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Solvent Isotope Effect on the Quartet → Doublet Intersystem Crossing Efficiencies of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ [1]

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In the course of our continuing investigation into the effect of solution medium on the photophysics and photochemistry of polypyridyl complexes of Cr(III),[2-4] we have observed that the intensity of luminescence from the ^2E state[5] of $Cr(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine) is significantly lower in D_2O than in H_2O, although the lifetime of ^2E is virtually unchanged. Inasmuch as the intensity of luminescence reflects the population of ^2E, the effect indicates that $^4T_2$, which is the precursor to ^2E, is sensitive to the isotopic nature of the solvent. Because of the very short lifetime (~10 ps)[6] of $^4T_2$ and its nonfluorescent nature in aqueous solution, very few other probes are available for its examination. While there are examples of enhancement of fluorescence yields for rare-earth complexes[7] and an increase in phosphorescence lifetimes in simple Cr(III)-ammine complexes[8] when the solvent is changed from H_2O to D_2O, this appears to be the first report where the quantum yield of luminescence is *reduced* by the presence of D_2O.

Solutions of 1.1×10^{-5} M $Cr(bpy)_3^{3+}$ or $Cr(phen)_3^{3+}$ (phen = 1,10-phenanthroline), available as ClO_4^- salts from previous studies,[9] were prepared from concentrated stock solutions in H_2O (distilled and passed through a Millipore purification train) to D_2O mole fractions (χ_D) from 0.00 to 0.99 using 99.9% D_2O (Alfa) which had been distilled under N_2 from $KMnO_4$ and BaO. The solutions were deaerated with Ar for 30 min, and all measurements of ^2E lifetime ($^2\tau$) and luminescence intensity (I) were made at 22 ± 1 °C. Emission lifetimes (at 727 nm) were measured by using 347-nm excitation from a frequency-doubled ruby laser pulse; emission intensities (at 727 nm) were determined for the same solutions by using a Perkin-Elmer MPF-2A recording spectrofluorimeter (excitation 310 nm)[10] equipped with a temperature-controlled cell compartment and a red-sensitive photomultiplier tube. The reproducibility error in the emission decay data, which were strictly first order, was <±2%. Measurements taken with different samples of the complexes and D_2O on different days were reproducible to better than ±10%. The results are shown in Table I. The reported values of $^2\tau$ are the average of three independent runs. The values of I are the average of two independent runs with reproducibility of <±10%.

Table I. Emission Intensities and Lifetimes of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ in Deaerated H_2O-D_2O Mixtures at 22 °C

compd	χ_D	I, arb units	$^2\tau$, ms	Φ_{rad} (rel)
$Cr(bpy)_3^{3+}$	0.00	60.5	0.066	1.0
	0.20	46.6	0.067	0.77
	0.40	37.3	0.066	0.62
	0.60	26.5	0.066	0.44
	0.80	18.0	0.063	0.32
	0.99	12.6	0.061	0.23
$Cr(phen)_3^{3+}$	0.00	53.0	0.23	1.0
	0.50	45.5	0.20	0.99
	0.99	45.0	0.19	1.0

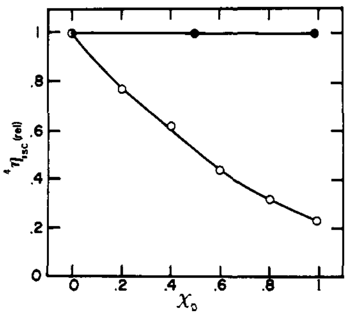

Figure 1. Values of $^4\eta_{isc}$ (relative to χ_D = 0.0) vs. χ_D for $Cr(bpy)_3^{3+}$ (○) and $Cr(phen)_3^{3+}$ (●) at 22 °C.

Our previous studies[2-4,9,11] of these complexes have led to the formulation of the following photophysical mechanism for $Cr(NN)_3^{3+}$ complexes:

$$\begin{array}{ll} {}^4A_2 \xrightarrow{h\nu} {}^4T_2, & I_a \\ {}^4T_2 \rightarrow {}^2E, & {}^4k_{isc} \\ {}^4T_2 \rightarrow {}^4A_2, & {}^4k_{nr} \\ {}^2E \rightarrow {}^4A_2 + h\nu', & {}^2k_{rad} \\ {}^2E \rightarrow {}^4A_2, & {}^2k_{nr} \\ {}^2E \rightarrow \text{photoproducts}, & {}^2k_{rx} \end{array}$$

The mechanism assumes negligible $^2E \rightarrow {}^4T_2$ back intersystem crossing and, at the moment, does not distinguish between Franck-Condon thermally equilibrated quartet excited states. It should be noted that ground-state quenching[4] of ^2E is negligible at the substrate concentrations used in the absence of a high concentration of Cl^-.

