

SOLVENT ISOTOPE EFFECT ON THE FLUORESCENCE OF AZOALKANES

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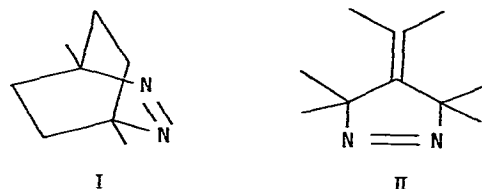
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A study of fluorescence quantum yields and fluorescence lifetimes of the cyclic azoalkanes I and II reveals a striking dependence of Φ_F and τ_F on solvent and on isotopic substitution (OH \rightarrow OD). A mechanism involving specific deactivation of the fluorescent state from a hydrogen bonded complex is proposed to rationalize the data. The observation that the quantum yield for decomposition of I does not correlate with the variation of fluorescence parameters with solvent and isotopic change leads to the conclusion that the state responsible for photoreaction *precedes* the fluorescent state.

Excited state lifetimes and quantum yields display both intramolecular and intermolecular deuterium isotope effects. For instance, an intramolecular isotope effect has been established for the phosphorescence lifetimes of aromatic hydrocarbons [1]. Usually, replacement of hydrogen by deuterium results in an increase of the excited state lifetime by an order of magnitude by slowing down radiationless pathways for deactivation. External (intermolecular) deuterium isotope effects have only been reported for a few systems, the most striking examples of which involve singlet oxygen ($^1\Delta_g$) [2], transition metal complexes [3] and proton transfer reactions in the excited state [4].

In this note, we wish to report such an exceptionally large external isotope effect which was observed during the course of an investigation of the spectroscopy of cyclic and bicyclic azoalkanes [5]. As shown in table 1, large deuterium isotope effects were noted on the fluorescence quantum yield and lifetime of 3,6-dimethyl-1,2-diaza-[2.2.2] bicyclooctene (I) [6] ‡.

‡ All solvents were commercial products (Aldrich Chem. Co.). All solutions were nitrogen saturated using a N_2 -purging technique (see ref. [5] for details). Lifetimes were determined by single photon counting and quantum yields were measured by Parker's method [7].



In alcohols, the deuterium isotope effects on the quantum yield ratio $[\phi_{fl}(D)/\phi_{fl}(H)]$ range from 4 to 20, depending upon the nature of the alcohol and degree of deuteration. This effect is smaller for water (≈ 2) than for alcohols (≈ 10) and nearly absent in acidic solutions although fluorescence was quenched † by H^+ (D^+) with a rate constant of approximately $10^8 \text{ mol}^{-1} \text{ s}^{-1}$. In contrast to OH containing solvents, no isotope effect was observed for benzene or acetonitrile. Most interestingly, the quantum yields of azoalkane disappearance shows no isotope effect even in alcoholic solutions. Finally, the radiative lifetimes (τ_0^{fl}), as determined by the equation

$$\tau_0^{fl} = \tau / \phi_{fl}, \quad (1)$$

vary by less than a factor of two ‡.

† Quenching experiments were carried out with HCl and DCl solutions in H_2O and D_2O , respectively. The Stern-Volmer plots were linear.

‡ It is not clear whether the small changes in τ_0^{fl} are a real effect or due to quenching by impurities in different solvents.

Table 1
Isotope effect on the spectroscopic properties of (I)

Solvent	Isotopic purity	ϕ_{fl}	$\phi_{\text{d}}^{\text{a)}$	τ (ns)	$\phi_{\text{fl}}(\text{D})/\phi_{\text{fl}}(\text{H})$	$\tau_{\text{f}}^{\text{fl}}$ (ns)
benzene		0.5		660		1200
benzene- d_6	99%	0.5		980	1.0	1960
acetonitrile		0.7	0.15	780		1100
acetonitrile- d_3	99%	0.65		1000	0.93	1550
methanol		0.01	0.25	14		1400
methanol- d_1	99.5%	0.1 ₀	0.20	165	10	1650
methanol- d_4	99.5%	0.2 ₀		440	20	2200
ethanol		0.01 ₅			5	
ethanol- d_1	99.5%	0.07 ₅				
isopropanol		0.01 ₅			3.7	
isopropanol- d_1	98%	0.05 ₅				
<i>t</i> -butanol		0.05 ₅		100		1800
<i>t</i> -butanol- d_1	98%	0.3 ₄		560	6.2	1650
water		0.25	0.025	335		1350
deuterium oxide	99%	0.55	0.03	700	2.2	1280
H ⁺ in H ₂ O		$k_{\text{q}}=0.07 \times 10^8$				
D ⁺ in D ₂ O		$k_{\text{q}}=1 \times 10^8$			0.7	

a) Quantum yield for azoalkane disappearance ($\text{mol}^{-1} \text{s}^{-1}$).

