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Relaxation Pathways of Chromium(III) Quartet Excited States

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The photoracemization of $(+)_D$-$Cr(en)_3^{3+}$ in aqueous solution at 25 °C has been examined under ligand field excitation in the presence and absence of OH^- ion as a specific ^2E_g doublet-state quencher. For excitation wavelengths between 436 and 496.5 nm essentially constant percent reaction quenching by OH^- ion was observed (57%). In contrast, a marked decrease in quenching occurred for irradiations at 514.5 nm (38%) yielding a percent quenching ratio of 0.65 for 514.5 nm vs. 436 nm. The overall racemization quantum yield (ϕ_{rac}) at 25 °C remained constant (0.4) over this wavelength region and was identical with that observed for hydrolysis. These racemization results are interpreted on the basis of a model which indicates that $^4T_{2g} \rightarrow {}^2E_g$ intersystem crossing competes successfully with $^4T_{2g}$ vibrational equilibration. Independent support for this analysis comes from the relative phosphorescence yields (P) on 514 nm vs. 436 nm excitation ($P_{514}/P_{436} = 0.63$), a value in close agreement with the percent reaction quenching ratio (0.65).

Introduction

It has been recently found that a limited number of Cr(III) complexes display readily observable phosphorescence in room-temperature fluid solution.[1,2] This knowledge has been subsequently applied with marked success[3-6] to photoreactive excited-state identification, by comparing phosphorescence and photolysis quenching in the presence of specific doublet (^2E_g) excited-state quenchers. Analysis of these quenching data for the O_h and D_3 systems so far examined strongly supports the contention that photoreaction originates solely out of the quartet ($^4T_{2g}$) excited level.

We explore in this report a promising extension of this quenching technique which provides a clearer insight into the details of $^4T_{2g}$ excited state relaxation in aqueous solution (see Figure 1). Up to the present it has been generally assumed that subsequent to $^4A_{2g} \rightarrow {}^4T_{2g}$ excitation, vibrational equilibration of the $^4T_{2g}$ state is very rapid ($<10^{-10}$ s).[7] The implication has been that chemical reaction and $^4T_{2g} \rightarrow {}^2E_g$ intersystem crossing (ISC) are competitive processes out of the vibrationally equilibrated (Thexi) quartet.[8] Adamson et al.[9,10] have commented, however, on the possibility of ISC occurring prior to complete quartet relaxation—but except for very low-temperature studies on the Reinecke's salt system,[9] strong experimental support has been lacking.

We have chosen to examine this question for the complex $Cr(en)_3^{3+}$, in view of the extensive photochemical and emission data already available on this system. The experimental probe used was the wavelength dependence of $(+)_D$-$Cr(en)_3^{3+}$ photoracemization, in the presence of hydroxide ion as a specific doublet quencher. The reaction quenching results are interpreted on the basis of a model developed in the Discussion. The relative phosphorescence quantum yields in aqueous solution over this wavelength region have also been determined, to provide supportive data for the reaction quenching results. The evidence to be presented is consistent with ISC competing successfully with $^4T_{2g}$ vibrational equilibration.

Experimental Section

Materials. Racemic and optically active $[Cr(en)_3]Cl_3 \cdot 2H_2O$ were prepared according to literature procedures[11,12] with samples in each case recrystallized at least twice. Tris(bipyridine)ruthenium(II) chloride ($[Ru(bpy)_3]Cl_2$) was purchased from G. F. Smith Chemical Co. and used without further purification. All other reagents were of reagent grade quality.

