

Mechanism of the Photochemistry and Photophysics of the Tris(2,2'-bipyridine)chromium(III) Ion in Aqueous Solution

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Abstract: The photochemical and photophysical behavior of $\text{Cr}(\text{bpy})_3^{3+}$ in aqueous solution was investigated using the techniques of continuous and flash photolysis and the measurement of luminescence intensity and lifetime. Continuous irradiation in deaerated basic solution results in the release of one bpy ligand ($\Phi = 0.15$ at 11 °C and pH 9.6); the complex is photochemically stable in acidic medium ($\Phi \sim 10^{-3}$ at 11 °C and pH 4.3). The functional dependence of Φ on pH is the same as that observed for the rate constant of the thermal aquation reaction. Flash excitation reveals a transient absorption which is identified as the lowest excited doublet state, 2E , through comparison with the lifetime of the 727-nm phosphorescence emission ($\tau = 77 \mu\text{s}$ at 22 °C). At least 97% of the photoreaction is quenched under conditions in which the phosphorescence emission is completely quenched. It is suggested that the quenchable part of the reaction originates directly from the 2E state. Decay of the 2E absorption yields a solution slightly bleached of ground state; in basic solution the bleaching is permanent. In acidic solution the ground state is recovered via H^+ -dependent pseudo-first-order kinetics with a second-order rate constant of $4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Both the photochemical and thermal reactions are believed to involve a common ground-state intermediate with acid-base properties; a seven-coordinate $\text{Cr}(\text{bpy})_3(\text{H}_2\text{O})^{3+}$ species generated via an associative mechanism with ground or excited (2E) $\text{Cr}(\text{bpy})_3^{3+}$ is most plausible. Inasmuch as the final products in alkaline solution appear to be formed within the lifetime of the 2E state, the photochemical quantum yield is taken to be the fraction of 2E states that decay via the reactive pathway.

Introduction

Parallel photochemical and photophysical investigations on the same system under the same experimental conditions can make significant contributions toward the complete understanding of the factors which determine the excited state behavior of transition metal complexes.²⁻¹⁴ Particularly useful are comparisons between the quenching behavior of the photochemical reaction and that of the luminescence emission; Cr(III) complexes are especially suitable for this kind of thorough investigation inasmuch as they luminesce in aqueous solution at room temperature under the experimental conditions in which photochemistry is usually studied.^{7,9,11,13-15}

$\text{Cr}(\text{bpy})_3^{3+}$ (bpy = 2,2'-bipyridine) is known^{15,16} to exhibit a relatively strong luminescence in aqueous solution at room temperature; however, its photochemical behavior has not been investigated. The use of $\text{Cr}(\text{bpy})_3^{3+}$ in energy transfer processes^{17,18} and the extraordinary oxidation properties of its lowest excited state^{19,20} make a detailed understanding of the photochemical and photophysical behavior of this complex even more necessary. In this paper we report the results obtained from systematic experiments using continuous and flash photolysis and luminescence intensity and lifetime techniques.²¹ The role played by the various excited states, the nature of the ground-state intermediates, the mechanism of the observed photoaquation reaction, and the relationship to the mechanism of the thermal aquation reaction²² are discussed in detail.

Experimental Section

Materials. Tris(2,2'-bipyridine)chromium(III) perchlorate hemihydrate, $[\text{Cr}(\text{bpy})_3](\text{ClO}_4)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, was prepared by the method of Baker and Mehta.²³ Anal. Calcd for $\text{C}_{30}\text{H}_{25}\text{N}_6\text{Cl}_3\text{O}_{12.5}\text{Cr}$: C, 43.52; H, 3.04; N, 10.15; Cl, 12.85; O, 24.45; Cr, 6.28. Found:²⁴ C, 43.56; H, 3.06; N, 10.00; Cl, 12.75; O, 23.86; Cr, 6.45. The absorption spectrum of the complex was in agreement with that reported by König and Herzog.²⁵ Bis(2,2'-bipyridine)chromium(III) perchlorate, $[\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_3$, was prepared photochemically as previously described.²² The visible spectra of the acidic and basic forms of this complex, $\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2^{3+}$ and $\text{Cr}(\text{bpy})_2(\text{OH})_2^{2+}$, were in agreement with those reported by Inskeep and Bjerrum.²⁶ All chemicals and solvents used were of reagent grade quality.

Apparatus. Absorption spectra were measured with Perkin-Elmer 323 and Cary 118 spectrophotometers. Luminescence spectra were recorded with a Perkin-Elmer MPF 3 spectrofluorimeter equipped with an R 446 tube and a thermostated cell holder. Some experiments were also carried out with a Raman laser instrument²⁷ which was also equipped with an R 446 tube. Emission decay measurements were performed with an apparatus previously described.²⁸ The pH of the solutions was measured with a pH M 64 Radiometer or Beckman Expandomatic SS-2 instrument. Continuous photolysis experiments were carried out using 313-, 365-, 405-, or 464-nm exciting radiation.²⁹ The intensity of the incident light was measured by means of the ferrioxalate actinometer.³⁰ The flash photolysis and flash spectroscopy experiments were performed with an apparatus previously described.³¹

Procedure. Unless otherwise noted, the experiments were carried out in aqueous solutions at 22 °C. Britton-Robinson or phosphate buffers (generally $8 \times 10^{-3} \text{ M}$) were used for the experiments in the pH range 4.5-10.7. The experiments at lower or higher pH were carried out in perchloric or hydrochloric acid and sodium hydroxide solutions. The ionic strength was adjusted to 1.0 M with NaCl. Deoxygenation of the solutions was carried out by bubbling a stream of purified N_2 for 30 min; in some cases, the freeze-pump-thaw method was used.

Luminescence experiments were carried out on 10^{-3} M solutions with either right angle or frontal illumination.³² The exciting wavelength was 440 nm in the former case and 312 nm in the latter. In the frontal illumination experiments the exciting light was absorbed in a very small volume of the solution.

In the flash photolysis and flash spectroscopy experiments, the xenon flash (1/e decay time = 30 μs) was filtered through a Pyrex optical cell with quartz end windows (path length = 22 cm). The analyzing light was filtered through a monochromator or 6 mm of Pyrex. The solution in the sample cell was replaced after each flash. The concentration of the complex was 10^{-5} - 10^{-6} M . Solutions were prepared immediately before use and deoxygenated in the dark in order to eliminate unwanted photolysis of the complex. For temperature dependence studies, a jacketed quartz cell was employed. A stream of cooled water from a constant-temperature bath was pumped continuously through the outer jacket to maintain the temperature of the precooled solution between 0 and 22 °C within ± 0.5 °C.

