Photophysical and Photochemical Properties of $Rh(NH_3)_5Cl^{2+}$ in Nonaqueous Solvents. Solvent Control of the Photolabilization Pathways of the Ligand Field Excited States[1]

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Abstract: Reported are the photoluminescence spectrum, lifetime, quantum yield, and ligand photosubstitution reaction quantum yield for $Rh(NH_3)_5Cl^{2+}$ at ambient temperature in several solvent systems. It is demonstrated that the identity of the ligand labilized from the ligand field excited states of $Rh(NH_3)_5Cl^{2+}$ is a function of the solvent medium, with Cl^- substitution predominating in water and formamide solutions but NH_3 substitution dominating in dimethylformamide, dimethyl sulfoxide, and methanol solutions. The results allow the calculation of rate constants for the excited-state processes including radiative, nonradiative, and reactive deactivation. These indicate that the greater solvent dependence of the chloride substitution rate is responsible for changes in the nature of the predominant photoreaction. Notably, a comparison of the excited state ligand substitution rate constants with those of the analogous thermal reactions shows the excited-state reactions to be faster by over 14 orders of magnitude.

Introduction

The photochemical properties of "Werner-type" transition-metal complexes have long been an area of active interest.[2] Ligand field (LF) excited states, especially for complex ions having the d^3 or low-spin d^6 ground state (gs) configurations, have received much of this attention. Until recently the principal information obtained from these studies has been the nature of the photoproducts and the quantum yields for forming these products under specified reaction conditions. Such results have led to a number of theoretical interpretations and predictions of the reactivity of the excited states.[3] Quantitative photophysical studies of the same complexes have added to the wealth of information regarding the excited-state processes.[4-10] However, until recently the correlation between the photophysical and photochemical data has been hampered by the markedly different conditions under which the two types of measurements were carried out: low-temperature glasses for the luminescence studies and ambient-temperature, fluid solutions for the photochemistry studies. A limited number of cases have been reported in which the photophysics and photochemistry of charge transfer,[11-15] intraligand,[16-18] and most recently ligand field[19-24] lowest energy reactive excited states have been measured under identical conditions. These measurements allow calculation of the rate constants for the excited-state processes, providing a more fundamental data set than photoreaction quantum yields for evaluating current theories and for generating new or improved treatments.[25]

One reaction commonly observed for ligand field excited states is the photosubstitution of one ligand for another. The majority of the studies to date have dealt with the nature of the labilized ligand, product stereochemistry, the dependence upon irradiation wavelength, and absolute quantum yield. A factor which is generally overlooked, especially in the theoretical modeling, is the solvent. The solvent obviously plays a crucial role, both as the reaction medium and, for many photosubstitution reactions, as the species replacing the labilized ligand in the product metal complex. In a preliminary communication,[1b] we demonstrated that the product mixture from the photosubstitution reactions induced by the LF excitation of $Rh(NH_3)_5Cl^{2+}$ was a dramatic function of the solvent medium, *despite* the insensitivity of the LF absorption spectrum to the solvent. Here we report quantitative pulse laser and continuous photolysis studies of the photochemical and photophysical properties of $Rh(NH_3)_5Cl^{2+}$ in several solvents. These results allow one to extract rate constants for the key excited state deactivation processes and thus to evaluate quantitatively how each of these individual rate constants is responding to changes in the solvent medium.

