Electron Localization or Delocalization in the MLCT Excited States of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$. Consequences to Their Photochemistry and Photophysics in Fluid Solution

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Received July 31, 1997

Introduction

It is now known that the generation of the lowest energy, thermally equilibrated metal-to-ligand charge-transfer (MLCT) excited state of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine), which arises from the initially populated Franck−Condon excited state, is essentially complete in ∼300 fs.[1] Electroabsorption (Stark effect) studies by Oh and Boxer[2] showed that MLCT excitation resulted in a significant change in the dipole moment, suggesting that the transferred electron is localized on a single ligand even in the initial state. Recently, Karki and Hupp[3] performed the same type of experiments on $Ru(phen)_3^{2+}$ (phen = 1,10-phenanthroline) and found that the initially populated excited state was also localized; their results suggested that the separated charge of the thermally equilibrated excited state was localized on one ligand.

Turró et al.[4] proposed on the basis of resonance Raman spectral evidence that the luminescent $^*Ru(phen)_3^{2+}$ state either is delocalized or is very rapidly hopping within vibrational times among the phen ligands, whereas $^*Ru(bpy)_3^{2+}$ exists with electron localization on just one ligand. If this were so, one would expect there to be profound differences in the photochemical and photophysical behavior of the excited states of these complexes. Electron localization in $^*Ru(bpy)_3^{2+}$, represented as $(bpy)_2Ru^{III}(bpy^{\bullet-})^{2+}$, would result in a large dipole moment, which has been estimated to be 14 D with a dipole length of 3 Å due to the asymmetry of the structure.[5] On the other hand, delocalization or very rapid hopping in $^*Ru(phen)_3^{2+}$, represented as $Ru^{III}(phen^{\bullet-/3})_3^{2+}$, would be expected to have a very small dipole moment, if any. In fluid solution, where the solvent dipoles interact with the excited state, the photochemistry and photophysics of Ru−diimine complexes are strongly affected by the nature of the solution medium.[6] Variations in the dipole−dipole interactions cause changes in the energy gaps involving the MLCT state, the ground state, and the metal-centered excited state, resulting in an alteration of the rates of the processes and their temperature dependencies;[7] the interactions also affect the values of the solvent reorganization energies in the excited-state electron-transfer reactions.[8] The detailed photochemical and photophysical behavior of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ would be expected to be functions of the extent to which the electron is localized on the ligands in the excited state.

To explore this question, we have examined the effect of the variation of temperature on the photophysics of $^*Ru(phen)_3^{2+}$ in H_2O-CH_3CN mixtures and on the rate constants for oxidative quenching by methylviologen (MV^{2+}) and reductive quenching by the phenolate ion (PhO^-) in aqueous solution. Comparisons are made with the same data for $^*Ru(bpy)_3^{2+}$. It is important to note that the ground- and excited-state oxidation and reduction potentials and excited-state energies for these complexes are virtually identical.[9]

Experimental Methods

$[Ru(bpy)_3]Cl_2$ (GFS Chemicals) was recrystallized from water and dried over silica gel; $Ru(phen)_3^{2+}$, as the PF_6^- salt, was available from our laboratory reserves. Methylviologen dichloride (MV^{2+}; Aldrich) was recrystallized three times from methanol and dried under vacuum; phenol (PhOH; Aldrich) was purified by sublimation. Distilled water was further purified by passage through a Millipore purification train. CH_3CN (Baker HPLC grade) was purified and dried as described in the literature;[10] Na_2SO_4, KCl, and NaOH were Fisher or Baker Analyzed reagents.

Emission lifetime and transient absorption measurements were made with a pulsed Nd:YAG laser (λ_{exc} = 532 nm) that has been described before.[11] The temperature of the solutions was controlled to ±0.1 °C. The measurement of the lifetime of $^*Ru(phen)_3^{2+}$ as a function of temperature was performed on Ar-purged solutions of H_2O, CH_3CN, and their mixtures. Reductive and oxidative quenching experiments were performed as a function of temperature on Ar-purged aqueous solutions containing 40 μM complex and 0.5−5.0 mM MV^{2+} at ambient pH and ionic strength or 0.6−6.0 mM PhO^- at pH 12.0 and μ = 50 mM (Na_2SO_4).

