Photochemistry of Tris(2,2'-bipyridyl)ruthenium(II) in Aqueous Solutions

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The photochemical reaction of $Ru(bpy)_3^{2+}$ has been studied in 0.1 M HCl at temperatures between 313 and 368 K. The effects of ligand and solvent deuteration are reported in detail, along with a description of the effects of other variables such as ionic strength. The photosubstitution reaction of $Ru(bpy)_3^{2+}$ has been found to be thermally activated with a quantum yield of 10^{-3}–10^{-5} depending upon conditions. The reaction involves ligand field levels which lie 3560 cm^{-1} above the lowest charge-transfer levels. The complex is simultaneously luminescent and photoactive (hence the term "luminactive"), which has allowed a simultaneous, quantitative determination of photochemical and photophysical excited-state decay parameters. This report also includes a description of a technique for measuring photochemical quantum yields which takes advantage of the fact that the complex emits light while undergoing photochemistry. This allows the disappearance of the starting material to be followed continuously in situ by simply monitoring the luminescence intensity as a function of photolysis time.

I. Introduction

Excited-state processes of the tris(2,2'-bipyridyl)ruthenium(II) ion have been the subject of much research interest during the past 2 decades. The $Ru(bpy)_3^{2+}$ ion has been used extensively as a sensitizer[2] of photochemical and photophysical processes. Its selection for such an application has been based upon several criteria: a strong absorption in the visible region, an easily detected emission which facilitates quenching studies, solubility in aqueous media, and thermal and photochemical stability. Sensitization by $Ru(bpy)_3^{2+}$ has been shown to occur by either an energy-transfer or an electron-transfer mechanism, and the latter may involve either oxidation or reduction of the complex. Recently, $Ru(bpy)_3^{2+}$ and related complexes have been proposed[3-6] as catalysts in energy conversion schemes involving the photochemical decomposition of water.

It is agreed generally that the low-temperature emission arises from a charge transfer to ligand (CTTL) excited state.[7,8] The exact spin multiplicity of this state may be a moot question due to the magnitude of spin–orbit coupling[9] in ruthenium complexes. In fluid aqueous solution, the excited state of $Ru(bpy)_3^{2+}$ has been postulated[10,11] to involve some participation by solvent, and hydrated electrons have been detected as transients in flash photolysis.[12] The temperature dependence of the luminescence of $Ru(bpy)_3^{2+}$ in fluid aqueous solution may be explained by an excited-state model consisting of two sets of electronic energy levels.[11] The lower set of levels is derived from the model used[7] to fit the luminescence behavior observed at temperatures below 77 K. It consists of a set of charge-transfer levels which decay with a radiative rate constant of 6.8×10^5 s^{-1} and with a radiationless rate constant of 1.22×10^6 s^{-1}. A second set of ligand field levels lies 3560 cm^{-1} (42.6 kJ/mol) above the CT levels and decays to the ground state with a radiationless decay constant of 10^{13} s^{-1}. The presence of the LF levels accounts for the temperature dependence of the luminescence properties; the deuterium effects have been interpreted in terms of decreases in the nonradiative rate of the CT levels.

Recent reports[7,13-15] have shown that the complex is not as stable photochemically as had been assumed previously. In fact, $Ru(bpy)_3^{2+}$ has recently been proposed[14] for use as a chemical actinometer with laser irradiation. The nature of the photochemical reactions of $Ru(bpy)_3^{2+}$ and their relationship to the other excited-state processes are the subject of this report. This study includes measurements of the effects on the photochemical quantum yield of such parameters as temperature, deuteration, acid concentration, ionic strength, and dissolved oxygen. All of this information is necessary before this system would be suitable as a chemical actinometer,[14] and the data may also be relevant to the optimization of solar energy conversion schemes[3-6] using $Ru(bpy)_3^{2+}$ or its analogues.

II. Experimental Section

Photolysis samples were prepared fresh daily. Solutions of $\sim 5 \times 10^{-5}$ M $Ru(bpy)_3^{2+}$ in 0.1 M HCl were used to give an absorbance of 0.5–1.0 for a 1-cm path length at 436 and 454 nm. The solutions were deoxygenated with a stream of chromous-scrubbed nitrogen and transferred to 1-cm square fluorescence cells which were sealed under a nitrogen atmosphere. The absorbance of each sample was determined spectrophotometrically at 436 nm (the irradiation wavelength), 454 nm (the maximum of the dominant CT absorption of the starting material), and 500 nm (corresponding to a shoulder which developed during the course of the photolysis). Initial sample concentrations were calculated from the measured absorbance at 454 nm.

