2502 *Inorg. Chem.* **1983**, *22*, 2502–2509

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Photochemical, Photophysical, and Thermal Behavior of the Tris(1,10-phenanthroline)chromium(III) Ion in Aqueous Solution

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Received October 22, 1982

The rate constant of the thermal aquation of $\mathrm{Cr(phen)_3^{3+}}$ (phen = 1,10-phenanthroline) has been determined as a function of pH and temperature; the quantum yield of the photoaquation has been evaluated as a function of excitation wavelength, as a function of pH in the presence of excited-state quenchers ($\mathrm{I^-}$, $\mathrm{O_2}$), and as a function of substrate concentration. The luminescence lifetime and intensity from the $^2T_1/^2E$ excited states have been measured as a function of pH, $[\mathrm{O_2}]$, $[\mathrm{I^-}]$, and $[\mathrm{Cr(phen)_3^{3+}}]$. The absorption spectrum of the $^2T_1/^2E$ excited states has been obtained; the decay of the absorption has been monitored as a function of temperature and solution medium. The thermal, photochemical, and photophysical behavior of $\mathrm{Cr(phen)_3^{3+}}$ in aqueous solution is very similar to that exhibited by $\mathrm{Cr(bpy)_3^{3+}}$ (bpy = 2,2′-bipyridine) and is interpreted in terms of analogous mechanistic steps. It is believed that excitation into spin-allowed states yields $^4T_2$, which undergoes very efficient intersystem crossing to $^2T_1/^2E$; these latter states can depopulate via nonradiative decay (including ground-state quenching) or interact with $\mathrm{H_2O}$ and $\mathrm{OH^-}$ to yield a $\mathrm{Cr(phen)_3(H_2O)^{3+}}$ intermediate, which is the direct precursor of the aquation products. Back intersystem crossing is not regarded as an important process. The thermal aquation of the ground state is visualized as occurring via the same intermediate. The relationship of the results reported here to photoracemization and thermal racemization observations in the literature is made.

Introduction

Polypyridyl complexes of transition metals have been extensively utilized as photosensitizers and electron-relay species in photochemical systems directed toward the conversion and storage of solar energy.[2] In view of this potential applicability in practical systems for the splitting of water,[3] for example, detailed knowledge of the ground- and excited-state properties of these complexes is required.

In previous studies we have thoroughly investigated the thermal,[4,5] photochemical,[6-9] and photophysical[7,10-17] behavior of $\mathrm{Cr(bpy)_3^{3+}}$ (bpy = 2,2′-bipyridine) as a function of temperature, pH, and solution medium. As part of the examination of the photophysics and photochemistry of polypyridyl complexes of Cr(III), $\mathrm{Cr(NN)_3^{3+}}$, in general,[18,19] we have also noted in the past some of the properties of $\mathrm{Cr(phen)_3^{3+}}$ (phen = 1,10-phenanthroline) as have other investigators.[20-25] In this paper we focus on this latter complex so as to derive a detailed picture of the ground- and excited-state behavior and to compare these details with those obtained for $\mathrm{Cr(bpy)_3^{3+}}$.

Experimental Section

Materials. Tris(1,10-phenanthroline)chromium(III) perchlorate was synthesized by a modification of the literature procedure.[26] In a $\mathrm{N_2}$-purged glovebag, a solution of 1.08 g (8.79 mmol) of $\mathrm{CrCl_2}$ dissolved in 150 mL of deoxygenated distilled water containing a few drops of 70% $\mathrm{HClO_4}$ was added to a solution of 5.17 g (26.1 mmol) of 1,10-phenanthroline hydrate in 50 mL of deoxygenated $\mathrm{CH_3OH}$. The resulting dark olive green mixture was stirred for 15 min, after which it was removed from the glovebag and $\mathrm{Cl_2}$ was bubbled through it for 40 min. Upon the addition of 2 mL of a saturated $\mathrm{NaClO_4}$ aqueous solution, a crude solid yellow product separated from the yellow solution. After filtration, the crude product was recrystallized from hot water containing a few drops of concentrated HCl. The hot solution was filtered, and the filtrate was allowed to cool in order to induce crystallization. Filtration and recrystallization yielded 4.3 g (53% yield) of $\mathrm{[Cr(phen)_3](ClO_4)_3{\cdot}2H_2O}$. Anal. Calcd for $\mathrm{CrC_{36}H_{28}N_6Cl_3O_{14}}$: C, 46.64; H, 3.04; N, 9.07. Found (Galbraith Laboratories): C, 46.93; H, 3.02; N, 9.11. The absorption spectrum of the complex is shown in Figure 1.

All chemicals used were reagent grade quality.

Apparatus. Details of the facilities for the determination of absorption spectra, emission spectra, pH, continuous-photolysis quantum yields, flash-photolysis transient absorption spectra, and excited-state emission and absorption lifetimes have been presented before.[7,15,18]

Procedures. All thermal aquation, photochemistry, and luminescence experiments were carried out in 0.008 M Britton–Robinson buffer[27] in the pH range 4.5–12.2; in more alkaline solutions for the thermal reactions, the buffer was absent. The complex concentration was in the range $(0.3\text{–}50) \times 10^{-4}$ M, and the ionic strength was adjusted to 1 M with NaCl. In the flash-photolysis experiments, which

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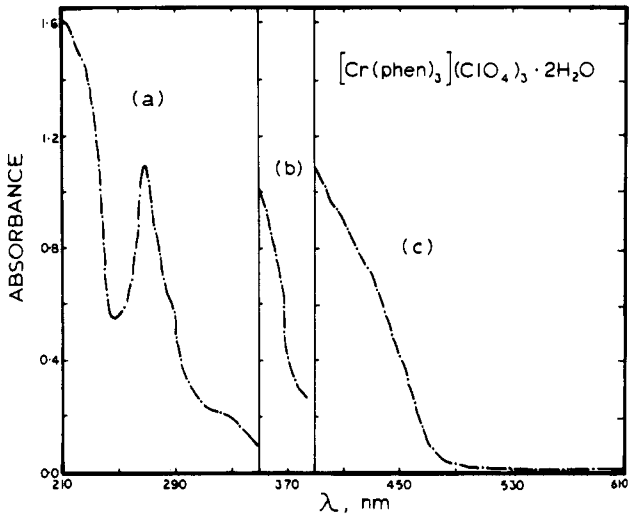

Figure 1. Absorption spectrum of $Cr(phen)_3(ClO_4)_3{\cdot}2H_2O$ in 0.1 M HCl (1-cm optical path length): (a) 1.7×10^{-5} M; (b) 2.1×10^{-4} M; (c) 1.1×10^{-3} M.

were conducted in a 22-cm Pyrex-jacketed cell, no buffer was used and the pH was regulated with $HClO_4$ or NaOH. Where appropriate, deoxygenation was achieved by the passage of a stream of purified N_2 through the solutions for at least 30 min. The thermal reactions were performed at 31.1 ± 0.1 °C in order to obtain reasonable rates, the continuous-photolysis and luminescence experiments at 15.0 ± 0.1 °C in order to reduce the thermal component and the flash-photolysis experiments at 22 ± 1 °C. Activation parameters were obtained through the variation of the temperature.

The thermal reaction was followed either by spectrophotometry or through the determination of the concentration of free phen released into the solution using an extraction procedure with *n*-heptane and absorbance calibration plots for each of the solution media used.