Results and Discussion

Photophysics. The lifetime of $^*Ru(phen)_3^{2+}$ in the absence of quencher ($\tau_0 = 1/k_0$) was measured at 25 °C in H_2O-CH_3CN mixtures (χ_{AN} = 0.0−1.0); Figure 1 shows the results in comparison with those for $^*Ru(bpy)_3^{2+}$.[7] $^*Ru(bpy)_3^{2+}$ is longer lived in CH_3CN than in H_2O at room temperature, which is the general behavior of Ru and Os complexes.[12] $^*Ru(phen)_3^{2+}$, on the other hand, shows the opposite effect, which is similar to that exhibited by $^*Ru(bpz)_3^{2+}$ (bpz = 2,2′-bipyrazine),[13] the excited state of which is believed to be localized.[14] To probe the origin of this lifetime effect, values of k_0 were measured as a function of temperature, and were fitted to the model described by Van Houten and Watts ($k_0 = k_1 + k_2 \exp(-\Delta E/RT)$),[15] where k_1 is the rate constant for the decay of the MLCT excited state directly to the ground state via radiative (k_{rd}) and nonradiative (k_{nr}) modes and $k_2 \exp(-\Delta E/RT)$ ($=k'$) is the overall rate constant for the thermally activated population of the metal-

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S0020-1669(97)00959-2 CCC: $15.00

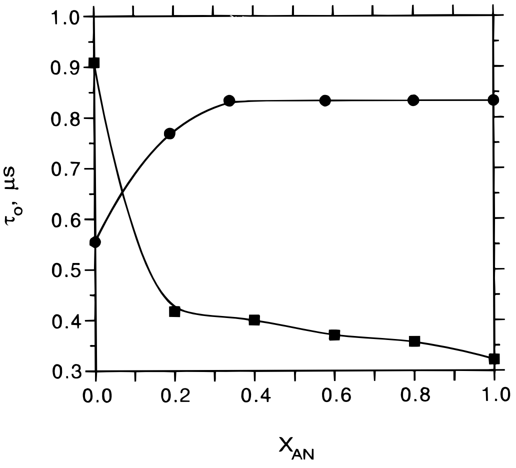

Figure 1. τ_0 for $*Ru(phen)_3^{2+}$ (■) and $*Ru(bpy)_3^{2+}$ (●) as a function of χ_{AN} in H_2O-CH_3CN mixtures at 25 °C.

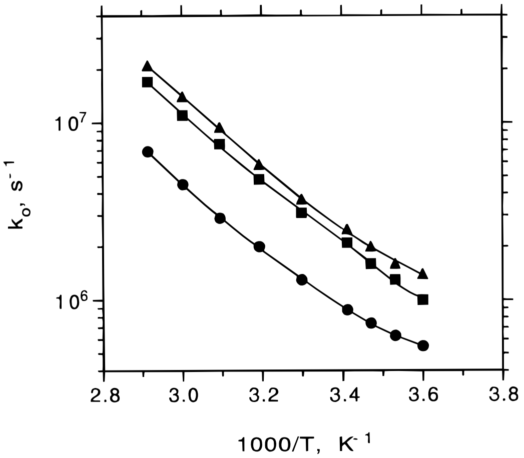

Figure 2. Plot of log k_0 vs $1/T$ for the decay of $*Ru(phen)_3^{2+}$ at χ_{AN} = 0.0 (●), 0.2 (■), and 1.0 (▲) in H_2O-CH_3CN mixtures.

