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Supplementary Material Available: A listing of final thermal parameters for **1** (1 page); a listing of final observed and calculated structure factors for **1** (12 pages). Ordering information is given on any current masthead page.

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Pressure Effects on the Excited-State Reaction Dynamics of *cis*-Bis(bipyridine)dichlororhodium(III), *cis*-$Rh(bpy)_2Cl_2^+$

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Pressure effects on the photosubstitution quantum yields and luminescence lifetimes of the *cis*-$Rh(bpy)_2Cl_2^+$ ion (bpy = 2,2′-bipyridine) were studied over the range 0–200 MPa in aqueous solution. The combined results of these measurements lead to a calculated activation volume of -9.7 ± 0.8 cm^3 mol^{-1} for chloride aquation from the ligand field excited state. The principal photoproduct is the *cis*-$Rh(bpy)_2(H_2O)Cl^{2+}$ ion, but spectroscopic data are described that support partial isomerization to give *trans*-$Rh(bpy)_2(H_2O)Cl^{2+}$ as a minor photoproduct as well. These and related data are discussed in terms of possible excited-state mechanisms.

Introduction

Our interest in the photophysical and photochemical properties of d^6 metal complexes has led to a series of detailed investigations of the mechanisms of the excited-state reactions of rhodium(III) ammine ions using high-pressure techniques.[3–6] In these studies, rate constants and volumes of activation ($\Delta V^{\ddagger}$) for the different physical and chemical decays from the lowest energy excited states (ligand field triplet states, ^{3}LF) were determined from photoreaction quantum yields (ϕ_p) and luminescence lifetimes (τ) measured as functions of pressure. The resulting data were compared with reaction profiles drawn from partial molar volumes obtained by density measurements, and mechanistic conclusions concerning the nature of the excited-state processes were drawn and were correlated with earlier assignments.[7–15] In general, the observations concerning photosubstitution and photoisomerization reactions of such rhodium(III) ammine complexes could be interpreted in terms of a limiting dissociative ligand labilization from the ^{3}LF state.

The present study deals with the pressure effects on the photochemistry and photophysics of the *cis*-$Rh(bpy)_2Cl_2^+$ ion, which has previously been reported to undergo photoaquation to the monoaquo complex *cis*-$Rh(bpy)_2(H_2O)Cl^{2+}$ in acidic aqueous solution[16] and to show a weak emission from the lowest energy ^{3}LF state under such conditions.[17] Determination of reaction quantum yields, emission lifetimes, and the pressure dependencies of these parameters under the same conditions enable calculation of rate constants (k_i) and activation volumes ($\Delta V_i^{\ddagger}$) for ligand substitution and nonradiative deactivation. Density measurements were also carried out to determine partial molar volumes of the reactant and of the major product *cis*-$Rh(bpy)_2(H_2O)Cl^{2+}$. In addition, NMR analyses of the photochemical reaction solutions revealed evidence for the formation of a minor photoproduct concluded to be the *trans*-$Rh(bpy)_2(H_2O)Cl^{2+}$ isomer.[18]

Table I. UV/Vis Data for the Synthesized Compounds

complex^a	λ_{max}, nm	ϵ, M^{-1} cm^{-1} × 10^{-4}
cis-$[Rh(bpy)_2Cl_2]^+$	384 (sh)	1.04 × 10^{-2}
	311	2.73
	302 (sh)	2.35
	252	2.32
cis-$[Rh(bpy)_2(H_2O)Cl]^{2+}$	316 (sh)	2.12
	307	2.58
	248	2.44
cis-$[Rh(bpy)_2(H_2O)_2]^{3+}$	319	2.68
	306	2.75
	299 (sh)	1.99
	243	2.77

^{a}Spectra obtained as perchlorate salts in dilute aqueous solution, at pH 2 and 25 °C.

Experimental Section

Materials. The complexes *cis*-$[Rh(bpy)_2Cl_2]Cl\cdot 2H_2O$, *cis*-$[Rh(bpy)_2Cl(H_2O)](ClO_4)_2\cdot H_2O$, and *cis*-$[Rh(bpy)_2(H_2O)_2](ClO_4)_3\cdot H_2O$ were prepared and recrystallized according to published procedures[19,20] with the modifications noted below for the aqua chloro complex. The salt *cis*-$[Rh(bpy)_2Cl_2](ClO_4)\cdot 2H_2O$ was prepared from an aqueous so-

