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Photochemistry and Photophysics of *cis*- and *trans*-Diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III) Ions in Acidified Aqueous Media under Different Pressure and Temperature Conditions

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The photochemical and photophysical behaviors of the complex ions *cis*- and *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$, where cyclam is 1,4,8,11-tetraazacyclotetradecane, have been investigated in acidified aqueous media by pulsed-laser techniques in conjunction with conductivity and near-UV–visible optical detection methods and by steady-state photolytic procedures carried out under different pressure and temperature conditions. The lowest doublet electronically excited state for the cis complex has been characterized in terms of its absorption and emission properties and of the effects of pressure and temperature on its lifetime: $\Delta V^{*}_{obs}(\tau^{-1}) = +2.9 \pm 0.4$ cm^3 mol^{-1}, and $E_a(\tau^{-1}) = 36 \pm 1$ kJ mol^{-1}. The decay of the doublet state yields an intermediate that subsequently reacts to release ammonia. The values of the ammonia quantum yield (0.15 ± 0.05) and of the associated volume of activation (+0.6 ± 0.4 cm^3 mol^{-1}) are independent of the irradiating wavelength, including that for the lowest spin-forbidden doublet band. The trans complex shows very little chemical reactivity of either a transitory or permanent nature; however, the lifetime of the lowest doublet excited state does exhibit a strong dependence on temperature, and correspondingly the observed volume of activation varies significantly with temperature: $\Delta V^{*}_{obs}(\tau^{-1}) = +1.5 \pm 0.3$ and $+6.6 \pm 0.6$ cm^3 mol^{-1} at 4.0 and 57.8 °C, respectively. Contributions of different possible excited-state processes to the observed volumes and energies of activation are discussed.

Introduction

The photochemistry and photophysics of octahedral type chromium(III) complex ions in liquid and solid phases have been under active investigation from both experimental and theoretical viewpoints for many years, and a number of recent reviews have appeared that describe the diversity of photobehavior encountered in such systems.[2-7] This sustained interest arises in part because the photosubstitutional mechanisms and excited-state properties of chromium(III) complexes continue to elicit considerable debate on several key issues: the relative chemical importance of the lowest electronically excited states (spin-forbidden doublet and spin-allowed quartet states), the types and roles of nonradiative processes such as the possible involvement of thermally activated back-intersystem crossing (bisc) from the lowest doublet to a low-lying quartet state(s), and the potential occurrence of chemically reactive ground-state intermediates.

In this latter context, we have reported in a recent communication on the presence of a chemically reactive intermediate in the photoaquation of *cis*-$[Cr(cyclam)(NH_3)_2]^{3+}$ (eq 1) where

$$cis\text{-}[Cr(cyclam)(NH_3)_2]^{3+} + H_2O \xrightarrow{h\nu} cis\text{-}[Cr(cyclam)(NH_3)(H_2O)]^{3+} + NH_3 \quad (1)$$

$$NH_3 + H^+ \rightarrow NH_4^+ \quad (2)$$

cyclam is the macrocyclic tetraamine 1,4,8,11-tetraazacyclotetradecane.[8,9] In acidic aqueous solutions, the extremely rapid protonation of released ammonia will lead to a change in conductivity. For changes in proton concentration down to about 0.1 μM, the associated conductivity movements can be readily discerned by using ac and dc detection techniques having microsecond and submicrosecond time resolutions, respectively.[10] In correlation with measurements of phosphorescent emission from the doublet state, these methods can be used to follow the evolutionary sequence of events for the reacting system.

In the present study, these time-resolved approaches have been used and extended to include near-UV–visible absorption detection in order to try to obtain different, but complementary, perspectives about the photodynamic behavior of the cis and trans complexes. We have also undertaken steady-state photolytic experiments under differing conditions of pressure and temperature with the aim of obtaining insight into the intimate mechanisms. The trans isomer, in contrast to the cis form, is reported not to undergo net photochemical change,[9] and thus the study of the former affords a propitious opportunity to investigate radiative and nonradiative processes associated with the lowest doublet excited state in a situation potentially unencumbered by chemical reaction.

Experimental Section

Actinometry and Apparatus. The time-resolved apparatus using conventional flash photolysis and pulsed-laser sources (argon ion with cavity dumping (488 and 514 nm); frequency-doubled Q-switched neodymium–YAG (530 nm); frequency-doubled ruby (347 nm)) coupled with UV-visible absorption–emission and conductivity detection methods have been described elsewhere.[10-13] For excitation at 308 nm, a Lumonics Hyper EX-400 instrument with Xe/HCl gas was used, and this output was also employed as a pump source for the dye Coumarin440 (Exciton), having lasing centered around 436 nm (fwhm ca. 9 nm). In pulsed measurements, the conductivity signals were calibrated against the signal for

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photorelease of ammonia from $[Cr(NH_3)_6]^{3+}$ in acidified media with $\phi(NH_3)$ equal to 0.45.[14] For steady-state photolytic experiments, the light sources were CW modes of an Ar ion laser (476.5 nm) and of a DCM dye laser (646.0 nm) or a 500-W mercury arc lamp (437 nm isolated with a combination Bausch-Lomb H9-436 interference filter and a Corning CS 3-75 cutoff filter), and actinometry was performed by the reineckate procedure.[15]

Quantum yields for the release of ammonia in acidic media under steady-state irradiation were based upon measurements for changes in pH using an Orion digital ionanalyzer (model 301A) with a Fisher Accuphast or Corning semimicro combination electrode with reference to calibration curves. Emission spectra, quantum yield determinations, and quenching experiments were performed with a Spex Fluorolog 222 or Shimadzu RF 540 spectrofluorometer. Emission yields were determined relative to that for $[Cr(NH_3)_6]^{3+}$ ($\phi_{em} = 5.5 \times 10^{-5}$)[16] by using procedures described by Demas and Crosby.[17] UV-visible absorption spectra were recorded on Cary 2315 or 118C spectrophotometers.

