Observation of Transient Intermediates in the Photochemical Decomposition of Substituted s-Tetrazines

Sir:

In this communication we report the observation of diffuse transient absorption extending over the visible region of the spectrum for dimethyl-, phenyl-, and diphenyl-s-tetrazine following pulsed excitation with 3371-Å radiation. Considerable attention has been given to the photochemistry of s-tetrazine and its derivatives which, despite undergoing photochemical decomposition following excitation with visible light, exhibit sharp, highly structured visible absorption spectra.[1-5]

In addition, we have found that the photodecomposition of s-tetrazine, the parent system, is linear in excitation intensity in solution at room temperature, but the derivatives dimethyl-s-tetrazine and phenyl-s-tetrazine exhibit a quadratic dependence on excitation intensity under identical conditions. Our experiments on matrix isolated s-tetrazine at 4.2 K indicate a linear dependence of tetrazine disappearance on light intensity under broad-band illumination but a quadratic dependence when only the origin region (0-0 band) is excited. Recent work by Burland[6] also showed that the photochemistry of s-tetrazine and dimethyl-s-tetrazine in mixed crystals at 2 K is biphotonic.

These unusual results may be explained by a mechanism whereby the chromophore first absorbs a photon and then decays to an intermediate state or species which under the proper conditions requires absorption of a second photon to achieve decomposition into products. To more fully understand the mechanism of photochemical decomposition of s-tetrazine and its derivatives we probed for the existence of this intermediate via flash photolysis techniques.

The output of a 900-kW peak power NRG nitrogen superradiator was focused through a long focal length lens onto a 1-mm^2 aperture. Under these conditions a peak power density of 0.1 GW/cm^2 was obtained. A 1000-W xenon arc was aligned to be colinear with the output of the NRG and also focused onto the aperture. Ethanolic solutions of dimethyl-, phenyl-, or diphenyl-s-tetrazine (0.6, 0.01, and 0.001 M, respectively) were placed in a 1-mm path length cell directly behind the aperture. The transmitted light was filtered to remove the laser radiation and focused onto the slit of a spectrometer set to pass 6100-Å light which is on the long wavelength edge of the parent compound absorption. The output was detected photoelectrically, amplified by a wide-band preamplifier, and observed directly on an externally triggered oscilloscope.

Transient absorption for phenyl-s-tetrazine exhibited peak optical densities as high as 0.4, corresponding to an extinction coefficient of ~7000 L^{-1} M cm^{-1}. The rise and decay times for the transient absorption in degassed solutions were observed to be 80 and 500 μs, respectively. The transient signal strength was observed to depend linearly on the intensity of the N$_2$ laser, indicating that this reaction pathway does not occur through simultaneous two photon absorption. Considerably weaker signals with a substantially (ca. ÷ 3) shorter rise and fall times were observed under nondegassed conditions. Measurements at different detection wavelengths revealed a diffuse absorption spectrum which extended from the edge of the phenyl-s-tetrazine absorption at 610 nm to at least 700 nm with a maximum at 635 nm. In addition, weaker absorption was observed in the near-ultraviolet region between the first and second singlet. Transient absorption for dimethyl-s-tetrazine exhibited rise and decay times of 6 and 500 μs, respectively. Stronger signals were observed for diphenyl-s-tetrazine with rise and decay times of 22 μs and 2.2 ms, respectively. In all cases the transient spectrum was diffuse, the absorption

maximum being red shifted to ~650 nm for diphenyl-s-tetrazine. We also succeeded in observing a transient absorption from mixed crystals of diphenyl-s-tetrazine, the observed decay time being 10 ms at both room temperature and at 4.2 K.

The observation of these new metastable species with diffuse visible absorption spectra can be used in an explanation of the previous results obtained for s-tetrazine and its derivatives. Thus we propose that a photochemically produced intermediate first arises in the decomposition of s-tetrazine just as with its derivatives. In the case of s-tetrazine the parent molecule first absorbs a photon at some arbitrary energy, decays to the zero-point level of the first singlet,[3] and then rearranges to the intermediate. In solution at room temperature we propose that this intermediate decays thermally to products (N$_2$ and HCN) without absorption of a second photon. However, at helium temperature this intermediate is more stable to thermal decomposition and requires absorption of a second photon to generate products efficiently. In the cases of dimethyl-, phenyl-, and diphenyl-s-tetrazine the intermediate is sufficiently stable to thermal decomposition at room temperature to require the absorption of a second photon to result in efficient dissociation. If no second photon is available[7] the intermediate may simply regenerate the starting material more efficiently.

