Temperature Dependence of the Photophysical and Photochemical Properties of the Tris(2,2′-bipyridyl)ruthenium(II) Ion in Aqueous Solution

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Abstract: Luminescence lifetimes and quantum yields of $Ru(bipy)_3^{2+}$ in aqueous solution between 0 and 100 °C are reported. The study includes both the perprotio and perdeuterio complex in H_2O and D_2O. Although the luminescence lifetimes and quantum yields are found to be solvent and temperature dependent, the radiative lifetime is insensitive to these parameters. The temperature dependence of the lifetime and quantum yield data is correlated with a model which assumes a lower set of luminescent levels which undergo weak-coupled radiationless deactivation and a higher set of nonluminescent levels which undergo strong-coupled radiationless deactivation. Although the complex ion is essentially photoinert at 25 °C in 0.1 M HCl, photolysis at 95 °C with 436-nm irradiation results in labilization of 2,2′-bipyridine. Photophysical and photochemical data suggest that the lower set of levels in our model are charge-transfer-to-ligand states, which are modified by mixing with charge-transfer-to-solvent configurations. These levels are photoinert, whereas the upper set of levels, which are ~3600 cm^{-1} above the lower set, give rise to ligand substitution photochemistry. The upper set of levels is assigned to d–d orbital parentage.

I. Introduction

The luminescence of the tris(2,2′-bipyridyl)ruthenium(II) ion has been the subject of a large number of experimental studies, and the assignment of this luminescence has been vacillatory. The emission was initially assigned as a charge-transfer fluorescence by Paris and Brandt.[1] This assignment was disputed by later authors who assigned the emission as "d–d" phosphorescence,[2] "d–d" fluorescence,[3] charge-transfer,[4] charge-transfer fluorescence,[5] and charge-transfer phosphorescence.[6] More recent studies by Harrigan, Hager, and Crosby[7,8] now indicate that the emission at −196 °C originates from a set of three thermally equilibrated levels of charge-transfer orbital parentage. When the effects of spin–orbit coupling are included, these levels are labeled as A_1, E, and A_2 in the D_3 symmetry group of the complex ion. At −196 °C, 89.9% of the emission originates from the A_2 level which has a formal spin singlet parentage.[8] Hence, in a formal sense the emission is now believed to be primarily due to a charge-transfer fluorescence. This classification is only formal however, since the spin–orbit interaction is large enough to cause a large mixing of the singlet and triplet spin states.[9] Studies of the luminescence polarization of the complex at −196 °C have led Fujita and Kobayashi[10] to the conclusion that the correct assignment of the emitting state is to a ^3E charge-transfer state. This is in opposition to the formal assignment of the emitting triplet as a $^3A_2$ (giving rise to A_1 and E under spin–orbit coupling) by Crosby et al.,[7,8] and would suggest that the luminescence properties arise from sublevels of ^3E. Hence, it appears that the assignment of the low-temperature emission of the complex is not yet fully resolved, although there seems to be little doubt that it arises largely from a charge-transfer-to-ligand (CTTL) excited state.

In addition to the low-temperature studies of this complex, which have been used in the assignments of its luminescence, several studies of the luminescence at elevated temperatures have been reported. Lytle and Hercules[11] have reported the luminescence properties of the complex in several different solvents between −193 and 12 °C, and have concluded that a thermally activated process through a higher energy charge-transfer state with polarization parallel to the C_3 axis contributes to the deactivation of the perpendicular polarized charge-transfer state at elevated temperatures. Van Houten and Watts[12] have studied the effects of ligand and solvent deuteration on the luminescence of the complex in water at 25 °C and have concluded that the luminescence under these conditions includes contributions from charge-transfer-to-solvent (CTTS) configurations in addition to the charge-transfer-to-ligand (CTTL) configuration.

The $Ru(bipy)_3^{2+}$ complex ion has also found widespread use as a sensitizer for the photoluminescence and photochemistry of other transition metal complexes in aqueous solutions. Studies by various authors of the quenching of the luminescence have led to the conclusion that the excited state of the complex may give rise to either electron-transfer[13-18] or energy-transfer processes.[19-28] Quenching of the luminescence by oxygen has been found to give rise to the production of singlet oxygen[29] and the complex has been used to photosensitize a redox reaction in the nonspontaneous direction, even though neither reactant absorbs appreciably in the region photolyzed.[30] This latter process has been claimed to represent a useful inorganic model for photosynthesis.[30]

In spite of the accumulation of a large body of information on the use of $Ru(bipy)_3^{2+}$ as a donor to photosensitize the formation of excited states of a wide variety of acceptors, the photophysics and photochemistry of the complex itself have not been well characterized in fluid solutions. In particular, very little is known about the photochemical and photophysical properties of the $Ru(bipy)_3^{2+}$ complex ion in aqueous solutions, although water is generally the solvent used in studies which employ the complex as a sensitizer. In a previous communication[12] we reported the luminescence lifetime and quantum yield of the complex and its perdeuterated analogue in both H_2O and D_2O at 25 °C. In this paper we report a study of the photophysics of these systems over the entire temperature range of fluid water under atmospheric pressure.