Experimental Section

Syntheses. $[Rh(NH_3)_5L](ClO_4)_3$ (L = Cl^-,[26] H_2O,[27] and DMF[28]) and *trans*-$[Rh(NH_3)_4(H_2O)Cl](ClO_4)_2$ were all synthesized according to previously published procedures.[29] $[Rh(NH_3)_5Me_2SO](ClO_4)_3$ was prepared by analogy to a previously published procedure.[28] $[Rh(NH_3)_5H_2O](ClO_4)_3$ (320 mg) was dissolved in Me_2SO (1 mL) and heated at 35 °C for 3 h. The solution was allowed to cool to room temperature and H_2O plus concentrated $HClO_4$ (2 mL) were added. The resulting deep yellow precipitate was collected by filtration, washed with $EtOH/Et_2O$, and vacuum dried. The complex was twice recrystallized from Me_2SO as above. The infrared absorption spectrum shows bands at 982 and 943 cm^{-1} characteristic of oxygen coordinated Me_2SO.[30] $Rh(NH_3)_5fma^{3+}$ was synthesized in situ by a photochemical technique. $Rh(NH_3)_5H_2O^{3+}$ in fma was exhaustively photolyzed at 313 nm until no further spectral changes occurred. The photolysis solution was concentrated by rotary evaporation and concentrated $HClO_4$ was added to precipitate the product. (That $Rh(NH_3)_5\,fma^{3+}$ was the only product was checked by heating a known amount of product in 1.0 N HCl to generate only (>98%) $Rh(NH_3)_5Cl^{2+}$.) The infrared absorption spectrum shows bands at 1715 and 1390 cm^{-1} characteristic of coordinated fma. The *trans*-$Rh(NH_3)_4SCl^{2+}$ ions (S = DMF, Me_2SO) were prepared by a similar photochemical method utilizing [*trans*-$Rh(NH_3)_4H_2OCl](ClO_4)_2$ as the starting material. The stereochemical integrity of these products was checked by monitoring the quantitative stereoretentive[29,31] conversion to *trans*-$Rh(NH_3)_4Cl_2^+$ (>98%) upon heating the final photolysis solution with Cl^-. The trans solvent products were isolated as perchlorate salts from the photolysis solutions by rotary evaporation. The infrared absorption spectra for these complexes show peaks, 982 and 943 cm^{-1} for Me_2SO and 1650 and 1370 cm^{-1} for DMF, characteristic of the oxygen coordinated solvent species.[30] Their electronic absorption spectra are noticeably different from that of *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$. Upon heating in aqueous solution the trans solvent complexes quantitatively convert to *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$. The electronic absorption spectra of all the complexes are given in Table I.

Solvents. The solvents formamide (fma), methanol (MeOH), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (Me_2SO) were analytical reagent grade (Mallinckrodt Inc.) and were used without further purification. The water was doubly distilled.

Photolysis Procedures. Photolyses at 350 and 366 nm were carried out utilizing a photolysis apparatus previously described in detail.[20,32] Light intensities were determined by ferrioxalate actinometry.[33]

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Table I. Electronic Absorption Spectra of Rh(III) Complexes in Various Solvent Systems

complex	solvent	λ_{max} (ϵ)[a]
$Rh(NH_3)_5Cl^{2+}$	H_2O	347 (103), 277 (109)
	DMF	349 (122), 277 (146)
	Me_2SO	351 (117), 278 (135)
	fma	347 (113), 277 (128)
	MeOH	349 (101), 278 (118)
$Rh(NH_3)_5H_2O^{3+}$	H_2O	316 (104), 263 (89)
	DMF	316 (156)
$Rh(NH_3)_5Me_2SO^{3+}$	H_2O	327 (114)- , 260 sh (120) 215 (1.79×10^3)
	Me_2SO	326 (103)
$Rh(NH_3)_5fma^{3+}$	fma	319 (116) 266 (107)
$Rh(NH_3)_5DMF^{3+}$	H_2O	323 (185), 260 (151)
	DMF	323 (216)
trans-$Rh(NH_3)_4(H_2O)Cl^{2+}$	H_2O	389 (55), 284 (114)
trans-$Rh(NH_3)_4(DMF)Cl^{2+}$	H_2O	386 (94), 276 sh (150)
	DMF	392 (88), 286 (132)
trans-$Rh(NH_3)_4(Me_2SO)Cl^{2+}$	Me_2SO	405 (73)

[a] Wavelength of intensity maximum in nanometers; extinction coefficient in M^{-1} cm^{-1}.

Temperature control to better than ±0.5 °C was maintained with a Forma Scientific recirculating water bath. The photochemical quantum yield values were obtained from spectral changes[10,20,32] monitored on a Cary 118C spectrophotometer with a thermostated cell compartment. Incremental quantum yields were plotted vs. percent reaction and these plots were extrapolated to the 0% reaction intercept.[10] The initial quantum yields thus calculated are values independent of perturbations (secondary photoreactions, inner filtering, etc.) possibly introduced by products. Dark reactions monitored under identical conditions displayed no spectral changes.

