Quenching of Aromatic Hydrocarbon Singlets by Alkyl Azides[1]

Frederick D. Lewis[2] and J. Christopher Dalton[3]

Contribution from the Department of Chemistry, Columbia University,
New York, New York 10027. *Received May 9, 1969*

Abstract: Hexyl azide was found to be an efficient quencher of aromatic hydrocarbon fluorescence. The rate of fluorescence quenching is related to the singlet energy of the donor in accord with an endothermic collisional exchange energy transfer mechanism. Energy transfer by donors with low singlet energies is more efficient than expected for classical endothermic energy transfer as was previously observed for triplet sensitization of alkyl azides. Both singlet and triplet results are best explained by vertical energy transfer to a bent azide ground state generating a bent excited state. Singlet sensitization leads to decomposition of the azide with an efficiency similar to that for the direct photolysis.

Alkyl azides decompose thermally[4] and photolytically[5,6] to give nitrogen and a nitrene (eq 1). One

$$R\text{-}N_3 \xrightarrow[\text{or }\Delta]{h\nu} R\text{-}N\colon + N_2 \qquad (1)$$

of us has recently reported that the photodecomposition of alkyl azides can be sensitized by a variety of known triplet sensitizers.[7,8] An approximately linear relationship between sensitizer triplet energy and the rate constant for energy transfer to the azides was observed for several aryl ketone sensitizers. Phenanthrene, however, gave an anomalously large value for the rate constant of triplet energy transfer and for the quantum yield of sensitized decomposition.[8] Since phenanthrene is known to have a moderately long singlet lifetime in solution ($\tau_F = 56.0 \times 10^{-9}$ sec in degassed benzene[9]) it was felt that singlet energy transfer to the azides might be occurring. This possibility prompted an investigation of the behavior of alkyl azides as quenchers of aromatic hydrocarbon singlets.

Hexyl azide was found to decrease both the intensity and the lifetime of phenanthrene fluorescence. The observed quenching is consistent with the reaction scheme given by eq 2-7, where S is the sensitizer and A the azide. First-order sensitizer decay processes other than fluorescence and intersystem crossing have been neglected. A standard Stern-Volmer treatment of the quenching yields eq 8, where $\tau_F{}^0$ and τ_F are the fluorescence lifetimes of phenanthrene in the absence and presence of azide, F^0 and F are the fluorescence intensities in the absence and presence of azide, and k_q is the rate constant for singlet quenching. $\tau_F{}^0$ was determined by the single photon counting technique[10] to be 55×10^{-9} sec in degassed benzene, in good agreement with the published value.[9] Figure 1 gives a plot of $\tau_F{}^0/\tau_F$ and F^0/F for phenanthrene as a function of azide concentration. The data obtained by the two methods are in excellent agreement. From the slope in Figure 1 and eq 8 k_q is determined to be 5.8×10^8 l. mole^{-1} sec^{-1}. This rate is somewhat below that for exothermic (diffusion controlled) singlet transfer in solution.[11]

