planar units into dimers or extended chains) have been found for parallel-planar chloro- and sulfur-bridged copper complexes.[28] On the basis of the ϕ/R^0 quotient of 39.4 for the Cu_2O_2 unit in $Cu_2L(CH_3COO)_2{\cdot}2CH_3OH$, as compared to the corresponding values of 42.6 for the hippurato compound and 35.0 (mean value) for the $(L')^-$ derivative, it may be tentatively suggested that a J value of $-1.50\ cm^{-1}$, intermediate between those for the other two compounds, would not be inappropriate for the Cu_2O_2 unit in the present system.

Acknowledgment. O.P. thanks W.E.H. for his hospitality during his stay at The University of North Carolina at Chapel Hill.

Registry No. $Cu_2[(C_6H_5)(C_6H_4O)C{=}N(CH_2)_2NHCH_2-]_2(CH_3COO)_2{\cdot}2CH_3OH$, 84928-97-2.

Supplementary Material Available: Listings of the hydrogen atom coordinates and the observed and calculated structure factor amplitudes for $Cu_2L(CH_3COO)_2{\cdot}2CH_3OH$ (11 pages). Ordering information is given on any current masthead page.

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Pulsed-Laser Photochemical Study of Tris(2,2′-bipyridine)chromium(III) Ion in Acidic and Alkaline Aqueous Media

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Received August 10, 1982

The photochemistry and photophysics of tris(2,2′-bipyridine)chromium(III) ion, $Cr(bpy)_3^{3+}$, following pulsed-laser excitation at 347 nm, have been studied in acidic (pH 2.3–5.4) and alkaline (pH 9.4–11.0) aqueous media by using conductivity and visible optical detection methods. Evidence is presented to show that the lowest doublet excited state(s) is primarily responsible for chemical change, where in basic solution it accounts for about 93% of the photoaquation reaction. This state exhibits phosphorescence emission at 727 nm and an excited-state absorption band with a peak at 380 nm and a molar absorption coefficient of about 7000 $M^{-1}\ cm^{-1}$. The decay of the absorption band and that of emission obey first-order rate laws with the respective rate constants of 1.5×10^4 and $1.6 \times 10^4\ s^{-1}$. The concomitant change in conductivity also follows a first-order rate law ($k \simeq 1.8 \times 10^4\ s^{-1}$). In acidic media, the change involves an increase in conductivity associated with release of proton with a quantum yield of ca. 0.08. At longer times, the conductivity decreases, and this is described by a two-term rate law: $k_{obsd}(\text{acid}) = k_i' + k_a[H^+]$, with $k_i' = 39 \pm 9\ s^{-1}$ and $k_a = (8.7 \pm 0.4) \times 10^4\ M^{-1}\ s^{-1}$. In basic solution, the conductivity decreases in two stages and leads to net chemical change. The slower stage exhibits a two-term rate law: $k_{obsd}(\text{base}) = k_i + k_b[OH^-]$, with $k_i = 0.75 \pm 0.08\ s^{-1}$ and $k_b = (3.8 \pm 0.1) \times 10^3\ M^{-1}\ s^{-1}$. Two possible mechanistic interpretations of the results are presented, one of which invokes the participation of an electronically excited intermediate that undergoes acidic dissociation with a pK_a value less than 2.

Introduction

A number of studies have appeared within recent years on the photochemistry and photophysics of aqueous and nonaqueous solutions containing chromium(III) complex ions with nitrogen heterocyclic ligands, the premier example being tris(2,2′-bipyridine)chromium(III), $Cr(bpy)_3^{3+}$.[2-19] Interest in this and related systems derives both from the fundamental chemical and spectroscopic opportunities afforded by their study and from their relevance to solar energy conversion processes. Several excellent reviews have appeared recently covering these aspects.[2-4] The results reported here focus on the photoaquation reaction of $Cr(bpy)_3^{3+}$ where the overall process is in basic media

$$Cr(bpy)_3^{3+} + 2OH^- \xrightarrow{h\nu} Cr(bpy)_2(OH)_2^{+} + bpy \qquad (1a)$$

and in acidic solution

$$Cr(bpy)_3^{3+} + 2H_2O + H^+ \xrightarrow{h\nu} Cr(bpy)_2(H_2O)_2^{3+} + Hbpy^+ \qquad (1b)$$

The photochemical and photophysical details of this and related complex ions provide intriguing differences from those of the other major type of chromium(III) complex ions so far studied, namely systems with NH_3, amine, halogen, and pseudohalogen ligands. For $Cr(bpy)_3^{3+}$, the photoaquation quantum yield attains a maximum limiting value in base (Φ_{bpy}

