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Quartet vs. Doublet Excited-State Reactivity in $Cr(bpy)_3^{3+}$. Temperature Dependence of Quenchable and Unquenchable Photoaquation

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Abstract: Iodide ion quenches the photoaquation reaction of $Cr(bpy)_3^{3+}$ in mildly alkaline solution. At $[I^-] \sim 0.1$ M, Φ_{rx} reaches a plateau value of 2×10^{-3}. The dependence of the unquenchable quantum yield on pH reveals a "titration" curve (low reactivity in acidic medium, higher reactivity in alkaline solution, with a transition at pH ~7) similar to that observed previously for the quenchable quantum yield and the rate constant of the thermal aquation reaction, arguing that all three modes of reaction occur via a common intermediate. The unquenchable photoreaction occurs from a short-lived excited state, and several models are examined in order to reconcile the quenchable and unquenchable modes and the temperature dependences of their quantum yields: (A) unquenchable reaction from $^4T_2$ state, intersystem crossing to $^2T_1/^2E$ states, and quenchable reaction from these latter long-lived states; (B) quenchable reaction from $^2T_1/^2E$ populated via intersystem crossing from the quartet manifold; (C) all reaction from $^4T_2$ repopulated from long-lived $^2T_1/^2E$ via back intersystem crossing. It is concluded that on the basis of the evidence available, it is not necessary to invoke any reaction mode at this time other than that represented by A.

A continuing controversy in the photochemistry and photophysics of chromium(III) complexes centers around the specific roles played by the excited quartet and doublet states in defining the photochemical behavior.[1] Further complicating the issue are the questions of prompt reaction from non thermally equilibrated excited states and back intersystem crossing from the doublet to the quartet. Reactivity modes may or may not be different from states with different spin multiplicities and different extents of thermal equilibration. Only where the photochemical behavior is known in sufficient detail would it be possible to make photophysical distinctions.

In the case of $Cr(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine) in aqueous solution, a model has evolved[2] to account for an extensive array of experimental results. According to this model, the lowest excited doublet states ($^2T_1/^2E$) are populated by nearly quantitative intersystem crossing from the very short-lived[3] lowest quartet state ($^4T_2$) with back intersystem crossing not being an important process. The ultimate photochemical aquation product is viewed as arising from an interaction of $^2T_1/^2E$ with the solvent that produces, in the first instance, an intermediate ($Cr(bpy)_3(H_2O)^{3+}$) that undergoes, in alkaline solution, rapid deprotonation followed by rapid, irreversible, and quantitative bpy labilization; the final product is ($Cr(bpy)_2(OH)_2^+$). Kirk[1] has suggested that prompt intersystem crossing to $^2T_1/^2E$ may be very efficient inasmuch as initially produced states may have mixed doublet and quartet character. In this case, prompt intersystem crossing may not be a kinetically distinguishable process.

There have been indications in the past that ($^4T_2$)$Cr(bpy)_3^{3+}$ is photoactive although the mechanistic details of its reactions have not been elucidated. The quenching of ($^2T_1/^2E$)$Cr(bpy)_3^{3+}$ by I^- ($k_q = 1.4 \times 10^9$ M^{-1} s^{-1})[4] causes the parallel diminution of the lifetime, luminescence, and photoreaction of that state. However, a correlation of these quenching effects[5] reveals an unquenchable component representing ~3% of the total photoreaction. Furthermore, the quenching of ($^2T_1/^2E$)$Cr(phen)_3^{3+}$ (phen = 1,10-phenanthroline) by I^- ($k_q = 1.6 \times 10^9$ M^{-1} s^{-1})[4] reduces the quantum yield of photoracemization of the optically active complex to less than 10% of the total value.[6] The unquenchable quantum yield in the presence of I^- has an apparent activation energy of 2.2 kcal mol^{-1} while the total quantum yield in the absence of I^- has an apparent activation energy of 10.1 kcal mol^{-1}.[7]

In the work described in this paper, we have used I^- to quench ($^2T_1/^2E$)$Cr(bpy)_3^{3+}$ virtually completely in order to examine the pH and temperature profiles of unquenchable photoaquation.

[†] Concordia University.

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(1) For a recent review, see: Kirk, A. D. *Coord. Chem. Rev.* **1981**, *39*, 225.

(2) For a recent review, see: Jamieson, M. A.; Serpone, N.; Hoffman, M. Z. *Coord. Chem. Rev.* **1981**, *39*, 121.

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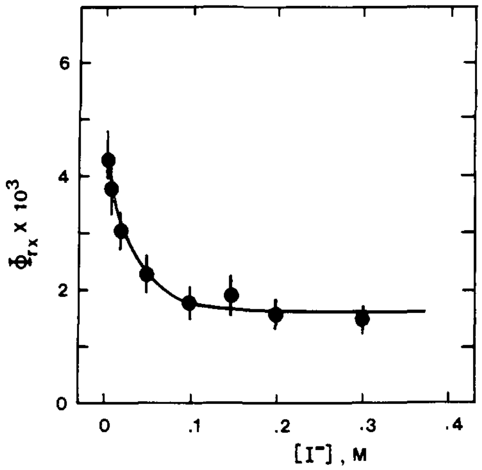

Figure 1. Φ_{rx} as a function of [I⁻] in the 313-nm photolysis of Ar-purged solutions of 1.6×10^{-4} M $Cr(bpy)_3^{3+}$ containing 0.008 M Britton–Robinson buffer (pH 9.3) at 22 °C; ionic strength controlled at 1.0 M with NaI and NaCl. Value of Φ_{rx} for $Cr(bpy)_3^{3+}$ in the absence of I⁻ under identical conditions is 0.13 (ref 9). Error bars represent the standard deviation (±15%) of the average of two to four determinations.

