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Energy of the Photosubstitutionally Reactive Excited State of Pentaammine(pyridine)ruthenium(II)

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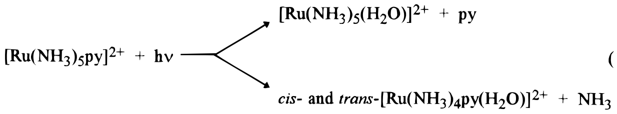
The photosensitized aquation of pentaammine(pyridine)ruthenium(II) by several dyes has been studied under conditions where only the sensitizers absorb light. The ratio of the quantum yields for ammine and pyridine substitution was the same as that for direct photoaquation. Sensitization was effective with singlet sensitizers Rhodamine-B (17 452 cm^{-1}) and Safranine-T (17 690 cm^{-1}), as well as the triplet sensitizer biacetyl (19 000 cm^{-1}), but no reaction was observed with Neutral-Red (16 900 cm^{-1}). The results indicate that the excited state precursor of the observed photosubstitution in the complex lies in the energy range between 17 000 and 17 700 cm^{-1}.

Introduction

The photochemistry of ammineruthenium(II) complexes with pyridine-like ligands has been extensively studied since 1969.[1−10] The main representative complex of this class of complexes is $[Ru(NH_3)_5py]^{2+}$ (py = pyridine), which has been subject to extensive study.[1−5,7−10] The visible spectra of $[Ru(NH_3)_5L]^{2+}$ (L = pyridine or pyridine-like ligand) are dominated by intense metal-to-ligand-charge-transfer (MLCT) absorption bands which are both ligand and solvent dependent.[4,11,12] In these complexes, the nonobserved lowest energy ligand field (LF) absorption band was estimated to lie at ∼390 nm. The complexes were irradiated with light energies corresponding to the MLCT absorption energies and were classified as “reactive” or “unreactive”. It was shown that "reactive" $[Ru(NH_3)_5L]^{2+}$ complexes have irradiation wavelength independent, relatively higher, photosubstitution quantum yields and have MLCT absorption band maxima at wavelengths shorter than 460 nm in aqueous solution.[4] On the other hand, the "unreactive" are those having lower and irradiation wavelength dependent quantum yields of photosubstitution and having MLCT absorption bands at longer wavelengths. These observations led Ford to propose the tuning model.[4] According to this model, in which a LF excited state was assigned as responsible for the photosubstitution reactions, the reactive complexes are those which have a LF excited state as lowest energy excited state (LEES), while the unreactive complexes would be those with a MLCT excited state as LEES.

The UV−vis spectrum of the pyridine complex, $[Ru(NH_3)_5py]^{2+}$, displays a MLCT band at 408 nm ($\epsilon = 7800\ M^{-1}\ cm^{-1}$) and an intraligand, $\pi-\pi^*$, band at 246 nm ($\epsilon = 4600\ M^{-1}\ cm^{-1}$).[11] The photoaquation of $[Ru(NH_3)_5py]^{2+}$ in its MLCT absorption energy range was found to be wavelength independent and resulted exclusively in the loss of coordinated ammonia and pyridine ligands. In addition, a pH dependence of the pyridine quantum yields was observed, suggesting competitive acid-catalyzed reaction pathways for pyridine aquation and acid-independent reaction pathways for ammonia aquation[1b]



$$[Ru(NH_3)_5py]^{2+} + h\nu \longrightarrow \begin{cases} [Ru(NH_3)_5(H_2O)]^{2+} + py \\ cis\text{- and } trans\text{-}[Ru(NH_3)_4py(H_2O)]^{2+} + NH_3 \end{cases} \qquad (1)$$

One proposed mechanism[9] for the acid-dependent path involves an intermediate formed by rehybridization and protonation of the pyridine nitrogen in the MLCT state to form a Ru(III)-coordinated free radical species. Studies on the charge-transfer excited species $\{[Ru(NH_3)_5L]^{2+}\}^*$ showed evidence for a reactive ligand field excited state and indicated that the MLCT was substitutionally unreactive.[4] Flash photolysis experiments on the $[Ru(NH_3)_5py]^{2+}$ complex ion showed the formation of a long-lived transient.[5] This transient was proposed to be an intermediate (not an excited state) in which the pyridine ring is bonded to the Ru(II) through the pyridine π system, leaving the nitrogen lone pair free for reversible protonation and further aquation of the complex. At the time this mechanism was proposed, such bonding had little precedent among “classical”