In the continuous-photolysis experiments, the reaction cell was filled with 3 mL of solution and placed in the thermostated cell holder of the irradiation apparatus. A sample of the solution was maintained in the dark at the same temperature in order to provide a control for the thermal component of the reaction and to serve as a reference for spectrometric measurements. During irradiation, the solution was stirred by bubbling N_2 or air, as appropriate. After suitable irradiation periods, the irradiated solutions were analyzed for the concentration of free phen. In all cases in which the quantum yield of reaction (Φ_{rx}) was determined (relative to ferrioxalate actinometry;[28] $I_0 \sim 10^{-6}$ einstein min^{-1}), the irradiation period was chosen so that <10% decomposition of $Cr(phen)_3^{3+}$ occurred. In the luminescence quenching experiments, weighed amounts of solid KI were added to the solution of the complex.

Results

Luminescence. In fluid solution at room temperature, $Cr(phen)_3^{3+}$ exhibits a relatively strong emission, which consists of two bands centered at 699 and 727 nm. These bands have been assigned to phosphorescence from the lowest doublet excited states, $^2T_1$ and ^2E, respectively.[22] Inasmuch as the lifetimes of the two emission bands are identical, the two doublet states are viewed as being in thermal equilibrium and will be designated hereafter as $^2T_1/^2E$.

Under all the experimental conditions used to determine the lifetime (τ_{obsd}) of $^2T_1/^2E$, the emission undergoes strictly first-order decay. The intensity of the emission determined at both 699 and 727 nm and its lifetime in air-equilibrated solution at 15 °C do not depend on pH in the range 4–11 (Figure 2), but they decrease about 10% at pH 12.2. However, it has been noted before[23] that the emission intensity in O_2-free solution is dependent on pH, decreasing from a plateau maximum in acidic solution to a lower plateau in alkaline solution with an inflection point at pH ~9; recently we have observed[29] that the lifetime of the emission in O_2-free solution, measured at 5 °C, follows the same profile.

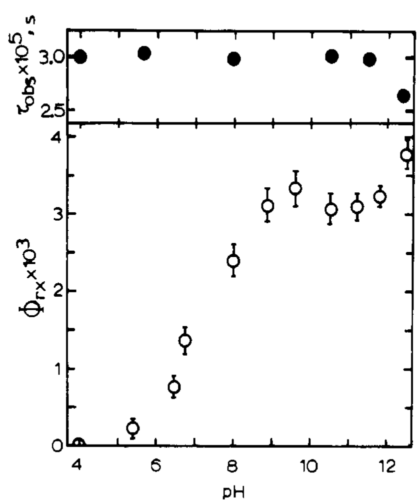

Figure 2. Dependence of Φ_{rx} (○) and τ_{obsd} (●) on pH for 1.2×10^{-3} M $Cr(phen)_3^{3+}$ in air-equilibrated solution at 15 °C containing 0.008 M Britton–Robinson buffer and 1 M NaCl.

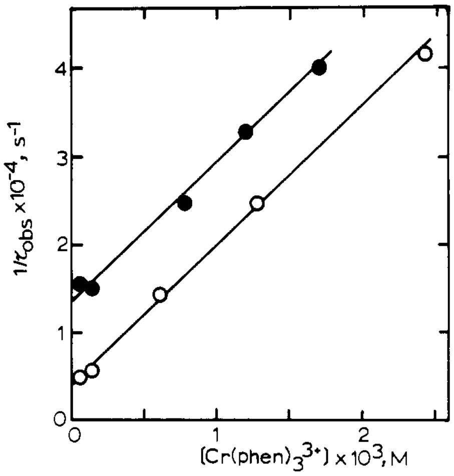

Figure 3. Dependence of τ_{obsd}^{-1} on $[Cr(phen)_3^{3+}]$ at pH 10.5 and 15 °C in deoxygenated (○) and air-equilibrated (●) solutions containing 0.008 M Britton–Robinson buffer and 1 M NaCl.

It is already known that emission intensity and lifetime depend on temperature[23] and $[Cr(phen)_3^{3+}]$[13,18] and are quenched by O_2 and I^-.[12,15,23] These effects have been observed again in this independent study. Figure 3 shows that $1/\tau_{obsd}$ ($=k_{obsd}$) increases linearly with $[Cr(phen)_3^{3+}]$ in both deaerated and air-equilibrated solutions containing 1 M NaCl. From the slope of the plots, we evaluate the ground-state quenching rate constant (k_g) at pH 10.5 and 15 °C to be $(1.6 \pm 0.1) \times 10^7$ M^{-1} s^{-1} in 1 M NaCl. Previously published values[18] of k_g for $Cr(phen)_3^{3+}$ at 22 °C in deoxygenated solutions are 3.0×10^6, 2.3×10^6, and 6.1×10^6 M^{-1} s^{-1} in 5 M HCl, 1 M HCl, and 1 M NaCl at pH 9.5, respectively. Our recent study[30] of the ground-state quenching of $(^2T_1/^2E)Cr(bpy)_3^{3+}$ in alkaline solution shows that k_g increases as pH is increased, and it is not unreasonable to expect the same phenomenon with $Cr(phen)_3^{3+}$; we regard the various values of k_g to be consistent. Extrapolation of the line for the deaerated solution in Figure 3 to $[Cr(phen)_3^{3+}] = 0$ yields the rate constant for

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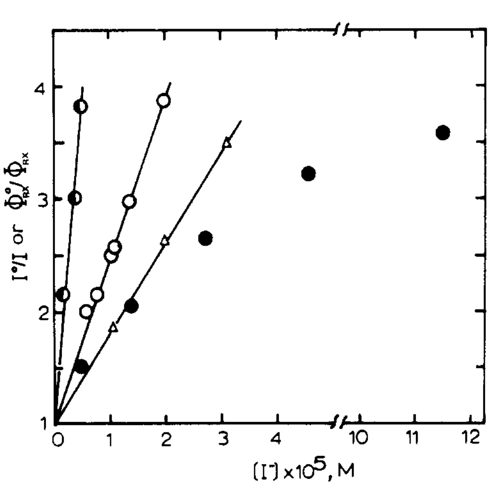

Figure 4. Stern–Volmer plots for the quenching of emission intensity (I) and Φ_{rx} by I^- at pH 10.5 and 15 °C in solutions containing 0.008 M Britton–Robinson buffer and 1 M NaCl: ◐, I^0/I for deoxygenated 1.0×10^{-4} M $Cr(phen)_3^{3+}$; ○, I^0/I for deoxygenated 1.1×10^{-3} M $Cr(phen)_3^{3+}$; △, I^0/I for air-equilibrated 1.1×10^{-3} M $Cr(phen)_3^{3+}$; ●, Φ_{rx}^0/Φ_{rx} for deoxygenated 1.1×10^{-3} M $Cr(phen)_3^{3+}$. Superscript zero refers to solutions without I^-.

the inherent decay of $^2T_1/^2E$ ($k_0 = (4 \pm 1) \times 10^3$ s^{-1}) corresponding to $\tau_0 = 0.25 \pm 0.09$ ms at pH 10.5 and 15 °C; at pH 9.5 and 22 °C, $\tau_0 = 0.23$ ms.[18] Taking $[O_2] = 3.0 \times 10^{-4}$ M for air-equilibrated solutions at 15 °C[31] and the data of Figure 3, we calculate the rate constant for the quenching of $^2T_1/^2E$ by O_2 (k_q) to be approximately 3×10^7 M^{-1} s^{-1}. We have reported a value of $k_q = 2.7 \times 10^7$ M^{-1} s^{-1} for the quenching of $^2T_1/^2E$ by O_2 in air-equilibrated solutions containing 1 M HCl at 25 °C. Figure 4 shows the linear Stern–Volmer plots that were obtained for the quenching of the emission intensity by I^- at pH 10.5. It must be noted that the slopes of the lines, corresponding to values of the Stern–Volmer constant (k_{SV}), are dependent upon the presence of O_2 and $[Cr(phen)_3^{3+}]$ inasmuch as $k_q = k_{SV}/\tau_{obsd}$. We find the value of $k_q(I^-) = (2.8 \pm 0.4) \times 10^9$ M^{-1} s^{-1}, independent of $[O_2]$ and $[Cr(phen)_3^{3+}]$; the corresponding value of $k_q(I^-)$ in 1 M HCl at 25 °C is 2.1×10^9 M^{-1} s^{-1}.[15] In all cases, emission lifetimes and intensities parallel each other.

