

istically large difference between ΔA_1 in pure NaNO_3 and in pure KNO_3 in order to be accounted for in this way. In our opinion the apparent temperature dependence of ΔA_1 is largely due to configurational entropy contributions in excess of those predicted by the quasi-lattice model.

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Supplementary Material Available: Tables IV-VI, giving all experimental data from solubility and emf measurements (10 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

Evidence of a Chromium(II) Intermediate in the Photolysis of Tris(2,2'-bipyridyl)chromium(III) in Dimethylformamide

GERALD B. PORTER* and J. VAN HOUTEN

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The mechanism for the photochemical reaction of $[\text{Cr}(\text{bpy})_3]^{3+}$ in DMF has been found to be strikingly different from that obtained in aqueous solution. The primary difference stems from the initial formation of a Cr(II) intermediate in DMF which does not occur in water. This leads to a large photochemical quantum yield in DMF. Experimental evidence supports an autocatalytic chain reaction with a Cr(II)-bipyridine complex as the chain carrier. The luminescence lifetime and quantum yield are smaller in DMF than in water, and, in mixed H_2O -DMF systems, they have been found to vary monotonically with solvent composition.

Introduction

The study of excited states of tris(bipyridyl) transition-metal complexes in nonaqueous solvents has demonstrated that the nature of the solvent can exert large effects on the processes observed. These effects can arise without change in the energy of the lowest excited state(s) with variation in solvent properties.

In some relatively simple cases, the solvent effects can be traced to variations in the kinetics of nonradiative decay of the excited state. For example, the luminescence lifetime and quantum yield, the racemization quantum yield, and the photochemical quantum yield of $[\text{Ru}(\text{bpy})_3]^{2+}$ are all found to be greater in D_2O than in H_2O .¹⁻⁴ In this case the effect has been attributed to a decrease in the efficiency of nonradiative deactivation of the excited state via O-D vibrations vis-à-vis O-H vibrations. On the other hand, no such deuterium isotope effect has been observed for the excited-state decay of $[\text{Cr}(\text{bpy})_3]^{3+}$.^{5,6}

The use of nonhydroxylic solvents can lead to a more complicated situation. Inasmuch as O-H vibrations are important in radiationless decay, there will naturally be an alteration of the lifetime and quantum yields. Furthermore, differences in the chemical properties of various solvents (ligating ability, redox potential, etc.) can provide pathways for photochemical reactions which are inaccessible in water. The recent literature provides several examples of the effect of nonhydroxylic solvents on the photo processes of $[\text{Ru}(\text{bpy})_3]^{2+}$. In aqueous solution the photochemical quantum yield of this complex is too small to be detected ($<10^{-5}$) at room temperature. As the temperature is raised, the quantum yield increases, although it remains small ($\Phi = 5.3 \times 10^{-4}$ at 90 °C in 0.1 M HCl).³ On the other hand, photosubstitution of $[\text{Ru}(\text{bpy})_3]^{2+}$ proceeds much more readily in nonhydroxylic solvents. In chlorinated hydrocarbons, $\text{Ru}(\text{bpy})_2\text{Cl}_2$ is formed at room temperature with $\Phi = 0.02$.⁷ In neat DMF, photosolvation of $[\text{Ru}(\text{bpy})_3]^{2+}$

occurs at room temperature with $\Phi \approx 10^{-4}$ and the complex also undergoes photoanation with an increase in quantum yield when NCS^- is added.⁸ The increase in photochemical quantum yield for $[\text{Ru}(\text{bpy})_3]^{2+}$ in nonhydroxylic solvents is accompanied by an increase in the luminescence lifetime; for example, at 25 °C $\tau = 0.60, 0.80, 0.82,$ and $1.03 \mu\text{s}$ in $\text{H}_2\text{O}, \text{CH}_3\text{CN}, \text{DMF},$ and Me_2SO , respectively.^{2,9}

