

to tetramethyl-1,4-dithiin. In the presence of acetone the photolysis of 3 does not lead to 4 and traps the dithiolene ligand and $(\text{H}_3\text{C})_2\text{C}_2\text{S}_2\text{C}(\text{CH}_3)_2$ is presumably formed. A similar type of ligand exchange was thermally observed¹⁷ for $\text{M}(\text{S}_2\text{C}_2(\text{CN})_2)_2^-$ and $\text{M}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2^-$ ($\text{M} = \text{Cu}, \text{Ni}, \text{Pd}$).

Thus, we demonstrate the photoinduced bimolecular bidentate ligand migration reaction with the example of the 1,2-dithiolene ligand migration to a new metal center to form a photochemically stable peridithiolene complex.

Registry No. 3, 12116-98-2; 4, 12090-33-4.

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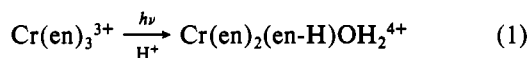
Evidence for Doublet-State Reactivity of the Tris(ethylenediamine)chromium(III) Ion in Aqueous Solution

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The identification of the ligand-field excited state(s) responsible for the photosubstitutional behavior of chromium(III) complexes has been a central and long-standing problem in inorganic photochemistry.^{2,3} Early workers postulated that the doublet state, $^2\text{E}_g$,^{4,5} was photoreactive, but subsequent quenching and sensitization studies,⁶⁻¹¹ buttressed by theoretical models,¹²⁻¹⁴ have provided some persuasive arguments that the lowest quartet excited state, $^4\text{T}_{2g}$, is the main or sole precursor to ligand labilization.¹⁵

A particularly contentious system has been $\text{Cr}(\text{en})_3^{3+}$ (en is ethylenediamine). Irradiation into the lowest energy quartet absorption band ($^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}$) of the complex in aqueous solutions causes both phosphorescent (doublet) emission and Cr-N bond cleavage (reaction 1).¹⁶⁻¹⁸ Addition of various



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quenchers effects substantial quenching of the emission, whereas a smaller reduction in the reaction yield, ϕ , is observed.¹⁰ While the unquenchable portion of the reaction must originate from directly formed $^4\text{T}_{2g}$, the quenchable component could result from (i) thermal repopulation of the reactive $^4\text{T}_{2g}$ state via back intersystem crossing from $^2\text{E}_g$ or (ii) direct reaction from $^2\text{E}_g$.

Detailed studies of the excited-state behavior of $\text{Cr}(\text{en})_3^{3+}$ were undertaken in an attempt to assess the relative importance of these two pathways. On the basis of a kinetic analysis of quenching data, Ballardini et al.¹⁰ concluded that all photochemistry originates from $^4\text{T}_{2g}$. The $^4\text{T}_{2g} \xrightarrow{\text{M}} ^2\text{E}_g$ and $^2\text{E}_g \xrightarrow{\text{M}} ^4\text{T}_{2g}$ intersystem crossing steps were assigned efficiencies of ~ 0.6 and ~ 1 , respectively, so that essentially all of the excited molecules reaching $^2\text{E}_g$ ultimately return to $^4\text{T}_{2g}$ where reaction occurs (e.g., path i). Thus the chief role of the $^2\text{E}_g$ state is that of a temporary repository for excitation energy. Fukuda et al.¹⁹ adopted the opposite view from a pulsed laser study of primary photoproduct formation. These workers concluded that the thermally equilibrated $^4\text{T}_{2g}$ state is formed directly with $\sim 70\%$ efficiency from the initially populated Franck-Condon state and then undergoes reaction 1 with a quantum yield of 0.17 ± 0.03 ; the thermally equilibrated $^2\text{E}_g$ state, on the other hand, is produced with $\sim 30\%$ efficiency via prompt intersystem crossing and subsequently reacts with a quantum yield of 0.8 ± 0.2 (e.g., path ii). Back intersystem crossing from $^2\text{E}_g$ to $^4\text{T}_{2g}$ was taken to be negligible.