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= 0.13, pH 9.3, deaerated) and considerably reduced values ($\Phi_{bpy} \leq 0.038$, pH ≤4.0) in acidic media.[2,11] In contrast, the amine complexes are generally found to be more reactive toward photosubstitution in acidic solutions. In part, this difference seems to be a reflection of the fact that hydroxide ion is not a particularly effective excited-state quenching agent for $Cr(bpy)_3^{3+}$ ($k_q \leq 2 \times 10^4$ M^{-1} s^{-1}) whereas for amine complexes the quenching rates can be near those for diffusion-controlled limits.[3,8,20,21] For the latter, at least part of the photochemistry appears to originate in ligand field quartet state(s), but for $Cr(bpy)_3^{3+}$ the photoaquation reaction appears to be derived nearly exclusively from the lower lying doublet level(s).[2,8] Electronically excited $Cr(bpy)_3^{3+}$ is considered to react with water to subsequently yield a reactive ground-state intermediate, which is also common to the thermal aquation mechanism.[2,8,9,22,23] Evidence has been mounting in favor of the intermediate being a seven-coordinate species involving a Cr–O bond; however, the possibility continues to exist that the species is a ligand covalent hydrate, similar to the types originally discussed by Gillard.[24]

In this study, we have sought to further elucidate the photoaquation mechanism of $Cr(bpy)_3^{3+}$ in acidic and basic solutions through a new approach involving pulsed-laser excitation at 347 nm coupled with time-resolved conductivity detection. This has been complemented by emission and excited-state absorption measurements. While the results are in the main consistent with earlier interpretations, they introduce a number of new facets. Of particular importance is the realization that the promptly developed chemistry in acidic media is at level comparable to that in alkaline solutions and that this may involve the occurrence of an excited-state acidic dissociation reaction.

Experimental Section

The samples of tris(2,2′-bipyridine)chromium(III) perchlorate $[Cr(bpy)_3](ClO_4)_3 \cdot {}^1/_2H_2O$, used in this study, were kindly provided by Dr. V. Balzani and by Drs. N. Serpone and M. A. Jamieson. The samples were used as received: Their UV–visible absorption spectra for the ground and excited states (^2E) and their emission characteristics agreed with those reported in the literature.[2,6,8,10–13,17–19,25] The concentrations of the solutions, prepared from water purified by a Millipore Super-Q system and deaerated by bubbling with argon, ranged from 20 to 101 μM. The pH of the solutions was adjusted by the addition of perchloric acid or sodium hydroxide, and the temperature range was 20.0–23.2 °C. All solutions were prepared just prior to use and were exposed to as little extraneous light as possible.

Irradiation of the solutions at 347 nm employed a frequency-doubled ruby laser (Korad K1QP) with ca. 70-mJ pulses (duration ca. 15 ns). The flow-through 1-cm^2 quartz cell, used in the optical and conductivity measurements, is described elsewhere along with the dc conductivity bridge.[26] The ac conductivity apparatus, employed at times exceeding 1 μs, is nearly the same as that applied in pulse radiolysis investigations.[21,27]

Results

Irradiation of $Cr(bpy)_3^{3+}$ at 347 nm leads initially to population of an upper state level, assigned as a-$^4T_1$.[2,8,25] Prevailing evidence indicates a subsequent and rapid relaxation to the lowest doublet states, ^2E and $^2T_1$, which are sufficiently close in energy so as to be in thermal equilibrium.[2] For simplicity, we shall refer to these closely spaced levels as the ^2E, although it has been proposed that the photoreactive state is in fact the $^2T_1$ one.[2,7,9] Our observations commence with the decay of the ^2E level as monitored by its emission at 727 nm, by its excited-state absorption spectrum (ESA), and with the associated changes in conductivity. The shape of the ESA band with a peak near 380 nm ($\epsilon \simeq 7000$ M^{-1} cm^{-1}) found in this work is similar to that reported by others.[10,28] In addition, we observed an isosbestic point at 365 nm with prompt bleaching at 360 nm. Both the ESA spectrum and the emission decayed via first-order rate laws, and the rate constants are presented in Table I. Within experimental error, the values are the same for both phenomena, and they agree with previously reported values.[2,6,8] Subsequently, small amounts of residual bleaching were found in the 360–440-nm range with the extent being greatest at 360 nm.

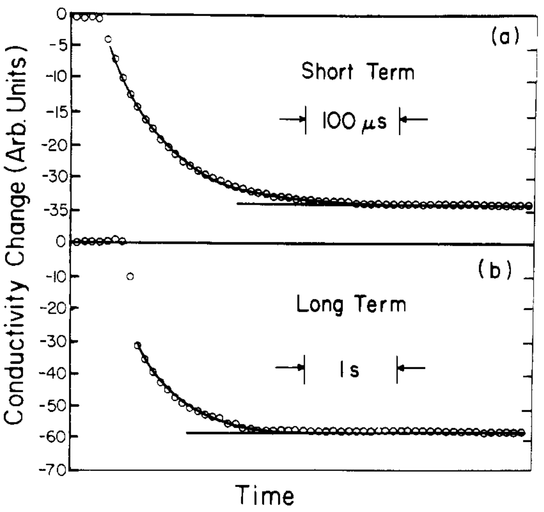

Figure 1. Conductivity changes occurring on irradiation of a deaerated solution containing 97 μM $Cr(bpy)_3^{3+}$ at pH 10.6 and 21 °C: (a) short-term decrease in conductivity; (b) long-term decrease in conductivity.

