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Received September 1, 1976

Excited State Relaxation and Chromium(III) Photochemistry

Sir:

Implicit in discussions of Cr(III) photochemistry has been the assumption that a unique chemical species is involved in all of the photochemical and photophysical processes.[1] At any instant, a variety of solvent arrangements obtains about a transition metal complex. If the interconversion rates between the solvates are rapid compared to the reaction rate, it is appropriate to speak of a single solvated chemical species. Multiple emission decays observed from $Cr(CN)_6^{3-}$ in rigid glass solvents were ascribed to different environments, but, as the solvent became fluid, the nonexponentiality disappeared, as would be expected if a single species were present.[2] We now present evidence for multiple solvates of $Cr(CN)_6^{3-}$ in H_2O at room temperature with interconversion rates less than 10^7 s^{-1}.

$^2E \rightarrow {}^4A_2$ emission was excited at several wavelengths (Figure 1) by an Avco C-950 N_2 laser or tuned dye lasers (BBOT and POPOP) pumped by the N_2 laser. The decay profiles were monitored by a C-31034 photomultiplier with a 50 Ω load and a Tektronix 7904-7A19 oscilloscope. The $Cr(CN)_6^{3-}$ ^2E lifetimes at different excitation wavelengths are shown in Figure 2 for two solvents, water, and 80% (v/v) glycerol-water. The decays were all exponential in the time intervals that could be used (~2 τ). The emission spectra, recorded with a Jarrell-Ash 0.25-m monochromator (without slits) and a PAR Model 160 boxcar integrator, are also dependent on the excitation wavelength (Figure 3).

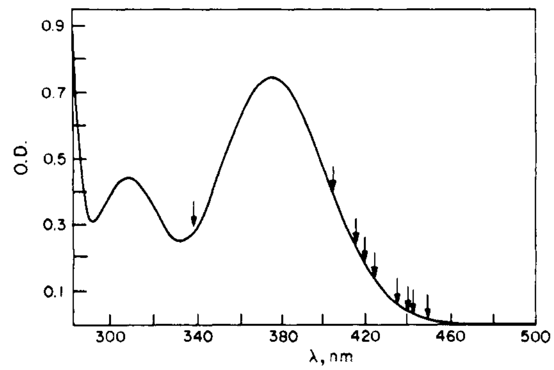

Figure 1. $Cr(CN)_6^{3-}$ absorption spectrum (from ref 3).

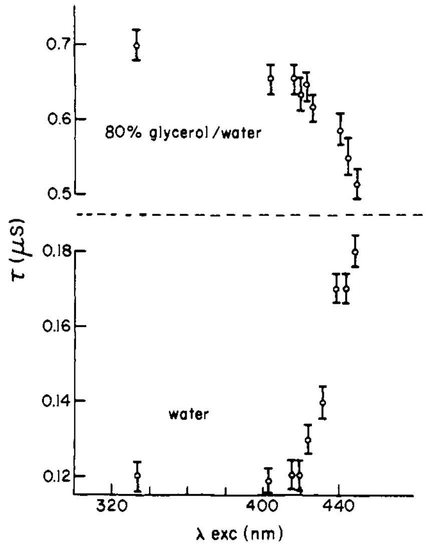

Figure 2. ^2E lifetimes in different solvents as a function of excitation wavelength.

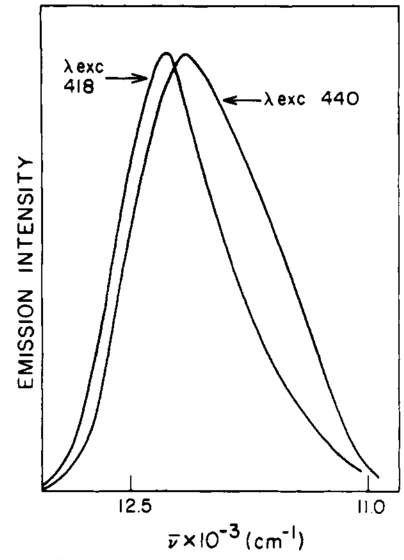

Figure 3. $Cr(CN)_6^{3-}$ emission spectra in water for different excitation wavelengths.

Since the major changes in lifetimes occur upon excitation in the red edge of the $^4T_2 \leftarrow {}^4A_2$ absorption band, the possibility that impurities and/or photoproducts were responsible for the effect was carefully examined. The absorption spectrum of twice-recrystallized $K_3Cr(CN)_6$ (City Chemical Corp., Electronic Grade) agreed very well with the published spectrum,[3] and the lifetimes were unchanged upon repeated recrystallization from water. The lifetime at 337 nm was the same after 1 and 80 laser pulses. Finally, any impurity or photoproduct and $Cr(CN)_6^{3-}$ would have to exhibit almost identical emission spectra. For the foregoing reasons, we believe that all of the lifetimes arise from $Cr(CN)_6^{3-}$.

The multiple lifetimes in the same solvent clearly point to the existence of more than one species with interconversion times exceeding the ^2E lifetime. A slow equilibrium between conformers[4] can be ruled out by the time scale, >0.1 μs. However, exchange rates between hydrogen bonded solvent molecules and bulk solvent as small as $\sim 10^5$ s^{-1} have been found in amine-alcohol complexes.[5] Water is an efficient quencher of $Cr(CN)_6^{3-}$ luminescence, $\tau = 6.5$ ms in DMF,[6] suggesting a strong solute-solvent interaction in aqueous media and the slow solvent exchange time is not too surprising.

