

at longer wavelength. This strongly suggests that the copper centers in these molecules are bonded to less than three chloro ligands.

(4) Thus, very low y in complexes IX, XI, and XIII is attributed to copper(II) coordinated by two chloro ligands, μ -oxo, and H_2O . The absence of DENC at site Y is supported by $z > y$ and $R_x < R_y$ (Table III).

Spectral evidence for weak copper-chlorine bonds at site Y is only apparent in complexes VII, IX, XI, and XIII, all of which contain a $Ni(\mu-O, Cl, Cl)Cu$ "dimer" unit in the top face. Loosening of this top unit from the core of each molecule would give ground-state entropies $S_{VII} > S_{IX}$ and $S_{XI}, S_{XIII} > S_{VII}$. A requirement for formation of copper-chlorine bonds in the activation process for isomerization to give structures more like II and III would lead to a decrease in entropy: as anticipated, ΔS^\ddagger (Table V) is strikingly negative and similar in all systems. We much prefer this description of activation to the "polar-activated complex" hypothesis presented earlier.⁷

Isomerizations VII \rightarrow VI, XI \rightarrow X, and XIII \rightarrow XII all require breaking of a $Cu(\mu-O)$ bond. Four of the six ΔH^\ddagger values are essentially the same (Table V). The higher ΔH^\ddagger for isomerizations XI \rightarrow X and XIII \rightarrow XII in methylene chloride suggest a more significant, solvent-induced $Cu\gamma-(\mu_4-O)$ interaction in complexes XI and XIII, in line with higher absorptivity y in this solvent (Table III).

Conclusions. Molecular structures I-III (Chart I) are different and distinguishable. Introduction of nickel into complexes II (to give VII) and III (to give IX) apparently increases the entropy of $Cu(\mu-O, Cl, Cl)$ sites. This does not appear to be the case for $Cu(\mu_4-O, Cl, Cl, Cl)$ sites, which are thermodynamically preferred by copper. It is this preference that is probably responsible for disproportionation to complex V on attempted crystallization of complexes I-IV and any of their transmetalated derivatives containing copper.

Acknowledgment. This work was supported by Biomedical Research Support Grant RR07143 from the Department of Health and Human Services and Grant INT-8512210 from the

National Science Foundation, which are gratefully acknowledged. We wish to thank Professor William Orme-Johnson and co-workers for assistance with EPR measurements.

Appendix

From inspection of the spectra in Figures 5 and 6 we assume that the site of transmetalation of III by $Ni(NS)_2$ is Z, X, X, and Y in eq 8-11, respectively. If ϵ_{III} and ϵ_8 are the measured molar absorptivities at 850 nm of III and the tetranuclear product of eq 8 etc., then from the data in Figure 5 for methylene chloride we can write eq A1-A5. Thus, $z - z' = 90$, $x - x' = 260$ or 345

$$\epsilon_{III} = 2x + y + z = 770 \text{ M}^{-1} \text{ cm}^{-1} \quad (\text{A1})$$

$$\epsilon_8 = 2x + y + z' = 680 \text{ M}^{-1} \text{ cm}^{-1} \quad (\text{A2})$$

$$\epsilon_9 = x + x' + y + z' = 335 \text{ M}^{-1} \text{ cm}^{-1} \quad (\text{A3})$$

$$\epsilon_{10} = 2x' + y + z' = 75 \text{ M}^{-1} \text{ cm}^{-1} \quad (\text{A4})$$

$$\epsilon_{11} = 2x' + y' + z' = 64 \text{ M}^{-1} \text{ cm}^{-1} \quad (\text{A5})$$

(av 300 ± 40) and $y - y' = 11 \text{ L (mol of metal)}^{-1} \text{ cm}^{-1}$. We could then assume that $x' = y' = z' = \epsilon_{11}/4 = 16 \text{ L (mol of Ni)}^{-1} \text{ cm}^{-1}$. This gives $x = 316 \pm 40$, $y = 27$, and $z = 106 \text{ L (mol of metal)}^{-1} \text{ cm}^{-1}$. A better approximation is $x \gg x'$, $y \gg y'$ and $z \gg z'$, which gives $x = 325$, $y = 12$, $z = 100$, $x' = 25$, $y' = 1$ and $z' = 10 \text{ L (mol of metal)}^{-1} \text{ cm}^{-1}$, each with an average error of ca. $\pm 13\%$ arising from the alternative choices, 260 or 345 L (mol of metal)⁻¹ cm⁻¹, for $x - x'$. These average x' , y' , and z' values are different, as expected, and each is 8-10% of the corresponding value for copper, which supports the approximation. The same analysis for the data in Figure 6 gives $x - z'$ in nitrobenzene (Table III). A complete summary of observed and calculated molar absorptivities is given in Table IV.¹⁸

Supplementary Material Available: Table IV, observed and calculated molar absorptivities (ϵ , $M^{-1} \text{ cm}^{-1}$) of reactants and products at 850 nm in methylene chloride and nitrobenzene solution at 25 °C (1 page). Ordering information is given on any current masthead page.

