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Photochemical Activity of Tris(2,2′-bipyridine)chromium(III) Ion in Acidic Aqueous Solution[1]

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The quantum yield (Φ) of photoaquation of $Cr(bpy)_3^{3+}$ in deaerated acidic aqueous solution at 22 °C has been measured as a function of pH (0–5), ionic strength (up to 1 M NaCl), and the presence of ClO_4^- (up to 1 M) and $H_2PO_4^-$ (up to 1 M). In the limit of high acidity, Φ reaches a plateau value of 0.007; Φ increases with increasing pH, ultimately reaching an upper plateau value of 0.18 at pH 9–10. Increasing the ionic strength of the acidic solution decreases Φ; the presence of ClO_4^- or $H_2PO_4^-$ also decreases Φ. The results indicate that the previously proposed mechanism for the photoaquation of $Cr(bpy)_3^{3+}$ must be modified to include (1) H^+-assisted formation of $Cr(bpy)_2(H_2O)_2^{3+}$ from $Cr(bpy)_3(H_2O)^{3+}$ ($k = 2 \times 10^4\ M^{-1}\ s^{-1}$), (2) $H_2PO_4^-$-assisted conversion of $Cr(bpy)_3(H_2O)^{3+}$ to $Cr(bpy)_3^{3+}$ ($k = 8 \times 10^3\ M^{-1}\ s^{-1}$), and (3) HPO_4^{2-}-assisted conversion of $Cr(bpy)_3(OH)^{2+}$ to $Cr(bpy)_2(OH)_2^+$ ($k \sim 8 \times 10^5\ M^{-1}\ s^{-1}$). The pseudo-first-order rate constant for the conversion of $Cr(bpy)_3(OH)^{2+}$ to products at pH 5 is estimated to be $\sim 2 \times 10^3\ s^{-1}$ and the pK_a of $Cr(bpy)_3(H_2O)^{3+}$ is estimated to be of the order of 5–6.

Introduction

In a recent publication,[2] we reported that the quantum yield of photoaquation (Φ) of $Cr(bpy)_3^{3+}$ at λ 313–464 nm is strongly pH dependent: $\Phi \sim 10^{-3}$ at pH 4.3 and 0.11 at pH 9.6 (air-saturated 1 M NaCl solutions buffered with phosphate at 11 °C). The value of Φ in alkaline (pH 9–10) solution is increased in the absence of air and with increase in temperature; $\Phi = 0.18$ (± 0.02) in deaerated solutions at room temperature.[3]

The low activity of $Cr(bpy)_3^{3+}$ toward photoaquation in acidic solution, a property that appears to be general for polypyridyl complexes of Cr(III),[4] is rationalized by Scheme I in which reaction I_a represents the excitation of the complex to the lowest energy ^2E excited state with unitary efficiency[2] via spin-allowed excited states and efficient intersystem crossing.[5] Inasmuch as the emission quantum yield[2] from the ^2E state is $<10^{-3}$, decay of ^2E is via competing reactive (reaction 1) and nonradiative (reaction 2) modes. The proposed seven-coordinate intermediate $Cr(bpy)_3(H_2O)^{3+}$ is believed to undergo deprotonation (reaction 5) which leads ultimately to the loss of bpy and the formation of the final product (reaction 6) in competition with $[H^+]$-dependent (reaction 4) and -independent (reaction 3) paths which re-form the substrate. Reaction 4 is the primary reaction leading to the relative stability, both photochemical[2] and thermal,[6] of $Cr(bpy)_3^{3+}$ in acid solution.

The photochemical behavior of $Cr(bpy)_3^{3+}$ in alkaline solution is extremely dependent on the nature of the solution medium;[7] the value of Φ is lowered in the presence of ClO_4^- and Cl^-. In this paper we examine in detail the photochemical activity of $Cr(bpy)_3^{3+}$ in acidic aqueous solution as a function of pH, ionic strength, and the presence of anions.