When $[\text{Cr}(\text{bpy})_3]^{3+}$ is irradiated in neat argon-saturated DMF at room temperature, a number of effects are observed which indicate that the excited-state processes of this complex are quite different from those which occur in aqueous solution. These effects are more dramatic than those reported for the Ru(II) analogue. The luminescence lifetime and quantum yield of $[\text{Cr}(\text{bpy})_3]^{3+}$ in DMF are a factor of 15 smaller than they are in water.¹⁰ The photochemical quantum yield for disappearance of substrate in DMF is greater than it is in water ($\Phi_{\text{aq}} = 0.18$ at pH 9-10).¹¹

The increase in photochemical quantum yield of $[\text{Cr}(\text{bpy})_3]^{3+}$ in DMF is the focus of this report. Our data support the hypothesis that the kinetics of radiationless deactivation are solvent dependent. Furthermore, in DMF the initial photoreduction of the substrate to form a kinetically labile Cr(II) complex plays a major role in the overall reaction mechanism. Reduction of the excited $[\text{Cr}(\text{bpy})_3]^{3+}$ complex by H_2O is also thermodynamically feasible, although it has never been reported. In aqueous solution $[\text{Cr}(\text{bpy})_3]^{2+}$ has been observed in flash photolysis experiments using $[\text{Cr}(\text{bpy})_3]^{3+}$ in the presence of reducing agents such as ferrous ion.¹² In that case, the ${}^2\text{E}$ $[\text{Cr}(\text{bpy})_3]^{3+}$ excited state was quenched, and a transient absorption spectrum with maxima at 470 and 560 nm was observed and assigned as $[\text{Cr}(\text{bpy})_3]^{2+}$.^{12,13} Similar behavior of the Cr(III) complex has

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been reported with use of $[\text{Ru}(\text{bpy})_3]^{2+}$ as the reducing quencher,^{12,14} however, this system is complicated by the fact that the ruthenium complex absorbs a significant fraction of the exciting light. In aqueous solution the Cr(II) species decays by electron back-transfer before it can undergo any other reaction.^{12,14}

Experimental Section

All materials in this study were the same as used previously.¹⁰ Solutions were prepared as needed by using freshly distilled DMF. Solutions were deoxygenated in a Zwickel flask by bubbling for at least 1 h with chromous-scrubbed, dried argon. All experiments were performed at room temperature with samples sealed under argon in a 1-cm² fluorescence cell. Solutions were stirred vigorously during and after irradiation.

Luminescence Measurements. Excitation for both photolysis and luminescence measurements was with a He-Cd laser at 442 nm ($I_0 = 8 \times 10^{-8}$ einstein s⁻¹). For luminescence intensity measurements, the laser beam was chopped with a rotating sector, and the emission was detected at a right angle to the beam with a RCA 8645 photomultiplier mounted on a Bausch and Lomb grating monochromator with appropriate filters. The photomultiplier output was fed into a Brookdeal PM322A/LA350 lock-in amplifier and then into a strip-chart recorder.

The same detection system was used for lifetime measurements, except that a small pulsed nitrogen laser was used for excitation at 337 nm, and the photomultiplier output was fed directly into a fast oscilloscope with a 50 Ω termination. The decay traces were photographed, and the lifetimes were determined by a least-squares fit of \ln (intensity) vs. time.

In Situ Absorbance Measurements. A small tungsten lamp operated from a constant-voltage source was used to produce an analyzing beam at a right angle to the He-Cd laser beam. The filtered output of the lamp was focused on the monochromator entrance slit after passing through the stirred photolysis cell. For prevention of interference from sample luminescence or scattered laser light, the cell was masked and the geometry of the system was arranged so that the analyzing beam and the laser beam did not intersect. Furthermore, the rotating sector was moved to a position between the tungsten lamp and the cell, and the photomultiplier output was fed into the lock-in amplifier. The laser beam was not chopped in these experiments. The intensity of the tungsten lamp was kept low to prevent photolysis by that source.

Simultaneous in Situ Absorbance and Luminescence during Photolysis. Luminescence intensity was measured in the manner described above. Sample absorbance was determined by monitoring the transmitted power of the laser beam passing through the sample with use of a power meter placed behind the cell. The output of the power meter was fed directly into a second strip-chart recorder. Thus a single experimental run yielded two plots: one showing luminescence intensity as a function of time and a second showing sample absorbance at 442 nm as a function of time.