The samples were photolyzed at 436 nm with the same apparatus[10] which had been used for luminescence measurements. However, the excitation slits were opened to 12 mm (40-nm band-pass) to give an incident intensity at the cell face of 2×10^{-6} einstein/min. This intensity was measured daily with 0.006 M potassium ferrioxalate[16,17] as a chemical actinometer, and it was checked occasionally by an alternative technique utilizing Reinecke's salt.[18] The samples were placed in the thermostated cell holder of the apparatus and allowed to reach the desired temperature. They were then photolyzed for 15–60 min and the emission at 610 nm was monitored continuously and recorded on a strip chart. Since the rate of disappearance of starting material is proportional to the quantum yield[19]

$$-dc/dt = \Phi I_m \qquad (1)$$

the slope of plots of emission intensity vs. photolysis time could be related directly to the photochemical quantum yield.

The data were used to calculate the quantum yield, Φ (mol/einstein), by use of eq 2, where V is the volume (mL) of the solution

$$\Phi = V A_m s / (1000 \epsilon_m L I_0' (1 - 10^{-A_i})) \qquad (2)$$

photolyzed (determined gravimetrically), A_m is the initial measured absorbance at the monitored wavelength (454 nm) using a 1-cm cell, s is the slope of the plot of emission intensity vs. time (min^{-1}), ϵ_m is the extinction coefficient of the starting material at the monitored wavelength (M^{-1} cm^{-1}), L is the initial measured luminescence intensity, I_0' is the incident radiation intensity at the cell face (einsteins/min), and A_i is the average measured absorbance at irradiation wavelength (436 nm).

Comparison of results obtained by this technique with quantum yields measured by conventional techniques showed the two to be in good agreement. Corrections for thermal dark reactions were found to be unnecessary since the starting material could be refluxed overnight in dilute acid with no apparent spectra changes.

A similar technique for measuring quantum yields has been outlined recently by Demas,[14] although his mathematical treatment differs somewhat because he used optically dilute solutions with the powerful 457.9-nm irradiation of an argon ion laser.

III. Results

The results summarized in Table I demonstrate the effect of temperature and deuteration on the photochemical quantum yield for disappearance of $Ru(bpy)_3^{2+}$ or $Ru(bpy-d_8)_3^{2+}$ in 0.1 M HCl or DCl. The ordering of the deuterium effects on the

Table I. Photochemical Quantum Yield for Disappearance of Tris(bipyridyl)ruthenium(II) in Aqueous Acid Solutions[a]

| | quantum yield × 10⁴ | | | |
| | 0.1 M HCl | | 0.1 M DCl | |
T, K	Ru-(bpy)₃²⁺	Ru-(bpy-d₈)₃²⁺	Ru-(bpy)₃²⁺	Ru-(bpy-d₈)₃²⁺
313	0.4	1.2	1.3	2.7
323	1.2	1.8	1.8	2.7
333	1.9	2.4	2.9	3.9
343	2.9	3.5	4.2	5.8
353	4.4	5.6	6.3	6.7
363	5.3	5.8	7.5	8.5

[a] These data represent averages of at least three determinations for each set of conditions. Standard deviations were typically less than ±10%.

photochemical quantum yield parallels the previously reported ordering of the deuterium effects on the luminescence quantum yield and lifetime; however, the relative magnitude of the effects on the photochemical results is not as dramatic as it was[11] for the luminescence. Now the effect of solvent deuteration on the photochemical quantum yield is only slightly larger than the effect of ligand deuteration, whereas for the luminescence results,[11] the solvent deuterium effect was almost double the ligand deuterium effect. As the temperature is raised, the photochemical quantum yield increases; however, unlike the luminescence results,[11] the deuterium effect does not disappear.

For the purpose of determining the effect of conditions such as pH, ionic strength, anions of acids other than HCl, and dissolved oxygen, a preliminary study was conducted involving a series of photolyses at 343 K in which these parameters were systematically varied. This temperature was chosen because it gave a reasonably high quantum yield which could be measured accurately, yet without the difficulties associated with runs at higher temperatures that present problems. Deuterated materials were not used extensively in this portion of the study. On days when these studies were conducted, a sample of Ru(bpy)₃²⁺ in degassed 0.1 M HCl was often run as a simultaneous control. The results are summarized in Table II.

