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Photosubstitution Reactions of Ruthenium(II) Polypyridyls at High Pressures

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The photosubstitution reactions of $Ru(bpy)_3Cl_2$ and $Ru(phen)_3Cl_2$ have been monitored by loss of luminescence intensity in acetonitrile at 1 atm and 300 MPa and 15, 25, and 60 °C. The effect of pressure is to slow down the rate of photoreaction at all temperatures. The magnitudes of the pressure dependence, expressed as apparent activation volumes, are 12 and 22 mL/mol for $Ru(bpy)_3Cl_2$ and 9 and 27 mL/mol for $Ru(phen)_3Cl_2$ at the respective temperatures of 15 and 60 °C. The large temperature dependence of $\Delta V_{app}^{\ddagger}$ is related to ion association in the Cl^- addition step. The influence of ion pairing is supported by comparative P–T studies with the PF_6^- counterion and with aqueous and CH_2Cl_2 solutions.

Introduction

Two recent reviews[1,2] attest to the relatively few pressure investigations of inorganic photochemical systems. One of the more complete pressure studies concerns the photosubstitution reactions of Rh(III) halo ammine complexes,[3-5] in which the photophysical and photochemical processes originate from the same lowest energy excited ligand field state. This pressure work confirms the mechanistic conclusion that the ligand displacement reactions are dissociative. Other systems studied at high pressures include Co(III) halo ammine and cyano complexes,[6-8] halo ammine, cyano, thiocyano, and bipyridyl complexes of Cr(III),[6,7,9-11] and Fe(II) cyano complexes.[12] These studies demonstrate the difficulty in developing universal principles for P–V effects on photosubstitution reactions of transition-metal complexes.

Observed pressure effects on kinetic processes are conveniently compared and summarized in terms of apparent activation volumes, $\Delta V_{app}^{\ddagger}$. Interpretation of these measured activation volumes requires considerable caution since precise information about the efficiencies of various pathways, the volume of various intermediates, and the volumes of transition states is typically nonexistent. Only in the simplest cases can conclusions be stated with confidence.[8,11] Until more P–V data become available about the individual kinetic steps, the present results are necessarily accompanied by incomplete analyses.

The photochemistry of Ru(II) polypyridyl complexes differs from that of the other systems mentioned above because the photophysically active state is not the reactive state. As seen from previous work,[13-15] the photoreaction results from thermal activation to the higher energy ligand field state out of the metal-to-ligand charge-transfer state. We have already reported the pressure effects on the Ru(II) photophysical processes[16,17] and find them consistent with current perspectives of nonradiative decay in polypyridyl complexes. The point was stressed that simultaneous variations in P and T are necessary to draw conclusions about the photophysical steps. Large P–T sensitivities are also observed for the photosubstitution reactions, which help to identify ion association equilibria as the major pressure-sensitive factor.

Table I. Photochemical Rate Constants in CH_3CN at 0.1 MPa ($k°$) and 300 MPa (k)[a]

	$k°$, 10^{-5} s^{-1}			k, 10^{-5} s^{-1}		
	15 °C	25 °C	60 °C	15 °C	25 °C	60 °C
$Ru(bpy)_3Cl_2$	6.5	13.0	38.1	1.4	2.2	3.1
$Ru(phen)_3Cl_2$	1.2	1.7	9.1	0.4	0.2	0.5

[a] Estimated error is ±0.3 × 10^{-5} s^{-1} for all values.

Experimental Section

The acetonitrile was used as received from Burdick-Jackson (B&J Brand High Purity Solvents) and stored under nitrogen. The sources of $Ru(bpy)_3Cl_2$ and $Ru(phen)_3Cl_2$ as well as LiCl have been listed previously.[16,17] The H_2O used in this work was purified to greater than 10 MΩ cm resistivity.

