the same for all solvent systems and is consistent with a single explanation. Irradiation of *cis*- or *trans*-$Ru(dmpe)_2Cl_2$ results in loss of chloro ligand from the lowest ligand field excited state[20] as the primary photochemical event. The five-coordinate fragment $[Ru(dmpe)_2Cl^+]^*$, in a ligand field excited state, shows a thermodynamic preference for Cl to appear in the apical position of the square pyramid ($e_\sigma^{\mathrm{P}} > e_\sigma^{\mathrm{Cl}}$[2–4]). Apparently, the excited-state, five-coordinate fragment is long-lived enough that the basal isomer, formed by Ru–Cl dissociation in the cis starting material, undergoes the thermodynamically preferred basal → apical isomerization. The trans starting complex generates the apical isomer directly upon Ru–Cl bond breaking, and the apical isomer, in both cases, undergoes electronic relaxation and ligand addition to form the observed photolysis products.[21] It should be noted that, under conditions where $Ru(dmpe)_2Cl_2$ and $Ru(dppe)_2Cl_2$[11] undergo cis to trans photoisomerization, $Os(dppe)_2Cl_2$ does not.[14] This is due, presumably, to a combination of a larger barrier for basal → apical isomerization and more rapid electronic relaxation (spin–orbit coupling) for the third-row congener.

In the weakly coordinating alcohol solvents, ligand addition is just recoordination of the previously dissociated chloro ligand. In aqueous solution or water/alcohol mixtures, aquo ligand is added to $[Ru(dmpe)_2Cl^+]^*$ to form *trans*-$Ru(dmpe)_2(H_2O)Cl^+$ as the sole photolysis product. In Me_2SO, irradiation of the *cis*- or *trans*-$Ru(dmpe)_2Cl_2$ gives a complex with electronic spectrum, a ^{13}C NMR spectrum with a methylene peak in roughly the same place as the trans isomer in Figure 1, and a peak due to coordinated Me_2SO as well as solvent Me_2SO. All indications are that irradiation of either isomer leads to *trans*-$Ru(dmpe)_2(Me_2SO)Cl^+$ via $[Ru(dmpe)_2Cl^+]^*$ as the photolysis product.

Conclusion

The stereochemical model[2–4] correctly predicts the product geometry when *cis*- or *trans*-$Ru(dmpe)_2Cl_2$ is irradiated in the ligand field spectral region in a variety of solvents. In the case of $Ru(dmpe)_2Cl_2$, the solvents used in this study did have some effect on the quantum yield but did not alter the nature of the leaving group or the stereochemistry of the photolysis product. Although there is still no direct evidence for the existence of a five-coordinate, excited-state fragment along the reaction coordinate for photosubstitution reactions, a continued amount of experimental data[3,5–11] strongly suggests that this type of mechanism is correct and that it may be operable for systems other than d^6 complexes.[4]

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Registry No. *trans*-$Ru(dmpe)_2Cl_2$, 19206-05-4; *cis*-$Ru(dmpe)_2Cl_2$, 84172-85-0; *trans*-$Ru(dmpe)_2(H_2O)Cl^+$, 84130-50-7; *trans*-$Ru(dmpe)_2(Me_2SO)Cl^+$, 84130-51-8; $[Ru_2(Cl)_3(PEt_2Ph)_6]Cl$, 84130-52-9.

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[20] The use of the given model[2–4] to describe the photochemistry does not require the assumption of either a spin-singlet or spin-triplet excited state for the five-coordinate fragment. However, it is far more likely that the triplet state is the reactive excited state since the longer lifetime of this state may be necessary for the isomerization reaction to occur.

[21] An alternate explanation for the photochemical formation of *trans*-$Ru(dmpe)_2Cl_2$ from *cis*-$Ru(dmpe)_2Cl_2$ in pure alcohol would be a nondissociatve twist mechanism. Although this mechanism cannot be ruled out, the exclusive formation of *trans*-$Ru(dmpe)_2SCl^+$ in the other solvent systems make this possibility unlikely.

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Pressure Effects on the Photochemical and Photophysical Properties of the Rhodium(III) Complexes RhA_5X^{2+} ($A = NH_3, ND_3$; $X = Cl, Br$) in Aqueous Solution

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The effect of pressure up to 200 MPa was studied for ligand labilizations resulting from the ligand field photoexcitation of $Rh(NH_3)_5X^{2+}$ ($X = Cl, Br$) and of the perdeuterio analogues $Rh(ND_3)_5X^{2+}$ in H_2O or D_2O solutions, respectively. Quantum yields for halide photoaquation displayed negative volumes of activation (ΔV^*) ranging from -10.3 cm^3 mol^{-1} for Br^- aquation from $Rh(NH_3)_5Br^{2+}$ in H_2O to -4.2 cm^3 mol^{-1} for Cl^- loss from $Rh(ND_3)_5Cl^{2+}$ in D_2O. In contrast, ammonia photolabilization quantum yields gave positive ΔV^* values ranging from $+3.4$ cm^3 mol^{-1} for ND_3 loss from $Rh(ND_3)_5Br^{2+}$ in D_2O to $+12.7$ cm^3 mol^{-1} for NH_3 loss from $Rh(NH_3)_5Cl^{2+}$ in H_2O. In addition, the pressure dependence of the luminescence lifetimes τ was studied under conditions comparable to those of the photochemical investigations for the perdeuterio complexes $Rh(ND_3)_5Cl^{2+}$ and $Rh(ND_3)_5Br^{2+}$ in D_2O. The volumes of activation for the total deactivation rates τ^{-1} were calculated as -3.5 and $+4.1$ cm^3 mol^{-1} for $X = Cl$ and Br, respectively. Combination of lifetime and quantum yield pressure effects allows the estimation of ΔV^* values for rates of the individual excited-state deactivation processes, ligand aquation, and nonradiative deactivation. Comparison of these data with calculated reaction volume profiles supports the view that the key ligand labilization pathways from the ligand field excited states are dissociative in character.