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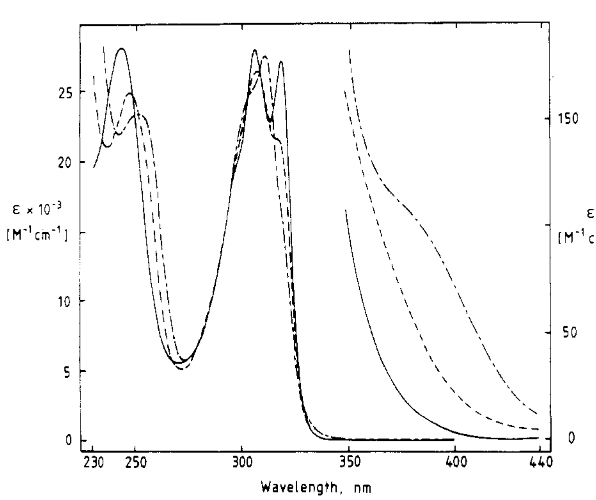

Figure 1. UV/vis spectra: *cis*-$[Rh(bpy)_2Cl_2]ClO_4\cdot 2H_2O$ (----); *cis*-$[Rh(bpy)_2(H_2O)Cl](ClO_4)_2\cdot H_2O$ (---); *cis*-$[Rh(bpy)_2(H_2O)_2](ClO_4)_3\cdot H_2O$ (—).

lution of the analogous chloride species by precipitation with perchloric acid and recrystallization from dilute aqueous $NaClO_4$ solution. All other chemicals were of analytical reagent grade, and doubly distilled water was used throughout the investigation.

The base hydrolysis of the dichloro complex to produce the hydroxo chloro species (the key step in the synthesis of the *cis*-$Rh(bpy)_2(H_2O)Cl^{2+}$ ion)[20] was monitored spectrophotometrically because of reproducibility difficulties. Samples were taken and acidified and the UV/vis spectra recorded. As soon as the UV absorption band (Figure 1) showed a shoulder at 316 nm, the reaction was quenched by cooling to prevent the formation of the dihydroxo complex. The pH of this solution was then adjusted to pH 10 by adding $HClO_4$. The immediate precipitate was removed and found to be the unreacted dichloro complex. The filtrate solution was allowed to stand in the refrigerator for 2 days leading to formation of a yellow crystalline solid, presumably the chloro hydroxo complex. This was recovered by filtration and then redissolved in hot water. Sufficient concentrated $HClO_4$ was then added to give an acid concentration of about 0.5 M. After the solution was allowed to stand in the refrigerator, pale yellow needles of the aquo chloro salt *cis*-$[Rh(bpy)_2Cl(H_2O)](ClO_4)_2$ were obtained. These were dried in vacuo over $CaCl_2$ at 80 °C.

The synthesized compounds were characterized by UV/vis and ^1H NMR spectroscopy (270 MHz), and their purity was checked by chemical analysis.[21] Electronic spectral data are given in Table I. The reported λ_{max} values for each complex agreed well with the literature,[17,20] and extinction coefficients agreed quantitatively for the $Rh(bpy)_2Cl_2^+$ ion;[17] however, ϵ_{max} values somewhat different from those initially reported[20] were obtained for the *cis*-$Rh(bpy)_2(H_2O)Cl^{2+}$ and *cis*-$Rh(bpy)_2(H_2O)_2^{3+}$ ions. Nonetheless, the NMR spectra of each of these complexes in D_2O could be fully analyzed in terms of expected chemical shifts and coupling constants and showed no evidence of any other complexes being present. In particular, the spectrum of the *cis*-aquochloro salt displayed no resonances corresponding to those characteristic of either the *cis*-dichloro or the *cis*-diaquo analogues (see below). This is an important point, given that the difference method used here for quantum yield measurements depends on accurate spectral properties of the known species and that the extinction coefficients reported here for aquo chloro species differ by about 10% from those reported previously (Table I).