II. Experimental Section

A. Lifetime Measurements. Nitrogen-saturated solutions of $Ru(bipy)_3^{2+}$ or $Ru(bipy\text{-}d_8)_3^{2+}$ in H_2O or D_2O[12] were irradiated at 337 nm with a pulsed nitrogen laser. The temperature of the solutions was controlled to ±0.1° with a circulating water bath. Lifetimes were calculated from the slope of a plot of ln intensity vs. time taken from

Table I. Luminescence Quantum Yields, Measured Lifetimes, Radiative Lifetimes, and Quenching Constants for the Tris(2,2′-bipyridyl)ruthenium(II) Complex Ion in Aqueous Solutions

	$Ru(bipy)_3^{2+}/H_2O$				$Ru(bipy\text{-}d_8)_3^{2+}/H_2O$			
T, °C	Q[a]	τ_m,[b] μs	τ_r,[c] μs	k_q,[d] μs^{-1}	Q[a]	τ_m,[b] μs	τ_r,[c] μs	k_q[d] μs^{-1}
5	0.049 ± 0.003	0.73 ± 0.039	14.9	1.30	0.057 ± 0.003	0.89 ± 0.008	15.6	1.06
10	0.046 ± 0.003	0.71 ± 0.053	15.4	1.34	0.054 ± 0.002	0.85 ± 0.035	15.7	1.11
15	0.044 ± 0.002	0.67 ± 0.020	15.2	1.43	0.052 ± 0.003	0.82 ± 0.017	15.7	1.16
20	0.042 ± 0.002	0.64 ± 0.020	15.2	1.50	0.049 ± 0.002	0.76 ± 0.011	15.5	1.25
25	0.042 ± 0.002	0.58 ± 0.019	13.8	1.65	0.047 ± 0.003	0.69 ± 0.036	14.7	1.38
30	0.040 ± 0.002	0.58 ± 0.007	14.5	1.66	0.043 ± 0.002	0.66 ± 0.033	15.3	1.45
40	0.036 ± 0.001	0.51 ± 0.030	14.2	1.89	0.036 ± 0.002	0.54 ± 0.031	15.0	1.79
50	0.027 ± 0.001	0.39 ± 0.008	14.4	2.49	0.029 ± 0.001	0.41 ± 0.020	14.1	2.37
60	0.020 ± 0.002	0.30 ± 0.018	15.0	3.27	0.021 ± 0.0006	0.32 ± 0.022	15.2	3.06
70	0.017 ± 0.004	0.22 ± 0.015	12.9	4.47	0.015 ± 0.0006	0.23 ± 0.011	15.3	4.28
80	0.011 ± 0.0008	0.15 ± 0.005	13.6	6.59	0.0097 ± 0.0002	0.16 ± 0.008	16.5	6.19
90	0.0075 ± 0.0006	0.10 ± 0.008	13.3	9.93	0.0066 ± 0.0003	0.11 ± 0.005	16.7	9.03
		$Ru(bipy)_3^{2+}/D_2O$				$Ru(bipy\text{-}d_8)_3^{2+}/D_2O$		
5	0.086 ± 0.004	1.35 ± 0.033	15.7	0.677	0.10 ± 0.005	1.79 ± 0.042	17.7	0.502
10	0.083 ± 0.004	1.35 ± 0.098	16.3	0.679	0.098 ± 0.005	1.65 ± 0.032	16.8	0.547
15	0.082 ± 0.004	1.23 ± 0.044	15.4	0.748	0.090 ± 0.004	1.56 ± 0.053	17.3	0.583
20	0.075 ± 0.004	1.09 ± 0.033	14.5	0.849	0.085 ± 0.004	1.46 ± 0.102	17.2	0.627
25	0.070 ± 0.003	1.02 ± 0.047	14.6	0.912	0.079 ± 0.006	1.25 ± 0.040	15.8	0.737
30	0.063 ± 0.002	0.97 ± 0.022	15.4	0.966	0.070 ± 0.005	1.16 ± 0.032	16.6	0.802
40	0.050 ± 0.001	0.74 ± 0.002	14.8	1.28	0.051 ± 0.005	0.85 ± 0.002	16.7	1.12
50	0.038 ± 0.002	0.55 ± 0.021	14.5	1.75	0.037 ± 0.004	0.60 ± 0.016	16.2	1.61
60	0.024 ± 0.004	0.38 ± 0.022	15.8	2.57	0.025 ± 0.002	0.39 ± 0.028	15.6	2.50
70	0.020 ± 0.005	0.25 ± 0.020	12.5	3.92	0.016 ± 0.001	0.26 ± 0.025	16.3	3.78
80	0.012 ± 0.0005	0.16 ± 0.007	13.3	6.18	0.011 ± 0.0006	0.17 ± 0.019	15.5	5.82
90	0.0077 ± 0.0006	0.10 ± 0.003	13.0	9.92	0.0069 ± 0.0003	0.11 ± 0.006	14.5	9.03

[a] Photoluminescence quantum yield excited at 436 nm. [b] Measured luminescence lifetime excited at 337 nm. [c] Radiative lifetime calculated from τ_m/Q. [d] Quenching rate constant calculated from $\tau_m^{-1} - \tau_r^{-1}$.

oscilloscope tracings of the decay.[31] The kinetics were found to be strictly exponential under all conditions.