Results and Discussion

Photochemistry. Figure 1 shows the changes in absorption and emission at selected wavelengths as a function of time during the photolysis of $[\text{Cr}(\text{bpy})_3]^{3+}$ in DMF. The complete absorption spectra obtained at selected times after the photolysis of this system have been published previously.¹⁰ These plots provide evidence that the reaction of the substrate occurs via a multistep process. This is particularly evident in the 450–650-nm region where an induction period characterized by an initial gradual increase in absorbance is observed, followed by a sudden drop (dogleg) in optical density. It should be noted that the occurrence of the dogleg in the visible absorbance is coincident with the time when the 725-nm emission of the substrate drops to zero (Figure 1b). Thus, the absorbance increases steadily as long as substrate photolysis continues, with the dogleg occurring as soon as all the substrate has been consumed. The length of the induction period in-

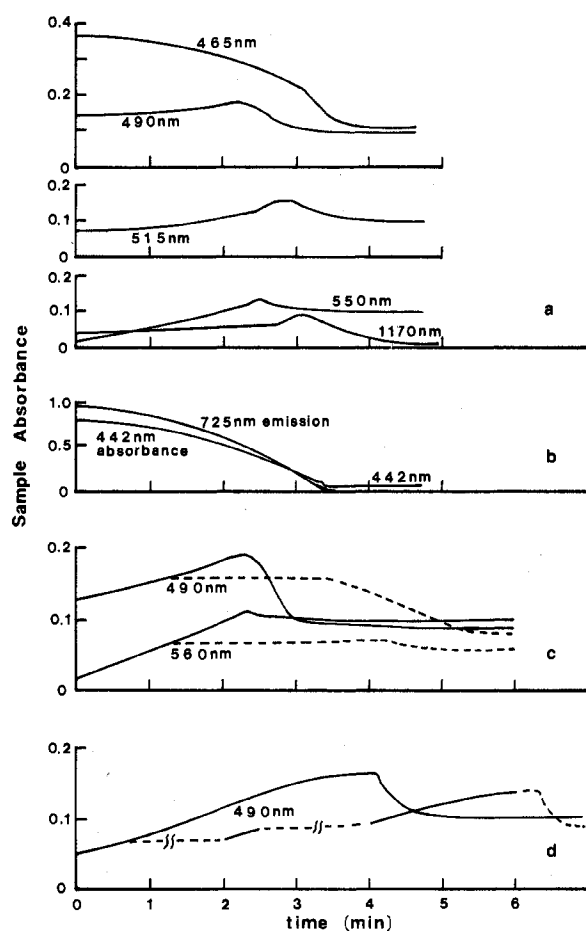


Figure 1. In situ absorbance and emission profiles vs. time during the photolysis of $[\text{Cr}(\text{bpy})_3]^{3+}$ in neat DMF (argon saturated, room temperature, 422-nm irradiation) (— laser on, --- laser off). Panel a: large absorbance at selected wavelengths, 465 nm corresponding to large decreases in ϵ between substrate and product, 490–515 nm corresponding to the region of largest deviation from isobestic behavior, 550 nm corresponding to a large increase in ϵ during the reaction (see Figure 1 of ref 9), and 1170 nm corresponding to a maximum in the absorption spectrum of $[\text{Cr}(\text{bpy})_3]^{2+}$ (see ref 21). Panel b: simultaneous substrate absorbance and emission (arbitrary units) during a single run (the dogleg in absorbance at 442 nm does not appear to be very pronounced due to the large overall change in absorbance at this wavelength). Panel c: absorbances at selected wavelengths showing a comparison between continuous photolysis and runs in which the laser beam was interrupted after an initial irradiation period. Panel d: absorbances at 490 nm illustrating the behavior observed under continuous and intermittent photolysis conditions. The data in this figure represent the results of individual typical experimental runs, and each curve is from a separate run, with the exception of the two curves in panel b which were recorded simultaneously. Variability in total time to reach the dogleg has been attributed to traces of oxygen in the system and to variations in laser intensity and sample concentration. The samples in panel d were less concentrated than the others. The first two dark intervals in panel d were each 2.5 min in length, but they have been compressed as indicated. All traces were recorded in the manner described in the Experimental Section with the exception of the trace at 1170 nm. The data at 1170 nm were recorded in a Cary 14 spectrophotometer using the unfiltered "white" light from the near-IR source of the spectrophotometer as the photolysis source. This procedure is the same as that used in recording the spectra reported in the inset of Figure 1 of ref 9. The time scale for the 1170-nm trace has been compressed to compensate for the lower intensity of the Cary source relative to that of the laser used in all other determinations; the tick marks on the abscissa correspond to 3-min intervals for the 1170-nm trace only.