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coordination compounds, but it is now accepted, as illustrated by the similarly bonded intermediates proposed to occur in the linkage isomerization of isonicotinamide,[13] from amido bonded to pyridyl bonded, in pentaammineruthenium(II). The other striking example is the analogously bonded benzene reported to occur in the stable $Os^{II}(NH_3)_5(C_6H_6)$ complex.[14]

The nonobservance[10] of the pyridine radical anion resonance peaks in Raman scattering of $[Ru(NH_3)_5py]^{2+}$, at 340 nm, did not prove that the photoactive LF state lies below the MLCT state in $[Ru(NH_3)_5py]^{2+}$, although it is consistent with Ford's model. Creutz and co-workers,[7] reported studies on picosecond absorption spectroscopy of $[Ru(NH_3)_5py]^{2+}$. These experiments suggested a very short lifetime ($\tau << 20$ ps) for the MLCT state. The ligand field excited state is not observed directly and was inferred to be short-lived.

An unknown detail of this system is the approximate energy of the excited state(s) responsible for its photochemistry. Because sensitization and quenching have been very useful tools for the analysis of the photochemical fates of inorganic molecules[15] and since the excited state precursor(s) of the photochemistry observed in ruthenium(II) ammines is (are) not directly observed, we decided to run some sensitization and quenching experiments in order to determine the energy range of this (these) states(s) in pentaammine(pyridine)ruthenium(II), which would provide a wider experimental basis for mechanistic discussion.

Experimental Section

Chemicals. The $[Ru(NH_3)_5py](BF_4)_2$ salt was prepared from $[Ru(NH_3)_5Cl]Cl_2$ and recrystallized according to published procedures.[11] Rhodamine-B (Aldrich) was recrystallized twice from diethyl ether and air-dried. Safranine-T, Neutral-Red, and biacetyl (2,3-butanedione) were purchased from Aldrich and used without further purification. Solutions for photolysis and luminescence studies were prepared using doubly distilled water containing 0.2 M NaCl at pH 4.0 (10^{-4} M HCl). Solutions were deareated with argon previously passed through a chromous bubbler. Reinecke's salt[16] $(NH_4)[Cr(NH_3)_2(SCN)_4]$ (Eastman), used for actinometry at 519 nm, was converted to the potassium salt by recrystallizing from KNO_3 solution. Potassium tris(oxalato)-ferrate(III), used in actinometry at 405 nm, was prepared according to Calvert and Pitts.[17]

Instruments. Monochromatic irradiations at 405 and 519 nm were carried out with a 150 W xenon lamp in a Oriel Model 6253 universal arc lamp source, using Oriel interference filters for monochromatization at the appropriate wavelengths. The progress of the photoreactions was monitored spectrally on a HP Model 8452A diode array spectrometer. Tris(oxalato)ferrate(III) was used as the actinometer for the 405 nm irradiations and Reinecke's salt for the 519 nm irradiations. Emission spectra were recorded on a Aminco-Bowman Model J4-8960A spectrofluorimeter, with a high-pressure xenon lamp and an IP28 type photomultiplier. The electrochemical data were obtained using a PAR Model 273 potentiostat/galvanostat, a plotting system recorder, and an IBM XT microcomputer. Measurements were carried out in 0.2 M NaCl solutions at pH 4.0 (10^{-4} M HCl), using a cell containing Ag/AgCl (−17 mV vs SCE) as the reference electrode, Pt wire as the auxiliary electrode, and a glassy carbon electrode with an area of 0.082 cm^2 as the working electrode. The solutions were 1×10^{-4} M in $[Ru(NH_3)_5py]^{2+}$ and 1×10^{-4} M for the dye. Solutions were deaerated using an argon stream. The diffuse reflectance spectrum was recorded vs $MgCO_3$ reference on a SPECORD M40 spectrometer equipped with an integrating sphere.

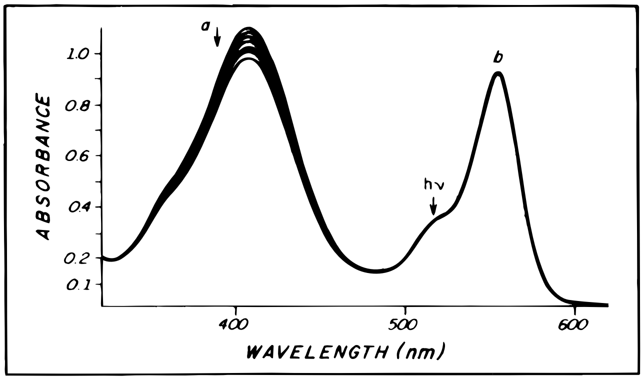

Figure 1. Electronic spectral changes for 9.41×10^{-6} M Rhodamine-B and 1.44×10^{-4} M $[Ru(NH_3)_5py]^{2+}$ in 0.2 M NaCl, pH 4.0 (10^{-4} M HCl), under 519 nm irradiation: (a) absorption band of the complex; (b) absorption band of the dye; $h\nu$ = irradiation wavelength.