The high-pressure apparatus, employing quartz optics for spectrophotometric and photolytic measurements, has been described elsewhere.[11,13] Observed volume-changes $\Delta V^{\ddagger}_{\mathrm{obs}}(X)$, where X is the reciprocal of the lifetime (τ) or of the quantum yield of reaction (ϕ_{rx}), were calculated from plots of ln X versus pressure. The plots were found to be linear on the basis of unweighted least-squares regression analysis, and $\Delta V^{\ddagger}_{\mathrm{obs}}(X)$ is defined as

$$\Delta V^{\ddagger}_{\mathrm{obs}}(X) = -RT\left[\frac{\partial \ln X}{\partial P}\right]_T \qquad (3)$$

where R is the gas constant and T is temperature (K). Where the effects of pressure were small, values of $\Delta V^{\ddagger}_{\mathrm{obs}}(X)$ were calculated by using the integrated form of eq 3 at the two pressure limits and on the presumption that $\Delta V^{\ddagger}_{\mathrm{obs}}(X)$ is independent of pressure.

Materials and Solutions. The cis and trans forms of $[Cr(cyclam)(NH_3)_2]^{3+}$ were prepared as nitrate–hexafluorophosphate salts by the methods described by Kane-Maguire and co-workers.[9] Because photochemical results for the trans compound as described below implicate a reaction involving the nitrate anion, the salt of *p*-toluenesulfonate (OTs), *trans*-$[Cr(cyclam)(NH_3)_2](OTs)_3$, was prepared by replacing in the synthesis the precipitating agent NH_4PF_6 by *p*-toluenesulfonic acid (BDH; material recrystallized from water): attempts to prepare in this manner the analogous cis salt were not successful. The presence of dissolved oxygen in aqueous media is reported not to effect the room-temperature emission lifetime of *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$.[9] Our results involving comparisons between aerated and deaerated media, in addition to confirming this, also showed that the presence or absence of oxygen has no apparent effects on the lifetime of phosphorescence or chemical quantum yield for the cis complex ion: deaeration was achieved by bubbling the solutions with argon or dinitrogen.

Water purified by a Millipore Super-Q type of system was used to prepare the solutions, and these were prepared just prior to use and were exposed to as little extraneous light as possible. Adjustments to pH were made by addition of perchloric or nitric acids of reagent or ultrapure quality (Merck or Alfa Products).

Results

Photobehavior of *trans*-$[(Cr(cyclam)(NH_3)_2)]^{3+}$. This complex has a doublet-state lifetime of 43 ± 2 μs (23–27 °C; λ(excit) 347 and 530 nm). Its associated phosphorescence yield is (9.1 ± 0.2) × 10^{-4} (22 °C, λ(excit) = 421 nm), and thus this species is one of the strongest emitting chromium(III) complex ions in aqueous acidic media.[2,16] Information available as supplementary material shows that the emission band for the doublet to quartet ground-state transition and that for the corresponding ground-state absorption are vibrationally structured, and the spectra exhibit a strong mirror-image quality to each other: the 0–0 positions occur at 669.3 nm for absorption and at 670.2 nm for emission. The emission spectrum and intensity as well as the lifetime are found generally to be independent of the presence or absence of dissolved oxygen, the concentration of the chromium complex (1–6 mM), the pH (1–4), and the nature of the acid used (HNO_3, $HClO_4$). Furthermore, the emission spectra and lifetimes are the same within experimental error for the samples of the tosylate salt and of the hexafluorophosphate–nitrate salt.

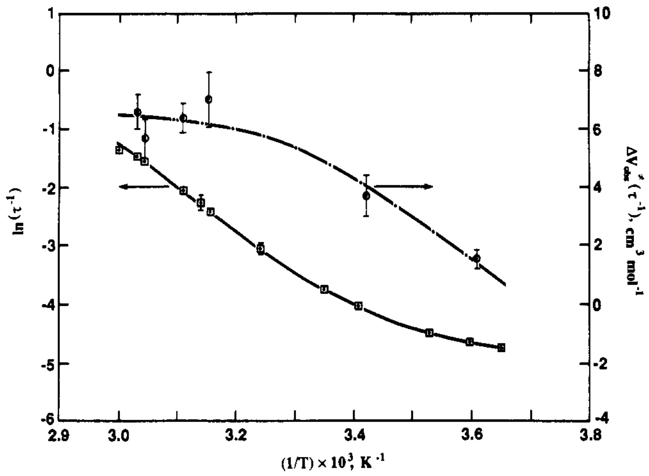

Figure 1. Plots of the natural logarithm for the reciprocal of the lifetime in microseconds and of the observed volume of activation $\Delta V^{\ddagger}_{\mathrm{obs}}(\tau^{-1})$ versus the reciprocal of the absolute temperature for *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$. Conditions: 0.5–5.7 mM complex; 0.01–0.1 M $HClO_4$; 0.9–60.2 °C; λ(em) 680 nm; λ(excit) flashlamp, 488 (Argon-Ion Laser) and 308 nm (Excimer-Xe/HCl laser). The solid curve is the fit to eq 4 and that of the dash–dot curve is the fit to eq 5: see text for parameters.