Introduction

The photosubstitution reactions resulting from the ligand field (LF), i.e. d to d, excitations of d^3 and d^6 Werner-type transition-metal complexes have been the subject of considerable experimental and theoretical investigation. However, despite these efforts, information regarding the intimate mechanisms of the excited-state reactions leading to substitution products has not been fully elucidated. In the interest of providing such mechanistic information, the effects of pressure on the photoaquation and photoisomerization reactions of some Cr(III) and Rh(III) amine complexes were investigated in several recent studies.[3–6] In general, quantum

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yield determinations were performed as a function of pressure according to procedures usually adopted for such measurements at ambient pressure but with specially designed high-pressure equipment.

For reaction from a single, thermally equilibrated excited state the photoreaction quantum yield can be defined by[7] eq 1, where ϕ_{ic} denotes the efficiency of internal conversion/intersystem crossing from states initially excited to the reactive state, τ is the lifetime of the reactive excited state, k_p is the rate constant for the primary photoreaction, and k_n and k_r are the rate constants for nonradiative and radiative deactivations, respectively.

$$\phi = \phi_{ic}\frac{k_p}{k_p + k_n + k_r} = \phi_{ic}k_p\tau \qquad (1)$$

The measurements of pressure effects on the photoreaction quantum yields noted above can be interpreted in terms of possible excited-state reaction mechanisms. However, the fact that pressure may affect any of the parameters of eq 1 adds to the ambiguities of such interpretation. For example, in the studies noted above, it was assumed that the observed pressure effects are principally due to the pressure dependence of k_p and that $\Delta V^{\ddagger}$ for the major deactivation pathway, nonradiative decay, is very small (0 ± 2 cm^3 mol^{-1}).[8] This assumption may indeed be in error and, as such, influence the mechanistic interpretation of the obtained quantum yield data. In this context we chose to investigate pressure effects on both the photoreaction quantum yields and the dynamic photophysical properties of the pentaamminerhodium(III) complexes $Rh(NH_3)_5X^{2+}$ (X = Cl, Br) when subjected to ligand field (LF) excitation. Reported here are the studies in aqueous solution.

Earlier studies in the UCSB laboratories have measured luminescence lifetimes and quantum yields and photoreaction quantum yields of the $Rh(NH_3)_5X^{2+}$ ions in fluid solutions under ambient temperature and pressure conditions.[9] Furthermore, it has been demonstrated that excitation into singlet ligand field absorption bands is followed by efficient internal conversion and intersystem crossing to the lowest energy excited state ($\phi_{ic} \simeq 1$), a ligand field triplet state,[10] from which reaction or deactivation to the ground state occurs. Quantum yields for emission are quite small[9] ($<10^{-4}$), hence $k_r << (k_n + k_p)$, and eq 1 can be rewritten as

$$\phi = k_p\tau \qquad (2)$$

where

$$\tau = (k_p + k_n)^{-1} \qquad (3)$$

These relationships allowed calculation of the excited-state rate constants for reaction (ligand aquation in this case) and nonradiative deactivation to the ground state from the measured quantum yield and excited-state lifetimes. Such parameters also were calculated from similar data[9] for the perdeuterio complexes $Rh(ND_3)_5X^{2+}$, which display somewhat longer excited-state lifetimes. In the present study, the above relationships will allow determination of the activation volumes for k_p and k_n from the pressure dependencies of ϕ and τ.

Experimental Section

Materials. The pentaamminerhodium(III) complexes $[Rh(NH_3)_5Cl](ClO_4)_2$,[11] $[Rh(NH_3)_5Br](ClO_4)_2$,[12] and $[Rh(NH_3)_5H_2O](ClO_4)_3$[13] and the tetraamminerhodium(III) species *trans*-$[Rh(NH_3)_5(H_2O)Cl]S_2O_6$[14] and *trans*-$[Rh(NH_3)_5(H_2O)Br]S_2O_6$[14] were all prepared and recrystallized according to published procedures. Chemical analyses[15] and UV–visible absorption spectra were in agreement with the theoretically expected values and those reported elsewhere,[14,16] respectively. The perdeuterated compounds $[Rh(ND_3)_5Cl](ClO_4)_2$ and $[Rh(ND_3)_5Br]ClO_4)_2$ were prepared by repeated recrystallization from D_2O,[17] and the UV–visible spectra were in good agreement with their perprotio analogues. All other chemicals were of analytical reagent grade, and doubly distilled water was used throughout the investigation.

Instrumentation. The photochemical measurements were performed at the University of Frankfurt by employing a high-pressure photolysis unit described in detail elsewhere.[6] Light at 366 nm was selected from a high-pressure mercury lamp (Osram HBO 100/2) using Oriel interference filters. UV–visible spectra were recorded on a Perkin-Elmer 555 spectrophotometer. pX (X = H, Br) measurements were performed on a WTW pMX 500 ion meter by using the appropriate ion-selective electrodes. Partial molar volumes were determined from density measurements on a Paar DMA 02/C digital precision density apparatus at 25.000 ± 0.002 °C.