Procedures. The same general procedure was used for the study of both the direct and photosensitized photolysis of $[Ru(NH_3)_5py]^{2+}$. A weighed amount of the complex was dissolved in a solution of 1×10^{-5} M Rhodamine-B in 0.2 M NaCl at pH 4.0 (10^{-4} M HCl). The solutions were deaerated by bubbling argon prior to photolysis and stirred during irradiation. The deaerated solutions were photolyzed up to approximately 10% conversion in 1.0 cm and 0.5 cm cells at 25 °C. The quantum yields for substitution of py were calculated from the decrease in the MLCT band as described in the literature.[1c,4] The spectroscopic technique does not provide any reliable information regarding ammonia photoaquation (eq 1) under the experimental conditions described. For this reason, it was necessary to monitor the ammonia photoaquation by pH changes in the acidic (pH 4) photolysis solution, since each equivalent of ammonia released will neutralize 1 equiv of acid. Thus, after photolysis, the pH values of the irradiated solutions were determined, and the quantum yields for the acid consumption were calculated from the pH differences. The quantum yield of ammonia was corrected for the pH changes due to the protonation of the basic pyridine released, taking into account its pK_a. Analogous samples were allowed to react in the dark , under the same conditions of the photolyzed solutions, in order to correct quantum yields.

Results

Continuous Photolysis. The photoaquation quantum yields for $[Ru(NH_3)_5py]^{2+}$, irradiated at 405 nm both in the presence and in the absence of Rhodamine-B, were determined with $(1-5) \times 10^{-4}$ M $[Ru(NH_3)_5py]^{2+}$ solutions. In the solutions with no sensitizer, the ammonia aquation quantum yield was found to be 0.060 ± 0.005 mol/einstein and that for pyridine 0.040 ± 0.004 mol/einstein, in good agreement with the reported[4] values of 0.063 ± 0.005 and 0.040 ± 0.004 mol/einstein, respectively.

Figure 1 shows the result of the photolysis at 519 nm of a 1.44×10^{-4} M deaerated solution of $[Ru(NH_3)_5py]^{2+}$ in the presence of 9.41×10^{-6} M Rhodamine-B. At this wavelength, only the dye absorbs the incident radiation. The spectral changes obtained on irradiation were exactly those expected for reaction 1, *i.e.*, a continuous decrease of the absorbance of the complex (at 408 nm) and no change in the absorbance of Rhodamine-B (at 554 nm). A spectrophotometric check of the photochemical stability of Rhodamine-B in these experiments showed that changes were negligible under the conditions used in this work. On the basis of the light absorbed by Rhodamine-B, the quantum yield for the sensitized reaction, Φ_r^s, was obtained. The variation of reciprocal quantum yield for the sensitized reaction as a function of the complex concentration is shown in Figure 2.

Experiments were also performed using Safranine-T as sensitizer. Carefully dearated aqueous solutions containing 1.2×10^{-5} M Safranine-T and $6 \times 10^{-5}-2 \times 10^{-4}$ M $[Ru(NH_3)_5$-

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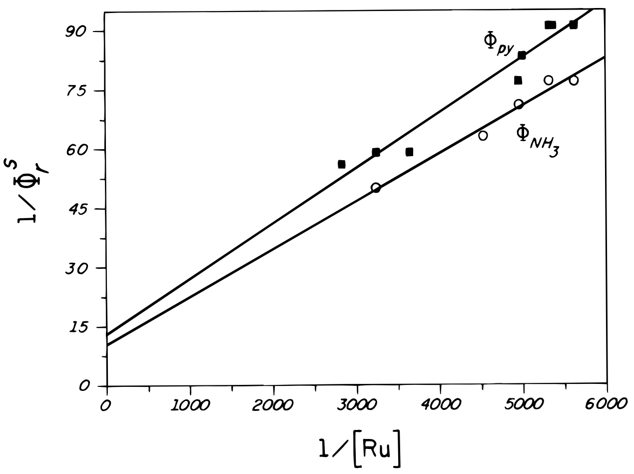

Figure 2. Variation of the quantum yield of the Rhodamine-B-sensitized aquation of $[Ru(NH_3)_5py]^{2+}$: (■) pyridine aquation; (○) ammonia aquation.