For the continuous photolysis experiments, the complex concentration was generally 10^{-3} M and the intensity of the incident light impinging on the front surface of the cell was $\sim 1 \times 10^{-6} \text{ Nh}\nu \text{ min}^{-1}$. The reaction cell (optical path = 1.0 cm) was filled with 3.0 mL of solution and placed in the thermostated (11.0 ± 0.1 °C) cell holder

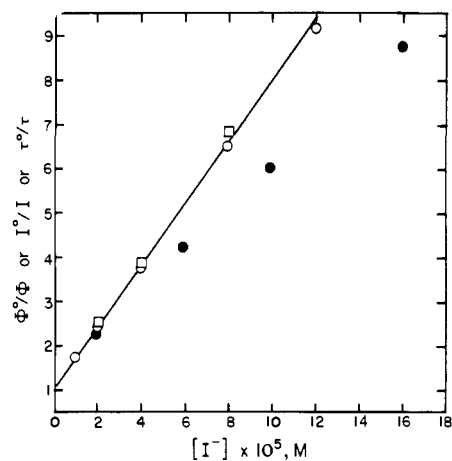


Figure 1. Stern-Volmer plot of the quenching by I^- of the emission intensity (○), emission lifetime (□), and photochemical quantum yield (●) of $Cr(bpy)_3^{3+}$; 11 °C, air-equilibrated solutions, $\mu = 1.0$ M.

Table I. Comparison of the Properties of the Phosphorescence Emission from $Cr(bpy)_3^{3+}$ and the Primary Flash Photolysis Transient

	Primary transient (temp, °C)	Phosphorescence emission (temp, °C)
Lifetime in water, ^a μs	63 ^b (22) 126 ^b (11)	77 ^c (22) 136 ^c (11) 51 ^d (22) 80 ^d (11)
Lifetime in 7 M $NaClO_4$, μs	330 ^b (22)	353 ^c (22)
E_a , kcal mol ⁻¹	+8.3 ^b (0-22)	-9.1 ^c (11-40) -7.1 ^d (11-40)
k_q for I^- , 10^9 M ⁻¹ s ⁻¹	1.2 ^b (22)	1.1 ^d (22)
k_q for O_2 , 10^7 M ⁻¹ s ⁻¹	1.7 (22)	~2 (22)

^a Lifetime independent of pH. ^b N_2 -purged solutions. ^c Freeze-pump-thaw deaerated solutions. ^d Air-equilibrated solutions.

of the irradiation equipment. Under these conditions, the incident light was completely absorbed at each of the irradiation wavelengths. A sample of the solution was maintained in the dark at the same temperature in order to provide a control for thermal reactions and a reference for spectrophotometric measurements. The solutions were air equilibrated unless otherwise noted. During the irradiation, these solutions were stirred by bubbling a stream of air; deoxygenated solutions were not stirred. After suitable irradiation periods, the light beam was interrupted and the irradiated solution was analyzed either spectrophotometrically or for its free bipyridine concentration using a standardized procedure based on extraction with *n*-heptane.²² In all cases in which the quantum yield of bipyridine release was determined, the irradiation period was chosen so that <10% decomposition of $Cr(bpy)_3^{3+}$ occurred.

Results

Luminescence Experiments. In agreement with Kane-Maguire et al.,¹⁶ we have found that the emission spectrum of $Cr(bpy)_3^{3+}$ in aqueous solution consists of two bands peaking at 695 and 727 nm. O_2 quenches the emission (Table I), leaving the relative intensity of the two bands unchanged. The emission intensity at 727 nm and the relative intensity of the two peaks do not vary with pH (1.0–10.7) or buffer concentration (≤ 0.1 M). As previously reported,¹⁵ the emission intensity decreases with increasing temperature; in carefully deoxygenated solution, the apparent activation energy (284–318 K) is -9.1 kcal mol⁻¹ (Table I). The relative emission yield at 727 nm, measured at pH 3 with the method described by Kane-Maguire et al.,¹³ was found to be the same for 312-, 350-, and 450-nm ir-

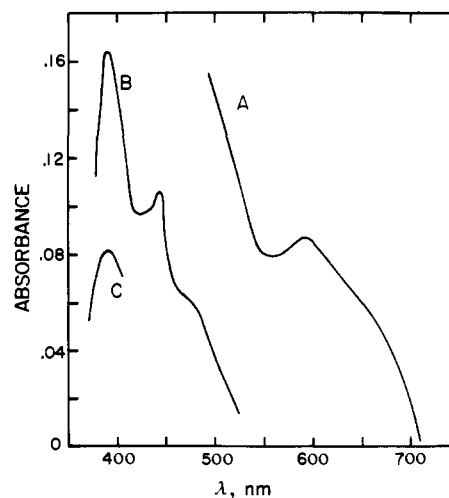


Figure 2. Absorption spectrum of the primary transient measured 150 μs after the flash photolysis of $Cr(bpy)_3^{3+}$ in 0.93 M $HClO_4$ and 1.0 M $NaCl$. [$Cr(bpy)_3^{3+}$]: A = 1.3×10^{-4} M; B = 1.7×10^{-5} M; C = 6.7×10^{-6} M. Optical path length = 22 cm. The spectrum is derived from points taken at 38 individual wavelengths; in the case of curve C, the points are 2 nm apart and 5–10 nm apart for the other curves. Absolute error in absorbance values = ± 0.003 units; reproducibility = ± 0.005 units.

radiation. Using right angle illumination, emission intensity at 727 nm was quite stable in acid media during irradiation, but a small decrease was observed in alkaline solutions after long irradiation periods.

In aqueous, air-equilibrated solution, I^- quenches both emission bands with the same rate constant. From Stern-Volmer quenching plots (Figure 1) $k_q = 8.5 \times 10^8$ M⁻¹ s⁻¹ at 11 °C and 1.1×10^9 M⁻¹ s⁻¹ at 22 °C. Fe_{aq}^{2+} also quenches the emission intensity with $k_q = 4.1 \times 10^7$ M⁻¹ s⁻¹.²⁰ High concentrations of ClO_4^- (> 1.2 M) cause a significant increase in the emission intensity (about a factor of 5 for $[ClO_4^-] = 7$ M in deaerated solution).

The presence of Me_2SO decreases the emission intensity at 695 and 727 nm, as previously observed by Kane-Maguire et al.¹⁶ With a Raman laser instrument these authors^{16,33} also observed a broad, structureless emission band centered at about 580 nm in Me_2SO solutions. In Me_2SO solutions, with our conventional spectrofluorimeter, we observe only the two peaks at 695 and 727 nm; with a Raman laser instrument we also observe a broad emission band, centered at about 570–580 nm, which is much more intense than the 727-nm peak (note that the laser instrument and the conventional spectrofluorimeter are both equipped with R 446 PM tube). Continuous irradiation with the laser causes a small decrease in the 727-nm band and an increase in the broad emission. In aqueous solution, no emission is observed in the 500–650-nm range even upon laser irradiation. In Me_2SO or methanol at 77 K, the 727-nm peak is very intense but no emission is observed in the 500–650-nm region with the conventional spectrofluorimeter.

The emission decay is the same at 695 and 727 nm and follows good first-order kinetics. The emission lifetime is independent of pH within the experimental error, and exhibits the same temperature dependence as the emission intensity (Table I). Oxygen and I^- quench the emission lifetime in the same way as they quench the luminescence intensity. The lifetime is increased in the presence of ClO_4^- ; $\tau = 353$ μs at 22 °C for carefully deoxygenated solutions containing 7 M ClO_4^- .