Scheme I

$$Cr(bpy)_3^{3+} \xrightarrow{h\nu} (^2E)Cr(bpy)_3^{3+} \qquad (I_a)$$

$$(^2E)Cr(bpy)_3^{3+} \xrightarrow{H_2O} Cr(bpy)_3(H_2O)^{3+} \qquad (1)$$

$$\rightarrow Cr(bpy)_3^{3+}\ \text{(nonradiative)} \qquad (2)$$

$$Cr(bpy)_3(H_2O)^{3+} \rightarrow Cr(bpy)_3^{3+} + H_2O \qquad (3)$$

$$\xrightarrow{H^+} Cr(bpy)_3^{3+} + H_2O \qquad (4)$$

$$\rightleftarrows Cr(bpy)_3(OH)^{2+} + H^+ \qquad (5)$$

$$Cr(bpy)_3(OH)^{2+} \xrightarrow[OH^-]{H_2O} Cr(bpy)_2(OH)_2^+ + bpy \qquad (6)$$

Experimental Section

Materials. $Cr(bpy)_3(ClO_4)_3 \cdot {}^1/_2H_2O$ was available from our previous work[2,7] with the compound. Spectral grade *n*-hexane was used for the bpy analysis. All other chemicals and reagents were of analytical grade.

Apparatus. Continuous photolyses were performed with a 200-W superpressure mercury lamp and a Bausch and Lomb high-intensity grating monochromator. Excitation was at 313 nm with a 10-nm band-pass. The photolyte was contained within a serum-capped 1-cm path length quartz spectrophotometer cell and was magnetically stirred. Incident light intensities were measured for individual runs with a solution of $Cr(bpy)_3^{3+}$ buffered at pH 9.5 as the reference actinometer which had been calibrated against ferrioxalate. Typical I_a values were $\sim 2 \times 10^{-4}$ einstein L^{-1} min^{-1}.

Flash photolysis experiments were performed in a Pyrex-jacketed 22-cm path length cell with the apparatus previously described.[2]

Procedures. Solutions were deaerated by using deoxygenated (Cr^{2+}-scrubbed) Ar or N_2 for 30 min prior to photolysis; in the continuous photolysis experiments, the bubbling was continued during the irradiations. Quantum yield measurements were made with at

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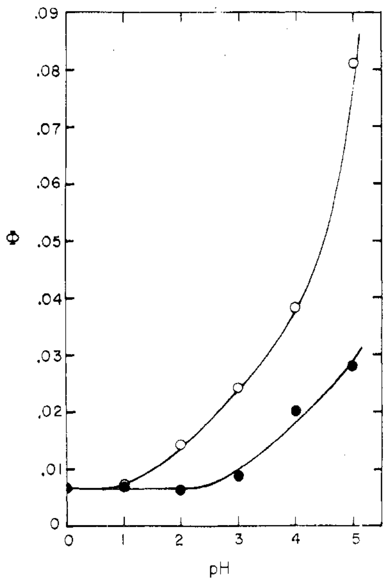


Figure 1. Quantum yield of photoaquation of $Cr(bpy)_3^{3+}$ as a function of pH in deaerated solution at 22 °C: ○, acidity adjusted with HCl (pH 0, 1) and $HClO_4$ (pH 2–5); ●, same but ionic strength adjusted to 1 M with NaCl or HCl. Irradiation wavelength is 313 nm.

Table I. Values of Φ in Aqueous Acidic Solutions at 22 °C[a]

	Φ	
pH	deaerated solution	air-saturated solution
0.0	0.0025	0.0011
1.1	0.0034	0.0019
2.0	0.014	0.011
3.0	0.024	0.021
4.0	0.038	0.027
5.1	0.081	0.061

[a] pH adjusted with $HClO_4$; ionic strength not controlled.

least 99% absorbance of the incident light for ≤10% destruction of the substrate. The pH of the solutions was controlled to ±0.02 pH unit. The experiments were performed at 22 °C unless otherwise noted. All solutions were freshly prepared from the solid complex; new aliquots were used for each flash and continuous photolysis experiment.