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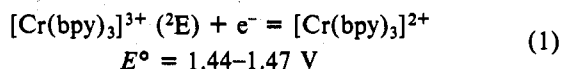
creases substantially with the introduction of traces of oxygen, and the reproducibility of the data is dependent on rigorous deoxygenation.

In other experiments, the beam from the photolysis source was interrupted prior to the dogleg. After the irradiation was stopped, but before complete reaction, the 450–650-nm absorption maintained a constant value for several minutes before undergoing a sudden drop. The time delay before the drop was found to increase as the initial irradiation time decreased; see Figure 1c. Figure 1d illustrates the behavior of a sample which was irradiated briefly and then irradiated again later after an intervening period in the dark. This experiment shows that the increase in absorbance during the induction period occurs only during irradiation.

Because of the postirradiation decomposition observed (Figure 1c), only an overall quantum yield for disappearance of $[\text{Cr}(\text{bpy})_3]^{3+}$ can be measured. We have established that 3 mL of 10^{-3} M $[\text{Cr}(\text{bpy})_3]^{3+}$ can be completely decomposed with 45 s of irradiation at 442 nm with $I_a = 6 \times 10^{-8}$ einstein s^{-1} but only partly decomposed, including the postirradiation effect, with 30-s irradiation. Thus the overall quantum yield is of the order of unity.

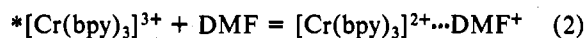
The general mechanism we propose for the photosolvation of $[\text{Cr}(\text{bpy})_3]^{3+}$ in DMF involves $[\text{Cr}(\text{bpy})_3]^{2+}$ as an intermediate. Absorption of 442-nm radiation by $[\text{Cr}(\text{bpy})_3]^{3+}$ populates the 4T_2 state. (The T_{2g} state in O_h symmetry is split into A_1 and E states upon reduction to D_3 symmetry. However the splitting is too small to be resolved in fluid solution at room temperature, so we have chosen to retain the T_2 symmetry label, but we have dropped the gerade subscripts.) In this transition, an electron is promoted from a t_2 orbital to an e^* antibonding orbital; it is the 4T_2 state that gives rise to part of the photoaquation reactions observed for Cr(III) complexes in general.^{15–17}

The $[\text{Cr}(\text{bpy})_3]^{3+}$ complex in basic aqueous solution undergoes photoaquation via the 2E state.^{13,18,19} Maestri et al.¹³ cite evidence that the aquation reaction proceeds in both photoreaction and thermal reaction modes through the same intermediate: $[\text{Cr}(\text{bpy})_3(\text{H}_2\text{O})]^{3+}$. Previous work¹² summarized above has demonstrated that 2E $[\text{Cr}(\text{bpy})_3]^{3+}$ can act as a strong oxidizing agent. In aqueous solution, the reduction potential of this 2E state, which is formed with close to unit quantum yield, is given by eq 1.^{5,13,20} Although it is therefore



capable of oxidizing water, no net oxidation occurs (in common with other powerful oxidizing agents such as $\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^{2-}). This apparent redox stability may be due either to rapid electron back-transfer, giving no net reaction, or to a relatively high activation barrier to electron transfer so that redox cannot compete kinetically with other decay processes.

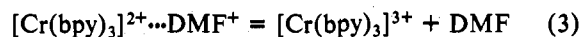
Since we do find $[\text{Cr}(\text{bpy})_3]^{2+}$ in our photolysis system, it is apparent that reaction 2 must occur (the right-hand side



of eq 2 represents a cage pair). We cannot say whether eq 1 is kinetically or thermodynamically controlled nor say, in

fact, what the actual electron donor is—it could be DMF itself or some impurity remaining, although the latter seems unlikely in view of the rigorous purification procedure we have used.¹⁰ We cannot state what excited state is responsible for reaction 2.