The different wavelength dependence of τ in the two solvents warrants comment. Since water is a quencher, the longer lifetime in 80% glycerol-water is to be expected. If long wavelength excitation in the mixed solvent selects solvates with higher proportions of water in the solvation sphere, the lifetime should approach that found in aqueous solution. It is possible that at even longer wavelengths the lifetimes would be the same in the two solvents.

It is of interest to compare the behavior of $Cr(en)_3^{3+}$ and $Cr(CN)_6^{3-}$. In spite of the hydrogen bonding propensities of amines, water is a weaker quencher of the $Cr(en)_3^{3+}$ emission, $\tau = 1.59$ μs in H_2O and 2.26 μs in a glycerol-water solution of approximately 50 mol %. Furthermore, τ is the same with 460- and 520-nm excitation, although the latter wavelength is well past the absorption maximum. The solvent exchange rate for water-amine hydrogen bonds exceeds 10^9 s^{-1} [5] and multiple lifetimes are therefore not anticipated.

In order to underscore the relevance of the foregoing to photochemistry, it is useful to distinguish three classes of relaxation processes: (i) intramolecular, where the solvent sphere is unchanged; (ii) solvent, characterized by translation and rotation times of the bulk solvent; and (iii) solvate. Intramolecular relaxation times, e.g., vibrational relaxation, are $>10^{11}$ s^{-1} while solvent relaxation times vary with viscosity but typically range from 10^8 to 10^{11} s^{-1}. Adamson has discussed the pertinence of solvent relaxation in the photochemical context.[7] The distinction between solvent and solvate relaxation is not sharp, but solvate relaxation designates processes that are strongly dependent upon both solute and solvent. It should be emphasized that solvates are not exciplexes, which are stable only in excited states.

Much, if not all, Cr(III) photochemistry originates in the $^4T_2$ state. While the lifetimes of the solvent relaxed $^4T_2$ are not known, they are likely to be shorter than ^2E lifetimes. If solvate relaxation is slow enough to lead to multiple ^2E lifetimes, multiple solvates should also prevail on the time scale appropriate to $^4T_2$ reactions. It is then possible that photochemical and photophysical measurements do not pertain to the same species. Also, comparison of direct and photosensitized processes may be misleading if one solvate is preferentially excited or is a more efficient acceptor in energy transfer. The absence of multiple ^2E lifetimes does not, however, preclude multiple solvates in $^4T_2$ for photoreactions that take place promptly in $^4T_2$ without passing through ^2E. The results of Kane-Maguire et al.[8] may refer to a single species, but one cannot be certain.

It would be surprising if $Cr(CN)_6^{3-}$ were the only metal complex with long-lived solvates. However, $Cr(CN)_6^{3-}$ may be unique in having a τ with such a large environmental sensitivity.[9] The most direct method to determine the effect, if any, of multiple solvates on photochemistry is to measure the photochemical yields as a function of exciting wavelength, including red-edge excitation.

Acknowledgments. This work was supported by the National Science Foundation (Grant MPS 74-18553).

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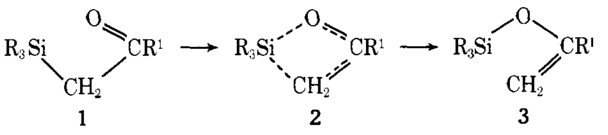
Received August 25, 1976

Revaluation of Evidence Bearing on the Mechanism of the β-Ketosilane to Siloxyalkene Thermal Rearrangement

Sir:

Various accounts[1-4] of the course of thermal rearrangement of β-ketosilanes, **1**, to siloxyalkenes, **3**, present evidence purporting to be fully consistent with the intramolecular, four-center mechanism shown in eq 1. This claim is based essentially



1 2 3 (1)

on the following experimental facts: (a) When the carbonyl substituent R^1 in **1** varies in a series of para-substituted acetophenone derivatives, the Hammett $\rho = -0.78$[3] at 393 K; when one silicon substituent R in **1** is varied in a similar series of 1-(aryldimethylsilyl)-2-propanones, $\rho = +0.54$[4] at 433 K. (b) When **1** possesses a chiral silicon center, the configuration in the product of thermal rearrangement is completely retained. Though the possibility of a five-coordinate silicon intermediate involving d-orbital participation as well as pseudorotation has been considered[2] this was ruled out as inconsistent with the Hammett ρ constants[3,4] which have been interpreted as an indication of almost no negative charge development on both the silicon and the carbonyl carbon. Moreover, molecular orbital calculations, stated[3] to be in harmony with this interpretation, have been advanced to justify a sigmatropic rearrangement of silicon bridging the allylic framework with its d_{xz} and d_{yz} orbitals.

The analogous rearrangement of allylsilanes has been characterized[5] as a fully concerted, orbital symmetry controlled migration of silicon involving a bridging 3_p orbital. The evidence for this conclusion is twofold: (i) the complete insensitivity of the experimental activation parameters to vari-

Table I. Effect of Solvent Composition on the Activation Parameters in the Rearrangement of Trimethylsilylacetophenone

Solvent composition	Medium dielectric ϵ	E_a (kcal)	Frequency factor A	$\Delta S^{\ddagger}$ (eu)
Benzene-d_6	2.28^a	30.6 ± 0.1	8.89×10^{13}	2.7 ± 0.3
Nitrobenzene-benzene-d_6 (4:1)	$28.3^{a,b}$	22.9 ± 0.8	1.25×10^{10}	−14.9 ± 2.0

[a] CRC Handbook (20 °C). [b] Weighted average; nitrobenzene (ϵ = 34.8) and benzene values.