Through comparison with corresponding values for the total unquenched photoaquation,[5,8] we have been able to evaluate various mechanistic models of the photochemistry and photophysics of $Cr(bpy)_3^{3+}$.

Experimental Section

$[Cr(bpy)_3](ClO_4)_3 \cdot 0.5H_2O$ was available from previous studies.[4] All other chemicals were of reagent or spectrograde quality, and water was monodistilled.

Continuous photolyses were carried out at 313 nm with an Oriel 1-kW Hg Xe lamp and a 0.25-m Bausch & Lomb grating monochromator (22-nm bandwidth). The light beam was passed through an 8-cm path of cooled, distilled water in order to avoid infrared heating of the sample. All measurements were made at temperatures controlled (±0.5 °C) with a circulating water bath. Spectrometric determinations were performed with a Perkin-Elmer Model 552 UV/VIS spectrophotometer. All procedures were carried out in dim red light.

For determination of the quantum yields of photoaquation (Φ_{rx}) as a function of [I⁻] at pH 9.3 (0.008 M Britton–Robinson buffer), argon-purged solutions of $Cr(bpy)_3^{3+}$ at a concentration (1.6×10^{-4} M) chosen to insure complete absorption of the 313-nm radiation were photolyzed at 22 °C; the ionic strength was maintained constant at 1.0 M by use of NaCl/NaI mixtures.

Values of Φ_{rx} were determined spectrophotometrically; $\Phi_{rx} = 0.10$ for air-equilibrated solutions of $Cr(bpy)_3^{3+}$ in the absence of quencher under identical conditions was taken[9] as the actinometric standard. The thermal component[10] of the aquation process was negligible. Photolyses were carried out to ~10% decomposition of substrate.

The pH dependence of Φ_{rx} was obtained in the same manner as above in the presence of 0.15 M I⁻. Owing to the oxidation of I⁻ by O_2,[11] the preparation of the samples was carried out by the addition of enough solid NaI to previously argon-purged solutions of the appropriate pH to give 0.15 M I⁻. The temperature dependence of Φ_{rx} was determined at pH 9.6 in the presence of 0.15 M NaI and 0.85 M NaCl in the temperature range 15–40 °C.

Results

Figure 1 illustrates the dependence of Φ_{rx} on [I⁻] at 22 °C for $Cr(bpy)_3^{3+}$; plateau values of Φ_{rx} ($\sim 2 \times 10^{-3}$) are reached at [I⁻] > 0.1 M. At 0.5 M I⁻, Φ_{rx} diminishes further to 7×10^{-4} and reaches a value more than an order of magnitude lower at 1 M I⁻. The dependence of Φ_{rx} in the presence of 0.15 M I⁻ upon pH at 22 °C is shown in Figure 2. The values of Φ_{rx} at pH 9.6 in 0.15 M NaI and 0.85 M NaCl are temperature dependent and are given in Table I; for comparison, the values of Φ_{rx} in the absence of I⁻, adapted from a previous publication,[8] are also presented.

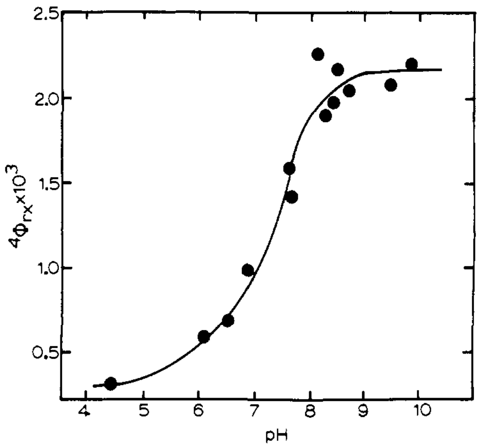

Figure 2. Φ_{rx} as a function of pH in the 313-nm photolysis of Ar-purged solutions of 1.6×10^{-4} M $Cr(bpy)_3^{3+}$ containing 0.008 M Britton–Robinson buffer and 0.15 M NaI at 22 °C; ionic strength controlled at 1.0 M with NaI and NaCl.

Table I. Quantum Yields of Photoaquation at 313 nm of $Cr(bpy)_3^{3+}$ as a Function of Temperature

	Φ_{rx}	
T, °C	in the absence of I⁻ [a]	in the presence of I⁻,[b] $\times 10^3$
6.3	0.089	
11.1	0.095	
15.2		1.7
22.0		2.4
22.1	0.12	
27.8	0.13	
28.9		4.2
32.6	0.12	
34.8		4.7
36.2	0.12	
40.4		6.7

[a] Values adapted from those given in ref 8 through reevaluation of the actinometric calibration. Experimental conditions: $\sim 1 \times 10^{-3}$ M $Cr(bpy)_3^{3+}$, pH 9.8, 0.008 M Britton-Robinson buffer, 1 M NaCl. Values of Φ_{rx} represent the average of two to four determinations (standard deviation ±10%). [b] Experimental conditions: 1.6×10^{-4} M $Cr(bpy)_3^{3+}$, pH 9.6, 0.008 M Britton-Robinson buffer, 0.15 M NaI and 0.85 M NaCl. Values of Φ_{rx} represent the average of two to four determinations (standard deviation ±15%).