The fact that the transients exhibit buildup times in the microsecond range indicates they are not formed directly from the singlet state of the parent compound (fluorescence lifetime is 6 and 14 ns, respectively, for dimethyl- and phenyl-s-tetrazine[4]). It is unlikely that the formation of the intermediate proceeds through a relaxed triplet state of tetrazine since the intersystem crossing quantum yield is <10^{-3}; yet the photochemical quantum yield is near unity.[8,9] This possibility, however, has not been experimentally eliminated for phenyl- and diphenyl-s-tetrazine. The possibility of triplet–triplet absorption being responsible for the observed transient can be eliminated since the observed transient lifetime in solution of 500 μs is much longer than the 2 K neat crystal phosphorescence lifetimes (i.e., 60 and 85 μs, respectively, for dimethyl- and phenyl-s-tetrazine). Thus we have no indications that a tetrazine triplet state is involved in photochemistry following excitation into the singlet manifold.[9]

It has been previously shown that 1,4-nitrogen bonding plays a negligible overall role in the photochemistry of tetrazine.[10] Mechanisms involving diradical intermediates (e.g., homolytic bond cleavage) are consistent with the shorter lifetimes and reduced signal strengths observed in nondegassed solutions as well as with the observed visible absorption spectra. Consequently, it may be possible to trap such intermediates with suitable scavengers; such chemical experiments are in progress. The results presented here are consistent with previously published experiments,[3,4] but they do indicate that the assumptions[4] used to evaluate reaction rates from lifetime data are incorrect in some instances (e.g., the quantum yields in Table VI of ref 4 more likely refer to relative yields of formation of the intermediate).

Finally these results raise the intriguing possibility that apparently simple photoprocesses can involve intermediates that are metastable on normal laboratory time scales and which even at temperatures close to 0 K can tunnel back to the starting material. Studies of the Raman and IR spectra of these intermediates at low temperatures are presently underway.[11]

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References and Notes

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(7) Obviously the model proposed here predicts differences in the quantum yield and rate of the photodissociation for appropriately pulsed vs. CW illumination. For example a N_2-laser running at 50 pps would not intercept the intermediate in the case of diphenyl-*s*-tetrazine.
(8) J. H. Meyling, R. P. van der Werf, and D. A. Wiersma, *Chem. Phys. Lett.*, **28**, 364 (1974).
(9) The intersystem crossing quantum yield value is based on knowledge of the relative amounts of fluorescence and phosphorescence. The triplet state could be involved if an intersystem crossing occurred to levels that then undergo reaction rather than relaxation to potentially phosphorescent states.
(10) D. S. King, C. T. Denny, R. M. Hochstrasser, and A. B. Smith, III, *J. Am. Chem. Soc.*, **99**, 271 (1977).
(11) NOTE ADDED IN PROOF. A requirement for any proposed intermediate is that its transient absorption be in the red region of the optical spectrum. Possible examples are i and ii. Structure ii was suggested by the recent spectral
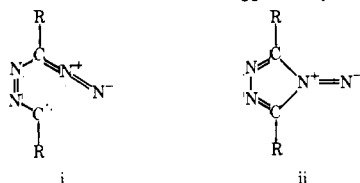
properties reported by Dervan for a 1,1-dialkyldiazene; see W. D. Hinsberg, III, and P. B. Dervan, *J. Am. Chem. Soc.*, **100**, 1608 (1978). Interestingly, this diazene and its dimethyl and diphenyl derivatives (ii, R = H, CH_3, and C_6H_5) have been suggested to be the intermediate in the oxidative $(Pb(OAc)_4)$ fragmentation of the corresponding 4-amino-1,2,4(4*H*)-triazole; see K. Sakai and J.-P. Anselme, *Tetrahedron Lett.*, 3851 (1970).

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Fluorescence and Photochemistry of the Charge-Transfer Band in Alcoholic Vanadium Trichloride Solution

Sir:

The primary photochemical and photophysical processes derived from the charge-transfer excited states of transition metal complexes have been the subject of extensive investigations in the past decade.[1] At present, however, our understanding of the photophysical properties of the charge-transfer excited state is still relatively limited because of the few luminescence data available.