Continuous Photolysis. Irradiations were performed by using light of 313-, 365-, and 404-nm wavelengths,[32] which primarily populate the lowest intraligand excited state, the spin-allowed $^4T_1$ ligand-field excited state, or the lowest energy spin-allowed $^4T_2$ excited state, respectively;[15] the stoichiometry of the photoreaction and the observed quantum yields were independent of the wavelength used. Irradiation of alkaline solutions of $Cr(phen)_3^{3+}$ causes spectral changes (Figure 5) characterized by isosbestic points at 222, 235, 256, 302, and 475 nm and by a small increase in absorbance at around 500 nm. In addition, free phenanthroline is detected in the irradiated solutions. The overall stoichiometry of the photoreaction is given in reaction 1; spectral changes are consistent with the

$$Cr(phen)_3^{3+} \xrightarrow[OH^-]{h\nu} Cr(phen)_2(OH)_2^+ + phen \qquad (1)$$

formation of the dihydroxy complex.[33] At pH 5–7, phenanthroline is again released upon irradiation, but different spectral changes are observed due to the protonation of the products.[33] At pH <5, small spectral changes are observed only after very long irradiation periods (greater than 5 h).

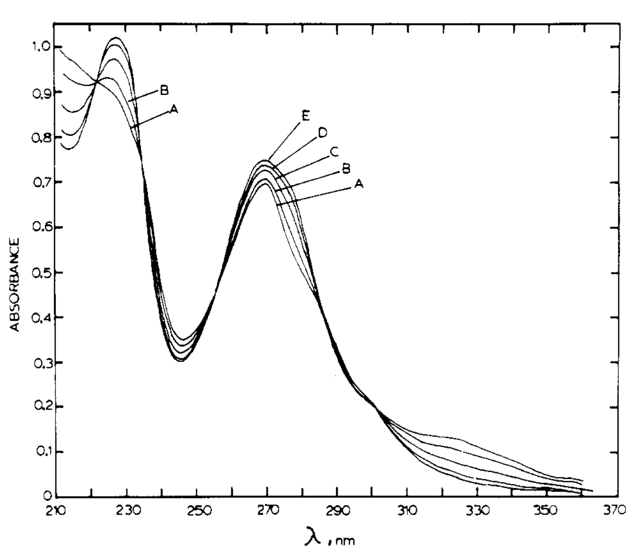

Figure 5. Spectral variations upon 365-nm irradiation of 2.2×10^{-5} M $Cr(phen)_3^{3+}$ at pH 10.4 and 15 °C in 0.008 M Britton–Robinson buffer and 1 M NaCl. Irradiation time: (A) 0 (unirradiated); (B) 8 min; (C) 20 min; (D) 40 min; (E) 180 min.

Table I. Quantum Yields for the Photoaquation of $Cr(phen)_3^{3+}$ at pH 10.5 and 15 °C

$[Cr(phen)_3^{3+}]$, mM	Φ_{rx}[a]	$[Cr(phen)_3^{3+}]$, mM	Φ_{rx}[a]
1.1[b]	0.0045	3.3[b]	0.0017
1.1[c]	0.0031	5.0[c]	0.0017

[a] Accuracy 10%. [b] Deoxygenated solution, N_2 purged. [c] Air-equilibrated solution.

At pH >5, the amount of phenanthroline released upon photolysis increases linearly with increasing irradiation time for more than 10% of photoreaction. The quantum yield of the photoreaction (Φ_{rx}) is independent of the wavelength of irradiation (313–404 nm) but is strongly dependent on pH as shown in Figure 2. The value of Φ_{rx} rises from a negligible value in acidic solution to a plateau in alkaline solution; a small but significant rise is seen at pH 12.5. The value of Φ_{rx} at constant pH is decreased due to the presence of O_2 and an increase in $[Cr(phen)_3^{3+}]$ as seen in Table I; previously published values[18] of Φ_{rx} in deaerated solutions at 22 °C containing 1 M NaCl and 1.5 mM $Cr(phen)_3^{3+}$ are 0.0005, 0.005, and 0.006 at pH 5.1, 9.2, and 10.4, respectively.

Reaction 1 is quenched by I^- but the Stern–Volmer plot for quantum yield (Φ_{rx}^0/Φ_{rx} vs. $[I^-]$; Figure 4) is not linear. A comparison of the quenching of emission intensity and quantum yield under the same experimental conditions (open and filled points in Figure 4) clearly shows that the extent to which the photoreaction is quenched by I^- is less than that exhibited by the emission intensity and, by extension, its lifetime. This effect is a common feature for many Cr(III) complexes and has been observed for the photoaquation of $Cr(bpy)_3^{3+}$[7] and the photoracemization of $(+)_{589}Cr(phen)_3^{3+}$.[21,23,24] The fact that the value of Φ_{rx} approaches a lower limit at high $[I^-]$ at which point the emission from $^2T_1/^2E$ has been completely quenched, a phenomenon well characterized in $Cr(bpy)_3^{3+}$,[34] is explained by there being two sources of reaction 1, one quenchable by I^- (and other doublet-state quenchers) and one unquenchable. Thus, $\Phi_{rx} = \Phi_u + \Phi_q$. A kinetic steady-state treatment of this model[35] yields the expression $\Phi_{rx} = \Phi_u + \Phi_q'(I/I^0)$, where Φ_{rx} is the observable quantum yield of pho-

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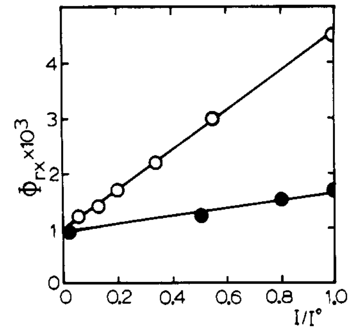

Figure 6. Plot of Φ_{rx} vs. I/I^0 (see text) for experiments in the presence of I^- at pH 10.5 and 15 °C in 0.008 M Britton–Robinson buffer and 1 M NaCl: ○, deoxygenated solutions containing 1.1×10^{-3} M $Cr(phen)_3^{3+}$; ●, air-equilibrated solutions containing 5.0×10^{-3} M $Cr(phen)_3^{3+}$.