Luminescence Procedures. The procedures and equipment for measurement of emission spectra and luminescence lifetimes have been described previously.[19,20,34] Luminescence quantum yields were also measured on this instrument (vide supra) by a modified Parker-Rees technique[35,36] using a 5-nm excitation bandwidth centered at 366 nm. A 7-cm $CuSO_4$ (150 g/L) solution filter and a Corning 7-60 glass filter were used to assure spectral purity of the exciting light. Quinine bisulfate (5×10^{-5} M) in 1.0 N H_2SO_4 was used as the standard with a yield of 0.55 for 366-nm excitation at 25 °C.[37] The working equation is

$$Q_x = Q_r \left(\frac{\eta_x}{\eta_r}\right)^2 \left(\frac{E_x}{E_r}\right)\left(\frac{D_x}{D_r}\right)\left(\frac{A_r}{A_x}\right) \qquad (1)$$

where Q is the absolute quantum yield, η is the solvent refractive index, E is the emission intensity, D is the integrated area under the corrected emission spectrum, and A is the absorbance per centimeter at the exciting wavelength. The subscripts x and r refer to the unknown and the known, respectively. The technique described by Parker and Rees was employed for estimating D under the actual quantum yield conditions.[36]

Thermal Substitution Reactions of $Rh(NH_3)_5Cl^{2+}$. The thermal substitution reactions were monitored on a Cary 118C spectrophotometer. Samples were thermostated at 80 ± 1 °C with a Haake FE constant-temperature water bath. The spectrum was taken periodically and the spectral changes at several different wavelengths were used in calculating substitution rate constants.

Results

Photosubstitution Quantum Yields of $Rh(NH_3)_5Cl^{2+}$. The irradiation of the lowest singlet ligand field band of $Rh(NH_3)_5Cl^{2+}$ leads to photosubstitution as the only observed reaction (eq 2). The quantum-yield values are listed in Table II. The magnitude of the photosubstitution quantum yield changes as the solvent medium is varied but more importantly the nature of the substitution photoreactions is dependent upon the solvent. In aqueous solution, Cl^- photosubstitution (eq 2a)[20,38] is the principal photoreaction, although solution pH changes indicate small quantum yields for NH_3 labilization. In formamide (fma) solution Cl^- photosubstitution again predominates to give $Rh(NH_3)_5fma^{3+}$ as the rhodium(III) product. However, a marked behavioral reversal is noted in dimethylformamide, dimethyl sulfoxide, and methanol solutions, where NH_3 photosubstitution (eq 2b) predominates to give *trans*-$Rh(NH_3)_4Cl_2^+$ in each case. The electronic and infrared absorption spectra of the products along with the ability to convert these to *trans*-$Rh(NH_3)_4Cl_2^+$ through the known stereoretentive thermal reaction[31] with Cl^- (see Experimental Section) support the assignment of the trans stereochemistry. The photoreactions studied at low temperatures show a decrease in the overall quantum yield but very little, if any, change in the nature of the substitution reactions.

Table II. Quantum Yields for Photosubstitution of $Rh(NH_3)_5Cl^{2+}$ in Various Solvent Systems

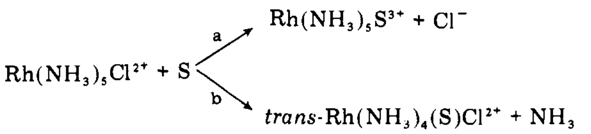
solvent	T, K	Φ_{Cl^-}[a]	Φ_{NH_3}[a]	R[b]
H_2O	298	0.18 ± 0.01 (23)	0.02 ± 0.01 (23)	9
	278	0.14 ± 0.01 (6)	<0.02 (6)	>7
fma	298	0.057 ± 0.004 (5)	<0.011 (5)	>5
	278	0.033 ± 0.003 (4)	<0.008 (4)	>4
Me_2SO	298	<0.006 (5)	0.029 ± 0.006 (5)	<0.2
MeOH	298	0.008 ± 0.002 (4)	0.110 ± 0.010 (4)	0.07
DMF	298	0.004 ± 0.001 (7)	0.070 ± 0.007 (7)	0.06
	278	0.002 ± 0.001 (3)	0.038 ± 0.005 (3)	0.04