It should be noted that the quenching of $^2T_1/^2E$ emission by I⁻ follows strictly Stern–Volmer kinetics. When suffficient I⁻ is added, the $^2T_1/^2E$ emission cannot be detected; no residual emission is ever seen under those conditions.

The value of the unquenchable quantum yield is independent of excitation wavelength between 313 and 435 nm.

Discussion

The fact that Φ_{rx} reaches a residual, unquenchable value at [I⁻] > 0.1 M indicates that this portion of the photoaquation reaction occurs from short-lived, presumably quartet, excited states. Under the conditions where the plateau values of Φ_{rx} are observed, $^2T_1/^2E$ is quenched to greater than 99.99%. Thus, for $Cr(bpy)_3^{3+}$, which exhibits[9] $\Phi_{rx} = 0.13$ in the absence of I⁻, the maximum quantum yield from unquenched $^2T_1/^2E$ would be $\sim 1 \times 10^{-5}$. The unquenchable portion of the quantum yield ($\sim 2 \times 10^{-3}$) constitutes ~2% of the total yield under identical conditions of temperature, pH, and ionic strength. For further discussion, we will designate the unquenchable quantum yield as $^4\Phi_{rx}$ and the total quantum yield in the absence of I⁻, which represents photoreaction that occurs due to population of $^2T_1/^2E$ from the short-lived states, as $^{4\rightarrow 2}\Phi_{rx}$. The further diminution of $^4\Phi_{rx}$ at [I⁻] ≥ 0.5 M may be due to the quenching of the short-lived quartet state by I⁻,

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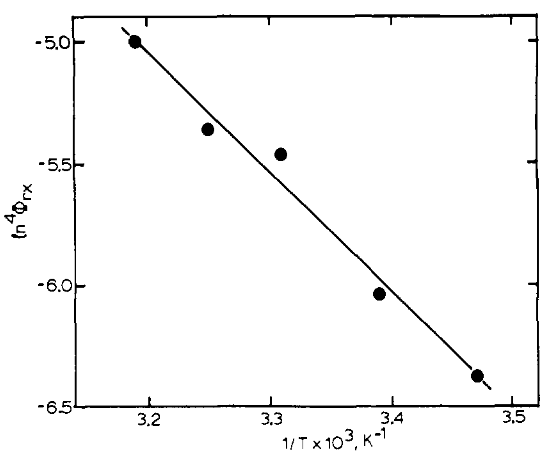

Figure 3. Plot of $\ln {}^4\Phi_{rx}$ vs. $1/T$.

possibly by a static, ion-pairing mechanism.

The fact that $^4\Phi_{rx}$ and $^{4\to2}\Phi_{rx}$ show the same pH profile (as well as the same as for the rate constant of the thermal aquation reaction)[10] argues strongly for the existence of a common intermediate that renders the overall reaction efficient in alkaline solution and inefficient in acidic solution. If it is accepted that the common intermediate is $Cr(bpy)_3(H_2O)^{3+}$, then it must be true that photochemical reactions from long-lived $^2T_1/^2E$ and short-lived quartet excited states (as well as thermal reaction from $^4A_2$) are mechanistically indistinguishable except for the efficiencies and temperature dependences of formation of the intermediate.

With regard to the latter point, a plot of $\ln {}^4\Phi_{rx}$ vs. $1/T$ (Figure 3) yields an apparent activation energy of 9.6 kcal mol^{-1} while a similar plot for $^{4\to2}\Phi_{rx}$ yields a value of 1.9 kcal mol^{-1}. If the common intermediate is a ground-state species irrespective of its origins and all subsequent deprotonation and ligand labilization reactions are the same, then the difference in the temperature dependences of $^4\Phi_{rx}$ and $^{4\to2}\Phi_{rx}$ must arise from reactions that lead to the intermediate. Such reactions would have to be the interaction of excited states with the solvent to form the intermediate or back intersystem crossing from $^2T_1/^2E$ to $^4T_2$ in competition with other modes of decay. It is the nature of the quantum yield of a photochemical reaction, which reflects the cumulative steps of the mechanism leading to the final products, not to reflect the temperature dependence of any steps that occur quantitatively irrespective of the activation energy of those steps. Therefore, the temperature dependences of $^4\Phi_{rx}$ and $^{4\to2}\Phi_{rx}$ must arise from mechanistic steps that are different and in competition with nonproductive reactions. The efficiency of any one of the steps leading ultimately to product can be expressed in terms of a ratio of rate constants of the competing reactions; the temperature dependences of these competing reactions lead to the temperature dependence of the quantum yield. At the same time it must be noted that prompt processes occurring from Franck–Condon states are, almost certainly, temperature independent.[12] One is left with an intriguing paradoxical possibility: could it be that reactions of high-energy, highly distorted $^4T_2$ have higher activation energies than those of low-energy, undistorted $^2T_1/^2E$? Or are the temperature effects the result of the energy gap between $^4T_2$ and $^2T_1/^2E$ that must be overcome upon back intersystem crossing?