B. Quantum Yields. The samples were irradiated at 436 nm with a 1000-W Hg–Xe lamp and the desired line was isolated with a monochromator and appropriate filters.[12] The yields were measured by a modified Parker-Rees method[32,33] using fluorescein purified by the method of Orndorff and Hemmer[34] as the standard with a yield of 0.90.[35] Solutions were prepared fresh daily and irradiated as briefly as possible to minimize photodecomposition. The desired temperature was maintained with a water bath.

C. Time-Resolved Spectra. Samples dissolved in glycerol, H_2O, or D_2O were excited at 337 nm with the pulsed N_2 laser. The emission was sampled at various delay times after the excitation pulse using a boxcar integrator.[36] By scanning the emission monochromator while simultaneously monitoring at a given delay time, time-resolved emission spectra were recorded. The spectra were corrected for variations in instrumental response as a function of wavelength.[33] Temperatures below 0 °C were maintained with a Dewar and appropriate low-temperature slush baths.[37,38]

D. Photochemistry. The photochemical reactions were performed with 436-nm irradiation in the same apparatus as was used to measure quantum yields. However, the slits of the excitation monochromator were opened to give an incident intensity at the photolysis cell of 5×10^{17} quanta/min as determined by either ferrioxalate[39] or Reineckate[40] actinometry. The disappearance of starting material was monitored continuously by following the decrease in emission intensity at 610 nm vs. time and the absorbance spectrum of the photolyte was measured hourly.

III. Results

A. Luminescence Quantum Yields and Lifetimes Between 0 and 100 °C. The results of our study of the luminescence lifetimes and quantum yields of $Ru(bipy)_3^{2+}$ in aqueous solution between 0 and 100 °C are compiled in Table I. The ratio of the measured lifetime, τ_m, to the quantum yield, Q, has also been tabulated as the radiative lifetime, τ_r.[41] From the values of τ_m and τ_r we have calculated and listed values of the quenching rate constant, k_q, at each temperature.

B. Analysis of Temperature Dependence of Luminescence Quantum Yields and Lifetimes. Plots of log τ_m^{-1} or log Q vs. $1/T$ are nonlinear, indicating the data are not fit by a simple Arrhenius-type equation.[42] We also attempted to fit our data by adding one more level to the three-level model used by Harrigan and Crosby[7] to interpret the low-temperature luminescence lifetime and quantum yield of $Ru(bipy)_3^{2+}$. We found, however, that the addition of a new term to their equation to account for thermal population of higher energy levels at elevated temperatures could not fit our data when we maintained the same values of τ_{mi}, τ_{ri}, and Q_i for the lowest three levels as reported by these authors.[7] The problem is best illustrated by using the reported values of τ_{mi}, τ_{ri}, and Q_i for the lowest three levels and the energy gaps between them to calculate τ_m, τ_r, and Q between 0 and 100 °C, assuming no additional levels are thermally populated. This procedure leads to a calculated radiative lifetime which varies from 8.0 μs at 0 °C to 7.6 μs at 100 °C. The value of τ_m ranges from 3.2 to 3.0 μs, and Q varies from 0.39 to 0.40 between 0 and 100 °C according to this calculation. These results clearly indicate that the 0–100 °C temperature range is in the high-temperature limit of the Harrigan–Crosby three-level model, and very little temperature dependence is predicted by this model. Our results indicate that a fourth level must be added to this model to explain the temperature dependence above 0 °C, and that a temperature independent value of about 14 μs for τ_r, the total radiative lifetime, must result from addition of a fourth level to the model. It is impossible to assign a set of parameters for a fourth level which would satisfy these requirements while maintaining the values assigned[7] to the three lower levels.

In order to obtain an adequate fit of our experimental data and retain a model which includes the three levels which give

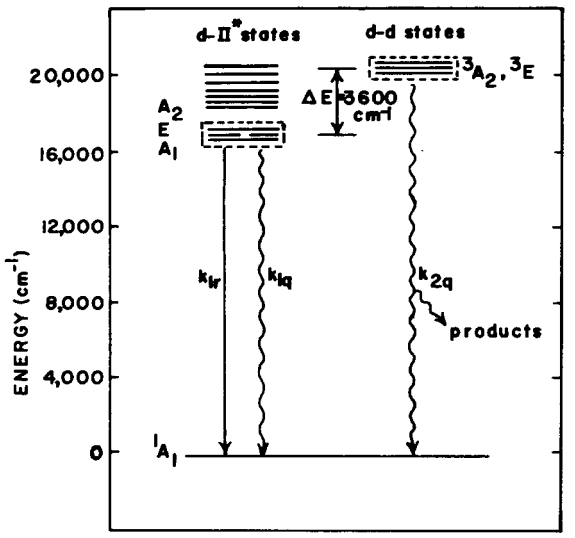

Figure 1. Schematic representation of the model used to interpret the temperature dependence of the luminescence lifetime and quantum yield of $Ru(bipy)_3^{2+}$ between 0 and 100 °C.