The photophysical measurements were performed at the University of California, Santa Barbara. Luminescence lifetimes in a pressure cell were measured with a DCR-1A Nd/YAG laser described previously.[18] A Corning 7.37 band-pass filter was used to ensure spectral 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 at 705 nm with a fast response time photomultiplier (EMI 9816A) positioned perpendicular to the excitation beam. The output signal was displayed as emission intensity vs. time on a Tektronix 7904 oscilloscope and photographed. The high-pressure cell was a Novaswiss Model 545.0040 (four sapphire optical windows; 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 sample was contained in a cylindrical quartz capsule (d = 0.9 cm), equipped with a shrinkable Teflon cap, and placed in the high-pressure cell filled with water. All experiments were carried out at ambient temperature (298 ± 3 K).

Calculations. Photochemical quantum yields were calculated from experiments performed at nine different pressures over the range 1–200 MPa. The degree of conversion was determined from differential spectral measurements[19] at ambient pressure and from pX (X = H, Br) measurements for reactions that included the release of NH_3 and Br^-, respectively. 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 photographic traces of the luminescence decay were digitized and analyzed (as exponential decays) with a DEC PDP 11 computer. From the lifetimes τ so measured, the pressure-independent volumes of activation $\Delta V^{\ddagger}_{\tau^{-1}}$ were determined by using a linear fitting routine for eq 4, where τ and τ_0 are the lifetimes at pressure P and atmospheric pressure, respectively.

$$\Delta V^{\ddagger}_{\tau^{-1}} = -RT\frac{d\ln(\tau_0/\tau)}{dP} \qquad (4)$$

Results and Discussion

Ligand field photoexcitation of the halopentaamminerhodium(III) complexes leads to competitive photoaquation of halide or ammine (eq 5), where X = Cl or Br and A = NH_3

$$S + RhA_5X^{2+} \xrightarrow{h\nu} RhA_5S^{3+} + X^- \qquad (5a)$$

$$S + RhA_5X^{2+} \xrightarrow[H^+\ (\text{or } D^+)]{h\nu} trans\text{-}RhA_4(S)X^{2+} + NH_4^+\ (\text{or } ND_4^+) \qquad (5b)$$

for S = H_2O or A = ND_3 for S = D_2O. The application of

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Table I. Pressure Dependence of the Photochemical Quantum Yields for the Ligand Field Photolysis of $Rh(NH_3)_5X^{2+}$ and $Rh(ND_3)_5X^{2+}$ (X = Cl, Br) in Aqueous Solution at 25 °C

photolysis product	press., MPa	no. of expts	quantum yield, mol einstein^{-1}	photolysis product	press., MPa	no. of expts	quantum yield, mol einstein^{-1}
	$Rh(NH_3)_5Cl^{2+}$ [a]				$Rh(NH_3)_5Br^{2+}$ [a]		
$Rh(NH_3)_5H_2O^{3+}$	1	8	0.20 ± 0.01	$Rh(NH_3)_5H_2O^{3+}$	1	5	0.022 ± 0.004
	25	2	0.22 ± 0.01		25	5	0.025 ± 0.008
	50	5	0.23 ± 0.01		50	8	0.029 ± 0.008
	75	5	0.26 ± 0.01		75	6	0.030 ± 0.009
	100	5	0.26 ± 0.01		100	6	0.033 ± 0.004
	125	4	0.28 ± 0.01		125	6	0.037 ± 0.011
	150	5	0.27 ± 0.01		150	6	0.042 ± 0.006
	175	3	0.29 ± 0.01		175	4	0.049 ± 0.005
	200	5	0.31 ± 0.01		200	6	0.050 ± 0.008
trans-$Rh(NH_3)_4(H_2O)Cl^{2+}$	1	10	0.036 ± 0.005	*trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$	1	4	0.21 ± 0.01
	25	3	0.036 ± 0.003		25	4	0.20 ± 0.02
	50	5	0.034 ± 0.002		50	6	0.19 ± 0.02
	75	6	0.025 ± 0.005		75	5	0.19 ± 0.02
	100	7	0.020 ± 0.005		100	5	0.17 ± 0.02
	125	2	0.015 ± 0.005		125	5	0.16 ± 0.02
	150	7	0.018 ± 0.004		150	4	0.15 ± 0.01
	175	3	0.013 ± 0.004		175	3	0.15 ± 0.01
	200	4	0.014 ± 0.005		200	4	0.14 ± 0.02
	$Rh(ND_3)_5Cl^{2+}$ [b]				$Rh(ND_3)_5Br^{2+}$ [b]		
$Rh(ND_3)_5D_2O^{3+}$	1	3	0.33 ± 0.02	$Rh(ND_3)_5D_2O^{3+}$	1	2	0.031 ± 0.007
	25	2	0.35 ± 0.02		25	2	0.036 ± 0.005
	50	2	0.37 ± 0.02		50	3	0.043 ± 0.008
	75	2	0.40 ± 0.02		75	2	0.037 ± 0.008
	100	3	0.41 ± 0.03		100	3	0.045 ± 0.006
	125	2	0.44 ± 0.01		125	2	0.044 ± 0.008
	150	2	0.43 ± 0.02		150	2	0.062 ± 0.007
	175	2	0.48 ± 0.01		200	3	0.070 ± 0.010
	200	3	0.46 ± 0.02	*trans*-$Rh(ND_3)_4(D_2O)Br^{2+}$	1	2	0.37 ± 0.01
trans-$Rh(ND_3)_4(D_2O)Cl^{2+}$	1	4	0.092 ± 0.011		25	3	0.37 ± 0.01
	25	2	0.090 ± 0.009		50	3	0.26 ± 0.03
	50	3	0.086 ± 0.009		75	3	0.34 ± 0.01
	75	2	0.058 ± 0.008		100	3	0.33 ± 0.01
	100	4	0.062 ± 0.011		125	2	0.34 ± 0.01
	125	3	0.057 ± 0.015		150	3	0.32 ± 0.01
	150	3	0.064 ± 0.013		200	3	0.28 ± 0.02
	175	2	0.040 ± 0.014				
	200	3	0.045 ± 0.012				