In order to attempt to resolve these questions, we will examine the various models in detail.

A. $^4\Phi_{rx}$ from $^4T_2$. Let us assume that the unquenchable photoaquation originates from the $^4T_2$ state, which is populated with unitary efficiency from the initially excited Franck–Condon states via vibrational relaxation. Let us further assume that $^4T_2$ undergoes reaction with the solvent in competition with nonradiative decay to $^4A_2$ and intersystem crossing to the doublet manifold. With regard to the fate of $Cr(bpy)_3(H_2O)^{3+}$, we will take the pH dependences of $^4\Phi_{rx}$ and $^{4\to2}\Phi_{rx}$ (as well as the rate constant of the thermal aquation reaction) as representing the titration of that species so that deprotonation is quantitatively accomplished at pH 9.6. Our argument that $Cr(bpy)_3(OH)_2^+$ converts rapidly, quantitatively, and irreversibly to $Cr(bpy)_2(OH)_2^+$ rather than returning to $Cr(bpy)_3^{3+}$ is based on the following facts: (1) OH^- is a much stronger base than is bpy so that labilization of coordinated OH^- would be significantly less probable than labilization of one end of coordinated bpy; replacement of coordinated OH^- by open-ended bpy would be extremely unlikely; (2) formation of $Cr(bpy)_2(OH)_2^+$ occurs within the time frame of the decay of $^2T_1/^2E$ ($\tau \sim 70$ μs);[4] (3) direct reaction of $^2T_1/^2E$ with OH^-, which presumably proceeds via the deprotonated intermediate, yields a value of the quantum yield that approaches unity at high $[OH^-]$.[13]

Reactions 1–7 summarize the mechanism.

$$Cr(bpy)_3^{3+} \xrightarrow{h\nu} {}^4T_2 \qquad I_a \tag{1}$$

$$^4T_2 \rightarrow {}^4A_2 \qquad {}^4k_{nr} \tag{2}$$

$$^4T_2 \rightarrow {}^2T_1/^2E \qquad {}^4k_{isc} \tag{3}$$

$$^4T_2 \xrightarrow{H_2O} Cr(bpy)_3(OH_2)^{3+} \qquad {}^4k_{rx} \tag{4}$$

$$Cr(bpy)_3(OH_2)^{3+} \rightleftarrows Cr(bpy)_3^{3+} + H_2O \tag{5}$$

$$Cr(bpy)_3(OH_2)^{3+} \rightleftarrows Cr(bpy)_3(OH)^{2+} + H^+ \tag{6}$$

$$Cr(bpy)_3(OH)^{2+} \xrightarrow{OH^-} Cr(bpy)_2(OH)_2^+ + bpy \tag{7}$$

For reaction that occurs exclusively from $^4T_2$, $^4\Phi_{rx}$ is equal to $^4\eta_{rx}$, the efficiency of reaction from $^4T_2$, which can be written in terms of the rate constants of all processes out of that state. Thus, $^4\Phi_{rx} = {}^4k_{rx}/({}^4k_{rx} + {}^4k_{nr} + {}^4k_{isc})$. Inasmuch as $^4\Phi_{rx}$ is very small and the efficiency of intersystem crossing $({}^4\eta_{isc} = {}^4k_{isc}/({}^4k_{rx} + {}^4k_{nr} + {}^4k_{isc}))$ is ~ 1, $^4k_{rx}$ and $^4k_{nr}$ must be small compared to $^4k_{isc}$. This expression can now be written in terms of the classical kinetics formulation:

$$^4\Phi_{rx} = \frac{(kT/h)e^{\Delta S^*_{rx}/R}e^{-\Delta H^*_{rx}/RT}}{(kT/h)e^{\Delta S^*_{isc}/R}e^{-\Delta H^*_{isc}/RT}}$$

so that $\ln {}^4\Phi_{rx} = (\Delta S^*_{rx} - \Delta S^*_{isc})/R - (\Delta H^*_{rx} - \Delta H^*_{isc})/RT$, indicating that the linear plot of $\ln {}^4\Phi_{rx}$ vs. $1/T$ has a slope of $-(\Delta H^*_{rx} - \Delta H^*_{isc})/R$ and an intercept $= (\Delta S^*_{rx} - \Delta S^*_{isc})/R$. From the plot in Figure 3 (slope $= -4.90 \times 10^3$, intercept $= 10.6$), substitution leads to values of 9.6 kcal mol^{-1} for $(\Delta H^*_{rx} - \Delta H^*_{isc})$ and +21 cal deg^{-1} mol^{-1} for $(\Delta S^*_{rx} - \Delta S^*_{isc})$. It is clear that according to this model, $\Delta H^*_{rx} \geq 9.6$ kcal mol^{-1}. It can be argued that rapid intersystem crossing, being isoenergetic crossing from the quartet to the doublet manifolds and occurring in the picosecond time frame, has a zero or near zero value of ΔH^*_{isc}. If so, $\Delta H^*_{rx} = 9.6$ kcal mol^{-1}. It could also be argued that the large change in geometry that must occur when the system crosses from $^4T_2$ to $^2T_1/^2E$ leads to an energy barrier at the crossing point of the potential surfaces that could be substantial. At the present time, the exact energetics and degree of distortion of $^4T_2$ are unknown as are the kinetics parameters of its decay. Irrespective of the details of these conjectures, it remains a fact that this model demands a rather large value of ΔH^*_{rx} for the reaction of an excited, highly distorted state.