In a previous study[11] it was found that photolysis of Ru(bpy)₃²⁺ in 0.1 M HCl at elevated temperatures resulted in an initial color change from yellow-orange to red-orange followed by bleaching of all visible absorption bands under prolonged photolysis. It was noted that the initial red-orange color disappeared even if the solution was stored in the dark at room temperature after a short initial period of irradiation, indicating the red-orange product formed initially was not thermally stable.

Due to the thermal instability of the initial red photoproduct formed in the photolysis of Ru(bpy)₃²⁺, it was found in this study to be formed best for isolation purposes by use of high light intensities, high HCl concentration, and high temperatures for short irradiation times. Hence, 3-mL solutions of deoxygenated 10⁻³ M Ru(bpy)₃²⁺ in 1 M HCl were photolyzed with the full, focused output of the 1000-W Hg–Xe lamp filtered by 6 cm of CuSO₄ solution. At 363 K, maximum product yields were obtained at 15–20-min photolysis times; further photolysis resulted in bleaching of the 500-nm absorption. Under these irradiation conditions, the absorption spectrum of the solution after 15-min photolysis typically showed an intense peak at ~500 nm due to the photoproduct and a weak shoulder at ~450 nm due to the starting material. The decrease in absorption at 450 nm showed that more than 70% of the initial Ru(bpy)₃²⁺ was typically photolyzed under these conditions. A typical series of absorption spectra of a high-intensity photolysis are shown in Figure 1.

Table II. Photochemical Quantum Yields for Disappearance of Ru(bpy)₃²⁺ under Selected Conditions

solvent	T, K	10⁴Φ	remarks
H₂O	343	<0.1	experimentally zero; limit of detection Φ ≈ 10⁻⁵
0.001 M HCl	343	0.41	
0.01 M HCl	343	0.44	
0.1 M HCl	343	2.93	
1.0 M HCl	343	18	
12 M HCl[a]	343	>62[b]	reacted to 75% completion in 16 min
1.0 M HCl	298	1.9	
12 M HCl[a]	298	>15	reacted to 25% completion in 15 min
1.0 M DCl	343	22	
1.0 M DCl	343	29	sample = Ru(bpy-d₈)₃²⁺
1.0 M DCl	298	3.6	
0.1 M HCl	343	11	0.9 M NaCl added (μ = 1.0)
0.1 M NHO₃	343	2.1	
1.0 M HNO₃	343	6.2	
0.1 M HNO₃	343	7.8[c]	0.9 M NaNO₃ added (μ = 1.0)
0.1 M HClO₄	343	1.3[c]	
0.1 M HCl	343	1.0[c]	air saturated
1.0 M HCl	298	0.72[c]	air saturated

[a] Solutions prepared with 12 M HCl became visibly lighter during degassing, possibly due to photodecomposition in room light or to sample precipitation. [b] Slope of the plot of emission intensity vs. time was not constant. The curve was concave upward with some discontinuities; therefore the initial quantum yield may be larger than the reported value. [c] No 500-nm shoulder observed.
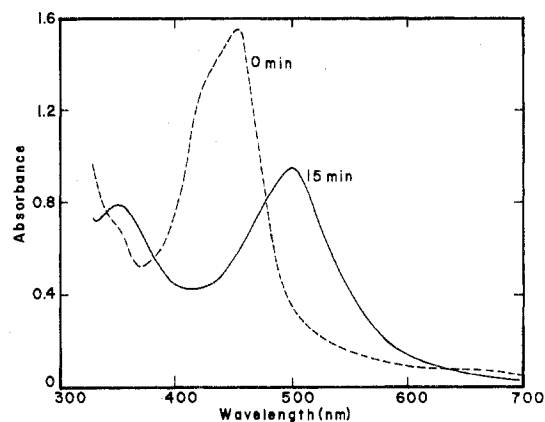

Figure 1. Absorption spectra of Ru(bpy)₃²⁺ in 1 M HCl as a function of photolysis time at 363 K with high-intensity irradiation: (- - -) absorption prior to photolysis; (—) absorption after 15 min of photolysis.

