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Pulsed Laser Conductivity and Emission Studies of Tris(ethylenediamine)chromium(III) Ion in Aqueous Media

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Numerous investigations into the photochemical and photophysical processes of tris(ethylenediamine)-chromium(III) ion, $Cr(en)_3^{3+}$, (and related octahedral Cr(III) systems) have now been carried out [1–10 and references therein]. These efforts have shown that irradiation of the ligand field or charge transfer bands leads to photoaquation with a quantum yield of 0.4 (independent of wavelength)

$$Cr(en)_3^{3+} + H_2O \xrightarrow{h\nu} Cr(en)_2(en)(H_2O)^{3+} \qquad (1)$$

In acidic media, protonation of the monodentate ethylenediamine ligand occurs

$$Cr(en)_2(en)(H_2O)^{3+} + H^+ \rightarrow Cr(en)_2(enH)(H_2O)^{4+} \qquad (2)$$

Notwithstanding the extensive interest in such systems, only recently has the first direct measurement of the rate of primary photoproduct formation of a Cr(III) coordination compound been reported [3]. The formation was observed by monitoring the growth in absorption of $Cr(en)_2(enH)(H_2O)^{4+}$ following pulsed laser excitation (530 nm) of the first quartet ligand field band of $Cr(en)_3^{3+}$ ($^4L_1$, λ_{max} = 456 nm). Under the conditions used (pH 2), the protonation rate (reaction (2)) was too fast to be measured. An important observation was that product formation occurred in two distinct stages. The lifetime of the slower stage had the same value as that of phosphorescence emission from the lowest doublet thexi state (D_1^o). The prompt increase in absorption (present at the end of the laser pulse) was attributed to reaction from the lowest vibrationally equilibrated quartet state (Q_1^o, $\tau < 5$ ns). The situation was however complicated by the occurrence of excited state absorption (E.S.A.) from the relatively long-lived doublet state, and such E.S.A. has been observed with other chromium(III) systems [11].

We wish to report here the results of a study into the photobehavior of $Cr(en)_3^{3+}$ involving conductivity detection of the photoproduct, a new approach which may prove of general benefit in avoiding complications introduced by the presence of E.S.A.. We have confirmed by this independent means the earlier results obtained by optical detection, and in addition have extended the investigation of the time dependent processes to those manifested upon irradiation of the second quartet ligand field band ($^4L_2$, λ_{max} = 350 nm). The approach used here has been to monitor the conductivity changes associated with reaction (2) following laser excitation at 347 or 530 nm. This has provided the opportunity to study the protonation dynamics of the partially coordinated ethylenediamine ligand. Because proton transfer processes are of general importance in thermal complexation kinetics but are often difficult to separate from competing reactions (ring closure and loss of ligand), pulse laser photolysis coupled with conductivity detection offers an attractive means to generate such entities and to characterize their reactions.

Experimental

Tris(ethylenediamine)chromium(III) perchlorate was prepared from the commercially available chloride salt (Ventron, Alpha Division) [2]. Aqueous solutions containing added amounts of $HClO_4$ were deaerated by bubbling with argon gas, and the pH's of the solutions were measured on a Knick pH meter, calibrated against standard buffer solutions. Laser photolysis experiments were carried out using a frequency doubled Q-switched Neodym-Yag laser (System 2000, JK-Laser Ltd.), which delivered 100 mJ pulses (duration 20 ns) at 530 nm, and with a frequency doubled Ruby laser (Korad K1QP) with 70 mJ pulses (duration 15 ns) at 347 nm. The solutions were irradiated in a flow-through 1 cm^2 quartz cell, which contained a pair of platinum electrodes between which the laser beam passed. Conductivity changes were observed by applying a 100 V pulse of 5 ms duration to the electrodes, and by measuring the current changes induced by the laser pulse. With a 180 ohm matched system, the time response was 15 ns [12]. The optical detection system, which was used to monitor phophorescence emission in the region of 670 nm, had a rise time of 10 ns [13]. Data from both emission and conductivity experiments were digitized and evaluated on a PDP 11/40