The quantum yields were calculated on the basis of the amount of bpy released into solution upon continuous photolysis. The photolyzed solutions were brought to pH ~10 with 0.1 M NaOH in order to deprotonate the free bpy which was then quickly extracted with *n*-hexane. In a typical experiment, 2.5 mL of ~1 × 10^{-4} M $Cr(bpy)_3^{3+}$ solution was photolyzed for 2 min, 2.0 mL of the photolyzed solution was neutralized with NaOH, and the mixture was shaken vigorously for 2 min with 5 mL of *n*-hexane. After 1 min, the organic layer was carefully transferred to a 1-cm spectrophotometer cell and the solution absorbance at 282 nm was measured against *n*-hexane as the reference. An aliquot of the photolyte solution was kept in the dark and carried through the same analytical procedure; no appreciable absorption at 282 nm was ever seen. The amount of free bpy released was calculated from a calibration plot derived from the quantitative extraction procedure. Duplicate and triplicate runs yielded values of Φ within ±10%.

Results

Continuous Photolysis. The value of Φ in acidic aqueous solution is dependent upon the pH and ionic strength of the solution and the presence of anions such as $H_2PO_4^-$ and ClO_4^-. Figure 1 shows the dependence of Φ on pH for deaerated solutions in which the ionic strength is not controlled (acidity adjusted with HCl at pH 0 and 1, and with $HClO_4$ at pH 2–5) and for solutions with ionic strength adjusted with HCl and NaCl to 1 M. In comparison, Φ = 0.18 ± 0.02 at pH 9.5 in the presence or absence of 1 M NaCl. As has been seen before in alkaline solution,[2,7] the presence of high concentrations of ClO_4^- diminishes the value of Φ; Φ = 0.0034 in 0.1 M $HClO_4$ (no NaCl present) and 0.0025 in 1.0 M $HClO_4$. In addition, the presence of O_2 causes a diminution in the value of Φ (Table I).

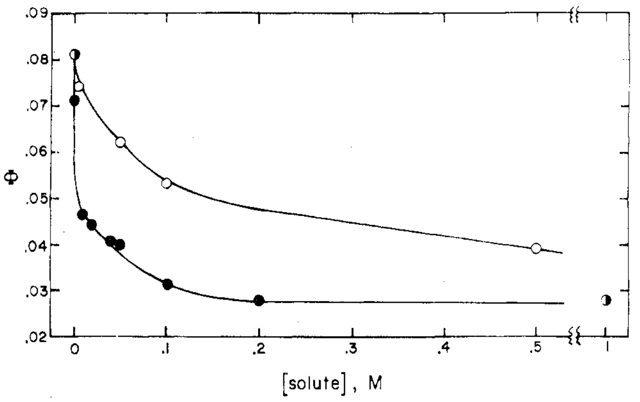


Figure 2. Quantum yield of photoaquation of $Cr(bpy)_3^{3+}$ as a function of the concentration of added solute (○, NaCl; ●, NaH_2PO_4) in deaerated solution at 22 °C and pH 5.0. Irradiation wavelength is 313 nm.

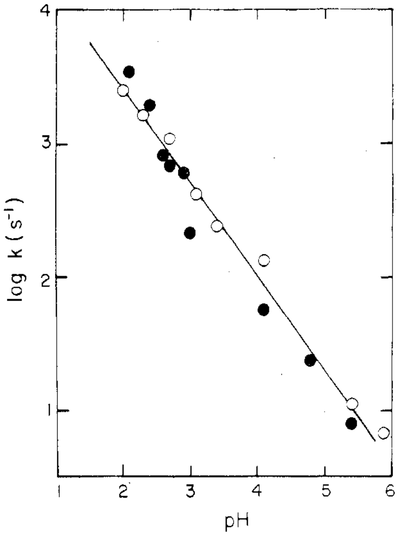


Figure 3. First-order rate constant for the decay of transient bleaching as a function of pH in the flash photolysis of deaerated solutions of: $Cr(bpy)_3^{3+}$ containing 1 M NaCl at 22 °C, ○; $Cr(bpy)_3^{3+}$ containing 1 M NaCl and 8 × 10^{-3} M total phosphate at 22 °C, ●. Monitoring wavelength is 365 nm. The line is drawn for the convenience of the eye.