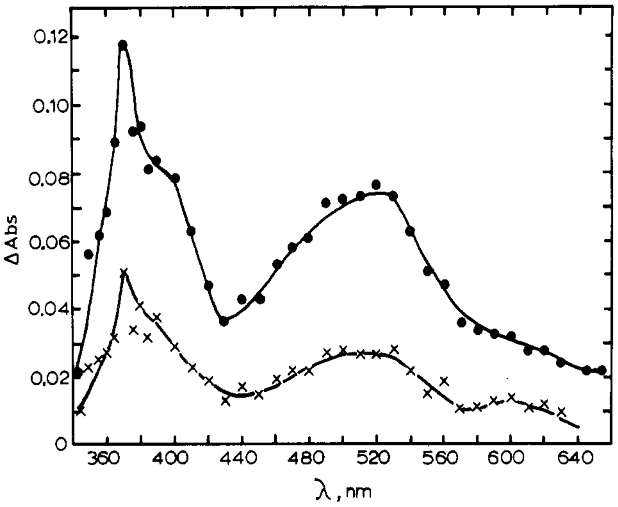

Figure 7. Absorption spectrum of $(^2T_1/^2E)Cr(phen)_3^{3+}$ from the Pyrex-filtered flash photolysis of deoxygenated 1×10^{-5} M $Cr(phen)_3^{3+}$ at pH 2.4 and 22 °C (22-cm optical path length): ●, spectrum measured 0.2 ms after the flash; ×, spectrum measured 0.5 ms after the flash.

toreaction, Φ_u is the quantum yield of the unquenchable photoreaction, Φ_q' is the quantum yield of the quenchable photoreaction in the absence of quencher (I^-), and I and I^0 are the intensities of the emission from $^2T_1/^2E$ in the presence and absence of quencher, respectively. Thus, a plot of Φ_{rx} vs. (I/I^0) is predicted to be linear; Figure 6 shows that this is so for both deaerated and air-equilibrated solutions at pH 10.5 and 15 °C. Both lines extrapolate to the same intercept, which yields the value of $\Phi_u = (1.0 \pm 0.2) \times 10^{-3}$, independent of $[O_2]$ and $[Cr(phen)_3^{3+}]$; the corresponding value of Φ_u for $Cr(bpy)_3^{3+}$ at 22 °C and pH 9.6 is 2×10^{-3}.[34] The slopes of the lines in Figure 6 represent Φ_q', the value of which is dependent upon the experimental conditions inasmuch as both O_2 and $Cr(phen)_3^{3+}$ quench $^2T_1/^2E$. The value of Φ_q' is expected to increase with decreasing $[Cr(phen)_3^{3+}]$, reaching its intrinsic value (Φ_q^0) at infinite substrate dilution; this phenomenon has been demonstrated for $Cr(NN)_3^{3+}$ in general.[18] The value of Φ_q^0 can be evaluated from the expression $\Phi_q^0 = \Phi_q'(\tau_0/\tau)$, where τ_0 is the intrinsic lifetime of $^2T_1/^2E$ and τ is the emission lifetime under the same experimental conditions (concentration of substrate) used to determine Φ_q. By using the Φ_q values from Figure 6 and values of τ known as a function of $[O_2]$ and $[Cr(phen)_3^{3+}]$, we evaluate the intrinsic quenchable quantum yield of photoaquation at infinite substrate dilution at 15 °C to be 0.018 ± 0.002; the corresponding value at 22 °C is 0.028.[18]

Flash Photolysis. Figure 7 shows the absorption spectrum obtained upon the flash photolysis of a deoxygenated solution of 1×10^{-5} M $Cr(phen)_3^{3+}$ at pH 2.4 (HCl). The absorption decayed completely to the base line, following excellent first-order kinetics with $k = (2.8 \pm 0.4) \times 10^3$ s^{-1} ($\tau = 0.36$ ms) at 22 °C. The decay of the absorption was accelerated at pH 11.4 ($k = 6.6 \times 10^3$ s^{-1}) and retarded in 11.7 M $HClO_4$ ($k = 1.5 \times 10^3$ s^{-1}). The absorption was significantly quenched by O_2 ($k_q = 3.5 \times 10^7$ M^{-1} s^{-1} at pH 2.2 in $HClO_4$) and SCN^- ($k_q = 1.0 \times 10^8$ M^{-1} s^{-1} at pH 2.7 in HCl). Permanent spectral changes were observed after the flash in alkaline solution corresponding to the formation of $Cr(phen)_2(OH)_2^+$, but no transient bleaching of the solution was observed at pH 5, as had been noted in the case of $Cr(bpy)_3^{3+}$.[7] The temperature dependence of the decay of the transient absorption at pH 3 ($HClO_4$) is shown in Figure 8, from which is derived an activation energy of 8.2 kcal mol^{-1}. Figure 8 also illustrates the temperature dependence of the transient decay in deoxygenated water at natural pH. The data show that the value of k is solution medium dependent but that the value of E_a remains unaffected.

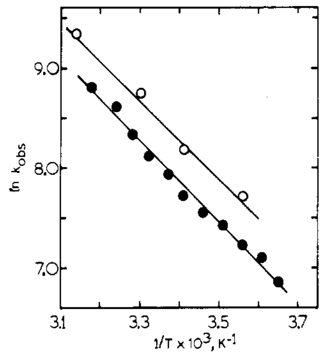

Figure 8. Arrhenius plot of the decay of $(^2T_1/^2E)Cr(phen)_3^{3+}$ in deoxygenated 0.001 M $HClO_4$ (●) and water at natural pH (○). Monitoring wavelength was 370 nm.

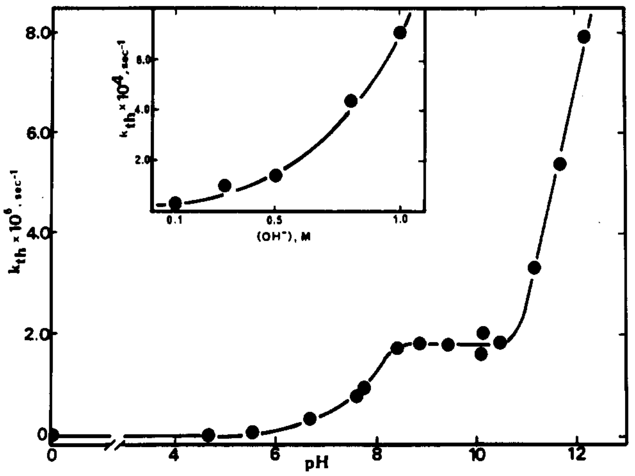

Figure 9. Plot of pH and [OH⁻] dependence of k_{th} for the thermal aquation of $Cr(phen)_3^{3+}$ at 31.1 °C. Ionic strength was controlled at 1 M with NaCl.

As in the case of $Cr(bpy)_3^{3+}$ and other $Cr(NN)_3^{3+}$ complexes,[7,15] comparison of the temporal behavior of the transient absorption and emission allows the flash-photolysis transient to be assigned as absorption by $^2T_1/^2E$. The value of E_a is very similar to the value obtained previously[23] from the temperature dependence of the intensity of emission from $^2T_1/^2E$.

Thermal Reaction. At pH ≤5, no spectral changes are observed nor is phenanthroline released into the solution. However, in more alkaline medium, thermal aquation is observed with the same stoichiometry as given in reaction 1. The spectral changes and isosbestic points are identical with those of the photochemical reaction (Figure 5). The value of the observed first-order rate constant of thermal aquation (k_{th})

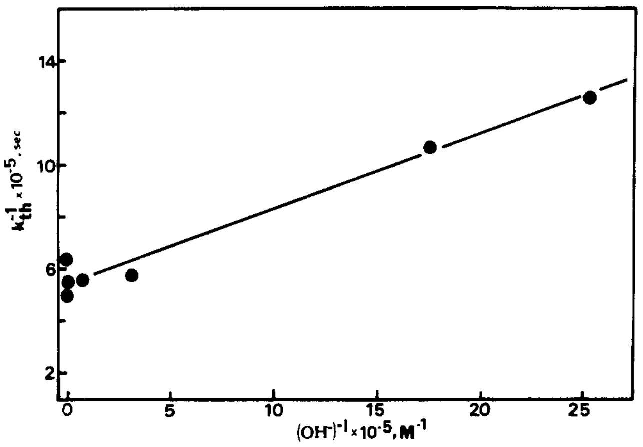

Figure 10. Dependence of k_{th}^{-1} on $[OH^-]^{-1}$ for the thermal aquation of $Cr(phen)_3^{3+}$ at 31.1 °C in the pH range 6.6–10.5. Ionic strength was controlled at 1 M with NaCl.