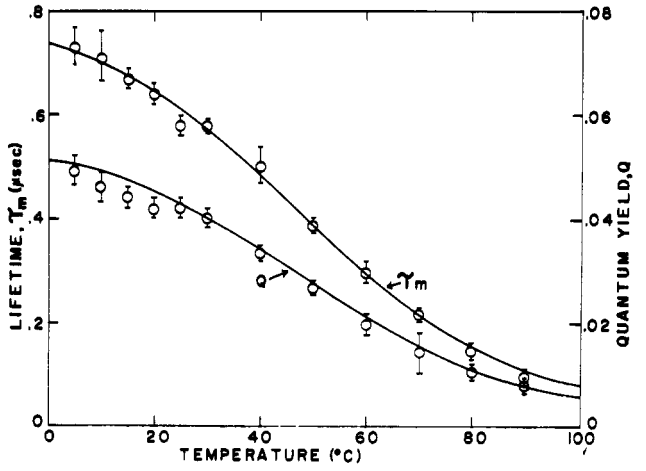

Figure 2. Computer generated fit of luminescence lifetime and quantum yield of $Ru(bipy)_3^{2+}$ in H_2O using eq 1 and 2: Φ, experimental points; —, computer fit.

rise to the low-temperature luminescence, we found it necessary to modify the high-temperature limit of the Harrigan–Crosby model and to add one additional level. The equations used in our fitting procedure for τ_m and Q are

$$\tau_m(T) = [k_{1r} + k_{1q} + k_{2q}e^{-\Delta E/kT}]^{-1} \quad (1)$$

$$Q(T) = k_{1r}\tau_m(T) \quad (2)$$

The model used to obtain these equations is shown in Figure 1. Within the context of our model we have retained the three levels which have been proposed to account for the low-temperature luminescence properties and the small energy gap between them (~61 cm^{-1}). Because $kT \gg 61$ cm^{-1} in the temperature range 0–100 °C (vide supra), we have represented the average values the radiative and nonradiative rate constants for the low-energy set of three levels by the single-rate constants k_{1r} and k_{1q}. The values of these two rate constants have been altered from the Harrigan–Crosby values to fit our experimental data. We have added a fourth level characterized by a second quenching rate constant, k_{2q}, which represents the sum of all photophysical and photochemical (vide infra) radiationless processes from this upper level. The level is presumed to have a radiative rate constant which is much less than k_{2q}, and hence does not emit light. As a result, the average

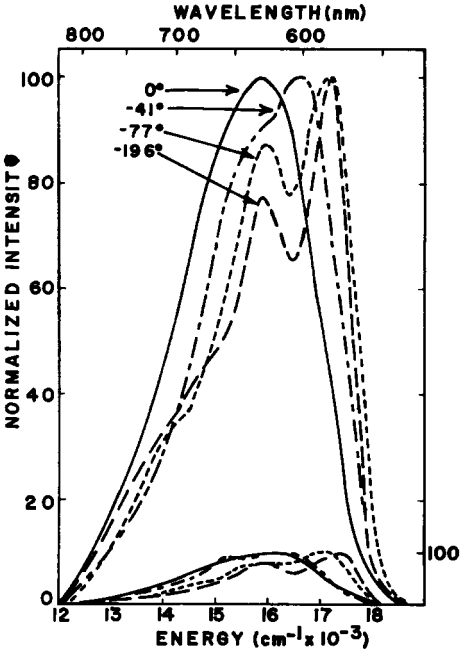

Figure 3. Time resolved emission spectra of $[Ru(bipy)_3]Cl_2$ in glycerol at various temperatures (°C): Upper curves (left ordinate), initial emission measured 0.2 ± 0.025 μs after the excitation pulse; lower curves (right ordinate), spectra taken after sufficient delay for the emission to decay to less than 2% of its initial intensity.

Table II. Values of Rate Constants and Energy Gaps to Fit Experimental Lifetime of $Ru(bipy)_3^{2+}$ from 0–100 °C

Sample/Solvent	H_8/H_2O	D_8/H_2O	H_8/D_2O	D_8/D_2O
τ_r, μs	14.4	15.4	14.7	16.4
k_{1q}, μs^{-1}	1.222	0.965	0.567	0.407
k_{2q}, μs^{-1}	10^7	10^7	10^7	10^7
ΔE, cm^{-1}	3559	3543	3568	3574

value of the radiative lifetime, $\tau_m(T)/Q(T)$, is independent of temperature and is equal to k_{1r}^{-1} as required by our results.

