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Environmental Effects on the Phosphorescence Lifetime of Cationic Cr(III) Complexes

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Several recent reports have stressed the importance of obtaining photochemical and photophysical data on Cr(III) species under comparable experimental conditions [1–5]. However, although most photochemical studies have been in solution near room temperature, relatively little photophysical data are available under these circumstances. Unfortunately, direct room temperature detection of the photochemically active $^4T_2$ quartet excited state via $^4T_2 \rightarrow {}^4A_2$ fluorescence has proven an elusive goal [5–7]. In contrast the ^2E doublet excited state is reasonably amenable to study via $^2E \rightarrow {}^4A_2$ phosphorescence [8], and may also have an active role in photochemical deactivation [2, 5]. Somewhat surprisingly the effect of environmental factors on the ^2E lifetime has received limited attention [1–3, 9, 10], and we wish to report here our observations on the solvent dependence of the ^2E lifetime for nine cationic Cr(III) species.

Experimental

In each instance recrystallized perchlorate salts of the complexes were employed. Deuterated samples of $Cr(NH_3)_6^{3+}$ and $Cren_3^{3+}$ were prepared by precipitation from 99.85 percent D_2O solution with anhydrous $NaClO_4$ and subsequent drying on a vacuum line. IR analysis indicated greater than 80 percent deuteration at the amine positions for both compounds. A 250 kW N_2 laser (Molectron UV-12) was used as the excitation source. Emission was monitored at right angles using a J–Y Optics H-10V monochromator followed by a Corning CS3-66 filter and Hamamatsu 666 photomultiplier tube (operated at 1100 V). The signal was fed into a tektronix 466 DM 44 storage oscilloscope using a load resistor whose size was varied from 100 Ω to 5 kΩ depending on the time response required. An RC time constant for the system was experimentally determined using the procedure recommended by Demas *et al.* [12]. The stored decay signals were traced onto plastic overlays and analyzed assuming exponential decay. The least-squares program used generally yielded correlation coefficients greater than 0.995 and a reproductibility significantly better than 10 percent. Fresh solutions were made up immediately prior to irradiation and a satisfactory storage display of each decay curve required less than 20 seconds of excitation (10 Hz). The average 610 nm lifetime value obtained for an aqueous solution of $[Rubipy_3]Cl_2$ (0.58 μsec at 24 °C) was in excellent agreement with that reported [13].

Results and Discussion

The ^2E lifetimes obtained for a range of different solvents are collated in Table I. Doublet lifetimes in water solution near 24 °C have been reported previously for $Cr(NH_3)_6^{3+}$, $Cren_3^{3+}$, $Crbipy_3^{3+}$ and $Crphen_3^{3+}$. The values from the present study are in good agreement with these earlier findings. Our results for $Crbipy_3^{3+}$ and $Crphen_3^{3+}$ in other solvents are in disagreement with those provided by Henry and Hoffmann [11], where lifetimes were reported essentially independent of solvent. Following the terminology of Adamson *et al.* [2], 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} and k_{nr} are the rate constants for direct chemical reaction from ^2E, back intersystem crossing ($^2E \longrightarrow {}^4T_2$) and nonradiative relaxation from $^2E \longrightarrow {}^4A_2$, respectively. For each complex investigated it is expected that $k \gg k_r$ under room temperature solution conditions, and thus the data should primarily reflect variations in the non-radiative rate constants with change in solvent and extent of deuteration.

It is apparent from inspection of Table I that solvent effects are most strongly felt for complexes containing ligands high in the nephelauxetic series. This is consistent with the notion that delocalization of the metal t_{2g} electrons onto the ligand will enhance communication between the complex and the solvent. The marked room temperature solvent dependences noted earlier for $Cr(CN)_6^{3-}$ and *trans*-$Cr(NH_3)_2(NCS)_4^-$ are also in accord with this view [9, 2]. However, the exact nature of the solvent effects are difficult to assess. It has been suggested that good ligand to solvent hydrogen bonding leads to a large k and short lifetimes [2]. The reduced lifetimes of *cis*-$Cren_2(CN)_2^+$ and *trans*-$Cren_2(NCS)_2^+$ in water may in fact be rationalized on this basis, but no obvious correlation is seen for the remaining systems. Likewise, no correlation is evident between τ and solvent viscosity or dielectric constant. For example, lifetimes in acetonitrile and ethylene glycol are in general very similar, despite a factor of 70 difference in their relative viscosities.

It is of interest to explore the possible photochemical implications of the present study. The

TABLE I. ^2E Lifetimes (in μsec at 24 °C).