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TABLE I. Lifetimes for Long Term Conductivity Change and Emission, and Values of f_D.[a]

Band Irradiated (Excit. λ)	τ_L, μs (Conductivity)	τ_p, μs (Emission)	f_D (This Work)	f_D (Literature)
$^4L_1$ (530 nm)[b]	1.8 ± 0.3 (8)	1.54 ± 0.06 (5)	0.67 ± 0.08 (8)	0.70 ± 0.03[d], 0.6[e]
$^4L_2$ (347 nm)c	1.6 ± 0.3 (13)	1.66 ± 0.07 (7)	0.69 ± 0.08 (13)	0.6[e]

[a] Numbers in parenthesis are number of determinations. [b] pH 2.3–3.1; 20.8–23.5 °C; $[Cr(en)_3^{3+}]$ = 2.0, 4.0 mM; Emission wavelength: 670, 675 nm. [c] pH 2.3–3.05; 21.4–23.0 °C; $[Cr(en)_3^{3+}]$ = 4.0 mM; Emission wavelength: 670 nm. [d] [3]. [e] [4].

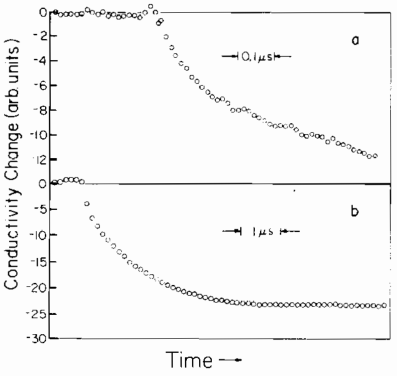

Fig. 1. Conductivity changes on pulse irradiation of 4 mM $Cr(en)_3^{3+}$ at 347 nm and pH 2.5: a) Short term, b) Long term.

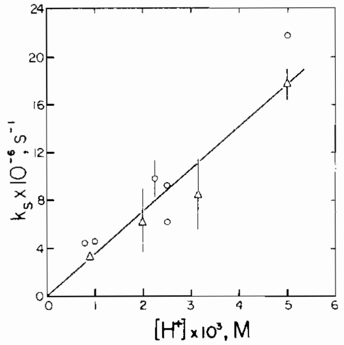

Fig. 2. Plot of the rate constant for the short term conductivity change (k_s) *versus* concentration of proton: (○) 530 nm radiation, (△) 347 nm radiation.

computer. The conductivity results were further analyzed in terms of a double exponential function using a non-linear least square fitting program run on a DEC-2050 computer.

Results and Discussion

On pulse irradiation at 347 or 530 nm of acidic aqueous $Cr(en)_3^{3+}$ solutions, the resultant conductivity decreased in two stages as shown in Fig. 1. These stages became better resolved in time as the pH was decreased from 3.1 to 2.3. It was found that the normalized change in conductivity could be described by

$$(C_\infty - C_t)/C_\infty = A\{\exp(-k_s t)\} + B\{\exp(-k_L t)\} \quad (3)$$

where C_t and C_∞ were the conductivity values at time, t, and at time where no further change occurred. The parameters A, B, k_s and k_L were computed using a non-linear least square fitting procedure. The latter two represent the apparent first-order rate constants for the short and long term changes respectively. The values of k_L were independent of pH whereas those for the short term change, k_s, increased with decreasing pH. Fig. 2 shows the linear dependence of k_s on the concentration of proton: a least square fit of 21 data points yielded slope = 3.6 ± 0.4 × 10^9 M^{-1} s^{-1} and intercept = −0.1 ± 1.2 × 10^6 s^{-1}.