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Pulsed-Laser Photochemical Study of Tris(1,10-phenanthroline)chromium(III) Ion in Acidic and Alkaline Aqueous Media

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The photochemistry and photophysics of tris(1,10-phenanthroline)chromium(III) ion, $Cr(phen)_3^{3+}$, following pulsed-laser excitation at 347 nm, have been studied in deaerated acidic and alkaline aqueous media (pH 3.0-11.1) at room temperature by using conductivity and visible optical detection methods. The lifetimes of the lowest doublet excited state(s) from which is derived the major portion of the photochemistry are little affected by changes in pH as monitored by emission and excited-state absorption nor are the initial intensity levels of these phenomena noticeably altered by pH changes. Alterations in pH do have significant effects on the conductivity signals, which correlate to photoaquation. Conductivity studies for natural pH (ca. pH 7.1) provide evidence for a ground-state intermediate with a pK_a value around 7. In basic media, an apparent single stage of conductivity occurs, and the values of the observed rate constant and the resulting overall change in conductance are dependent upon the concentration of hydroxide ion. The quantum yield for aquation at the highest pH of 11.1 is determined as 0.08 ($\pm 20\%$). By contrast, photochemical reaction in acidic media is found to be very much reduced relative to that occurring in alkaline solutions. A mechanism, incorporating a six-coordinate, monodentate phenanthroline intermediate, is proposed, and it is used to discuss the occurrence of photoracemization and to compare the behavior of $Cr(phen)_3^{3+}$ to that previously reported for the congeneric system $Cr(bpy)_3^{3+}$, where bpy designates the 2,2'-bipyridine ligand.

Introduction

A number of studies have been presented recently pertaining to the photochemistry and photophysics of tris(2,2'-bipyridine)-chromium(III) ion, $Cr(bpy)_3^{3+}$, and tris(1,10-phenanthroline)-chromium(III), $Cr(phen)_3^{3+}$, as well as related complexes.²⁻²⁶ Such efforts have been engendered in part by the opportunities

afforded to investigate fundamental chemical and spectroscopic aspects for these materials, representing a broad class of sub-

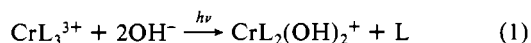
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stances, and ones of relevance to solar energy conversion processes. Several reviews have appeared covering various facets of their photobehavior.²⁻⁴

This particular study focuses on the photoaquation reaction of $\text{Cr}(\text{phen})_3^{3+}$, and it employs a relatively new approach involving conductivity detection techniques to monitor in conjunction with optical methods time-resolved changes induced by pulsed-laser excitation. Because aquation processes are frequently accompanied by changes in the concentrations of proton and hydroxide ion, species having large equivalent ionic conductivities, we have recently used conductivity detection as a means to obtain mechanistic insight into the photobehavior of the congeneric $\text{Cr}(\text{bpy})_3^{3+}$ ion and another major category of chromium(III) complex ions, ones containing saturated amine ligands.^{15,27} This report provides a basis for further comparison among these types of systems.

Such comparisons reveal intriguing differences both within and between these major categories. For example, with the aromatic heterocyclic systems, the photoaquation quantum yields attain maximum limiting values in basic solutions, and the overall process is



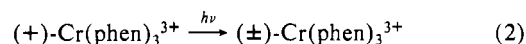
where L is phen, bpy, or their substituted forms.^{2,5,7,11,16} In contrast for the saturated amine cases, photosubstitution is maximal in acidic solutions, and this stems in part from their greater sensitivity to quenching of the longer lived doublet states by hydroxide ion even though the lifetimes of the corresponding states for $\text{Cr}(\text{phen})_3^{3+}$ and $\text{Cr}(\text{bpy})_3^{3+}$ are generally longer and greater percentages of photoreaction are associated with these states (here more than 90%).^{2,3,15} Our earlier conductivity study of $\text{Cr}(\text{bpy})_3^{3+}$ did indicate, however, levels of transitory reactivity in acidic media comparable to those for net chemical change found in alkaline solutions, and the presence of the former has been proposed to be associated with the occurrence of an excited-state ionization process with a $\text{p}K_a$ value of 2 or less.¹⁵ The current investigation was undertaken in part to discern if a similar situation might occur for $\text{Cr}(\text{phen})_3^{3+}$, but the results indicate that this is not the case, and they reveal other points of difference.

Table I. Summary of Values of Observed Rate Constants^a

pH	$k_{\text{obsd.}} \cdot 10^{-3} \text{ s}^{-1}$		
	emission ^b	excited-state abs ^c	conductivity
3.0-4.3	3.3 ± 0.4 (5)	3.3 ± 0.3 (14)	see text
natural		3.5 ± 0.2 (4)	4.0 ± 0.2 (4) (incr cond)
pH ^d			
9.2-9.4	4.5 (1)	4.0 ± 0.3 (8)	2.3 ± 0.2 (9) (decr cond)
11.1	4.8 ± 0.3 (3)	4.9 ± 0.3 (4)	4.0 ± 0.1 (5) (decr cond)

^a Conditions: deaerated media; $[\text{Cr}] = 40\text{--}98 \mu\text{M}$; room temperature $20.5\text{--}28.0 \text{ }^\circ\text{C}$. ^b Emission wavelength 726/727 nm. ^c Absorption wavelength 515 nm, except at pH 4.3, where ESA was monitored also at 369-400 nm. ^d pH ca. 7.1.