The emission lifetime does exhibit a marked dependency on temperature over the range of 0.9 to 60.2 °C as shown in Figure 1. The solid curve connecting the data points represents the fit achieved by using a two-term expression (eq 4). The first term

$$\tau^{-1} = k_{\mathrm{obs}} = k_0 + k_T e^{-(E_a/RT)} \qquad (4)$$

has been taken to be temperature-independent because earlier studies have shown that, at temperatures below 250 K, the lifetime varies little with temperature or with the nature of the media.[9,18] For the purpose of fitting the data, the k_0 value has been taken as 5.71×10^3 s^{-1}, the average of the reciprocal lifetimes reported for different media at 77 K.[9] The second term expresses the temperature dependence in the form of an Arrhenius function with k_T of (5 ± 3) × 10^4 s^{-1} and the apparent activation energy E_a being 59 ± 2 kJ mol^{-1}.

The effect of applied pressure on the lifetime has been studied from room pressure to 207 MPa. For a given temperature, plots of ln k_{obs} versus pressure are found to be linear with positive slopes; i.e., the lifetime increases with increasing applied pressure. The observed volumes of activation $\Delta V^{\ddagger}_{\mathrm{obs}}(\tau^{-1})$ have been calculated from the linear slopes by using the definition of $\Delta V^{\ddagger}_{\mathrm{obs}}(\tau^{-1})$ given in eq 3. The resulting values are shown in Figure 1, and they exhibit a dramatic increase in proceeding from the low-temperature region ($\Delta V^{\ddagger}_{\mathrm{obs}}(\tau^{-1}) = +1.5 \pm 0.3$ cm^3 mol^{-1}, 4.0 °C) to the high-temperature region ($\Delta V^{\ddagger}_{\mathrm{obs}}(\tau^{-1}) = +6.6 \pm 0.6$ cm^3 mol^{-1}, 57.8 °C). To model this behavior, the definition of the volume of activation (eq 3) has been applied to form of k_{obs} given by eq 4 to yield eq 5. The assumption made in this derivation is that

$$\Delta V^{\ddagger}_{\mathrm{obs}}(\tau^{-1}) = (k_0 \Delta V^{\ddagger}_0 + \Delta V^{\ddagger}_T k_T e^{-(E_a/RT)})/k_{\mathrm{obs}} \qquad (5)$$

the parameters $\Delta V^{\ddagger}_0$ and $\Delta V^{\ddagger}_T$, representing the intrinsic volumes of activation for the lower and higher temperature regimes, respectively, are independent of pressure, and the linearity found in the plots of ln k_{obs} versus pressure at all temperatures indicates that this assumption is a reasonable approximation over our range of pressures. The dot–dash curve shown in Figure 1 demonstrates that eq 5 provides a good description of the variation of $\Delta V^{\ddagger}_{\mathrm{obs}}(\tau^{-1})$ with temperature. The value of $\Delta V^{\ddagger}_0$ is negative, but small (−1.8 ± 1.1 cm^3 mol^{-1}) whereas that for $\Delta V^{\ddagger}_T$, which is associated with the higher temperature region, has a relatively large, positive value of +6.7 ± 0.3 cm^3 mol^{-1}.

In view of these substantial changes in lifetimes and volumes of activation with temperature, it is essential to their interpretation to discern if this behavior arises from the presence of chemical

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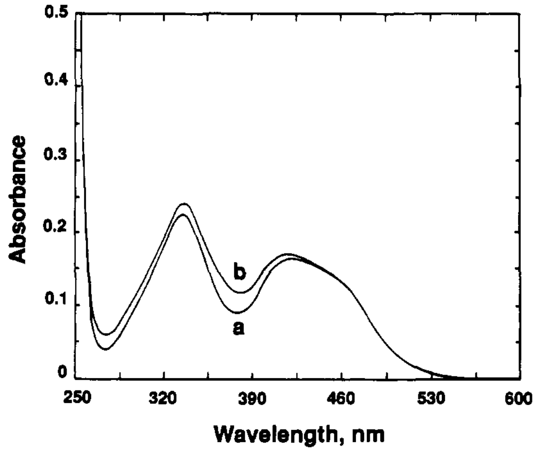

Figure 2. Absorbance of 4.9 mM *trans*-$[(Cr(cyclam)(NH_3)_2](PF_6)(NO_3)_2$ in aerated 1 mM HNO_3 solution at 54 °C and 1 cm path length: curve a, unirradiated solution; curve b, solution irradiated at 476.5 nm (1.0×10^{-7} einstein s^{-1}) for 1 h.

processes of either a permanent or a transitory nature. To address the possible occurrence of short-lived species, pulsed laser experiments have been carried out in conjunction with conductivity and UV–visible optical detection techniques. The wavelengths of radiation were 530 and 347 nm, corresponding to irradiation of the first- and second-quartet ligand-field bands, respectively. Over the 180-μs timeframe following the end of the laser pulse (<20-ns duration), during which period the phosphorescent decay from the doublet state is completed, no discernible conductivity change has been observed. Thus the yield of any process that might give rise to chromium–nitrogen heterolytic bond cleavage such as loss of ammonia ligand or the partial loss of coordination by cyclam, which in turn would give rise to detectable proton concentration changes, is very small ($\phi(\Delta[H^+]) \leq 0.007$). Furthermore, no absorption changes in the range 340–750 nm were detected in these time-resolved experiments.

