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Solid State Emission Lifetimes – Implications for Cr(III) Photochemistry

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Despite the recent development of increasingly sophisticated theoretical models for transition metal complex photoreactivity [1], the identity of the photoactive state under ligand field excitation remains a controversial issue. This is especially true of octahedral Cr(III) systems with respect to the reaction component that is quenched on selective doublet quenching. Two alternative explanations [2] – *direct* doublet reaction or 'delayed' quartet reaction *via* $^2E \rightsquigarrow {}^4T_2$ back intersystem crossing (ISC) – have been suggested for this reaction component [3]. Both pathways have been advanced as rationalizations of the apparent activation energies observed for $^2E \rightarrow {}^4A_2$ phosphorescence intensities and lifetimes in fluid solution. More recently, Adamson and coworkers [4] have proposed a set of empirical rules for correlating observed solution emission lifetimes for Cr(III) ammines. The rules are based, however, on the supposition that direct reaction out of the ^2E level controls the ^2E lifetime in room temperature solution [4, 5]. There is clearly urgent need for effective, experimental procedures for establishing the actual photochemical role of the ^2E level. Adamson and coworkers have very recently described one such procedure which involved monitoring the rate of primary photoproduct formation [6]. We present here experimental data for a potentially valuable new approach which involves measurement of solid state lifetimes for deuterated and undeuterated samples. The systems chosen for study were $Cr(NH_3)_6^{3+}$ and $Cren_3^{3+}$.

Experimental

Undeuterated ClO_4^- and PF_6^- salts of $Cr(NH_3)_6^{3+}$ were obtained by addition of $NaClO_4$ and NH_4PF_6 solutions, respectively, to an aqueous solution of purified $[Cr(NH_3)_6](NO_3)_3$. The materials were recrystallized from water until constant $^2E \rightarrow {}^4A_2$ emission lifetimes for the solids were obtained. A pure sample of $[Cren_3](ClO_4)_3$ was prepared in similar fashion from $[Cren_3]Cl_3$ as starting material. However, solubility restrictions prevented isolation of satisfactory samples of $[Cren_3](PF_6)_3$. Deuterated ClO_4^- salts of $Cr(NH_3)_6^{3+}$ and $Cr\,en_3^{3+}$ were prepared following methods described earlier [7]. An analogous procedure was adopted for $[Cr(ND_3)_6](PF_6)_3$, with solid NH_4PF_6 replacing anhydrous $NaClO_4$ as the precipitating agent from D_2O solutions. Infrared analysis indicated greater than 90 percent deuteration at the ammine positions for all samples.

A 250 kW N_2 laser (Molectron UV-12) with a pulse width of 10 ns was used as the excitation source. The pulsed laser light was guided into the sample compartment using a 12 inch quartz fiber light pipe. For room temperature studies an Aminco solid-sample accessory (C73-62140) was used as the sample compartment while a specially constructed Dewar was used for 77 K measurements. The $^2E \rightarrow {}^4A_2$ emission was monitored at right angles using a J-Y Optics H-10V monochromator followed by a Corning CS 3-66 filter and an RCA 31034 A photomultiplier tube (operated at 1700 V). The signal was fed into a Tektronix 5441 storage oscilloscope (with 5A 45 amplifier and 5B 40 time base plug-ins) using a load resistor whose size was varied from 100 Ω to 10 kΩ depending on the time response required [7, 8]. Emission lifetimes were obtained using procedures described elsewhere [7]. Correlation coefficients were generally greater than 0.997 with reproducibilities of 10 percent or better. Freshly packed UV cells or nmr tubes were used for samples studied at room temperature or 77 K, respectively. Satisfactory storage displays of emission decay curves were obtained following 5–20 seconds of excitation (20 Hz).