$$S \xrightarrow{h\nu} {}^1S \qquad (2)$$

$${}^1S \xrightarrow{k_F} S + h\nu \qquad (3)$$

$${}^1S \xrightarrow{k_{ST}} {}^3S \qquad (4)$$

$${}^1S + A \xrightarrow{k_q} S + {}^1A \qquad (5)$$

$${}^1A \xrightarrow{k_p} \text{products} \qquad (6)$$

$${}^1A \xrightarrow{k_o} A \qquad (7)$$

$$\frac{\tau_F{}^0}{\tau_F} = \frac{F^0}{F} = 1 + k_q\tau_F{}^0[A] \qquad (8)$$

$$\tau_F{}^0 = \frac{1}{k_F + k_{ST}} \qquad (9)$$

Several possible mechanisms may be considered whereby hexyl azide could quench phenanthrene singlets.[12] Long-range or resonance electronic energy transfer to yield an excited azide singlet can be ruled out due to the very weak azide absorption in the region of overlap with the phenanthrene fluorescence. Collisional exchange energy transfer is a possibility even though the long wavelength azide absorption maxima at 2880 Å (99 kcal/mole) would seem to make energy transfer from phenanthrene (E_S = 83.0 kcal/mole) strongly endothermic. If "nonclassical" singlet energy transfer were to occur, as has been observed for triplet energy transfer from aryl ketones to alkyl azides,[8] then the likelihood of a collisional exchange energy transfer mechanism would be greatly enhanced. Finally, the possibility that the quenching occurs by an "exciplex" mechanism, such as that suggested by Hammond and coworkers[13] for the quenching of aromatic singlets by conjugated dienes, should be considered. This process would not lead to formation of an excited azide singlet, but rather a sensitizer-azide complex in which the electronic energy of the sensitizer is converted into vibrational energy in the complex, possibly resulting in "hot ground state" azide chemistry.

If the mechanism for quenching of aromatic singlets

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(2) National Institutes of Health Postdoctoral Fellow, 1968–1969; inquiries should be directed to the Department of Chemistry, Northwestern University, Evanston, Ill. 60201.

(3) National Institutes of Health Predoctoral Fellow, 1966–1969.

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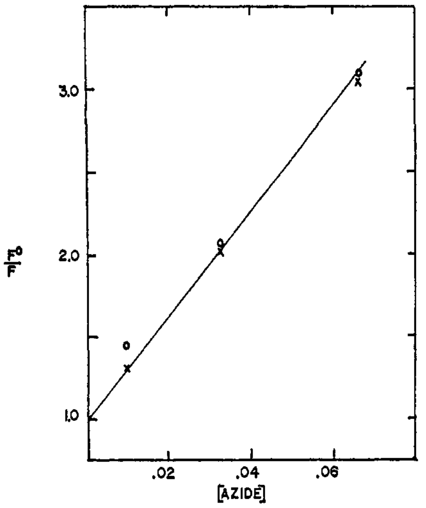

Figure 1. Stern–Volmer plot for quenching of phenanthrene fluorescence lifetime (O) and intensity (X) by hexyl azide.

by hexyl azide is collisional exchange energy transfer, a definite correlation would be expected between the sensitizer singlet energy and k_q, the rate of energy transfer. If, on the other hand, the Hammond exciplex mechanism is operating, no such correlation would be expected, since only a few aromatic singlets are quenched by dienes and no dependence of quenching rate on sensitizer singlet energy is observed.[14] In addition, because the collisional exchange mechanism generates excited azide singlets we might expect the quantum yield for singlet sensitized azide decomposition to be related to the quantum yield for direct azide photodecomposition if this mechanism is operating. In order to distinguish between these two mechanistic possibilities we have measured the rate of singlet quenching for various singlet sensitizers and also the quantum yield for singlet sensitized decomposition of hexyl azide.

The fluorescence of naphthalene, triphenylene, pyrene, and 1,2-benzanthracene in degassed benzene solutions is quenched by hexyl azide. Fluorescence lifetimes in the absence of azide were measured for each of the sensitizers by the single photon counting technique. These values are compared with representative fluorescence lifetime values from the literature in Table I. The pyrene value is probably low due to some exciplex formation at the concentration used.[15] Also given in Table I are the sensitizer singlet energies (E_S) measured from the fluorescence spectra in benzene solution. In all cases the values are in good agreement with literature values in alkane solvents.

Stern–Volmer treatment of the quenching data, such as that shown in Figure 1, yielded the values of $k_q\tau_F^0$ for each of the sensitizers given in Table II. No correction for competitive absorption by azide was necessary as nearly all the exciting irradiation was absorbed by the sensitizers. From the slopes of the Stern–Volmer plots and the fluorescence lifetimes singlet quenching rates (k_q) were determined and are given in Table II. A plot of the log of the rate constant for fluorescence quenching *vs.* the donor singlet energy is given in Figure 2. An approximately linear dependence of quenching rate constant upon donor singlet energy is observed. Even with naphthalene whose singlet energy is ~88 kcal/mole a diffusion-controlled rate is not obtained. The diffusion-controlled rate for