Flash Photolysis Experiments. Upon flash excitation, a solution of $Cr(bpy)_3^{3+}$ in 0.93 M $HClO_4$ initially displays the transient absorption spectrum shown in Figure 2 (primary transient); no further absorption could be observed up to 800 nm, the limit of photomultiplier response. The entire spectrum (370–700 nm) decays via first-order kinetics returning exactly to the absorption level that existed before the flash. In less

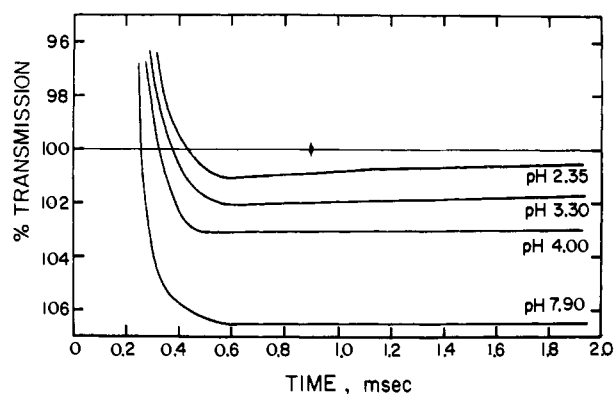


Figure 3. Time-dependent behavior of the solution absorption at 390 nm as a function of pH after flash photolysis. $[\text{Cr}(\text{bpy})_3^{3+}] = 4 \times 10^{-5} \text{ M}$. The 100% transmission line is the baseline before the flash, arbitrarily taken to be an absorbance of zero. The small vertical double-headed arrow indicates the noise level of the oscilloscope traces under the prevailing experimental conditions.

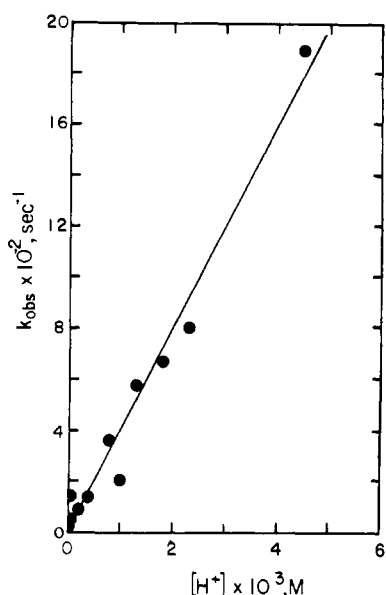


Figure 4. Dependence of the observed rate constant for the decay of the secondary transient on $[\text{H}^+]$.

acidic, neutral, and alkaline solution the same primary transient spectrum is obtained which also disappears via the same first-order kinetics. The rate constant for the decay of the primary transient equals $1.6 \times 10^4 \text{ s}^{-1}$ (std dev = 0.3×10^4) at 22 °C and is independent of pH (−0.4 to 13.1), monitoring wavelength, and buffer concentration (<0.1 M). The value of k increases with increasing temperature corresponding to $E_a = 8.2 \text{ kcal mol}^{-1}$ at pH 5.5; the same data, plotted in the form $\ln(k/T)$ vs. $1/T$, yield $\Delta H^\ddagger = 8.0 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -12 \text{ cal K}^{-1} \text{ mol}^{-1}$. At pH 0.3, the same results are obtained within experimental error.

The primary transient is quenched by O_2 ($k_q = 1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), I^- ($k_q = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), and OH^- ($k_q \leq 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 5 °C). It is also quenched by $\text{Fe}_{\text{aq}}^{2+}$ ($k_q \sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$) to produce a product absorbance at 560 nm²⁰ which is quenched by $\text{Fe}_{\text{aq}}^{3+}$. If the product is assumed to be $\text{Cr}(\text{bpy})_3^{2+}$ ($\epsilon_{560} 4850 \text{ M}^{-1} \text{ cm}^{-1}$), $k(\text{Cr}(\text{bpy})_3^{2+} + \text{Fe}_{\text{aq}}^{3+}) = 4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. It is interesting to note that quenching by I^- does not reveal any absorption that can be attributed to $\text{Cr}(\text{bpy})_3^{2+}$ or I_2^- ($\lambda_{\text{max}} 385 \text{ nm}$). High concentrations of ClO_4^- cause a significant decrease in the rate constant of decay of the primary transient absorption (about a factor of 5 for 7 M ClO_4^-).³⁴

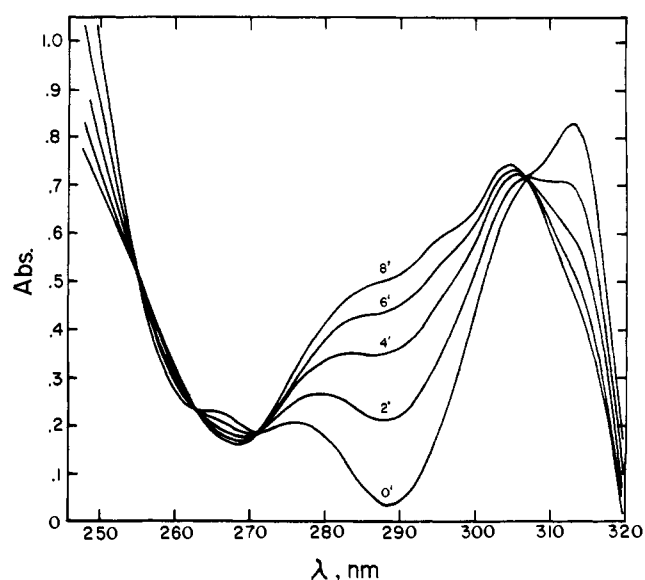


Figure 5. Spectral changes resulting from the irradiation of $7 \times 10^{-5} \text{ M}$ $\text{Cr}(\text{bpy})_3^{3+}$ at 365 nm, 11 °C, pH 9.6. Irradiation times are as shown.

At pH >2, the decay of the primary transient results in a solution with less absorbance than that of the unflashed solution in the wavelength region $\lambda 360\text{--}400 \text{ nm}$; no positive absorption was ever seen after the decay of the primary transient. This negative absorption effect is very small compared with the positive primary transient absorbance and can only be measured for ground-state absorbance >0.002 (22-cm path length) (Figure 3). The bleaching of the solution is taken as representing the depletion of the ground-state $\text{Cr}(\text{bpy})_3^{3+}$ and the formation of a secondary transient. Both the extent of the bleaching and the rate at which the ground state is recovered from the secondary transient are pH dependent. At pH 2.35, the original baseline is almost completely recovered within 3 ms. As the pH is increased, the rate of recovery is decreased; at pH 4, in fact, the return of the signal to the original baseline is not quite complete. At pH 2.35–5.35, recovery of the ground-state absorbance occurs via first-order kinetics. In the absence of phosphate buffer, k_{obsd} is a linear function of $[\text{H}^+]$ (Figure 4) fitting an equation of the form $k_{\text{obsd}} = k_0 + k_a[\text{H}^+]$ where a least-squares fit gives $k_0 \leq 10 \text{ s}^{-1}$ and $k_a = 4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. The rate of decay of the secondary transient is not affected by the presence of I^- or O_2 ; however, the amount of transient is reduced. The fraction of the secondary transient signal lost (measured immediately after the decay of the primary transient) is equal to the fraction of the primary transient quenched (measured immediately after the flash) by I^- or O_2 . In the presence of $8 \times 10^{-3} \text{ M}$ phosphate, the return of the signal at pH >3.5 is faster than in the absence of phosphate and the dependence of k_{obsd} on $[\text{H}^+]$ is far from linear; at pH <3.5, the presence of phosphate has virtually no effect on k_{obsd} .