Results and Discussion

In a previous communication we have examined the effect of deuteration on the ^2E state *solution* lifetimes of several Cr(III) ammines [7]. Following the terminology of Adamson *et al.*, [5] the ^2E lifetimes may be written as $\tau = 1/(k_r + k)$, where k_r is the radiative rate constant and k is the summed rate constant for all non-radiative processes involving the ^2E level, *i.e.* $k = k_{cr} + k_{bisc} + k_{nr}$, where k_{cr}, k_{bisc}, k_{nr} are the rate constants for direct chemical reaction from ^2E, back ISC $^2E \rightsquigarrow {}^4T_2$, and $^2E \rightsquigarrow {}^4A_2$ radiationless deactivation, respectively [9]. Since $k \gg k_r$ under all experimental conditions, the lifetime data reflect variations in the non-radiative rate constants. The results obtained for $Cr(NH_3)_6^{3+}$ in room temperature solution were typical and revealed

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only a small deuteration effect in contrast to the marked response reported previously by Flint and coworkers at 77 K [11]. In accordance with recent theoretical discussions of radiationless transitions in transition metal systems [12, 13], these findings are consistent with a weak coupling mechanism operative at low temperature being replaced by a strong coupling mechanism at room temperature. The weak coupled deactiviation mode dominant at 77 K is expected to be $^2E \rightsquigarrow {}^4A_2$ relaxation. However, a decay via either back ISC or direct ^2E reaction would satisfactorily account for the room temperature data, since either pathway should display minor deuteration effects characteristic of strong coupling between the initial and final states. It was concluded [7] therefore that such studies are ineffective in distinguishing between these two room temperature decay modes.

In this present communication we explore how extension of those studies to include corresponding *solid-state* emission lifetimes may provide information for assessing the relative importance of the k_{bisc} and k_{cr} terms for ^2E non-radiative decay. The potential value of solid state studies is that under appropriate circumstances one of the terms in contention (k_{cr}) may be eliminated. Thus for the complexes $Cr(NH_3)_6^{3+}$ and $Cren_3^{3+}$, provided the counter-ions are poorly coordinating anions such as ClO_4^- and PF_6^-, any k_{cr} term is effectively eliminated (since the solid salts exhibit no detectable photodecomposition on ligand field excitation and lifetimes display no dependence on irradiation time [14]). As a result, for solid samples k reduces to $k = k_{bisc} + k_{nr}$, where k_{nr} may contain contributions from purely intramolecular (k_{intra}) and environment-related (k_{envir}) paths, *i.e.* $k_{nr} = k_{intra} + k_{envir}$.

Our emission lifetime results are presented in Table I. The solid state data for $[Cr(NH_3)_6](ClO_4)_3$ are especially dramatic. The room temperature lifetime for the undeuterated ClO_4^- salt (27 μs) is more than an order of magnitude longer than that in solution (2.2 μs), and differs little from that at 77 K (35 μs). The temperature independence of the solid state data alone eliminates back ISC as a significant deactivation pathway in the solid state (and by inference also in solution*), since k_{bisc} is a thermally activated process. Doublet excited state deactivation is thus principally via $^2E \rightsquigarrow {}^4A_2$ relaxation (*i.e.* $k = k_{nr}$ for solid state), with the k_{nr} term being almost temperature independent. This temperature insensitivity is to be contrasted with the marked temperature dependence reported in solution [16]. However, these phase differences may be readily reconciled if the primary fate of ^2E molecules in solution is direct chemical reaction. Thus the much shorter solution lifetime at room temperature is associated with a dominant chemical reaction path which is absent in the solid. A substantial activation energy for this chemical reaction would then account for the strong temperature dependence in solution [5]. Furthermore, this interpretation is an accord with the corresponding deuteration data. In the solids, a very strong, approximately constant, deuteration effect is operative over the greater than 200° temperature range studied, consistent with $^2E \rightsquigarrow {}^4A_2$ decay as the dominant relaxation mechanism even at room temperature. The small deuteration effect in solution

TABLE I. Emission Lifetimes for Cr(III) Systems (μsec).

Complex	Solid		0.02 *M* $HClO_4$ Solution[b] 297 K
	77 K	297 K	
$[Cr(NH_3)_6](ClO_4)_3$	35[a]	27	2.2
$[Cr(ND_3)_6](ClO_4)_3$	600[a]	538	3.1
$[Cr(NH_3)_6](PF_6)_3$	40	23	2.2
$[Cr(ND_3)_6](PF_6)_3$	940	535	3.1
$[Cr\,en_3](ClO_4)_3$	54	17	1.7
$[Cr\,D\text{-}en_3](ClO_4)_3$	290	28	1.8

[a]These values are in reasonable agreement with values reported by C. D. Flint (Ref. 11). [b]References 7.