[a] Measured in 10^{-3}-10^{-2} M $HClO_4$ in H_2O. [b] Measured in 10^{-3}-10^{-2} M $DClO_4$ in D_2O.

pressure did not lead to any new photoproducts but did alter the quantum yields of the various reactions. Values of ϕ for the above reactons in H_2O and D_2O are summarized in Table I as a function of pressure. It should be noted that the quantum yields for the reactions are different when the systems are perdeuterated and D_2O is used for the reaction medium. This observation is in agreement with earlier measurements at ambient pressure and is largely due to the effect of ammine perdeuteration on excited-state nonradiative deactivation rates. The luminescence lifetimes of the species $Rh(ND_3)X^{2+}$ (X = Cl, Br) were measured as a function of pressure in D_2O, and the results are summarized in Table II. Both tables illustrate that pressure has a significant influence on the values of ϕ and τ, respectively. Plots of ln ϕ and ln τ^{-1} vs. pressure were found to be linear within the experimental error limits concerned. $V^{\ddagger}_{\phi}$ and $V^{\ddagger}_{\tau^{-1}}$ were estimated from the slopes of such plots in the usual way, and their values are summarized in Table III.

From eq 2, by following the previously outlined derivations,[4,6] it can be shown that the volume of activation for the excited-state substitutions (k_p) and for nonradiative decay (k_n) are given, respectively, by

$$\Delta V^{\ddagger}_{p} = \Delta V^{\ddagger}_{\phi} + \Delta V^{\ddagger}_{\tau^{-1}} \qquad (6)$$

and

$$\Delta V^{\ddagger}_{n} = \Delta V^{\ddagger}_{\tau^{-1}} - \frac{\phi}{1-\phi}\Delta V^{\ddagger}_{\phi} \qquad (7)$$

Table II. Pressure Dependence of the Luminescence Lifetime of $Rh(ND_3)_5X^{2+}$ (X = Cl, Br) in D_2O at 25 °C (10^{-3} M DCl)

press., MPa	no. of measmts	τ, ns
	$Rh(ND_3)_5Cl^{2+}$	
0.1	7	29.5 ± 1.4
69.3	3	26.8 ± 0.6
116.3	7	24.3 ± 0.5
163.3	3	22.8 ± 1.1
210	7	21.9 ± 1.1
282	3	20.4 ± 1.1
	$Rh(ND_3)_5Br^{2+}$	
0.1	4	23.8 ± 0.7
69.3	2	27.9 ± 0.7
104.5	2	30.0 ± 0.2
108.5	2	28.8 ± 0.2
139	2	30.2 ± 0.6
198	2	34.0 ± 0.6

In the case where two photochemical reactions occur with different quantum yields ϕ_1 and ϕ_2, eq 5 must be modified to

$$\Delta V^{\ddagger}_{n} = \Delta V^{\ddagger}_{\tau^{-1}} - \frac{\phi_1\Delta V^{\ddagger}_{\phi_1} + \phi_2\Delta V^{\ddagger}_{\phi_2}}{1-\phi_1-\phi_2} \qquad (8)$$

The $\Delta V^{\ddagger}_{\tau^{-1}}$ and $\Delta V^{\ddagger}_{\phi}$ data listed in Table III allow calculation of $\Delta V_p^{\ddagger}$ by using eq 5 for both ammine and halide aquation from the excited states of the perdeuterated complexes. In addition $\Delta V_n^{\ddagger}$ values can be calculated by using

Table III. Volumes of Activation from Photochemical and Photophysical Measurements on the Photoaquation Reactions of $Rh(NH_3)_5X^{2+}$ and $Rh(ND_3)_5X^{2+}$ (X = Cl, Br) in Aqueous Solution at 25 °C[a]