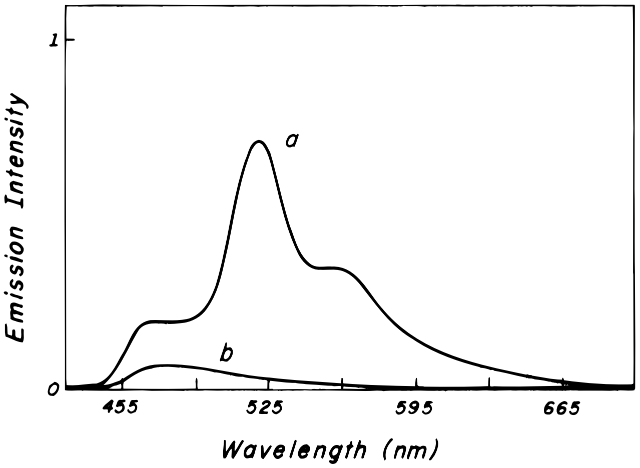

Figure 3. Emission spectra for 0.29 M biacetyl in 0.2 M NaCl, pH 4.0 (10^{-4} M HCl): (a) biacetyl alone; (b) biacetyl with added 8.89 × 10^{-5} M $[Ru(NH_3)_5py]^{2+}$.

$py]^{2+}$ were irradiated with 519 nm light, which was only absorbed by the dye. Irradiation resulted in reactions similar to those observed in the case of Rhodamine-B.

The need to keep irradiation times short (<15 min) to avoid complications due to biacetyl photolysis made it impossible to irradiate this system long enough to obtain a good plot of $1/\Phi_r^s$ vs 1/[Ru] for py and NH_3 aquation.

Luminescence Studies. Irradiation of deaerated aqueous solutions of Rhodamine-B or Safranine-T with 510 nm light (S_1 band), resulted in intense fluorescence emission bands at 578[18] and 588 nm,[19] respectively. The fluorescence of these dyes was quenched by the complex and was plotted on Stern−Volmer diagrams (I^0/I vs [Ru]), which yielded Stern−Volmer quenching constants, K_{SV}, of 229 M^{-1} for Rhodamine-B and 280 M^{-1} for Safranine-T. On the other hand, addition of (1−3) × 10^{-4} M of the ruthenium(II) complex had no effect on the fluorescence of Neutral-Red. The phosphorescence of a 0.3 M solution of biacetyl was completely quenched by the presence of 8.89 × 10^{-5} M $[Ru(NH_3)_5py]^{2+}$ (see Figure 3). The absorption spectrum of the mixture remains the same before irradiation.

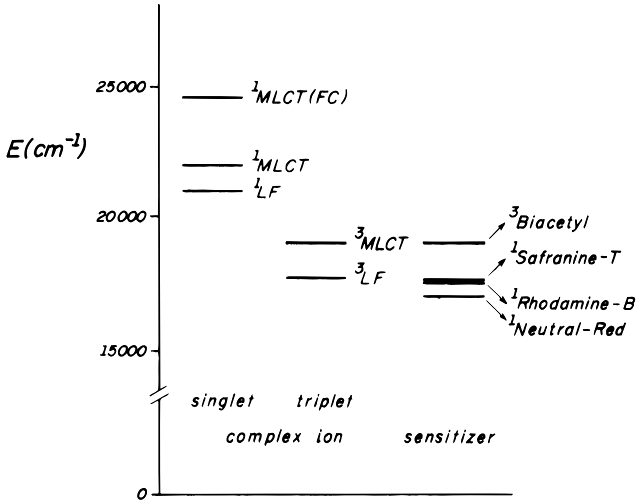

Figure 4. Energy-level diagram of the donor dyes and complex ion acceptor.

Discussion

The electronic states of the dyes and $[Ru(NH_3)_5py]^{2+}$ which may be involved in the reactions occurring in the experiments described above are represented in the energy diagram of Figure 4. The energy values of the singlet states (^{1}S) of Rhodamine-B (17 500 cm^{-1}), Safranine-T (17 700 cm^{-1}), and Neutral-Red (16 900 cm^{-1}) were derived from the 0,0 band, assumed to correspond to the point where the normalized absorption spectrum and the normalized and corrected emission spectrum cross. The emission spectrum of biacetyl consists of a low fluorescence band at about 470 nm (21 300 cm^{-1}) and a very intense phosphorescence band with a maximum at about 525 nm (19 000 cm^{-1}). The triplet yield for biacetyl is known to be near 1 in condensed media.