Compound	H_2O	D_2O	0.02 *M* $HClO_4$	DMF	DMSO	CH_3CN	Ethylene Glycol	Methanol	Acetone
$Cr(NH_3)_6^{3+}$	2.3		2.2	3.0	3.9				
$Cr(ND_3)_6^{3+}$			3.1						
$Cren_3^{3+}$	1.6		1.7	1.4	1.5	1.3	2.3		
$Cr(D\text{-}en)_3^{3+}$			1.8						
$Crbipy_3^{3+}$									
air saturated	41	37		2.0	1.9	28	37	29	28
N_2 purged	60			3.0	2.1	51		39	
$Crphen_3^{3+}$									
air saturated	62	48		12	10	28	39	22	24
N_2 purged	180			20	15	40		34	
cis-$Cren_2(CN)_2^+$	1.7[a]	1.7		7.0	11.0[b]	5.8	6.9		
trans-$Cren_2(NCS)_2^+$	2.5	3.0		6.4	4.1	6.0	5.1		
cis-$Cren_2(NCS)_2^+$	0.49	0.60		0.37	0.47	0.30	0.42		

[a] 1.9 μsec (N_2 purged solution). [b] 11.4 μsec (N_2 purged solution).

identity of the Cr(III) photoreactive level(s) is still a controversial issue, in particular with regard to the reaction component that is quenched on selective doublet quenching. With the exception of $Cr(CN)_6^{3-}$, this component constitutes a major fraction of the total reaction quantum yield; and has been variously ascribed to direct doublet reaction of 'delayed' quartet reaction via $^2E \longrightarrow {}^4T_2$ back intersystem crossing. There has been much interest therefore in assessing the relative importance of the k_{bisc} term in the overall expression for nonradiative decay from the ^2E level ($k = k_{cr} + k_{bisc} + k_{nr}$). For the compounds listed in Table I it has been argued that back intersystem crossing is the dominant deactivation mode for the ^2E state [9]. This conclusion has been based in part on the high apparent activation energy experimentally observed for phosphorescence intensities and lifetimes. However, a similar activation energy has been reported for $Cr(CN)_6^{3-}$ [10]. Since for this species the k_{bisc} and k_{cr} terms are insignificant, it must be concluded that radiationless deactivation to the ground state (k_{nr}) may display a strong temperature independence. Furthermore, Gutierrez *et al.* [2] have recently suggested at 10–14 kcal mol^{-1} activation energy for k_{cr} for the complex *trans*-$Cr(NH_3)_2(NCS)_4^-$. Thus, temperature dependence studies alone are not likely to resolve the photochemical problem posed above.

An alternative approach might be to examine the effect of deuteration on the doublet lifetimes. Recent theoretical discussions of intramolecular decay in transition metal systems [14] suggest that the coupling of the initial and final states can be analyzed in terms of two limiting models – strong coupling and weak coupling. The strong coupling limit corresponds to a large horizontal displacement of the potential wells for the two states, and results in no isotope effect being predicted for deuteration of the ligand amine hydrogens (N–H). In contrast a substantial deuterium isotope effect is expected for the weak coupling limit, where the two states are essentially undistorted with respect to each other. For $Cr(NH_3)_6^{3+}$, a marked deuteration effect has been reported previously at 80 K (τ $Cr(NH_3)_6^{3+}$ = 32 μsec; τ $Cr(ND_3)_6^{3+}$ = 662 μsec [15]. This result is consistent with a dominant weak-coupled deactivation mode and may be reasonably assigned to $^2E \longrightarrow {}^4A_2$ relaxation. However, the corresponding data for $Cr(NH_3)_6^{3+}$ and $CrD\text{-}en_3^{3+}$ in 0.02 *M* $HClO_4$ at 24 °C clearly indicate the importance of a strong coupled relaxation pathway at room temperature. Similar conclusions may be inferred from the comparative lifetime data for *cis*-$Cren_2(CN)_2^+$ and *cis*- and *trans*-$Cren_2(NCS)_2^+$ in H_2O and D_2O. Solvent deuteration alone is not expected to have a large influence on lifetimes [16], and is consistent with the findings for $Crphen_3^{3+}$ and $Crbipy_3^{3+}$ in H_2O and D_2O. Unfortunately, the lack of a deuterium effect for the systems containing N–H protons does not distinguish between back intersystem crossing or direct chemical reaction as the major decay route for the ^2E level. Either pathway should provide strong coupling between the initial and final states. For several Cr(III) systems the actual photochemical role played by the ^2E level remains a challenging question.

Finally we note that for none of the complexes investigated was evidence found for a rise-time for sample phosphorescence. Even when employing a 50 Ω load resistor (corresponding to an RC time constant of 3.9 nanoseconds) emission was instantaneous with the pulse. The observation provides further confirmation of the rapidity of $^4T_2 \longrightarrow {}^2E$ intersystem crossing [4, 18].

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