

Figure 8. The ratio, f , of the relative proportion of quenched probes to unquenched in metal ion/SDS solutions is plotted, as a function of $[A^{2+}]/[M]$. The points are calculated from eq 16, which assumes that the probes and quasi-static metal ions are both distributed among the micelles following Poisson statistics.

proportions³⁵ can be obtained from the semilog plots as in Figures 3, 4, and 6. By extrapolating the longer lived decay back to zero, we obtained the relative proportion of unquenched probes and consequently the fraction that is quenched. Note, this is only valid for the curves which are minimally affected by the micelle-micelle collisional-exchange process.

In Figure 8, experimental f values have been plotted against $[A^{2+}]_{tot}/[M]$ and compared with those of the expected curve based on 16. As can be seen, the agreement is quite good and gives independent support for the Poisson distribution for metal ions

(35) Time zero for the emission quenching plots is taken at the end of the laser pulse. This introduces some error into the calculation of the relative proportions because quenching of the fluorescence signal occurs during the finite (~25 ns at 10% of pulse height) duration of the pulse. However, this is relatively small in the range of $[A^{2+}]/[M]$ ratios studied.

bound to micelles in a quasi-static state.

This could be shown equally well from eq 17, the reduced form of eq 11, which has a linear approximation at large values of t . Extrapolation of the slower linear component such as in Figure 3 gives at $t = 0$ an intercept equal to $-\bar{n}$.

$$\ln \left(\frac{I_t}{I_0} \right) = -(\bar{n} + k_{qt}t) \quad (17)$$

By applying these last two equations to calculate the aggregation number of $C_{12}(EtO)_3S$ micelles, we obtained a value of 56 ± 5 . This value compares favorably with that of 61 ± 2 obtained by the Turro and Yekta method.³⁶

Summary and Conclusions

The fluorescence quenching data clearly shows that the more highly charged the metal ion the greater is its tendency to bind to the micelle surface, as one would expect on purely electrostatic considerations. This conclusion is also supported by the data obtained from the reaction rates of the hydrated electron in metal ion/SDS solutions. The strength of metal ion binding to SDS micelles, suggested by the pyrene fluorescence quenching results, follows the order $Eu^{3+} > Cu^{2+} > Ni^{2+} > Mn^{2+}, Fe^{2+} > Tl^+, Ag^+$.

Evidence for the migration of bound metal ions through micelle-micelle collisions has also been found from the characteristics of the fluorescence quenching curves. It is found to be relatively fast at high micelle concentrations. Thus it is a process that should not be neglected when metal ion reactions in micellar systems are interpreted, particularly over an expanded micelle concentration range.

Experimental support that the distribution of strongly bound metal ions (i.e., bound during the lifetime of the excited pyrene) follows Poisson statistics has also been found.

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Determination of Rate Constants for Photosolvation Reactions: Solvent Dependence of Chloride Substitution Rates for Excited States of *cis*-Dichlorobis(2,2'-bipyridine)iridium(III)

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Abstract: Emission quantum yields, lifetimes, and spectra as well as photosolvation yields have been determined for *cis*-dichlorobis(2,2'-bipyridine)iridium(III), $IrCl_2(bpy)_2^+$, and its deuterated analogue $IrCl_2(bpy-d_8)_2^+$ in water, methanol, dimethylformamide, and acetonitrile. Both charge-transfer and ligand-field excited states contribute to the decay properties in fluid solutions. Rates of photosolvation are strongly solvent dependent, consistent with a dissociative or dissociative interchange mechanism. Rates of radiationless decay are also strongly solvent dependent as are the intensity distributions in the emission spectra. Upward movement of the charge-transfer state in water solutions accounts for the large contribution of the ligand-field emission in this solvent relative to nonaqueous media.