The preparation of $Ru(bpy)_3(PF_6)_2$ was based on a previously described procedure.[18] Approximately 1 g of the $Ru(bpy)_3Cl_2$ was dissolved in a minimum of H_2O. A saturated solution of NH_4PF_6 (Aldrich Chemical) was added slowly until precipitation was complete. Anion exchange leads to a dramatic difference in H_2O solubility between starting material and product. The solid was recrystallized twice from acetonitrile/toluene (1:1) solvent.

The high-pressure optical cell and pressure-generating equipment as well as the luminescence station, temperature controller, and sample encapsulation techniques have been described previously.[16,19] A small quartz capsule is loaded with a freshly prepared, N_2-purged sample. A stainless-steel piston is placed in the capsule end, which allows the pressure to be transmitted to the sample. The capsule is placed in the high-pressure cell, which has been filled with the sample solvent and attached to the pressure system. The temperature is regulated to ±0.2 °C and fixed at 15, 25, and 60 °C for pressure up to 300 MPa (1 MPa = 10 bar = 10.1 atm).

The sample is irradiated at 436 nm for typically 1 h as the luminescence intensity I is monitored at right angles. The time dependence of the intensity is obtained directly from the recorder output at selected temperatures and pressures. These $I(t)$ data are analysed by assuming a first-order reaction:[14,15]

$$\ln (I/I_0) = -kt \tag{1}$$

where

$$k = 2.303 I_i s \epsilon \Phi \tag{2}$$

Here I_0 is the initial (t = 0) luminescence intensity, t is the photolysis time, ϵ is the molar extinction coefficient of the Ru(II) complex at the excitation wavelength of 436 nm, and Φ is the photochemical quantum yield. The parameter s, dependent on sample geometry, and the irradiance I_i need not be known for this analysis. A simple linear least-squares fit of the data was used to obtain the observed photochemical rate constant k.

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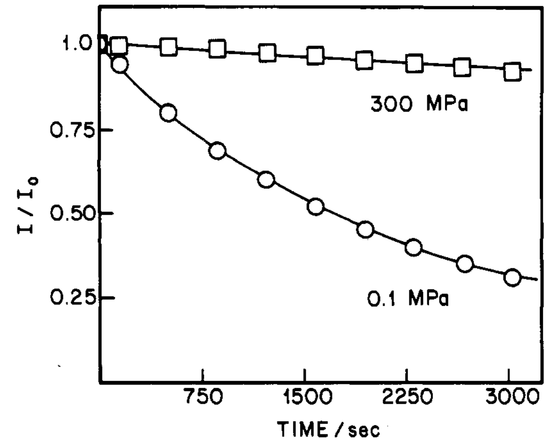

Figure 1. Time dependence of the luminescence intensity ratio of Ru(bpy)$_3$Cl$_2$ in CH$_3$CN at 60 °C and at pressures of 0.1 MPa (○) and 300 MPa (□).

Table II. Photochemical Quantum Yield in CH$_3$CN at 0.1 MPa ($\Phi°$) and 300 MPa (Φ)

	$\Phi/\Phi°$		
	15 °C	25 °C	60 °C
Ru(bpy)$_3$Cl$_2$	0.23	0.18	0.088
Ru(phen)$_3$Cl$_2$	0.34	0.12	0.054

The relative change in reaction quantum yield Φ with pressure is related to the observed rate by eq 3. The reference pressure of 0.1 MPa

$$\Phi/\Phi° = k\epsilon°/k°\epsilon \qquad (3)$$

is denoted herein by a degree sign. The extinction coefficient ratio $\epsilon°/\epsilon$ is nearly unity; e.g., the ratio equals 1.073 and 1.015, respectively, for the bpy and phen complexes in CH$_3$CN at P = 300 MPa.[16]

Results

In Figure 1, the relative luminescence intensity is plotted as a function of time for Ru(bpy)$_3$Cl$_2$ in CH$_3$CN at 60 °C. The effect of pressure on the photolysis rate is dramatic: the 1-atm intensity loss of ≈70% is decreased to ≈8% at 300 MPa. The photolyzed solution, monitored for more than 3 h subsequent to photolysis, showed no recovery of lost luminescence intensity. This supports the assumption that the photoproducts are thermally stable for the duration of the present experiments. Photolysis below 15 °C would require unduly long irradiation times, which would introduce unacceptable errors in the evaluation of the rate constant k. In all experiments, the I/I_0 vs. time plots were exponential over the entire photolysis, implying the lack of interference from products.