The values of $^2\tau$ reflect the competing modes of decay of ^2E: $1/^2\tau = {}^2k_{rad} + {}^2k_{nr} + {}^2k_{rx}$. Inasmuch as $\Phi_{rad} \sim 10^{-3}$ for both complexes[9,12] and Φ_{rx} = 0.18 for $Cr(bpy)_3^{3+}$ [13] and 0.010 for $Cr(phen)_3^{3+}$,[14] the virtual independence of $^2\tau$ on the solvent isotopic composition, which has been noted before,[2,15,16] reflects the independence of $^2k_{nr}$. The small *decrease* in $^2\tau$ which is almost within the error envelope, observed from H_2O to D_2O, may be due to low concentrations of adventitious quenching impurities in the D_2O.

The intensity of luminescence, which is proportional to Φ_{rad}, reflects the steady-state concentration of ^2E. Table I also shows the dependence of Φ_{rad}, relative to its value in H_2O, as a function

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of χ_D. In obtaining these values, small corrections in Φ_{rad} have been made for the extent to which $^2\tau$ is different in each solution. Now, $\Phi_{rad} = {}^4\eta_{isc}({}^2k_{rad}/{}^2k_0)$ where $^4\eta_{isc}$ is the efficiency of forming ^2E via intersystem crossing from $^4T_2$. Although radiative transition probabilities ($^2k_{rad}$ in this case) are proportional to the square of the index of refraction of the medium,[17] the virtual identity of $n_D{}^{20}$ for H_2O (1.3330) and D_2O (1.3283) and the independence of Φ_{rad} with χ_D for $Cr(phen)^{3+}$ rule out any variation of $^2k_{rad}$. We must conclude that *$^4\eta_{isc}$ for $Cr(bpy)_3{}^{3+}$ decreases with increasing χ_D* and, in contrast, *$^4\eta_{isc}$ for $Cr(phen)_3{}^{3+}$ remains constant*. Thus, Figure 1 shows the dependence of $^4\eta_{isc}$ (relative to its value in H_2O) as a function of χ_D.

If $^4\eta_{isc}$ for $Cr(bpy)_3{}^{3+}$ is taken[18] as ~ 1 in H_2O, Figure 1 shows that $^4\eta_{isc}$ varies with χ_D to ~ 0.2 in D_2O. Inasmuch as $^4\eta_{isc} = {}^4k_{isc}/({}^4k_{isc} + {}^4k_{nr})$, $^4k_{isc} \gg {}^4k_{nr}$ in H_2O but $^4k_{isc} < {}^4k_{nr}$ in D_2O. *The transition from H_2O to D_2O results in a change in the relative values of $^4k_{isc}$ and $^4k_{nr}$ in the two solvents.* Designating the rate contants in pure H_2O as $^4k_{isc}{}^H$ and $^4k_{nr}{}^H$ and those in pure D_2O as $^4k_{isc}{}^D$ and $^4k_{nr}{}^D$, we see from Figure 1 that $^4k_{nr}{}^D/{}^4k_{isc}{}^D \sim 4$; inasmuch as $^4\eta_{isc}{}^H \sim 1$, $^4k_{nr}{}^H/{}^4k_{isc}{}^H \leq 0.1$. If the intersystem crossing process is not sensitive (or at most, only mildly sensitive)[19] to the change in the isotopic composition of the solvent, so that $^4k_{isc}{}^H \sim {}^4k_{isc}{}^D$, then it is readily seen that $^4k_{nr}{}^D \gg {}^4k_{nr}{}^H$. For values of $^4k_{nr}{}^H/{}^4k_{isc}{}^H$ in the range from 0.1 to 0.01, representing $^4\eta_{isc}{}^H$ values of 0.91–0.99, $^4k_{nr}{}^D/k_{nr}{}^H$ has values ranging from ~ 10 to ~ 100.

In order to account for this very large deuterium-favored solvent isotope effect on the nonradiative decay of $^4T_2$ to $^4A_2$, it should be noted that $^4T_2$, having $t_{2g}{}^2e_g{}^1$ orbital population, is distorted (increased Cr–N bond distance) relative to $^4A_2$ ($t_{2g}{}^3$ orbital population). We view $^4T_2$ as having solvent molecules within the opened interligand pockets exhibiting a weak electronic interaction between lone-pairs and the vacant t_{2g} orbital that points into the pockets; the interligand solvent molecules represent the isotopic composition of the bulk solvent. The direction and magnitude of the solvent isotope effect argues against the coupling of the vibrational levels of $^4T_2$ and $^4A_2$ by the solvent; because of the lower vibrational frequencies of D_2O relative to H_2O, D_2O is less efficient in its coupling and would favor a modest hydrogen-favored effect. The solvent involvement in the nonradiative process could arise from the microstructure of the solvent in the immediate vicinity of the complex ion; D_2O is a more structured solvent than is H_2O.[20] If the nonradiative process is entropically more favorable in D_2O than in H_2O with little or no enthalpic difference, then $^4k_{nr}{}^H < {}^4k_{nr}{}^D$. That the entropic effect is significant is supported by our observation that $^4\eta_{isc}$ in D_2O is *increased* in the presence of salts in a manner that parallels the ability of these salts to modify the solvent structure.[20]