The photoproduct was found to be sufficiently thermally stable to isolate in usable quantities when photolysis times at 363 K were limited to 15–20 min. Isolation of the photoproduct was accomplished by immediately cooling the solutions to ice temperature following the 15-min photolysis and evaporating the 1 M HCl with a small freeze-drying apparatus. The solid purple-red residue was then dissolved immediately in 1 mL of methanol and purified by column chromatography on a 2.5 cm × 50 cm column of Sephadex LH-20 using 0.01 M HCl in methanol for elution. The chromatography was carried out under dark conditions at room temperature to prevent further photoreactions of the product. A complete evaporation and purification of a 3-mL photolysis solution was generally completed within 1 h of the time the photolysis was finished. During column chromatography, unreacted Ru(bpy)₃²⁺ appeared as the first band to be eluted; this was followed by the purple-red product which we isolated; a third, yellow band sometimes appeared which was formed in larger proportion at longer photolysis times (vide infra).

Solutions of the red photoproduct in 0.01 M HCl–CH₃OH could be successfully stored for several days by freezing them in liquid nitrogen. However, solutions stored at ice temperature
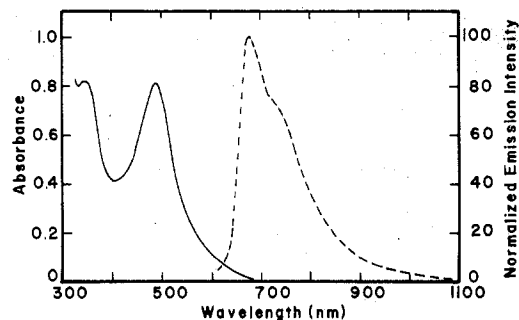
Figure 2. Absorption and emission spectra of the primary product of photolysis of Ru(bpy)$_3$$^{2+}$ in 1 M HCl at 363 K: (—) absorption in aqueous 1 M NaCl and 0.01 M HCl solution at 295 K; (---) corrected emission in aqueous 0.01 M HCl, 1 M NaCl–CH$_3$OH glass at 77 K.

were found to be unstable over a period of 2 days. Both absorption and emission studies of solutions of the purified photoproduct showed no sign of Ru(bpy)$_3$$^{2+}$ when freshly prepared; however, after 2 days at ice temperature, Ru(bpy)$_3$$^{2+}$ could be easily detected in these solutions.

The absorption and low-temperature emission spectra of freshly purified solutions of the photoproduct are shown in Figure 2. Both absorption and emission spectra of the freshly prepared photoproduct were found to be independent of pH over the range 1–8 when 1 M NaCl was used as a supporting electrolyte. In the absence of supporting NaCl, the 495-nm absorption of the photoproduct was found to be red shifted to about 510 nm by adjustment of the pH to 8 with 0.01 M NaHCO$_3$. Addition of HClO$_4$ to the pH 8 solution to readjust the pH to 2 did not regenerate the original 495-nm absorption of the photoproduct but led to a new absorption at 480 nm. Addition of 1 M NaCl to either the pH 8 or pH 2 solutions led to shifts in the respective absorption bands back to 495 nm. The 495-nm absorption band in aqueous solutions was shifted to 508 nm in methanol. Evaporation of the methanol followed by dissolution in 0.01 M HCl with 1 M NaCl supporting electrolyte regenerated the 495-nm absorption band. However, when the photoproduct was dissolved in acetonitrile, two new bands appeared at 480 and 540 nm. Evaporation of the acetonitrile followed by partial dissolution of the residue in water gave a solution with an absorption band at 455 nm and an emission characteristic of Ru(bpy)$_3$$^{2+}$. The water-insoluble portion of the residue was redissolved in acetonitrile and was found to have an absorption band at 545 nm.

Solutions of the purified photoproduct were photolyzed at 363 K in deoxygenated 1 M HCl in order to characterize further the overall photochemistry resulting from irradiation of Ru(bpy)$_3$$^{2+}$. Irradiation of the photoproduct with the CuSO$_4$-filtered output of the 1000-W Hg–Xe lamp resulted in disappearance of the absorption band at 495 nm and appearance of a new band at 370 nm. This band appears at nearly the same wavelength as that observed after extensive photolysis of Ru(bpy)$_3$$^{2+}$ and is also seen in the absorption spectrum of the third band from the Sephadex purification of the photoproduct. A dark reaction was also observed at 363 K which led to disappearance of the 495-nm absorption and appearance of a new absorption band at 370 nm. The rate of the dark reaction was substantially less than that of the high-intensity photolysis.