At least two plots like Figure 1 were prepared at each temperature for both Ru(bpy)$_3$Cl$_2$ and Ru(phen)$_3$Cl$_2$ in CH$_3$CN. The results are given in Table I. The phen complex has smaller $k°$ values relative to the bpy complex, as previously observed for the two complexes in CH$_2$Cl$_2$.[15] The 1-atm $k°$ values increase with increasing temperature, giving rise to apparent activation energies of 30 and 37 kJ mol^{-1} for the bpy and phen complexes, respectively. The values for the bpy complex can be compared to 22 kJ mol^{-1} in CH$_2$Cl$_2$[15] and 24 kJ mol^{-1} in 0.1 M HCl.[14]

High pressures result in large decreases in the photochemical rates for both complexes. This is illustrated in terms of the ratio of quantum yields (eq 3) for loss of starting material as listed in Table II. We note that Φ is more sensitive to pressure at the higher temperatures for both complexes. For example, the pressure-induced decrease in the Ru(bpy)$_3$Cl$_2$ photolysis quantum yield is 13-fold at 60 °C but only 4-fold at 15 °C for ΔP = 300 MPa.

Apparent activation volumes are evaluated from eq 4, where $P°$ = 0.1 MPa and P = 300 MPa. Only if $\Delta V_{app}^{\ddagger}$ is pressure-

$$\Delta V_{app}^{\ddagger} = -RT[\ln(\Phi/\Phi°)]/(P - P°) \qquad (4)$$

independent, would the integrated form (eq 4) correspond to the activation volumes normally evaluated from the differential form at 1 atm. A test study of the bpy complex in CH$_3$CN at 25 °C as a function of pressure (50-MPa intervals) revealed a curved ln k vs. P plot. The tangent at 1 atm of this plot gives a value for $\Delta V^{\ddagger}$ that is 30% higher than the result from eq 4. Hence, the activation volumes for the bpy and phen complexes listed in Table III represent lower limits and only have comparative significance. For both complexes, $\Delta V_{app}^{\ddagger}$ increases as the temperature is raised, this trend being more pronounced for the phen complex.

Table III. Apparent Activation Volumes of the Photoreaction in CH$_3$CN

	$\Delta V_{app}^{\ddagger}$, mL/mol		
	15 °C	25 °C	60 °C
Ru(bpy)$_3$Cl$_2$	12	14	22
Ru(phen)$_3$Cl$_2$	9	18	27

Table IV. Photochemical Parameters of Ru(bpy)$_3^{2+}$ in Different Environments

	60 °C		25 °C		60 °C	
	Cl$^-$ H$_2$O	Cl$^-$ 9 M LiCl	Cl$^-$ CH$_2$Cl$_2$	PF$_6^-$ CH$_3$CN	PF$_6^-$ CH$_3$CN	PF$_6^-$ H$_2$O
$k°$, 10^{-5} s^{-1}	4.2	21.8	≈380	1.5	16.5	0
$\Delta V_{app}^{\ddagger}$, mL/mol	9.5	12	≈17	8	10	

The photolysis of the bpy complex is also studied at high pressures with a change in solvent or counterion. The results for aqueous solutions and the PF$_6^-$ counterion are listed in Table IV. The rate constant at ambient pressure is greatly reduced in H$_2$O relative to CH$_3$CN (38 × 10^{-5} s^{-1} vs. 4.2 × 10^{-5} s^{-1}) but 9 M LiCl addition give $k°$ intermediate between those of the two solvents. The pressure dependence of the photolysis rate constant in aqueous systems at 60 °C corresponds to $\Delta V_{app}^{\ddagger}$ at 15 °C in CH$_3$CN.