Hollebone and co-workers[12] have developed a tensorial model for mechanisms of the reactivity of coordination compounds. Two limiting cases were considered: (1) excited-state decay via random coordinate selection (DERCOS) and (2) excited-state decay on specific nuclear coordinates (DOSENCO). This latter case predicts that excitation of $Cr(bpy)_3^{3+}$ into the quartet manifold is rapidly accompanied by the t_{1u} buckle vibrational mode causing facial exposure of the central metal atom. The exposed Cr(III)

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[12] Hollebone, B. R.; Langford, C. H.; Serpone, N. *Coord. Chem. Rev.* **1981**, *39*, 181.

[13] Jamieson, M. A.; Serpone, N.; Hoffman, M. Z.; Sriram, R. 184th National Meeting of the American Chemical Society, Kansas City, Missouri, September 12–17, 1982; Abstract INOR185.

core on the stretched faces of the octahedron could be subjected to facile nucleophilic attack by the solvent leading to an associative reaction. The time frame for the DOSENCO process makes it competitive with vibrational relaxation down the quartet manifold. Indeed, DOSENCO decay may be the origin of the reactive mode and perhaps intersystem crossing from the quartet manifold.

B. $^{4\to2}\Phi_{\mathrm{rx}}$ from $^{2}\mathrm{T}_1/^{2}\mathrm{E}$. Efficient intersystem crossing, either prompt or delayed, from the quartet manifold populates the luminescent $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ states with a yield that is close to unity. If the quantum yield in the absence of I^- occurs primarily due to reaction of $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ in competition with radiative and nonradiative modes, eq 8–10 can be written:

$$^{2}\mathrm{T}_1/^{2}\mathrm{E} \rightarrow {}^{4}\mathrm{A}_2 \qquad {}^{2}k_{\mathrm{nr}} \tag{8}$$

$$^{2}\mathrm{T}_1/^{2}\mathrm{E} \rightarrow {}^{4}\mathrm{A}_2 + h\nu' \qquad {}^{2}k_{\mathrm{rad}} \tag{9}$$

$$^{2}\mathrm{T}_1/^{2}\mathrm{E} \xrightarrow{\mathrm{H_2O}} \mathrm{Cr(bpy)_3(OH_2)^{3+}} \qquad {}^{2}k_{\mathrm{rx}} \tag{10}$$

This sequence is followed by reactions 5–7 and the formation of the final aquation product. In a previous communication,[8] we reported the temperature dependence of the lifetime of $^{2}\mathrm{T}_1/^{2}\mathrm{E}$, which according to this model equals $1/(^{2}k_{\mathrm{nr}} + {}^{2}k_{\mathrm{rad}} + {}^{2}k_{\mathrm{rx}})$. Inasmuch as the quantum yield of luminescence from $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ is $\sim 10^{-3}$,[14] $^{2}k_{\mathrm{rad}} \ll (^{2}k_{\mathrm{nr}} + {}^{2}k_{\mathrm{rx}})$. Quantitative formation of the final aquation product dictates that $^{4\to2}\Phi_{\mathrm{rx}}$ is equal to the efficiency of reaction from $^{2}\mathrm{T}_1/^{2}\mathrm{E}$, $^{2}\eta_{\mathrm{rx}}$, which, in turn, is equal to $^{2}k_{\mathrm{rx}}/(^{2}k_{\mathrm{rx}} + {}^{2}k_{\mathrm{nr}})$. From the knowledge of $^{4\to2}\Phi_{\mathrm{rx}}$ as a function of temperature (Table I), one can extract $^{2}k_{\mathrm{rx}}$ as a function of temperature. The plot of ln $(^{2}k_{\mathrm{rx}}/T)$ vs. $1/T$ is linear with a slope corresponding to $\Delta H^{*}_{\mathrm{rx}} = 9.7$ kcal mol^{-1} and an intercept corresponding to $\Delta S^{*}_{\mathrm{rx}} = -11$ cal deg^{-1}/mol^{-1}.[8]

Inasmuch as $\Delta H^{*}_{\mathrm{rx}}$ from $^{4}\mathrm{T}_2$ could have a value of $\sim$9.6 kcal mol^{-1} from the model in section A, it is clear that the enthalpic barrier of activation toward reaction from $^{4}\mathrm{T}_2$ and $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ could be identical. It is also clear that the large difference in the values of the apparent activation energies of the quantum yields in the presence and absence of I^- may be totally illusory due to the fact that quantum yields reflect kinetic competitions among reactions with differing temperature coefficients. The apparent low activation energy of $^{4\to2}\Phi_{\mathrm{rx}}$ (1.9 kcal mol^{-1}) arises simply from $(\Delta H^{*}_{\mathrm{rx}} - \Delta H^{*}_{\mathrm{isc}})$ according to this model. Irrespective of the validity of the model, it must be pointed out that mechanistic conclusions based merely on the apparent activation energies of quantum yields may have limited utility.