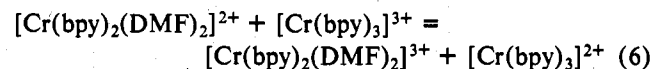
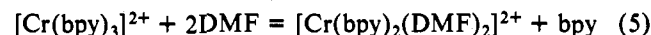
Electron back-transfer, resulting in overall quenching (eq 3), can compete with diffusion from the cage (eq 4). In our



experiments, the entire reaction is completed in a short time, so that the reverse of eq 4 or the equivalent with the final oxidized species is unimportant.

To establish a value for the quantum yield for production of cage-free $[\text{Cr}(\text{bpy})_3]^{2+}$, we measured the absorption continuously during a photolysis. The absorption was monitored at 700 nm, where neither $[\text{Cr}(\text{bpy})_3]^{3+}$ nor other Cr(III) species in this system absorb and where $[\text{Cr}(\text{bpy})_3]^{2+}$ has a large extinction coefficient: $2300 \text{ M}^{-1} \text{ cm}^{-1}$.²¹ The optical density (OD) at 700 nm increased regularly during the irradiation to 0.19 at the point that the substrate had just disappeared and then decreased slightly and leveled off at 0.16. Admission of air at this stage to oxidize Cr(II) species resulted in an immediate drop of the OD to zero again. The quantum yield for formation of $[\text{Cr}(\text{bpy})_3]^{2+}$ was 6×10^{-3} .

Once $[\text{Cr}(\text{bpy})_3]^{2+}$ has escaped from the solvent cage in which it was formed, it can participate in the sequence (5)–(6)



which is the main pathway by which $[\text{Cr}(\text{bpy})_3]^{3+}$ is solvated to $[\text{Cr}(\text{bpy})_2(\text{DMF})_2]^{3+}$, the bis product. $[\text{Cr}(\text{bpy})_3]^{2+}$ is a labile species and loses one ligand in reaction 5 to form $[\text{Cr}(\text{bpy})_2(\text{DMF})_2]^{2+}$. Both $[\text{Cr}(\text{bpy})_3]^{2+}$ and $[\text{Cr}(\text{bpy})_2(\text{DMF})_2]^{2+}$ would undergo rapid electron transfer with $[\text{Cr}(\text{bpy})_3]^{3+}$ and $[\text{Cr}(\text{bpy})_2(\text{DMF})_2]^{3+}$, but two of the four reactions will lead to no net change.

Provided that some $[\text{Cr}(\text{bpy})_3]^{3+}$ remains in solution, the reverse of reaction 5 is prevented by competition with reaction 6. As soon as all of the $[\text{Cr}(\text{bpy})_3]^{3+}$ has been consumed, the equilibrium between $[\text{Cr}(\text{bpy})_3]^{2+}$ and $[\text{Cr}(\text{bpy})_2(\text{DMF})_2]^{2+}$ can be established. Although Cr(II) is somewhat stable in our carefully degassed DMF solutions, it does decay thermally with a half-life of about 1 h. Technical problems associated with handling DMF solutions of Cr(II) species have frustrated our attempts to measure quantitatively the equilibrium constants and the kinetics of reactions involving these compounds.

It is difficult to rationalize our data in terms of any mechanism which does not involve $[\text{Cr}(\text{bpy})_3]^{2+}$. $[\text{Cr}(\text{bpy})_3]^{2+}$ is almost black with $\epsilon = 2000\text{--}5000 \text{ M}^{-1} \text{ cm}^{-1}$ throughout the visible region.²¹ On the other hand, $[\text{Cr}(\text{bpy})_3]^{3+}$ is yellow; its absorbance decreases rapidly to $\epsilon < 10 \text{ M}^{-1} \text{ cm}^{-1}$ at wavelengths greater than 500 nm.²¹ At the concentrations used here, neither the substrate nor the final product (a pink solution) absorbs significantly at wavelengths greater than 500 nm. Thus, the initial gradual increase in absorbance (Figure 1) corresponds to the formation of small amounts of $[\text{Cr}(\text{bpy})_3]^{2+}$ by photoreduction of the substrate in reactions 1, 2, and 4. The labile Cr(II) complex can decompose by reaction 5; however, it is immediately regenerated by reaction 6, thereby maintaining a steady-state rather than an equilibrium concentration as long as excess substrate remains. As soon as all the substrate is consumed, reaction 5 goes to equilibrium,