Apparatus. A modified Aminco-Bowman spectrophotofluorimeter (vide infra) was employed for 365- and 436-nm irradiations, the excitation monochromator being followed by Corning 7-51 and 5-60 band-pass filters, respectively. An argon ion laser (Coherent Radiation, Model 52) was used for photolysis studies at 457.9, 476.5, 488.0, 496.5, 501.7, and 514.5 nm. Optical rotation measurements were obtained at 589 nm using a Bendix automatic polarimeter (Model 1144) with digital readout to 0.0002°. Relative phosphorescence intensity data

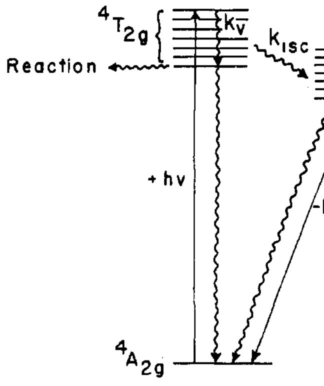

Figure 1. Principal processes that may occur subsequent to vertical excitation ($+h\nu$) to a $^4T_{2g}$ Franck–Condon excited state. The states here and in the text are labeled assuming approximate octahedral microsymmetry. k_V and k_{isc} are the rate constants for $^4T_{2g}$ vibrational equilibration and $^4T_{2g} \rightarrow {}^2E_g$ intersystem crossing, respectively. A wavy line represents a radiationless process.

were collected using an Aminco-Bowman spectrophotofluorimeter (Model 48203D) which had the following modifications incorporated: a red-sensitive Hamamatsu 666 phototube replacing the conventional 1 P21, a 750-nm blazed emission monochromator replacing the normal 500-nm blaze, a Hg lamp instead of the Xe lamp, and the emission monochromator offset to cover the region 300–900 nm (in lieu of 200–800 nm). The alterations were specifically chosen so as to maximize the sensitivity of the instrument toward materials emitting in the red region.

Visible and uv absorption spectra were obtained with the use of a Perkin-Elmer 202 spectrophotometer.

Procedures. Percent Reaction Quenching. In aqueous solution under ligand field (LF) excitation, $Cr(en)_3{}^{3+}$ is known to undergo facile substitution to yield *cis*-$Cr(en)_2(enH)(H_2O)^{4+}$ as the initial photoproduct.[2] Subsequent thermal hydrolysis to *cis*-$Cr(en)_2(H_2O)_2{}^{3+}$ is slow at 30 °C,[13] the process being negligible under our experimental conditions (25 °C and irradiation times less than 15 min). The quantum efficiency of the photostep has been determined previously from spectral or pH changes. In the initial phase of this study spectral and optical rotation changes were both monitored during several photolysis experiments. As a precautionary measure, the photoreaction was followed spectrally at 390 nm, since Jorgensen and Bjerrum[14] reported the extinction coefficients of *cis*-$Cr(en)_2(enH)(H_2O)^{4+}$ and *cis*-$Cr(en)_2(H_2O)_2{}^{3+}$ are identical at this wavelength (ϵ 26.1). Solutions were acidified prior to absorbance measurement to ensure solvent coordination is by water. Within experimental error, the percents reaction obtained by the spectral and polarimetric methods were identical in aqueous solution (vide infra). Since the polarimetric procedure is simpler and is of higher precision, the reaction quenching data were collected solely by this method. Ferrioxalate[15] and Reineckate[16] actinometries were employed when absolute light intensities were required.

The choice of hydroxide ion (OH^-) as a selective ^2E_g excited-state quencher requires comment. Thermal base hydrolysis of $Cr(en)_3{}^{3+}$ is independent of $[OH^-]$[17] and under our experimental conditions makes an insignificant contribution to the observed net reaction. The $Cr(en)_3{}^{3+}$ phosphorescence signal is completely suppressed at the 0.1 M NaOH concentration primarily used in these studies. In fact, for a solution of $[Cr(en)_3]Cl_3$ adjusted to pH 10.60 with OH^- ion, greater than 99% phosphorescence quenching is still observed. It is therefore highly improbable that quenching is associated with >99% conversion to a nonphosphorescent deprotonated $Cr(en)_3{}^{3+}$ species, since this would indicate a coordinated ethylenediamine pK_a value of ~8.6. Although a direct pK_a experimental determination would be difficult,[18] comparison with the analogous Co(III) system argues for the pK_a being ≥13.[19,20] Further, the absorption spectra of $[Cr(en)_3]Cl_3$ aqueous solutions at pH 3.0 and 10.6 are essentially superimposable over the wavelength range 240–650 nm—an observation inconsistent with formation of the amido complex under basic conditions.[21] At higher $[OH^-]$ (e.g., 0.05 M) there is some spectral evidence below 270 nm for $Cr(en)_3{}^{3+},OH^-$ ion-pair formation.