Table II. Activation Parameters for the Thermal Aquation of $Cr(phen)_3^{3+}$ [a]

	pH[b] 10.10[c]	pH[b] 12.17[d]	0.80 M NaOH[e]
E_a, kcal mol^{-1}	23.9 ± 0.7	22.2 ± 1.4	21.5 ± 0.4
$\Delta S^{\ddagger}_{298}$, cal deg^{-1} mol^{-1}	−8.4 ± 2.3	−10.6 ± 1.4	−5.4 ± 1.2
$\Delta H^{\ddagger}_{298}$, kcal mol^{-1}	23.3 ± 0.7	21.6 ± 1.4	20.9 ± 0.4
k_{th}, s^{-1} (298 K)	7.9×10^{-7}	4.3×10^{-6}	1.9×10^{-4}

[a] Ionic strength adjusted to 1.0 M with NaCl; standard errors are shown. [b] Solution contains 0.008 M Britton-Robinson buffer. [c] Temperature range 31.1–71.0 °C. [d] Temperature range 21.2–48.1 °C. [e] Temperature range 15.5–30.6 °C.

at 31.1 °C as a function of pH and, in very alkaline solution, $[OH^-]$ is illustrated in Figure 9. The pH dependence of k_{th} reveals four distinct regimes. At pH ≤5, k_{th} is very small with a value estimated as $<1 \times 10^{-8}$ s^{-1}. In the pH 6.6–10.5 range, $1/k_{th}$ is proportional to $1/[OH^-]$ (Figure 10) and follows eq 2. In the pH 11.1–12.2 range, k_{th} is linearly proportional to

$$k_{th}\ (s^{-1}) = \frac{[OH^-]}{2.8 \times 10^1 + 5.4 \times 10^5 [OH^-]} \qquad (2)$$

$[OH^-]$ (Figure 11, bottom) as described by eq 3. In the range

$$k_{th}\ (s^{-1}) = 3.2 \times 10^{-4}[OH^-] + 3.3 \times 10^{-6} \qquad (3)$$

$[OH^-]$ = 0.10–1.0 M, k_{th} is proportional to $[OH^-]^2$ (Figure 11, top), as described by eq 4. Temperature-dependence

$$k_{th}\ (s^{-1}) = 6.9 \times 10^{-4}[OH^-]^2 + 3 \times 10^{-6} \qquad (4)$$

studies of k_{th} in each of the three reactive regimes yield the activation parameters given in Table II.

Discussion

The thermal, photochemical, and photophysical behavior of $Cr(phen)_3^{3+}$ in aqueous solution is very similar to that observed for $Cr(bpy)_3^{3+}$ under similar experimental conditions.[4-17] The only significant difference between the two complexes is the magnitude of ground-state quenching of $^2T_1/^2E$ in 1 M NaCl; the effect is nil for $Cr(bpy)_3^{3+}$ but is of consequence for $Cr(phen)_3^{3+}$. This distinction is not due to differences in the chemistry of the complexes but, rather, to the relative lifetimes of $^2T_1/^2E$; the longer lifetime of $(^2T_1/^2E)Cr(phen)_3^{3+}$ renders it more susceptible to interactions with the solution medium.

Both $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ display patterns of behavior that demand specific analogous mechanistic interpretations: (1) the emission lifetime and photoreaction quantum yield are independent of the wavelength of excitation within the 313–436-nm region; (2) a very small portion (~5%) of the photoreaction cannot be quenched by I$^-$, an efficient doublet quencher; (3) despite the fact that the lifetime and intensity of emission are independent of pH in air-saturated solution (and only mildly dependent on pH in deoxygenated solution), the quantum yield of photoreaction is strongly dependent on pH; (4) the pH dependence of the quantum yield parallels the pH dependence of the rate of the thermal aquation reaction (pH ≤11); (5) in strongly alkaline solution, the rate of the thermal aquation reaction is greatly accelerated. The interpretation of the results reported in this paper will parallel that already given for $Cr(bpy)_3^{3+}$.

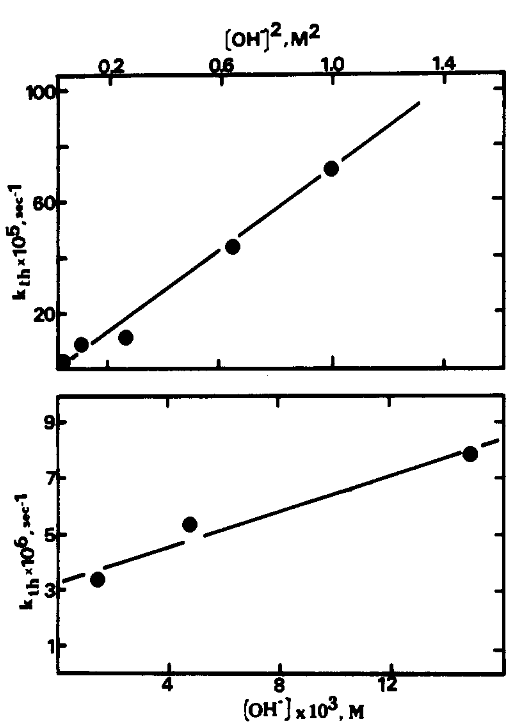

Figure 11. Bottom: Dependence of k_{th} on $[OH^-]$ for the thermal aquation of $Cr(phen)_3^{3+}$ in the pH range 11.1–12.2. Top: Dependence of k_{th} on $[OH^-]^2$ for the thermal aquation of $Cr(phen)_3^{3+}$ in 0.10–1.0 M OH$^-$. Temperature = 31.1 °C. Ionic strength was controlled at 1 M with NaCl.

Thermal Aquation. The dependence of k_{th} on pH (≤11) resembles a "titration" curve and argues that the rate-determining step involves nucleophilic attack by H_2O at the Cr(III) center (reaction 5) to form an intermediate that can undergo

$$Cr(phen)_3^{3+} + H_2O \rightleftharpoons Cr(phen)_3(H_2O)^{3+} \qquad (5)$$

deprotonation (reaction 6); in acidic solution, $Cr(phen)_3(H_2O)^{3+}$

$$Cr(phen)_3(H_2O)^{3+} \rightleftharpoons Cr(phen)_3(OH)^{2+} + H^+ \qquad (6)$$

is unstable with respect to re-formation of the substrate. Thus, the plateau region (pH 9–10.5) reflects the complete titration of $Cr(phen)_3(H_2O)^{3+}$ and strongly suggests that $Cr(phen)_3(OH)^{2+}$ quantitatively and irreversibly leads to loss of phen and the formation of the final product (reaction 7). In this case, k_{th} represents the rate constant for the