The absence of long-term changes to proton concentration have been confirmed by the results obtained from steady-state laser-irradiation (476.5 nm) experiments performed at 10 and 54 °C. Under these conditions of prolonged irradiation, small absorption changes did occur for the complex having hexafluorophosphate–nitrate counterions as shown in Figure 2; however, irradiation of the corresponding tosylate salt under the same photolytic conditions led to far less change (by at least a factor of 6).[19,20] The presence of the nitrate anion is definitely a contributing factor because when sodium nitrate is added to solutions of the tosylate salt, they become photosensitive in the manner shown in Figure 2. This situation may be similar to that reported recently by Ruminski and co-workers for the occurrence of photoredox for a series of chromium(III) ammine complexes in the presence of nitrate anion to yield small amounts of nitrite and chromate products ($\phi \ll 0.01$).[21] Since chromate ions absorb intensely in the region of maximum absorption change (ca. 370 nm) shown in Figure 2, their presence could account for the small level of change observed here. Notwithstanding the occurrence of some photochemistry, the conclusion is that its presence does not have a major, direct bearing on the behavior of the doublet excited state because its emission spectra and lifetime are independent of the nature of the complex salt whereas the photoinduced absorption changes do depend upon the nature of the salt. These features in conjunction with the radiative decay being a minor process and the absence of detectable intermediates show that the decay of the doublet state is primarily determined by at least two nonradiative processes, one of which involves thermal activation.

Table I. Emission and Lifetime Characteristics of the Doublet State for Aerated *cis*-$[Cr(cyclam)(NH_3)_2]^{3+}$ Solutions

characteristic	value
emission quantum yield[a]	$\phi_{em} = (1.7 \pm 0.1) \times 10^{-4}$
activation energy for ϕ_{em}^{-1} [b]	$E_a(\phi_{em}^{-1}) = 43.1 \pm 0.8$ kJ mol^{-1}
observed lifetime[c]	$\tau = 1.51 \pm 0.02$ μs
activation energy for τ^{-1} [d]	$E_a(\tau^{-1}) = 36 \pm 1$ kJ mol^{-1}
volume of activation[e]	$\Delta V^{\ddagger}_{obs}(\tau^{-1}) = +2.9 \pm 0.4$ cm^3 mol^{-1}
radiative lifetime[f]	$\tau_0 = 8.9 \pm 0.5$ ms
activation energy for τ_0^{-1} [f]	$E_a(\tau_0^{-1}) = 7 \pm 1$ kJ mol^{-1}

[a] Conditions: λ(excit) = 468 nm; 22.0 ± 0.1 °C; 0.1 M HNO_3; 3.0 mM $[Cr]^{3+}$. [b] 8–47 °C.[9] [c] Conditions: λ(excit) = 488 nm; 22.0 ± 0.1 °C, 1.0 mM $HClO_4$; 5.0 mM $[Cr]^{3+}$. [d] Conditions: λ(excit) = 488 nm; 10.0–39.8 °C; 0.1 M $HClO_4$. [e] Conditions: λ(excit) = 488 nm; 11.0–39.8 °C; room pressure to 207 MPa; 1.0 mM $HClO_4$; 5.0 mM $[Cr]^{3+}$. [f] See text.

Photobehavior of *cis*-$[(Cr(cyclam)(NH_3)_2]^{3+}$. The cis complex, like that of the trans form, is notable for its relatively strong phosphorescent emission in aqueous media at room temperature. The quantum yield for emission along with other parameters characterizing the doublet excited state are presented in Table I. The decay of emission obeys a first-order rate law, and the associated lifetime is found in general to be independent of complex concentration (0.6–10.3 mM), pH (1–5.4), and the presence or absence of dissolved oxygen. The τ value is also independent of the excitation wavelength from 347 to 530 nm, corresponding to irradiation of first- and second-quartet ligand-field bands having peak maxima at 468 and 356 nm, respectively. Lifetime measurements made by other investigators on aqueous mixtures of alcohols and dimethyl sulfoxide fluids and glasses show that the transition from the low- to the high-temperature regions, unlike that for the trans complex, occurs around 200 K, and thus our results pertain to the high-temperature region.[9,18] Consistent with this is that the observed volume of activation $\Delta V^{\ddagger}_{obs}(\tau^{-1})$ is independent of temperature over our range of 11.0–39.8 °C. The value of $\Delta V^{\ddagger}_{obs}(\tau^{-1})$ and that for the apparent activation energy $E_a(\tau^{-1})$ are given in Table I, and they were determined from the slopes of the linear plots of ln τ^{-1} versus pressure or the reciprocal of the absolute temperature, respectively.

Information available as supplementary material shows that the absorption and emission bands corresponding to the transitions between the quartet ground state and the lowest doublet excited state are vibrationally structured with the 0–0 positions being at 671.1 (absorption) and 670.2 nm (emission). For both *cis*- and *trans*-$[(Cr(cyclam)(NH_3)_2]^{3+}$, the 0–0 band widths are relatively narrow (fwhm = 100–210 cm^{-1}), and their positions for the two isomers are within 2 nm of each other. This close proximity coupled with the narrow band width indicates that the emitting doublet levels in the case of each isomer are likely to be derived from the ^2E_g level in O_h parentage.[22,23]

The results presented in our earlier communication on the transitory photobehavior of the cis complex show that the decay in emission from the doublet state leads to subsequent conductivity changes, indicative of the formation of a chemical intermediate.[8] Reaction of the intermediate gives rise to release of ammonia and formation of the final product *cis*-$[(Cr(cyclam)(NH_3)(H_2O)]^{3+}$ (see Discussion). To discern if the intermediate absorbs in the near-UV-visible range, time-resolved experiments were carried out by using 530-nm radiation. On pulse irradiation, an absorption band with a peak at 320 nm as shown in the inset to Figure 3 had fully developed within the time response of the apparatus (<20 ns). Its subsequent decay obeyed a first-order law with the as-