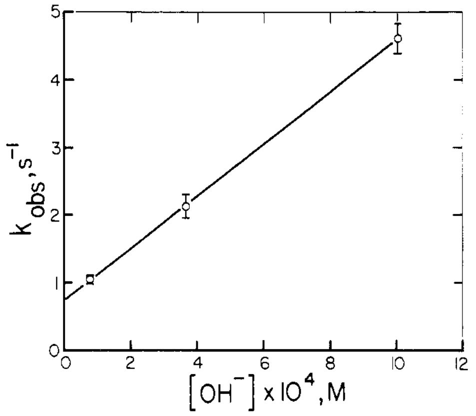

Figure 2. Plot of the observed first-order rate constant for the long-term decrease in conductivity vs. the concentration of hydroxide ion at 21 °C. The values of the intercept and slope are 0.75 ± 0.08 s^{-1} and (3.8 ± 0.1) × 10^3 M^{-1} s^{-1}, respectively.

Concomitant with the decay of the excited state (^2E), there were changes in conductivity. The sign of the initial change (increase or decrease) depended upon pH; however, in all instances the rate laws obeyed first-order kinetics. The values

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(28) Determinations of the initial concentrations of the ^2E state, used to estimate the ϵ value at 380 nm, were based on earlier reported ESA data for 460 nm[6] and a ground-state ϵ value of 230 M^{-1} cm^{-1} at 460 nm. The concentration measurements were made under conditions where the absorbance of the ESA spectrum varied linearly with the laser intensity.

Table I. Summary of First-Order Rate Constants Associated with the Decay of the ^2E State[a]

phenomenon	$10^{-4}k$, s^{-1} [b]	pH range	concn of $Cr(bpy)_3^{3+}$, μM	variation in laser intens	comments
conductivity	2.0 ± 0.3 (18)	2.3-5.4	20-101	14	conductivity increase
	1.7 ± 0.2 (7)	9.4-11.0	71-97	3	conductivity decrease
emission	1.5 ± 0.2 (9)	2.3-4.0	20-101	14	wavelength 727, 732 nm
	1.5 ± 0.1 (4)	9.6-11.0	72-97	3	wavelength 727 nm
excited state	1.6 ± 0.1 (4)	3.5-4.0	91-97	5	wavelength 360-460, 780 nm[c]
absorption	1.6	10.7	93		wavelength 460 nm

[a] Temperature range 20.0-23.2 °C. [b] Numbers in parentheses are the numbers of separate determinations. Each determination is itself an average of several measurements. [c] An isosbestic point occurs at 365 nm with an increase in absorption at 360 nm and with a decay in absorption at wavelengths longer than 365 nm.

of the rate constants are given in Table I. They are within experimental error the same as those representing the decay of the excited state. As this decay is not affected by changes in our experimental conditions, notably pH, and yet leads at the same rate to subsequent chemical change, it can be concluded that exiting from the ^2E state is rate determining and that, while this can involve reaction with water (vide infra), there are also subsequent fast chemical processes.[29]

In basic media, the initial manifestation of this was a decrease in conductivity as shown in Figure 1a, and the rate was unaffected by changes in pH (9.4–11.0) (Table I). At much longer times, a further decrease in conductivity took place as exemplified in Figure 1b. This latter change obeyed first-order kinetics; however, a plot of the observed first-order rate constant vs. concentration of hydroxide ion as shown in Figure 2 indicates a linear dependence on $[OH^-]$. A linear least-squares analysis of this data with an index of 0.99 yields for this plot an intercept value of 0.75 ± 0.08 s^{-1} and a slope of $(3.8 \pm 0.1) \times 10^3$ M^{-1} s^{-1}. The ratio of the signal height for the first conductivity change to that of the overall movement is 0.52 ± 0.08. This ratio is consistent with that expected[30] for a sequential consumption of 2 equiv of OH^- to yield the known photoproducts $Cr(bpy)_2(OH)_2^+$ and free bpy (eq 1a).[2,8,9,32]

The foregoing conductivity changes pertain to processes associated with the ^2E state; however, the possibility exists of some prompt reaction from the higher lying quartet levels such as the nascently populated a-$^4T_1$. We have looked for such at shorter times (200-ns scale). While there may have been a vestige of a prompt component, it was very small. The results indicate that greater than ca. 93% of the initial change in conductivity is associated with the decay of the ^2E level. This agrees with the estimate of at least 97% as determined by Maestri and co-workers through iodide quenching of the photoreaction and of emission.[8]