Table I. Sensitizer Fluorescence Lifetimes and Singlet Energies

Sensitizer (M)	λ_{ex}, A	$\tau_F^0 \times 10^9$ sec[a]	$\tau_F^0 \times 10^9$ sec[b]	E_S, kcal/mole[f]
Naphthalene (0.01)	3150	93	110,[c] 96[d]	87.7
Phenanthrene (0.03)	3500	55	56[e]	83.0
Triphenylene (0.01)	3400	38	36.6[d]	81.9
Pyrene (2.5×10^{-4})	3460	215	300[c]	77.7
1,2-Benzanthracene (1.5×10^{-3})	3860	45	44.1[c]	73.3

[a] Measured by single photon counting technique. [b] Values from literature for hydrocarbon solvents. [c] Reference 10. [d] I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965. [e] Reference 9. [f] Energy of shortest wavelength fluorescence band in benzene solution.

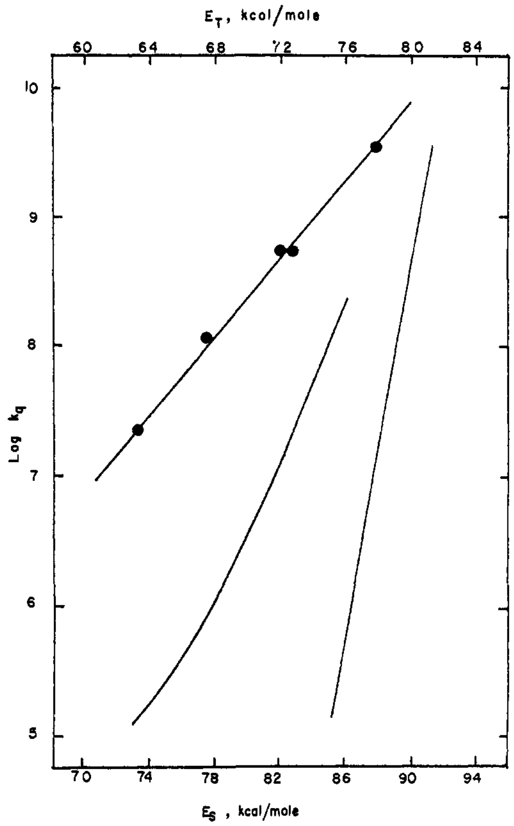

Figure 2. Plot of log k_q *vs.* sensitizer energy for energy transfer to hexyl azide. Left to right: singlet transfer, triplet transfer (ref 8), and classical endothermic transfer (eq 11).

Table II. Kinetic Data for Singlet Quenching by Hexyl Azide

Sensitizer	Azide concn, M	$k_q\tau_F^0$ [a]	k_q
Naphthalene	0.01–0.001	371 ± 23[b]	4.0×10^9
Phenanthrene	0.067–0.01	32 ± 3[b,c]	5.8×10^8
Triphenylene	0.1–0.01	22.4 ± 2.5[b]	5.9×10^8
Pyrene	0.1–0.01	25.3 ± 2.6[b]	1.2×10^8
1,2-Benzanthracene	0.1–0.01	1.0 ± 0.1[b]	2.3×10^7

[a] Standard deviation for least-square fit. [b] Determined from quenching of fluorescence intensity. [c] Determined from quenching of fluorescence lifetime.

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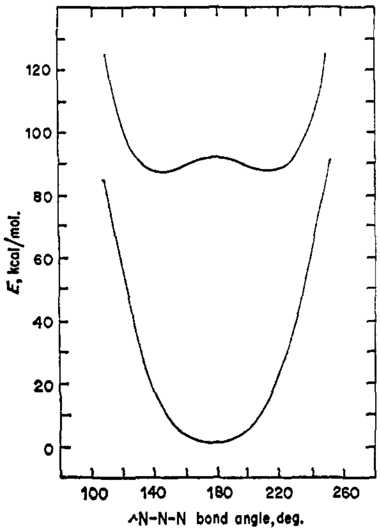

Figure 3. Plot of energy *vs.* N–N–N bond angle for methyl azide as determined by extended Hückel calculations: lower curve, ground state; upper curve, first excited state (ref 8).

singlet energy transfer in benzene is calculated from the modified Debye equation (eq 10) to be 1.5 × 10^{10} l.

$$k_{\text{diff}} \sim \frac{8RT}{2000\eta} \tag{10}$$

mole^{-1} sec^{-1}.[11] Extrapolation of the plot for singlet quenching in Figure 2 to this value gives a singlet energy of about 91–92 kcal/mole. This result is entirely reasonable in view of the broadness of the azide absorption which maximizes at 99 kcal/mole.