complex	photolysis product	solvent	$\Delta V^{\ddagger}{}_{\phi}$[b]	$\Delta V^{\ddagger}{}_{\tau^{-1}}$[c]	$\Delta V_p{}^{\ddagger}$[d]	$\Delta V_n{}^{\ddagger}$[e]
$Rh(NH_3)_5Cl^{2+}$	$Rh(NH_3)_5H_2O^{3+}$	H_2O	−5.2 ± 0.4	(−3.4)	−8.6 ± 1.6	(−2.6)
	trans-$Rh(NH_3)_5(H_2O)Cl^{2+}$		+12.7 ± 1.2		+9.3 ± 1.9	
$Rh(ND_3)_5Cl^{2+}$	$Rh(ND_3)_5D_2O^{3+}$	D_2O	−4.2 ± 0.5	−3.5 ± 1.1	−7.7 ± 1.6	−2.6 ± 1.0
	trans-$Rh(ND_3)_4(D_2O)Cl^{2+}$		+9.5 ± 1.6		+6.0 ± 2.2	
$Rh(NH_3)_5Br^{2+}$	$Rh(NH_3)_5H_2O^{3+}$	H_2O	−10.3 ± 1.2	(+3.5)	−6.8 ± 1.6	(+2.5)
	trans-$Rh(NH_3)_4(H_2O)Br^{2+}$		+4.6 ± 0.6		+8.1 ± 1.2	
$Rh(ND_3)_5Br^{2+}$	$Rh(ND_3)_5D_2O^{3+}$	D_2O	−9.4 ± 1.5	+4.1 ± 0.6	−5.3 ± 1.8	+2.5 ± 1.2
	trans-$Rh(ND_3)_4(D_2O)Br^{2+}$		+3.4 ± 0.5		+7.5 ± 1.1	

[a] All volume quantities are given in $cm^3\ mol^{-1}$. [b] Determined from plots of ln ϕ vs P for all experimental data points (mean values are quoted in Table I). [c] Determined from plots of ln τ^{-1} vs. P for the data in Table II; values in parentheses were calculated according to eq 9—see Results and Discussion. [d] Calculated from eq 6—see Results and Discussion. [e] Calculated from eq 8; values in parentheses were assumed equal to perdeuterio analogues—see Results and Discussion.

Table IV. Estimated Volume Changes for the Photoaquation Reactions of $Rh(NH_3)_5X^{2+}$ (X = Cl, Br) in Aqueous Solution at 25 °C[a]

overall reacn	$\Delta\overline{V}$[b]	$\Delta\overline{V}_D$[c]	$\Delta V_p{}^{\ddagger}$[d]
$Rh(NH_3)_5Cl^{2+} + H_2O \xrightarrow{h\nu} Rh(NH_3)_5H_2O^{2+} + Cl^-$	−17.8 ± 1.0	+2.7 ± 1.0[e]	−8.6 ± 1.6
$Rh(NH_3)_5Cl^{2+} + H_2O \xrightarrow[+H^+]{h\nu}$ *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+} + NH_4{}^+$	+3.9 ± 1.6	+24.8[f]	+9.3 ± 1.9
$Rh(NH_3)_5Br^{2+} + H_2O \xrightarrow{h\nu} Rh(NH_3)_5H_2O^{3+} + Br^-$	−19.4 ± 1.8	+1.1 ± 1.8[e]	−6.8 ± 1.6
$Rh(NH_3)_5Br^{2+} + H_2O \xrightarrow[+H^+]{h\nu}$ *trans*-$Rh(NH_3)_4(H_2O)Br^{2+} + NH_4{}^+$	+0.3 ± 2.3	+24.8[f]	+8.1 ± 1.2

[a] All volume quantities are given as $cm^3\ mol^{-1}$. [b] Estimated from the following: $\overline{V}[Rh(NH_3)_5Cl^{2+}] = 82.3 \pm 0.5$;[21] $\overline{V}[Rh(NH_3)_5Br^{2+}] = 91.5 \pm 1.6$;[21] $\overline{V}[Rh(NH_3)_5H_2O^{3+}] = 60.7 \pm 0.9$;[21] $\overline{V}$[*trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$] = 85.5 ± 1.8;[6] $\overline{V}$[*trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$] = 91.1 ± 1.7;[6] $\overline{V}(Cl^-) = 21.8$;[22] $\overline{V}(Br^-) = 29.4$;[22] $\overline{V}(NH_3) = 24.8$;[23] $\overline{V}(H^+) = 4.523$; $\overline{V}(NH_4{}^+) = 14.2$.[22] [c] Estimated volume change for a dissociative reaction mode—see Results and Discussion. [d] From Table III. [e] Assume $\overline{V}[Rh(NH_3)_5{}^{3+}] = 63.2 \pm 0.9$.[21] [f] Assume $\overline{V}[Rh(NH_3)_4X^{2+}] = \overline{V}[Rh(NH_3)_5X^{2+}]$; $\Delta\overline{V}_D$ values for NH_3 dissociation do not assume protonation of the released ammonia—see Results and Discussion.

eq 8. However, the shorter lifetimes and weaker emissions from the perprotio complexes in H_2O prevented the measurements of accurate lifetimes for these species in the pressure cell. Therefore, for the sake of discussion, the $\Delta V_n{}^{\ddagger}$ values for these complexes were assumed to be the same as those calculated for their perdeuterio analogues, and values of $\Delta V^{\ddagger}{}_{\tau^{-1}}$ and of $\Delta V^{\ddagger}{}_p$ were therefore estimated by the sequential application of eq 9 and 6, respectively. Notably the $\Delta V^{\ddagger}{}_{\tau^{-1}}$ values

$$\Delta V^{\ddagger}{}_{\tau^{-1}} = \Delta V_n{}^{\ddagger} + \frac{\phi_1 \Delta V^{\ddagger}{}_{\phi_1} + \phi_2 \Delta V^{\ddagger}{}_{\phi_2}}{1 - \phi_1 - \phi_2} \qquad (9)$$

so estimated for the perprotio complexes are not significantly different from those determined directly for the perdeuterio analogues, consistent with the observation that deuteration had relatively minor effects on values for $\Delta V^{\ddagger}{}_{\phi}$ as well.