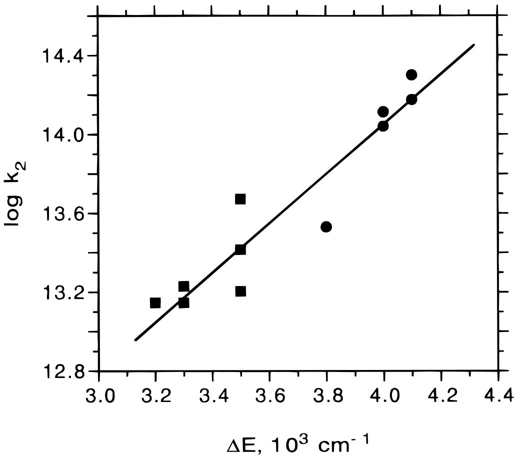

Figure 3. Plot of log k_2 vs ΔE for $*Ru(phen)_3^{2+}$ (■) and $*Ru(bpy)_3^{2+}$ (●).

centered (MC) excited state. The values of k_1 and ΔE, the energy gap between the MLCT and MC excited states, obtained from the fitting of the data in H_2O are in excellent agreement with the literature values;[16] the values of k_2, which are subject to much greater uncertainty, are quite comparable. Table 1 gives the values of k_0 at 25 °C, k_1, k_2, and ΔE for $*Ru(phen)_3^{2+}$ as a function of χ_{AN}, with corresponding data for $*Ru(bpy)_3^{2+}$.[7] Inasmuch as the quantum yields for emission of the excited states are ~5%,[17] $k_1 \sim k_{nr}$.

The plot of log k_0 vs $1/T$ (Figure 2), which is nonlinear for both complexes, shows that the rate of decay of $*Ru(phen)_3^{2+}$ increases as χ_{AN} is increased across the entire temperature range (4.6−70 °C) with no evidence of an isokinetic point; for $*Ru(bpy)_3^{2+}$, however, the decay is faster in CH_3CN-rich mixtures at higher temperatures (35−65 °C) but faster in H_2O-rich mixtures at lower temperatures (7−35 °C).[7] This difference in behavior is due to the effect of the solution medium on the relative importance of the various decay pathways of the excited states; k' is always the major contributor to k_0 for $*Ru(phen)_3^{2+}$ whereas k_1 and k' are the dominant quantities at low and high temperatures, respectively, for $*Ru(bpy)_3^{2+}$. In fact, the effect of solvent deuteration in aqueous solution has shown[18] that at room temperature the decay of $*Ru(bpy)_3^{2+}$ is predominantly via nonradiative transition to the ground state while the decay of $*Ru(phen)_3^{2+}$ is mainly through the MC state.

Comparison of the parameters for $*Ru(phen)_3^{2+}$ and $*Ru(bpy)_3^{2+}$ in the different solution media (Table 1) reveals some important differences. The value of k_1 in H_2O is significantly smaller for $*Ru(phen)_3^{2+}$ than for $*Ru(bpy)_3^{2+}$; however, systems with more rigid ligands but about the same MLCT−ground-state energy gap, as is the case here, have slower nonradiative decays.[19] For both complexes, k_1 exhibits its greatest change as χ_{AN} is increased in H_2O-rich solution where preferential solvation by H_2O would be important, although k_1 increases for $*Ru(phen)_3^{2+}$ but decreases for $*Ru(bpy)_3^{2+}$. It has been pointed out[12] that solvent reorganization in the vicinity of the excited state is an important factor in mediating nonradiative decay processes; it would appear that the changes in solvent reorganization as χ_{AN} is increased in H_2O-rich solution are different for the two excited states. It should be noted that k_1 *decreases* as χ_{AN} is increased for hetero- and homoleptic complexes of bpz and bpm (2,2′-bipyrimidine) where hydrogen-bonding exists between the N-heteroatom and water.[7] The *increase* in k_1 for $*Ru(phen)_3^{2+}$ as χ_{AN} is increased could be attributed to its somewhat greater hydrophobicity in comparison to that of its less conjugated analogues. This difference in behavior of $*Ru(phen)_3^{2+}$ and $*Ru(bpy)_3^{2+}$ could also be taken as an indication that their electron localizations are different, although the rather small differences in k_1 for such large presumed differences in structure do not provide a very strong argument.