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*The present data cannot unambiguously exclude back ISC as an important process in *solution.* Since we anticipate back ISC to be primarily an intramolecular phenomenon, it seems improbable that the room temperature solution value for k_{bisc} would be an order of magnitude greater than that in the solid phase. However, should the extent of $^4T_2$ state distortion relative to the ^2E level differ significantly between solid and solution, this may affect the corresponding k_{bisc} values. If our present interpretation is correct (*i.e.* that k_{bisc} is insignificant in solution) the room temperature solution lifetime of $Cr(NH_3)_6^{3+}$ in non-nucleophilic solvents should approximate the solid state value. Unfortunately, a wide variety of $Cr(NH_3)_6^{3+}$ salts tested (including the ClO_4^-, PF_6^-, BF_4^-, tetraphenylborate, paratoluenesulfonate and trifluoromethanesulfonate) are all insoluble in the non-nucleophilic solvents listed by Gutmann [15].

is then diagnostic of a strong coupling mechanism such as anticipated for direct chemical reaction (*i.e.* $k \simeq k_{cr}$ for solution). Alternative arguments that the short solution lifetimes are associated with solvent enhanced $^2E \rightsquigarrow {}^4A_2$ relaxation (*i.e.* $k = k_{nr} \simeq k_{envir}$) are negated by the absence of a strong isotope effect.

Similar conclusions may be derived from an analysis of the corresponding solid state results for $[Cr(NH_3)_6](PF_6)_3$. Again the undeuterated salt has a room temperature lifetime an order of magnitude greater than that in solution. Furthermore, a very strong essentially constant deuterium isotope effect is observed over the entire temperature range, indicating an insignificant role for back ISC. However, the undeuterated room temperature lifetime is detectably shorter than that for the ClO_4^- salt, while the reverse is true at 77 K. These trends are associated with a more pronounced (though minor) temperature dependence in both the deuterated and undeuterated samples (lifetimes for both samples have approximately doubled on going to 77 K). These small differences between the ClO_4^- and PF_6^- salt data may be attributed to differing crystal lattice effects included in the k_{envir} term for k_{nr}.

We next consider the corresponding results for $Cren_3^{3+}$. Again the room temperature lifetime for the undeuterated species is an order of magnitude longer in the solid state than in solution. However, the solid state lifetimes are significantly temperature dependent – although substantially less than that reported in solution [16, 17]. Furthermore, in contrast to our $Cr(NH_3)_6^{3+}$ observations, only a modest deuteration effect is noted for the solid at room temperature, but is more marked at 77 K. Although these latter results may in part reflect the fewer number of active N-H hydrogens present [12], the temperature dependencies suggest a substantial deactivation role for back ISC in the room temperature solid*. We therefore conclude that back ISC is also important in room temperature solution, but not to the extent formally believed [16–18]. The reduced solution lifetimes indicate that direct reaction is again the major relaxation route in solvent media.

In conclusion, the present study suggests the potential value of solid state lifetime data in analyzing complex solution photochemical behavior. The evidence presented for $Cr(NH_3)_6^{3+}$ and $Cren_3^{3+}$ are in general agreement with recent suggestions concerning a *direct* photochemical role for the ^2E state [4–6]. However, we also conclude that for $Cren_3^{3+}$ the reaction component that is quenched on selective doublet quenching contains *some* contributions from a 'delayed' quartet pathway. We note that a more prominent role for back ISC in $Cren_3^{3+}$ is consistent with the D_3 symmetry of the system which allows for more rapid back ISC along a single potential energy surface (adiabatically) [19, 20]. We are therefore examining the general applicability of these solid state studies to other Cr(III) systems of reduced symmetry.

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*A detailed temperature dependence investigation of these ^2E lifetimes is in progress, and the results support the present conclusions. Thus, the solid state lifetimes at 60 °C for $[Cr(NH_3)_6](ClO_4)_3$ and $[Cr(NH_3)_6](PF_6)_3$ are 24 μsec and 19 μsec, respectively, *i.e.* little changed from the 24 °C value. In contrast, the corresponding 60 °C lifetime for $[Cren_3](ClO_4)_3$ is 2.2 μsec, which indicates that above room temperature back ISC becomes the dominant deactivation mode for the solid phase.

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