Instrumentation. Photolyses were carried out in a thermostated (25.0 ± 0.2 °C) high-pressure cell compartment[22] positioned on top of a magnetic stirrer. Test solutions were irradiated in a pillbox spectrophotometer cell[23] (2.54-cm^3 volume at ambient pressure), and mixing during irradiation was effected by vigorous stirring with a Teflon-coated magnetic bar (2 × 6 mm). The mixing effectiveness at all pressures could be confirmed by visual examination through the sapphire windows of the high-pressure cell compartment. For such examinations, the pillbox cell was positioned higher; i.e., the distance from the magnetic stirrer was greater than during the photolysis experiments, where care was taken to prevent interference between the stirrer and the photolysis beam. Light at 313 nm was selected from an Osram HBO 100/2 high-pressure mercury lamp using Oriel interference filters (bandwidth 12 nm at half of the maximum transmission). A nearly collimated light beam was focused into the pressure cell with the aid of quartz lenses and a pinhole. A PRA TX 7 electronic feedback system coupled to a PRA M302 lamp power supply was employed to stabilize the light flux by monitoring a small fraction of the light beam split off with the aid of a quartz plate. The quantum flux of the absorbed light was determined by measuring the photocurrent of a PIN 10 (Silicon Detector Corp.) photodiode. Calibration was effected with the aid of the HCD actinometer.[24] All spectra were recorded on a Perkin-Elmer 555 spectrophotometer.

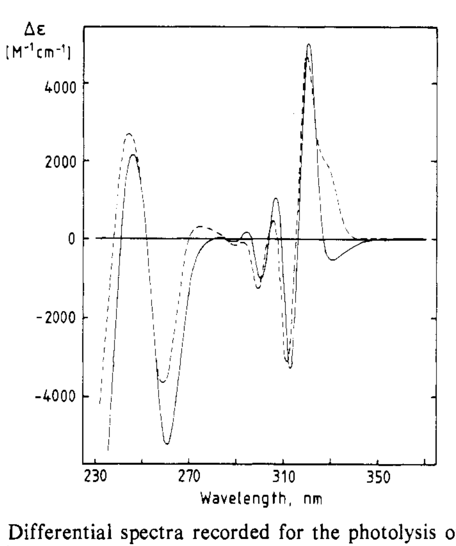

Figure 2. Differential spectra recorded for the photolysis of *cis*-$[Rh(bpy)_2Cl_2]^+$ in acidic aqueous solution: (---) total photolysis spectrum; (—) expected spectrum if *cis*-$[Rh(bpy)_2(H_2O)Cl]^{2+}$ were the exclusive product.

Density measurments for the determination of partial molar volumes were carried out with a digital densitometer, Anton Paar DMA 02, thermostated at 25.000 ± 0.002 °C.

The pressure dependence of the luminescence lifetimes was measured by pulse laser techniques as previously described.[4,5] The excitation wavelength was 266 nm (fourth harmonic of the Nd/YAG laser source).

NMR spectra were recorded on a 270-MHz instrument operating in the FT mode.

Calculation of Quantum Yields. Photolysis experiments were performed at five different pressures in the range of 5–200 MPa. Complex concentrations were varied in the range (6–9) × 10^{-5} M. Small spectral changes in the course of irradiation required the degree of photochemical conversion to be kept in the range of 10–20%, and quantum yields were corrected for inner-filter effects.[25] For each series of pressure dependence measurements, all other parameters were kept constant. The degree of photochemical conversion was determined according to a differential spectral method.

Results and Discussion

Analysis of the Observed Photoproducts. Photolysis of *cis*-$Rh(bpy)_2Cl_2^+$ in acidic aqueous solution ($HClO_4$, pH 2.7, λ_{irr} 313 nm) led to the formation of a product with an electronic spectrum close to that of *cis*-$Rh(bpy)_2(H_2O)Cl^{2+}$. However, careful examination of a differential spectrum using the unphotolyzed starting solution as the reference showed measurable differences from the behavior expected if eq 1 were the sole photoreaction

$$cis\text{-}Rh(bpy)_2Cl_2^+ + H_2O \xrightarrow{h\nu} cis\text{-}Rh(bpy)_2(H_2O)Cl^{2+} + Cl^- \tag{1}$$

(Figure 2). One possible explanation might be that the initial photoproduct undergoes secondary photolysis to the diaquo species *cis*-$Rh(bpy)_2(H_2O)_2^{3+}$. This possibility was examined in a separate

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[21] Hoechst AG Analytical Laboratory, Frankfurt. Determined (and theoretical) values for the complex [*cis*-$Rh(bpy)_2(H_2O)Cl](ClO_4)_2\cdot H_2O$ ($C_{20}H_{20}O_{10}N_4Cl_3Rh$): C, 34.9 (35.0); H, 2.9 (2.9); N, 8.0 (8.2); O, 22.9 (23.3); Cl, 15.9 (15.5); Rh, 15.2 (15.0). Determined (and theoretical) values for the complex $[Rh(bpy)_2(H_2O)_2](ClO_4)_3\cdot H_2O$ ($C_{20}H_{22}O_{14}N_4Cl_3Rh$): C, 30.8 (31.3); H, 2.7 (2.9); N, 7.2 (7.3); Cl, 14.0 (13.9); Rh, 13.6 (13.4).