The similarities between the changes in the overall quantum yields for ligand release for both complex ions as a function of pH with the corresponding variations of the rate constants for thermal aquation have provided a major line of evidence for the proposed presence of a ground-state intermediate(s) common to both photolytic and thermal mechanisms.^{2,5,16} The results found here for natural-pH solutions of $\text{Cr}(\text{phen})_3^{3+}$ offer a direct indication of such an intermediate(s). Considerable discussion has ensued as to the nature of such species for these and related complexes, and the proposals have generally focused on the species being of a seven-coordinate type or of a ligand covalent hydrate form.^{2,5,15,16,28,29} The dissimilarities as well as similarities observed here and earlier studies of $\text{Cr}(\text{phen})_3^{3+}$ and $\text{Cr}(\text{bpy})_3^{3+}$ have led us to place emphasis on the involvement of six-coordinate intermediates with one of the heterocyclic ligands being monodentate rather than bidentate; however, in so doing, this is not meant to preclude the occurrence of other forms, particularly at the earlier stages of reaction. The proposed mechanism also attempts to relate in a more detailed manner an earlier proposal as to the interconnection between photoaquation and loss of optical activity for (+)- $\text{Cr}(\text{phen})_3^{3+}$.⁵ While the apparent loss of optical activity is largest in basic media as is the case for aquation, the former remains significant in acidic solutions as well.^{11,12,18} Given the much lower level of photoaquation under acidic conditions, the implication is that the loss of optical activity reflects the predominant role of a process involving intramolecular racemization as for



However, in alkaline solutions where photoaquation is now significant, change in optical activity can now be associated with net chemical reaction. In support of this, the quantum yields presented here for aquation in basic media are very similar in value to those estimated for the intrinsic photoracemization yield (eq 2) as derived from the observed yields in acidic media.

Experimental Section

Three separate samples of tris(1,10-phenanthroline)chromium(III) perchlorate dihydrate, $[\text{Cr}(\text{phen})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, were used in this study. Two of these samples were kindly provided by Professors R. D. Gillard and M. Z. Hoffman, and the third sample was prepared by a method reported in the literature.⁵ The properties of these materials were essentially identical in terms of their ground-state and excited-state absorption spectra, their excitation-emission spectra, and their kinetic behavior.³⁰ The values of the observed first-order rate constants for decay of emission and excited-state absorption (ESA) of the doublet states (${}^2\text{T}_1/{}^2\text{E}$) are given in Table I: The corresponding lifetimes (τ) are given by k_{obsd}^{-1} .³¹ Where comparisons between the lifetimes and spectral

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- (30) While the sample, prepared by us, exhibited the same properties and kinetic behavior as those of the other samples, it did decompose thermally in basic media (ca. pH 10) on two separate occasions over about a 2-h period whereas the other samples were thermally stable under the conditions used here. We have no explanation for this erratic behavior; however, the sample was not employed in any of the studies in alkaline solutions.

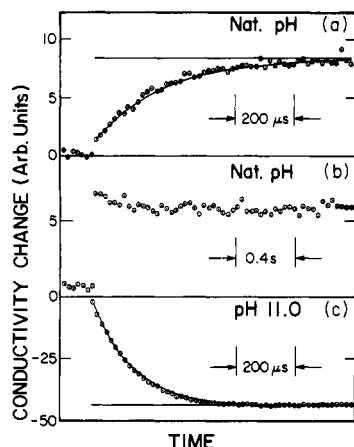


Figure 1. Conductivity changes occurring on irradiation of deaerated solutions of $41 \mu\text{M Cr}(\text{phen})_3^{3+}$: (a) short-term changes at natural pH; (b) long-term changes (without flow) at natural pH; (c) decrease at pH 11.0. Solid curves represent first-order kinetic fits.

features, measured in this work, could be made with those reported for similar conditions, there was good agreement.^{2,5,7,22,25,26} The concentrations of the solutions, prepared from water purified by a Millipore Super-Q system and deaerated by bubbling with argon, ranged from 40 to $98 \mu\text{M}$. The pHs of the solutions were adjusted by the addition of reagent grade perchloric acid or sodium hydroxide, and the temperature range was 20.5–28.0 °C. All solutions were prepared just prior to use, and they were exposed to as little extraneous light as possible.

The irradiation of the solutions at 347 nm employed a frequency-doubled ruby laser (Korad K1QP) with ca. 70-mJ pulse (duration ca. 15 ns), and the reaction vessel was a flow-through 1-cm² quartz cell. Changes in laser intensity, typically two- to fivefold, did not alter the results with one exception. At the highest laser intensities attainable, there appeared in basic media a prompt drop in conductivity following the laser pulse (less than about 20% of the overall conductance change). This seems to be associated with significant ground-state bleaching. Such was not observed at lower intensities as used in this work. The ac conductivity and optical detection apparatus is described elsewhere along with the computer-based system, employed for collection and analysis of the data.²⁷ Quantum yields as measured from conductivity measurements were determined relative to those of tris(2,2'-bipyridine)chromium(III) ion¹⁵ and of the system benzophenone-tetranitromethane (3:1 water-2-propanol, pH 3).³² The equivalent ionic conductivities for H⁺ and OH⁻ are 350 and 198 Ω⁻¹ cm² equiv⁻¹, respectively, and those for Cr(phen)₃³⁺ and related ions have been taken as about 50 Ω⁻¹ cm² equiv⁻¹.³³ Numbers given in parentheses are the number of separate determinations, and errors are cited as estimated standard deviations.

Results

In this study of the photobehavior of Cr(phen)₃³⁺, three different facets have been investigated over a pH range of 3.0–11.1, and they are emission and absorption (ESA) of the doublet level (²T₁/²E) and the change in conductivity. Whereas emission and ESA monitor directly the excited state, changes in conductivity provide potential insight into both excited- and ground-state chemical reactions. In general, the latter phenomenon was found in this study to be markedly dependent upon pH. Only minor changes in conductivity took place in acidic media; however, much larger changes transpired at natural pH (ca. 7.1) and in alkaline solution as shown in Figure 1. Of note here is that, at natural pH, an increase in conductivity occurred, and this was concomitant with decay of the doublet state (Table I). Subsequently, about a 25% decrease took place (Figure 1b). In alkaline solution, the conductivity not only decreased but also the values of the associated rate constants depended upon pH (see below).