I. Introduction

The rate constants and mechanistic details of a vast number of thermal ligand substitution processes in transition-metal complexes have been studied and established with some certainty.²

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While it is clear that the ligand-field excited states of low-spin d^6 complexes are far more labile toward ligand substitution than are the ground states,³ interpretation of this enhanced lability has been hampered by a dearth of quantitative kinetic data, stemming from inherent difficulties in the measurement of excited-state lifetimes under conditions relevant to the photochemistry. Several notable exceptions include determinations of rate constants for

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photoinduced ligand substitution in chloropentaammine- and bromopentaamminerhodium(III),^{4,5} tris(bipyridyl)chromium(III),⁶ tris(bipyridyl)ruthenium(II),⁷ and (triphenylstannyl)- and (triphenylgermanyl)tricarboxyl(1,10-phenanthroline)rhenium(I).⁸ In each of these cases, the complexes are believed to luminesce from the reactive excited state (es) or one in thermal equilibrium with the reactive state, and combined measurements of luminescence lifetimes τ and photochemical quantum yields Φ_p have been a key feature in determining es reaction rate constants. In the case of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$, measurements of Φ_p and τ values have been extended to several nonaqueous solvents, and solvent-dependent reaction rate constants have been correlated with changes in the free energy of solvation of the photolabilized chloride ion.⁹

Recent studies¹⁰ of the photophysics of *cis*-dichlorobis(2,2'-bipyridine)iridium(III), $\text{IrCl}_2(\text{bpy})_2^+$, and its deuterated analogue $\text{IrCl}_2(\text{bpy-}d_8)_2^+$ indicate that these ions have low-energy ligand-field (LF) excited states. These states are believed to give rise to the chloride photoaquation which has been reported in several studies.¹¹⁻¹⁴ Low-energy charge-transfer (CT) excited states are also present in these complexes, at energies slightly above those of the LF states.¹⁰ These CT states make measurable contributions to the emission spectra in fluid solutions, as do the lower energy LF states.

We have made a quantitative study of the photochemistry and photophysics of $\text{IrCl}_2(\text{bpy})_2^+$ and $\text{IrCl}_2(\text{bpy-}d_8)_2^+$ in several different solvents. Our purpose in undertaking this study was to begin a quantitative characterization of the kinetics of photosolvation processes in complexes of Ir(III) and to identify the effects of the low-energy charge-transfer states on these processes. We report here the results of that study.

II. Experimental Section

A. Chemicals. The synthesis and purification of $[\text{IrCl}_2(\text{bpy})_2]\text{Cl}$ and $[\text{IrCl}_2(\text{bpy-}d_8)_2]\text{Cl}$ have been described previously.¹⁵ $[\text{IrCl}_2(\text{bpy-}d_8)_2]\text{Cl}$ was prepared from perdeuterio-2,2'-bipyridine (Merck, Sharp and Dohme) and iridium trichloride (Matthey Bishop, Inc.) and purified according to the procedure used for $[\text{IrCl}_2(\text{bpy})_2]\text{Cl}$.¹⁴ The chloride salts were converted to perchlorates by adding perchloric acid to saturated solutions of the chloride salts. Crystals of the less soluble perchlorate salts formed immediately and were collected on glass filter frits, washed with cold water, and dried. Reagent or spectroquality grade solvents were used without further purification, and deionized water was distilled from an all-glass distillation apparatus.

B. Photolysis Procedures. The substrate concentration of the photolysis solution was in the range $(1.5-2.5) \times 10^{-4}$ M. Aqueous photolysis solutions were 10^{-2} M in nitric acid. All solutions were prepared immediately prior to photolysis, and dark reactions were checked after each photolysis. Stirred solutions were photolyzed at 366 nm in 10-cm quartz cells mounted in thermostated cell holders. The photolysis apparatus has been described in previous publications.^{3,16} Light intensities were determined by ferrioxalate actinometry,¹⁷ and quantum yields were obtained from spectral changes^{3,16,18} monitored by a Cary 118C spectro-