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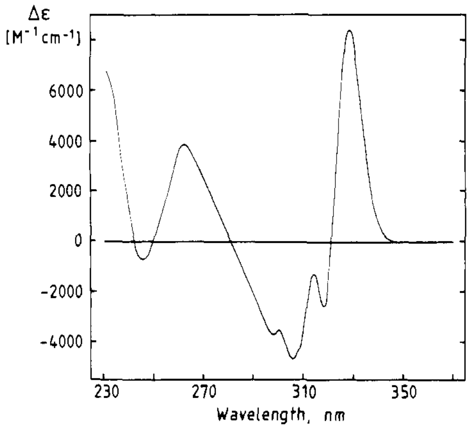

Figure 3. Differential spectrum recorded for the photolysis of *cis*-$[Rh(bpy)_2(H_2O)Cl]^{2+}$ in acidic aqueous solution.

experiment by photolyzing an authentic sample of *cis*-$Rh(bpy)_2(H_2O)Cl^{2+}$ in acidic aqueous solution. The spectral changes thereby observed with the differential technique (Figure 3) were inconsistent with the formation of the diaquo product but did agree with those differences noted in the photolysis of the dichloro complex. Thus, another product must be invoked to explain these spectral observations. Nonetheless, while the lesser product from the photolysis of the dichloro complex appears to be the same as that produced by direct photolysis of the *cis*-aquochloro complex, the consistency of the spectra recorded periodically during the course of the photolysis of *cis*-$Rh(bpy)_2Cl_2^+$ strongly suggests that both the *cis*-aquochloro complex and the minor second product are formed competitively as primary photoproducts of the system.

The ^1H NMR spectrum (270 MHz) of the product solution from the exhaustive photolysis (313 nm) of *cis*-$Rh(bpy)_2Cl_2^+$ in $D_2O/DClO_4$ solution displayed four resonances in the aromatic region, two doublets and two double doublets of equal intensities, at frequencies (Figure 4) different from those noted for the bipyridine hydrogens of *cis*-$Rh(bpy)_2(H_2O)Cl^{2+}$ and representing about 10% of the total photoproduct. The same resonances were also generated directly by photolysis of *cis*-$Rh(bpy)_2Cl(H_2O)^{2+}$ in solution, and the difference spectrum between those of an authentic sample of *cis*-$Rh(bpy)_2(H_2O)Cl^{2+}$ and the product photolysis solution is shown in Figure 4b. The frequencies of these bands are different from those found in the NMR spectra of authentic samples of the *cis*-dichloro or *cis*-diaquo complexes or of free bipyridine. However, the pattern of relative intensities and frequencies of these new resonances is very similar to that reported[26] for the well-characterized ruthenium(II) ion *trans*-$Ru(bpy)_2(CH_3CN)_2^{2+}$, an observation that suggests the unknown product may be the *trans*-$Rh(bpy)_2(H_2O)Cl^{2+}$ ion. All attempts to isolate this product (via crystallization or ion-exchange chromatography) were unsuccessful. Such an assignment is therfore tenuous, given the possibility that key NMR resonances in the more complicated spectra expected for species such as a monodentate bipyridine complex might be obscured by the resonances of the major product. Nonetheless, we believe such to be unlikely and that the symmetry of the detected NMR spectrum points strongly toward assignment as the *trans*-$Rh(bpy)_2(H_2O)Cl^{2+}$ configuration.

Although there are no known *trans*-bis(bipyridine) complexes of Rh(III) that have been characterized, *trans*-$Rh(bpy)_2(H_2O)Cl^{2+}$ would be the product for photoaquation of Cl^- from *cis*-$Rh(bpy)_2Cl_2^+$ predicted by the model described for the photoisomerization of d^6 complexes.[7,14,15] According to this model, the square-pyramidal, electronically excited, pentacoordinate intermediate $[Rh(bpy)_2Cl^{2+}]^*$ resulting from Cl^- dissociation from the lowest energy ^3LF state would have a site preference for the stronger field ligands in the basal positions as the result of orbital energy considerations. This preference would put Cl^- in the apical site, a configuration that would be the precursor to *trans*-$Rh(bpy)_2(H_2O)Cl^{2+}$ when trapped by the solvent. This model does not address other considerations such as steric effects that may prevent the trans species from being the predominant product. Nonetheless, the observation of partial cis to trans isomerization, concomitant with Cl^- photoaquation from the *cis*-dichloro complex or with H_2O photolabilization from *cis*-$Rh(bpy)_2(H_2O)Cl^{2+}$, would be consistent with similar observations[27] with $RhA_4Cl_2^+$ and $RhA_4(H_2O)Cl^{2+}$ complexes, where A is NH_3, en/2, etc. The same model also explains the observation that the ruthenium(II) ion *cis*-$Ru(bpy)_2(H_2O)_2^{2+}$ undergoes cis to trans photoisomerization.[28]