Table I. Wavelength Dependence of $Cr(en)_3{}^{3+}$ Phosphorescence and Photoracemization Quenching at 25 °C

λ, nm	% reactn quenching[a]	Rel quenching[b]	Rel phosphoresence intens[c]
436	58.4 ± 3.4 (2)[d]	0.65	0.63
457.9	57.6 ± 3.0 (5)	0.65	
476.5	57.6 ± 4.6 (4)	0.65	
488.0	56.5 ± 4.8 (4)	0.67	
496.5	55.0 ± 6.0 (10)	0.69	
501.7	49.8 ± 2.9 (5)	0.76	
514.5	37.7 ± 5.4 (9)	1.00	1.00

[a] $[OH^-]$ = 0.10 M; the number of independent determinations is given in parentheses, with the standard deviations providing a measure of the error limits involved. [b] Percent reaction quenching at 514.5 nm relative to that at excitation wavelength. [c] Phosphorescence intensity at 514.5 nm relative to that at excitation wavelength. [d] The corresponding value for $[OH^-]$ = 0.01 M is 58.0%.

Phosphorescence quenching due to ionic strength effects may also be eliminated, since the emission signal is unaffected by the presence of up to 1 M NaCl. The absence of quartet excited-state deactivation by OH^- is experimentally supported by incomplete photoreaction quenching under conditions of total phosphorescence extinction. Furthermore, for a particular excitation wavelength (e.g. 436 nm) the percent reaction quenching remains constant (58%) as the $[OH^-]$ is increased from 0.01 to 0.10 M (Table I). It is also noteworthy that the presence of OH^- has no observable effect on the spectral distribution of $Cr(en)_3{}^{3+}$ emission. Although the exact mechanism of OH^- doublet quenching is not known, deactivation may proceed in a manner similar to that suggested for $Cr(NH_3)_6{}^{3+}$ as substrate.[3] In a previous study by Ballardini et al.[6] $CoCl_2{\cdot}6H_2O$ was employed as a ^2E_g excited-state quencher. The alternative use of OH^- appears to offer several advantages in view of (i) a considerably greater quenching efficiency, enabling small OH^- concentrations to be employed, and (ii) the absence of light absorption and $^4T_{2g}$ excited-state quenching at high OH^- concentrations.

In a typical experiment, equimolar solutions of $[Cr(en)_3]Cl_3$ in water and 0.1 M NaOH were successively irradiated for identical time periods at the wavelength of interest. Complex concentrations and cell path lengths were such that initial solution absorbances were ≥1.5, while photolysis times were adjusted to minimize the extent of reaction (generally ≤12%). Percent reaction quenching was determined from the difference in percent photoracemization for the two solutions.

Relative Phosphorescence Yields. A fresh aqueous solution of $[Cr(en)_3]Cl_3$ was prepared for each phosphorescence measurement at 25 °C. Excitation wavelengths of 436 and 514 nm were examined, the light from the excitation monochromator first passing through Corning 5-60 and 3-72 filters, respectively. In addition, a Corning 3-74 cutoff filter inserted just prior to the emission monochromator eliminated spurious signals associated with second-order grating phenomena. Light absorption by $Cr(en)_3{}^{3+}$ at the two excitation wavelengths was equalized by absorbance matching. The complex displayed a strong phosphorescence signal centered around 680 nm, consistent with literature reports.[1,2] Provided the relative light intensities at the excitation wavelengths are known, a direct comparison of the relative $Cr(en)_3{}^{3+}$ phosphorescence efficiencies is then possible. These relative incident light intensities were determined by comparing emission signals of absorbance-matched aqueous solutions of $[Ru(bpy)_3]Cl_2$ under identical slit conditions. Demas and Crosby[22] have previously demonstrated the wavelength independence of the $Ru(bpy)_3{}^{2+}$ phosphorescence yield over a wide wavelength range (including that of the present investigation). For all emission experiments the sample compartment slits employed yielded excitation and emission bandwidths of 2 and 24 nm, respectively.