A conceptually straightforward test for distinguishing between these alternative proposals involves direct irradiation into the doublet region of $\text{Cr}(\text{en})_3^{3+}$. Selective population of $^2\text{E}_g$ would be expected to enhance the observed quantum yield for Cr-N bond breaking were path ii important but should leave ϕ essentially unchanged if path i dominates.²⁰ We report here the results of this doublet irradiation experiment.

Experimental Section

Commercially available (Alfa Inorganics) $[\text{Cr}(\text{en})_3]\text{Cl}_3 \cdot 3.5\text{H}_2\text{O}$ was twice recrystallized from concentrated perchloric acid solution. The resulting perchlorate salt was washed several times with absolute ethanol and dried over calcium sulfate in an evacuated desiccator. The electronic absorption spectrum of the complex in pH ~ 2.7 HClO_4 (maxima at 459 nm, $\epsilon = 76.0 \text{ M}^{-1} \text{ cm}^{-1}$, and 350 nm, $\epsilon = 61.2 \text{ M}^{-1} \text{ cm}^{-1}$) agrees closely with literature reports.²¹ All spectral measurements were taken on a Cary 15 or 219 spectrophotometer.

Several light sources were used in the photochemical studies. Radiation centered at 404 nm with an 18-nm band width was provided by a 200-W high-pressure mercury-arc lamp in conjunction with interference and blocking filters. A CW Radiation 5-mW helium-neon laser was used for photolyses at 632.8 nm. Excitation at 669.2 nm with a power of 15-18 mW was accomplished with a Coherent Radiation Model 590 dye laser (containing Rhodamine B) pumped with a spectra Physics Model 164 argon ion laser; the output wavelength was determined to within ± 0.2 nm by means of a Spex 1401 double monochromator.

Solutions of $\text{Cr}(\text{en})_3^{3+}$ in pH 2.0-2.7 perchloric acid were irradiated in a 2-cm (404 nm) or a 20-cm (632.8 and 669.2 nm) jacketed cell. Temperature was maintained to ± 0.2 °C by means of a circulating water bath or to ± 0.8 °C by conducting the photolysis at ambient conditions in a constant-temperature darkroom. The contents of the cell were stirred periodically during irradiation to avoid bleaching of $\text{Cr}(\text{en})_3^{3+}$ in the light beam. The extent of reaction 1 (generally

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(20) Several years ago Chen and Porter^{20b} reported that the quantum yield for reaction 1 remains unchanged upon shifting the wavelength of irradiation from the quartet to the doublet (specifically, 632.8 nm) region. This preliminary result, though quoted by others in the literature,¹⁰ was never published by the original workers. (b) Chen, S.; Porter, G. B. Abstracts of the Xth Informal Conference on Photochemistry, Stillwater, OK, May 1972, p 155.

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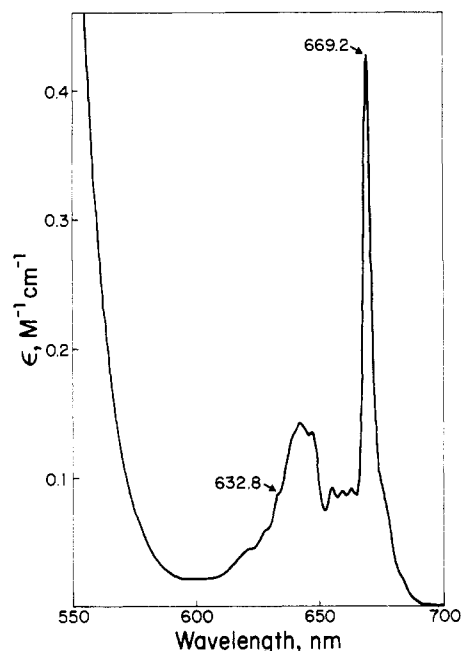


Figure 1. Electronic absorption spectrum of $\text{Cr}(\text{en})_3^{3+}$ in the doublet region. The solvent is pH ~ 2.7 perchloric acid.