Table I. Quantum Yields for Photosolvation of $\text{IrCl}_2(\text{bpy})_2^+$ and $\text{IrCl}_2(\text{bpy-}d_8)_2^+$

solvent	temp, °C	photosolvation quantum yield, mol/einstein $\times 10^2$	
		$\text{IrCl}_2(\text{bpy})_2^+$	$\text{IrCl}_2(\text{bpy-}d_8)_2^+$
10^{-2} M HNO_3	5	4.1 ± 0.5	5.1 ± 0.5
	25	9.2 ± 0.8	9.2 ± 0.8
	50	13.4 ± 2.0	15.2 ± 2.0
methanol	5	1.0 ± 0.1	1.1 ± 0.2
	25	1.9 ± 0.2	2.1 ± 0.1
	50	3.5 ± 0.2	3.5 ± 0.1

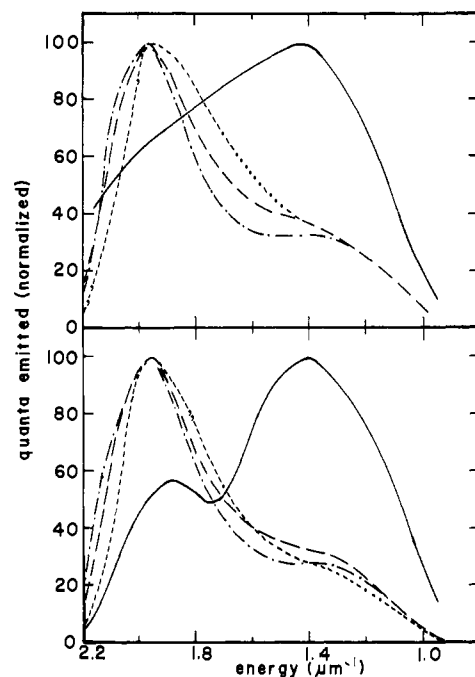


Figure 1. Corrected emission spectra of $\text{IrCl}_2(\text{bpy})_2^+$ (lower) and $\text{IrCl}_2(\text{bpy-}d_8)_2^+$ (upper) at 298 K: (—) in H_2O ; (---) in methanol; (- - -) in acetonitrile; (- · -) in dimethylformamide.

photometer with a thermostated cell compartment. Incremental quantum yields were determined as a function of percent reaction and extrapolated to 0% reaction to give values independent of perturbations caused by labilized chloride ion, inner filtering, secondary photoreactions, etc. which might be caused by the buildup of photoproducts. Dark reactions displayed no spectral changes during the photolysis time periods.

Extinction coefficients used in quantum yield determinations were obtained for solutions of $\text{IrCl}_2(\text{bpy})_2^+$ and $\text{IrCl}_2(\text{bpy-}d_8)_2^+$ in 10^{-2} M nitric acid, methanol, dimethylformamide, acetonitrile, and dimethyl sulfoxide. Extinction coefficients for $\text{IrCl}_2(\text{bpy-}d_8)_2^+$ were determined by direct dissolution of the isolated complex in 10^{-2} M nitric acid. The photoproduct from photolysis of $\text{IrCl}_2(\text{bpy})_2^+$ in methanol, $[\text{IrCl}(\text{CH}_3\text{OH})(\text{bpy})_2]^{2+}$, was prepared in situ by refluxing $[\text{IrCl}(\text{H}_2\text{O})(\text{bpy})_2]^{2+}$ in methanol to a constant absorption spectrum (2 days). Extinction coefficients were calculated for the resulting solution. Extinction coefficients of the perdeuterated photoproducts were assumed to be equivalent to those for the perprotonated photoproducts.