Results

Preliminary experiments involving spectral and polarimetric measurements on the same test aqueous solutions indicated that photoracemization and photoaquation of $Cr(en)_3{}^{3+}$ proceed at essentially identical rates. Thus, after 6 min of 476.5-nm excitation, reaction percents of 16.3 (spectral) and 14.1 (polarimetric) were observed, while corresponding values of 35.4 and 31.4 were obtained following 5-min irradiation at 514.5 nm. Further, a racemization quantum yield (ϕ_{rac}) of

0.43 was determined for 365-nm excitation, in good agreement with the literature value for hydrolysis (ϕ_{hyd}). A tabulation of the results for percent quenching by OH^- of $Cr(en)_3{}^{3+}$ photoracemization is provided in Table I for all irradiation wavelengths investigated. These values are compared with the corresponding relative phosphorescence intensities of $Cr(en)_3{}^{3+}$ at these excitation wavelengths. Previous investigations reveal a wavelength independence for $Cr(en)_3{}^{3+}$ photoreaction upon irradiation into either the ${}^4T_{1g}$ or ${}^4T_{2g}$ excited states (250–442 nm).[6] A more recent report[23] also indicates photoreaction proceeds with identical efficiency when excitation is into the ${}^2E_g$ band. We have extended the wavelength range examined in the quartet region by measuring ϕ_{rac} on excitation into the long-wavelength tail of the ${}^4T_{2g}$ band (514.5 nm). The ϕ_{rac} value (0.40) is essentially unchanged from the corresponding yield at 365 nm (0.43, vide supra).

Discussion

A primary objective of the present investigation has been to examine the question as to whether or not ${}^4T_{2g} \rightarrow {}^2E_g$ ISC can compete successfully with ${}^4T_{2g}$ vibrational equilibration in aqueous solution near room temperature—using the $Cr(en)_3{}^{3+}$ system as a test case. We suggest an experimental distinction between these alternative relaxation pathways may be possible, provided a Boltzmann equilibrium does not pertain between the excited levels involved. The very short lifetimes of these states[6,24] for $Cr(en)_3{}^{3+}$ as well as the large energy gap between the ${}^4T_{2g}$ and ${}^2E_g$ zero vibrational levels (~14 kcal)[10] enhance the probability of this latter condition being met. The experimental parameter examined was the wavelength dependence of hydroxide quenching of $(+)_D\text{-}Cr(en)_3{}^{3+}$ photoracemization.

An essential requirement is that the wavelengths chosen populate the ${}^4T_{2g}$ state and bracket a crossover point between the ${}^4T_{2g}$ and ${}^2E_g$ surfaces. The excitation wavelengths employed were 436, 457.9, 476.5, 488.0, 496.5, 501.7, and 514.5 nm. Inspection of the visible spectrum of $Cr(en)_3{}^{3+}$ (Figure 2) indicates that all of these wavelengths fulfill the requirement of absorption into the ${}^4T_{2g}$ excited state. We anticipate the longest wavelength, 514.5 nm, corresponds to generation of the ${}^4T_{2g}$ level near its vibrationally equilibrated (Thexi) configuration. Although the energy of the Thexi ${}^4T_{2g}$ state has not been experimentally determined (due to the absence of $Cr(en)_3{}^{3+}$ fluorescence), Fleischauer et al.[10] have recently advanced an empirical procedure for predicting this value. This method predicts an energy of 56.4 kcal for the Thexi ${}^4T_{2g}$ state, corresponding to a wavelength of 504 nm. The validity of this empirical approach for N_6 chromophoric systems receives support from the recent observation of $Cr(bpy)_3{}^{3+}$ (bpy ≡ 2,2'-bipyridine) fluorescence at a wavelength in agreement with that predicted.[25] Further, some unusual features arising from a biacetyl sensitization study of $Cr(en)_3{}^{3+}$ [2] suggest[10] a nearly isoenergetic relationship between the biacetyl triplet level (56.1 kcal; 508 nm) and the Thexi ${}^4T_{2g}$ state.