$<5\%$) was determined by pH measurements at $\sim 20^\circ\text{C}$ with a Corning combination electrode and Digital 112 pH meter. The pH difference between the irradiated and dark solutions corresponds to uptake of H^+ by the uncoordinated end of the en ligand.¹⁶ For minimization of thermal aquation of the photoproduct and the accompanying further uptake of protons,²² all operations were performed as rapidly as possible. Irradiation times were limited to 5 min at 404 nm, 30–120 min at 632.8 nm, and <9 min at 669.2 nm, while the pH measurements were completed within 15–20 min after the cessation of photolysis. Light intensity was measured by Reineckate actinometry.²³ So that light scattering by suspended particulate matter could be avoided, all solutions used for spectral and photochemical (including actinometry) measurements were filtered at least once through a 0.22- μm Millipore disk filter.

Results and Discussion

The portion of the absorption spectrum of $\text{Cr}(\text{en})_3^{3+}$ corresponding to the spin-forbidden $^4A_{2g} \rightarrow ^2E_g$ transition is shown in Figure 1. The sharp peak at 669.2 nm lies very close to the 0–0 transition, while the other features down to 600 nm represent transitions to higher vibrational levels of 2E_g .²⁴ Most importantly, the components of the doublet transition are sufficiently well separated from the tail of the more intense quartet band to ensure selective population of 2E_g upon irradiation at 632.8 nm and, especially, at 669.2 nm.

Accurate determination of the extremely low extinction coefficients of $\text{Cr}(\text{en})_3^{3+}$ in the 600–700-nm region requires particulate-free solutions so as to avoid a high background of light scattering. Such scattering increases the apparent absorbance of the sample and thereby results in a lowering of the observed quantum yield.²⁵ Absorption measurements of carefully filtered solutions provide what we consider to be reliable extinction coefficients at 632.8 nm ($\epsilon = 0.085 \pm 0.002$

Table I. Quantum Yields for Cr–N Bond Breaking upon Irradiation of $\text{Cr}(\text{en})_3^{3+}$ in Acidic Solution

| temp, $^\circ\text{C}$ | quantum yields (ϕ) ^a | | |
|------------------------|--|---------------------------------|-------------------------------|
| | 404 nm | 632.8 nm | 669.2 nm |
| 10.0 ± 0.2 | <i>b</i> | 0.55 ± 0.05^c (7 values) | <i>d</i> |
| 21.0 ± 0.8 | 0.36 ± 0.00 (3 values) | 0.59 ± 0.03 (4 values) | <i>d</i> |
| 23.0 ± 0.5 | <i>d</i> | <i>d</i> | 0.53 ± 0.00 (2 values) |
| 25.0 ± 0.2 | 0.38 ± 0.01 (2 values) | <i>d</i> | <i>d</i> |

^a Concentration of $\text{Cr}(\text{en})_3^{3+}$ was 0.055–0.07 M; ϕ was independent of initial pH in the range 2.0–2.7. ^b A quantum yield of 0.367 ± 0.002 has been reported for photolysis at 434 nm and 10 $^\circ\text{C}$.¹⁶ ^c Uncertainties represent deviation from the mean. ^d No data were collected under the stated conditions.

$\text{M}^{-1} \text{cm}^{-1}$) and 669.2 nm ($\epsilon = 0.42 \pm 0.01 \text{ M}^{-1} \text{cm}^{-1}$). These values remain essentially unchanged in the temperature interval 10–25 $^\circ\text{C}$.

Quantum yield data for reaction 1 are compiled in Table I. In close agreement with previous studies,^{16,18} we find that irradiation (404 nm) into the first quartet ligand field band of $\text{Cr}(\text{en})_3^{3+}$ causes Cr–N bond breaking with $\phi \approx 0.37$. The key finding, however, is that direct excitation of the doublet region enhances the reaction efficiency by 40–60%.^{26,27} The result at 669.2 nm is especially significant since, as noted above, essentially all of the incident radiation populates the 2E_g state with little or no competitive absorption by the quartet band.