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yielding the dogleg in Figure 1. This accounts for the slight drop in OD at 700 nm at the end of the reaction which was observed by continuous monitoring during photolysis. The fact that the dogleg coincides with the disappearance of the 725-nm emission of the substrate (see Figure 1b) serves to confirm this aspect.

The catalytic activity of the mixture is maintained after all the substrate has been consumed. This was demonstrated by sealing a portion of a degassed solution of $[\text{Cr}(\text{bpy})_3]^{3+}$ in DMF in a cell having two compartments. The material in one compartment was photolyzed, and the absorption spectrum of the resulting pink solution was recorded. The unphotolyzed yellow solution from the second compartment was then mixed with the photolyzed portion. The mixture quickly turned pink, and the resulting absorption spectrum was identical with that of the original photolysate. Hence it is apparent that some Cr(II) species capable of acting in a catalytic role remains after the substrate has been consumed.

Reductive quenching of $[\text{Cr}(\text{bpy})_3]^{3+}$ (^2E) by a variety of species in aqueous solution has been extensively investigated,^{5,12,14,20,22} and transient spectra of $[\text{Cr}(\text{bpy})_3]^{2+}$ have been observed;²³ however, no analogous autocatalytic decomposition has ever been reported in any of the studies involving water. The basic difference between our results in DMF and the previous reductive quenching experiments in H_2O stems from the fact that the consumption of the transient by rapid, second-order, electron back-transfer is consistently observed^{12,20,22} in aqueous systems. This back-reaction has generally been assumed to occur while the reactants remain in a solvent-caged pair before the $[\text{Cr}(\text{bpy})_3]^{2+}$ can undergo any further reactions such as ligand loss. On the other hand, in the DMF system which we have investigated, the radical ion resulting from oxidation of a solvent molecule in the inner solvation sphere (reaction 2) can quickly "escape" from the cage (reaction 4) by self-exchange with molecules in the outer solvent sphere and eventually with the bulk solvent. This process involves merely the transfer of an electron from the bulk solvent into the inner solvent sphere, and it would be driven entropically as well as electrostatically since it accomplishes the spatial separation of two cations. Such a mechanism will naturally be more efficient when the oxidized species is a solvent molecule (e.g., DMF) than when it is a solute in low concentration, as is the case for the aqueous studies. Thus, although $[\text{Cr}(\text{bpy})_3]^{2+}$ can be produced photochemically in neat DMF, neat methanol,²³ basic solution,²³ or aqueous solutions containing reductive quenchers,^{5,12,14,20,22,23} it is not surprising that its eventual fate is quite different in the two systems. When $[\text{Cr}(\text{bpy})_3]^{3+}$ is photolyzed in neat methanol, the behavior is apparently similar to what we have reported for DMF solutions;²⁴ however, the investigators chose not to pursue their examination of this reaction "because of the formation of Cr(II)".¹⁸

Thermal Reactions with Added $[\text{Cr}(\text{bpy})_3]^{2+}$. As we have noted previously,¹⁰ the addition of solid $[\text{Cr}(\text{bpy})_3](\text{ClO}_4)_2$ to a solution of $[\text{Cr}(\text{bpy})_3]^{3+}$ in DMF results in a reaction which mimics the photoreaction in all details. This was taken as strong evidence that $[\text{Cr}(\text{bpy})_3]^{2+}$ is an active participant in the photoreaction. Efforts at a quantitative determination of the amount of Cr(II) present in reaction mixtures and the kinetics of the catalysis step have been only partly successful. The main problems concern the sensitivity of solutions of Cr(II) complexes to aerobic oxidation and the irreproducibility attributed to traces of oxygen.