A series of experiments were performed at pH 5.0 to test the dependence of Φ on ionic strength (adjusted with NaCl) and $[H_2PO_4^-]$. As Figure 2 shows, Φ diminishes with increasing [NaCl]; the effect of $H_2PO_4^-$ is even more marked with Φ = 0.071 and 0.046 at $[H_2PO_4^-]$ = 0.005 and 0.01 M, respectively.

Flash Photolysis. Absorption due to the ^2E state is seen upon the flash photolysis of $Cr(bpy)_3^{3+}$; it decays via pH-independent (up to pH 13) first-order kinetics (k = 1.6 × 10^4 s^{-1} at 22 °C in deaerated solution).[2] As described previously,[2] decay of ^2E in acidic solution results in transient bleaching of the solution in the 360-nm spectral region. The subsequent increase in the absorbance of the solution is via first-order kinetics; at pH <4 in solutions containing 1 M NaCl, the absorbance at $t = \infty$ is indistinguishable from that at t = 0. At pH >4, the extent of permanent bleaching of the solution increases smoothly with increasing pH; at pH 7, decay of ^2E results only in permanent bleaching. We had previously shown[2] that the first-order rate constant for the re-formation

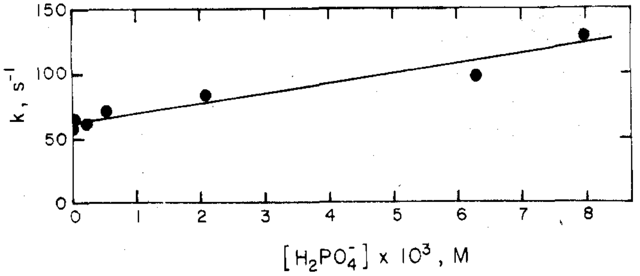


Figure 4. First-order rate constant for the decay of transient bleaching as a function of $[H_2PO_4^-]$ in the flash photolysis of deaerated solutions of $Cr(bpy)_3^{3+}$ containing 1 M NaCl at pH 4.0 and 21 °C. Monitoring wavelength is 365 nm.

of the solution absorbance from the transient bleaching was linearly dependent on $[H^+]$ (1×10^{-4}–5×10^{-3} M) with a slope of 4×10^5 M^{-1} s^{-1} in solutions containing 1 M NaCl. Figure 3 shows the rate constant data for solutions containing 1 M NaCl over an extended range of pH in the presence and absence of phosphate. Careful examination of the data reveals a small, but real, dependence of the first-order rate constant on $[H_2PO_4^-]$ in solutions containing 1 M NaCl at pH 4.0 (Figure 4); the slope of the least-squares line (correlation coefficient = 0.95) equals 8×10^3 M^{-1} s^{-1}.

The rate constant for the decay of the transient bleaching was measured as a function of temperature (0–22 ± 0.5 °C) for solutions containing 1 M NaCl from which values of E_a were derived from Arrhenius plots. At pH 2.1 and 3.1, E_a = 9.8 and 8.3 kcal mol^{-1}, respectively. In the presence of 8×10^{-3} M phosphate and 1 M NaCl at pH 5.5, E_a = 19.0 kcal mol^{-1}.

Discussion

Inasmuch as the quantum yield of formation[5] of ^2E is ~1, the limiting value of Φ in deaerated *alkaline* solution at 22 °C (0.18) represents the fraction of ^2E that ultimately produces final products via reactions 1, 2, 5, and 6; reaction 3 is very slow ($k_3 \leq 10$ s^{-1})[2] and reaction 4 ($k_4 = 4 \times 10^5$ M^{-1} s^{-1} at 22 °C in 1 M NaCl)[2] is operative only in acidic solution. If, as is believed,[2] reactions 5 and 6 quantitatively yield products in alkaline solution, then the limiting value of Φ must arise from a partitioning of ^2E according to reactions 1 and 2; $k_1/(k_1 + k_2) = 0.18$. Therefore, the quantum yield of formation of $Cr(bpy)_3(H_2O)^{3+}$ must be equal to 0.18 and must be independent of pH inasmuch as the lifetime of ^2E ($1/(k_1 + k_2)$) is pH independent. In air-saturated solutions ($[O_2] = 2.5 \times 10^{-4}$ M), ^2E is quenched by O_2 ($k_q = 1.7 \times 10^7$ M^{-1} s^{-1})[2] via primarily energy transfer[4,8] so that ~20% of ^2E is lost via that route; $Cr(bpy)_3(H_2O)^{3+}$ and its reactions are not affected by the presence of O_2.[2]