The values of ΔE for the two complexes in the H_2O-CH_3CN mixtures are different but are well within the "normal" range for Ru(II)−diimine complexes.[20] Of importance is the relationship between k_2 and ΔE; despite the large uncertainties in the values of k_2, a plot of log k_2 vs ΔE (Figure 3) shows a respectably linear Barclay−Butler correlation, suggesting that the mechanism of population of the MC state from the MLCT state is the same for both excited states despite any differences or similarities in electronic nature.

Photochemistry. The oxidative quenching of $*Ru(phen)_3^{2+}$ or $*Ru(bpy)_3^{2+}$ by MV^{2+} gave good linear plots of k_{obs}, the observed decay rate constant, vs $[MV^{2+}]$ as a function of temperature under the conditions of low, but variable, ionic

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Table 1. Photophysical Parameters for $^*\mathrm{Ru(phen)_3}^{2+}$ and $^*\mathrm{Ru(bpy)_3}^{2+}$ as a Function of χ_{AN} in H_2O-CH_3CN Mixtures

	χ_{AN}								
	0.00	0.19	0.20	0.34	0.40	0.58	0.60	0.80	1.0
			$^*\mathrm{Ru(phen)_3}^{2+}$						
k_0, 10^6 s^{-1} (25 °C)	1.1		2.4		2.5		2.7	2.8	3.1
k_1, 10^6 s^{-1}	0.35 (0.37)[a]		0.54		0.41		0.59	0.53	0.42
k_2, 10^{13} s^{-1}	1.6 (2.3)[a]		1.7		1.4		4.7	2.6	1.4
ΔE, 10^3 cm^{-1}	3.5 (3.6)[a]		3.3		3.3		3.5	3.4	3.2
			$^*\mathrm{Ru(bpy)_3}^{2+}$ [b]						
k_0, 10^6 s^{-1} (25 °C)	1.8	1.3		1.2		1.2		1.2	1.2
k_1, 10^6 s^{-1}	1.4	0.85		0.71		0.65		0.59	0.56
k_2, 10^{13} s^{-1}	3.4	15		11		13		13	20
ΔE, 10^3 cm^{-1}	3.8	4.1		4.0		4.0		4.0	4.1

[a] Reference 16. [b] Reference 7.

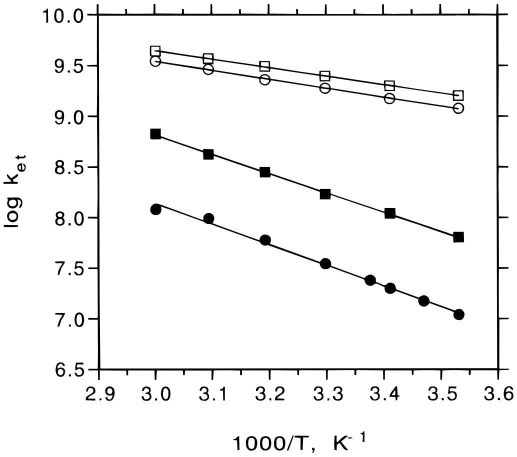

Figure 4. Plot of log k_{et} vs $1/T$ for the quenching of $^*\mathrm{Ru(phen)_3}^{2+}$ (□, ■) and $^*\mathrm{Ru(bpy)_3}^{2+}$ (○, ●) by MV^{2+} (open symbols) and PhO^- (closed symbols) in H_2O.

strength; values of the quenching rate constants (k_q) were obtained from the slopes of the lines. Electron-transfer quenching can be represented by the diffusional formation of a precursor complex (k_d) followed by the diffusional breakup of the complex (k_{-d}) in competition with the electron-transfer step (k_{et}); the rate constants are related by eq 1, where $K_d = k_d/k_{-d}$.

$$\frac{1}{k_q} - \frac{1}{k_d} = \frac{1}{K_d k_{\mathrm{et}}} \tag{1}$$

Values of k_d and k_{-d} were calculated as before[21] from the equations of Smoluchowski, Debye, and Eigen,[22] from which was obtained k_{et} as a function of temperature; these rate constants are given in the Supporting Information.