Examination of the activation volumes reported in Table III indicates some interesting patterns of behavior. First, $\Delta V^{\ddagger}{}_{\phi}$ and $\Delta V_p{}^{\ddagger}$ are consistently negative for halide aquation but consistently positive for ammine aquation. Moreove, $\Delta V^{\ddagger}{}_{\tau^{-1}}$ and $\Delta V_n{}^{\ddagger}$ follow the pattern set for the major photoreaction pathway; i.e., negative values are seen for $Rh(ND_3)_5Cl^{2+}$ where chloride photoaquation dominates but positive values are found for $Rh(ND_3)_5Br^{2+}$ where ammine aquation dominates as the antithermal photoreaction. At first, one is tempted to attribute the negative or positive character of $\Delta V^{\ddagger}{}_{\tau^{-1}}$ to the effect of pressure on the dominant photoreaction in determining pressure effects on the lifetime. However, examination of eq 9 and of the numerical values of the activation parameters demonstrates that the largest contribution to $\Delta V^{\ddagger}{}_{\tau^{-1}}$ is from $\Delta V_n{}^{\ddagger}$, consistent with the fact that the most significant deactivation pathway under all conditions investigated is nonradiative deactivation. The absolute values of $\Delta V_n{}^{\ddagger}$ are small, in agreement with the assumption taken in earlier studies[3-6] that this value would be small (see Introduction). However, the nonzero values of $\Delta V_n{}^{\ddagger}$ are experimentally significant and, more importantly, have opposite signs for the chloro (negative) and bromo (positive) complexes. These signs parallel the signs of the $\Delta V_p{}^{\ddagger}$ values of the predominant reactions in each case and suggest a relationship between the mechanisms of the nonradiative deactivation (k_n) and reactive deactivation (k_p) pathways. Previous papers have addressed this question by suggesting that one significant contribution to nonradiative deactivation is a so-called "strong coupling" mechanism perhaps related to the ligand labilization pathway to the extent of showing similar activation parameters.[17,20] (The competing "weak coupling" mechanism would be expected to be relatively temperature and pressure insensitive.) Thus, the parallel between the signs of the $\Delta V^{\ddagger}$ values for the dominant k_p pathway and for k_n of the haloamine complexes may in fact represent an experimental indication of the parallel character of k_p and the strong coupling contribution to k_n.

Evaluation of the mechanistic significance of the $\Delta V_p{}^{\ddagger}$ values calculated for the excited-state ammine and halide aquations will be aided by consideration of the reaction volume profiles. In Table IV are listed the overall volume changes $\Delta\overline{V}$ for the two aquation pathways depicted in eq 5 calculated from the measured partial molar volumes of the reactants and products.[6,21-23] It is noteworthy that halide aquation, which gives X^- plus $Rh(NH_3)_5H_2O^{3+}$, has negative values of $\Delta\overline{V}$ owing to solvation changes induced by charge creation, i.e., a dication $Rh(NH_3)_5X^{2+}$ reacting to give a trication plus an anion. In contrast ammine photoaquation in acidic solutions gives *trans*-$Rh(NH_3)_4(H_2O)X^{2+}$ plus $NH_4{}^+$ and exhibits a small positive $\Delta\overline{V}$. Differences between the $\Delta\overline{V}$ values of ammine vs. halide photoaquation are about 20 $cm^3\ mol^{-1}$ for X = Cl or Br.

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Volume changes between the initial complexes and those species produced as the result of a hypothetical ligand dissociation ($\Delta\bar{V}_D$, eq 10) or as the the result of a hypothetical

$$RhA_5X^{2+} \rightarrow RhA_5^{3+} + X^- \text{ (or } RhA_4X^{2+} + A) \quad (10)$$

association of a solvent molecule (ΔV_A, eq 11) can be calcu-

$$RhA_5X^{2+} + H_2O \rightarrow RhA_5X(H_2O)^{2+} \quad (11)$$

lated by using the somewhat controversial assumptions[24,25] that the 5- and 7-coordinated rhodium(III) species produced have about the same volume as hexacoordinate Rh(III) ammines with the same electrostatic charge. (Note that the $\Delta\bar{V}_D$ calculation for ammine dissociation ignores the eventual protonation of the ammonia released since no pH effects were found for quantum yields in acidic solution.[9]) The $\Delta\bar{V}_D$ values so calculated are listed in Table IV and again show NH_3 labilization to give a predicted volume change more than 20 cm^3 mol^{-1} greater than that for X^- dissociation, since in the latter case the volume effects of charge creation nearly cancel those expected from generating an additional particle. In contrast, the volume change for a limiting H_2O association would be expected to have consistent values of about −18 cm^3 mol^{-1} in each case. Thus, the fact that there are considerable differences between the measured $\Delta V_p^\ddagger$ values for the competitive NH_3 and X^- labilizations from the same $Rh(NH_3)_5X^{2+}$ ions is particularly significant. The magnitude of these differences, ~18 cm^3 mol^{-1} for X = Cl and ~15 cm^3 mol^{-1} for X = Br, $\Delta V_p^\ddagger$ for NH_3 loss being the more positive in each case, strongly suggests a substantially dissociative character for the transition state of NH_3 and X^- labilization from the ligand field excited states.