The fact that Φ reaches a lower limit at high acidity that extends over almost three pH units in the presence of 1 M NaCl indicates that a step must be added to the mechanism to account for the release of bpy from $Cr(bpy)_3(H_2O)^{3+}$ which parallels the $[H^+]$ dependence of reaction 4. Without such a dependence for the new reaction, the value of Φ would decrease as $[H^+]$ is increased according to Scheme I. Reaction 7 is the acidic analogue of reaction 6. One can visualize a

$$Cr(bpy)_3(H_2O)^{3+} \xrightarrow[H_2O]{H^+} Cr(bpy)_2(H_2O)_2^{3+} + bpyH^+ \qquad (7)$$

H^+-promoted release of one end of a coordinated bpy with the ultimate loss of the monodentate ligand. Such a mechanism is well-known for the acid-catalyzed aquation of $Fe(bpy)_3^{2+}$[9] and can give rise to a rate expression that is primarily first order in $[H^+]$. Therefore, reactions 4 and 7 can have the same dependence on $[H^+]$ so that the ratio of rate 4/rate 7 will maintain a constant value across at least three pH units. The limiting value of Φ in deaerated acidic solution containing 1 M Cl^- indicates that ~4% of $Cr(bpy)_3(H_2O)^{3+}$ disappears via reaction 7 under conditions where reactions 3, 5, and 6 are noncompetitive. Thus, $k_7/(k_4 + k_7) = 0.04$ so that $k_7 = 2 \times 10^4$ M^{-1} s^{-1}.

The effect of ClO_4^- on Φ at pH 0 and 1 can be attributed to the reduction in the quantum yield of formation of $Cr(bpy)_3(H_2O)^{3+}$ caused by a lowering of the value of k_1; k_2 is also lowered which results in the prolongation of the lifetime of ^2E.[7,10] Chloride does not exhibit such an effect except at concentrations significantly greater than 1 M.

The effect of the presence of air on Φ (Table I) at pH 2–5 is to cause a reduction in Φ averaging 22% showing that the effect can be attributed solely to the quenching of ^2E by O_2. The data in more acidic solution (0.1–1 M $HClO_4$) reflect the prolonged lifetime of ^2E in that medium[7,10] so that the fraction of ^2E quenched by O_2 is increased.

Increasing the ionic strength of the solution with NaCl diminishes Φ to a significant extent, particularly at low $[H^+]$ where the natural ionic strength of the solution is near zero. The direction of the effect is consistent with the ionic nature of reactions 4 and 7 and equilibrium 5; reactions between cations are accelerated upon an increase in ionic strength. At the same time, any reactions involving oppositely charged species, as could occur in some direct involvement of OH^- in reaction 6 and equilibrium 5, are retarded upon increase of ionic strength. Unfortunately, the relative contributions of these ionic reactions at pH 5, where the ionic strength effect is at a maximum, is not apparent although it is most likely that reaction 7 is no longer important.

In principle, the Φ data at constant 1 M ionic strength could be used to deduce values for the unknown rate and equilibrium constants. Unfortunately, the complexity of the scheme precludes an exact mathematical analysis of the mechanism at this time. However, if it is assumed, to a first approximation, that (1) the ratio of rate 4/rate 7 remains constant over the entire pH range, (2) the rate of reaction 6 remains constant over the pH range studied, and (3) equilibrium 5 is very rapid, then it can be readily shown that $\Phi_{calcd} = [\phi_a/(1 + K_5/[H^+]) + \phi_b/(1 + [H^+]/K_5)]$ where ϕ_a and ϕ_b are the acidic and basic limiting values of Φ (0.007 and 0.18, respectively). With $K_5 = 5 \times 10^{-6}$, the values of Φ_{calcd} at pH 0, 1, 2, 3, 4, and 5 are 0.007, 0.007, 0.007, 0.008, 0.02, and 0.06, respectively. Clearly, the observed and calculated values of Φ at pH 5 are not in accord. However, despite the oversimplicity of this treatment, it is probably not unreasonable to conclude that pK_5 is of the order of 5–6, depending upon the ionic strength of the solution. This value is well within the range for pK_a values of aquo complexes of trivalent metal centers[11] and lends credence to the proposal[2] that $Cr(bpy)_3(H_2O)^{3+}$ represents a seven-coordinate species with a water molecule coordinated to, rather than "closely associated with", the metal center.