Table 2
Isotope effects on the spectroscopic properties of (II)

Solvent	ϕ_{fl}	$\phi_{\text{d}}^{\text{a)}$	τ_{fl} (ns)	$\phi_{\text{fl}}(\text{D})/\phi_{\text{fl}}(\text{H})$
acetonitrile	0.1 ₅	0.7	225	1.2
acetonitrile- d_1	0.1 ₈			1.2
methanol	0.01	0.2	13	4.5
methanol- d_1	0.04 ₅			
methanol- d_4				
ethanol	0.01 ₀			
ethanol- d_1	0.02 ₀			2
isopropanol	0.01			
isopropanol- d_1	0.02			2
<i>t</i> -butanol	0.09 ₅			
<i>t</i> -butanol- d_1	0.2 ₅			2.6
water	no detectable emission $<10^{-3}$			
deuterium oxide	0.003			
H ⁺ in CH ₃ CN/H ₂ O	$k_{\text{q}}=4 \times 10^8$			
D ⁺ in CH ₃ CN/D ₂ O	$k_{\text{q}}=3 \times 10^8$ (1.3)			

a) Quantum yield for azoalkane disappearance ($\text{mol}^{-1} \text{s}^{-1}$).

The fluorescence quantum yields for 4-isopropylidene-3,3,5,5-tetramethyl-1-pyrazoline (II) are listed in table 2 [6]. The results are similar to those of (I), although smaller in magnitude.

The results in tables 1 and 2 clearly indicate that an interaction between the azo moiety and an OH group is necessary in order to produce a significant isotope effect. Since the absorption spectra of (I) and (II) are identical in ROH and ROD, a ground state complex is ruled out. Thus, an interaction between the excited azoalkane and the solvent must be responsible for this effect. The most obvious assumption is that a hydrogen bond is formed between an excited azo and a solvent molecule. This complexation provides an additional pathway for radiationless deactivation. Proton or deuteron transfer cannot be responsible for this isotope effect since both H⁺ and D⁺ are equally efficient at quenching fluorescence. *Another key implication of these results is that the fluorescent state and the reactive state of (I) are not the same.* Thus, as the solvent varies from acetonitrile to methanol, the fluorescence of (I) is quenched by 98%, but the quantum yield of decomposition remains un-

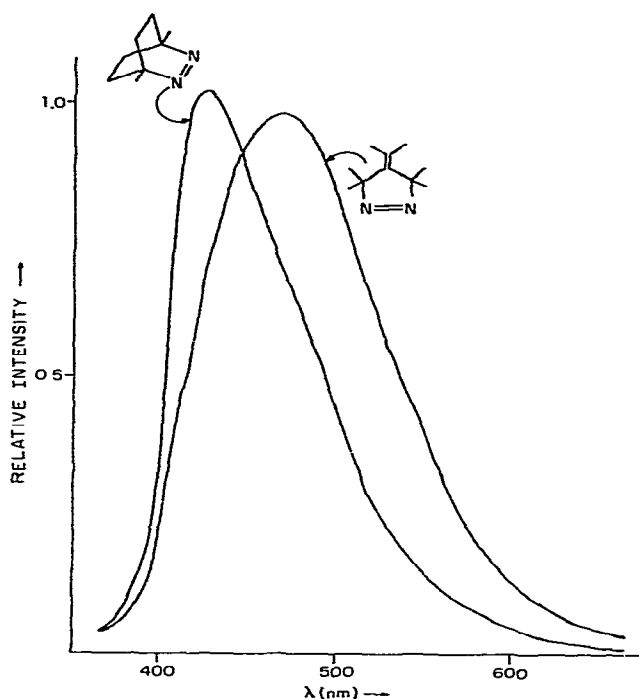
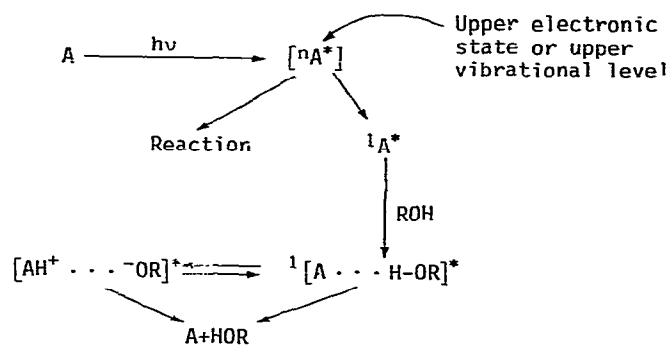