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(19) The change in the absorption spectrum upon irradiation (Figure 2) can not be accounted for solely on the basis of the occurrence of trans to cis isomerization or that of ammonia aquation based upon the reported spectra for the resulting products.[9]

(20) Kane-Maguire and co-workers found no discernible photoreaction after 30 h of 365-nm irradiation from a Hg-Xe lamp, so it seems probable that our detection of a small amount of absorption change under laser-irradiation conditions points to the presence of a process(es) having a very low quantum yield.[9]

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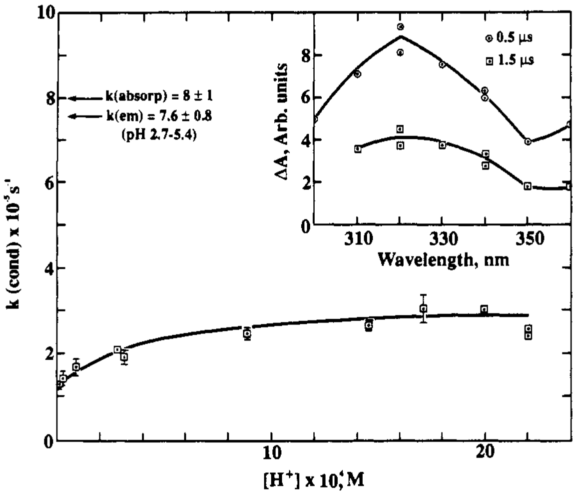

Figure 3. Plot of observed first-order rate constants versus proton concentration and the doublet-state absorption spectrum associated with irradiation of *cis*-$[Cr(cyclam)(NH_3)_2]^{3+}$. Conditions: (a) Absorption kinetics and spectrum, deaerated, pH 3.0 solution at 22–24 °C for 530-nm irradiation with complex concentration of 3.0 mM (spectrum) and, for kinetics, 3.0 and 10.3 mM; (b) conductivity rate constants, deaerated, pH 2.65–5.43 solutions at complex concentrations of 0.6–3.0 mM and at 22–27 °C, λ(excit) = 347 and 530 nm; (c) emission rate constant, deaerated, pH 2.7–5.4 solutions at complex concentration of 0.6–10.3 mM at 22–27 °C, λ(em) = 680 nm and λ(excit) = 347 and 530 nm.

sociated rate constant of $(8 \pm 1) \times 10^5\ s^{-1}$ being independent of wavelength (310–360 nm) and complex concentration (3.0–10.3 mM). The rate constant for emission from the doublet excited state, measured under the same experimental conditions, is found to be $(7.6 \pm 0.8) \times 10^5\ s^{-1}$, and thus the decay rates for absorption and emission are within experimental error identical. For wavelengths between 310 and 750 nm, no additional absorption on the microsecond and longer time scale was detected.[24] The absorption that is encountered has the decay rate of the doublet state, and it can reasonably be assigned to doublet excited-state absorption (ESA). The fact that the ESA is fully developed by the end of the laser pulse upon irradiation of the first-quartet band shows that intersystem crossing from the first-quartet excited state to the doublet level is very rapid, probably on the picosecond (or less) time frame as found for related systems.[2]

The photochemical quantum yield for release of ammonia (eq 1) and the associated volume of activation $\Delta V^{\ast}_{obs}(\phi(NH_3))$ have been measured under steady-state irradiation conditions at room pressure and at 207 MPa. The laser wavelengths used of 476.5 and 646.0 nm correspond to irradiation of the first-quartet ligand-field band and of the spin-forbidden doublet band, respectively. The results are presented in Table II along with the values of $\phi(NH_3)$ reported by Kane-Maguire and co-workers for steady-state photolysis of the second-quartet ligand-field band and by ourselves using pulsed laser conductivity methods.[8,9] The quantum yield and volume of activation are found to be independent of wavelength, and the values of $\phi(NH_3)$ determined by different procedures (steady-state versus time-resolved measurements) are the same.

Discussion

Our previously reported results on the photobehavior of the cis complex obtained by time-resolved conductivity measurements provide several salient features that need to be considered in conjunction with those found here in the pulsed laser absorption and steady-state photolysis experiments.[8] Between pH 4.0 and 5.4, the conductivity signal increases following pulse irradiation of the first- and second-quartet ligand-field bands (see Figure 1 of ref 8), and the value of the associated first-order rate constant ($(8.1 \pm 0.5) \times 10^5\ s^{-1}$) is the same as those for the decay in emission and ESA for the doublet state as given in the Results. While the value of the conductivity rate constant is independent of pH, the maximum development of the signal height decreases in a manner indicating that the proton-release process, which gives rise to the conductivity increase, has a pK_a value of ca. 4.6. At slightly longer times, a decrease in conductivity obeying an observed first-order rate law occurs, and at pH <4, this is the only conductivity change encountered over our longest period of observation (1 s). Below about pH 3, the decrease in conductivity reflects the release of ammonia and its subsequent protonation (eq 2) although at higher pH some contribution will occur from the acid–base reaction of the final product *cis*-$[Cr(cyclam)(NH_3)(H_2O)]^{3+}$ having a pK_a of 4.0.[8]

Table II. Quantum Yields at Room Pressure and Volumes of Activation for Release of Ammonia for *cis*-$[Cr(cyclam)(NH_3)_2]^{3+}$

ligand-field band	irradn wavelength, nm	$\phi(NH_3)$	$\Delta V^{\ast}_{obs}$-($\phi(NH_3)$), $cm^3\ mol^{-1}$	ref
doublet	646.0[a]	0.15	+0.6[b]	this work
1st quartet[c]	530[d]	0.16 ± 0.04		8
1st quartet[c]	476.5[a]	0.15 ± 0.01	+0.6 ± 0.4	this work
2nd quartet[c]	365[e]	0.2		9
2nd quartet[c]	347[d]	0.14 ± 0.02		8