A key question that must be addressed is whether the actual $\Delta V_p^\ddagger$ values are consistent with the limiting dissociative model for ligand labilization from the LF excited states of d^6 complexes. Such a model has been proposed[14,26] to account for stereochemical rearrangements associated with ligand photoaquation in systems such as the disubstituted tetraammines $Rh(NH_3)_4XY^{n+}$ and is consistent with the preponderance of experimental observations and theoretical interpretations related to the LF photochemistry of d^6 complexes.[27] According to the arguments presented in the Introduction, LF excitation leads to efficient formation of the hexacoordinate triplet ligand field excited state (eq 12). Aquation by a limiting dissociative

$$RhA_5X^{2+} \xrightarrow{h\nu} [RhA_5X^{2+}]^* \quad (12)$$

mechanism would lead to pentacoordinate intermediates (eq 13), which subsequently react with solvent to give the products

$$[RhA_5X^{2+}]^* \xrightarrow{k_p} [RhA_5^{3+}]^* + X^- \text{ (or } [RhA_4X^{2+}]^* + A) \quad (13)$$

in eq 5. The volume difference between $[RhA_5X^{2+}]^*$ and the transition state of eq 13 represents $\Delta V_p^\ddagger$.

The partial molar volume $\bar{V}$ of $[RhA_5X^{2+}]^*$ is unknown; however, recent analyses of the vibrational structure of low-temperature electronic absorption and emission spectra of octahedral d^6 complexes conclude that the triplet LF states of such species have metal–ligand bond lengths more than 0.1 Å longer than those of the ground state.[28] From this information and the $\bar{V}$ values of ground-state ions, excited-state volume increases by as much as +10 cm^3 mol^{-1} can be estimated, the magnitude depending on whether the bond lengthening is isotropic or anisotropic. It has been argued that the pentacoordinate intermediates generated in eq 13 remain in triplet LF states. However, since the other ligand–metal bonds are expected to shorten toward ground-state lengths as the excitation becomes channeled along the bond undergoing dissociation, we conclude that $\bar{V}$ for the excited pentacoordinate intermediates would have volumes similar to those for the respective analogous ground-state species. Hence, the $\Delta\bar{V}_D$ that was calculated for the ground-state dissociation (eq 10, Table IV) should be more positive than that of the excited-state analogue eq 13) by an amount approximately equal to the volume difference between RhA_5X^{2+} and $[RhA_5X^{2+}]^*$.

The substantially negative $\Delta V_p^\ddagger$ values reported here for halide aquation from $[RhA_5X^{2+}]^*$ are consistent with previous observations[29] of marked solvent effects in the photoreactions of $Rh(NH_3)_5Cl^{2+}$. While Cl^- aquation is the predominant photosubstitution pathway for this complex in aqueous media, NH_3 labilization dominates in less ionizing solvents such as dimethylformamide. Calculations of k_p values based on combined quantum yield/luminescence lifetime measurements indicate that k_{Cl} varies by several orders of magnitude and parallels the solvents' abilities to solvate Cl^-. In contrast, k_{NH_3} is relatively solvent insensitive.[29] With regard to the $\Delta V_p^\ddagger$, the values for X^- labilization suggest that a negative solvational term, the result of solvent collapse to facilitate the charge creation, is the factor dominating volume changes in achieving the transition state for aquation of the anion from the hexacoordinate excited state.

Concluding Remarks

The results described in this article have lead to the following observations and conclusions. First, the substantial differences between the $\Delta V_p^\ddagger$ values calculated for NH_3 and X^- aquations from the ligand field excited state of RhA_5X^{2+} (A = NH_3, ND_3; X = Cl, Br) point to a mechanism with substantially dissociative character for these substitution reactions. Second, once the expanded volume of the ligand field excited state is taken into account, the actual values of $\Delta V_p^\ddagger$ appear to be quite consistent with a limiting dissociative mechanism for this reaction. In addition, it appears that solvent rearrangements due to charge creation dominate the volume parameters for X^- labilizations. Third, the observation that the signs for the activation volumes for nonradiative deactivation $\Delta V_n^\ddagger$ parallel those for the $\Delta V_p^\ddagger$ of the principal reaction pathways from the chloro or bromo complexes suggests that a significant contribution to nonradiative deactivation may be a strong coupling mechanism related to the ligand dissociation pathway.

Last, from a phenomenological standpoint it is interesting to note that measurement of the ϕ_p and τ under the same conditions allows one to calculate k_p values from eq 2 and to examine directly the pressure effects on these. For example, at nearly ambient pressure, k_{Cl^-} and k_n for the LF excited state of $Rh(ND_3)_5Cl^{2+}$ have the respective values 1.1×10^7 s^{-1} and 3.1×10^6 s^{-1}, while at 200 MPa, k_{Cl^-} increases by about a factor of 2 (to 2.1×10^7 s^{-1}) while k_n decreases by a comparable factor (to 2.0×10^6 s^{-1}).

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Registry No. $Rh(NH_3)_5Cl^{2+}$, 15379-09-6; $Rh(ND_3)_5Cl^{2+}$, 50513-49-0; $Rh(NH_3)_5Br^{2+}$, 15337-80-1; $Rh(ND_3)_5Br^{2+}$, 50513-50-3; $Rh(NH_3)_5H_2O^{3+}$, 15337-79-8; *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$, 38781-25-8; $Rh(ND_3)_5D_2O^{3+}$, 83967-60-6; *trans*-$Rh(ND_3)_4(D_2O)Cl^{2+}$, 83967-61-7; *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$, 71424-39-0; *trans*-$Rh(ND_3)_4(D_2O)Br^{2+}$, 83967-62-8; Cl^-, 16887-00-6; NH_4^+, 14798-03-9; Br^-, 24959-67-9.