In the pH range 4–6, the return of the signal to the original baseline is incomplete and a permanent change in the absorbance of the solution results. Moreover, at pH >6, no return of the signal is seen after the decay of the primary transient for at least up to 20 ms. Apparently, the bleaching of the solution occurs within the decay of the primary transient ($\sim 300 \mu\text{s}$ after the flash). At pH 9.6, no further change at 360 nm is observed for up to 10 s after the flash.

The absorption spectrum of a repeatedly flashed solution at pH 9.6 shows spectral changes, identical with those reported for the thermal aquation²² and with those obtained for the continuous photolysis (Figure 5 and following section), with well-defined isobestic points (for $\sim 36\%$ decomposition) at 255, 263, 274, and 307 nm. No changes were detected between

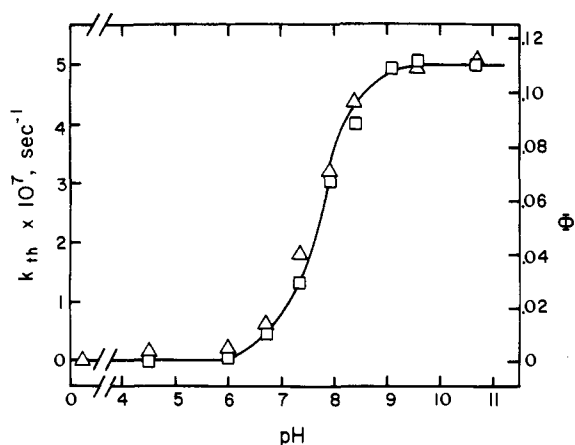
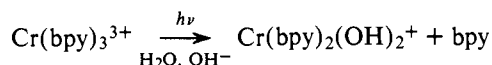


Figure 6. Dependence of the quantum yield (Φ) of the photochemical reaction (Δ) on pH, 11 °C, air-equilibrated solutions, $\mu = 1.0$ M. For comparison, values of the rate constant of the thermal substitution reaction (\square) from ref 22 are also presented.

spectra recorded immediately (50 s) after the flash and 8 min later for a solution at pH 9.6 containing 8.3×10^{-6} M $\text{Cr}(\text{bpy})_3^{3+}$ and 8×10^{-3} M phosphate buffer. Continuous monitoring of the absorbance at 290 nm (absorbance scale 0–0.02), at which the largest spectral changes occur (see Figure 5), showed no further changes, beyond the very large increase in absorbance generated by the photochemical reaction, from 44 s to 7 min after the flash.

Continuous Photolysis Experiments. In basic solution (pH 7.33–10.70), irradiation (λ 313, 365, 405, and 464 nm) causes noticeable spectral changes as well as the formation of free bpy; the same spectral changes are observed in flashed alkaline solutions (see preceding section). Good isobestic points are observed as above (Figure 5). The isobestic points are exactly the same as those obtained in the thermal reaction of the complex in basic solution.²² The overall photochemical stoichiometry is therefore identical with that of the thermal aquation reaction:



For irradiation at 365 nm, where the molar absorptivities of $\text{Cr}(\text{bpy})_3^{3+}$ and $\text{Cr}(\text{bpy})_2(\text{OH})_2^+$ are ~ 3000 and $\sim 400 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, isobestic points are maintained for the transformation of $>90\%$ of the $\text{Cr}(\text{bpy})_3^{3+}$; in fact, photolysis is a very convenient way of preparing the bis-bpy complex.²² In weakly acidic solution (pH 6.03 and 6.71), the spectral changes are slightly different from those shown in Figure 5 owing to the acid–base equilibria of $\text{Cr}(\text{bpy})_2(\text{OH})_2^+$.²² In more acidic solutions (pH ≤ 4.5), small spectral changes and some bpy release are observed only after very long irradiation periods.

The quantum yield of the photochemical reaction is determined from measurements of the concentration of free bpy released into solution. For 365-nm irradiation, the quantum yield is strongly dependent on pH: $\Phi = 0.11 (\pm 0.01)$ at pH 9.6 and 11 °C; $\Phi \sim 10^{-3}$ at pH 4.3 and 11 °C (Figure 6). At pH 9.3, Φ is independent of the wavelength of irradiation. Deaeration of the solution by repeated freeze–pump–thaw cycles causes an increase in Φ of $\sim 40\%$ (pH 9.3, 11 °C, and 365-nm irradiation; $\Phi = 0.15$). I^- quenches the photoreaction as shown in Figure 1. The presence of 7 M ClO_4^- causes Φ to decrease by a factor of ~ 10 (pH 9.6 and 313-nm irradiation).

Discussion

The continuous photolysis of neutral and basic aqueous solutions of $\text{Cr}(\text{bpy})_3^{3+}$ leads to the substitution of a bidentate bpy molecule by two molecules of H_2O or OH^- ; the complex

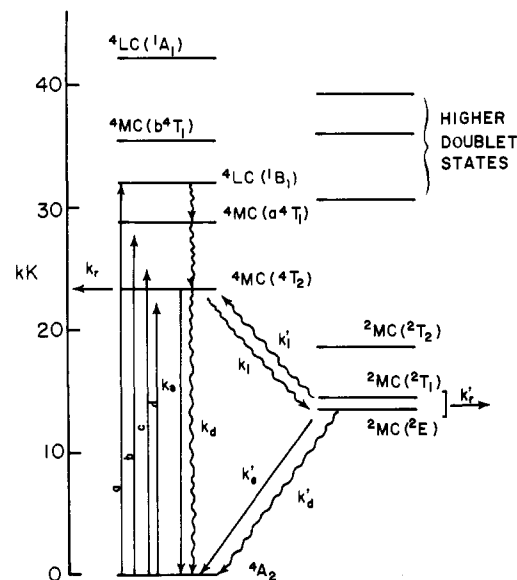


Figure 7. Energy level diagram of $\text{Cr}(\text{bpy})_3^{3+}$ following the assignments given in ref 25; MC = metal-centered states, LC = ligand-centered states. Arrows a, b, c, and d indicate the wavelengths of radiation used (313, 365, 405, and 465 nm, respectively). $k_e, k_d, k_r,$ and k_i are the rate constants of emission, internal conversion, reaction, and intersystem crossing for the lowest excited quartet state (4T_2). $k'_e, k'_d, k'_r,$ and k'_i are the corresponding rate constants for the thermally equilibrated 2E and 2T_1 excited states.

is virtually photoinert in acidic media. Consideration of the results, the known excited states, and reactions involving possible ground-state intermediates makes it clear that the simple overall stoichiometry is the result of a complicated sequence of elementary steps involving excited and ground-state intermediates. As for any other photochemical reaction, the most important problems to solve are (1) the role played by the various excited states, (2) the manner in which the reactive excited state gives rise to ground-state intermediates, and (3) the secondary reactions of the ground-state intermediates which yield the final products. The results obtained here permit us to draw some important conclusions and formulate reasonable mechanisms.