In acidic media (pH 2.3–5.4), the decay of the ^2E level was now commensurate with an increase in conductivity (Figure 3a), representing generation of proton (vide infra). A first-order rate law was obeyed, and the value of the rate constant is essentially the same as those for emission and ESA decay (Table I). There were however indications of a possible additional minor process(es). The value of the rate constant seemed slightly higher in the pH range of 3–4, and there was a drop of ca. 10% (relative to the maximum conductivity increase) at about 500 μs. These features were less apparent at lower pH. At longer times, a major decrease in the conductivity transpired, as shown in Figure 3b. At pH 4, the signal returned to the base line; however, the return was less complete at lower pH, with a maximum residue of ca. 10% at the lowest pH used. This decrease obeyed apparent first-order kinetics; however, the observed rate constant was found to be linearly dependent upon proton concentration, as exemplified in Figure 4. Linear regression analysis of this plot

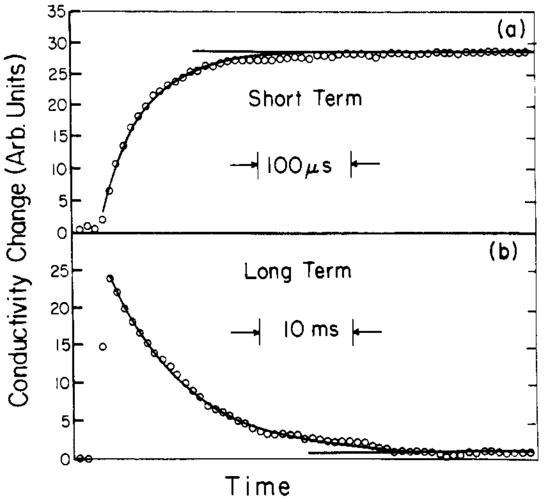

Figure 3. Conductivity changes occurring on irradiation of a deaerated solution containing 101 μM $Cr(bpy)_3^{3+}$ at pH 3.0 and 21 °C: (a) short-term increase in conductivity; (b) long-term decrease in conductivity.

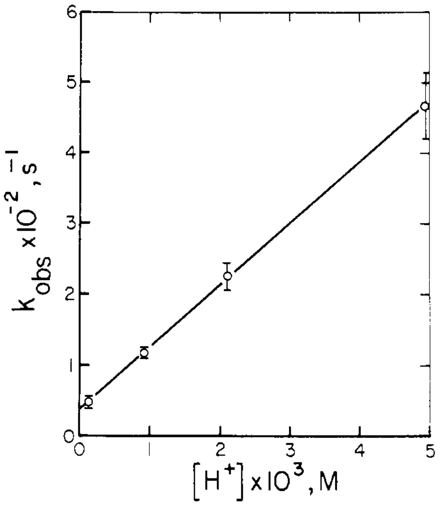

Figure 4. Plot of the observed first-order rate constant for the long-term decrease in conductivity vs. the concentration of proton at 21 °C. The values of the intercept and slope are 39 ± 9 s^{-1} and $(8.7 \pm 0.4) \times 10^4$ M^{-1} s^{-1}, respectively.

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(29) The rate constant for OH^- quenching of the ^2E state is equal to or less than 2×10^4 M^{-1} s^{-1} [8] so that, for our pH conditions, the rate of this process will have been negligible.

(30) The equivalent ionic conductivities of the complex ions involved are not known; however, from values reported for similar Cr(III) ions[31] and a value of 198 Ω^{-1} cm^2 $equiv^{-1}$ for OH^-, the ratio is expected to be in the range of 0.50–0.58.

(31) "Landolt-Börnstein, Zahlenwerte and Funtionen", 6th ed.; Springer-Verlag: Berlin, 1960; Vol. II, Part 7, pp 259–260.

(32) On the basis of the reported pK_a values for $Hbpy^+$ and for $Cr(bpy)_2(H_2O)_2^{3+}$, these species will occur in basic media in the forms of bpy and of $Cr(bpy)_2(OH)_2^+$.[33,34]

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(index of fit 0.98) gives an intercept value of 39 ± 9 s^{-1} and slope value of $(8.7 \pm 0.4) \times 10^4$ M^{-1} s^{-1}.

At pH 4, the observed rate constant for the conductivity change was the same as that describing the decrease in the optical bleaching at 360 nm. This latter aspect has been studied in detail by Maestri and co-workers.[8] They also found a two-term rate constant expression: $k_{obsd} = k_0 + k_a[H^+]$, with $k_0 \leq 10$ s^{-1} and $k_a = 4 \times 10^5$ M^{-1} s^{-1}. The rate law is proposed to reflect relaxation of a ground-state species with a coordination number of 7 to the more stable six-coordinate form via acid-independent (eq 2) and acid-catalyzed pathways. The

$$Cr(bpy)_3(H_2O)^{3+} \rightarrow Cr(bpy)_3^{3+} + H_2O \qquad (2)$$

conductivity results indicate that the rate law involves consumption of proton rather than just acid catalysis. The slight numerical differences between the two studies vis-à-vis the values of the terms in the observed rate constant expression and the trends in the differences seem attributable to the marked disparity in the ionic strength conditions between the two studies (see below).