C. Lifetime and Quantum Yield Determination. The instrumentation and procedures used in the measurement of luminescence lifetimes have been described in previous publications.^{5,9,15} Luminescence quantum yields were determined by a modified Parker-Rees method,^{19,20} using purified fluorescein²¹ in 0.1 M NaOH as a standard with a yield of 0.90 for 436-nm excitation.²²

III. Results

Photolysis of the starting complexes in acetonitrile, dimethylformamide, and dimethyl sulfoxide resulted in no meas-

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Table II. Photophysical Parameters for the Decay of $\text{IrCl}_2(\text{bpy})_2^+$ and $\text{IrCl}_2(\text{bpy-d}_8)_2^+$ at 298 K

	water (pH 2)		methanol		dimethylformamide		acetonitrile	
	H ^a	D ^b	H	D	H	D	H	D
τ , ^c ns	$\sim 1.2^d$	$\sim 2.0^d$	36	44	330	710	344	894
Φ_e ^e	3.0×10^{-5}	4.1×10^{-5}	9.2×10^{-4}	1.1×10^{-3}	9.8×10^{-3}	1.7×10^{-2}	6.6×10^{-3}	1.3×10^{-2}
τ/Φ_e , μs	$\sim 41^f$	$\sim 50^f$	38	40	33	42	52	69
k_{Cl_2} , ^g s ⁻¹	$\sim 8 \times 10^7$	$\sim 5 \times 10^7$	5.3×10^5	4.7×10^5	$<10^3$	$<10^3$	$<10^3$	$<10^3$
k_n , ^h s ⁻¹	$\sim 7.5 \times 10^8$	$\sim 4.5 \times 10^8$	2.7×10^7	2.2×10^7	3.0×10^6	1.4×10^6	2.9×10^6	1.1×10^6

^a H = $\text{IrCl}_2(\text{bpy})_2^+$. ^b D = $\text{IrCl}_2(\text{bpy-d}_8)_2^+$. ^c Measured lifetime. ^d Estimated from τ/Φ_e and Φ_e . ^e Measured luminescence quantum yield, fluorescein standard. ^f Average value taken from methanol, dimethylformamide, and acetonitrile. ^g Photosolvation rate constant calculated from Φ_p/τ . ^h Quenching rate constant.

urable absorption changes over the entire time period used (6–16 h). Photosolvation quantum yields are estimated to be less than 10^{-4} in these solvents. Values of Φ_p in 10^{-2} M nitric acid and methanol at 5, 25, and 50 °C are listed in Table I. Apparent activation energies for photosolvation based upon the temperature dependence of these quantum yields are about 4.6 kcal/mol in 10^{-2} M HNO_3 and 5.0 kcal/mol in methanol.

Luminescence lifetimes and quantum yields (Φ_e) of $\text{IrCl}_2(\text{bpy})_2^+$ and $\text{IrCl}_2(\text{bpy-d}_8)_2^+$ in the four solvents employed are listed in Table II. Values of τ/Φ_e , which represent Boltzmann-averaged radiative lifetimes of the CT and LF emitting states, are also listed in Table II. Although luminescence lifetimes in acidic water were too short to measure directly with our apparatus, estimates based upon the luminescence quantum yields, which are measurable, and τ/Φ_e values transferred from other solvents have been used to estimate τ 's in water. These values represent lower limits for τ in water (vide infra). The fact that the luminescence decay curves cannot be resolved with the nitrogen laser implies an upper limit of about 10 ns for these lifetimes.

Emission spectra of the complexes in the four solvent systems employed are illustrated in Figure 1. The broad maxima in the near-infrared region ($\sim 1.4 \mu\text{m}^{-1}$) are assigned to transitions from the low-energy LF states and the narrower bands in the green region ($\sim 2.0 \mu\text{m}^{-1}$) are assigned to the higher energy CT emissions. Small variations in the ratio of LF to CT emission intensity are seen in the nonaqueous solvents whereas a major enhancement of the ligand-field emission intensity relative to the charge-transfer intensity is evident in aqueous solutions.