However, since little of substance is known concerning the shape of Cr(III) excited-state surfaces, it is a moot point if a crossing point actually exists between the ${}^4T_{2g}$ and ${}^2E_g$ surfaces of $Cr(en)_3{}^{3+}$. Further, even should this latter condition be met, the question remains as to the position of the excitation wavelengths with respect to this point. Four distinct cases may then be envisaged.

Case I. The shapes of the two surfaces are sufficiently different for no crossing to occur.

Case II. All excitations correspond to population of the ${}^4T_{2g}$ state above the crossover point.

Case III. All excitations populate the ${}^4T_{2g}$ level below the crossover point.

Case IV. The wavelengths used span the crossing point.

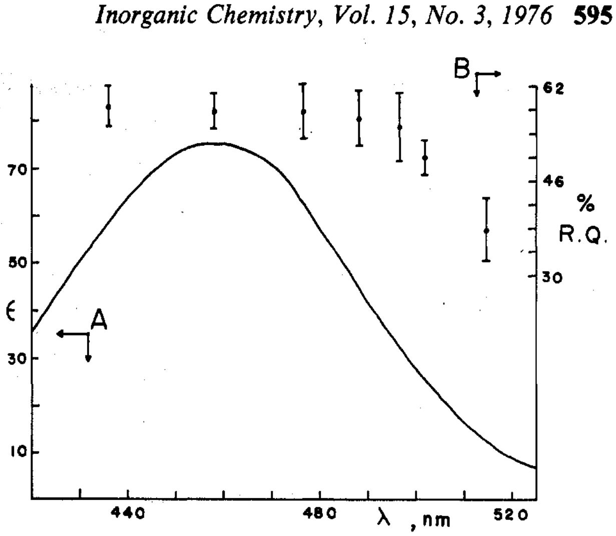

Figure 2. (A) Absorption spectrum of $[Cr(en)_3]Cl_3$ in the region of the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (O_h) band. (B) Variation of percent reaction quenching (% R.Q.) by OH^- of $(+)_D\text{-}Cr(en)_3{}^{3+}$ photoracemization with change in irradiation wavelength.

For cases I–III, irrespective of the relative rates of ISC and quartet vibrational relaxation, no wavelength dependence for percent reaction quenching or phosphorescence intensity is expected. However, for case IV two alternative (and experimentally distinguishable) situations may be considered.

Alternative A. If ISC competes successfully with quartet relaxation, a higher resultant doublet concentration would be expected for irradiations above the crossover point. For excitations below this point, population of the doublet would be dependent on ISC over the small activation barrier imposed by the crossing point. Recent work[6] has convincingly demonstrated that ${}^2E_g \rightarrow {}^4T_{2g}$ back-ISC makes a major contribution to the net photoaquation of $Cr(en)_3{}^{3+}$. Provided the overall reaction yield is wavelength independent (as we observe), the component associated with back-ISC will increase for wavelengths yielding higher doublet populations. The presence of a selective doublet quencher such as OH^- will terminate this alternate reaction pathway. The model predicts then a decrease in the observed percent reaction quenching as the excitation wavelength passes from above to below the crossover point. Furthermore, this decrease should be accompanied by a parallel reduction in phosphorescence efficiency.

Alternative B. If rapid quartet vibrational equilibration occurs prior to ISC, the doublet population will bear no relationship to the position on the quartet surface initially reached by excitation. The percent reaction quenching (and also relative phosphorescence yields) would then be independent of irradiation wavelength. However, such an experimental observation would not lead to an unambiguous interpretation. It would result also if ISC occurred before or during quartet relaxation, provided the two states are now in Boltzmann thermal equilibrium.