The time-resolved measurements of the conductivity and optical changes show that, in acidic media, the changes are of a transitory nature and in the main reversible. Qualitatively this is consistent with the findings that the overall quantum yields for the release of bipyridine (eq 1b) are low. between pH 2.0 and 4.0, the yields range from 0.014 to 0.038.[11] They are notably lower than that in basic solution of 0.13 (pH 9.3, eq 1a)[2] where the conductivity and optical changes are also now of a more permanent character.

Of principal interest here has been the measurement of the quantum yield associated with the short-term maximum change encountered in acidic solutions (Figure 3a) and the discernment of any dependence of its value on pH. Considering the latter aspect first, the maximum level of increase in conductivity did decrease somewhat on going from pH 4.1 to 2.4: On the basis of a relative value of 1.0 for the conductivity change at pH 4.1, the values were 0.73 ± 0.09 (pH 3.1), 0.69 ± 0.06 (pH 2.7), and 0.69 ± 0.05 (pH 2.4). This relatively constant level coupled with the fact that this pertained to an increase in conductivity indicates the presence of a proton-ionization reaction with a pK_a below 2. The question of whether this reflects the behavior of an excited-state or a ground-state species will be condidered below.

To estimate the quantum yield associated with the initial conductivity increase, comparative measurements were made against two different reference reactions. The first of these involved the comparison of the conductivity change of $Cr(bpy)_3^{3+}$ in acid relative to that taking place in basic solution. Our results in basic media are consistent with the first conductivity change (Figure 1a) leading quantitatively to the final products. Consequently, we have assumed that the overall quantum yield of 0.13 applies also to the nascent change. The second comparison has been referenced to the photolysis of $Cr(en)_3^{3+}$. A laser conductivity study of the formation of the product, which contains a monodentate and monoprotonated ligand (enH), has been reported earlier by us.[26] A quantum yield of 0.48 has been taken for the formation of the product (eq 3), on the basis of the value of 0.40 ± 0.05 at 15 °C and

$$Cr(en)_3^{3+} + H_3O^+ \xrightarrow{h\nu} Cr(en)_2(enH)(H_2O)^{4+} \qquad (3)$$

with allowance being made for our higher temperature (21 °C).[35] In order to make these comparisons, knowledge of the equivalent ionic conductivities of the ions involved is required. These are 350 and 198 Ω^{-1} cm^2 $equiv^{-1}$ for H^+ and OH^-, respectively.[31] The values for the complex ions of interest here are apparently not known, but values reported for similar Cr(III) complex ions range between ca. 20 and 120 Ω^{-1} cm $equiv^{-1}$.[31] If one takes an average of about 65 Ω^{-1} cm^2 $equiv^{-1}$, then the quantum yield for proton generation is estimated to be 0.08 by comparison to $Cr(bpy)_3^{3+}$ reaction in base and that of 0.07 with reference to eq 3. With allowance being made for the uncertainty in the equivalent ionic conductivities for the chromium(III) ions, a lower limit for the yield would be 0.05. The important feature that arises from these comparisons is that the quantum yields associated with the nascent conductivity changes in alkaline and acidic solutions (Figures 1a and 3a) are quite comparable (within about a factor of 2).

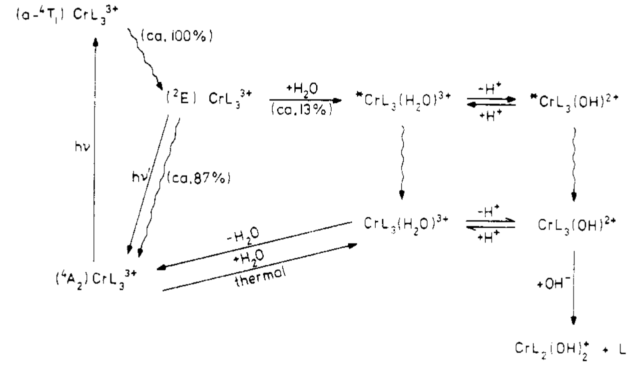

Figure 5. Proposed mechanistic scheme.

Discussion

In Figure 5, are portrayed the major features to be discussed below. Previous studies have shown that irradiation of $Cr(bpy)_3^{3+}$ ($^4A_2$ ground state) with near-UV–visible light yields on our experimental time scales the prompt formation of the ^2E state with almost unitary efficiency. The subsequent reaction of this state then leads via substitution processes to the overall aquation products (eq 1a,b). The fact that the features of the ^2E state (emission yield and lifetimes for emission and ESA decay) are not affected over moderate ranges of pH such as in this work (pH 2.3–11.0) can be taken to indicate that the chemistry of this state involves reaction with water. The product of this reaction (eq 4) has generally

$$(^2E)Cr(bpy)_3^{3+} + H_2O \rightarrow {}^*Cr(bpy)_3(H_2O)^{3+} \qquad (4)$$

been considered to be a seven-coordinate species with the water bound to the metal center; however, the possibility also exists that the water may be incorporated into the structure of the bipyridyl ligand. On the basis of a limiting photosubstitution quantum yield being attained in basic media (pH ≥9) and the phosphorescence yield being quite low ($\Phi_p < 10^{-3}$), it is estimated that the chemical reaction (eq 4) accounts for ca. 13% of the loss for the ^2E state and that the nonradiative transition to the ground state ($^4A_2$) encompasses the major loss (ca. 87%).[2,8] In addition, Jamieson and co-workers[9] have proposed from the temperature dependency of the photoaquation reaction in alkaline media that the product of eq 4 is an electronically excited species $^*Cr(bpy)_3(H_2O)_3^+$. This species then decays to a seven-coordinate ground state intermediate (eq 5).