The observed linear decrease in log k_q with E_S implies that the mechanism for quenching of aromatic hydrocarbon singlets by alkyl azides is endothermic collisional exchange singlet energy transfer. For endothermic energy transfer to occur an activation energy must be supplied. Assuming vertical excitation of the ground-state acceptor the requirement of an activation energy leads to the prediction that the slope of the plot of log k_q *vs.* E_S should obey eq 11.[16] This equation pre-

$$\frac{\Delta \log k_q}{\Delta E_S} = \frac{1}{2.303RT} \tag{11}$$

dicts a slope of 0.74 for the endothermic portion of the log k_q *vs.* E_S plot. Acceptors such as biacetyl[17] and *trans*-stilbene[16] which obey eq 11 for triplet energy transfer are referred to as "classical" acceptors. The observed slope for singlet transfer to hexyl azide is 0.16, implying that the rate of endothermic singlet energy transfer to hexyl azide by low singlet energy sensitizers is much faster than predicted for classical energy transfer. This type of behavior has been observed for triplet transfer to *cis*-stilbene and related olefins[16] and to organic azides[8] and has been referred to as "nonclassical" energy transfer.

Whereas the observation of nonclassical energy transfer seems well documented, its explanation is far from clear. Herkstroeter and Hammond[16] have explained nonclassical behavior for olefins such as *cis*-stilbene by postulating "that flexible molecules can undergo "nonvertical" transitions to produce twisted geometric forms directly." Lewis and Saunders[8] favored an interpretation based upon ideas suggested by Liu[18] that nonclassical triplet energy transfer to alkyl azides can be explained by invoking vertical excitation of a vibrationally excited bent azide ground state to form a low-energy bent excited state. Such an explanation has the advantage of not being a formal violation of the Franck–Condon principle. By analogy, the same explanation is favored for the observed nonclassical behavior in singlet energy transfer as well.

Extended Hückel calculations on methyl azide showed that the first excited state has energy minima where the angle of the N_1–N_2–N_3 bond (θ) is 140 or 220° and a small maximum for a linear azide, whereas the linear conformation is the most stable ground state.[9] The results of these calculations, which do not include spin, are shown in Figure 3. If the excited-state potential well had the same shape as the ground state, then excitation of vibrationally excited states would lead to classical behavior. However, vertical excitation of a vibrationally excited bent ground state to a bent excited state benefits by simultaneous rising of the ground-state and lowering of the excited-state energies, thus making the energy transfer process more efficient than predicted for classical energy transfer by eq 11.

That the same sort of nonclassical endothermic energy transfer should occur from both singlets and triplets to alkyl azide is entirely reasonable. There is no compelling reason to believe that the shape of the potential wells of the excited singlet and triplet states of alkyl azides should differ greatly. The difference in the slopes of the singlet and triplet energy transfer plots (Figure 2) may be indicative of small differences in the singlet and triplet potential wells. However, in the absence of calculations including spin, such conjectures are hazardous.

Having established that the most probable mechanism for the observed fluorescence quenching by hexyl azide is collisional exchange energy transfer to the bent ground-state azide it remained to be determined if singlet transfer leads to decomposition of the azide and if the quantum yield for singlet sensitized decomposition was consistent with the proposed mechanism. The quantum yield of phenanthrene singlet sensitized azide decomposition was determined by including enough piperylene to quench totally triplet energy transfer to the azide. Since the triplet energy of piperylene is 2–3 kcal/mole below that of phenanthrene, energy transfer from phenanthrene triplets should occur at close to the diffusion-controlled rate. On the other hand, endothermic triplet energy transfer from phenanthrene to hexyl azide should occur with a rate constant several orders of magnitude slower than that for diffusion control.[8] Thus inclusion of a concentration of piperylene equal to that of azide should ensure that triplet sensitization of azide by phenanthrene does not occur. Any sensitized decomposition observed should be coming from singlet energy transfer.