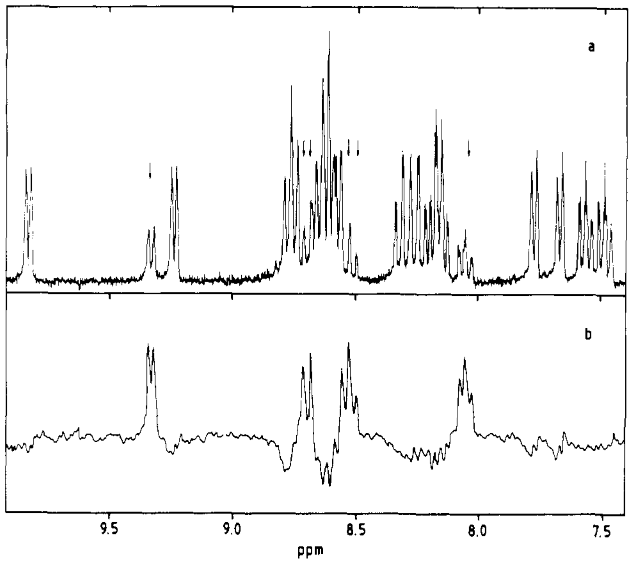

Figure 4. (a) ^1H NMR spectrum (270 MHz) of a photolyzed solution of *cis*-$[Rh(bpy)_2(H_2O)Cl](ClO_4)_2$ in $D_2O/DClO_4$. (b) Difference of the ^1H NMR spectra of an acidic solution of *cis*-$[Rh(bpy)_2(H_2O)Cl](ClO_4)_2$ in $D_2O/DClO_4$ before and after irradiation with light at 313 nm.

Ambient Pressure Measurements. From the exhaustive photolysis of *cis*-$Rh(bpy)_2(H_2O)Cl^{2+}$, the extinction coefficients for the proposed trans species were estimated from spectral changes and the conclusion drawn from ^1H NMR analysis of a similarly photolyzed solution that the latter species represented about 10% of the total product. Quantum yields (λ_{irr} 313 nm) could then be calculated by assuming Cl^- aquation gave 90% *cis*-$Rh(bpy)_2(H_2O)Cl^{2+}$ plus 10% of the second product. The results for overall photoconversion calculated at various wavelengths were, within experimental uncertainty, the same as those obtained at 317 nm, an isosbestic point for the two products (Figures 2 and 3).

At ambient pressure the quantum yield for Cl^- aquation (ϕ_p) was determined to be 0.056 ± 0.008 mol/einstein in acidic aqueous solution. The phosphorescence observed by pulse laser techniques was weak; thus, the photosubstitution and nonradiative deactivation are by far the dominant pathways for deactivating the lowest energy excited state, also concluded to be the ^3LF state in this case.[17] Therefore, a good approximation for the fraction of nonradiative decay ϕ_n is $1 - \phi_p$. The measured lifetime τ under these conditions was 39 ± 2 ns. If intersystem crossing/internal conversion from upper states to the ^3LF state is assumed efficient (as seen for other Rh(III) complexes),[12] then the excited-state rate constant for labilization of Cl^- (eq 2) can be calculated from eq 3. This value is $(1.4 \pm 0.2) \times 10^6$ s⁻¹, significantly smaller

$$[cis\text{-}Rh(bpy)_2Cl_2^+]^* \xrightarrow[H_2O]{k_p} Rh(bpy)_2(H_2O)Cl^{2+} + Cl^- \quad (2)$$

$$k_p = \phi_p \tau^{-1} \quad (3)$$

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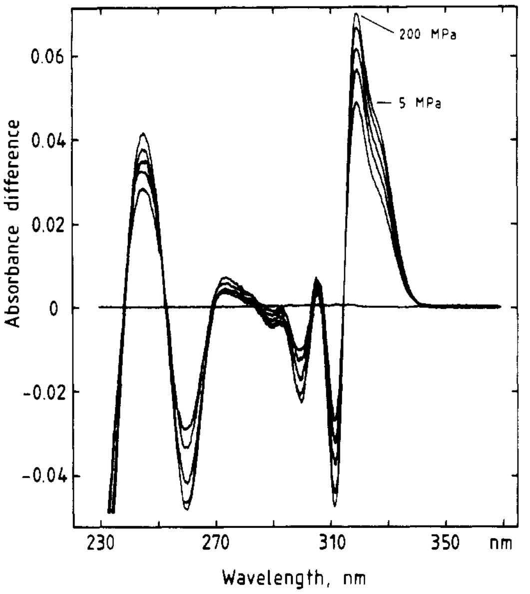