Solutions of Ru(bpy)$_3$$^{2+}$ in 0.1 M HCl which had been photolyzed at 360 K overnight were analyzed by fluorescence spectroscopy. These solutions were almost colorless, and the emission intensity at 610 nm due to the starting material had dropped to less than 1% of its initial value. When excited at 313 nm at room temperature, these samples displayed an emission band centered at 400 nm. This spectrum is very similar to that of a fresh sample of 2,2'-bipyridine in 0.1 M

HCl. The ultraviolet absorption spectrum of the photoproduct is also similar to that of the ligand. Dark thermal control solutions of Ru(bpy)$_3$$^{2+}$ showed no detectable changes in either absorption or emission. Unfortunately, the fluorescence of free bipyridine could not be used to quantitatively study the early stages of the photoreaction because this fluorescence is quenched by Ru(bpy)$_3$$^{2+}$.

IV. Discussion

The photochemical reaction of Ru(bpy)$_3$$^{2+}$ occurs in competition with measurable light emission by the complex; thus it has been termed luminactive. These results require that the parameters (energy gaps and decay constants) for any model which describes the photochemical behavior must be self-consistent with those proposed to describe the luminescence behavior and vice versa. The apparent activation energies obtained from plots of ln Φ vs. 1/T are similar in magnitude to the energy gaps found[11] in the evaluation of the luminescence data. This observation was taken as an indication that the energy levels involved in the luminescence quenching might also be implicated in the photochemical reaction. Since apparent activation energies obtained from plots of ln Φ vs. 1/T are always less than the true activation energy,[20] a more sophisticated analysis of the data was undertaken to obtain a better estimate of the true activation energy. This was particularly necessary since, in cases when the physical deactivation processes show some activation energy (which is known to be true in this case), the relationship between the apparent activation energy and the true activation energy of a photochemical reaction becomes quite complex.[20]

These results are consistent with a kinetic model which assumes that the photochemical reaction occurs from a set of LF levels which are in thermal equilibrium with the lower energy CT levels. A general kinetic treatment of the photochemical quantum yield from an equilibrium mixture of two excited states has been presented by Wagner,[21] and we have adopted his nomenclature for the following discussion. A general mechanism for the decay process is indicated in eq 3–8.

$$R_1{}^* \xrightarrow{k_i} R_0 \qquad (3)$$

$$R_1{}^* \xrightarrow{k_{r1}} P \qquad (4)$$

$$R_1{}^* \underset{k_{31}}{\overset{k_{13}}{\rightleftharpoons}} R_3{}^* \qquad (5)$$

$$R_3{}^* \xrightarrow{k_d} R_0 \qquad (6)$$

$$R_3{}^* \xrightarrow{k_{r3}} I \qquad (7)$$

$$I \xrightarrow{P_p} P \qquad (8)$$

As applied to the present study, R_0, $R_1{}^*$, and $R_3{}^*$ represent the ground state, lowest CT state, and lowest LF state of Ru(bpy)$_3$$^{2+}$, respectively. The primary photoproduct is represented by P, and I is a potential metastable ground-state intermediate which may be formed from R_3 and then form P with a probability P_p.

The general expression for the quantum yield for product formation, Φ_p, arising from two excited states in equilibrium is given by[21]

$$\Phi_p = \frac{X_1 k_{r1} + X_3 P_p k_{r3}}{X_1(k_{r1} + k_i) + X_3(k_{r3} + k_d)} \qquad (9)$$

where X_1 and X_3 are defined by eq 10 and 11. Due to the

$$X_1 = k_{31}/(k_{31} + k_{13}) \qquad (10)$$

$$X_3 = k_{13}/(k_{31} + k_{13}) \qquad (11)$$

Table III. Results for Computer Fitting of Photochemical Quantum Yields of Tris(bipyridyl)ruthenium(II) to Equation 14

sample/solvent	$\Delta E_a{}^{\ddagger}$, μm^{-1}	$10^{-12}P_pA$, s^{-1}	$10^{-6} \cdot$ $k_i{}^a$, s^{-1}	$10^{-12} \cdot$ $k_d{}^a$, s^{-1}	Δ $E_{LF}{}^a$ μm^{-1}
Ru(bpy)$_3$$^{2+}$/ 0.1 M HCl	0.20 ± 0.01	19 ± 1.0	1.3	10	0.36
Ru(bpy-d_8)$_3$$^{2+}$/ 0.1 M HCl	0.16 ± 0.01	4.4 ± 0.2	1.0	10	0.36
Ru(bpy)$_3$$^{2+}$/ 0.1 M DCl	0.21 ± 0.01	37 ± 2.0	0.64	10	0.36
Ru(bpy-d_8)$_3$$^{2+}$/ 0.1 M DCl	0.15 ± 0.01	4.0 ± 0.2	0.48	10	0.36