IV. Discussion

A. Photochemical Considerations. Previous photochemical quantum yield data for $\text{IrCl}_2(\text{bpy})_2^+$ are limited to the chloride photoaquation yield (0.07–0.13) reported by Muir and Huang.¹¹ The photophysics of the complex have been studied at 77 K in rigid glasses^{23,24} where, due to the failure of the system to attain thermal equilibrium between the excited CT and LF states, luminescence properties are associated primarily with emissions from the higher energy CT states. Time-resolved emission spectroscopy indicates¹⁰ that a small contribution also occurs from the lower energy LF states at 77 K. In fluid solutions near room temperature, thermal equilibration of these states occurs,¹⁰ and significant contributions of the LF states to the emission properties are evident.

In many ways, the photochemistry and photophysics of $\text{IrCl}_2(\text{bpy})_2^+$ appear to be analogous to those of $\text{IrCl}_2(\text{phen})_2^+$, where more detailed photochemical studies^{11,25} have been performed. Chloride photoaquation of the latter complex has been attributed²⁵ to a LF excited state, and although some debate concerning the energy of this state relative to the CT state has occurred,^{26,27} recent studies^{28,29} indicate that the LF state is the

lower of the two. The marked similarity between the photophysical and photochemical properties of $\text{IrCl}_2(\text{bpy})_2^+$ and $\text{IrCl}_2(\text{phen})_2^+$ indicate that chloride photosolvation in the former arises from a LF excited state just as it does in the latter.

The potentially important kinetic processes which may contribute to the decay of the excited states of these complexes are summarized in Scheme I. In this scheme both the CT and LF excited states relax to the ground state (G) with rate constants $k_i = k_{in} + k_{ir}$ and $k_d = k_{dn} + k_{dr}$, respectively. Each of these constants are the sum of a radiative (k_{ir} , k_{dr}) and nonradiative (k_{in} , k_{dn}) component. The CT state is assumed to be photoinert, whereas the LF state can form an intermediate (I) with rate constant k_{r3} .³⁰ Once formed, the intermediate can form the product ($\text{P} = \text{IrClH}_2\text{O}(\text{bpy})_2^{2+}$, in water) with rate constant k_p or relax to G with rate constant k_4 . This mechanism assumes that, once formed, the intermediate and product do not undergo back-reaction with free chloride in solution. Correction for this possible complication has been accomplished in the quantum yields reported in Table I by extrapolation to zero free chloride concentration.

Scheme I



Since lifetime measurements indicate that the LF and CT states are thermally equilibrated, the ratio k_{13}/k_{31} may be expressed as an equilibrium constant K_{eq} . A general treatment of the decay kinetics of two excited states in equilibrium where only one reacts has been presented,³¹ and the treatment has been applied⁷ to the decay kinetics of $\text{Ru}(\text{bpy})_3^{2+}$ in water. The essential results of this treatment are presented in eq 9 and 10. In these equations

$$\Phi_p = \frac{k_{r3}P_p}{K_{\text{eq}}^{-1}k_i + k_{r3} + k_d} \quad (9)$$

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(30) No direct characterization of the intermediate I is presently available. One possible formulation which would be consistent with the present data on solvent effects would be a solvent-caged ion pair which could either recombine via k_4 or dissociate and yield product via k_p .

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$$1/\tau = K_{\text{eq}}^{-1}k_i + k_{r3} + k_d \quad (10)$$

Φ_p and τ represent the measured quantum yield for product formation and measured luminescence lifetime, respectively. The quantity P_p , which represents the fraction of I which forms P, is given by $k_p/(k_p + k_d)$. Hence, measurement of Φ_p and τ will yield an observed rate constant for product formation, Φ_p/τ , which represents the product $k_{r3}P_p$.