By contrast, the effects of pH on the emissions and ESA features were smaller. Pulse irradiation at 347 nm that populates

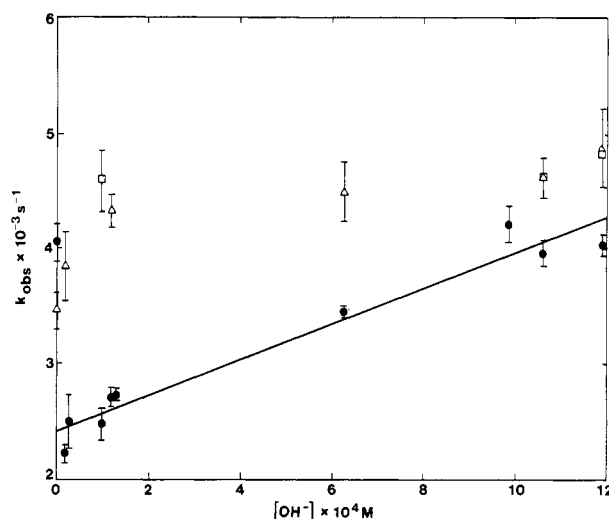


Figure 2. Plots of observed first-order rate constant vs. concentration of hydroxide ion for deaerated, 40–50 $\mu\text{M Cr}(\text{phen})_3^{3+}$: (●) conductivity; (□) emission (726 nm); (Δ) ESA (515 nm). Points on the left vertical axis are for natural pH. Unweighted least-squares regression analysis (solid line): index of fit 0.952; intercept $(2.4 \pm 0.1) \times 10^3 \text{ s}^{-1}$; slope $(1.5 \pm 0.1) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

principally a quartet level (^a-⁴T₁, in analogy to the case for the congeneric Cr(bpy)₃³⁺)² gave rise to the prompt occurrence (within the time duration of the laser pulse) of emission at 727 nm and ESA at 369–515 nm. This was followed by relatively slow decays that obeyed apparent first-order rate laws. In Table I, a summary of the corresponding observed rate constants for various pHs is given, and within experimental error, the values for both phenomena are the same. While they do show about a 45% increase on going from pH 3.0 to 11.1, the initial levels of emission and absorption remained nearly constant (less than 15% change) over this pH range. Because the growth and decay of these features for the doublet state are well separated in time,^{2,13,17,19} the approximately constant behavior indicates that the intersystem crossing(s) efficiency from the nascent quartet to the doublet states remains relatively unaffected over our range in pH. A notable difference between Cr(bpy)₃³⁺ and Cr(phen)₃³⁺ in acidic media is that whereas for Cr(bpy)₃³⁺ transitory bleaching of absorption is observed subsequent to the decay of ESA,^{15,16} no such feature has been observed for Cr(phen)₃³⁺ by Bolletta and co-workers or by us.⁵

A second significant difference between these two complex ions is found in the conductivity behavior in acidic solutions. For Cr(phen)₃³⁺, there was a slight but prompt increase in conductivity, following excitation. Subsequently some decay occurred at pH 4.0 on a time scale comparable to that for emission decay, but at pH 3.0, the rate of conductivity decrease was now considerably slower although the low levels of change precluded accurate, kinetic measurements. By contrast for Cr(bpy)₃³⁺, a significant increase occurs with the same rate as that for emission decay of the doublet excited state, and the subsequent conductivity kinetics match that of the aforementioned bleaching of absorption.¹⁵ On the basis of the maximum level of change in acidic solution, that for Cr(phen)₃³⁺ was about 2% of that for Cr(bpy)₃³⁺ even though in basic media (see below) the overall conductivities differed only by approximately a factor of 2.

For experiments carried out in alkaline solutions, the most notable feature was a relatively large decrease in conductivity on the 200- μs time scale (Figure 1). This change obeyed an apparent first-order rate law; however, there are several prominent features associated with it. At pH 9.2–9.4, the observed rate constant was about a factor of 2 smaller than those for emission and ESA and also for the conductivity change encountered at natural pH (Table I). While only small increases in the values of the observed rate constants for emission and ESA occurred on going to higher pHs, a more substantial increase in that for conductivity transpired as portrayed in Figure 2. The change in k_{obsd} (conductivity) can

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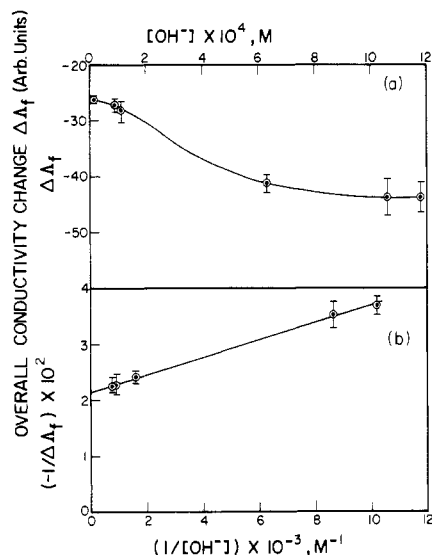


Figure 3. Overall conductivity changes $\Delta\Delta_f$ as a function of concentration of hydroxide ion for a deaerated solution of $41 \mu\text{M Cr}(\text{phen})_3^{3+}$: (a) plot of $\Delta\Delta_f$ vs. $[\text{OH}^-]$; (b) plot of $-\Delta\Delta_f^{-1}$ vs. $[\text{OH}^-]^{-1}$. Unweighted least-squares regression analysis for solid line of part b: index of fit 0.998; intercept $(2.16 \pm 0.02) \times 10^{-2}$; slope $(1.52 \pm 0.04) \times 10^{-6} \text{ M}$.

be represented as a linear function of hydroxide ion concentration as shown by the solid line; however, the index of fit (0.952) suggests that the linearity is an approximation to a more complex situation.