^{a} See ref 11.

absence of any measurable photochemistry at low temperatures, we assume that the CT state, R_1^*, is not photoactive. By substituting (10) and (11) into (9) and setting $k_{r1} = 0$, we obtain (12) where K_{eq} is the equilibrium constant for popu-

$$\Phi_p = \frac{K_{eq}P_pk_{r3}}{k_i + K_{eq}(k_{r3} + k_d)} \quad (12)$$

lation of R_1^* and R_3^* given by

$$K_{eq} = k_{13}/k_{31} \quad (13)$$

There are two apparent sources for the temperature dependence of Φ_p. These are through the equilibrium constant, K_{eq}, and through the rate constant for reaction of the LF levels, k_{r3}. With the assumption of the normal Boltzmann expression for the temperature dependence of K_{eq} and an Arrhenius form for k_{r3}, the temperature dependence of the quantum yield for product formation is given by eq 14, where A is the normal

$$\Phi_p(T) = \frac{P_pAe^{-(\Delta E_{LF}+\Delta E_a{}^{\ddagger})/kT}}{k_1 + Ae^{-(\Delta E_{LF}+\Delta E_a{}^{\ddagger})/kT} + k_d e^{-\Delta E_{LF}/kT}} \quad (14)$$

Arrhenius preexponential factor, ΔE_{LF} is the energy gap between the CT and LF levels, and $\Delta E_a{}^{\ddagger}$ is the activation energy for reaction of the LF levels.

Values of k_i, k_d, and ΔE_{LF} in eq 14, which are available from previous studies of the temperature dependence of the luminescence lifetime and luminescence quantum yield of Ru(bpy)$_3$$^{2+}$, are listed in Table III. To establish values of P_pA and $\Delta E_a{}^{\ddagger}$, experimental values of $\Phi_p(T)$ (Table I) were fit to eq 14 by a nonlinear least-squares computer-fitting routine, allowing P_pA and $\Delta E_a{}^{\ddagger}$ to vary to give the best fit. In all four cases good agreement between the experimental $\Phi_p(T)$ values and eq 14 was obtained by adjustment of P_pA and $\Delta E_a{}^{\ddagger}$ to the values in Table III.

Isolation of the red photoproduct whose absorption and emission spectra are shown in Figure 2 by high-intensity photolysis for a short period of time indicates that this is the primary photoproduct. Photolysis of this species to yield a product with an absorption peak at 370 nm shows that the peak which grows in at 365 nm in the Ru(bpy)$_3$$^{2+}$ photolysis is indeed due to a secondary photolysis product and not simply a second primary product which forms at a slower rate. The pH-independent absorption spectrum of the primary photoproduct over the pH range 1–8 in 1 M NaCl indicates it is not an aquated Ru(II) or Ru(III) species, since these would have pK_a's in this range. We therefore believe that the photoproduct is due to anation of Ru(II) by Cl$^-$. Since RuCl$_2$(bpy)$_2$ is insoluble in water and has absorption maxima at 553 and 380 nm in acetonitrile[22,23] as well as an emission maximum of 14.0×10^3 cm^{-1},[24] this species is eliminated from consideration as the primary photoproduct. The red shift of the charge-transfer absorption of Ru(bpy)$_3$$^{2+}$ from 455 to 553 nm in RuCl$_2$(bpy)$_2$ and the appearance of a new band at 380 nm clearly illustrate that a π-donating ligand such as Cl$^-$ in

the coordination sphere of Ru(II) lowers the energy of the charge transfer from Ru(II) to the π-accepting bpy ligand. On the basis of absorption data, we conclude that the photoproduct we have isolated has one Cl$^-$ ligand and one monodentate bpy ligand bound to Ru(II). The other four coordination sites are occupied by two bidentate bpy ligands in this formulation. This is consistent with the charge-transfer absorption band at 495 nm which is intermediate between the charge-transfer absorptions of Ru(bpy)$_3$$^{2+}$ and RuCl$_2$(bpy)$_2$ and with the band at 350 nm. The occurrence of an emission at 14.8×10^3 cm^{-1}, between the 17.1×10^3 cm^{-1} emission of Ru(bpy)$_3$$^{2+}$ and the 14.0×10^3 cm^{-1} emission of RuCl$_2$(bpy)$_2$, shows the same effect on the MLCT as seen in absorption. Furthermore, the formulation is consistent with the absence of a pH dependence on the absorption and emission spectra in 1 M NaCl.