Values of the observed rate constants for product formation at 25 °C, k_{Cl} , are tabulated in Table II as are values of the observed rate constants for radiationless deactivation of the excited states (k_n). These rate constants display a significant solvent dependence with maximum values in water and minimum values in the nonreactive solvents. However, the reaction rate constants are much more sensitive to solvent changes than are k_n values. It is clear that the enhanced photosolvation yields observed in water are due to enhancement of the product $k_{r3}P_p$ and not to a decrease in the radiationless deactivation rate. However, the absence of major deuterium effects on either the luminescence or solvation quantum yields in the reactive solvents (water and methanol) does not clarify whether the photosolvation process is a direct reaction of an excited-state species, as reported in studies^{5,9} of halopentaammines of Rh(III), or a reaction of a hot ground state.³²

The nature of the solvent dependence of the observed reaction rate does yield some general information regarding mechanistic details of photosolvation. There is no correlation of the observed reaction rates with the electron-donating ability of the solvent, as reflected in Gutmann's donor numbers,³³ but there is qualitative correlation with Gutmann's acceptor numbers³³ and with $\Delta\Delta G_{\text{Cl}^-}$ (the free energy of solvation of Cl^- in a given solvent relative to methanol). This suggests that the ability of the solvent to stabilize the charge separation along the Ir(III)--- Cl^- bond during the solvation process is a key feature in the reaction mechanism. This conclusion parallels that drawn in a previous study⁹ of photosolvation of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ and is consistent with a dissociative or dissociative interchange mechanism.

The upward movement of the CT state in aqueous solutions should lead to an increase in Φ_p even if k_{Cl} were independent of the solvent. This would result from the higher population of the reactive LF state in water and is reflected in an enhanced value of K_{eq} . If this enhancement of K_{eq} were the only factor responsible for the increase in Φ_p , $1/\tau$ would decrease according to eq 8 to maintain a solvent-independent Φ_p/τ ratio. This mode of enhancement of Φ_p is a unique one not available in complexes where the reactive excited state lies substantially below all other es, as in $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$. Hence, a comparison of the solvent effects on the photophysical and photochemical rate constants in $\text{IrCl}_2(\text{bpy})_2^+$ and $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ may lend some insight into the effect of movement of the CT state in the former. This comparison is limited to methanol and water due to the absence of detectable photoactivity of the Ir(III) complex in the other nonaqueous solvents studied.

The previous study⁹ of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ indicates that the chloride photosolvation yield increases from 0.008 in methanol to 0.18 in water, primarily as a result of an increase in the observed rate constant for aquation of Cl^- from the LF excited state. Only minor effects on the rates of photophysical processes leading to ground-state formation were observed. The present study indicates a somewhat smaller solvent effect on Φ_p for $\text{IrCl}_2(\text{bpy})_2^+$, which increases from 0.019 in methanol to 0.092 in water. Hence, upward movement of the CT state in the Ir(III) complex does not lead to an enhanced solvent effect on the photosolvation yield when compared to the Rh(III) data. However, k_{Cl} increases from $5.3 \times 10^5 \text{ s}^{-1}$ in methanol to $8 \times 10^7 \text{ s}^{-1}$ in water for the Ir(III) complex as compared to values of $4.6 \times 10^5 \text{ s}^{-1}$ and $1.3 \times 10^7 \text{ s}^{-1}$, respectively, for the Rh(III) complex.⁹ Hence, the solvent effect in the Ir(III) complex as compared to the Rh(III) complex is manifested in the rate rather than the yield for photosolvation.

The reduced effect on Φ_p in the Ir(III) complex arises from a large k_n increase not paralleled in the Rh(III) complex.

As a result of this analysis we conclude that while movement of the CT state has major effects on the luminescence properties of $\text{IrCl}_2(\text{bpy})_2^+$, it is not important with regard to the photosolvation yield. Rather, modifications of k_{Cl} and k_n from the LF state are the dominant features of the solvent effect in $\text{IrCl}_2(\text{bpy})_2^+$. Further, the somewhat similar solvent effects on both k_{Cl} and k_n in $\text{IrCl}_2(\text{bpy})_2^+$ suggest that a substantial fraction of the photophysical decay follows a pathway through an intermediate species which may yield the photosolvation product as well as return to the ground state. These processes are represented by eq 6–8 in Scheme I.