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

rate-determining attack of H_2O on $Cr(phen)_3^{3+}$. In the pH range 11.1–12.2, k_{th} is linearly dependent on $[OH^-]$, and the slope of the plot in Figure 11 (bottom) is identified with the rate constant for the direct nucleophilic attack of OH$^-$ on $Cr(phen)_3^{3+}$ ($k_8 = 3.2 \times 10^{-4}$ M^{-1} s^{-1}); the reverse of reaction 8 is rendered inoperative due to the quantitative nature of reaction 7.

$$Cr(phen)_3^{3+} + OH^- \rightleftharpoons Cr(phen)_3(OH)^{2+} \qquad (8)$$

In the [OH$^-$] range 0.10–1.0 M, where k_{th} varies linearly with [OH$^-$]^2, a plausible mechanism involves the formation of ion-pair aggregates between the substrate and OH$^-$ (reaction 9) that are attacked by OH$^-$ to form a seven-coordinate intermediate (reaction 10) followed by irreversible loss of phen to yield the final product (analogous to reaction 7).

$$\mathrm{Cr(phen)_3{}^{3+} + OH^- \rightleftarrows \{Cr(phen)_3{}^{3+},OH^-\}} \qquad (9)$$

$$\mathrm{\{Cr(phen)_3{}^{3+},OH^-\} + OH^- \rightleftarrows} \\ \mathrm{\{Cr(phen)_3(OH)^{2+},OH^-\}\ or\ Cr(phen)_2(phen-)(OH)_2{}^+} \qquad (10)$$

It should be noted that a [OH$^-$]^2-dependent path at pH >13 was observed in the reduction of Ru(bpy)$_3{}^{3+}$.[36]

A comparison of the activation parameters for the thermal aquation of Cr(phen)$_3{}^{3+}$ (Table II) with those of Cr(bpy)$_3{}^{3+}$ [5] indicates that a common mechanism is involved. The slight decrease in ΔH^* with increasing involvement of OH$^-$ is consistent with the greater nucleophilicity of OH$^-$ compared to H$_2$O and the resulting stronger Cr–OH bond (compared to Cr–OH$_2$) in the transition state leading to the intermediate. An associative mechanism is suggested by the negative values of ΔS^*; a strictly dissociative mechanism is expected to exhibit positive values of ΔS^*.[37] The variations in ΔS^* at pH 10.10 and 12.17 are, no doubt, within experimental error, but the less negative value in highly alkaline medium can be construed to arise from the somewhat more random structures possible in the transition state leading to the ion-paired aggregate seven-coordinate intermediate.

Photochemistry. The parallel between the thermal and photochemical behaviors argues for a common mechanism and, in particular, a common intermediate from which both the pH dependences of Φ_{rx} and k_{th} derive. Although an examination of the pH dependence of Φ_u was not performed in this study, the unquenchable quantum yield for Cr(bpy)$_3{}^{3+}$ follows the same pH profile[34] and is not unexpected for Cr(phen)$_3{}^{3+}$. This expectation finds support in the fact that Φ_u at pH 10.5 (1 × 10^{-3}) is higher than the total Φ_{rx} at pH 5.6 (2.3 × 10^{-4}). Thus, it appears that both the quenchable and the unquenchable quantum yields, which may or may not derive from different excited states (this point is discussed in the following section), as well as the thermal reaction, can be seen as proceeding through the same intermediate. In the photochemical process, reaction 11 replaces reaction 5; reaction −5 must still be operative.

$$\mathrm{{}^*Cr(phen)_3{}^{3+} + H_2O \rightarrow Cr(phen)_3(H_2O)^{3+}} \qquad (11)$$

$$\mathrm{Cr(phen)_3(H_2O)^{3+} \rightleftarrows Cr(phen)_3{}^{3+} + H_2O} \qquad (-5)$$

Reactions 6 and 7 serve as the source of the plateau of Φ_{rx} at pH 9–12. By analogy with reaction 8, it should be expected that Φ_{rx} will increase beyond the plateau in more alkaline medium through the involvement of reaction 12.

$$\mathrm{{}^*Cr(phen)_3{}^{3+} + OH^- \rightarrow Cr(phen)_3(OH)^{2+}} \qquad (12)$$

Figure 2 shows the start of such a rise. For Cr(bpy)$_3{}^{3+}$,[30] the rise is precipitous and, at 1 M NaOH, Φ_{rx} approaches unity. It is very likely that reactions analogous to eq 9 and 10 can be written for *Cr(phen)$_3{}^{3+}$. These observations reinforce the original proposal[7] that conversion of the deprotonated intermediate to product is quantitative, rapid, and irreversible.

The effect of [Cr(phen)$_3{}^{3+}$] on Φ_{rx} at pH 10.5 in 1 M NaCl is significant, as shown in Table I. In fact, at 3.3 mM substrate, Φ_u (1 × 10^{-3}) is greater than Φ_q (0.7 × 10^{-3}). It is predicted that at sufficiently high [Cr(phen)$_3{}^{3+}$], the value of Φ_{rx} will approach Φ_u. As has been shown previously,[7,18] the quenching of Φ_{rx} in general, and Φ_q in particular, can be directly linked to the quenching of ${}^2T_1/{}^2E$ by O$_2$, I$^-$, or the substrate.

Photophysics. The wavelength independence of τ_{obsd} and Φ_{rx} in the range investigated indicates that the spin-allowed excited states populated by the absorption of light deactivate to a common state with virtually unitary efficiency. The lowest spin-allowed excited state is ${}^4T_2$, which is taken as the starting point of the photophysical and photochemical schemes. The lifetime of ${}^4T_2$ is unquestionably very short with intersystem crossing to ${}^2T_1/{}^2E$ being the predominant pathway; the efficiency of intersystem crossing (η_{isc}), evaluated from direct doublet excitation,[14] is close to unity for both Cr(bpy)$_3{}^{3+}$ [10] and Cr(phen)$_3{}^{3+}$. Thus, both nonradiative decay to the ${}^4A_2$ ground state and prompt unquenchable photoreaction (Φ_u) are minor decay paths with the ${}^2T_1/{}^2E$ thermally equilibrated excited states being populated with almost unitary efficiency.

${}^2T_1/{}^2E$ luminesces with low efficiency ($\Phi_{rd} \sim 10^{-3}$),[15,38] competing with nonradiative decay to ${}^4A_2$ and other modes of deactivation. The question of whether ${}^2T_1/{}^2E$ are the reactive states or whether ${}^4T_2$, repopulated via back intersystem crossing, is the reactive state has been long standing in Cr(III) photochemistry,[39] with much evidence directed toward one position of another. Suffice it to say, the quenching of ${}^2T_1/{}^2E$ will be reflected in the values of Φ_{rx} irrespective of which mechanism is operative.

The photochemical behavior of Cr(bpy)$_3{}^{3+}$,[6–9] including the temperature dependence of the quenchable and unquenchable photoaquation reaction that has been determined recently,[34] finds its simplest explanation in the hypothesis that the quenchable part of the photoreaction takes place directly from ${}^2T_1/{}^2E$ with back intersystem crossing being an insignificant process. By extension, we believe that the same hypothesis is valid in the case of the similar Cr(phen)$_3{}^{3+}$ complex.