We have, however, been able to establish that less than 200

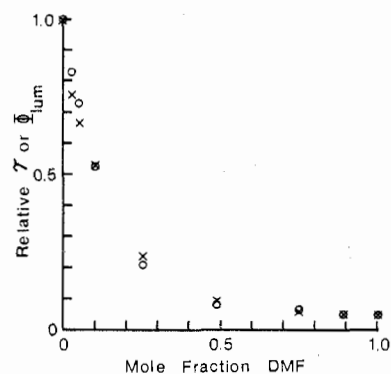


Figure 2. Relative luminescence quantum yield (O) and lifetime (X) data versus χ_{DMF} for $[\text{Cr}(\text{bpy})_3]^{3+}$ in mixed DMF- H_2O systems (argon saturated).

μg of $[\text{Cr}(\text{bpy})_3](\text{ClO}_4)_2$ (10^{-4} M) will catalyze the decomposition of 3 mL of 10^{-3} M $[\text{Cr}(\text{bpy})_3]^{3+}$ in DMF. In fact, the catalyst is probably much more efficient, as that amount of $[\text{Cr}(\text{bpy})_3]^{2+}$ represents a larger concentration than that present in photolysis samples, based on absorbance observations. However, it was technically impossible to weigh and transfer anaerobically a smaller sample of the solid. Neither serial dilution techniques to prepare less concentrated samples of $[\text{Cr}(\text{bpy})_3]^{2+}$ nor conventional flow methods were practical, owing to the necessity to exclude oxygen rigorously and to the instability of DMF solutions of the Cr(II) complex even in an oxygen-free environment. The procedure we chose was one in which a small weighed sample of solid $[\text{Cr}(\text{bpy})_3](\text{ClO}_4)_2$ was placed in a spectrometer cell attached to a Zwickel flask containing a solution of $[\text{Cr}(\text{bpy})_3]^{3+}$ in DMF. The entire system was flushed with argon for at least 1 h, and the solution was then transferred to the cell where it was mixed with the solid and the reaction was monitored. However, even this approach was less than ideal because the solid sometimes appeared to deliquesce by absorbing DMF from the argon stream. The damp solid then began to decompose before it could be mixed with the solution. Nevertheless, it was possible to establish by this technique that small amounts of $[\text{Cr}(\text{bpy})_3]^{2+}$ do catalyze the decomposition of solutions containing large (>10-fold) excesses of $[\text{Cr}(\text{bpy})_3]^{3+}$ in a manner which parallels the photoreaction.

Luminescence in Mixed Solvents. The lifetime and quantum yield of phosphorescence are decreased by a factor of 15 in DMF relative to those in aqueous solution. Since the ratio of phosphorescence quantum yield to the lifetime is the same in DMF as in water (see Figure 2), it follows that the solvent affects the ^2E state alone.

The excited-state decay of this complex has been found to be sensitive to other aspects of solvent composition. The effect of added anions on the decay kinetics of aqueous solutions has been reported in detail. It has been observed^{18,22,25} that high concentrations of various anions (chloride and perchlorate in particular) prolong the lifetime of the ^2E state by 50–840%.

Organic solvents and mixed aqueous organic solvents have recently been found to perturb the rates of decay processes of tris(bipyridyl) metal complexes, although they have little effect on the energies of excited states observed in emission.^{10,18,25–29} In addition to ourselves,¹⁰ Henry and Hoff-

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man^{18,25} have been actively investigating the effect of mixed solvents on the decay kinetics of $[\text{Cr}(\text{bpy})_3]^{3+}$. Although there is good agreement on a value of 63 μs for the lifetime of $[\text{Cr}(\text{bpy})_3]^{3+}$ in pure, oxygen-free water,^{10,18,25} there are differences between our data and theirs in mixed DMF-H₂O solutions.