The PF$_6^-$ counterion in CH$_3$CN decreases $k°$ by 88% and 55% at 25 and 60 °C, respectively, over the values of the Cl$^-$-bound complex at the same temperatures. This decrease is consistent with previous experiments.[15] Also, the $\Delta V_{app}^{\ddagger}$ values are smaller for this counterion. Noteworthy is the negligible temperature effect on the $\Delta V_{app}^{\ddagger}$ values for the PF$_6^-$ complex (Table IV). By contrast, an increase of 8 mL/mol is observed for the photolysis of Ru(bpy)$_3$Cl$_2$/CH$_3$CN in the same temperature range (Table III). Irradiation of Ru(bpy)$_3$(PF$_6$)$_2$/H$_2$O over a 1-h period produced no measurable loss of starting material at ambient or high pressures.

The photochemistry observed for Ru(bpy)$_3$Cl$_2$ in methylene chloride is much more rapid than in the previous solvents.[15] The I/I_0 vs. time plots are not exponential, suggesting that product buildup complicates our simple analysis. However, at 25 °C, pressure slowed the photosubstitution reaction by 80%, which results in an activation volume slightly larger than the measured pressure dependence in CH$_3$CN at the same temperature.

Discussion

The salient features of this work are (1) that pressure strongly reduces the photoreaction rate of Ru(II) polypyridyls and (2) that increasing temperatures enhance this pressure effect. These observations fit the hypothesis that pressure perturbs ion association equilibria in the photochemical reaction.

The photosubstitution process is assumed to originate from the LF state, which is strongly coupled to the MLCT luminescent state.[20] In our previous photophysical studies of Ru(II) complexes at high pressures, we reported an activation volume of about 11 mL/mol for the thermally activated nonradiative MLCT → LF step.[16,17] It is anticipated that the critical transition state along the reaction path occupies a volume equal to or larger than that of the LF state. The results in Table III confirm this conclusion.

The strong increase in the photochemical $\Delta V_{app}^{\ddagger}$ at elevated temperatures parallels the previously reported P–T effect on the luminescent lifetime τ.[16,17] This photophysical behavior is attributed to an increased efficiency θ for the thermally activated

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MLCT → LF step. Since the ligand field state is also an intermediate in the photosubstitution reaction, it can be suggested that this energy barrier is dominant along the reaction coordinate and responsible for the temperature dependence of the photochemical $\Delta V_{\mathrm{app}}^{\ddagger}$. Unfortunately, this assumption cannot be tested quantitatively because the relative efficiencies and activation volumes of the several individual reaction steps required for the mechanistic analysis outlined by Kirk et al.[8] are unavailable.

The Meyer–Durham model[15] for $\mathrm{Ru(bpy)_3Cl_2}$ photolysis starts with metal–ligand bond cleavage to form a five-coordinate intermediate to which ligating counterions and solvent molecules can sequentially add to give the major product $[\mathrm{Ru(bpy)_2(CH_3CN)Cl]Cl}$:[21]

$$*\mathrm{Ru(bpy)_3}^{2+} + \mathrm{Cl}^- \rightarrow *\mathrm{Ru(bpy)_2bpy{\cdot}Cl}^+ + \mathrm{CH_3CN} \rightarrow \mathrm{Ru(bpy)_2(CH_3CN)(Cl)}^+ + \mathrm{bpy} \quad (5)$$

If chloride addition represents a critical step in the reaction sequence insofar as the volume profile is concerned, then counterion solvation, Ru(II) complex ion solvation, and association with the excited complex are important physical properties easily perturbed by pressure.[22]

Evidence for ion pairs and triplets in the photochemistry of Ru(II) polypyridyls has been previously cited.[23,24] As a consequence of electrostriction, the effect of pressure on ion association is invariably a shift in the equilibria: contact ion pairs ↔ solvent-shared ion pairs ↔ solvent-separated ions.[22,25,26] Compressing a polar solvent will increase its dielectric constant ϵ and thus weaken ion binding. Hence pressure will reduce the probability of chloride addition and contribute a positive volume increment to the overall observed $\Delta V_{\mathrm{app}}^{\ddagger}$.