The slope of the plot of log k_{et} vs $1/T$ is a measure of the free energy of activation of electron transfer, which, according to Marcus theory, is made up of the driving force ($\Delta G_{\mathrm{et}}^{\circ}$) and the reorganization energy (λ) of the reaction.[23] Figure 4 shows that the slopes of the plots for the reactions of $^*\mathrm{Ru(phen)_3}^{2+}$ and $^*\mathrm{Ru(bpy)_3}^{2+}$ with MV^{2+} are the same; inasmuch as $\Delta G_{\mathrm{et}}^{\circ}$ is the same for both systems, we can conclude that the values of λ are the same. The magnitude of k_{et} is also nearly the same, implying that the values of the electronic coupling coefficients for the transfer of an electron from a reduced ligand of the excited state to the viologen acceptor are, at a minimum, very similar.

The same treatment was applied to the values of k_q for the reductive quenching by PhO^- at pH 12 as a function of temperature (Supporting Information). Figure 4 shows that the slopes of the plots are virtually identical, indicating that the values of λ for the reductive electron-transfer quenching are the same for $^*\mathrm{Ru(phen)_3}^{2+}$ and $^*\mathrm{Ru(bpy)_3}^{2+}$; the larger value of λ for quenching by PhO^- than for MV^{2+} is mainly due to hydrogen-bonding to the solvent by PhO^- and will be discussed in detail in a future publication.[24] It is particularly interesting to note that the values of k_{et} for the quenching by PhO^- are a factor of ~5 larger for $^*\mathrm{Ru(phen)_3}^{2+}$ than for $^*\mathrm{Ru(bpy)_3}^{2+}$, suggesting that the electronic coupling coefficients for the transfer of an electron from the π orbital of the phenolate donor to a t_{2g} orbital of the metal center in the excited states are different. Molecular modeling shows a possible basis for the greater orbital overlap in the case of $^*\mathrm{Ru(phen)_3}^{2+}$; the greater inflexibility of the phen ligands increases somewhat the distortion of the structure of the complex from the octahedral, opening up the intraligand pockets in which electron transfer occurs. This difference in behavior has been observed in an analogous system; the reductive quenching of $^*\mathrm{Ru(phen)_3}^{2+}$ and $^*\mathrm{Ru(bpy)_3}^{2+}$ by ascorbate ion in H_2O has values of $k_q = 2.3 \times 10^8$ and 3.0×10^7 M^{-1} s^{-1}, respectively.[25]

Conclusions

The results show that the decay parameters of $^*\mathrm{Ru(phen)_3}^{2+}$ and $^*\mathrm{Ru(bpy)_3}^{2+}$ as a function of temperature in H_2O, CH_3CN, and their mixtures are quite similar and that the reorganization energies for their electron-transfer quenching, whether reductive or oxidative, are virtually identical. We conclude that even if the natures of the excited states of $^*\mathrm{Ru(phen)_3}^{2+}$ and $^*\mathrm{Ru(bpy)_3}^{2+}$ were very different, i.e., delocalized vs localized, such differences do not manifest themselves in their photophysics and electron-transfer photochemistry in fluid solution at and near room temperature. The paper by Turró et al.[4] proposes that differences exist on the vibrational time scale, but the results presented here indicate that these differences, were they to exist, do not affect the observed excited-state decay and electron-transfer chemistry.

Acknowledgment. This research was supported by the Division of Chemical Sciences, U.S. Department of Energy.

Supporting Information Available: A table giving values of k_q, k_d, k_{-d}, and k_{et} for the quenching of $^*\mathrm{Ru(phen)_3}^{2+}$ and $^*\mathrm{Ru(bpy)_3}^{2+}$ by MV^{2+} and PhO^- as a function of temperature in aqueous solution (2 pages). Ordering information is given on any current masthead page.

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