The Role of the Excited States. The peculiar excited state situation of Cr(III) complexes has been reviewed by several authors.^{5,35–37} The electronic absorption spectrum of $\text{Cr}(\text{bpy})_3^{3+}$ has been discussed in detail by König and Herzog.²⁵ The energy level diagram of Figure 7 has been constructed following their assignments of the various bands, assuming an octahedral microsymmetry. No exclusively ligand-to-metal charge transfer transitions below $4.0 \mu\text{m}^{-1}$ are assigned²⁵ which seems rather unlikely in view of the fact that $\text{Cr}(\text{bpy})_3^{3+}$ is not very difficult to reduce. Nevertheless, the presence of charge transfer excited states at relatively low energies does not affect this discussion. The doublet metal-centered excited states at low energy have the same electronic configuration as the ground state, so that they are not expected to be distorted with respect to the ground-state geometry.^{5,35–37} This is experimentally confirmed by the coincidence between the absorption and emission maxima.^{16,25} Therefore, the energies given in Figure 7 are the zero vibrational levels of the doublet states. The quartet metal-centered excited states, on the other hand, belong to excited electronic configurations and, thus, are expected to be strongly distorted with respect to the ground-state geometry.^{5,35–37} As a consequence, if the $^4T_2 \rightarrow ^4A_2$ fluorescence were strong enough to be observed, it would appear as a broad band with a large Stokes shift with respect to the corresponding absorption band. The broad emission observed at 580 nm ($\sim 1.72 \mu\text{m}^{-1}$) by Kane-Maguire et al.¹⁶ for $\text{Cr}(\text{bpy})_3^{3+}$ in Me_2SO upon laser excitation satisfied these

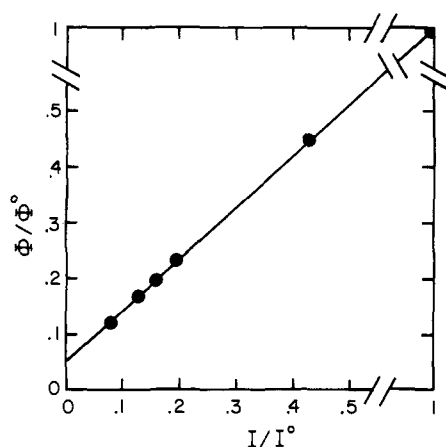


Figure 8. Plot of Φ/Φ^0 vs. I/I^0 for the quenching of the photoreaction and emission intensity by I^- : 11 °C, air-equilibrated solutions.

requirements and was, therefore, assigned as the ${}^4T_2 \rightarrow {}^4A_2$ fluorescence. Our luminescence experiments, however, cast serious doubts on this assignment and suggest rather that the emission band is due to some reaction product obtained upon laser excitation of Me_2SO solutions. The lack of a reliable fluorescence emission from $\text{Cr}(\text{bpy})_3^{3+}$ precludes an exact evaluation of the energy of the zero vibrational level of the 4T_2 state.

Inasmuch as the lifetime of the two emission peaks at 695 and 727 nm at 22 °C is the same, the 2T_1 and 2E states must be thermally equilibrated (see also ref 16). Therefore, for the sake of simplicity, these two levels will be considered hereafter as a single level and called 2E . It has been previously shown¹⁷ that the ${}^4T_2 \rightleftharpoons {}^2E$ intersystem crossing takes place with almost unitary (~ 0.95) efficiency. Similarly, we have found that the relative yield of the 2E phosphorescence is the same for both 312- and 450-nm excitation, which correspond to ligand- and metal-centered transitions, respectively (see Figure 7). Therefore, these excited states relax to 2E with almost unitary efficiency.

Inasmuch as the quantum yield of photoreaction is the same for irradiation at 313, 365, 405, and 464 nm, the state responsible for the photochemical reaction has to be either 4T_2 or a lower lying (doublet) excited state. A plot of Φ/Φ^0 vs. I/I^0 (or τ/τ^0) for the I^- -quenching experiments in air-saturated solutions at pH 9.6 shows that at least 95% of the photoreaction is quenched upon complete quenching of the phosphorescence emission (Figure 8). Owing to the oxygen quenching effect, this value is increased to $\geq 97\%$ for deaerated solution (see also ref 14). This means that the quantum yield of the "prompt" photoreaction from 4T_2 is, at most, 3% of the total quantum yield, and that at least 97% of the reacting molecules pass through the 2E state. For the quenchable part of the photoreaction, there are two possible paths:^{2,11,14} (a) direct reaction from 2E ; (b) reaction from 4T_2 by molecules which have passed (once or several times) through 2E ("delayed" 4T_2 reaction). If the quenchable part of the photoreaction, which is more than 30 times greater than the unquenchable part, were to take place from 4T_2 , both the forward (${}^4T_2 \rightleftharpoons {}^2E$) and back (${}^2E \rightleftharpoons {}^4T_2$) intersystem crossing steps would have to take place with almost unitary efficiency in order to allow the excited molecules to pass several times through 4T_2 . Quantitatively, it can be shown that for the above hypothesis, the ratio between the quantum yields of the quenchable and total photoreaction is equal to $\eta_i\eta_i'$, where η_i and η_i' are the efficiencies of forward and back intersystem crossing. This requires $\eta_i\eta_i' \geq 0.97$, which means that not only η_i ¹⁷ but also η_i' must be very close to unity. In other words, the 4T_2 and 2E states would be in thermal equilibrium. Under such conditions, the lifetime of the emitting

state is given¹¹ by the following equation (see Figure 7 for the assignment of the various rate constants):

$$\tau \approx \frac{k_i}{k_i(k_e' + k_d' + k_i') + k_i'(k_e + k_d + k_r)}$$

Combining this equation with equations for η_i and η_i' :