The energies of the excited states of the complex are somewhat uncertain. Two absorption bands can be observed in the spectrum of the $[Ru(NH_3)_5py]^{2+}$ complex ion, corresponding to $\pi-\pi^*$ and MLCT transitions, although the ligand field theory[20] also predicts LF electronic transitions for the d^6 low-spin configuration. For solid $[Ru(NH_3)_5py]^{2+}$ the diffuse reflectance spectrum shows a broad shoulder with a maximum around 385 nm and a peak at 410 nm. The maximum at 385 nm is comparable to that of the lower energy ligand field band of $[Ru(NH_3)_6]^{2+}$, $\lambda = 390$ nm, $\epsilon = 39$ M^{-1} cm^{-1}, which is ascribed to a $^1T_{1g} \leftarrow {}^1A_{1g}$ transition.[21 a] Thus, a similar assignment would be reasonable for this band in the spectrum of $[Ru(NH_3)_5py]^{2+}$. This reasoning is supported by a comparison of the Rh(III) ions, $[Rh(NH_3)_6]^{3+}$ and $[Rh(NH_3)_5py]^{3+}$, which are isoelectronic with their Ru(II) analogs and display LF absorptions at 305 and 302 nm, respectively.[21b] From the above arguments it can be concluded that the $[Ru(NH_3)_5py]^{2+}$ ion does indeed have a LF transition in the same region of the spectrum as $[Ru(NH_3)_6]^{2+}$, which is somehow hidden by the more intense MLCT band. For evaluation of the lowest energy singlet and triplet excited state(s), E_{0-0}, it should be noted that the maximum of the absorption band (i.e., the "vertical" transition from the ground state to the excited state) does not correspond to the difference in electronic energy between the excited state and the ground state but includes some vibrational energy, λ^*, that is related to E_{0-0} by $E_{op} = E_{0-0} - \lambda^*$ where,

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Table 1. Excited State and Electrochemical Data for Dyes and $[Ru(NH_3)_5py]^{2+}$ [a]

species	E_{0-0}	$\epsilon^*(^*D/D^-)$	$\epsilon^0(D/D^-)$	$\epsilon^0(D^+/D)$	$\epsilon^0(A^+/A)$	$\Delta\epsilon_r$	$\Delta\epsilon_b$
Rhodamine-B	2.16	1.45	−0.71	+0.64		1.36	0.80
Safranine-T	2.19	1.90	−0.29	−0.46		1.81	0.38
Neutral-Red	2.10	2.37	−0.27	−0.24		2.28	0.36
$[Ru(NH_3)_5py]^{2+}$	2.20				+0.09		

[a] All energies are given in volts. Electrochemical potentials are referred to Ag/AgCl (−17 mV (SCE)). All electrochemical measurements were made in 0.2 M NaCl at pH 4.0 (10^{-4} M HCl).

E_{op} is the maximum energy produced from direct light absorption. The E_{0-0} values for the singlet and triplet LF excited states were estimated using the ligand field theory,[22] the ligand field parameters $\Delta_0 = 26\,800$ cm^{-1}, and the Racah parameters $B = 0.454$ and $C = 1.82$ estimated by Ford[21] for $[Ru(NH_3)_6]^{2+}$ and using the relationship $\lambda^* = 4.5 \times 10^{-6}(\Delta_0)^2$. Thus, for the $[Ru(NH_3)_5py]^{2+}$ complex, the lowest energy singlet and triplet LF excited states were calculated to lie at 21 640 and 17 700 cm^{-1}, respectively, which are below the Franck−Condon excited states observed in the absorption spectrum. From the energy of the Frank-Condon MLCT state obtained directly by light absorption (24 500 cm^{-1}) and λ^*, Creutz[7] and co-workers estimated the E_{0-0} values for the singlet and triplet MLCT excited state as 21 700 and 19 000 cm^{-1}, respectively.

The results obtained from dyes strongly suggest that the observed quenching of the dye fluorescence and the sensitized photoreaction of the ruthenium complex occur as the result of an electronic energy transfer process. A trivial emission−reabsorption process can be ruled out in view of the insensitivity of the complex to irradiation in the wavelength range of the fluorescence emission of the dyes. The photochemical stability of the dyes in the presence of the complex rules out chemical processes, like reactions between excited dyes and the complex, or an irreversible electron transfer within a donor−acceptor molecular complex. On the other hand, a chemical exchange of energy by a reversible electron transfer process[23]

$$^*D + A \rightarrow D^{\pm} + A^{\mp} \qquad (2)$$

$$D^{\pm} + A^{\mp} \rightarrow D + {}^*A \qquad (3)$$

could account for the observations of no net chemical change in the irradiated solutions.