$$^*Cr(bpy)_3(H_2O)^{3+} \rightarrow Cr(bpy)_3(H_2O)^{3+} + \text{heat} \qquad (5)$$

Maestri and co-workers[8] have presented strong evidence to indicate that this ground-state intermediate is also common to the thermal aquation reaction.

Our conductivity, ESA, and emission results are consistent with this picture. The conductivity findings, which pertain to chemical reactions subsequent to eq 4, interject several new and important facts. First, the rates for the initial changes in conductivity are the same as those associated with the decay of the electronically excited doublet state (Table I), indicating that the subsequent processes have time constants smaller than

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(35) Ballardini, R.; Varani, G.; Wasgestian, H. F.; Moggi, L.; Balzani, V. *J. Phys. Chem.* **1973**, *77*, 2947.

the lifetime of the ^2E state (τ ca. 59 μs). In acidic media, the nascent conductivity increase (Figure 3a) can be ascribed to proton release from an excited-state intermediate or from a ground-state species (eq 6, 7). The quantum yield for release

$$^*Cr(bpy)_3(H_2O)^{3+} \rightleftharpoons {}^*Cr(bpy)_3(OH)^{2+} + H^+ \tag{6}$$

$$Cr(bpy)_3(H_2O)^{3+} \rightleftharpoons Cr(bpy)_3(OH)^{2+} + H^+ \tag{7}$$

of proton is found to be about 0.08, a value somewhat smaller but yet comparable to that of 0.13 representing consumption of OH^- (Figure 1a) in basic media. Furthermore, the yield is relatively insensitive to change over the range of pH 2.4–4.1. This feature indicates the occurrence of an ionization process with a pK_a value below 2, which can be attributed to either eq 6 or eq 7. In both instances, it is unlikely that the reverse processes for eq 6 and 7, involving protonation, will have rate constants (k_{-6} and k_{-7}) in excess of 5×10^9 M^{-1} s^{-1}.[36] On this basis, it follows that one of the forward rate constants (k_6 or k_7) has a value greater than 5×10^7 s^{-1}.

These features and those pertaining to alkaline media as well as results from earlier studies suggest for consideration two possible mechanistic schemes. The choice between them reflects in essence a judgement as to whether the pK_a value for the ground-state species (eq 7) lies below 2 or above 5. For the case where one presumes that the value lies below 2 and that ionization does not occur for the electronically excited species $^*Cr(bpy)_3(H_2O)^{3+}$, the following steps in addition to eq 2, 5, and 7 apply:

$$Cr(bpy)_3(H_2O)^{3+} + OH^- \rightleftharpoons Cr(bpy)_3(OH)^{2+} + H_2O \quad \text{(in basic media)} \tag{8}$$

$$Cr(bpy)_3(OH)^{2+} \rightarrow Cr(bpy)_3^{3+} + OH^- \tag{9}$$

$$Cr(bpy)_3(OH)^{2+} + OH^- \rightarrow Cr(bpy)_2(OH)_2^+ + bpy \tag{10}$$

$$Cr(bpy)_3(OH)^{2+} + H_2O \rightarrow Cr(bpy)_2(H_2O)(OH)^{2+} + bpy \tag{11}$$

$$Cr(bpy)_2(H_2O)(OH)^{2+} + OH^- \rightleftharpoons Cr(bpy)_2(OH)_2^+ + H_2O \tag{12}$$

Owing to the time frame of the initial conductivity changes, the reaction of eq 7 (and that of eq 8 in alkaline media) needs to be rapidly established. The observed rate constants describing the longer term conductivity changes, i.e. the decreases in base (Figure 1b) and in acid (Figure 3b), contain two terms for each situation: $k_{obsd}(\text{acid}) = k_i' + k_a[H^+]$ and $k_{obsd}(\text{base}) = k_i + k_b[OH^-]$ of Figures 4 and 2, respectively. In acidic media, k_a would be approximated by k_2/K_a of eq 7, implying that $k_2 \geq 8.7 \times 10^2$ s^{-1}. As an acid-independent term (k_i') is present, a reaction such as eq 9 (followed by rapid neutralization of released OH^-) also needs to be considered along with that of eq 11. Our value of $k_i' = 39 \pm 9$ s^{-1} is somewhat higher than that ($k_0 \leq 10$ s^{-1}) reported for the return of optical bleaching,[8] and two features may be noted in this connection. Measurements of k_i' made 1 year apart using different samples of $Cr(bpy)_3^{3+}$ gave agreement. So while a systematic error in our measurement of k_i' cannot be ruled out completely, it seems somewhat improbable. A more likely explanation appears to be associated with the fact that the ionic strengths of our solutions ($\leq$0.01 M) were at least a 100-fold less than that of 1.0 M used by other workers,[8,11] and thus the activity of water in our case would be higher. The influence of ionic strength also affords a reasonable explanation for our k_a value being less (ca. 5-fold) than that found earlier.