The values of k_{1r}, k_{1q}, k_{2q}, and ΔE obtained by using eq 1 and 2 to fit our experimental results are compiled in Table II. The computer generated fits of eq 1 and 2 to our experimental data with these parameters are illustrated in Figure 2 for the perprotio complex in H_2O.

C. Luminescence Spectra between −196 and 100 °C. The corrected, time-resolved emission spectra of $Ru(bipy)_3^{2+}$ in glycerol or water at several temperatures between −196 and 100 °C are shown in Figure 3. The spectrum broadens and red shifts as the temperature is raised, and the time-resolved spectra indicate that the luminescence decay is exponential at all temperatures.

D. Photochemistry of $Ru(bipy)_3^{2+}$ in H_2O at 95 °C. Irradiation of $Ru(bipy)_3^{2+}$ in 0.1 M HCl at 95 °C with 436-nm light resulted in disappearance of the dominant charge-transfer absorption band at 450 nm (see Figure 4) and a decrease in the emission intensity with no change in the measured lifetime. During the initial hour of irradiation the yellow-orange solution of $Ru(bipy)_3^{2+}$ turned to a red-orange color with the appearance of a new shoulder on the absorption spectrum at 500 nm. Continued irradiation (~2–7 h) resulted in further decreases in the 450-nm absorption as well as disappearance of the shoulder at 500 nm. During this time a new absorption band at 365 nm appeared and grew steadily in intensity with increasing irradiation time. A sample of the same solution held at 95 °C in the dark for 7 h showed no change in its absorption spectrum. Analysis of the solution photolyzed at 95 °C by

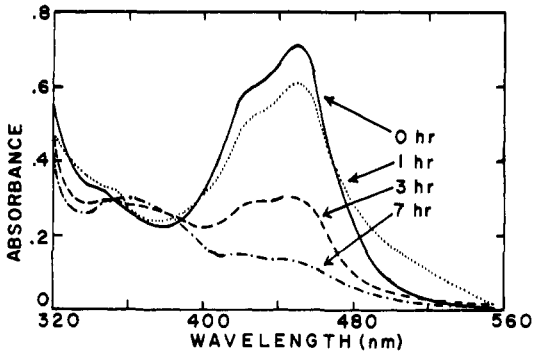

Figure 4. Absorption spectra of $Ru(bipy)_3^{2+}$ in 0.1 M HCl as a function of photolysis time at 95 °C with 436-nm irradiation.

fluorescence spectroscopy clearly showed the presence of free protonated 2,2′-bipyridine, providing conclusive evidence for labilization of the bidentate ligand from $Ru(bipy)_3^{2+}$ during photolysis. The dark thermal control solution contained no detectable free 2,2′-bipyridine. Irradiation of a 10^{-4} M solution of $Ru(bipy)_3^{2+}$ in 0.1 M HCl at 25 °C for 5 h resulted in no detectable disappearance of starting material.

IV. Discussion

A. Low-Lying Energy Levels in $Ru(bipy)_3^{2+}$. The low-lying CTTL states of $Ru(bipy)_3^{2+}$ are believed to arise from promotion of a d electron of Ru(II) to a ligand π^* orbital of a_2 or e symmetry.[43] Coupling of the promoted electron with the strongly spin-orbit coupled states of the d^5 core results in 16 levels which are comprised of 36 states. The lowest three levels of A_1, E, and A_2 symmetry, which arise from coupling of a $\pi^*(a_2)$ electron with the ground state of the d^5 core, are believed to be responsible for the luminescence properties at −196 °C.[43] *However, at ambient temperatures, as many as 36 spin-orbit coupled states of $d\pi^*$ orbital parentage could lie within about 3000 cm^{-1} of the lowest excited levels, and could therefore contribute to the net decay process (vide infra).*

In addition, the low-lying $^3T_1$ state of an octahedral d^6 complex will split into $^3A_2$ and ^3E components in the D_3 symmetry group of $Ru(bipy)_3^{2+}$, giving rise to a total of nine states of d–d orbital parentage. From the ligand f value of 2,2′-bipyridine and the metal g value of Ru(II),[44] we estimate Δ to be 26 600 cm^{-1}. The average energy of the $^3A_2$ and ^3E components is given by $\Delta - 3C$, where C is one of the Racah interelectronic repulsion parameters.[45] Reasonable values of C for this complex are estimated to lie between 2000 and 3000 cm^{-1},[35] which would place $\Delta - 3C$ between 17 600 and 20 600 cm^{-1} compared to a value of 17 100 cm^{-1} for the emitting CTTL levels at −196 °C. Although the $^3\pi\pi^*$ states of coordinated 2,2′-bipyridine lie at much higher energy (22 500 cm^{-1}), *as many as 45 electronic states of $d\pi^*$ and d–d orbital parentage may contribute to the thermally equilibrated excited state manifold at room temperature.* Although some of these may have a relatively small Boltzmann population at room temperature, they may still make large contributions to the decay of the excited-state manifold if their decay constants are much larger than those of the low-lying excited states.