The ability of an excited species to be involved in an electron transfer process is related to the excited state reduction and/or oxidation potentials. The reduction potentials of a D^*/D^- couple can be approached by the reduction potential of the corresponding couple in the ground state, $\epsilon°(D/D^-)$, plus the one-electron potential corresponding to the excited state spectroscopic energy, $E_{0,0}$:

$$^*\epsilon(^*D/D^-) = \epsilon°(D/D^-) + E_{0-0} \qquad (4)$$

Thus, the energy of the reductive quenching process, $\Delta\epsilon_r$, is given by the standard half-cell potential for reduction of the donor excited state, $^*\epsilon(^*D/D^-)$, minus the standard half-cell potential for the acceptor ground state, $\epsilon°(A^+/A)$, i.e., $\Delta\epsilon_r = {}^*\epsilon(^*D/D^-) - \epsilon°(A^+/A)$. The energy released by the back electron transfer reaction is given by

$$\Delta\epsilon_b = -\epsilon°(D/D^-) + \epsilon°(A^+/A) \qquad (5)$$

Table 1 summarizes the derived $\Delta\epsilon$'s. It can be seen that the dyes are, in principle, able to oxidize the complex. However, the energy released by the back electron transfer reaction is not enough to oxidize the complex. This implies that an electron transfer process cannot be the mechanism for the observed energy transfer.

Thus, the two other possible mechanisms for energy transfer are diffusional contact exchange and long-range resonance Förster energy transfer.[24] The photoactive excited states of Ru(II) ammine complexes have been widely described formally as triplet states,[4,7] and therefore, the spin-forbidden contact energy transfer should be very slow. This appears to be inconsistent with the large k_{et} values obtained for both dye−$[Ru(NH_3)_5py]^{2+}$ systems, which suggest that the singlet energy transfer is highly allowed. On the other hand, the quenching of the phosphorescence of biacetyl, as well as the energy relationships for this system, points to a significant amount of triplet character in that state. Crosby and co-workers[25,26] demonstrated that the charge-transfer states of platinum metal complexes must be described as spin−orbit states, with large contributions of both singlet and triplet characters. Furthermore, Demas and co-workers[27] also proposed a spin−orbit model for the charge-transfer excited states of $Ru(bpy)_3^{2+}$. Since the present results show an allowedness of singlet and triplet energy transfer to the sensitized state of $[Ru(NH_3)_5py]^{2+}$, the excited state precursor of the reactivity of the $[Ru(NH_3)_5py]^{2+}$ complex ion reached by sensitization must certainly be a spin−orbit state or, in other words, have both singlet and triplet character, which is consistent with an increase of the spin−orbit coupling with the increase of the atomic number, with the orbital and spin quantum numbers becoming less "good". Alternatively, Förster energy transfer, which is not limited by spin conservation rules, can also explain the results.

Many energy transfer processes in fluid solutions with transition metals occur via electron exchange mechanisms[24] and require molecular diffusion of *D and A to within collision distance as the rate-limiting feature of energy transfer. The role of the diffusional process can be evaluated by comparing the mean diffusion distance, x, of the dyes with the experimental average separation of donor and acceptor, $R_{o(exp)}$, for energy transfer in these systems. From the diffusion theory[24] it is found that x for a diffusing molecule during its emission lifetime is related to the diffusion coefficient,[28] D, of the dyes and the donor fluorescence lifetime, τ_D, according to

$$x = (2D\tau_D)^{1/2} \qquad (6)$$

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[28] (a) The diffusion coefficient, $D = kT/6\pi\eta r_0$, where k is the Boltzmann constant (1.36×10^{-22} cm^2 g K^{-1} s^{-2}), T is the temperature in K (298 K), η is the viscosity of water (1×10^{-8} g/cm s),[28b] and r_0 is the dye radius, considered to be similar for both dyes (6×10^{-8} cm).[28c] The D value of 3.61×10^{-6} cm^2 s^{-1} for the dyes was obtained at 25 °C. (b) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 62nd ed.; CRC Press Inc.: Boca Raton, FL, 1981. (c) Achari, A.; Neidle, S. *Acta Crystallogr.* **1976**, *B32*, 2537.