It is evident from the pH dependence of the absorption spectrum of the photoproduct in the absence of supporting Cl$^-$ that the Ru(II)-bound Cl$^-$ is very labile in this complex. Thus, substitution of OH$^-$ for Cl$^-$ to form Ru(bpy)$_2$OH(bpy)$^+$ is believed to account for the absorption band we observe at 510 nm in solutions containing NaHCO$_3$ without added Cl$^-$. The blue shift of this absorption to 485 nm upon addition of HClO$_4$ is consistent with formation of Ru(bpy)$_2$H$_2$O(bpy)$^{2+}$ at low pH. Thus, replacement of Cl$^-$ by the stronger π-donating OH ligand leads to a red shift in the charge-transfer absorption whereas the weaker π-donating H$_2$O ligand leads to a blue shift.

Re-formation of Ru(bpy)$_3$$^{2+}$ from the purified photoproduct strongly supports the formation of a Ru(II) species containing two bidentate bpy ligands and one monodentate bpy ligand in the photolysis. The function of acetonitrile in promoting formation of Ru(bpy)$_3$$^{2+}$ from the photoproduct is not fully understood, but the observed lability of the Cl$^-$ ligand suggests that a complex containing coordinated acetonitrile would be readily formed as an intermediate. The second product formed in acetonitrile has not been isolated in significant quantities, but its insolubility in water and the appearance of an absorption band at 445 nm suggest that it may be RuCl$_2$(bpy)$_2$. Due to the lability of Cl$^-$ in the photoproduct we have isolated, it is quite likely that several primary products may be formed in the aqueous-solution photolysis of Ru(bpy)$_3$$^{2+}$ depending upon the pH and the nature of the anions present. For example, Ru(bpy)$_2$H$_2$O(bpy)$^{2+}$ could be formed initially in the acid-solution photolysis of Ru(bpy)$_3$$^{2+}$ but would be rapidly converted to Ru(bpy)$_2$Cl(bpy)$^+$ in the presence of Cl$^-$. From the dependence of the quantum yields on Cl$^-$ concentration illustrated in Table II, it appears likely that direct photoanation rather than photoaquation followed by anation accounts for a portion of the quantum yield. The rapid rate of the photochemical pathway implies that the precursors may involve ion pairs such as those which have been implicated in the photochemistry of Ru(bpy)$_3$$^{2+}$ in nonaqueous solutions.[13,15]

Further evidence in support of a monodentate bpy complex of Ru(II) with sufficient stability to isolate comes from the recent isolation of a monodentate bpy complex of Ir(III).[25] The later complex has been isolated as a pure crystalline solid both in the acid Ir(bpy)$_2$H$_2$O(bpy)$^{3+}$ and in the base Ir-(bpy)$_2$OH(bpy)$^{2+}$ forms. We have recently found that photolysis of Ir(bpy)$_3$$^{3+}$ in aqueous OH$^-$ leads to formation of Ir(bpy)$_2$OH(bpy)$^{2+}$ [26] in analogy to the formation of Ru-(bpy)$_2$Cl(bpy)$^+$ from the aqueous Cl$^-$-solution photolysis of Ru(bpy)$_3$$^{2+}$.

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(bpy\text{-}d_8)_3^{2+}$, 67573-02-8.

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Photosubstitution Reactivity of a Series of Tetracarbonylbis(substituted pyridine)tungsten(0) Complexes Having Ligand Field or Charge-Transfer Lowest Excited States