In alkaline solutions (pH >9), the long-term decrease in conductivity would lead to the aquation product $Cr(bpy)_2(OH)_2^+$ and free unprotonated bipyridine ligand (eq 10–12). The dominant process will be that of eq 10 ($k_{10} = k_b$). The term independent of hydroxide ion concentration (k_i) will be associated in part with the minor process (eq 11), followed rapidly by deprotonation of $Cr(bpy)_2(H_2O)(OH)^{2+}$ (eq 12; pK_a = 6.1).[34] The reaction of eq 11 would also be operable in acidic solution and could account for the relatively small amount of overall aquation (eq 1b) observed at lower pH.[11] Such a situation would imply perhaps a slight *overall* decrease in conductivity owing to protonation of released bpy at a pH ca. 2.3 whereas we observed a slight increase ($\lesssim$10% of the short-term change). This difference and that of the minor drop in conductivity, which in the pH 3–4 range precedes the long-term decay, are features that suggest the presence of an additional secondary process(es). A related aspect is the possible intramolecular rearrangement(s) of $Cr(bpy)_3(OH)^{2+}$ as proposed by others subsequent to the complete release of bpy.[8,22,23] As such a rearrangement would not necessarily involve a conductivity change, it could occur without detection here. Our findings do however indicate that the final release of bpy does involve in part attack of OH^- (eq 10).

A key feature in considering the presence of $Cr(bpy)_3(H_2O)^{3+}/Cr(bpy)_3(OH)^{2+}$ as common intermediates to both the thermal and photoaquation of $Cr(bpy)_3^{3+}$ is that the thermal rate constants and quantum yields not only increase with pH but do so with sigmodial-shaped curves having a common inflection point near pH 8.[4,26,27] The foregoing mechanistic scheme can give rise to such an "S"-shaped curve; however, our kinetic data would imply that the inflection point is expected to be near pH 11–12. This difference seems unacceptably large even when allowance is made for the fact that the comparison involves results obtained under quite different experimental conditions and that our estimate is quite sensitive to the values of k_i and k_i'. A final point concerning this scheme whereby the ground-state intermediate $Cr(bpy)_3(H_2O)^{3+}$ is presumed to exhibit a pK_a of <2 is that this is more commensurate with the intermediate actually being a Gillard type of covalent-hydrate species as the thermal substitution results for $Cr(bpy)_3^{3+}$ suggest that, for such a species, the pK_a value would be very low ($pK_a \leq -6.4$).[22]

The second mechanistic scheme to be considered encompasses the foregoing reactions but with a different set of assumptions. They are as follows: The process with the pK_a value below 2 now pertains to the excited-state one (eq 6), with the forward reaction being rapid ($k_6 \geq 5 \times 10^7$ s^{-1}) and followed quickly by deexcitation of $^*Cr(bpy)_3(OH)^{2+}$

$$^*Cr(bpy)_3(OH)^{2+} \rightarrow Cr(bpy)_3(OH)^{2+} + \text{heat} \tag{13}$$

Secondly, the ground-state pK_a of $Cr(bpy)_3(H_2O)^{3+}$ is considered to be above 5, a facet more in keeping with arguments that this intermediate is a seven-coordinate species.[2,8] Under our conditions, the nascent ground-state product is $Cr(bpy)_3(OH)^{2+}$, and its presence is associated with the generation of proton, which gives rise to a prompt increase in conductivity in acid but a decrease (via reaction of H^+ and OH^-) in alkaline solutions. The longer term conductivity changes now reflect the subsequent behavior of $Cr(bpy)_3(OH)^{2+}$.

For our acid conditions, the equilibrium position of the ground-state dissociation reaction will lie to the left side of eq 7, and the linear relationship shown in Figure 3a will be a manifestation of several concurrent and competing processes. The slope, $k_a = 8.7 \times 10^4$ M^{-1} s^{-1}, is then that of the reverse process of eq 7, i.e. k_{-7}, with the rate of the subsequent water release reaction (eq 2) being more rapid. This aspect is a departure from previous intrepretations that have ascribed the acid dependence to acid-catalyzed release of water from $Cr(bpy)_3(H_2O)^{3+}$. An important implication of our interpretation is that within our experimental time frame (<1 s), the approach toward equilibrium for eq 7 is relatively slow: If we

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presume $pK_a \geq 5$ for eq 7, k_7 is anticipated to be smaller than $1\ s^{-1}$. The intercept value of $k_i' = 39\ s^{-1}$ now reflects at least in part the sum $k_{-8} + k_9 + k_{11}$. This sets an upper limit to $k_9 + k_{11}$; that is, k_i' is anticipated to be greater than k_i, which is in keeping with the experimental results. In basic resolutions (pH >9), the sequence of events follows that given for the first mechanistic scheme (eq 10–12).