The donor fluorescence lifetime, τ_D

$$\tau_D = \Phi_D/k_e \tag{7}$$

where Φ_D is the fluorescence quantum yield of the donor (0.32 for Rhodamine-B and 0.16 for Safranine-T),[18b,19] k_e is the radiative emission rate constant that can be evaluated from the absorption spectra[29]

$$k_e = \nu_{0(av)}^{\;\;2}\, \epsilon_{max}(\Delta\nu_{av})_{1/2}/2.5 \times 10^8 \tag{8}$$

where $\nu_{0(av)}$ is the average frequency (cm^{-1}) and $(\Delta\nu_{av})_{1/2}$ is the width of the band at half its absorbance maximum. Values of 1.55×10^8 and 1.13×10^8 s^{-1} were respectively obtained for Rhodamine-B and Safranine-T, at 25 °C in 0.2 M NaCl aqueous solution, at pH 4 (10^{-4} M HCl). Thus, the natural lifetimes obtained for Rhodamine-B and Safranine-T were 2.06×10^{-9} and 1.42×10^{-9} s, respectively. In aqueous solution, $(2D\tau_D)^{1/2}$ is 12 Å for Rhodamine-B and 10 Å for Safranine-T.

On the other hand, $R_{o(exp)}$ can be estimated experimentally[24] from the equation

$$R_{o(exp)} = 7.35/[A_{1/2}]^{1/3} \tag{9}$$

where $[A_{1/2}]$ is the concentration of the complex for which 50% of the dye emission is quenched. The experimental $R_{o(exp)}$ values obtained were 45 Å for Rhodamine-B and 48 Å for Safranine-T. The relationship $(2D\tau_D)^{1/2} << R_{o(exp)}$ indicates that the donors remain essentially immobile during their lifetimes. Thus, in aqueous solution, the diffusional energy transfer will be unlikely for these systems. Therefore, the high efficiency singlet energy transfer probably proceeds by a long-range resonance transfer mechanism, which is also sustained by the large experimental transfer radius (>40 Å). The theoretical Förster radii could not be calculated since the acceptor state of the complex cannot be reached by direct excitation, which hinders the calculation of the overlap integral in the Förster equation.

In conclusion, the following mechanism seems to be appropriate in accounting for both sensitization and quenching experimental results:

$$D(S_0) + h\nu \rightarrow {}^*D(S_1) \tag{10}$$

$${}^*D(S_1) \rightarrow D(S_0) + \Delta \tag{11}$$

$${}^*D(S_1) \rightarrow D(S_0) + h\nu'' \tag{12}$$

$${}^*D(S_1) + Ru \rightarrow D(S_0) + Ru(EE) \tag{13}$$

$$Ru(EE) \rightarrow Ru \tag{14}$$

$$Ru(EE) \rightarrow \text{products} \tag{15}$$

where $D(S_0)$ represents the donor ground state, $^*D(S_1)$ represents the donor excited state, Ru represents the acceptor ground state, and Ru(EE) represents the acceptor sensitized excited state.

According to this mechanism, the quantum yield of the dye-sensitized photolysis of $[Ru(NH_3)_5py]^{2+}$ (irradiation in the S_0 band of dye) can be written as

$$\Phi_r^{\,s} = ((k_{13}[Ru])/(k_{11} + k_{12} + k_{13}[Ru]))k_{15}/(k_{14} + k_{15}) \tag{16}$$

Table 2. Limiting Quantum Yields , Φ_{lim}, and Energy Transfer Rate Constants, k_{et}, for the Sensitization Reactions of Dyes with the $[Ru(NH_3)_5py]^{2+}$ Complex[a]

dye	$\Phi_{lim}(py)^b$	$\Phi_{lim}(NH_3)^b$	k_{et}, $M^{-1}\ s^{-1}$ [c]
Rhodamine-B	0.078 ± 0.015	0.095 ± 0.015	1.0×10^{11}
Safranine-T	0.072 ± 0.008	0.089 ± 0.008	1.6×10^{11}

[a] [dyes] = 1×10^{-5} M in 0.2 M NaCl, pH 4.0 (10^{-4} M HCl); $[Ru(NH_3)_5py^{2+}] = 1 \times 10^{-4}$ M. Irradiation at 519 nm. [b] Obtained from $1/\Phi_r^{\,s}$ vs 1/[Ru] plots. [c] $k_{et} = (1/\Phi_{lim}) \times$ slope. Slope from plots of $1/\Phi_r^{\,s}$ vs 1/[Ru].