Fig. 1. The normalized fluorescence spectra of I and II in air saturated acetonitrile.

changed [#]. In contrast, it appears the fluorescence and reactive states are the same in (II). Thus, both the fluorescence and decomposition are quenched in H₂O.

One possible interpretation of the former results is that the reaction occurs prior to the interaction of the excited azoalkane and the solvent. A plausible sequence is shown in scheme I. As indicated, decompo-



[#] There is a difference in our reaction quantum yields for the disappearance of compound I with those previously reported for nitrogen extrusion of I [8].

sition occurs from a species prior to the fluorescence state, i.e., reaction occurs from an upper electronic state or upper vibronic level of S₁. Before such an interpretation can be confirmed, investigations of variable wavelengths effects are necessary. We postulate that the azoalkane reaches the fluorescent state and then fluoresces or complexes with a solvent molecule. This complex now may deactivate either directly* or via a proton transfer complex to the ground state. For nonacidic solvents, i.e., H₂O, ROH, etc., deactivation occurs from the hydrogen bonded complex. Since the complex may be considered a supermolecule, the isotope effect can be explained in terms of varying Franck-Condon factors [9], i.e., electronic excitation energy is degraded by flowing into the O-H(D) stretching mode. Replacement of the methyl protons in methanol results in a slightly increased lifetime of the azo compound. This may either be a small primary isotope effect or a secondary isotope effect [10].

* We cannot exclude the possibility that the complex 3 is the emitting species. There is, however, no significant qualitative difference in the emission of I or II in deuterated and non-deuterated solvents (see fig. 2).

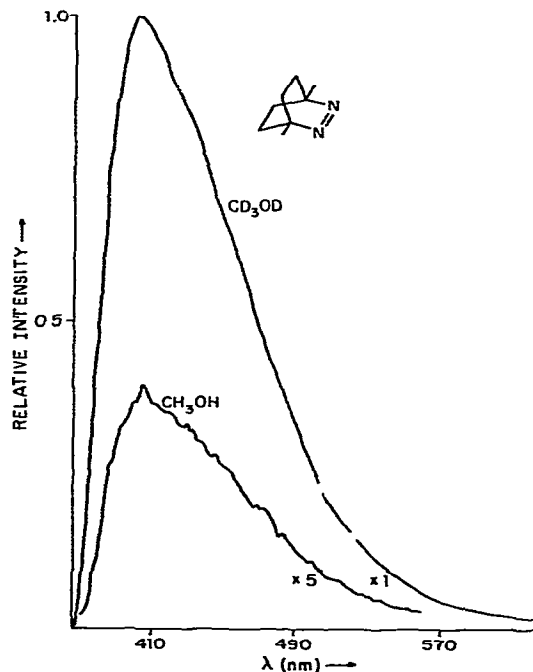


Fig. 2. The fluorescence spectrum of I in CH₃OH and CD₃OD.

In the case of acidic solutions, formation of the proton transfer complex is fast and the equilibrium greatly favors this complex. Vibrational relaxation occurs from this complex and no isotope effect is observed.

An alternative interpretation postulates that radiationless decay occurs exclusively from the proton transfer complex. In this case, the rate determining step must be the H^+ (D^+) transfer. This can account for the primary isotope effect but cannot explain the lack of an isotope effect for quenching by H_3O^+ versus D_3O^+ . Furthermore, H_2O would be expected to quench the fluorescence to a greater extent than CH_3OH . Again, this is contrary to the observed data.

In conclusion, we have presented data illustrating the fact that the quenching of fluorescence from azoalkanes exhibits an exceptionally large isotope effect. Furthermore, the fluorescence was shown to be different from the reactive state in the case of (I). The mechanism proposed for quenching involves formation of two distinct complexes, each with its own radiationless decay pathway. Further tests of the proposed mechanism are necessary and are now in progress.

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