C. Back Intersystem Crossing from $^{2}\mathrm{T}_1/^{2}\mathrm{E}$. The apparent similarities between the values of $\Delta H^{*}_{\mathrm{rx}}$ from both $^{4}\mathrm{T}_2$ and $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ according to the models in sections A and B immediately raise the question of whether *all* the observed photoreaction from $\mathrm{Cr(bpy)_3}^{3+}$ occurs from $^{4}\mathrm{T}_2$ with $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ being unreactive. Such a model requires $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ to engage in three decay paths: nonradiative (reaction 8), radiative (reaction 9), and back intersystem crossing (reaction 11). In this way the system passes many times

$$^{2}\mathrm{T}_1/^{2}\mathrm{E} \rightarrow {}^{4}\mathrm{T}_2 \qquad {}^{2}k_{\mathrm{bisc}} \tag{11}$$

through the reactive quartet leading to the observed quantum yield. The inherent lifetime of $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ would be equal to $1/(^{2}k_{\mathrm{rad}} + {}^{2}k_{\mathrm{nr}} + {}^{2}k_{\mathrm{bisc}})$. The total photoaquation quantum yield would be the sum of the immediate reaction from $^{4}\mathrm{T}_2$ ($^{4}\Phi_{\mathrm{rx}}$) as in section A and that resulting from passage of the system through $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ ($^{4\to2}\Phi_{\mathrm{rx}}$); $^{4}\Phi_{\mathrm{rx}} \ll {}^{4\to2}\Phi_{\mathrm{rx}}$. According to this mechanism, the system must pass through $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ approximately 50 times with each pass through $^{4}\mathrm{T}_2$, yielding a contribution to Φ_{rx} of $\sim 2 \times 10^{-3}$.

Before proceeding with the analysis, it is important to point out that reaction 8, the nonradiative decay of $^{2}\mathrm{T}_1/^{2}\mathrm{E}$, is an essential component of the mechanism in order to avoid the creation of a physically meaningless situation. With $^{4}\eta_{\mathrm{isc}} \sim 1$, the steady-state population of $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ is always maintained by very rapid reaction 3 in competition with inefficient reactions 2 and 4. Irrespective of the rate of reaction 11, if the only ultimate route of escape of $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ is via reaction 9 and the inefficient reactions 2 and 4 from $^{4}\mathrm{T}_2$, the quantum yield of luminescence would have to have a value close to unity. That is, clearly, not the case.

The scheme is now treated by using the approximation that during continuous irradiation the concentrations of $^{4}\mathrm{T}_2$ and $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ reach and remain at a steady state:

$$[^{4}\mathrm{T}_2]_{ss} = \frac{I_{\mathrm{a}} + {}^{2}k_{\mathrm{bisc}}[^{2}\mathrm{T}_1/^{2}\mathrm{E}]_{\mathrm{ss}}}{(^{4}k_{\mathrm{isc}} + {}^{4}k_{\mathrm{nr}} + {}^{4}k_{\mathrm{rx}})}$$

$$[^{2}\mathrm{T}_1/^{2}\mathrm{E}]_{\mathrm{ss}} = \frac{^{4}k_{\mathrm{isc}}[^{4}\mathrm{T}_2]_{\mathrm{ss}}}{(^{2}k_{\mathrm{rad}} + {}^{2}k_{\mathrm{nr}} + {}^{2}k_{\mathrm{bisc}})}$$

Noting that $^{4}k_{\mathrm{isc}} \gg (^{4}k_{\mathrm{rx}} + {}^{4}k_{\mathrm{nr}})$ because $^{4}\eta_{\mathrm{isc}} \sim 1$ and combining the equations, one obtains

$$[^{2}\mathrm{T}_1/^{2}\mathrm{E}]_{\mathrm{ss}} = \frac{I_{\mathrm{a}}}{^{2}k_{\mathrm{rad}} + {}^{2}k_{\mathrm{nr}}}$$

As above, irrespective of the value of $^{2}k_{\mathrm{bisc}}$ or its temperature dependence, the steady-state population of $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ is maintained by the high efficiency of the intersystem crossing reaction from $^{4}\mathrm{T}_2$. Since $^{2}k_{\mathrm{rad}} \ll {}^{2}k_{\mathrm{nr}}$, $[^{2}\mathrm{T}_1/^{2}\mathrm{E}]_{\mathrm{ss}} = I_{\mathrm{a}}/^{2}k_{\mathrm{nr}}$. The quantum yield of luminescence from $^{2}\mathrm{T}_1/^{2}\mathrm{E}$, $^{2}\Phi_{\mathrm{rad}}$, is seen to be equal to $^{2}k_{\mathrm{rad}}/^{2}k_{\mathrm{nr}}$. This latter statement predicts that a plot of ln $^{2}\Phi_{\mathrm{rad}}$ vs. $1/T$ yields a positive slope equal to $(\Delta H^{*}_{\mathrm{nr}} - \Delta H^{*}_{\mathrm{rad}})$. We know from the slope of such a plot[5] that this quantity equals 8.3 kcal mol^{-1}. Inasmuch as purely radiative decay will be temperature independent and will not have any activation enthalpy, $\Delta H^{*}_{\mathrm{nr}}$ from $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ is 8.3 kcal mol^{-1}.