The same value of k_4 (4×10^5 M^{-1} s^{-1}) is obtained from the data in Figure 3 at pH 2.0–3.4 in the presence or absence of phosphate; for H_3PO_4, pK_a = 2.0. Figure 4 shows that the conversion of $Cr(bpy)_3(H_2O)^{3+}$ to $Cr(bpy)_3^{3+}$ is accelerated by $H_2PO_4^-$ requiring the addition of reaction 8 to the

$$Cr(bpy)_3(H_2O)^{3+} \xrightarrow{H_2PO_4^-} Cr(bpy)_3^{3+} + H_2O \qquad (8)$$

mechanism where $k_8 = 8 \times 10^3$ M^{-1} s^{-1}. Clearly, reaction 8 does not compete with reaction 4 at low pH values under the conditions of the experiments in Figure 3 and can only be significant at low $[H^+]$. Thus, at pH 5, reaction 8 is competitive with reaction 4 at $[H_2PO_4^-] \geq 0.005$ M; the E_a data show that a new pathway has been introduced by the presence of phosphate. Reactions 4 and 8 demonstrate the general acid-catalyzed nature of the loss of H_2O from the seven-coordinate intermediate; both reactions may involve ephemeral protonation of the coordinated water with immediate loss of H_3O^+. Because reaction 8 involves oppositely charged ions, its inclusion in the mechanism introduces an effect of ionic strength opposite to that in the absence of phosphate. Irrespective of the intricacies of the ionic strength effect in solutions containing $H_2PO_4^-$ ($pK_a = 7.2$), the fact that Φ reaches an apparent lower limit at pH 5 at 0.2 M $H_2PO_4^-$ (Figure 2) means that the involvement of phosphate goes beyond reaction 8 which predicts that Φ should continue to decrease as $[H_2PO_4^-]$ is increased. One possible step involving $H_2PO_4^-$ is the analogue to reaction 7 in which $H_2PO_4^-$ promotes ring opening and loss by bpy. However, it is hard to visualize how that process could occur and yield a limiting quantum yield of 0.03; reaction 7 involving H^+, a much stronger acid than $H_2PO_4^-$, contributes only 0.007 to the quantum yield. We believe a more reasonable possibility is the involvement of HPO_4^{2-}, which is present to the extent of ~1% of the total phosphate at pH 5, in an analogue to reaction 6. The limiting value of Φ is achieved when $[HPO_4^{2-}] \sim 2 \times 10^{-3}$ M so that, taking into account the fact that HPO_4^{2-} is a much weaker base than OH^-, the factor of 10^6 difference in their concentrations could effect reaction 9. Therefore,

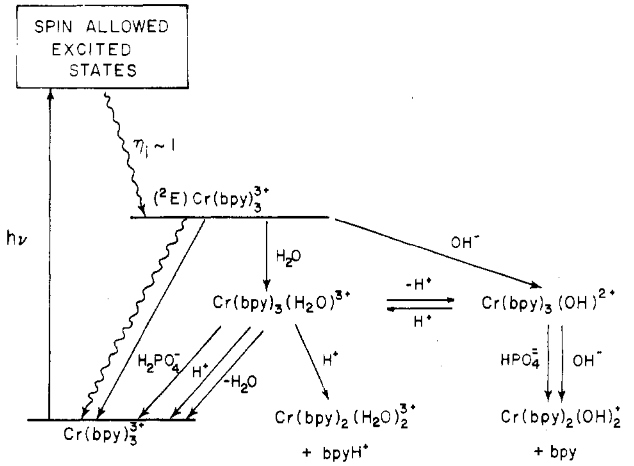
$$Cr(bpy)_3(OH)^{2+} \xrightarrow[HPO_4^{2-}]{H_2O} Cr(bpy)_2(OH)_2^+ + bpy \qquad (9)$$