Associated with this increase in k_{obsd} was a concomitant increase in the level of the conductivity as shown in Figure 3. No further movement to the conductivity level was observed up to 10 s after the laser pulse. The competitive role of hydroxide ion in establishing the overall level of the conductivity change is made more apparent by the plot of $-1/\Delta\Delta_f$ vs. $1/[\text{OH}^-]$ (Figure 3b): not shown is the point at the lowest concentration of hydroxide ion used ($16 \mu\text{M}$), which lies considerably off the line of best fit (index 0.998). In contrast to this behavior, the final level of conductivity change for $\text{Cr}(\text{bpy})_3^{3+}$ shows little if any dependence on hydroxide ion concentration under basic conditions similar to those for $\text{Cr}(\text{phen})_3^{3+}$.

The overall changes for this latter complex were compared to the changes encountered for two other systems, namely $\text{Cr}(\text{bpy})_3^{3+}$ in basic media and the benzophenone-tetranitromethane mixture (see Experimental Section). These comparisons provided two separate routes to estimate the chemical quantum yield for $\text{Cr}(\text{phen})_3^{3+}$. Within $\pm 20\%$, the calculated quantum yields as determined by the two approaches agreed, and the averaged values were 0.05 and 0.08 at the two pH extremes of 9.2 and 11.1, respectively. (In the comparison, the yield for deaerated $\text{Cr}(\text{bpy})_3^{3+}$ at pH 9.3 is 0.13.²) These calculations were performed on the presumption that the overall conductivity change does in fact represent the overall chemical reaction as in eq 1, and this seems appropriate in light of the fact that no further conductivity movement was found even up to relatively long times (10 s) and of the features discussed below.³⁴

Discussion

For both $\text{Cr}(\text{phen})_3^{3+}$ and $\text{Cr}(\text{bpy})_3^{3+}$, the overall stoichiometry for photoaquation is that of eq 1.^{5,16} In each case, plots of the observed rate constants for thermal aquation and of the apparent quantum yields for photoaquation vs. pH show the same type of sigmoidal-shaped curve: The respective values are very small in acidic media, for example $\phi_{\text{phen}} = 5 \times 10^{-4}$ (pH 5.1, deaerated, 22°C , 1 M NaCl),⁵ and then on progression to neutral and alkaline conditions, substantial increases occur with the devel-

opment of a plateau region in the range of about pH 9–11. While there are clear indications of some photoreaction from the quartet levels, this is small relative to that from the doublet states ($<10\%$), and intersystem crossing efficiencies (quartet to doublet states) for both complex ions exceed 90%.^{2,11,23,25}

Ground-State Intermediate. The similarities for these systems between their thermal and photolytic behaviors argue strongly in favor of the occurrence of a ground-state intermediate(s) that is common to both the photochemical and thermal mechanisms.^{2,5,16} We observe for a natural-pH solution of $\text{Cr}(\text{phen})_3^{3+}$ that there is an increase in conductivity, indicative of proton formation and accompanying the decay of the ${}^2T_1/{}^2E$ excited state, and this provides direct support for the presence of a ground-state intermediate(s) exhibiting an acid-base property. Estimates of the intensity of absorbed radiation and comparison of the conductivity changes here and in basic solutions point to a $\text{p}K_a$ value around 7, which is slightly higher than that estimated of 5–6 for the bipyridyl case.^{15,35} The fact that, subsequent to this initial conductivity increase, a drop of about 25% occurs (Figure 1b) and this is not followed by any further change up to 1 s after the laser pulse appears to reflect the experimental conditions and the acid-base characteristics of the final products. The formation of protons as a consequence of irradiation will cause the pH to decrease below its initial value of ca. 7.1. The extent of this decrease is somewhat problematical, but our estimates suggest the resulting pH to be around 5. As such, the solution will have the attributes of a buffer mixture owing to the properties of the final products: $\text{Hphen}^+/\text{phen}$ ($\text{p}K_a$ 4.9–5.0)³⁶ and $\text{Cr}(\text{phen})_2(\text{H}_2\text{O})_2^{3+}/\text{Cr}(\text{phen})_2(\text{H}_2\text{O})(\text{OH})^{2+}/\text{Cr}(\text{phen})_2(\text{OH})_2^+$ ($\text{p}K_{a1}$ 6.0; $\text{p}K_{a2}$ 3.4).³⁷

Basic Media. While there are similarities between the overall behaviors of $\text{Cr}(\text{phen})_3^{3+}$ and $\text{Cr}(\text{bpy})_3^{3+}$ as delineated above, the results given here and elsewhere^{2,15} point to the occurrence of significant kinetic differences, particularly with reference to the conductivity phenomena. In basic media, two distinct stages of decrease in conductance occur for $\text{Cr}(\text{bpy})_3^{3+}$, and they represent the sequential consumption of hydroxide ion to yield the long-term product $\text{Cr}(\text{bpy})_2(\text{OH})_2^+$ (eq 1). In contrast to the case for $\text{Cr}(\text{phen})_3^{3+}$, only one stage of decrease is discernible (Figure 1a,b) even out to the second time scale. Bolletta and co-workers report that permanent spectral changes transpire on flash photolysis of alkaline solutions.⁵ Although their time scale is not cited, there appears to be no reason for the presumption that the development of the final product $\text{Cr}(\text{phen})_2(\text{OH})_2^+$ does not occur within our observation period, and thus we assume that the observed conductivity change is in part associated with the formation of this product.