Focusing now on $^{4\to2}\Phi_{\mathrm{rx}}$, which represents the yield of product via passage of the system to and from $^{2}\mathrm{T}_1/^{2}\mathrm{E}$, one writes $^{4\to2}\Phi_{\mathrm{rx}} = {}^{4}k_{\mathrm{rx}}[^{4}\mathrm{T}_2]_{\mathrm{ss}}/I_{\mathrm{a}}$. Substitution and rearrangement of the equations lead to the following general expression:

$$^{4\to2}\Phi_{\mathrm{rx}} = \frac{^{4}k_{\mathrm{rx}}}{\left[{}^{4}k_0 - \left(\dfrac{^{4}k_{\mathrm{isc}}{}^{2}k_{\mathrm{bisc}}}{^{2}k_{\mathrm{bisc}} + {}^{2}k_{\mathrm{nr}}}\right)\right]}$$

where $^{4}k_0 = 1/^{4}\tau = {}^{4}k_{\mathrm{isc}} + {}^{4}k_{\mathrm{rx}} + {}^{4}k_{\mathrm{nr}}$. One can see that if nonradiative decay of $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ predominates over back intersystem crossing so that $^{2}k_{\mathrm{bisc}} \ll {}^{2}k_{\mathrm{nr}}$, $^{4\to2}\Phi_{\mathrm{rx}} = {}^{4}k_{\mathrm{rx}}/^{4}k_0$, which is identical with the unquenchable yield that arises from $^{4}\mathrm{T}_2$ before the first passage to the doublet manifold. If, however, as pointed out above, nonradiative decay of $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ were an unimportant process compared to back intersystem crossing, $^{4\to2}\Phi_{\mathrm{rx}}$ would have a value of 1.

Inasmuch as $^{4\to2}\Phi_{\mathrm{rx}}$ for $\mathrm{Cr(bpy)_3}^{3+}$ has a value (0.13)[15] intermediate between the values of the unquenchable quantum yield ($\sim 2 \times 10^{-3}$) and unity, this model requires that nonradiative decay of $^{2}\mathrm{T}_1/^{2}\mathrm{E}$ and back intersystem crossing compete with each other. Let us express $^{2}k_{\mathrm{bisc}}$ and $^{2}k_{\mathrm{nr}}$ in terms of each other: $^{2}k_{\mathrm{nr}} = X(^{2}k_{\mathrm{bisc}})$, where X is a fraction that is temperature dependent, then

$$^{4\to2}\Phi_{\mathrm{rx}} = \frac{(1 + X)}{X}\,\frac{^{4}k_{\mathrm{rx}}}{^{4}k_{\mathrm{isc}}}$$

Recognizing that $^{4}k_{\mathrm{rx}}/^{4}k_{\mathrm{isc}}$ is what we have designated as $^{4}\Phi_{\mathrm{rx}}$ in section A above, we write

$$^{4\to2}\Phi_{\mathrm{rx}} = \frac{(1 + X)}{X}\,{}^{4}\Phi_{\mathrm{rx}}$$

Comparison of the quenchable and unquenchable quantum yields (Table I) shows that $^{4}\Phi_{\mathrm{rx}}/^{4\to2}\Phi_{\mathrm{rx}} \sim 10^{-2}$ so that $(1 + X) \simeq 1$. Thus, $X = {}^{4}\Phi_{\mathrm{rx}}/^{4\to2}\Phi_{\mathrm{rx}} = {}^{2}k_{\mathrm{nr}}/^{2}k_{\mathrm{bisc}}$. Now, both rate constants can be written in their expanded forms such that a plot of ln X vs. $1/T$ is predicted to be linear with a slope that equals $-(\Delta H^{*}_{\mathrm{nr}} - \Delta H^{*}_{\mathrm{bisc}})/R$. Taking interpolated values for all the data points in Table I and evaluating X leads to the plot in Figure 4. From

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[14] Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* **1980**, *84*, 887.

[15] Note that the previously reported[8] value of Φ_{rx} of 0.18 has already been corrected.[9]

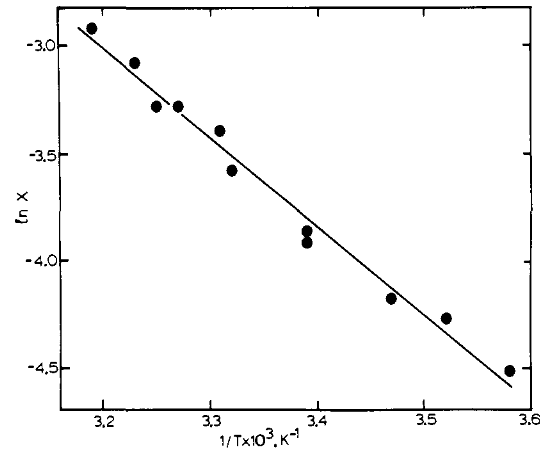

Figure 4. Plot of ln X vs. $1/T$.

the slope (-4.10×10^3) we evaluate ($\Delta H^{\ddagger}_{nr} - \Delta H^{\ddagger}_{bisc}$) to be 8.1 kcal mol^{-1}. Inasmuch as we evaluated above $\Delta H^{\ddagger}_{nr}$ from $^2T_1/^2E$ to be 8.3 kcal mol^{-1}, *we must conclude that the mechanism involving only quartet reactivity and back intersystem crossing from $^2T_1/^2E$ can be valid* only *if* $\Delta H^{\ddagger}_{bisc} \sim 0$.