[a] Conditions: pH 3 (HNO_3); [Cr] = 5.3 mM; 22.0 °C; aerated solution; Δ(pH) – measurement. [b] Pressure: room pressure and 207 MPa. [c] Peaks of 1st quartet and 2nd quartet are 468 and 356 nm, respectively. [d] Conditions: pH 2.7–3.3 ($HClO_4$); [Cr] = 0.6–3.0 mM; 22–26 °C; deaerated solution (Ar); $\phi(NH_3)$ measured relative to $\phi(NH_3)$ = 0.45 for $[Cr(NH_3)_6]^{3+}$. [e] Conditions: pH ~3 (HNO_3); 22 °C; Δ(pH) – measurement.

A plot of the observed first-order rate constant describing the decrease in conductivity *k*(cond) as a function of proton-concentration in the pH interval between 5.4 and 2.65 is shown in Figure 3. The value of *k*(cond) is found to increase with increasing acid concentration until pH 3 where a plateau is attained. A key observation is that the values of *k*(em) and *k*(ESA), which characterize the decay of the doublet excited-state, are always greater than that for *k*(cond): the closest approach occurs in the plateau region where *k*(em)/*k*(cond) = (2.7 ± 0.4)/1. The fact that the rate of release of ammonia as shown by the conductivity decrease is always smaller than that for the decay of the doublet excited state is *not* consistent with mechanisms commonly proposed to explain the photobehavior of related chromium(III) amine complexes, namely, ones involving the final products arising directly from the decay of the doublet level or from a rate-limiting back-intersystem crossing process to a low-lying quartet state, followed by prompt chemical reaction, because these mechanisms necessitate that at pH below 4, where the rate for ammonia protonation is not rate-limiting, *k*(cond) should equal *k*(em) (and *k*(ESA)), which is experimentally not found.[25]

The foregoing kinetic and pH results do indicate that there is a chemical intermediate derived from the decay of the doublet excited state and that the subsequent reaction of the intermediate gives rise to the release of ammonia and the formation of *cis*-$[Cr(cyclam)(NH_3)(H_2O)]^{3+}$. The intermediate's longevity (microsecond scale), the quenching effects of $[Cr(CN)_6]^{3-}$ on the emission and conductivity,[8] and the apparent absence of any emission (up to 800 nm) or ESA attributable to any other species except the doublet excited state argues against the intermediate being an electronically excited entity and perforce favors its description as a ground-state product.

The proposed mechanistic scheme based upon the results obtained from both time-resolved and steady-state measurements is shown in Figure 4. The symbols $[Cr]_{GS}$, $[{}^{\ast}Cr]_Q$ and $[{}^{\ast}Cr]_D$

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(24) Given the level of chemical yield found for the reaction of the cis complex, our expectation is that our equipment would be capable of detecting transitions with molar absorption coefficients at or in excess of $1 \times 10^3\ M^{-1}\ cm^{-1}$. It thus seems probable that the absence of detectable absorption attributable to the intermediate implies that it exhibits weakly absorbing bands, which are not greatly different from ligand-field transitions of the starting material ($\epsilon < 1 \times 10^2\ M^{-1}\ cm^{-1}$ in the visible region).

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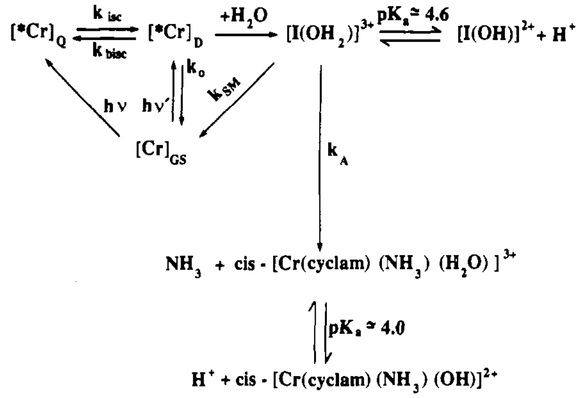

Figure 4. Proposed mechanistic scheme.

designate *cis*-$[Cr(cyclam)(NH_3)_2]^{3+}$ in its ground state and the lowest quartet and doublet states, respectively. For purposes of clarity, we have not shown the possible reaction (see below) of a thermally equilibrated quartet level to yield the intermediate $[I(OH_2)]^{3+}$. The intermediate has been shown as incorporating a coordinated water molecule in order to account for the fact that the intermediate exhibits an acid–base process with a pK_a of ca. 4.6; however, its specific structure is not known although it may be of a seven-coordinate type or alternatively it may be six-coordinate with one nitrogen position of the cyclam ligand being unbound. The pathway designated by k_0 represents the summation of radiative and nonradiative events leading from the doublet level to the ground state of the starting material. The value of k_0 can be approximated as the reciprocal of the observed lifetimes found in various media at 77 K, and as these lifetimes are considerably longer than that at room temperature, these events are not likely to contribute significantly to the deactivation of the doublet state observed under our conditions.[9,18] Allowance has also been made for the possibility that the intermediate $[I(OH_2)]^{3+}$ may revert to the starting material (pathway k_{SM}) as well as converting to the final products (pathway k_A). Because the cis complex is highly susceptible to rapid base hydrolysis (but it is thermally inert in acidic media), it has not been experimentally feasible to determine if the basic form of the intermediate $[I(OH)]^{2+}$ is chemically reactive.[9] To minimize this possible complication, we have used in the steady-state photolytic experiments solutions at or below pH 3.