Were $^4T_{2g}$ the sole precursor to reaction, ϕ should remain invariant to a change in the wavelength of irradiation from the quartet to the doublet region. The sharp rise in ϕ actually observed thus provides strong evidence that a significant portion of the photoreactivity of $\text{Cr}(\text{en})_3^{3+}$ originates from 2E_g .²⁸ Under the assumption that all photons absorbed at 632.8 or 669.2 nm cause 2E_g to be populated, our value of $\phi \approx 0.6$ falls at the lower end of the range proposed by Fukuda et al.¹⁹ for the inherent reactivity of this state.

The present study adds to the growing weight of evidence that chemical reaction can be a significant deactivation pathway for the 2E_g state in chromium(III) complexes.^{3,19,29–33}

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- (26) We attach no significance to the drop in ϕ between 632.8 nm (21 $^\circ\text{C}$) and 669.2 nm, since the two values are within the $\pm 10\%$ experimental accuracy of the quantum yield measurements.
 (27) Both the constancy of ϕ with time of irradiation and the excellent agreement between our 404-nm value of ϕ and that reported by Geiss and Schläfer at a slightly longer wavelength¹⁶ lead us to conclude that thermal aquation (estimated rate constant of $6.4 \times 10^{-5} \text{ s}^{-1}$ at 15 $^\circ\text{C}$)²² of the primary photoproduct formed in reaction 1 is negligible under the conditions employed in this study.
 (28) In a recent article²² published shortly after the submission of our results, Cimolino and Linck adopt the opposite viewpoint that the lowest quartet excited state in $\text{Cr}(\text{en})_3^{3+}$ is the sole precursor to reaction. They base their claim upon the invariance to excitation wavelength of the isomeric distribution of the photoproducts (Δ -*cis*-, Δ -*cis*-, and *trans*- $\text{Cr}(\text{en})_2$ - $(\text{en-H})\text{OH}_2^{4+}$ isomers are possible) formed in reaction 1. As noted by the authors themselves, such reasoning rests upon the *assumption* that reactions from the quartet and doublet would result in appreciably different stereochemical outcomes. Moreover, the determination of isomer ratios involved delicate and complex separations (by column chromatography) of product mixtures. In our view, this approach is inherently less accurate than the pH technique we employed to measure overall product quantum yields.
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The scope of this behavior and the factors that determine the relative contributions of quartet vs. doublet photochemistry remain to be delineated.

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Hydrolysis and Carbonate Complexation of Dioxouranium(VI) in the Neutral-pH Range at 25 °C¹

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A review of the data on the hydrolysis and carbonate complexation of uranyl(VI) ion, which are critical to any model attempting to describe the migration behavior of uranium in the geosphere, shows general agreement in regard to the existence of the following species:^{2a} UO₂²⁺, UO₂(OH)⁺, (UO₂)₂(OH)₂²⁺, (UO₂)₃(OH)₅⁺, UO₂CO₃, UO₂(CO₃)₂²⁻, and UO₂(CO₃)₃⁴⁻. Stability constants of the hydrolysis products^{2b} were obtained by potentiometric titrations up to a pH of 4.5, which marks the onset of precipitation of uranates. On the other hand, carbonate complexation constants have been derived from systems containing relatively high concentrations of this ligand. The uranium-carbonate system is also subject to the formation of solids near the neutral-pH region. It is apparent that an accurate representation, in an attempt to describe the behavior of uranium in natural waters on the basis of those species listed above, could not be made without some certainty that other species are not present in the neutral range and at relatively low partial pressures of CO₂ that are more representative of the medium under consideration. Tsymbal,³ in a study of carbonate complexation of the uranyl ion, performed potentiometric titrations that covered the neutral range and detected species additional to those listed above. He explained the data with the inclusion of (UO₂)₃(OH)₇⁻ and UO₂(CO₃)OH⁻. Reports on the existence of another species in the neutral range were also made by Blake et al.⁴ on the basis of spectrophotometric observations. These workers proposed U₂O₅(CO₃)OH⁻ as the formula for this species. The observations regarding this species were of a qualitative nature, and no attempt was made to obtain its stability constant. Finally, Porter⁵ also proposed the existence of U₂O₅(CO₃)OH⁻ on the basis of inflection points in plots of pH vs. volume of HCO₃⁻ added to UO₂(NO₃)₂ solutions.