as the total phosphate concentration is increased at constant pH, the $[H_2PO_4^-]/[HPO_4^{2-}]$ ratio remains constant so that, at some point, the competition of reactions 8 and 9 for the seven-coordinate acid–base pair reaches a constant level. That point occurs when $[H_2PO_4^-] \sim 0.2$ M and $[HPO_4^{2-}] \sim 2 \times 10^{-3}$ M so that if rate 8 = rate 9 and reaction 9 is first order in $[HPO_4^{2-}]$, $k_9 \sim 8 \times 10^5\ M^{-1}\ s^{-1}$. If at pH 5 the rate of reaction 6 is comparable to that of reaction 9 at the high-phosphate limit of Φ, the pseudo-first-order rate constant of reaction 6, k_6, is $\sim 2 \times 10^3\ s^{-1}$. The lifetime of reaction 6 calculated here is comparable to the value proposed earlier on the basis of the fact that the spectra of the final products are established within the decay of ^2E at pH ≥4.[2] Unquestionably, the rate of reaction 6 would also be accelerated as $[OH^-]$ is increased; however, the mechanistic details of reactions 6 and 9 are uncertain at this time.

Our present results at 22 °C in acidic deaerated solution containing 1 M NaCl are not inconsistent with those reported earlier[2] at 11 °C in acidic air-saturated solution containing 1 M NaCl and 8×10^{-3} M phosphate. The presence of air and phosphate causes a total reduction of ~60% in the value of Φ. Although the temperature dependence of Φ has not been determined in acidic solution as it has in alkaline solution,[3] if the major contribution toward minimization of Φ in the presence of phosphate is reaction 8 ($E_a = 19.0$ kcal mol^{-1}), then a reduction of temperature from 22 to 11 °C at pH 4–5 would cause a further lowering of Φ by a factor of 3–4. Therefore, from our data at pH 4 where $\Phi \sim 0.02$, we would predict that at 11 °C in air-saturated solutions containing 1 M NaCl and 8×10^{-3} M $H_2PO_4^-$, $\Phi \sim 0.002$.

Conclusions

Scheme II



The stability of $Cr(bpy)_3^{3+}$ toward photoaquation in acidic solution can be increased by (1) increasing the acidity of the solution, (2) increasing the ionic strength of the solution, (3) increasing the concentration of phosphate in the solution, especially at low acidities, (4) lowering the temperature of the solution, and (5) incorporating O_2 into the solution. In addition to the mechanism introduced previously,[2] steps are proposed for the (1) H^+-assisted formation of $Cr(bpy)_2(H_2O)_2^{3+}$ from $Cr(bpy)_3(H_2O)^{3+}$ ($k = 2 \times 10^4\ M^{-1}\ s^{-1}$), (2) $H_2PO_4^-$-assisted conversion of $Cr(bpy)_3(H_2O)^{3+}$ to $Cr(bpy)_3^{3+}$ ($k = 8 \times 10^3\ M^{-1}\ s^{-1}$), and (3) HPO_4^{2-}-assisted conversion of $Cr(bpy)_3(OH)^{2+}$ to $Cr(bpy)_2(OH)_2^+$ ($k \sim 8 \times 10^5\ M^{-1}\ s^{-1}$). The pseudo-first-order rate constant for the conversion of $Cr(bpy)_3(OH)^{2+}$ to products at pH 5 is estimated to be $\sim 2 \times 10^3\ s^{-1}$ and the pK_a of $Cr(bpy)_3(H_2O)^{3+}$ is estimated to be of the order of 5–6. The modified mechanism is summarized in Scheme II.

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Registry No. $Cr(bpy)_3^{3+}$, 15276-15-0.

References and Notes

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