The observed increase of $\Delta V_{\mathrm{app}}^{\ddagger}$ with T is consistent with contributions from ion pairing. According to the Bjerrum expression for ion association,[27] the equilibrium depends inversely on the cube of T and ϵ. The dielectric constant decreases with temperature elevation, but its pressure coefficient increases.[28] Thus, increasing temperature favors ion association and the observed increase in photochemical reaction rate. The large number of ion pairs leads to an increase in the activation volume for the step, which is reflected in the observed $\Delta V_{\mathrm{app}}^{\ddagger}$.

Table III shows a subtle difference between the bpy and phen ligands that is consistent with the influence of ion pairing. Since the rigid phen ligands prevent close proximity of the counterions, the ion association is weaker and hence more strongly perturbed by pressure. Thus, the phen ligand yields a greater volume change than the bpy complex at elevated temperatures.

The qualitative conclusions stated above are also supported by the results listed in Table IV. A change in counterion from Cl^- to $\mathrm{PF_6}^-$ reduces the photosubstitution rate in $\mathrm{CH_3CN}$ considerably, as expected for a nonligating ion.[15] Therefore, the exclusive substitution of solvent molecules is accompanied by a $\Delta V_{\mathrm{app}}^{\ddagger}$ of ≈ 10 mL/mol, which is temperature independent. The replacement of $\mathrm{CH_3CN}$ by $\mathrm{H_2O}$ creates a photoinert situation for the $\mathrm{PF_6}^-$ counterion.[15,20] The photoreaction of $\mathrm{Ru(bpy)_3Cl_2}$ in $\mathrm{H_2O}$ is reduced 9-fold relative to that in $\mathrm{CH_3CN}$ at 25 °C. By contrast, dissolution of the complex in $\mathrm{CH_2Cl_2}$ accelerates the rate 20-fold. The activation volumes observed for the strongly associated systems of $\mathrm{Cl^-/CH_2Cl_2}$ and 9 M LiCl are above the minimum value of ≈ 10 mL/mol. However, that for the weakly associated system of $\mathrm{Cl^-/H_2O}$ is at the minimum. Solvent polarity and electrostriction behavior are then consistent with the observed trends and total charge reduction of eq 5.

In summary, the volume profile of $\mathrm{Ru(bpy)_3Cl_2/CH_3CN}$ has its major contribution from the MLCT → LF photophysical process (labeled $\Delta V_3^{\ddagger}$ in ref 16 and 17) and from the transition state involving Cl^- addition. Electrostriction around this transition state will contribute to the overall activation volume such that $\Delta V_{\mathrm{app}}^{\ddagger} \geq \Delta V_3^{\ddagger}$. The five-coordinate intermediate has been viewed as being formed in a dissociative manner,[18] which should lead to a positive activation volume. Therefore, the results of this paper are consistent with dissociative formation of the intermediate.

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Registry No. $\mathrm{Ru(bpy)_3Cl_2}$, 14323-06-9; $\mathrm{Ru(phen)_3Cl_2}$, 23570-43-6; $\mathrm{Ru(bpy)_3(PF_6)_2}$, 60804-74-2; $\mathrm{CH_3CN}$, 75-05-8; LiCl, 7447-41-8; $\mathrm{H_2O}$, 7732-18-5; $\mathrm{PF_6}^-$, 16919-18-9; methylene chloride, 75-09-2.

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