Several reasons can account for the discernment or appearance of only one stage. Since we measure changes in conductivity rather than the levels themselves, an association of the complex ion with hydroxide ion prior to irradiation such as in the formation of an ion pair or a covalent hydrate species would not necessarily manifest itself on subsequent irradiation of the associated species; however, it is not apparent to us as to why such should prevail for the phenanthroline complex but not for the analogous bipyridyl system. Furthermore, while there are some changes to the lifetimes for ESA and for emission (and even larger changes for steady-state emission quantum yields)¹¹ with pH (Table I), they are relatively small and even more so with reference to the initial levels for ESA and emission. A second explanation, which seems more probable for our conditions (pH <11), is that, as for $\text{Cr}(\text{bpy})_3^{3+}$, there are also two stages for $\text{Cr}(\text{phen})_3^{3+}$ but they are not well-resolved in time. A significant indication of this possibility is that the observed rate constant for conductivity movement at pH 9.2 is about half the value of those for decay of emission and ESA and that the former increases more markedly with increasing hydroxide ion

(34) If the overall conductivity change reflects the consumption of one hydroxide ion as opposed to the proposed two units, then the chemical quantum yields would be a factor of 2 greater than those cited in the text.

(35) Sriram, R.; Henry, M. S.; Hoffman, M. Z. *Z. Inorg. Chem.* **1979**, *18*, 1727.

(36) *IUPAC Chem. Data Ser.* **1979**, No. 22.

(37) Inskip, R. G.; Bjerrum, J. *Acta Chem. Scand.* **1961**, *15*, 62.

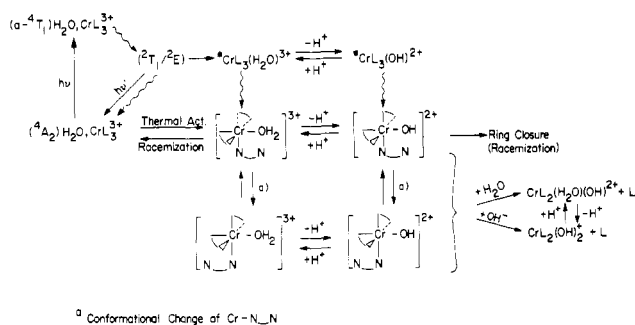
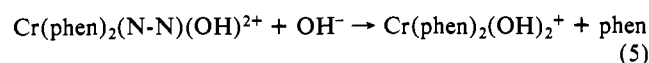
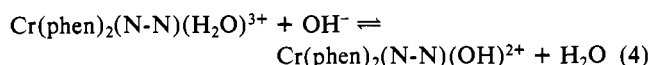
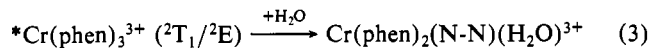


Figure 4. Proposed mechanistic scheme.

concentration (Figure 2). A computer simulation of the following scheme indicates that it is a plausible explanation:



where N-N is a monodentate phen. It is presumed here that, on the millisecond scale, eq 4 represents a near-equilibrium situation. If the rate associated with eq 3 is only marginally faster than that of eq 5, then the observed conductivity rate constant (with $[OH^-] \gg [Cr(phen)_2(N-N)(OH)^{2+}]$) will appear to be somewhat smaller than those monitoring the decay of the $^2T_1/2E$ species. On progression to higher concentrations of hydroxide ion, the observed rate constant describing the conductivity behavior will approach those for emission and ESA. This is the type of response that is shown in Figure 2.

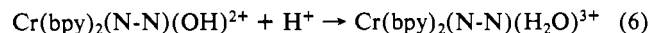
Generalized Mechanism. In order to elaborate on and to discuss further the mechanistic similarities and differences between $Cr(phen)_3^{3+}$ and $Cr(bpy)_3^{3+}$, we propose for consideration the general scheme depicted in Figure 4, where L and N-N represent respectively the bi- and monodentate ligands. Our development places emphasis on the potentially important interactive roles played by the degree of rigidity of the organic ligand and the microstructure of the solvent molecules surrounding these propeller types (D_3) of complexes, and in so doing, it expands on earlier suggestions made by others on the importance of these features.^{2,7,9,25,28,38} In this context, the species designated as H_2O, CrL_3^{3+} represent situations where water is in close proximity to the complex such as in the pocket regions, and those symbolized as $*CrL_3(H_2O)^{3+}$ infer new and stronger interactions. Considerable discussion has focused on whether or not such species represent seven-coordinate (Cr-O bond) or ligand covalent hydrate entities.^{2,28,29} Since in this regard our conductivity measurements do not provide an unequivocal distinction, it suffices perhaps to note that water molecules within or near the pocket regions are potentially well-placed to interact with the chromium center and the ligand, and thus the above designations represent limiting descriptions to what is likely to be highly cooperative circumstances. For simplicity, the ring-opening step is portrayed as being in association with nonradiative deactivation of $*CrL_3(H_2O)^{3+}/*CrL_3(OH)^{2+}$ although the latter could precede the former.