On the other hand, if ${}^4T_2$ is the reactive state with the system passing many times through ${}^2T_1/{}^2E$ via forward and back intersystem crossing and with the assumption that the Franck–Condon vibrational level of ${}^4T_2$ directly reached upon irradiation and the level indirectly populated via back intersystem crossing have the same efficiencies for reaction and intersystem crossing, a steady-state kinetic treatment leads to eq 13 and 14, where f is the ratio of $\Phi_q{}^0$ to Φ_{rx} ($=\Phi_u + \Phi_q{}^0$),

$$f = \eta_{isc}\eta_{bisc} \qquad (13)$$

$$k_{bisc} = \frac{1}{\tau_0}\,\frac{\eta_{isc}\eta_{bisc}}{1 - \eta_{isc}\eta_{bisc}} \qquad (14)$$

η_{bisc} is the efficiency of back intersystem crossing, and k_{bisc} is the rate constant of reaction 15. Using the values reported in this paper, we obtain $k_{bisc} \simeq 7 \times 10^4$ s^{-1} for Cr(phen)$_3{}^{3+}$ ($\simeq 2 \times 10^5$ s^{-1} for Cr(bpy)$_3{}^{3+}$).[7] If a preexponential factor of 10^{13} s^{-1} is assumed, the activation energy of k_{bisc} would be $\simeq$10 kcal mol^{-1}, a value far lower than expected on spectroscopic grounds, which would predict $E_a \simeq 20$ kcal mol^{-1}.[40]

$${}^2T_1/{}^2E \rightarrow {}^4T_2 \qquad (15)$$

According to the model proposed here, the quantum yield of formation of ${}^2T_1/{}^2E$ is essentially unity so that $\Phi_q{}^0 = k_{rx}\tau_0$ and $k_{nr} \simeq k_0 - k_{rx}$. From the data reported here at pH 10.5 and 15 °C, we evaluate k_{rx} to be 72 s^{-1} and k_{nr} as 3.9 × 10^3 s^{-1}; corresponding values reported[18] for pH 9.5 and 22 °C are 75 and 4.3 × 10^3 s^{-1}, respectively. Thus, in the absence of doublet quenchers, the decay of ${}^2T_1/{}^3E$ is primarily nonradiative with the temperature dependence reflecting k_{nr}. The flash-photolysis data from Figure 8, obtained under conditions where ground-state or other doublet quenching is negligible

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and plotted in the form ln (k_{obsd}/T) vs. $1/T$, yield $\Delta H^{*} = 7.9$ kcal mol^{-1} and $\Delta S^{*} = -16$ cal K^{-1} mol^{-1}; the corresponding values for $Cr(bpy)_3^{3+}$ are 8.0 kcal mol^{-1} and -12 cal K^{-1} mol^{-1}, respectively,[7] demonstrating that the difference in the rates of the nonradiative decays of the $^2T_1/^2E$ states lies in the entropic activation term. In $Cr(phen)_3^{3+}$, with its more rigid ligand structure, the solvent ordering upon formation of the activated complex along the nonradiative potential energy surface would be somewhat greater than for $Cr(bpy)_3^{3+}$.

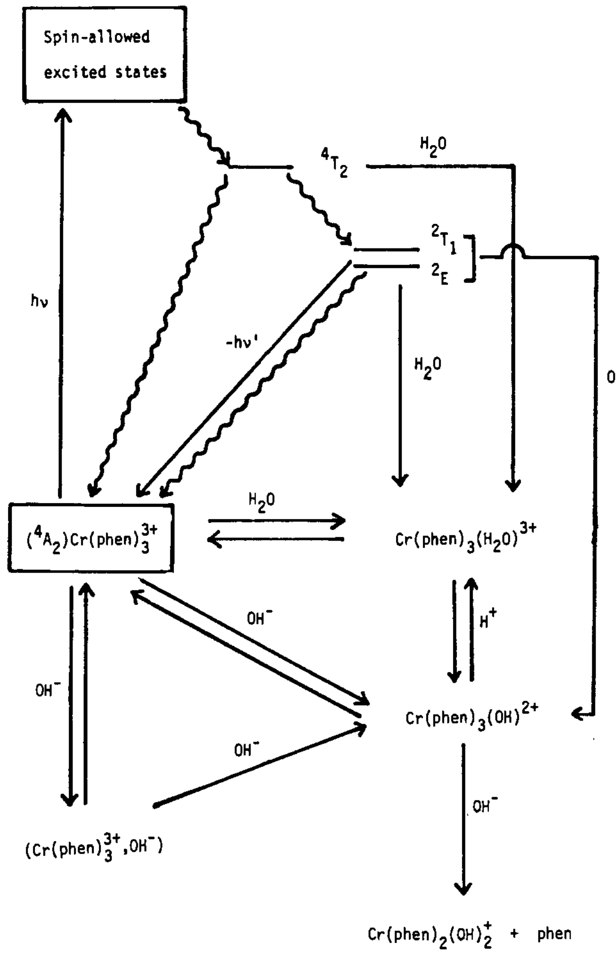
The absorption spectra of $^2T_1/^2E$ have been discussed before[7,15] in terms of doublet–doublet metal-centered transitions with some charge-transfer or ligand character. Flash photolysis decay of $(^2T_1/^2E)Cr(phen)_3^{3+}$ did not reveal transient ground-state bleaching at pH 5, as had been observed[7] for $Cr(bpy)_3^{3+}$. In the latter case, the repopulation of the ground state occurred with $[H^+]$-dependent and -independent kinetics. The $[H^+]$-independent rate constant (≤ 10 s^{-1}) was taken to represent the analogy to k_{-5}. In the case of $Cr(phen)_3^{3+}$, the quantum yield of formation of the $Cr(phen)_3(H_2O)^{3+}$ intermediate, even in the absence of any doublet quenching, is almost a factor of 10 lower than for $Cr(bpy)_3^{3+}$, thereby making the effect not detectable.

Relevance to Photoracemization and Thermal Racemization. $(+)_{589}Cr(phen)_3^{3+}$ undergoes a photoracemization reaction, which has been extensively studied by Langford and coworkers.[21,23,24] The quantum yield of photoracemization (Φ_{rac}) is quenched by O_2 and I^- to an unquenchable limit, increases with increasing pH, especially in alkaline solution, and decreases as the wavelength of excitation is increased across the first quartet absorption band (457.9–514.5 nm). On the basis of the temperature dependence of the quenchable and unquenchable photoracemization reaction, Langford concluded that $^4T_2$ is the reactive state that is thermally repopulated from $^2T_1/^2E$ by efficient back intersystem crossing.

Because of the difference in the mechanistic conclusions, it would be desirable to compare directly the photoracemization and photoaquation results for the same complex under similar conditions. Unfortunately, many of the conditions are explicitly not the same or have not been sufficiently specified so as to make a comparison. As one important example, 1 M NaCl was not present in the solutions for the Φ_{rac} determinations and, except when I^- was added, no solutes other than the substrate (as the Cl^- salt) were present. Therefore, it is likely that ground-state quenching was not an important component of $^2T_1/^2E$ decay in that case. As has been shown above, quenching by the substrate present in millimolar concentration decreases Φ_{rx} by about an order of magnitude from its intrinsic value. Nevertheless, it is quite clear that, in deaerated mildly acidic solution (pH 5.8), Φ_{rac} (0.037) is still significantly greater than Φ_{rx}. This point is less clear for mildly alkaline solution where the available Φ_{rac} data are for aerated conditions. It appears that Φ_{rac} and Φ_{rx} could have rather similar values under comparable conditions.