B. Interpretation of the Phenomenological Model Used in Analysis of the Luminescence Lifetime and Quantum Yield of $Ru(bipy)_3^{2+}$ Between 0 and 100 °C. It is clear that there is no hope of estimating all of the decay constants for as many as 45 thermally accessible levels in the excited-state manifold of $Ru(bipy)_3^{2+}$ from lifetime and quantum yield measurements. Most of these levels probably lie more than ~200 cm^{-1} above the lowest excited set of levels, and would have to either decay to the ground state or undergo photochemical processes very rapidly ($k > 10^9$ s^{-1}) to make any significant contribution to the decay at room temperature. Since the complex is photoinert at room temperature and shows a deuterium effect on its luminescence, the decay of the excited-state manifold is probably dominated by weak-coupled radiationless transitions to the ground state[46,47] at this temperature. It is unlikely that these weak-coupled processes would occur any more rapidly from the higher excited states than from the lowest excited state; thus the Boltzmann factors heavily favor decay via the lowest few levels. Hence, we anticipate that the number of levels responsible for the properties of the complex at room temperature is nearly the same as at −196 °C.

We now explore the origin of the difference between the high-temperature limit of the Harrigan-Crosby model[7,8] for the luminescence properties and the values of k_{1q}, τ_r, and Q_1 required by our model. The observed value of ~15 μs reported in Table II is substantially larger than the value of ~8 μs predicted by the Harrigan-Crosby model at 25 °C. Furthermore, our value of τ_{m_1}, $\tau_{m_1} = (k_{1q} + \tau_r^{-1})^{-1}$, is 0.78 μs compared to ~3 μs, and we require a Q_1, $Q_1 = \tau_{m_1}/\tau_r$, of ~0.05 compared to ~0.4 predicted by their model. Since there is little likelihood that these differences are attributable to depopulation of the excited-state manifold through higher-energy photoinert levels at room temperature, the discrepancies noted are due to the presence of new decay pathways in fluid solutions which are absent in rigid media. The following experimental results substantiate this view: (1) major changes occur in the shape of the luminescence spectrum when the solvent medium is transformed from a rigid glass to a fluid (see Figure 3); (2) the radiative lifetime undergoes a substantial change at the glass point in EPA;[11] (3) the area under the $d\pi^*$ absorption band centered at 450 nm is substantially larger at −196 °C than it is at room temperature.[41]

The results presented above as well as the value of τ_r we observed support the view that the radiative lifetime is sensitive to the viscosity of the solvent. In a previous communication[12] we suggested that the large solvent deuteration effect on the luminescent properties of $Ru(bipy)_3^{2+}$ was due to interaction of CTTS configurations with the CTTL states. This view presents a consistent interpretation of the effect of solvent medium on the radiative lifetime (i.e., that the radiative lifetime is altered on going from a rigid to a fluid medium due to structural changes in the solvation sphere which cause substantial mixing of the CTTL state with CTTS configurations). We also attribute changes in the quantum yield and quenching rate in fluid media to efficient radiationless decay pathways which are associated with the structure of the solvation sphere. The solvent deuteration effects indicate that these pathways dissipate energy through the O-H vibrations of water. Energy transfer to solvent is presumably moderated in a rigid medium by alterations of the solvation sphere.

We now consider the nature of the higher-energy nonradiative level characterized by k_{2q} responsible for the temperature dependence of the luminescence between 0 and 100 °C. Just as k_{1q} and τ_r are average properties of several closely spaced levels in our phenomenological model, k_{2q} could also represent an average property of several levels which are closely spaced relative to kT (~200 cm^{-1}). The importance of these levels in the decay pathways of $Ru(bipy)_3^{2+}$ as a function of temperature is given by the ratio $k_{2q}e^{-\Delta E/kT}/(k_{1q} + \tau_r^{-1} + k_{2q}e^{-\Delta E/kT})$, which represents the fraction of energy dissipated through the upper set of levels. Figure 5 shows that these levels provide the dominant pathway for decay above ~50 °C. This is perhaps surprising in view of the fact that these levels lie ~3560 cm^{-1} above the lowest set of levels, while kT is only ≲300 cm^{-1}. The unfavorable Boltzmann factor is offset by the extremely large value of k_{2q} of 10^{13} s^{-1}, roughly seven orders of magnitude larger than the values of k_{1q}. Thus, although the steady-state population of these levels is extremely small, 90–95% of the excited state energy is dissipated through this pathway at 100 °C.

Another important feature associated with the upper set of levels revealed in Table II is that the rate constant for deactivation of these levels, k_{2q}, is insensitive to perdeuteration of either the ligand or the solvent, whereas substantial deuteration effects on k_{1q} are indicated. We believe that this lack of a deuterium effect and the large value of k_{2q} are indicative of a strong-coupled radiationless decay process[47] which is thermally activated by population of the upper levels. Thus, we view the dissipation of excitation energy in aqueous Ru(bipy)$_3^{2+}$ as a combination of radiative and weak-coupled radiationless processes through a low-energy set of levels and a thermally activated strong-coupled radiationless process through a higher energy set.