The conductivity measurements do not provide here a clear basis for distinction; however, they do indicate direct evidence for an ionization process ($pK_a \lesssim 2$) for the case of $Cr(bpy)_3^{3+}$ that is attributed to proton release from $*Cr(bpy)_3(H_2O)^{3+}$ and that is in competition with nonradiative deactivation.¹⁵ The results of this study show no such corresponding phenomenon for $Cr(phen)_3^{3+}$ even though the lifetime of its doublet state is about 5 times larger than that for $Cr(bpy)_3^{3+}$ under essentially the same

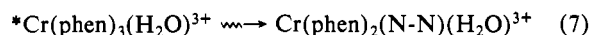
conditions. One does see for the phenanthroline case some conductivity increase in acidic media, but it is only a few percent of that in alkaline solution and its kinetic behavior is different from the major behavior of $Cr(bpy)_3^{3+}$ for acidic conditions. Important clues as to the possible origins of the remarkable differences between these two complex ions seem to appear in the effects of solvent, anions, and rigidity of the ligands on the quartet-doublet intersystem-crossing yields and in some instances the lifetimes of the doublet states.^{2,7,9,25,38} Sriram and co-workers²⁵ found that the substitution of D_2O for H_2O significantly decreased the intersystem-crossing yield for $Cr(bpy)_3^{3+}$ but left that for $Cr(phen)_3^{3+}$ unaffected. They interpreted this to indicate that water is less strongly bound for the phenanthroline complex. This type of picture was also used to discuss the markedly different lifetimes for $Cr(bpy)_3^{3+}$, $Cr(phen)_3^{3+}$, and related complex ions and the greater effect of ClO_4^- on the prolongation of the lifetime for $Cr(bpy)_3^{3+}$ than on that for $Cr(phen)_3^{3+}$.^{2,7,38} In the present context, deactivation entailing in part proton release is perceived to be more efficient for the bipyridyl complex than that for the phenanthroline system owing to the latter's less favorable solvation properties and the more rigid nature of the ligand.

The important kinetic aspect associated with this is that a route involving an excited-state ionization process is available to generate the ground-state intermediate of a base form in the case of $Cr(bpy)_3^{3+}$ even in acidic media ($pH > 2$) whereas for $Cr(phen)_3^{3+}$ such a pathway is insignificant. The formation and possible capture by hydroxide ion is believed to be an essential requirement to the subsequent release of the organic ligand;^{2,5,15,16} however, unlike previous interpretations, we suggest that one is predominantly dealing at the longer time scales with the six-coordinate species $CrL_2(N-N)(OH)^{2+}$ (and the aquo form), where N-N is a monodentate ligand, rather than a seven-coordinate entity. This perception offers a reasonable basis to explain several features, which are otherwise rather puzzling.

One of these features is that, for acidic solutions of irradiated $Cr(bpy)_3^{3+}$, transitory optical bleaching occurs,^{15,16} but such is not apparent for $Cr(phen)_3^{3+}$ in this and an earlier study.⁵ In the former case, the rates of restoration of both bleaching and conductivity are the same with $k_{obsd} = k_0 + k_a[H^+]$ ($k_0 = 39 \text{ s}^{-1}$, $k_a = 8.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$).¹⁵ In this context, the k_a term refers at least in part to the reaction of eq 6. This is associated with a pK_a value



in the range of 5-6 and is followed by ring closure. Since our estimate of the pK_a value for $Cr(phen)_3^{3+}$ is somewhat higher (pK_a ca. 7), its corresponding rate constant for eq 6 could be larger; however, the principal point is the absence in acidic media of formation of $Cr(phen)_2(N-N)(OH)^{2+}$; i.e., the dominant route to the ground state is that of eq 7.



Implied in eq 6 is protonation of the hydroxyl group rather than that of the uncoordinated nitrogen atom. While protonation of the latter is possible,³⁹ we suggest that this transpires at lower pHs. The reasons for this are that, for the coordinated but monodentate organic ligand, its situation is more analogous to that for the monoprotonated, free ligand than to that for the unprotonated form. Second, protonation of the monodentate ligand would be expected to hinder ring closure whereas protonation of coordinated hydroxide ion would facilitate closure as H_2O is generally a more facile leaving group than is OH^- . For $Cr(bpy)_3^{3+}$, the kinetic effect of increasing proton concentration is to enhance the rate of restoration. There is however a second facet to the effect of increasing acidity, which was previously unexplained¹⁵ but which now appears commensurate with the above statements, namely that the level of restoration becomes less complete at lower pHs: It is about 90% at pH 2.3 whereas it is complete at pH 4. Although such is barely discernible for $Cr(phen)_3^{3+}$, the pattern as mentioned in the Results section is

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similar, and its presence may be a reflection of the small amount of reaction arising from the nascently populated quartet level.