Figure 5. Differential spectral measurements for the photoaquation of *cis*-$[Rh(bpy)_2Cl_2]^+$ at various pressures (λ_{irr} = 313 nm, t = 8 min, incident light intensity 6.5 × 10^{14} quanta/s).

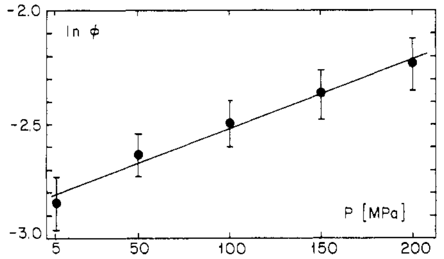

Figure 6. Plot of ln ϕ_p vs. P for the photolysis of *cis*-$[Rh(bpy)_2Cl_2]^+$ in aqueous solution.

Table II. Pressure Dependence of the Photoaquation Quantum Yield of *cis*-$[Rh(bpy)_2Cl_2]^+$ When Irradiated at 313 nm in Acidic (pH 2.7) Aqueous Solution at 298 K

pressure, MPa	no. of expts	$10\phi_p$, mol/einstein	pressure, MPa	no. of expts	$10\phi_p$, mol/einstein
5	18	0.58 ± 0.07	150	13	0.94 ± 0.11
50	13	0.72 ± 0.07	200	9	1.08 ± 0.12
100	13	0.83 ± 0.08			

than the k_p's for the analogous Cl^- labilization from the ^3LF states of $Rh(NH_3)_5Cl^{2+}$ (1.3 × 10^7 s^{-1})[9] and *cis*-$Rh(NH_3)_4Cl_2^+$ (3.0 × 10^8 s^{-1})[27] but larger than the value for labilization from the ^3LF state of $Rh(bpy)(trpy)Cl^{2+}$ (1.3 × 10^5 s^{-1})[29] (trpy = 2,2′:6′,2″-terpyridine).

Earlier studies by Sheridan[30] have shown that the photoreactivity of $RhA_4Cl_2^+$ complexes, where A_4 is a polydentate amine, depends strongly on the stereochemical configuration of the chelating amine ligand. Those configurations that would appear to inhibit distortion of the initial coordination sphere as a Cl^- dissociates displayed lower quantum yields for halide aquation. Lifetimes were not measured for Sheridan's complexes under photochemical conditions, so actual excited-state reactivities (i.e. rates) cannot be compared. However, studies by Sexton et al.[27] have noted that complexes of this type that most readily undergo photoisomerization are also those for which the ^3LF state is more labile, suggesting some synchronous nature in the ligand dissociation and isomerization mechanisms. Thus, a likely explanation of the above rates is that the relative rigidities of the bpy and trpy ligands reduce the excited-state reactivities of *cis*-$Rh(bpy)_2Cl_2^+$ and $Rh(bpy)(trpy)Cl^{2+}$ vs. those of *cis*-$Rh(NH_3)_4Cl_2^+$ and $Rh(NH_3)_5Cl^{2+}$, respectively.

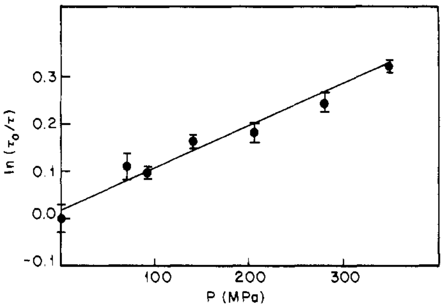

Figure 7. Pressure dependence of ln (τ_0/τ).