The percent reaction quenching results are presented in Table I and Figure 2. For excitation wavelengths from 436 to 496.5 nm essentially constant percent reaction quenching is observed. It is further noted that the average value (57%) is in accord with the extrapolated limiting value reported by Ballardini et al.[6] for 365-nm irradiation of $Cr(en)_3{}^{3+}$ with $CoCl_2{\cdot}6H_2O$ as doublet quencher (60%). In contrast, a marked decrease in quenching occurs for irradiation at 514.5 nm (38%). The experimental observations are difficult to rationalize in terms of cases I–III but are consonant with (i) excitations 436–496.5 nm corresponding to irradiation above a surface crossing point, while 514.5-nm absorption generates the ${}^4T_{2g}$ level below this point (case IV), and (ii) intersystem crossing competing with quartet vibrational relaxation (case IV, alternative A). Since $^2E_g \rightarrow {}^4T_{2g}$ back-ISC proceeds with near unit efficiency,[1,6] 0.57 and 0.38 are then the corresponding quantum yields for $^4T_{2g} \rightarrow {}^2E_g$ ISC for irradiation above and below, respectively, the surface crossing point. Thus, 0.38 represents the efficiency for ISC out of the vibrationally equilibrated $^4T_{2g}$ state. If this analysis is correct, independent experimental support should be forthcoming from the relative phosphorescence intensity studies at these wavelengths. The data in Table I are again in excellent agreement with this expectation. The ratio of the phosphorescence yields at 514 and 436 nm (0.63) matches closely the corresponding reaction quenching ratio (0.65). In addition, the 514-nm vs. 436-nm phosphorescence ratio reported here (0.63) is identical with that observed by Balzani et al.[2] for biacetyl-sensitized vs. direct emission for $Cr(en)_3{}^{3+}$. This information provides further evidence for the near-energetic equivalence of the biacetyl triplet and the Thexi $^4T_{2g}$ level.[10,26] The agreement between the phosphorescence and percent reaction quenching data in Table I is especially pleasing, in view of the clear-cut conclusions which can be drawn from the former. The higher phosphorescence yield associated with 436-nm irradiation clearly indicates a higher resultant doublet population to that obtained on 514-nm excitation. Although wavelength dependence studies of Cr(III) phosphorescence have been reported previously,[28] the present investigation appears to be the first in which yields have been compared across a common absorption band.

Although Beattie and co-workers[29,30] have demonstrated that ISC can be a rapid process, the present results are to our knowledge the first experimental evidence in Cr(III) systems for the step proceeding at a comparable rate to vibrational relaxation in aqueous solution at 25 °C. It has been argued by Adamson et al.[9,10] that a similar situation exists for most Cr(III) complexes at very low temperatures up to the solvent glass point region. The spin-multiplicity restrictions associated with organic photochemistry clearly do not apply rigidly to Cr(III) species, an observation consistent with substantial spin–orbit coupling.

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Registry No. (+)D-$Cr(en)_3{}^{3+}$, 41509-53-9; OH^-, 14280-30-9.

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Conformational Dynamics of Dioxodi-μ-oxo-aminopolycarboxylatodimolybdate(V) Complexes by Carbon-13 Nuclear Magnetic Resonance

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Carbon-13 nuclear magnetic resonance spectroscopy was employed to study the kinetic processes associated with the conformational interconversions of two isomeric forms of a molybdenum(V) complex of ethylenediaminetetraacetic acid, $(MoO_2)_2EDTA^{2-}$. The ^{13}C NMR spectra of the molybdenum(V) complex of *dl*-1,2-propylenediaminetetraacetic acid, $(MoO_2)_2PDTA^{2-}$, and a recently synthesized Mo(V) complex of *trans*-1,2-cyclohexanediaminetetraacetic acid, $(MoO_2)_2CyDTA^{2-}$, are also reported. The latter two complexes were found to be conformationally rigid over the temperature range studied (0–95 °C). Kinetic data for the $(MoO_2)_2EDTA^{2-}$ complex were collected and both rate constants and the corresponding activation parameters were determined by least-squares techniques.

Introduction

X-ray crystallographic studies[1] have established that the ethylenediaminetetraacetic acid (EDTA) complex of molybdenum(V) contains the dioxo-bridged Mo_2O_4 unit. The diamagnetism of the dioxo-bridged species is believed to be a consequence of either spin pairing through the oxo bridges or the formation of a direct metal–metal bond.[2-6] Since many complexes of molybdenum(V) exhibit diamagnetic charac-

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