We have found that vanadium(III) alcoholate complexes in the parent alcohol solution exhibit luminescence of relatively high quantum yield upon excitation at the charge-transfer band with competitive photoreduction[2] of vanadium(III) to vanadium(II). This appears to represent the first case of a transition metal complex displaying both photochemistry and luminescence from an upper excited state in fluid solution. Vanadium trichloride reacts with methanol, ethanol, and 1-propanol to form alcoholates, formulated in solution as $[V(RCH_2OH)_4-Cl_2]Cl$.[3] Absorption spectra of these complexes in solution show two distinct maxima at $\sim$670 (ν_1, ϵ_m 8) and 450 nm (ν_2, ϵ_m 15–16) in the visible region.[4] The ν_1 and ν_2 bands have been assigned as spin-allowed ligand-field transition attributable to $^3T_{2g} \leftarrow {}^3T_{1g}(F)$ and $^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$ of vanadium(III) in octahedral symmetry, respectively. In contrast, a broad
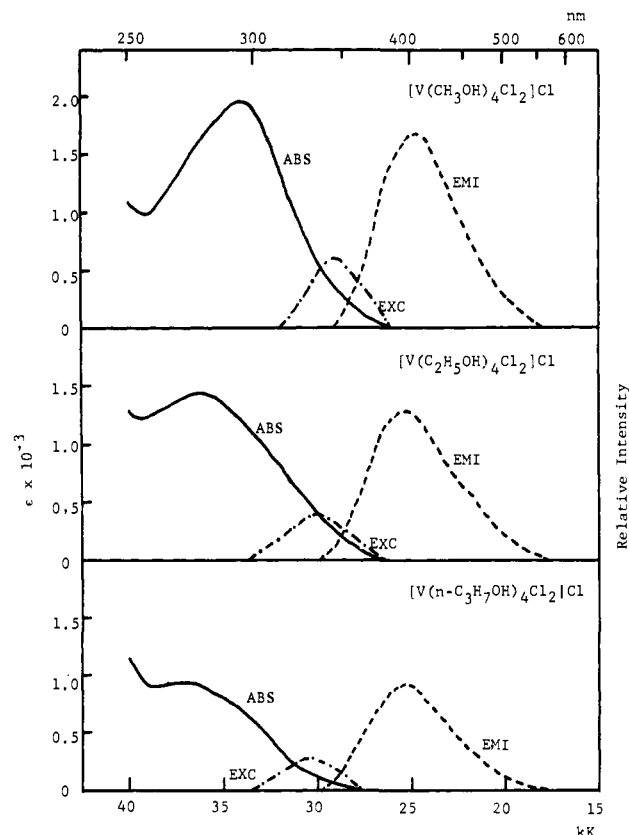

Figure 1. Absorption, emission, and excitation spectra of vanadium(III) alcoholates in room temperature solution.

Table I. Quantum Yields of Photoreduction and Fluorescence of Vanadium(III) Alcoholates in the Parent Alcohol at Room Temperature

Complex	$\Phi_r{}^a$	$\Phi_f{}^b$		
		290	330	345
$[V(CH_3OH)_4-Cl_2]Cl$	0.07 ± 0.01	0.000	0.002	0.004
$[V(C_2H_5OH)_4-Cl_2]Cl$	0.22 ± 0.02	0.000	0.008	0.010
$[V(n\text{-}C_3H_7OH)_4-Cl_2]Cl$	0.20 ± 0.02	0.000	0.020	0.021

a Quantum yields of photoreduction of vanadium(III) to vanadium(II) upon irradiation with 313-nm light. *b* Fluorescence quantum yields for excitation at different wavelengths (nm).

absorption band of relatively high intensity (ϵ_m 900–1950) lies in the ultraviolet region of 250–400 nm (Figure 1). This band can be identified as a spin-allowed charge-transfer transition from ligand to metal (CTTM), based on the following photochemical results.

Irradiation of alcoholic vanadium trichloride solutions with 313-nm light resulted in the absorption spectral changes. As irradiation proceeded, the ν_1 and ν_2 bands characteristic of vanadium(III) decreased in intensity, while new absorption bands appeared at 570 (ν_1') and 380 nm (ν_2').[5] The positions of the new absorption bands are in close agreement with the values[6] of alcoholic vanadium dichloride solutions. ν_1' and ν_2' may be assigned as spin-allowed ligand-field transitions attributable to $^4T_{1g}(F) \leftarrow {}^4A_{2g}$ and $^4T_{1g}(P) \leftarrow {}^4A_{2g}$ of vanadium(II) in octahedral symmetry, respectively. In addition, the photoreduction of vanadium(III) to vanadium(II) was confirmed by the appearance of the characteristic vanadium(II) EPR signal. Quantum yields Φ_r of the photoreduction upon irradiation with 313-nm light (Table I) were determined from