Table III. Pressure Dependence of τ^{-1} in Various Solvents at 296 K

solvent	$\Delta V_{\tau^{-1}}^*$, cm^3/mol	solvent	$\Delta V_{\tau^{-1}}^*$, cm^3/mol
formamide	0.2 ± 0.2	CH_3CN	0.9 ± 0.2
methanol	0.6 ± 0.2	H_2O	-2.2 ± 0.3

Table IV. Partial Molar Volumes, Determined by Density Measurements at 25.0 ± 0.002 °C in 10^{-2} M HCl Solutions[a]

complex	$\bar{V}$, cm^3/mol	$\bar{V}_{cation}$, cm^3/mol
cis-$[Rh(bpy)_2Cl_2]Cl$	300 ± 4	278 ± 4
cis-$[Rh(bpy)_2(H_2O)Cl](ClO_4)_2$	362 ± 4	261 ± 4

[a] For the anions Cl^- and ClO_4^- partial molar volumes of 21.8 and 50.7 cm^3/mol,[b] respectively, were used to calculate the partial molar volumes of the cations. [b] Horne, R. A., Ed. *Water and Aqueous Solutions, Structure, Thermodynamics and Transport Properties*; Wiley: London, 1972.

Pressure Effects. The effect of pressure on the quantum yield of the reaction is clearly demonstrated in Figure 5, which shows that overall product formation is larger at higher pressure with all other parameters constant. Quantum yields are summarized in Table II. Although ϕ_p increased at higher pressure, there appeared to be no changes in the differential spectra obtained (Figure 5). Thus, the product distribution is essentially pressure-independent. A plot of ln ϕ_p vs. P (Figure 6) is linear within the experimental error limits and gives the apparent volume of activation $\Delta V_\phi^* = -7.5 \pm 0.6$ cm^3 mol^{-1}, calculated according to eq 4. The emission lifetime measured in several solvents was also somewhat pressure-dependent, the largest pressure sensitivity being apparent in aqueous solution (Figure 7), where τ decreased from 39 ± 2 ns at 0.1 MPa to 27 ± 1 ns at 349 MPa and ΔV^* for the reciprocal lifetime was found to be −2.2 ± 0.2 cm^3 mol^{-1} (Table III). From these values the ΔV_p^* for the excited-state rate constant for Cl^- labilization in aqueous solution (eq 2) was calculated according to eq 4 and 5[4] to be −9.7 ± 0.8 cm^3 mol^{-1}.

$$\Delta V_\phi^* = -RT\left(\frac{d \ln \phi_p}{dP}\right)_T \tag{4}$$

$$\Delta V_p^* = \Delta V_\phi^* + \Delta V_\tau^* \tag{5}$$

The significantly negative ΔV^* value for Cl^- labilization from the LF excited state of *cis*-$Rh(bpy)_2Cl_2^+$ would appear to contradict the dissociative mechanism generally favored such d^6 complexes. Indeed, in the absence of other experimental tests, significant contributions from an associative mechanism such as described[31] for $Cr(bpy)_3^{3+}$ photosubstitutions, with water entering from pockets formed by the cis-oriented bpy ligands, cannot be unequivocally excluded. However, as we have previously noted for similar Rh(III) photoreactions,[4,5] the volume of activation

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consists of both intrinsic and solvational contributions, the latter being especially significant if there is charge creation or charge neutralization in the transition state. Thus, there would be considerable solvent electrostriction in the transition state for dissociation of Cl^- from the unipositive *cis*-$Rh(bpy)_2Cl_2^+$ ion to produce the dipositive $Rh(bpy)_2Cl^{2+}$ pentacoordinate complex and a uninegative Cl^-. Such electrostriction is evidenced in an overall volume change of -13.5 cm^3 mol^{-1} calculated for eq 1 from the partial molar volumes listed in Table IV. Furthermore, the overall volume change for the excited-state reaction (eq 2) would be significantly more negative, given that the ^{3}LF state must have a volume significantly larger than does the ground state.[4,32] Thus, we conclude that the ΔV_p^* value measured for eq 2 is indeed consistent with the dissociative photosubstitution mechanism predicted for such d^6 complexes and demonstrated in the photoreactions of similar Rh(III) halo amine compounds.[33]

The volume of activation for nonradiative decay was calculated from the sum of ΔV_r^* and the pressure dependence of ϕ_n (as in eq 4). The result is -1.5 ± 0.2 cm^3 mol^{-1}, having the same sign as that for photosubstitution but much smaller in magnitude. This is in accord with results for other amine complexes of rhodium(III)[4,34] and may indicate the parallel character of k_p and a strong coupling contribution to k_n. This point will be discussed in greater detail elsewhere.[34]

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(33) It is notable that the magnitude of ΔV_p^* is marginally greater for Cl^- photoaquation from *cis*-$Rh(bpy)_2Cl_2^+$ than for the analogous reaction of $Rh(NH_3)_5Cl^{2+}$ (-8.6 ± 1.6 cm^3 mol^{-1})[4] despite the smaller contributions from solvent electrostriction expected for the aquation of Cl^- from a +1 (rather than a +2) ion as evidenced by the smaller $\Delta \bar{V}$ for the former reaction.