As shown in Table II, the values of $\phi(NH_3)$ and $\Delta V^{*}_{obs}(\phi(NH_3))$ are independent of wavelength, including those found on irradiation of the lowest spin-forbidden band, which populates directly the doublet state ($^2E_g(O_h)$). Consequently the intersystem crossing efficiencies (η_{isc}) from the first- and second-quartet levels to the lowest doublet state are essentially unity. Furthermore, the implication is that, at least for the nascently populated quartet-states, they are chemically unreactive, and consistent with this conclusion is the finding in the time-resolved conductivity studies that no change proceeds at a rate faster than that for the decay of the doublet-excited state; i.e., no prompt chemical reaction from a quartet level is detected.

Through the recognition that η_{isc} is essentially one and from data presented in Table I, estimates of the radiative lifetime τ_0 and its associated activation energy $E_a(\tau_0^{-1})$ can be obtained by means of the relationships given in eqs 6 and 7, where τ and ϕ_{em}

$$\tau_0 = \eta_{isc}\tau/\phi_{em} = \tau/\phi_{em} \quad (\text{for } \eta_{isc} = 1) \qquad (6)$$

$$E_a(\tau_0^{-1}) = E_a(\phi_{em}^{-1}) - E_a(\tau^{-1}) \qquad (7)$$

are the observed lifetime and phosphorescent quantum yield, respectively. The room-temperature value of τ_0 of 8.9 ms is well within the range of values encountered at low temperatures for many related amine systems,[3,26] and the attendant expectation that the associated activation energy $E_a(\tau_0^{-1})$ will be very small is realized here (Table I). The τ_0 value is about 40 times larger than the observed lifetimes measured at 77 K in various media, and this clearly indicates that, even at low temperatures, nonradiative processes predominate.[9,18,26]

The observed phenomenological parameters $E_a(\tau^{-1})$ and $\Delta V^{*}_{obs}(\tau^{-1})$ that describe the effects of temperature and pressure on the lifetimes of the doublet levels for both *cis*- and *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ are composite quantities expressing the effects of temperature and pressure on all of the excited-state events.[2,11] While this feature complicates the interpretation of the phenomenological parameters, it is nevertheless instructive to consider possible contributions to them from the excited-state events. Kane-Maguire and co-workers have studied for both the cis and the trans complexes the effects of isotopic substitution of deuterium (N–D) for the proton (N–H).[9] For the trans complex ion at 283 K in aqueous medium, which as shown in Figure 1 corresponds to the upper end of the low-temperature region, there is a considerable isotopic effect with $k_H/k_D = 5.3/1$, and this feature in conjunction with results at even lower temperatures in nonaqueous media suggests that, in this low-temperature region, weak-coupled deactivation modes predominate and they are likely to be principally associated with the nonradiative decay of the doublet state to the ground state.[18] While the quantity ΔV^{*}_0 represents a composite effect of pressure on the nonradiative and radiative processes in the low-temperature region, its value of −1.8 cm^3 mol^{-1} is small. To our knowledge, the only other case where the volume of activation for the lifetime has been measured in the low-temperature region is that for *trans*-$[Cr(cyclam)(CN)_2]^+$.[2] (For this complex, the high-temperature region predominates at temperatures above 35 °C.)[27] At 23 °C, the value of $\Delta V^{*}_{obs}(\tau^{-1})$ is $+0.1 \pm 0.2$ cm^3 mol^{-1}, and the effects of isotopic substitution ($k_H/k_D = 4.5/1$ at 22 °C) are quite similar to those for the trans ammonia system.[11,28] These findings suggest the general possibility that volume changes in the weak-coupled regions may be small.

In the high-temperature regions, the effects of isotopic substitution on the lifetimes of the doublet levels for both *cis*- and *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ are considerably smaller: $k_H/k_D = 1.2/1$ for the cis complex at 20 °C with that ratio for the trans form being 1.3/1 at 60 °C. Kane-Maguire and co-workers have suggested on this basis that in the thermally activated regions, the decays of the doublet levels now reflect significant contributions from strongly coupled deactivation pathways.[9] Consistent with this view is our finding that for the trans complex in the thermally activated region where E_a is large (59 kJ mol^{-1}), the associated volume of activation ($\Delta V^{*}_T = +6.6$ cm^3 mol^{-1}) is considerably larger than that in the low-temperature regime ($\Delta V^{*}_0 = -1.8$ cm^3 mol^{-1}) and is also opposite in algebraic sign. The change in sign to a positive value on progressing to the high-temperature region indicates that one or more new processes are now controlling the exciting from the doublet state, and in association with this, the system experiences a significant increase in volume on progressing to the transition state(s). While one pathway could involve surface crossing from the doublet level to a ground-state intermediate, we have been unable to detect by either spectroscopic or conductivity means the occurrence of an intermediate.