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Magnetic Exchange Interactions Propagated by Saturated Bridges in Binuclear Dicyclopentadienyltitanium(III) Complexes

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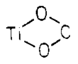
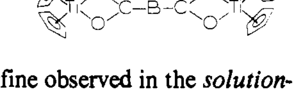
The single-crystal X-ray structures of one mononuclear and two binuclear dicyclopentadienyltitanium(III) carboxylate complexes have been determined. The mononuclear benzoate complex $(\eta^5\text{-}C_5H_5)_2Ti(O_2CC_6H_5)$ crystallizes in space group $P2_1/n$ with $a = 11.388$ (2) Å, $b = 11.564$ (2) Å, $c = 22.673$ (3) Å, $\beta = 105.09$ (1)°, and $Z = 8$. Diffraction data were collected with a Syntex $P\bar{1}$ automated diffractometer, and the structure was refined to $R_F = 0.054$ and $R_{wF} = 0.059$ for 2257 reflections with $I > 3\sigma(I)$ and $2\theta = 3\text{–}50.0°$ (Mo Kα radiation). There are two independent $(\eta^5\text{-}C_5H_5)_2Ti(O_2CC_6H_5)$ molecules in the unit cell; both have similar bond distances and angles. The angles and distances within the titanium coordination sphere are those expected for pseudotetrahedral coordination. The dihedral angles between the phenyl rings of the benzoate ligands and the



planes in the two different molecules are 12.8 and 11.3°. The binuclear complex bridged by the bicyclo[1.1.1]pentane-1,3-dicarboxylate dianion, $(\eta^5\text{-}C_5H_5)_2Ti(O_2CC_5H_6CO_2)Ti(\eta^5\text{-}C_5H_5)_2$, crystallizes in the space group $P2_1/c$ with $a = 8.136$ (2) Å, $b = 10.671$ (2) Å, $c = 17.553$ (3) Å, $\beta = 124.4$ (1)°, and $Z = 4$. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer, and the structure was refined to $R_F = 0.044$ and $R_{wF} = 0.061$ for 2083 reflections with $I > 3\sigma(I)$ and $2\theta = 3.5\text{–}55.0°$ (Mo Kα radiation). Normal pseudotetrahedral distances and angles are found for each of the Ti(III) ions in the binuclear complex. The binuclear complex is centrosymmetric with the bicyclo[1.1.1]pentane moiety disordered equally in two positions and with an *intra*molecular Ti–Ti distance of 9.8509 (6) Å. The nonbonding bridgehead C–C distance increases from 1.845 Å in bicyclo[1.1.1]pentane to 1.858 (4) Å in the dicarboxylate bridge of the binuclear complex. The binuclear complex bridged by the *trans*-cyclobutane-1,2-dicarboxylate dianion, $(\eta^5\text{-}C_5H_5)_2Ti(O_2CC_4H_6CO_2)Ti(\eta^5\text{-}C_5H_5)_2$, crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 11.096$ (2) Å, $b = 26.804$ (5) Å, $c = 8.049$ (1) Å, and $Z = 4$. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer, and the structure was refined to $R_F = 0.038$ and $R_{wF} = 0.052$ for 2355 reflections with $I > 3\sigma(I)$ and $2\theta = 3.5\text{–}55.0°$ (Mo Kα radiation). The cyclobutane ring of the bridging dicarboxylate dianion is nonplanar with a dihedral angle of 153°. The *intra*molecular Ti–Ti distance in the cyclobutanedicarboxylate-bridged binuclear complex is 7.8326 (11) Å. The origin of the weak ($J = -3.9$ cm^{-1} with $H = -2J\hat{S}_1\cdot\hat{S}_2$) antiferromagnetic exchange interaction for the "mononuclear" benzoate complex is examined with the X-ray results, as well as with characterization of analogous molecules such as $(\eta^5\text{-}C_5Me_5)_2Ti(O_2CC_6H_5)$. Variable-temperature (3–12 K) EPR results for toluene–benzene (4:1) glasses of five of the complexes, together with previously measured room-temperature EPR spectra, clearly indicate the presence of *intra*molecular magnetic exchange interactions in these binuclear dicyclopentadienyltitanium(III) complexes.

Introduction

In a series[3-5] of recent papers the question whether a saturated bridge could propagate a magnetic exchange interaction between two distant $(\eta^5\text{-}C_5H_5)_2Ti^{III}$ moieties was investigated. Sixteen binuclear complexes with saturated bridges and six with unsaturated bridges were examined. All 22 complexes are bridged by dicarboxylate dianions (where B is some hydrocarbon):



Titanium hyperfine observed in the *solution-state* EPR spectra for several of the binuclear complexes definitely established the presence of an *intra*molecular magnetic exchange interaction between the two Ti(III)-metallocene units. Antiferromagnetic exchange interactions ($J = -0.8$ to -3.0 cm^{-1}) were also evident in the magnetic susceptibility data for many of these complexes in the *solid-state*. It was difficult to decide whether the antiferromagnetic interaction seen for the solid-

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