$$\eta_i = \frac{k_i}{k_i + k_e + k_d + k_r}$$

$$\eta_i' = \frac{k_i'}{k_i' + k_e' + k_d' + k_r'}$$

one obtains

$$k_i' \approx \frac{1}{\tau} \frac{\eta_i\eta_i'}{1 - \eta_i\eta_i'}$$

With $\eta_i\eta_i' = 0.97$ and $\tau = 136 \mu\text{s}$, $k_i' \approx 2 \times 10^5 \text{ s}^{-1}$. Assuming a frequency factor of 10^{13} s^{-1} , the upper limit value for the activation energy of k_i' would be 10 kcal mol⁻¹. This means that the energy gap between the zero vibrational levels of 4T_2 and 2E is $\leq 10 \text{ kcal mol}^{-1}$, which would place the zero vibrational level of 4T_2 at $\leq 1.72 \mu\text{m}^{-1}$, i.e., more than $0.62 \mu\text{m}^{-1}$ lower than the energy of the center of gravity of the ${}^4A_2 \rightarrow {}^4T_2$ absorption.²⁵ Such a distortion, however, is very much higher than those encountered in the Cr(III) complexes for which fluorescence can be observed.³⁸ In fact, the empirical procedure proposed by Fleischauer et al.³⁹ predicts a value of $\approx 2.1 \mu\text{m}^{-1}$ for the zero vibrational level of the 4T_2 state of our complex. In such a case, the energy gap for the ${}^2E \rightleftharpoons {}^4T_2$ back intersystem crossing would be $> 20 \text{ kcal mol}^{-1}$, and this would cause $k_i' \leq 10^{-3} \text{ s}^{-1}$ (using a frequency factor of 10^{13} s^{-1}) and $\eta_i' < 10^{-6}$. Because of the large discrepancy between these values and those required by the hypothesis of the reactive quartet ($k_i' \approx 2 \times 10^5 \text{ s}^{-1}$, $E_a \leq 10 \text{ kcal mol}^{-1}$, $\eta_i' \approx 0.97$), we believe that the quenchable part of the photoreaction ($\geq 97\%$ of the total quantum yield) of $\text{Cr}(\text{bpy})_3^{3+}$ takes place directly from 2E .

For several Cr(III) complexes, including $\text{Cr}(\text{NH}_3)_6^{3+}$,⁸ $\text{Cr}(\text{en})_3^{3+}$,¹¹ and $t\text{-Cr}(\text{en})_2(\text{NCS})_2^+$,⁴⁰ evidence has been obtained showing that the quenchable part of the photoreaction derives from 4T_2 after back intersystem crossing from 2E . In all these cases, however, the observed photoreaction takes place in acidic medium and the reaction quantum yield decreases from acidic to alkaline solutions. $\text{Cr}(\text{bpy})_3^{3+}$, on the other hand, is photoinert in acidic solution and the quantum yield of ligand substitution increases from acidic to alkaline solutions. This difference in behavior between the amine complexes and $\text{Cr}(\text{bpy})_3^{3+}$ might be indicative of a different reactive excited state.

Further support for doublet reactivity comes from the behavior of the analogous $\text{Cr}(\text{phen})_3^{3+}$ complex. Kane-Maguire and Langford¹⁴ have observed that 5% of the photoracemization quantum yield of this complex is unquenchable, and we have found⁴¹ that the same is true for the photoreaction causing phen release (at pH 11). Again, if the quenchable part (95%) of the photoreaction had to take place from 4T_2 after back intersystem crossing from 2E , the product $\eta_i\eta_i'$ should be 0.95 for $\text{Cr}(\text{phen})_3^{3+}$. However, η_i was found to be only 0.2,¹⁷ which means the most (if not all) of the quenchable photoreaction has to take place directly from 2E , irrespective of the η_i' value. Evidence for direct reaction between the doublet state and OH^- has recently been obtained also for $t\text{-Cr}(\text{en})_2(\text{NCS})_2^+$.⁴⁰ In conclusion, even though direct proof is lacking, it is reasonable to assume that the state responsible for the photochemical release of bpy from $\text{Cr}(\text{bpy})_3^{3+}$ is 2E .⁴²

Identity of the Primary Transient. Inasmuch as the decay of the primary transient matches the decay of phosphorescence, the primary transient is identified as the 2E excited state.⁴⁴ This assignment is supported by the temperature dependences of

the transient and phosphorescence decays and by the O₂ and I⁻ quenching data.

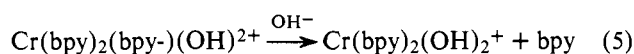
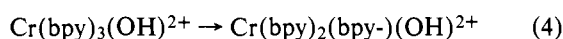
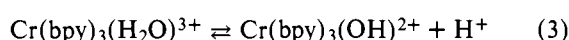
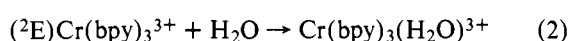
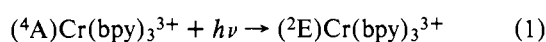
The absorption spectrum of the ²E excited state of Cr(III) complexes has been investigated only in a few cases.⁴⁵⁻⁴⁷ The best studied case is that of Cr(acac)₃, but the assignments given by Krause et al.⁴⁶ and Ohno and Kato⁴⁷ are in complete disagreement with each other. The absorption spectrum of the ²E level of Cr(bpy)₃³⁺ shows absorption bands at 590 (1.69 μm⁻¹), 445 (2.25 μm⁻¹), and 390 nm (2.56 μm⁻¹), and shoulders at ~650 (1.54 μm⁻¹) and ~475 nm (2.10 μm⁻¹). Inasmuch as the ²E state is 1.37 μm⁻¹ above the ground state, the excited states reached by ²E absorption are 3.0–4.0 μm⁻¹ above the ground state. The extinction coefficients of the bands shown in Figure 2 can be estimated knowing the intensity of the pumping flash, the quantum yield of doublet formation ($\phi(^2E) \sim 1$),¹⁷ the delay (150 μs) of the absorption measurements after the flash, the rate constant of ²E decay, and the bleaching due to the ground-state depletion. The values (lower limits) obtained for the extinction coefficients of the 390-, 445-, and 590-nm bands are about 7 × 10³, 3 × 10³, and 3 × 10² M⁻¹ cm⁻¹, respectively. Reference to Liehr's⁴⁸ and Perumareddi's⁴⁹ diagrams predicts the presence of five metal-centered doublet levels between 3.4 and 4.6 μm⁻¹ above the ground state. Thus, some of the observed transient absorption bands could correspond to doublet-doublet metal-centered transitions with some charge transfer character. The relatively high values of the extinction coefficients do not appear to be an obstacle to this assignment inasmuch as the spin-allowed metal-centered transitions from the ground state also give rise to intense bands.²⁵ As in the ground-state spectrum,²⁵ some of the observed features of the excited-state spectrum could correspond to vibrational components of the same electronic transitions. Some of the observed bands could also be due to ²E → ²(LMCT) transitions. Unfortunately, the location of exclusively charge transfer bands in the ground-state absorption spectrum has not been assigned.²⁵ However, the ligand-centered states at 3.0–4.5 μm⁻¹ have ⁴A₂ metal cores and so cannot be reached from ²E via one-electron transitions.