In our view, a more plausible route is a significant contribution from back-intersystem crossing from the doublet state to a low-lying quartet state, followed by prompt nonradiative decay to the ground state. Several considerations tend to support the existence of such a pathway. Low-lying, equilibrated quartet levels are generally perceived to be distorted with respect to the ground state and in the case of the trans complex also with respect to the doublet level because, as cited in the Results, the emission and absorption bands involving the transitions between the doublet and ground state are nearly mirror images of each other, implying that their potential energy surfaces are very similar.[2,6] On the presumption that ΔV^{*}_T pertains predominantly to one process, its positive algebraic sign, indicating volume expansion, would be consistent

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with a bisc process. The associated activation energy while it is relatively large (59 kJ mol^{-1}) is commensurate with the 0–0 energy gap of ca. 50 kJ mol^{-1} for the spacing between the doublet and quartet states that has been estimated by the procedure given by Fleischauer and co-workers.[29,30]

In the photoreaction of *cis*-[Cr(cyclam)(NH$_3$)$_2$]$^{3+}$ to yield *cis*-[Cr(cyclam)(NH$_3$)(H$_2$O)]$^{3+}$ as the eventual product, an intervening chemically reactive species is found. This intermediate is clearly derived from the decay of the doublet state, and furthermore, its formation appears to be associated with the incorporation of a water molecule. This process would not involve a change in overall electrostatic charge on the complex, and thus a contribution to the volume change due to electrostriction effects is anticipated to be quite small. In this circumstance, one anticipates that the incorporation of water may be attendant by a negative volume change and that if this process involves strong-coupled surface crossing directly from the doublet state to that the ground-state intermediate, then this negative volume change will contribute to the observed volume of activation. This consideration may account for the observed volume of activation (+2.9 cm^3 mol^{-1}) being smaller than that of +6.6 cm^3 mol^{-1} for the trans case; however, the overall algebraic sign for the observed volume of activation of the cis complex is positive, indicating in the general sense that dissociative contributions prevail over associative ones and thus at least one further pathway having a positive volume change must contribute.[31] It is notable in this context that the results found for the decay of the doublet-state emission in the *solid* phase where at 20 °C there is no detectable photochemistry suggest the influence of a strong-coupled relaxation process (other than direct decay to the ground state).[9] Consequently the possibility exists that in the thermally activated region, the decay of the doublet state for the cis complex may follow several strongly coupled pathways in solution although they may not all lead to the generation of the intermediate, and Lessard and co-workers have recently discussed in some detail this type of situation.[27]

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Supplementary Material Available: Tables listing the features of the absorption and emission bands for the transitions between the doublet state and the ground state for *cis*- and *trans*-[Cr(cyclam)(NH$_3$)$_2$]$^{3+}$ in aqueous media (2 pages). Ordering information is given on any current masthead page.

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(30) Lessard and co-workers, employing the same procedure as used by us, report a somewhat larger energy gap of ca. 60 kJ mol^{-1}.[27,29]

(31) The contribution here from a bisc process seems problematical at least from the viewpoint that the observed activation energy (36 kJ mol^{-1}) is less than the estimated energy gap between the quartet and doublet states of ca. 43 kJ mol^{-1}.[29]

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Electrochemical Parametrization of Rhenium Redox Couples

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The observed rhenium potentials for Re$^{IV/III}$, Re$^{III/II}$, and Re$^{II/I}$ reversible couples, for mononuclear species, are analyzed in terms of the electrochemical parametrization scheme based upon the Ru$^{III/II}$ couples. Two independent sets of Re$^{II/I}$ potentials are observed, which, if extended, would cross the Re$^{III/II}$ correlation line. The possible significance of these sets is explored. The Re$^{IV/III}$ couple correlation is roughly parallel to one of the Re$^{II/I}$ correlation lines. The analysis leads to some interesting avenues for future synthetic studies.

General Introduction

Recently[1] a ligand electrochemical series based upon the Ru$^{III/II}$ couple as an electrochemical standard was introduced. From this series of E_L(L) values, it was shown that many redox couples would fit a linear correlation:

$$E(\text{obs}) = S_M[\textstyle\sum E_L(L)] + I_M \qquad (1)$$

where for a given metal and oxidation state, S_M and I_M were constant for all derivatives of given coordination number, stereochemistry, and spin state. The sum $[\sum E_L(L)]$ is the sum of the E_L(L) values for all ligands binding to the metal ion. Thus, a series of linear correlations was presented for various couples, M$^{n+1/n}$, depending on the spin states and relative stereochemistries of M^{n+1} and M^n.

It was noted that, for a very limited data set, pairs of redox couples for the same metal ion had essentially parallel slopes. Thus, the S_M values for the couples Nb$^{V/IV}$ and Nb$^{IV/III}$ were identical. Clarke et al.[2] have demonstrated that the correlation lines for Tc$^{IV/III}$, Tc$^{III/II}$, and Tc$^{II/I}$ are also essentially parallel (Figure 1). However Cr$^{III/II}$ (low-spin Cr^{II}) is not parallel to[1] Cr$^{I/0}$ and some early work with closely related tris(dithiocarbamato)iron complexes showed that the Fe^{III}/Fe^{II} and Fe^{IV}/Fe^{III} couples were not parallel.[3] Thus the issue is unclear.

This report deals with data for Re$^{IV/III}$, Re$^{III/II}$, and Re$^{II/I}$ in order, in part to explore this issue in more detail, but also to obtain fresh insights into rhenium synthetic chemistry. The rhenium system is more complex than that observed for technetium. Two independent lines are observed for the Re$^{II/I}$ couples, and lines for Re$^{III/II}$ and Re$^{II/I}$, if extended, would cross, leading to some interesting synthetic and electrochemical predictions. The Re$^{IV/III}$ line is seen to be approximately parallel to one of the Re$^{II/I}$ lines.

All data are taken from the literature as referenced and are listed versus NHE. Standard corrections were used where other electrodes were involved.[4] Scatter in the figures may reflect some errors arising from poor reference electrodes, wet solvents, poor electrode design, etc., though scatter may also be a consequence of other factors discussed below.

Stereochemistry and Spin State in Rhenium Complexes

The complexes containing the rhenium(I) oxidation state, d^6, are almost invariably low spin and octahedral, but five-coordination is possible.[5] Rhenium(II) may exist in low-spin, d^5, paramagnetic,

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