[a] Quantum yields in mol/einstein; λ_{irr} 350 and 366 nm; mean value and average deviation with number of determinations in parentheses. [b] The quantum yield ratio for Cl^- and NH_3 photosubstitutions $R = \Phi_{Cl^-}/\Phi_{NH_3}$.

Table III. Luminescence Lifetime Values for $Rh(NH_3)_5Cl^{2+}$ in MeOH/H_2O Mixtures

% MeOH[b]	τ[a]	% MeOH[b]	τ[a]
0	14.2	50	17.6
33	16.3	75	19.6

[a] Measured lifetime in nanoseconds. [b] % MeOH by volume in MeOH/H_2O mixture.



$$\mathrm{Rh(NH_3)_5Cl^{2+}} + \mathrm{S} \begin{cases} \xrightarrow{a} \mathrm{Rh(NH_3)_5S^{3+}} + \mathrm{Cl^-} \\ \xrightarrow{b} trans\text{-}\mathrm{Rh(NH_3)_4(S)Cl^{2+}} + \mathrm{NH_3} \end{cases} \qquad (2)$$

Quantum yields calculated by the extrapolation method (see Experimental Section) represent in principle the intrinsic photoreactivities independent of perturbations introduced by the formation of products. One such product would be Cl^-_{sol}, which might undergo a secondary back reaction with the product $Rh(NH_3)_5S^{3+}$ or possible intermediates in the primary photoreaction to re-form starting material.[39] Although the method of quantum-yield calculation removes this potential contribuion to the photoreaction quantum yields, this possibility was further examined by measuring photosubstitution quantum yields over the Cl^- concentration range 0 to 8×10^{-3} M in both aqueous and methanol solution ($[Rh(NH_3)_5Cl^{2+}]_{initial} = 0.8$ to 4.0×10^{-3} M). At these concentrations the photoreaction quantum yields were observed to be independent of added Cl^-.

Luminescence Lifetimes of $Rh(NH_3)_5Cl^{2+}$. The excited-state lifetimes measured in the various fluid solutions are given in Table III. The instrumental limit is <10 ns so that the lifetimes were measurable in each case. The lifetime of $Rh(NH_3)_5Cl^{2+}$ in 100% methanol could not be measured directly owing to its limited solubility. A lower limit for the lifetime was determined using a series of MeOH/H_2O mixtures (see Table III). The lifetime increases as the percentage of methanol increases to a maximum value of 19.6 ns at 75% methanol. At higher percentages of methanol the complex is only sparingly soluble and the signal monitored is mostly scattered excitation light whose

Table IV. Luminescence Data for $Rh(NH_3)_5Cl^{2+}$ in Various Solvent Systems

solvent	T, K	τ^a	$\nu_{max}{}^b$	$\Delta\nu_{1/2}$
H_2O	298	14.2 ± 1.0 (19)	14.2	3.8
	278	21.9 ± 1.5 (4)		
fma	298	22.4 ± 1.0 (4)	14.2	5.6
	278	30.6 ± 1.1 (3)		
DMF	298	32.4 ± 1.4 (4)	14.2	5.3
	278	69.5 ± 5.4 (3)		
Me_2SO	298	35.1 ± 2.2 (4)	14.2	4.6
MeOH	298	$>19.6^c$	14.3	5.5

[a] Measured lifetime in nanoseconds; mean value and average deviation with number of determinations in parentheses. [b] Energy of emission intensity maximum (corrected) in 10^3 cm^{-1}. [c] A lower limit for τ in MeOH based upon the value of 19.6 ns measured in 75% MeOH/25% H_2O by volume (see Table III). Solubility of complex in 100% MeOH was too low to obtain a reliable value (see Results).

lifetime closely follows the laser pulse. The lower limit for the lifetime in methanol is taken as the value obtained in the 1:3 H_2O/MeOH solvent mixture. Emission lifetimes measured in doubly vacuumed distilled DMF were the same as those measured in reagent grade DMF.