(34) DiBenedetto, J.; Ford, P. C., manuscript in preparation.

Contribution from the Chemistry Department, Coal Research Center,
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Effect of Nitrilotriacetate on the Mechanism of Reduction of Copper(II) Ions by α-Hydroxyalkyl Free Radicals via Complexes with Copper–Carbon Bonds as Intermediates. A Pulse-Radiolytic Study[†]

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α-Hydroxyalkyl free radicals, $^{\bullet}CR_1R_2OH$, react with copper(II) nitrilotriacetate, $Cu(nta)^-(aq)$, in aqueous solutions to form the unstable intermediates $(nta)Cu^{III}{-}CR_1R_2OH^-(aq)$, or $(nta)Cu^{III}{-}CH_2O^{2-}(aq)$. These intermediates decompose by reducing a second $Cu^{II}(nta)^-(aq)$ complex, i.e. via the reaction $(nta)Cu^{III}{-}CR_1R_2OH^-(aq) + Cu^{II}(nta)^-(aq) \xrightarrow{H_2O} Cu^I(nta)^{2-}(aq) + Cu^{II}(nta)^-(aq) + CR_1R_2O + H_3O^+$. Unexpectedly, the intermediates do not decompose via first-order processes as expected. The spectrum of $(nta)Cu^{III}{-}CH_2OH^-(aq)$ is reported. The kinetics of reduction of $Co(NH_3)_6^{3+}$, $Ru(NH_3)_6^{3+}$, and $Fe(CN)_6^{3-}$ by the latter intermediate are reported.

Introduction

The addition of copper ions was shown to affect the nature of the products in a variety of reactions involving aliphatic free radicals, including catalytic processes, in protic and aprotic media.[3] The results were interpreted as indicating that aliphatic free radicals, $^{\bullet}R$, react with copper(II) and copper(I) ions to form short-lived intermediates with copper–carbon bonds, e.g.

$$^{\bullet}R + Cu^{2+}(aq) \rightarrow Cu^{III}{-}R^{2+}(aq) \qquad (1)$$

$$^{\bullet}R + Cu^{+}(aq) \rightarrow Cu^{II}{-}R^{+}(aq) \qquad (2)$$

Indeed, reactions 1 and 2 were observed for a variety of free radicals and several complexes.[4-9] However, no such intermediates were observed[4] in the reactions

$$^{\bullet}CR_1R_2OH + Cu^{2+}(aq) \rightarrow Cu^{+}(aq) + CR_1R_2O + H_3O^{+} \qquad (3)$$

It was however suggested that reaction 3 involves the formation of $Cu^{III}{-}CR_1R_2OH^{2+}(aq)$ as an intermediate but that its lifetime is too short to be observed. We decided to check wehther good σ-donating ligands, L, stabilize transients of the type $LCu^{III}{-}CR_1R_2OH$. Such an effect might be expected as such ligands stabilize complexes in higher oxidation states and therefore also decrease the free energy gain in reaction 3.

We wish to report that nitrilotriacetate, nta ($\equiv N(CH_2CO_2^-)_3$), indeed stabilizes such transients. Unexpectedly, the intermediates $(nta)Cu^{III}{-}CR_1R_2OH^{-}$[2] do not decompose via a first-order process as expected but by reduction of another $Cu^{II}(nta)^-$ complex.

Experimental Section

Materials. All chemicals used were of AR grade and were used without further treatment. All solutions were prepared with use of heat-distilled water, which was then passed through a Millipore setup, the final resistance being >10 MΩ. The N_2O used was bubbled through two bottles containing VSO_4 in dilute H_2SO_4 over Zn analgam, followed by two washing bottles containing pure water. Acetate buffer was used when required to maintain constant pH during the experiments.

[†] Dedicated to Professor Leon Dorfman on the occasion of his retirement.

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(2) The exact nature of the transient complexes found in the reactions of $^{\bullet}CR_1R_2OH$ free radicals with $Cu^{II}(nta)^-(aq)$ is unclear. The formula $(nta)Cu^{III}{-}CR_1R_2OH^-(aq)$ is used throughout; however, the transients might be $(nta)Cu^{III}{-}CR_1R_2O^{2-}(aq)$ as well (see Results and Discussion).

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