Since our model for energy dissipation in Ru(bipy)$_3^{2+}$ indicates that a strong-coupled radiationless process dominates the decay at elevated temperatures, we deduced that the complex might be photoactive. Although previous studies[13,14] as well as our own indicate that photochemistry in aqueous solution is negligible at room temperature, Figure 4 clearly indicates photoactivity at 95 °C. The appearance of an initial shoulder in the 500-nm absorption followed by disappearance of this shoulder and appearance of a peak at 365 nm indicates that the complex is photoactive and forms at least one secondary product. The appearance of a shoulder at 500 nm is symptomatic of a Ru(II) complex, which along with the appearance of uncomplexed 2,2′-bipyridine in the photolysis solution indicates that at least two ligand displacement reactions occur: (1) displacement of one end of the bipy ligand by water or perhaps Cl^- under our photolysis conditions, followed by protonation of the open end of the bidentate ligand in 0.1 M acid; and (2) subsequent reaction of the resulting complex leading to displacement of the bound end of the monodentate Hbipy$^+$ ligand and releasing unbound Hbipy$^+$ into the solution. Later stages of the photolysis may eventually lead to further displacements or formation of Ru(III) species in acidic solutions, but our study of the photochemistry is insufficient to either support or refute these possibilities.

Our limited study of the photolysis of Ru(bipy)$_3^{2+}$ at 95 °C provides strong evidence that the photoactivity is due to ligand displacement reactions rather than photoredox processes. Furthermore, it clearly shows that the lower set of levels in our model is photoinert while the upper set is photoactive. Our results also clearly indicate that photochemistry is not the only means for energy dissipation of the upper set of levels. For example, even though the upper levels account for 21% of the total energy loss following excitation at 25 °C in the H_8/H_2O system, no net photochemistry is observable under these conditions. Hence, photochemistry must account for only a small fraction of the radiationless pathway characterized by k_{2q} and the major fraction of this pathway presumably is radiationless deactivation to the ground state without photochemistry. This, of course, does not rule out the possibility of transient intermediates which lead to regeneration of starting material as reported by Natarajan and Endicott,[20] and this type of process is also possible for the lower set of levels.

There are three plausible classifications of the upper set of excited levels which are responsible for the temperature dependence of the luminescence and photochemistry in aqueous solutions: (1) charge-transfer levels arising from coupling of either a $\pi^*(a_2)$ or $\pi^*(e)$ electron with a state of the d^5 core; (2) d–d levels arising from either the $^3A_2$ or ^3E of the split $^3T_1$ state of the octahedral complex; (3) vibrationally excited levels of the low-energy dπ^* states. Of these, (1) and (3) are unlikely due to the lack of photoredox processes, which would be expected to be associated with the dπ^* excited states. Furthermore, (3) may be discounted due to the lack of any significant isotope effect on ΔE. The ligand displacement photochemistry of the upper set of levels provides evidence that these levels are either the $^3A_2$ or ^3E d–d state. This would place one of these states at about 20 600 cm^{-1}, well within the range of our estimate of the $^3T_1$ state of an octahedral complex (vide supra).

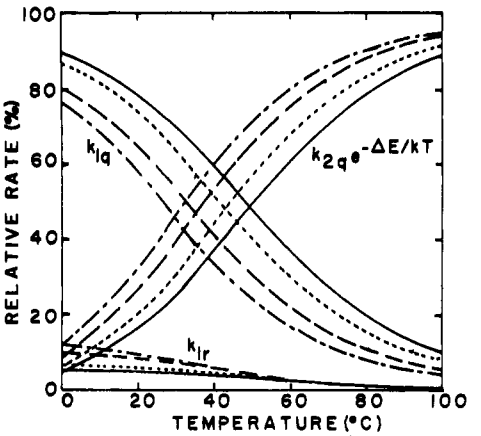

Figure 5. Relative contribution of each decay pathway to the total rate of deactivation as a function of temperature: (—), Ru(bipy)$_3^{2+}$ in H_2O; (- - -), Ru(bipy-d_8)$_3^{2+}$ in H_2O; (– –), Ru(bipy)$_3^{2+}$ in D_2O; (– · –), Ru(bipy-d_8)$_3^{2+}$ in D_2O.

V. Concluding Remarks

This study provides a characterization of the photophysical properties of Ru(bipy)$_3^{2+}$ over a temperature range of 0–100 °C, complementing its widespread use as a sensitizer in aqueous solution. It is quite natural to ask whether the sensitization properties are due to the lowest dπ^* set of levels or some other of the 45 low-lying dπ^* or d–d levels. The question is further complicated by the occurrence of both electron-transfer and energy-transfer processes from the excited state to various acceptors. Do both of these processes stem from the same set of levels or do they originate from different sets? Questions of this nature may be amenable to studies of the temperature dependence of the sensitization properties of Ru(bipy)$_3^{2+}$ under conditions where both types of sensitization are known to occur. Studies of this nature appear to be a logical extension of the current sensitization studies.