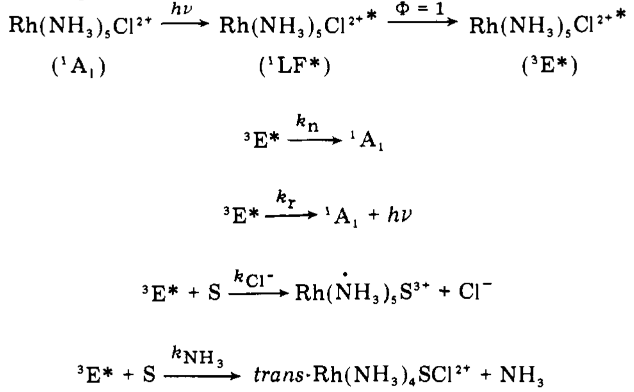
A decrease in the temperature of the solution resulted in significantly longer lifetimes in each case studied (Table IV).

Emission Spectra of $Rh(NH_3)_5Cl^{2+}$ at 298 K. The luminescence spectrum of $Rh(NH_3)_5Cl^{2+}$ was recorded in each of the solvent systems at 298 K. In each solvent the complex displayed a broad Gaussian band analogous to those previously assigned as LF emissions.[5,20] The lack of any solvent dependence upon the energy of the emission intensity maximum is further support for this assignment.[40] The corrected ν (max) values and the respective bandwidths at half height, $\nu_{1/2}$, are reported in Table IV. These results agree very well with emission spectra previously recorded for $Rh(NH_3)_5Cl^{2+}$ in low-temperature (77-85 K) H_2O-MeOH glasses and ambient-temperature spectra of solid samples.[5,7]

Emission Quantum Yields. The measurements of the emission quantum yields in the nonaqueous solvents could not be made under ideal conditions for optically dilute solutions owing to problems with solubility and solvent luminescence. The limited solubility of $Rh(NH_3)_5Cl^{2+}$ in methanol led to a very weak emission and therefore a larger degree of uncertainty in the measured quantum yield. For DMF, Me_2SO, and fma the absorbance of the exciting light by the solvent and the strong luminescence of the solvent required very high concentrations (10^{-2} M) of $Rh(NH_3)_5Cl^{2+}$ to be used. Corrections were also required in the measurement of the solvent blanks for the same reasons. Emission quantum yields were quite small and order of magnitude calculations place these in the 10^{-6}–10^{-5} range in each case.

Thermal Substitution Rates of $Rh(NH_3)_5Cl^{2+}$. The thermal substitution rates were measured at 80 °C.[41] In DMF and Me_2SO the spectral changes were very small even after 50 h reaction time. Regardless of whether Cl^- or NH_3 substitution is assumed, these changes correspond to substitution rates of less than 10^{-6} s^{-1} at 80 °C. For qualitative comparison to photochemical substitution rates, the thermal rates at 25 °C were calculated assuming an apparent activation energy of 25 kcal/mol. The rates at 25 °C calculated using this approximation were less than 10^{-8} s^{-1} for both DMF and Me_2SO. Spectral changes were so minor that the identity of the labilized ligand (if any) could not be determined. In fma and water the thermal pathway is Cl^- substitution to give $Rh(NH_3)_5fma^{3+}$ and $Rh(NH_3)_5H_2O^{3+}$, respectively. In fma the rate constant measured for thermal labilization of chloride is 1×10^{-5} s^{-1} at 80 °C. The spectrum at long reaction times (>50 h) corresponds to 96% conversion to $Rh(NH_3)_5fma^{3+}$. The data does not allow one to distinguish between complete conversion to $Rh(NH_3)_5fma^{3+}$ and an equilibrium being established at 96% conversion. The calculated rate at 25 °C, assuming an E_a value of 25 kcal/mol, is 1×10^{-8} s^{-1}. In water the previously measured[42] rate constant at 77 °C is 2.3×10^{-5} s^{-1}, which with an E_a value of 24.4 kcal/mol extrapolates to give 3.5×10^{-8} at 25 °C. We have confirmed these results with a measured rate constant of 5×10^{-5} s^{-1} at 80 °C.