We ascribe the short term change to the presence of some $Cr(en)_2(en)(H_2O)^{3+}$ formed at the end of the pulse and to the occurrence of reaction (2). This interpretation is in keeping with earlier results which indicate that on irradiation of the $^4L_1$ band, the resultant population of the thexi states (Q_1^o and D_1^o) and the subsequent chemical reaction from Q_1^o are extremely rapid processes ($\tau < 5$ ns) [3, 5, 8]. Our results (see also [5]) suggest a similar situation for irradiation of the $^4L_2$ band. While very few proton transfer rate constants have been reported for metal complex ions, the value of 3.6 × 10^9 M^{-1} s^{-1} is within the range expected for reaction (2) [14]. The value of K_a for the monodentate ethylenediamine of $Cr(en)_2(enH)(H_2O)^{4+}$ is not known*; however it is likely to be near 10^{-8} [15].

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*The coordinated water has a pK_a of 4.4 [16], and thus the extent of this ionization process will have been negligible here. Linck and Cimolino [17] have recently found that the primary photoproduct of reaction (1) is a combination of the *cis* and *trans*-isomers. The ratio of *trans/cis* forms is constant for irradiation at 365 and 540 nm. In view of the fact that the pK_a values of the two isomers are expected to be very close, our results could not distinguish between these products.

On this basis, the rate constant for the reverse process of reaction (2) is estimated to be small (*ca.* 10^2 s^{-1}), and the protonation of $Cr(en)_2(en)(H_2O)^{3+}$ will have gone to completion under the condition of $[H^+] >> [Cr(en)_2(en)(H_2O)^{3+}]$ prevailing here.

Considering in detail the results for the long term stage, the associated lifetimes ($\tau_L = 1/k_L$) are given in Table I along with those measured for the phosphorescence emission from the D_1^o state (τ_p). Within experimental error, the values are the same for irradiation of the $^4L_1$ and $^4L_2$ bands, and those for τ_p are in agreement with the reported ones [2, 4, 9]. The close correspondence between τ_L and τ_p demonstrates that the long term change is controlled by the exiting from the D_1^o state (under our conditions, this rate was slower than that for reaction (2)). The quantity, k_L, can be considered as the sum of first-order rate constants for radiative and non-radiative deactivation, back intersystem crossing ($D_1^o \rightarrow Q_1^o$) and chemical reaction from the D_1^o state [2, 4]. Considerable controversy presently surrounds the relative importance of these latter two processes [1–9]. In carrying our analysis further, we have assumed that these and the other processes occur and that the equivalent ionic conductivities of all the positive three charged species are the same. Within this context and presuming prompt chemical reaction from the Q_1^o state, the fraction of photoproduct (f_D) which arises from passage through the doublet state is given by $f_D = [B/(A + B)] [(k_s - k_L)/k_s]$. The calculated values of f_D are presented in Table I along with those reported in the literature. They are in good agreement with that obtained by optical absorption measurements for irradiation of the $^4L_1$ band [3], albeit somewhat higher than those derived from steady-state quenching experiments [4].

The concurrence of the f_D values for the irradiation of the $^4L_1$ and $^4L_2$ bands implies that the second excited quartet state is chemically unreactive. The constancy of f_D (and of the overall quantum yield for aquation) with excitation wavelength could be accounted for by rapid internal conversion from the second quartet state to the thexi state, Q_1^o, followed by intersystem crossing to D_1^o. Recent results suggest however that the relaxation of the Franck-Condon states competitively populates the thexi states, Q_1^o and D_1^o (see Figs. 4–3 of [1]). Our findings which now encompass the second excited quartet level would suggest a high degree of specificity associated with the formation of the vibrationally equilibrated Q_1^o and D_1^o states even though in principle there are a number of relaxation pathways potentially available. One possible explanation for such specificity may reside in the occurrence of distortion of the quartet levels with the concomitant lowering of symmetry from the near O_h symmetry of the ground state. Kane-Maguire and coworkers [8] have suggested in relationship to the competitive population of the Q_1^o and D_1^o states that owing to distortion, the presence of common irreducible representations (and of spin–orbit coupling) could lead to the generation of a common potential energy surface. Extending these arguments to the second excited state may account for the apparent lack of chemical reactivity from this state. Further studies are needed to substantiate such proposals, and ones directed at the time dependent photobehavior of chromium(III) systems hold considerable promise in this regard.

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