The most important feature revealed by this study is the interplay between the photophysical and photochemical pathways for energy degradation in the rare situation where the photophysical properties were measured under conditions where photochemistry occurs. *The study clearly indicates that the onset of photochemistry in this molecule is marked by a reduction of the deuterium effect on the lifetime.* We believe that this is a general feature which will emerge as symptomatic of the onset of photochemical activity in future studies of the temperature dependence of excited-state properties. As such, it may provide a clear link between photophysical and photochemical modes of energy conversion.

Changes in the nature of the solvation sphere appear to have major effects on both the radiative and radiationless decay processes of Ru(bipy)$_3^{2+}$ as the temperature and physical state of the medium are altered. Deuteration of water is known to have large effects on its hydrogen bonding properties,[48] and we believe that the solvent deuteration effects we observe are similar in origin to those in molecules which hydrogen bond to water. Space-filling models of Ru(bipy)$_3^{2+}$ indicate that a water molecule may make its closest approach to the metal center along the C_3 axis of the complex. Although the interaction between the electron-deficient hydrogen atom of water and the d electrons of Ru(II) along the C_3 axis is undoubtedly smaller than a normal hydrogen bond, it appears to be sufficient to impart significant CTTS character into the low-lying CTTL states of the complex with the net effect of lowering the energy of the charge-transfer states relative to the d–d states, thus hindering ligand substitution photochemistry via these

latter states. Lowering the solvent polarity would decrease the Ru(II)–solvent interaction along the C_3 axis leading to an increase in the energy of the CT states and an enhancement of the photochemical activity, as has been observed in dimethylformamide where $Ru(bipy)_3^{2+}$ undergoes photosubstitution at room temperature.[49] Hence, we conclude that the nature of the solvent–complex interactions may have a major effect on the photochemical activity of $Ru(bipy)_3^{2+}$ in fluid solution. A similar conclusion has been reached in studies of photosubstitution of pentaammine-3,5-dichloropyridineruthenium(II) in several solvents.[50]

The connections between the photophysics and photochemistry of metal complexes have been ill-defined in the past, but current experimental studies are beginning to clarify the situation. The difficulty in using spectroscopic results at −196 °C to interpret photochemical activity in fluid solution has been illustrated in a study of several iridium(III) complexes,[51] which has shown that the fluid solution photochemistry is due to d–d excited states, although the low-temperature photophysical properties arise from $d\pi^*$ or $\pi\pi^*$ excited states.[52] Studies of similar Ir(III) complexes in our laboratory suggest that radiationless transitions between states of different orbital parentage may be severely hindered in cases where the energy gap between them is small.[36,53] This may lead to thermal activation barriers to energy transfer between states of different orbital parentage, resulting in photophysical properties at −196 °C which do not reveal the existence of states responsible for photochemistry in fluid solution, even though these states may constitute the lowest excited state.[54]

The characterization of the molecular states responsible for the properties of "luminactive" complexes (those which are both luminescent and photochemically active under a given set of conditions) is of paramount importance to the development of a comprehensive theory of photophysical and photochemical energy conversion processes in metal complexes. Recent attempts to develop a theory to describe the photochemistry of transition metal complexes have been based on the fundamental postulate that the lowest excited level of a given multiplicity will be the dominant photoactive level of that multiplicity.[55,56] The present results and previous studies of Ir(III) complexes with π-bonding bidentate ligands[36,54,57] indicate that this postulate is invalid when states of orbital parentage different from that of the lowest excited state are thermally accessible from it. At the present it appears that *the lowest set of thermally equilibrated excited states of a given orbital parentage are the dominant states of that parentage involved in photochemistry or luminescence,* and we suggest that this would be a more appropriate postulate on which to base a theory of excited-state activity in metal complexes. This postulate de-emphasizes the importance of characterizing the excited states associated with energy-transfer processes in transition metal complexes by their spin multiplicity, as suggested by previous postulates,[55,56,58] and emphasizes the importance of orbital parentage. It offers the further advantage of accounting for a wavelength dependence of either photochemical[50,59] or photophysical processes.[36,57]

Although our study provides evidence for the occurrence of photosubstitution in $Ru(bipy)_3^{2+}$ at elevated temperatures, we do not have quantitative photochemical quantum yields in the temperature range of photochemical activity. A quantitative study of this photochemistry will complement our photophysical data and help to determine whether thermally activated photochemical and photophysical processes in this complex pass through the same intermediate levels, as we have assumed, or through different sets. A complete study of the photochemistry of this complex is currently in progress.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also acknowledge the partial support of this project provided by the Committee on Research of the University of California, Santa Barbara. We wish to thank Professors P. C. Ford and R. C. Millikan of this Department for their enlightening comments on this manuscript.

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