We have previously noted¹⁰ that in deaerated solutions, the luminescence lifetime and intensity of $[\text{Cr}(\text{bpy})_3]^{3+}$ are both smaller by factor of 15 in neat DMF as compared to water. Henry and Hoffman found¹⁸ that the ²E-state absorption is easily measured in aqueous solution, but it is too weak to be detected in DMF. However, they also assert that the decay rate of the ²E state is unchanged from water to $\chi_{\text{DMF}} = 0.1$. We find (see Figure 2) a large effect on the lifetime and phosphorescence intensity by small mole fractions of DMF such that, at $\chi_{\text{DMF}} = 0.1$, the lifetime has decreased from 63 μs in water to about half that value. In neat DMF $\tau = 4 \mu\text{s}$.

Figure 2 shows that the luminescence lifetime and intensity decrease in a parallel fashion as the mole fraction of DMF increases. All decays were strictly exponential. These data indicate that quenching by DMF must involve an increase in the rate of nonradiative decay of the ²E state. The behavior cannot be rationalized in terms of variations in the population of the ²E state due either to changes in the decay of the ⁴T₂

precursor or to changes in the efficiency of intersystem crossing to the ²E state.

Concluding Remarks

The photochemistry of $[\text{Cr}(\text{bpy})_3]^{3+}$ in DMF and the luminescence of the complex in mixed DMF-H₂O solutions have been investigated. We have observed that $[\text{Cr}(\text{bpy})_3]^{2+}$ formed by photoreduction in neat DMF plays an important autocatalytic role in the decomposition of the substrate. In mixed DMF-H₂O systems, new, efficient nonradiative pathways become available for the decay of the ²E state. The electron-transfer pathway in neat DMF probably does not play a significant kinetic role in the excited-state decay scheme; nevertheless this electron-transfer step is an important one since it is ultimately responsible for the formation of the trace amounts of $[\text{Cr}(\text{bpy})_3]^{2+}$ involved in the catalysis. It is clear that the study of excited-state processes of $[\text{Cr}(\text{bpy})_3]^{3+}$ in mixed-solvent systems is an area which is ripe for further careful investigation. Researchers in this area should pay particular attention to the role of dissolved oxygen.

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Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602, and the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

Mechanistic Photochemistry of Transition-Metal β -Diketonate Complexes. 2.^{1a} The Case of *trans*-Tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III)

CHARLES KUTAL,*^{1b} DARCHUN B. YANG,^{1b} and GUILLERMO FERRAUDI*^{1c}

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A detailed photochemical study of *trans*-Cr(tfa)₃ (tfa is the anion of 1,1,1-trifluoro-2,4-pentanedione) in several nonaqueous solvents is described. Both continuous and flash photolysis experiments reveal a more complex photoreactivity pattern than has heretofore been reported for chromium(III) β -diketonates. *Trans* to *cis* isomerization is the dominant process occurring upon irradiation at wavelengths $\geq 366 \text{ nm}$, on the other hand, results in both isomerization and redox decomposition, with the quantum efficiency of the latter pathway displaying a pronounced solvent dependence. The variation in the ratio of the quantum yields for the two processes with the excitation wavelength establishes the presence of two photoactive excited states in the complex. The lower energy state is assigned as the ligand field quartet, ⁴T_{2g}, whereas the higher lying state appears to contain appreciable ligand to metal charge-transfer character.

Introduction

Comparison of the reported photoreactivity patterns of first-row transition-metal β -diketonate complexes in nonaqueous solvents reveals an interesting dichotomy. Thus near-ultraviolet irradiation of the Mn(III),² Fe(III),³ Co(III),⁴ Ni(II),⁵ and Cu(II)⁶ complexes results in the one-electron reduction of the metal center by the ligand, whereas comparable excitation of the Cr(III)⁷⁻⁹ analogues induces only ste-

reochemical rearrangement. This apparent absence of a photoredox pathway in Cr(III) suggests that one or both of the following factors are operative. (i) The charge-transfer excited states of chromium(III) β -diketonates, though populated, are inherently unreactive in nonaqueous solvents. In other words, the principal relaxation pathways accessible to these excited states do not lead to redox products but instead terminate in the ground state of the original complex. (ii) The conditions under which past photochemical studies of chromium(III) β -diketonates were conducted tended to obscure any charge-transfer reactivity. This situation could obtain, for example, if the primary redox products undergo a rapid back-electron-transfer step to regenerate the parent complex.

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