Our results with $Cr(phen)_3{}^{3+}$ show an invariance of $^4\eta_{isc}$ toward χ_D. Inasmuch as $^4\eta_{isc}{}^H \sim 1$,[21] $^4k_{isc} \gg {}^4k_{nr}$ in both H_2O and D_2O suggesting that $^4k_{nr}$ here is less sensitive to solvent isotope substitution than in $Cr(bpy)_3{}^{3+}$. If $({}^4T_2)Cr(phen)_3{}^{3+}$ were somewhat less distorted than is $({}^4T_2)Cr(bpy)_3{}^{3+}$ due to the greater rigidity of the phen ligands, the interligand solvent molecules would be less strongly bound. This would result in a lessened contribution of the entropic effect in the nonradiative mode.

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(19) If it is assumed that variations in the overall values of $^4k_{isc}$ and $^4k_{nr}$ reflect the composition of bulk solvent in a linear way ($^4k_{isc} = {}^4k_{isc}{}^H\chi_H + {}^4k_{isc}{}^D\chi_D$ and $^4k_{nr} = {}^4k_{nr}{}^H\chi_H + {}^4k_{nr}{}^D\chi_D$ where $\chi_H + \chi_D = 1$), the use of the values of $^4\eta_{isc}$ as a function of χ_D leads to the result that $^4k_{isc}{}^H/{}^4k_{isc}{}^D \sim 4$. The direction and magnitude of this solvent isotope effect suggests that intersystem crossing may involve vibronic coupling to the solvent.

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Reluctant Azoalkanes: Short-Wavelength (185 nm) Liquid-Phase Photolysis and High-Temperature (400–1000 °C) Gas-Phase Pyrolysis of 3,3,5,5-Tetramethylpyrazolin-4-one

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Recently we demonstrated[1] that reluctant azoalkanes, such as those in which the azo linkage is contained in a six-membered ring,[2] undergo facile liquid-phase denitrogenation on irradiation with 185-nm light. It was, therefore, of interest to explore whether such short-wavelength photodenitrogenation was a general phenomenon of reluctant azoalkanes. For this purpose we chose 3,3,5,5-tetramethylpyrazolin-4-one (**1**), which represents one of the few reluctant substrates in which the azo linkage is contained in a five-membered ring. For example, this potential precursor to tetramethylcyclopropanone could not be efficiently denitrogenated ($\Phi = 0.012$ at 313 nm in benzene) via conventional photolysis, i.e., excitation of the n_-,π^* chromophore.[3] However, elevated temperatures or nonpolar solvents promoted nitrogen elimination under conventional photolysis conditions (≥300 nm).[4] We now report that short-wavelength (185 nm) radiation is effective in extruding nitrogen from pyrazolinone **1**. For comparison, we present also the results of its high-temperature (400–1000 °C) thermolysis.

Table I. Photolysis Conditions, Percent Consumption,[a] and Quantum Yields of the Photodenitrogenation of 3,3,5,5-Tetramethylpyrazolin-4-one (1)[b]

photolysis conditions			
λ, nm	$t \times 10^{-3}$, s	pyrazolinone consumption, %	quantum yield, %[c]
185[d]	0.6	75	63 ± 5[h] (56 ± 5)[i]
254[e]	54.0	5	0.05 ± 0.01
300[f]	27.0	14	0.24 ± 0.05
350[g]	28.8	6	0.11 ± 0.01

[a] Disappearance of **1** was monitored by GC on a 5 ft × $^1/_8$ in. stainless steel column, packed with 5% SE-30 on Chromosorb P, using column and injector temperatures of 105 and 130 °C, respectively, and a N_2 flow of 29 mL/min; $R_f = 173$ s for 1 under these conditions. [b] $\lambda_{max} = 356$ nm (ϵ 164) in hexane.[3d] [c] Quantum yields were determined by using 2,3-diazabicyclo[2.2.1]heptene (DBH) as actinometer, for which the photodenitrogenation efficiency is 100% at 185 and 350 nm.[1] [d] 50-W hot cathode mercury resonance lamp with relative intensities at 185 and 254 nm of 20% and 80%, respectively; solutions were not degassed. [e] RPR-2537-Å lamps with relative intensities at 185, 254, 313, and 365.4 nm of 0.8%, 100%, 1.9%, and 1.6%, respectively. [f] RPR-3000-Å lamps with relative intensities at 300 and 312 nm of 100% and 77%, respectively. [g] RPR-3500-Å lamps with relative intensities at 350–354 and 356 nm of 100% and 97%, respectively. [h] The cis–trans isomerization of cyclooctene was also used as actinometer, for which the isomerization efficiency is 35% at 185 nm.[6] [i] This quantum yield represents product formation (cf. Table II).

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