The present study was undertaken in an attempt to clarify the nature of the uranyl species formed in the neutral-pH range at relatively low CO₂ partial pressures; i.e., 10^{-3.5}-10^{-2.0} atm.

Experimental Section

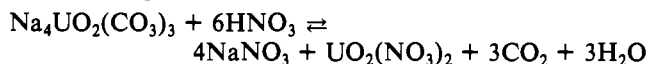
Uranyl dinitrate hexahydrate, Puratronic grade (a highly purified reagent) from Alfa Inorganics was used as starting material to prepare Na₄UO₂(CO₃)₃ according to a procedure described by Tsymbal.³ All other chemicals were AR grade and were used without further purification.

Visible spectra were recorded on a Unicam SP 8-100 spectrophotometer. Cyclic voltammograms were run with a Model 173 potentiostat driven by a Model 175 signal generator both from Princeton Applied Research. pH determinations were done with a Orion Model 701A pH meter using a combination glass electrode. In the potentiometric titrations section of this study the hydrogen ion concentration was determined with an electrode in which the AgCl-saturated 3 M KCl electrolyte filling the electrode was replaced by AgCl-saturated 0.1 M NaClO₄. This was done in order to minimize junction potentials with the titration medium, which contained NaClO₄ as background electrolyte to provide a 0.1 M ionic strength. During the course of the titrations the electrode was calibrated after each titrant addition with a 10⁻³ M HClO₄ solution in 0.1 M NaClO₄. Drift in the calibration readings, which typically were made every 2 h, did not exceed 1 mV. The titrations were conducted in a set of two jacketed cells connected in series and maintained at 25.0 ± 0.1 °C. The cells were provided with a sparge tube through which analyzed gas mixtures containing 0.03, 0.3, and 0.99% CO₂ by volume in nitrogen were passed in separate runs. The first cell served to saturate the gas stream with water vapor while the second was used as the titration vessel. Corrections due to the contribution of the partial pressure of water vapor and the daily changes in atmospheric pressure were taken into account for calculating the equilibrium CO₂ partial pressure for each run. The titrant, 0.1 M HClO₄, was introduced through a Teflon small-bore tube by means of a precision syringe from Micro Metric Instruments Co. A stock solution of 0.01 M U as uranyl tricarbonate with the sodium concentration increased to 0.048 M by the addition of NaHCO₃, for the prevention of hydrolysis, was used in the preparation of the solutions for the titration runs. The ionic strength of these solutions was adjusted to 0.1 M by the addition of NaClO₄.

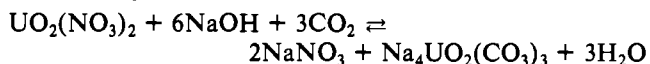
Results and Discussion

Exploratory Experiments. A number of experiments was conducted in order to confirm the presence of uranyl carbonate complexes in the neutral-pH range.

The method employed by Blake et al.⁴ in obtaining the species in question after the addition of 3.5 equiv of HClO₄ to a UO₂(CO₃)₃⁴⁻ solution can be described as an intermediate stage of the process



True equilibrium conditions dictate that the same intermediate stage could be achieved if the above process was reversed as described by



This approach was tried; addition of 2.5 equiv of NaOH/equiv of U to a 0.01 M U solution of uranyl nitrate maintained under 1 atm of CO₂ produced a solution with a pH of 5.0. When excess CO₂ was sparged off with an inert gas, the pH increased to 8.1 and a solution having a visible spectrum identical with that described by Blake et al.⁴ was produced.

Physicochemical changes occurring in the solution as the pH increases during the displacement of excess CO₂ were followed in a number of separate experiments done under the same conditions.

The carbon content of the solution showed an initial sharp drop; but, the change in carbon content as a function of pH slowed down and became asymptotic at a carbon content corresponding approximately to U/CO₃ = 2.0 (cf. Figure 1). The time dependence of the change in pH of the solution, while being sparged with an inert gas at a constant rate, was followed in a separate experiment (Figure 2). The pH values were expressed in terms of carbon content on the basis of the relation

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