While it is physically possible for there to be no enthalpic barrier to $^2T_1/^2E \rightsquigarrow {}^4T_2$ conversion, this requirement places severe restrictions on the relative energies and geometries of the states. It leads to the possibility that the zeroth energy level of $^4T_2$ lies *below* that of $^2T_1/^2E$ and that fluorescence from $^4T_2$, if it exists, is at longer wavelengths than emission from $^2T_1/^2E$. However, fluorescence has not been observed from Cr(bpy)$_3^{3+}$ in fluid solution or at low temperatures; in fact, no additional luminescence is observed at 740–1100 nm at 77 K upon excitation at $\lambda < 400$ nm.

Conclusions

From the temperature dependences of the quenchable and unquenchable quantum yields for the photoaquation of Cr(bpy)$_3^{3+}$, it does not appear necessary to invoke any reaction mechanism other than that in which the unquenchable yield arises out of the $^4T_2$ state and the quenchable yield comes from $^2T_1/^2E$ that have been populated from $^4T_2$ via rapid, efficient intersystem crossing. In order for all reactions to arise from $^4T_2$, populated after intersystem crossing via back intersystem crossing from $^2T_1/^2E$, the value of $\Delta H^{\ddagger}_{bisc}$ would have to be of the order of zero, thereby placing severe restrictions on the energy and distortion of $^4T_2$ relative to $^4A_2$ and $^2T_1/^2E$.

We continue to believe that the photoaquation of Cr(bpy)$_3^{3+}$ can be described by reactions 1–10. On the basis of the analysis of the data, $\Delta H^{\ddagger}_{rx}$ from $^4T_2$ is ≥ 9.6 kcal mol^{-1} and $\Delta H^{\ddagger}_{rx}$ from $^2T_1/^2E$ equals 9.7 kcal mol^{-1}; by assuming that $\Delta H^{\ddagger}_{isc}$ from $^4T_2$ has a zero or near-zero value, the conclusion is reached that reaction of the solvent with $^4T_2$ or $^2T_1/^2E$ to form the aquo intermediate has virtually the same enthalpic barrier. This comparison demonstrates that aside from the specific energetics of $^4T_2$ and $^2T_1/^2E$, the photoaquation activation mechanisms are identical. It could be argued that despite the distortion of $^4T_2$ relative to the ground and $^2T_1/^2E$ states, formation of the intermediate species requires a large degree of disruption of the structure of the ion and its associated solvent sheath to form the capped-octahedron or pentagonal-bipyramidal configuration.[16]

The positive value of ($\Delta S^{\ddagger}_{rx} - \Delta S^{\ddagger}_{isc}$) (+21 cal deg^{-1} mol^{-1}) for the reactions of $^4T_2$ indicates that $\Delta S^{\ddagger}_{rx}$ is more positive than $\Delta S^{\ddagger}_{isc}$. On the basis of the mechanism advocated here, $\Delta S^{\ddagger}_{rx}$ for $^2T_1/^2E$ is -11 cal deg^{-1} mol^{-1} [8] and $\Delta S^{\ddagger}$ for the thermal reaction from $^4A_2$ is -9 cal deg^{-1} mol^{-1};[10] these similar negative values are taken to indicate that addition of solvent to the geometrically similar $^4A_2$ and $^2T_1/^2E$ states forms a common intermediate. Since $^4k_0$ could have a value of $\sim 10^{11}$ s^{-1} [3] and $^4\Phi_{rx} \sim 2 \times 10^{-3}$, $^4k_{rx}$ could have a value of $\sim 10^8$ s^{-1}. In comparison, $^2k_{rx} = 1.6 \times 10^3$ s^{-1} for Cr(bpy)$_3^{3+}$ based upon this mechanism.[9] The factor of $\sim 10^5$ times greater reactivity of $^4T_2$ compared to $^2T_1/^2E$, there being similar values of $\Delta H^{\ddagger}_{rx}$ for both processes, must arise from differences in $\Delta S^{\ddagger}_{rx}$ from $^4T_2$ and $^2T_1/^2E$. If the rate constant factor is strictly entropic, then $\Delta S^{\ddagger}_{rx}$ from $^4T_2$ would be more positive than $\Delta S^{\ddagger}_{rx}$ from $^2T_1/^2E$ by ~ 23 cal deg^{-1} mol^{-1}. Thus, the driving force for the rapid reaction of $^4T_2$ would arise from the value of $\Delta S^{\ddagger}_{rx}$ of ca. +13 cal deg^{-1} mol^{-1}. Unlike reaction from $^4A_2$ and $^2T_1/^2E$, reaction from $^4T_2$ apparently involves an interaction with solvent to produce an activated complex that is more distorted than the $^4T_2$ and solvent reactants. Because the activated complex from $^4T_2$ must be of quartet multiplicity in order to satisfy an essential condition of the transition-state theory,[17] it must be distorted relative to the doublet activated complex from $^2T_1/^2E$. Such quartet-state distortion can permit a wide range of configurations in the activated complex. Intersystem crossing from this distorted quartet state into the doublet manifold would be accompanied by a tightening of the system and a negative value of $\Delta S^{\ddagger}_{isc}$; according to this analysis, $\Delta S^{\ddagger}_{isc} \sim -8$ cal deg^{-1} mol^{-1}.

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Registry No. Cr(bpy)$_3^{3+}$, 15276-15-0; iodide, 20461-54-5.

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