In alkaline solutions, the route followed to the ground-state intermediate, in particular $\text{CrL}_2(\text{N-N})(\text{OH})^{2+}$, whose presence can lead to net chemical reaction (Figure 4), becomes less critical, and the chemical quantum yields for the two complex ions are relatively close (0.08 (phen), 0.13 (bpy)) as found here and in earlier reports where the conditions are similar.^{2,15} There is however an additional feature to be considered that is potentially applicable to both acidic and basic circumstances. Considerable evidence exists for uncoordinated bipyridine exhibiting different conformations in solution involving rotation about the C(1)–C(1') bridging axis whereas such is precluded for phen owing to its fused ring system,^{40–42} and the corresponding possibility for the monodentate ligand seems probable. While the occurrence of different conformers for the bpy complex may not significantly affect aquation, it would be expected to statistically hinder ring closure, which represents a competitive process as does protonation in acidic media (Figure 4). This expectation seems fulfilled in that, for the complexes in basic solutions, the observed rate constants describing the conductivity decreases are of the form $k_{\text{obsd}} = k_i + k_s[\text{OH}^-]$. For $\text{Cr}(\text{bpy})_3^{3+}$, this applies to the second stage of the conductivity change.¹⁵ Presumably the intercept term reflects in part ring closure, and thus it is noteworthy that $k_i(\text{phen})/k_i(\text{bpy}) \approx 3 \times 10^3/1$.⁴³ Such may also aid in explaining the observation that the final level of conductivity change for the phen case depends upon hydroxide ion concentration (Figure 3) whereas this is not apparent for the bipyridyl system.

Comparison of Photoaquation and Photoracemization. Bolletta and co-workers have drawn attention to the possible interconnection between these two phenomena with reference to both the photolytic and the thermal behavior of $\text{Cr}(\text{phen})_3^{3+}$.⁵ In regard to the photobehavior, the conditions under which aquation and racemization were studied are sufficiently different so as to restrict such comparisons.^{5,11,12,18} The circumstances of the current investigation provide a more favorable basis to make comparisons. All of the available evidence points to strong similarities between the two phenomena, both photolytic and thermal.^{2,5,14,44} For instance, the major portions (>90%) of photoaquation and photoracemization both derive from the behavior of the $^2T_1/2E$ state, and change in optical activity as with the aquation yield increases with increasing basicity, although for the former, a plateau region at higher pHs is less discernible.¹¹ These and other features have

led to the proposal of a common ground-state intermediate(s),⁵ which we suggest to be of the monodentate type as portrayed in Figure 4.

A significant difference between the yields of photoracemization and photoaquation is that, in acidic solutions, the quantum yield for racemization is much larger than that for aquation: Our conductivity results indicate that aquation is less than a tenth of that for racemization (see also ref 11). Consequently, the major portion of the loss in optical activity is via an intramolecular racemization process in *acidic* media. Arguments for and against twist and one-ended dissociation mechanisms have been made,^{2,5,11,44} and we favor the involvement of monodentate species as shown in Figure 4. The comparison between the two phenomena is complicated by their sensitivity to experimental conditions with notable factors for photoracemization of $\text{Cr}(\text{phen})_3^{3+}$ being its dependency on wavelength of excitation, pH, and temperature,⁴⁵ and thus our comparisons are restricted to situations that most closely resemble the conditions employed in this investigation. Sasseville and Langford report for deaerated solutions (20–25 °C) values of $\Phi_{\text{rac}}(\text{obsd})$ such as 0.0372 (pH 5.9, λ_{ex} 457.9 nm) and 0.0367 (pH 3.0, λ_{ex} 488.0 nm).¹⁸ Earlier results have been done at 350-nm irradiation (closest to our position at 347 nm), where at natural pH, $\Phi_{\text{rac}}(\text{obsd}) = 0.048$ (deaerated) and 0.016 (aerated): The difference is ascribable to quenching by oxygen.¹¹ The change for aerated media from natural pH to 0.25 M HCl caused a 20% drop in $\Phi_{\text{rac}}(\text{obsd})$,⁴⁶ and one anticipates in the absence of oxygen quenching a yield of about 0.038, which is consistent with the aforementioned results, carried out at somewhat longer wavelengths.

Given the intramolecular nature of racemization (that is, $\Phi_{\text{rac}}(\text{obsd}) = \Phi_{\text{rac}}/2$), the actual value of Φ_{rac} is expected on the basis of the foregoing values to be in the neighborhood of 0.075. In aerated and basic media, $\Phi_{\text{rac}}(\text{obsd})$ increases, and we propose as in Figure 4 that this arises because the change in optical activity now occurs predominantly through net chemical reaction. In support of this is the observation that our determination of $\Phi_{\text{rx}} = 0.08$ (pH 11.1) is close to the estimated $\Phi_{\text{rac}} \approx 0.075$. These strikingly similar values provide a strong line of support for the interconnection mechanistically between photoaquation and photoracemization.

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 (41) Castellano, S.; Gunther, H.; Ebersole, S. *J. Phys. Chem.* **1965**, *69*, 4166.
 (42) Linnell, R. H.; Kaczmarczyk, A. *Z. Phys. Chem. (Leipzig)* **1961**, *65*, 1196.
 (43) Some caution, as noted in the Results section, appears to be warranted with reference to the specific values of k_i and k_s (Figure 2) for the phen system because the fit of the data to a linear function suggests that this may be an approximation to a more complex situation.
 (44) Lawrance, G. A.; Stranks, D. R. *Inorg. Chem.* **1977**, *16*, 929.

- (45) The quantum yield for aquation is independent of wavelength from 313 to 404 nm;⁵ however, to our knowledge, this aspect has not been reported at longer wavelengths where the quantum yield for racemization shows such dependency.¹⁸
 (46) Kane-Maguire, N. A. P., personal communication.