Scheme I



$$Rh(NH_3)_5Cl^{2+} \xrightarrow{h\nu} Rh(NH_3)_5Cl^{2+*} \xrightarrow{\Phi = 1} Rh(NH_3)_5Cl^{2+*}$$

$$({}^1A_1) \qquad ({}^1LF^*) \qquad ({}^3E^*)$$

$${}^3E^* \xrightarrow{k_n} {}^1A_1$$

$${}^3E^* \xrightarrow{k_r} {}^1A_1 + h\nu$$

$${}^3E^* + S \xrightarrow{k_{Cl^-}} Rh(NH_3)_5S^{3+} + Cl^-$$

$${}^3E^* + S \xrightarrow{k_{NH_3}} trans\text{-}Rh(NH_3)_4SCl^{2+} + NH_3$$

Discussion

Previous sensitization[38] and photophysical[20] studies have concluded that the common reactive LF excited state for $Rh(NH_3)_5Cl^{2+}$ is the lowest energy triplet LF state ${}^3E$ and that internal conversion/intersystem crossing from the initially populated singlets occurs with unit efficiency (Scheme I). It is this state from which emission is observed both in low- and ambient-temperature solutions. Thus, the combination of reaction and emission quantum yields and the lifetime measurements all made under identical conditions allow calculation of the first-order rate constants for the individual deactivation pathways shown in Scheme I: chemical reaction (k_{Cl^-} and k_{NH_3}) and radiative and nonradiative decay to the ground state (eq 3-6). Back reactions of Rh(III) intermediates or products formed in these photolyses with nucleophiles other than solvent (e.g., Cl^-) are insignificant under the experimental conditions.

$$k_{Cl^-} = \Phi_{Cl^-}\tau^{-1} \tag{3}$$

$$k_{NH_3} = \Phi_{NH_3}\tau^{-1} \tag{4}$$

$$k_r = \Phi_{em}\tau^{-1} \tag{5}$$

$$k_n = \tau^{-1} - k_{Cl^-} - k_{NH_3} - k_r \tag{6}$$

The calculated values for the radiative rate constants, k_r (10^3 s^{-1}), are at least three orders of magnitude smaller than the rates for the other pathways for deactivation and therefore are insignificant contributors to the overall deactivation of the excited state. The calculated values for k_{Cl^-}, k_{NH_3}, and k_n are summarized in Table V.

The ${}^3E$ LF excited state of $Rh(NH_3)_5Cl^{2+}$ can be viewed as having the excitation principally concentrated along the weak field NH_3—Cl^- axis,[3] a view which suggests labilization of *trans*-NH_3 or Cl^-. Various rationales including the relative σ and π donor strengths of the ligands[3,43] have been offered to explain the relative magnitudes of these two pathways in water and the analogues to eq 2a and 2b for other ML_5X^{2+} complexes. The LF absorption and emission spectra of $Rh(NH_3)_5Cl^{2+}$ are both insensitive to the solvent media (Tables I and IV), and hence provide no information that would explain the solvent-induced variations in quantum yields. More significantly, spectroscopic parameters and quantitative models using such information to interpret electronic redistribution in the reactive LF excited state are insufficient to

Table V. Rate Constants for Deactivation of Reactive Excited State of $Rh(NH_3)_5Cl^{2+}$

solvent	T, K	k_{Cl^-}[a]	k_{NH_3}[b] ($\times 10^{-6}$ s^{-1})	k_n[c]	$\Delta\Delta G_{Cl^-}$[d]
H_2O	298	12.7	1.4	56	−2.7
	278	6.4	0.9	39	
fma	298	2.5	0.5	45	−0.4
	278	1.1	0.3	31	
MeOH[e]	298	<0.46	<5.6	>45	0.0
Me_2SO	298	0.17	0.82	28	6.0
DMF	298	0.12	2.2	31	7.2
	278	0.03	0.55	14	