B. Photophysical Considerations. The energy gap between the LF and the higher energy CT states of $\text{IrCl}_2(\text{bpy})_2^+$ has been estimated¹⁰ to be $0.037 \mu\text{m}^{-1}$ in dimethylformamide. This is far smaller than the larger difference observed in the position of the emission band maxima arising from these two states ($\sim 0.6 \mu\text{m}^{-1}$) due to the massive Stokes shift associated with the ligand-field emission.³⁵ The sensitivity of the energy of CT states of low-symmetry metal complexes to solvent medium is well-known, as is the relative insensitivity of the energy of LF states. Given the small energy gap separating these states in dimethylformamide, major solvent effects on the luminescence spectrum as well as the quantum yields for the various photophysical and photochemical processes arising from these states are anticipated. This is manifested, for example, in the large enhancement of the LF to CT emission ratio (Figure 1), which is consistent with upward movement of the CT state in water. Solvent effects on the emission quantum yields can be interpreted in Scheme I primarily via recognition of the effect of movement of the CT state on step 3. The ratio k_{13}/k_{31} is given by $e^{-\Delta E/kT}$ and will increase with upward movement of the CT state, leading to reduced contributions from processes 1 and 2. As a result, the photophysical and photochemical parameters in water are more characteristic of the LF state than are these parameters in the nonaqueous solvents. This suggests that the reduction of the luminescence quantum yield in water arises from the fact that the intrinsic emission yield from the LF state, $k_{\text{dr}}/(k_{\text{d}} + k_{r3})$, is less than that from the CT state, $k_{\text{ir}}/(k_{\text{i}} + k_{13})$. It also suggests that the Boltzmann-averaged radiative lifetime τ/Φ_e in water could be different from that in the nonaqueous solvents. This is particularly important to our analysis since τ/Φ_e has been transferred from nonaqueous solvents to water in order to estimate τ values. Since k_{dr} for the Laporte-forbidden LF emission is expected to be somewhat smaller than k_{ir} for the CT emission, the value of τ/Φ_e in water may, in fact, be larger than the value transferred from the nonaqueous solvents. Hence, the τ values estimated by this procedure represent a lower limit. However, the upper limit of about 10 ns imposed by the time-resolution ability of the lifetime apparatus indicates that the 1–2-ns estimate of τ must be within an order of magnitude of the correct value. Thus our estimates of the reaction rate constant, k_p , could be no more than 1 order of magnitude too large. Even allowing for this large an error, our conclusion that k_p is greatly enhanced in water is unaltered.

V. Conclusion

The photochemical and photophysical properties of bis-bidentate complexes of Ir(III) such as $\text{IrCl}_2(\text{bpy})_2^+$ and $\text{IrCl}_2(\text{phen})_2^+$ are determined by the relatively unusual occurrence of light emission in competition with ligand substitution activity, coupled with the rare property of two close-lying emitting states of different orbital parentage. The primary ramification of the CT state in close proximity to the LF state appears to be enhanced emission intensity due to the combined increase of the radiative decay rate and substitutional unreactive nature of the CT state.

Solvent effects on the photochemical and photophysical properties of $\text{IrCl}_2(\text{bpy})_2^+$ can operate by two distinct modes: (1) movement of the CT transfer state relative to the LF state,

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changing the LF to CT emission intensity ratios owing to changes in the relative populations in each state; (2) direct solvent effects on photosolvation rates and nonradiative decay rates. The latter effects, especially with regard to the substitution rate k_{CT} , appear to be more important in determining photoreaction quantum yields. Clearly the enhanced photosolvation quantum yield of $\text{IrCl}_2(\text{bpy})_2^+$ in water relative to the nonaqueous solvents results from larger increases in k_{CT} than in k_n . The ability of the solvent to stabilize the developing charge separation along the $\text{Ir(III)}\cdots\text{Cl}^-$ bond appears to correlate with the rate of photosolvation, consistent with a dissociative or dissociative interchange mechanism from the LF es. However, because of the absence of any clear deuterium

isotope effect on the excited-states lifetimes and photosolvation rates in the reactive solvents, we cannot presently assert whether photosolvation and nonradiative deactivation are competing processes of the emitting LF excited state rather than competitive deactivation modes of an intermediate or hot ground-state species formed from the LF state.