The Photochemical Mechanism. On the basis of the discussion above, it appears that the excited state responsible for almost all of the observed photoreaction is the ²E state. Clearly, a reaction as complicated as the release of a bidentate bpy molecule and its replacement by H₂O or OH⁻ in the first coordination sphere of Cr(III) cannot take place in a single step. From the mechanistic point of view, a very important result emerges from a comparison of the photochemical and thermal²² reactions: the pH dependence of the quantum yield of the photoreaction is exactly the same as the pH dependence of the rate constant of the thermal reaction (Figure 6). This comparison eliminates the possibility that the pH dependence of Φ is due to acid-base properties of the excited states;⁵⁰ the absorption spectrum, emission spectrum, and lifetime of the ²E state are independent of pH. It further suggests that either the ground-state reactant is present in different acid-base forms in acidic and alkaline solutions, or that the thermal and photochemical reactions involve common, acid-dependent intermediates. Both these hypotheses can account for the kinetics of the thermal reaction. However, because of the pH independence of the absorption and emission spectrum of Cr(bpy)₃³⁺, *only the hypothesis of common, pH-dependent chemical intermediates in both the thermal and photochemical reactions remains valid.*

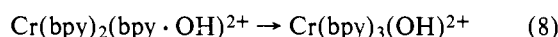
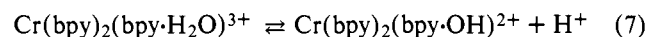
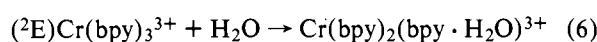
A dissociative mechanism, involving a five-coordinate intermediate, was considered implausible for the thermal reaction because no acid catalysis was observed.²² The lack of acid catalysis in the photochemical reaction serves to eliminate that alternative here also. In addition, the results obtained in the presence of ClO₄⁻ are difficult to reconcile with a dissociative mechanism. The increase in the ²E lifetime and the decrease

in Φ caused by ClO₄⁻ implies that this ion reduces the rate of deactivation of ²E that eventually leads to release of bpy. If the mechanism were dissociative, ClO₄⁻ would have to influence the metal–ligand bond breaking step, which seems rather unlikely. Finally, from a theoretical point of view a dissociative mechanism is unlikely as well because the reactive ²E state has the same metal–ligand bond distance as the ground state and, thus, is not expected to undergo facile metal–ligand bond rupture.

On the other hand, the formation of a seven-coordinate intermediate was proposed for the thermal reaction.²² This intermediate implies an associative mechanism involving coordination of a water molecule to the metal center as the rate-determining step. Deprotonation of the coordinated H₂O, rupture of a Cr–N bond forming a six-coordinate hydroxy complex with a monodentate bpy, followed by loss of bpy accounted for the final products. Applying this mechanism to the photochemical reaction yields, in the simplest terms, the following steps:



Another possible associative process is the so-called *Gillard mechanism*⁵² which involves the attack of H₂O at the C-6 position of a bpy ligand as the rate-determining step, with formation of a covalent hydrate which is susceptible to deprotonation of the quaternary nitrogen and intramolecular shift of OH to the metal center. Applying this mechanism to the photochemical reaction, step 1 would be followed by



Complete detachment of a bpy ligand would occur through reactions 4 and 5. This covalent hydrate mechanism was previously²² considered only on the basis of the equilibrium approach⁵³ and was thus eliminated. However, it also accounts for the pH dependence of the thermal and photochemical results if a more general kinetic treatment is used.⁵³

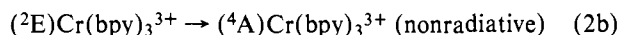
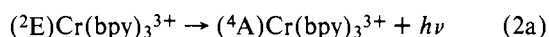
On the basis of the presently available data, a distinction cannot be made between the two associative mechanisms. However, the following speculations suggest that the most probable mechanism is the direct nucleophilic attack of H₂O on the central metal of the ²E state (reaction 2): (1) Although in O_h symmetry the t_{2g} orbitals are equally occupied in the ²E state,⁴⁹ this is not true in lower symmetries⁵⁴ owing to configuration interactions.⁵⁵ As a consequence of this lowering of the symmetry, the entering of H₂O with formation of a seven-coordinate intermediate should be facilitated.

(2) Ground-state substitution reactions generally occur⁵⁶ via associative mechanisms with activation energies smaller than the energy of the ²E state.

(3) Evidence for the direct reaction between the ²E state and OH⁻ has been obtained⁴⁰ for *t*-Cr(en)₂(NCS)₂⁺ which cannot undergo a Gillard-type reaction.

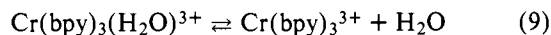
(4) Inasmuch as ²E is essentially a metal-centered excited state, it is difficult to visualize the driving force for nucleophilic attack of H₂O on the ligand. Such attack would be favored by ligand-to-metal charge-transfer excited states of which there are none below 4.0 μm⁻¹.²⁵

It must be noted that reaction 2 represents only one mode of decay of 2E ; reactions 2a and 2b must be competitive pathways.

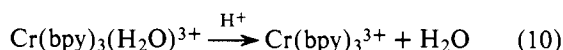


Inasmuch as the quantum yield of phosphorescence is $<10^{-3}$, reaction 2a does not contribute significantly to the decay of 2E . Therefore, the observed rate constant for the decay of 2E ($1.6 \times 10^4 \text{ s}^{-1}$ at 22°C) represents $k_{2b} + k_2[\text{H}_2\text{O}]$. Furthermore, inasmuch as the quantum yield of formation of 2E is ~ 1 , $\phi_2 + \phi_{2b} \sim 1$. The direct reaction of $({}^2E)\text{Cr}(\text{bpy})_3^{3+}$ and OH^- is not important until $\text{pH} > 13$ and has not been included in the mechanism; the direct attack of OH^- on $\text{Cr}(\text{bpy})_3^{3+}$ is known to be unimportant in the range $0 < \text{pH} < 10.7$.²² With regard to the ClO_4^- effect, we have shown³⁴ that both k_2 and k_{2b} are lowered in that medium.

The Ground-State Intermediates. The transient bleaching in acidic solution (secondary transient) implies the formation of $\text{Cr}(\text{bpy})_3(\text{H}_2\text{O})^{3+}$ via reaction 2 where the absorbance of the seven-coordinate species is less than that of the substrate in the absorbance window examined (360–400 nm). The return of $\text{Cr}(\text{bpy})_3(\text{H}_2\text{O})^{3+}$ to $\text{Cr}(\text{bpy})_3^{3+}$ takes place via acid-dependent and -independent paths. The acid-independent path (reaction 9) can be viewed as the relaxation of the seven-coordinate intermediate to the six-coordinate ground-state substrate via direct loss of the coordinated H_2O .



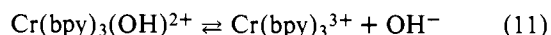
The reverse of reaction 9 is the rate-determining step of the slow thermal reaction.²² However, k_9 can be identified as k_0 (see Results section) with value of $\leq 10 \text{ s}^{-1}$. Thus, the intrinsic lifetime of $\text{Cr}(\text{bpy})_3(\text{H}_2\text{O})^{3+}$ toward reversion to $\text{Cr}(\text{bpy})_3^{3+}$ must be $\geq 0.1 \text{ s}$. The acid-dependent path can be represented by reaction 10 where k_{10} can be identified as k_a (see Results section) with a value of $4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Although the exact mechanism of reaction 10



is unknown, it probably involves H^+ -assisted Cr–O bond breaking. The fact that the rate of return of the ground-state absorbance is accelerated by the presence of H_2PO_4^- at low $[\text{H}^+]$ suggests that reaction 10 is a general-acid-catalyzed reaction. The relatively low value of k_{10} for a reaction involving H_3O^+ can be rationalized in terms of the charges of the reacting species and the very low basicity of the coordinated H_2O in the seven-coordinate species. Reactions 9 and 10 would also be operable in the thermal reaction²² and account for the fact that $\text{Cr}(\text{bpy})_3^{3+}$ is thermally as well as photochemically inert in acidic ($\text{pH} < 6$) media.