[a] Rate constant for Cl^- substitution from reactive excited state. [b] Rate constant for NH_3 substitution from reactive excited state. [c] Rate constant for nonradiative deactivation of excited state. [d] Free energy of solvation for chloride in given solvent relative to methanol (kcal/mol) (ref 50). [e] Based upon a lower limit of 19.6 ns for τ in 100% MeOH (see Table IV).

explain the change in the predominant photoreaction pathway from Cl^- substitution in H_2O and fma to NH_3 substitution in DMF, Me_2SO, and MeOH (Table II). The differences obviously lie in kinetic solvent effects on the various deactivation mechanisms (Table V).

On comparing the rate constants listed in Table V, it is seen that all these show some variation with solvent; however, the k_{Cl^-} term is by far the most solvent dependent. As a consequence, Φ_{Cl^-} is smaller in each of the nonaqueous solvents, but especially in Me_2SO, MeOH, and DMF, despite the longer excited-state lifetimes in these solvents which, according to eq 3, should favor larger quantum yields. In contrast, Φ_{NH_3} is larger in the last three solvents than in water, an observation reflecting both the relative solvent insensitivity of k_{NH_3} and the longer lifetimes (eq 4) in these media. Thus the photosubstitution behavior shows a crossover with NH_3 labilization favored ($R < 1$) in the less polar solvents Me_2SO, MeOH, and DMF. The difference in the ways which k_{Cl^-} and k_{NH_3} respond to changing the solvent can be rationalized by a mechanism for the Cl^- labilization from the LF excited state where considerable charge separation develops along the Rh(III)–Cl^- bond at the transition state, and the solvent's ability to stabilize this type of charge separation significantly influences the free energy of activation for this step. One acceptable measure of solvent's ability to stabilize this type of developing charge separation might be $\Delta\Delta G_{Cl^-}$,[44] the free energy of solvation of chloride ion in a given solvent relative to methanol. A clear, although qualitative, correlation between $\Delta\Delta G_{Cl^-}$ and k_{Cl^-} can be seen in Table V. In contrast, the ammine labilization should be much less solvent sensitive given the absence of major charge separation accompanying this pathway and the relative insensitivity of the ammonia solvation free energies to the nature of the solvent.[45] Thus the two solvents displaying the most favorable $\Delta\Delta G_{Cl^-}$ values are those for which Cl^- labilization is the favored photosubstitution pathway.

At 278 K the results for the solvent systems studied are similar to those at 298 K. The increases in excited-state lifetimes at the lower temperature for each solvent reflect rate decreases for all of the excited-state deactivation processes. The decreased photosubstitution quantum yields indicate that the activation energies (E_a) for these pathways (k_{Cl^-} and k_{NH_3}) are larger than that for nonradiative deactivation (k_n). It has been proposed [32] on the basis of deuterium isotope studies that nonradiative deactivation from the Rh(III) ammine excited states may occur by competing weak coupling and strong coupling mechanisms. Since the former mechanism is relatively temperature independent, the composite rate constant k_n should be less temperature sensitive than the ligand substitution rate constants.

The thermal substitution studies provide an interesting comparison with the photochemical ligand labilizations. The two solvents, water and fma, in which Cl^- photosubstitution is the dominant reactive deactivation pathway are also the solvents in which $Rh(NH_3)_5Cl^{2+}$ displays measurable thermal lability of Cl^-. In each of these solvents the excited state substitution reaction is 10^{14} faster than the thermal analogue. The solvents, DMF and Me_2SO, in which Cl^- substitution from the excited state is a minor deactivation process (NH_3 photosubstitution being the major reactive deactivation pathway) displayed no measurable thermal ligand labilization (Cl^- or NH_3); thus, again the excited-state rate constants are at least 14 orders of magnitude greater than the upper limit thermal rate constants. These rate increases on LF excitation are also reflected by the much smaller activation energies seen for the excited-state process. Notably, E_a for the thermal labilization of Cl^- in aqueous solution is 24.4 kcal/mol[42] while the analogous process from the LF excited state shows E_a values of ~6 kcal/mol in water and ~7 kcal/mol in fma. Previously, we have drawn the analogy between the reactivity of the ^3E state for Rh(III) complexes having the $(t_{2g})^5(e_g)^1$ electronic configuration and that of Rh(II) complexes having the $(t_{2g})^6(e_g)^1$ configuration.[20] The latter species which are generated by the pulse radiolysis of Rh(III) analogues also display very large rate constants for ligand labilization.[46] This observation might also be attributed to the tetragonal Jahn–Teller distortion of the species owing to the singular population of the σ^* e_g orbitals.