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Pressure Effect on Rate and Equilibrium Constants of Reversible Anionic σ -Complex Formation between Polynitroaromatics and Lyate Ions of Water and Methanol

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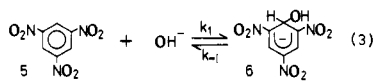
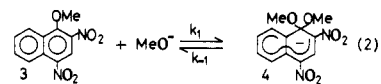
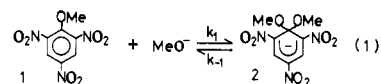
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Abstract: The kinetics of the following reversible anionic σ -complex formation reactions was studied by the high-pressure stopped-flow method up to 1500 bar at 25 °C: 2,4,6-trinitroanisole + $\text{MeO}^- \rightleftharpoons \mathbf{2}$ in methanol, 1-methoxy-2,4-dinitronaphthalene + $\text{MeO}^- \rightleftharpoons \mathbf{4}$ in methanol, and 1,3,5-trinitrobenzene + $\text{OH}^- \rightleftharpoons \mathbf{6}$ in water. The rate constants for complex formation in methanol increased with pressure, while that in water decreased slightly. Interestingly, the rate constants of reversion to reactants increased with pressure in all cases. It was concluded from the consideration of the volume of activation that the electronic charge is not completely delocalized into the ring system in the transition state and that local electrostriction in the vicinity of the nucleophile is still reflected in the volume. The pressure effect on the equilibrium constant for formation of $\mathbf{4}$ leads to a reaction volume consistent with that determined by the kinetic studies. The pressure-induced spectral red shifts of $\mathbf{2}$ and $\mathbf{4}$ are intelligible in terms of the density change of the solvent and the electronic character of the excited states. The anomalous pressure effect on the formation of $\mathbf{6}$ was explainable in terms of the strong solvation of OH^- in water.

The anionic σ complexes between polynitroaromatic substances and nucleophilic ions such as hydroxide and alkoxide ions have received much attention since the complex is often a reaction intermediate in nucleophilic substitutions.¹⁻⁵ The spectroscopic characteristics of these complexes have been extensively studied by means of electronic and NMR spectra,^{5,6} and voluminous studies have been reported on the kinetics of their reversible formation reaction and further transformation. It is found^{5,6} that their stability and reactivity are strongly dependent on the nucleophile as well as the solvent; however, the role of the solvent in each reaction step seems to remain uncertain.

High-pressure kinetic studies of chemical reactions in solution are recognized to give very important information about the reaction dynamism and the role of the solvent in activation.⁷ To date, the usual high-pressure techniques for thermal reactions have been restricted to these with half-lives longer than ca. 20 min, since it takes some time after compression to attain thermal equilibrium. We have developed a high-pressure stopped-flow method which is a different type from Heremans⁸ and succeeded

in following reactions as fast as several milliseconds up to 1500 bar,^{9,10} so it became possible to examine irreversible reactions or observable transient intermediate. This paper deals with the volume profile of some anionic σ -complex formations (1)–(3).



Experimental Section

Materials. 2,4,6-Trinitroanisole (**1**) was synthesized from 1-chloro-2,4,6-trinitrobenzene (**7**) and sodium methoxide in methanol. Into 30 mL of methanol was dissolved 5 g of **7**, and 4.8 g of 28% NaOMe in methanol was added, and then the mixture was refluxed for 4 h. After being cooled at room temperature, the mixture was neutralized by means of 0.5 N aqueous H_2SO_4 solution. The precipitate was recrystallized several times from methanol; mp 68.0 °C. 1-Methoxy-2,4-dinitronaphthalene (**3**) was synthesized according to the procedure of Fendler et al.¹¹ and recrystallized from methanol; mp 98.5 °C. Commercially obtained 2,4,6-trinitrobenzene (**5**) was recrystallized several times from methanol; mp

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