The conversion from transient bleaching to permanent bleaching of the flashed solutions takes place across the pH range in which the quantum yield of the photoreaction and the rate constant of the thermal reaction increase to their limiting values. If reaction 3 represents a rapid protonation–deprotonation equilibrium, then the seven-coordinate species can exist as $\text{Cr}(\text{bpy})_3(\text{OH})^{2+}$ depending on the pH of the solution. An exact evaluation of the $\text{p}K_a$ of $\text{Cr}(\text{bpy})_3(\text{H}_2\text{O})^{3+}$ cannot be made because of the uncertainties in the rate constants of reactions 4 and 9 and the lack of spectral data on this species.

Because OH^- is a better Lewis base than is H_2O , the intrinsic lifetime of $\text{Cr}(\text{bpy})_3(\text{OH})^{2+}$ toward loss of OH^- would be expected to be longer than that of $\text{Cr}(\text{bpy})_3(\text{H}_2\text{O})^{3+}$ so that k_{11} would be $\ll 10 \text{ s}^{-1}$.

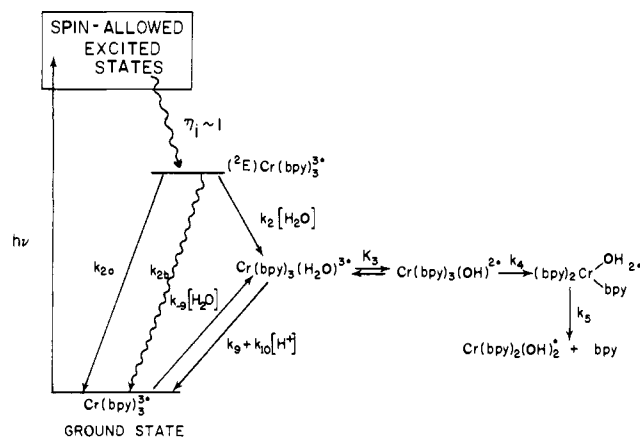


Inasmuch as no transient bleaching is seen in the flash photolysis of alkaline solutions and the spectra of the final products are established within the decay of the doublet state, it must be concluded that reactions 3–5 are completed within $\sim 300 \mu\text{s}$ and that the decay of 2E is the rate-determining step. In this case, reactions 3–5 are quantitative with no re-formation of $\text{Cr}(\text{bpy})_3^{3+}$ occurring in alkaline solution (where Φ reaches a plateau) once 2E has reacted via reactions 2 and 2b.

Conclusions

The photoaquation of $\text{Cr}(\text{bpy})_3^{3+}$ is visualized as proceeding according to Scheme I. The spin-allowed metal- or ligand-

Scheme I



centered excited states reached by the absorption of radiation deactivate to the lowest energy 2E excited state with unitary efficiency, presumably in less than 1 ns as has been found for other Cr(III) complexes.^{57,58} The reactive state leading to the photochemical release of bpy is believed to be the 2E state.

The 2E state reacts with H_2O , in competition with radiative and nonradiative decay to the ground state, to form a seven-coordinate intermediate, $\text{Cr}(\text{bpy})_3(\text{H}_2\text{O})^{3+}$, which has acid-base properties. This intermediate is also believed to be implicated in the thermal solvolysis of $\text{Cr}(\text{bpy})_3^{3+}$ (see Scheme I). Deprotonation to $\text{Cr}(\text{bpy})_3(\text{OH})^{2+}$ leads to ring opening and, ultimately, to loss of bpy. The final detachment of bpy from $\text{Cr}(\text{bpy})_2(\text{bpy})(\text{OH})^{2+}$ is expected to be a relatively slow process; inasmuch as this intermediate and $\text{Cr}(\text{bpy})_2(\text{OH})_2^+$ may have very similar spectra, no determination of the kinetics of this step is possible. $\text{Cr}(\text{bpy})_3(\text{H}_2\text{O})^{3+}$ also reacts via pH-dependent and -independent paths to re-form the substrate in acidic solution.

Finally, the limiting value of Φ of the photoreaction in deaerated alkaline solution (0.15) must represent ϕ_2 , the fraction of 2E that decays via the reactive pathway. By difference, the fraction of 2E that decays via a nonradiative pathway (ϕ_{2b}) must be 0.85.

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Photoinduced Substitution and Oxidative Addition Reactions of Pentacarbonylmanganese(-1) and Tetracarbonyl(triphenylphosphine)manganese(-1)

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Abstract: Photoinduced substitution and oxidative addition reactions of $Mn(CO)_5^-$ and $Mn(CO)_4PPh_3^-$ in tetrahydrofuran solutions are reported. Irradiation of $Mn(CO)_5^-$ as the bis(triphenylphosphine)iminium salt results in chemistry reflecting the intermediacy of $Mn(CO)_4^-$ or $Mn(CO)_4(\text{solvent})^-$. In the presence of PPh_3 or $P(OMe)_3$ the primary product is $Mn(CO)_4PPh_3^-$ or $Mn(CO)_4P(OMe)_3^-$, respectively. This photosubstitution chemistry is efficient chemically and with respect to quanta of light absorbed. Near-UV quantum yields exceed 0.2 for the process (254, 313, 366 nm). The $Mn(CO)_4P(OMe)_3^-$ appears to undergo further substitution upon irradiation, but the products were not characterized. However, $Mn(CO)_4PPh_3^-$ undergoes photoreactions reflecting the loss of PPh_3 , not CO, upon photoexcitation. Photolysis of $Mn(CO)_5^-$ in the presence of $HSiPh_3$ or $Ph_3SnSnPh_3$ results in high chemical yields of the oxidative addition products $cis\text{-}HMn(CO)_4SiPh_3^-$ and $cis\text{-}Mn(CO)_4(SnPh_3)_2^-$, respectively. Irradiation of $Mn(CO)_5^-$ as the Ph_4E^+ salt ($E = P, As$) results in the formation of $cis\text{-}PhMn(CO)_4EPh_3$. Irradiation of $Ph_3MeP[Mn(CO)_3]$ results in the formation of $cis\text{-}PhMn(CO)_4PPh_2Me$ as the only oxidative addition product. Competition between oxidative addition of Ph_4P^+ and substitution by PPh_3 suggests an important role for ion pairing in the oxidative addition of the cation.

Photoinduced substitution and oxidative addition reactions of metal carbonyls are numerous²⁻⁴ and are important in the preparation of new derivatives and are likely important in photocatalyzed reactions of olefins.⁴⁻⁹ We have undertaken

a study directed toward the comparison of the reactivity of intermediates resulting from irradiation of neutral and anionic isoelectronic metal carbonyls. The hope is that a coordinatively unsaturated metal carbonyl anion will participate in unusual