Cusumano and Langford[47] have recently reported the direct dependence of $Cr(en)_2(NCS)_2^+$ photosubstitution quantum yields on the Gutmann donor number values (DN)[48] of various solvent media and have argued for an associative mechanism. Their argument is consistent with other recent interpretations of the photosubstitution mechanisms for the d^3 Cr(III) complexes[47,49] but does depend on the assumption that deactivation rates are medium independent. In contrast there is no correlation between the present quantum-yield and rate-constant data for $Rh(NH_3)_5Cl^{2+}$ and the DN values or other similar solvent parameters. However, there is a good qualitative correlation between k_{Cl^-} and $\Delta\Delta G_{Cl^-}$ and this is consistent with the dissociative, or possibly dissociative interchange, photosubstitution mechanism commonly assumed[3] for hexacoordinate d^6 complexes such as those of rhodium(III).

In conclusion, we have shown that the identity of the ligand labilized from the lowest energy LF excited state of $Rh(NH_3)_5Cl^{2+}$ is a function of the solvent medium, with Cl^- substitution predominating in water and fma but NH_3 substitution being dominant in DMF, Me_2SO, and MeOH. We have measured the photoluminescence lifetimes and quantum yields of these systems under the photochemical conditions and have calculated rate constants for the excited state deactivation processes. These rate data indicate that whether Cl^- or NH_3 substitution is the dominant photoreaction depends upon the solvent sensitivity of the chloride substitution rate from the excited state and that this rate parallels the solvation free energy for chloride ($\Delta\Delta G_{Cl^-}$). The comparison of rates for ground-state and excited-state ligand labilization from $Rh(NH_3)_5Cl^{2+}$ shows the excited state reactions to be faster by more than 10^{14} with the marked decrease in E_a for Cl^- substitution providing further evidence for the increased reactivity of the excited state. Given that the solvent nature has relatively little influence on the LF absorption or emission spectra, these results demonstrate that spectroscopic parameters alone are insufficient for the quantitative rationalization of the LF photochemistry of d^6 complexes and illustrate the importance of considering the actual mechanism of the key excited state deactivation processes in such treatments.

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On Correlating Phosphorus Core Binding Energies, Phosphorus Lone Pair Ionization Potentials, and Proton Affinities of Tervalent Phosphorus Compounds

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Abstract: Phosphorus core binding energies have been determined for a wide variety of tervalent phosphorus compounds. These values are compared with literature values of the corresponding lone pair ionization potentials and proton affinities. No single correlation is found between all the core binding energies and the corresponding lone pair ionization potentials or proton affinities, but the lone pair ionization potentials are linearly correlated with the proton affinities. It is concluded that the electronic relaxations accompanying lone-pair ionization and proton attachment are similar in character and energy, whereas the electronic relaxation accompanying core ionization is of a somewhat different type, in which atomic orbital rehybridization plays a relatively unimportant role.

Introduction

Several groups of workers have shown that, for certain compounds of oxygen, nitrogen, and phosphorus with nonbonding "lone-pair" electrons on these atoms, the oxygen, nitrogen, and phosphorus core electron binding energies are linearly correlated with the corresponding proton affinities.[2-4] Indeed, it has been claimed that core binding energy shifts can be used to predict proton affinities.[4] However, there is evidence that such correlation only holds when considering compounds which are very closely related, such as those in a homologous series of compounds.[3] On the other hand, correlations have been observed between "lone pair" ionization potentials and proton affinities[5-8] which appear to be more general than those

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