If we apply the hypothesis that the quenchable photoracemization and photoaquation reactions originate from $^2T_1/^2E$, the source of racemization could very well be the $Cr(phen)_3(H_2O)^{3+}$ intermediate. Racemization via a twist mechanism from $^2T_1/^2E$ can be discarded because these states are not distorted with respect to the ground state and such a reaction should be pH independent. Racemization upon the formation of the $Cr(phen)_3(H_2O)^{3+}$ intermediate would be expected to occur. Release of H_2O in acidic solution from $Cr(phen)_3(H_2O)^{3+}$ would result in racemization, but the aquation yield would be low; in alkaline solution, aquation would cause loss of optical activity. The sharp rise in Φ_{rac} at pH >10 could be the result of the direct attack of OH^- on $^2T_1/^2E$. We also wish to note that the ratio of unquenchable to total racemization does not depend upon pH,[23] suggesting that photoracemization from both $^4T_2$ and $^2T_1/^2E$ occurs through a common pH-dependent intermediate, as we have suggested for the photoaquation.

Scheme I



Similarly, $(+)_{589}Cr(phen)_3^{3+}$ undergoes loss of optical activity in a manner that parallels the thermal aquation reaction. Kane-Maquire and Edwards[41] found that the rates of these thermal reactions were the same at 40 °C in 0.45 M KOH. The activation parameters of the process in which optical activity is lost are virtually the same as those presented here in Table II for the aquation processes, to the extent that they can be compared. Both processes show the same dependence on $[OH^-]$. In fact, the rate law in both cases contains the same $[OH^-]$ and $[OH^-]^2$ terms. It is clear that thermal aquation and loss of optical activity proceed via the same mechanism. We must reject the twist mechanism for the same reasons cited above and suggest that the thermal processes occur via formation of the common intermediate.

Summary

Scheme I shows the thermal, photophysical, and photochemical pathways we propose for $Cr(phen)_3^{3+}$. Some details, such as ground-state quenching, aquation in acidic solution, and ion-pair aggregate intermediates, have been omitted for the sake of clarity.

Comparison of analogous data for $Cr(bpy)_3^{3+}$ shows that $Cr(phen)_3^{3+}$ has the following characteristics: slower thermal reaction, longer $^2T_1/^2E$ intrinsic lifetime, lower intrinsic photoaquation quantum yields, greater propensity for ground-state quenching in highly ionic media. Inasmuch as the redox properties of the two complexes are practically the

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same in both the ground and excited states,[15] it would appear that $Cr(phen)_3^{3+}$ is a better candidate for use as a photosensitizer than $Cr(bpy)_3^{3+}$ as long as the phenomenon of ground-state quenching of $^2T_1/^2E$ is recognized.

Acknowledgment. Financial support from the European Community, the National Research Council of Italy, the North Atlantic Treaty Organization (Grant No. 046.81), the Natural Sciences and Engineering Research Council of Canada (Grant No. A-5443), and the National Science Foundation (Grant No. CHE79-18013) is gratefully appreciated.

Registry No. $Cr(phen)_2(OH)_2^+$, 86409-84-9; $Cr(phen)_3^{2+}$, 15276-16-1; O_2, 7782-44-7; I^-, 20461-54-5.

Contribution from the Department of Chemistry,
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Infrared Matrix Isolation Study of the SO_2F^-, SOF_3^-, and $SO_2F_3^-$ Anions Ion Paired with Cs^+

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Received January 19, 1983

The salt/molecule reaction technique has been coupled with the matrix isolation technique for the synthesis of several novel sulfur oxyfluoride anions. Reaction of CsF with SO_2 in argon matrices gave rise to a series of absorptions assigned to the SO_2F^- anion, in agreement with literature spectra. ^{18}O isotopic data confirmed the equivalence of the two oxygen atoms in this product anion. Reaction of CsF with thionyl fluoride, SOF_2, gave rise to absorptions at 623, 667, 695, and 1264 cm^{-1}, which have been assigned to the four stretching vibrations of the novel SOF_3^- anion, in a C_s geometry. The reaction of CsF with sulfuryl fluoride, SO_2F_2, gave rise to five product bands, which have been assigned to the $SO_2F_3^-$ anion, with a structure analogous to the known ClO_2F_3 species. Identification of this anion supports the claim that pentacoordinate sulfur anions play a role in the solution chemistry of SO_2F_2.

Introduction

Little is known about the complex oxyfluoride anions of sulfur, despite their likely intermediacy in solution reactions.[1] Of the several possible anions of this type, the fluorosulfinate anion, SO_2F^-, is one of the best characterized,[2–4] as it forms a stable solid at room temperatures with a variety of alkali metal cations. Thionyl fluoride, SOF_2, is known to exhibit some Lewis acid character through involvement of the sulfur d orbitals,[1] but there is no mention in the literature of the anion formed through fluoride ion addition, namely SOF_3^-. However, the isoelectronic chlorine analogue, $ClOF_3$, is well-known[5] and lends credence to the idea that the SOF_3^- anion should be stable. Sulfuryl fluoride, SO_2F_2, is known to be attacked by nucleophiles in solution, and a pentacoordinated intermediate anion has been postulated.[1] The fluoride ion addition to SO_2F_2 to form the $SO_2F_3^-$ anion has been studied in the gas phase by ion cyclotron resonance spectroscopy,[6,7] and the fluoride ion affinity of SO_2F_2 has been bracketed between 36 and 46 kcal/mol. However, this anion has never been isolated at room temperature and spectroscopically characterized, although again the isoelectronic species ClO_2F_3 is well-known.[8]

It is likely that the anions SOF_3^- and $SO_2F_3^-$ can be formed under appropriate experimental conditions, in a manner similar to that of the better known SO_2F^- anion. Matrix isolation provides a means for the study of such reactive species,[9] and in particular fluoride-containing anions, through the salt/molecule reaction technique.[10–12] In this approach, CsF is vaporized from a high-temperature oven and codeposited with a suitable fluoride ion acceptor diluted in a large excess of argon. Fluoride ion transfer has been shown to occur, leading to anion formation in an ion pair with the Cs^+ cation. The technique, then, provides a direct means for the formation and characterization of the oxyfluoride anions of sulfur. Consequently, such an investigation was undertaken to spectroscopically characterize these unusual anions and determine their structure to the degree possible.

Experimental Section

The experiments conducted in the course of this investigation were all carried out on a conventional matrix isolation system, which has been described previously.[13] The gas-phase reactants, SO_2 (Matheson), SOF_2 (PCR Research Chemicals), and SO_2F_2 and $S^{18}O_2$ (95% ^{18}O, Cambridge Isotope), were purified by repeated freeze/thaw cycles under vacuum prior to sample preparation. The SOF_2 was found to contain a considerable fraction of SO_2, and while the sample was distilled on the vacuum line, complete separation could not be achieved, due to similarities in boiling point. However, since separate experiments were conducted with SO_2 alone, product bands due to the reaction of SOF_2 could readily be identified. $S^{18}O_2F_2$ was prepared through the direct reaction of $S^{18}O_2$ with F_2 in a stainless-steel vacuum line. Complete separation of the product $S^{18}O_2F_2$ from the reactant $S^{18}O_2$ was not possible; the residual $S^{18}O_2$ did provide some complications to the resulting experiment and obscured a few regions of the spectrum. CsF was loaded into a stainless-steel Knudsen cell and outgassed under a vacuum prior to the start of an experiment. An oven temperature of 500 °C was sufficient to provide a vapor pressure of 1 μm of CsF. TlF was handled in a similar fashion; water absorption and outgassing were not as severe a problem as with CsF. Argon was used as the matrix gas in all experiments and was used without further purification.

Matrix samples were codeposited at roughly 2 mmol/h for 20–24 h before final scans were recorded on a Beckman IR-12 infrared

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