After rearranging terms

$$1/\Phi_r^{\,s} = (1/\Phi_{lim})(1 + 1/(k_q[Ru])) \tag{17}$$

$$\Phi_{lim} = k_{15}/(k_{14} + k_{15}) \tag{18}$$

$$k_q = k_{13}/(k_{11} + k_{12}) = k_{et}\tau_D \tag{19}$$

Plots of $1/\Phi_r^{\,s}$ vs 1/[Ru] were linear (see Figure 2 for Rhodamine-B) as expected from eq 17. The intercepts of these plots give the reciprocal quantum yields of the sensitized reaction, Φ_{lim}, which represents the quantum yield of the sensitized reaction when 1/[Ru] = 0 , i.e., when all the excited singlet dyes are scavenged by $[Ru(NH_3)_5py]^{2+}$. The products of the slopes of those plots times Φ_{lim} give the quenching rate constants for energy transfer, k_{et} ($k_q = k_{et}\tau_D = (1/\Phi_{lim}) \times$ slope). Table 2 summarizes the quantum yields and k_{et} values obtained for these systems.

The fluorescence emission intensity of the deaerated dye solution was found to decrease as $[Ru(NH_3)_5py]^{2+}$ concentration increased. Singlet to singlet energy transfer (eq 13) results in the quenching of the donor singlet by a Stern–Volmer quenching mechanism[24]

$$I°/I = 1 + K_{SV}[Ru] \tag{20}$$

$$K_{SV} = k_{13}/(k_{11} + k_{12}) = k_{et}\tau_D \tag{21}$$

The quenching rate constants for energy transfer, k_{et}, for both systems were obtained from the plots of I^0/I vs [Ru], eq 20, and eq 21 using the fluorescence lifetimes τ_D for the dyes. The values found were 1×10^{11} $M^{-1}\ s^{-1}$ for Rhodamine-B and 1.9×10^{11} $M^{-1}\ s^{-1}$ for Safranine-T, in very good agreement with the values calculated from the $1/\Phi_r^{\,s}$ vs 1/[Ru] plots (Figure 2 for Rhodamine B). The k_{et} values estimated from Stern–Volmer plots (eq 17) are equal the k_{et} values listed in Table 2. These similarities indicate that only one excited state is involved in the energy transfer process observed.

Flash photolysis studies[5] of $[Ru(NH_3)_5L]^{2+}$ complexes showed the formation of a long-lived transient only for those complexes showing net photoaquation. For $[Ru(NH_3)_5py]^{2+}$ the quantum yield of photoaquation obtained from the instantaneous bleaching was estimated to be 0.16 mol/einstein. The sum of the limiting aquation quantum yields, $\Phi_{py} + \Phi_{NH_3}$, obtained from sensitization experiments (~0.18 mol/einstein) is about twice the sum of the values obtained from direct photolysis (~0.10 mol/einstein) and very similar to that found in flash photolysis.[5] It should be noted that also the same products and the same ratio of products quantum yields, Φ_{py}/Φ_{NH_3}, were obtained from sensitization and from direct photolysis experiments (see Table 2). This indicates that all the reaction products arise from the same reactive excited state of the ruthenium(II) complex.

Direct photolysis of systems having the lowest LF absorption bands, namely $[Ru(NH_3)_6]^{2+}$ (which display absorption bands comparable to those of $[Ru(NH_3)_5py]^{2+}$), leads to substitution

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(29) Orchin, M.; Jaffé, H. H. *Symmetry, Orbitals, and Spectra (S.O.S.).* Wiley-Interscience: New York, 1971; p 312.

in aqueous solution.[30] This is consistent with the general observation that LF excitation of low-spin d^6 complexes leads to substitutional processes for the lower transition metals.

The higher quantum yields of the sensitized reaction suggest that the direct photolysis does not proceed by complete conversion of all higher excited states to the lowest reactive one but should be competitive with other deactivation pathways.

Due to the proximity of the energies of the LF or MLCT states, it is practically impossible to populate one of these excited states selectively. Therefore, there may be some doubt whether the acceptor state has LF or MLCT character. However, considering the general photoreactivity of ruthenium(II) ammines, the reactive state should have LF character. Considering that the singlet states of Rhodamine-B and Safranine-T are quenched by the complex, whereas no quenching of Neutral-Red is observed, it can be said that the energy of the sensitized excited state precursor of the photosubstitution reactions in $[Ru(NH_3)_5py]^{2+}$ lies between 17 000 and 17 700 cm^{-1}, in close agreement with the estimated values.

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[30] Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1978**, *17*, 1747.