While a clear choice between the two schemes does not appear to be feasible at this time, we favor, for the following reasons, the second one, where the pK_a values for $^*Cr(bpy)_3(H_2O)^{3+}$ and for $Cr(bpy)_3(H_2O)^{3+}$ are taken to be less than 2 and above 5, respectively. The pK_a assignment for $Cr(bpy)_3(H_2O)^{3+}$ is consistent with the recent estimate by Sriram and co-workers[11] that it is of the order of 5–6. In the context of the second mechanistic scheme (unlike the first scheme), our kinetic results are not directly applicable to the issue of the position of the inflection point observed in the plot of the steady-state quantum yields for the formation of free bipyridine vs. pH. Thus, the apparent discrepancy between the observed value near pH 8 and our higher estimate for the inflection point, made under the first scheme, is eliminated.

A final point concerns the quantum yield for release of proton where two different approaches to measuring this yield in acid both gave results that suggested the amount to be somewhat less than that in basic media. A plausible explanation for this within the second scheme is that the rate of deexcitation of $^*Cr(bpy)_3(H_2O)^{3+}$ (eq 5) may be only marginally slower than that for its acidic dissociation reaction (eq 6). Owing to the slowness of release of proton from the ground-state form $Cr(bpy)_3(H_2O)^{3+}$, less amount of proton will then be generated in acidic solution relative to that in alkaline solution. In the latter case, where the ground-state dissociation reaction pertains to eq 8, the amount of $Cr(bpy)_3(OH)^{2+}$ formed will be larger and can now provide a full measure of the nascent amount of $^*Cr(bpy)_3(H_2O)^{3+}$ produced. Parenthetically, if the estimate[11] for the ground-state pK_a value being in the range 5–6 is adopted along with an upper limit for k_{-8} of $39\ s^{-1}$ ($=k_i'$), then the value for k_8 is anticipated to be in the neighborhood of $10^{10}\ M^{-1}\ s^{-1}$. This level will meet the requirements under our conditions that the rate of the reaction between $Cr(bpy)_3(H_2O)^{3+}$ and OH^- (eq 8) be at least comparable to that for the decay of the ^2E state. The second scheme offers a consistent framework in which to interpret our and others' results and at the same time points to new areas of investigation on closely related systems.

Acknowledgment. We wish to thank the Natural Sciences and Engineering Research Council of Canada for financial support, and W.L.W. wishes to express his gratitude to the Hahn-Meitner-Institut and to the University of Saskatchewan for assistance. The kindness of Drs. V. Balzani, M. A. Jamieson, and N. Serpone in providing samples of the chromium compound is very much appreciated.

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

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Nuclear Magnetic Resonance Study of Ethylenediaminetetrakis(methylenephosphonic acid) and Some Metal Complexes

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Received July 14, 1982

The ^1H NMR spectra of ethylenediaminetetrakis(methylenephosphonic acid) and of some metal complexes were interpreted to indicate that the nitrogens are preferentially protonated in the free ligand whereas the phosphonate groups are protonated in the metal complexes. A single ABX pattern for lanthanide–ENTMP complexes is consistent with a time-averaged symmetry for the ligand about the metal involving long-lived Ln–N and short-lived Ln–O bonds. The ^{31}P NMR pattern also supports such averaged equivalence of all phosphonate groups. The CaENTMP complex has short-lived Ca–N and Ca–O bonds.

Introduction

Amino phosphonic acid ligands are of interest in biological systems and as chelating agents for metal ions. Protonation and metal ion complexation of some of these ligands have been reported by Martell et al.[2,3] using potentiometric titration and by Marov et al.[4,5] using ^1H NMR spectroscopy. These studies confirmed the existence of 1:1 metal-to-ligand complexes that became protonated at pH values below 8–10 depending on the cation. The resolution of the ^1H NMR spectra was insufficient to allow more extensive interpretation about the nature of the metal–donor atom bonding etc.

Proton resonance studies of the diamagnetic metal complexes of amino carboxylate ligands in aqueous solutions have provided information on the metal–ligand bond labilities and on structural features of the complexes.[6-9] In this paper we report the results of similar high-resolution NMR (^1H and ^{31}P) studies of ethylenediaminetetrakis(methylenephosphonic acid) and some of its metal complexes.

Experimental Section

Synthesis of ENTMP. Ethylenediaminetetrakis(methylenephosphonic acid), ENTMP, was prepared by a slight modification of the procedure reported by Krueger et al.[10] A 2.25-mol sample of phosphorous acid, 0.50 mol of H_4EDTA, and 400 mL of acetic anhydride were mixed together and heated to 130–140 °C for 1 h with vigorous stirring. The resulting lumpy mass was cooled, filtered, and rinsed with the minimum amount of water. The phosphonate ligand was dissolved in 4 equiv of sodium hydroxide solution and the

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