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Electronic absorption and emission spectra and photosubstitution efficiencies are reported for $cis\text{-}W(CO)_4X_2$ (X = 3,4-dimethylpyridine, 4-ethylpyridine, pyridine, 3-benzoylpyridine, 4-phenylpyridine, 3,5-dichloropyridine, 3,5-dibromopyridine, 4-benzoylpyridine, 4-cyanopyridine, 4-formylpyridine). The spectral data show that the tungsten → pyridine charge-transfer (CT) state moves smoothly to lower energy with more electron-withdrawing substituents on the pyridine, while the ligand field (LF) states are essentially insensitive to these changes. Photosubstitution of X occurs in all cases upon irradiation into the lowest energy absorption system, but the quantum efficiency for the substitution is very dependent on whether the lowest energy excited state is LF or W → XCT in character. The W → XCT state is virtually unreactive; e.g., $cis\text{-}W(CO)_4(4\text{-form-py})_2$ undergoes photosubstitution with a 436-nm quantum yield of ~0.0007. Complexes having LF lowest excited states are very photosubstitution labile; e.g., for X = 3,4-dimethylpyridine, 4-ethylpyridine, or pyridine the photosubstitution of X in $cis\text{-}W(CO)_4X_2$ occurs with a 436-nm quantum yield of ~0.4.

A large amount of work has been done to increase the understanding of the electronic structure and photochemistry of metal carbonyls[2] and particularly simply substituted d^6 metal carbonyl complexes. Studies of $W(CO)_5X$ (X = substituted pyridine) have shown that when the lowest excited state is ligand field (LF) in character, photosubstitution of both CO and X is found in fluid solution at room temperature.[3-6] The quantum yield for X dissociation is generally ≥0.5 in these cases,[3,4] and although the efficiency for CO substitution increases as the energy of irradiation increases, the predominant reaction remains loss of X. This is consistent with a substantial amount of reaction from the lowest excited state, even when upper excited states are directly populated. When the lowest excited state is clearly metal to ligand charge transfer (W → XCT) in character,[4] the quantum yield for substitution of X is several orders of magnitude smaller than the quantum yield associated with LF lowest excited states.
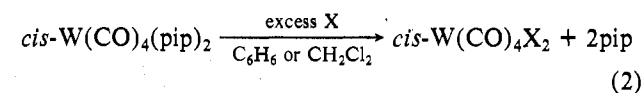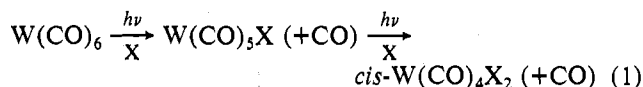
The red shift in the energetic position of the W → XCT absorption with the introduction of electron-withdrawing substituents onto the pyridine ring, which was used to elucidate the photosubstitution behavior of $W(CO)_5X$,[4] has also been found to occur in complexes of the type $Ru(NH_3)_5X^{2+}$,[7] $(\eta^5\text{-}C_5H_5)M(CO)_2X$ (M = Mn, Re),[8] and $Fe(CN)_5X^{3-}$.[9] In $Ru(NH_3)_5X^{2+}$, $(\eta^5\text{-}C_5H_5)Re(CO)_2X$, and $Fe(CN)_5X^{3-}$ complexes the photosubstitution results parallel those for $W(CO)_5X$; i.e., when the M → XCT excited state is higher than the LF state, efficient photosubstitution of X obtains, and

when the M → XCT is the lowest excited state, the quantum yield for photosubstitution is greatly reduced.

In this paper we wish to report an electronic spectral and photochemical study for complexes of the general formula $cis\text{-}W(CO)_4X_2$ (X = pyridine or a substituted pyridine). Aside from elaborating the number of systems for which photosubstitution lability can be manipulated by simple variation in X, the data allow a direct comparison of the relative LF and W → XCT positions in $W(CO)_5X$ and $cis\text{-}W(CO)_4X_2$.

Results and Discussion

a. Preparation of $cis\text{-}W(CO)_4X_2$. Synthesis of $cis\text{-}W(CO)_4X_2$ was by one of the two routes indicated in eq 1 or 2.

$$W(CO)_6 \xrightarrow[X]{h\nu} W(CO)_5X \ (+CO) \xrightarrow[X]{h\nu}$$
$$cis\text{-}W(CO)_4X_2 \ (+CO) \quad (1)$$

$$cis\text{-}W(CO)_4(pip)_2 \xrightarrow[C_6H_6 \text{ or } CH_2Cl_2]{\text{excess } X} cis\text{-}W(CO)_4X_2 + 2pip$$
$$(2)$$

Both routes have some precedence[3,10] even though only a few of the $cis\text{-}W(CO)_4X_2$ complexes studied have actually been reported. The major impurities are $W(CO)_5X$ and free ligand, and these can be separated from the desired product by chromatography on alumina and/or recrystallization. Four infrared band maxima, Table I, in the CO stretching region are consistent with the formulation of these compounds as C_{2v},