Degassed benzene solutions containing 0.03 *M* phenanthrene and 0.02 *M* hexyl azide and varying amounts of piperylene were photolyzed at 3130 Å. As a control experiment benzophenone, which should give only triplet sensitization due to its rapid rate of intersystem

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crossing, was used in place of phenanthrene. Quantum yields for azide disappearance were determined by gas chromatography using uranyl oxalate actinometry. The results are given in Table III. The quantum yield for phenanthrene-sensitized disappearance of the azide was found to be 0.24 in the absence of piperylene and 0.20 in the presence of either 0.01 or 0.1 M piperylene. Thus the quantum yield for singlet sensitized azide decomposition is 0.20. The observed lack of variation in the quantum yield in going from 0.01 to 0.1 M is strong evidence that all of the triplet-sensitized azide decomposition is being efficiently quenched. It also implies that hexyl azide is a much more efficient quencher of singlet phenanthrene than is piperylene. The benzophenone control demonstrates that there is no singlet sensitization by benzophenone and eliminates the unlikely possibility that the short-lived piperylene triplet could sensitize decomposition of the azide.

Table III. Quantum Yield for Sensitized Azide Disappearance

Piperylene, M	Phenanthrene, Φ	Benzophenone, Φ
0	0.24	0.054
0.01	0.20	0.008
0.10	0.20	0.001

The quantum yield for singlet sensitized azide decomposition, $\Phi'_{-\mathrm{A}}$, as derived from eq 2–7 is

$$\Phi'_{-\mathrm{A}} = \frac{k_\mathrm{q}[\mathrm{A}]}{k_\mathrm{q}[\mathrm{A}] + k_\mathrm{ST} + k_\mathrm{F}} \frac{k_\mathrm{p}}{k_\mathrm{p} + k_\mathrm{o}} \qquad (12)$$

where $k_\mathrm{p}/(k_\mathrm{p} + k_\mathrm{o})$ represents the efficiency with which singlet azide generated by energy transfer decomposes. Equation 12 may be rearranged to eq 13. From the

$$\frac{k_\mathrm{p}}{k_\mathrm{p} + k_\mathrm{o}} = \Phi'_{-\mathrm{A}} \frac{1 + k_\mathrm{q}\tau_\mathrm{F}^0[\mathrm{A}]}{k_\mathrm{q}\tau_\mathrm{F}^0[\mathrm{A}]} \qquad (13)$$

fluorescence quenching plot and the observed quantum yield for 0.02 M azide, a value of 0.57 is calculated for $k_\mathrm{p}/(k_\mathrm{p} + k_\mathrm{o})$. The direct photolysis quantum yield, a measure of the efficiency of decomposition of azide singlet generated by light absorption, is 0.86 for 2537-Å irradiation and 0.71 for 3130-Å irradiation in degassed methanol.[6] The relatively good agreement between the 3130-Å and the singlet sensitized values is entirely consistent with a collisional exchange singlet energy transfer mechanism. The slight decrease in efficiency for singlet sensitized *vs.* direct photolysis may be due to the smaller amount of singlet energy supplied by energy transfer. Such an explanation is in accord with the observed dependence of the efficiency of triplet-sensitized azide decomposition upon sensitizer triplet energy.[8]

Experimental Section

Materials and Sensitizers. Hexyl azide was prepared as previously described.[6] Benzene was spectro grade refluxed twice over fresh phosphorus pentoxide and fractionated, the middle 70% being retained. *trans*-1,3-Pentadiene (98%, Chemical Samples) was distilled under reduced pressure prior to use. Naphthalene (Baker, Photochemical Grade) was recrystallized several times from methanol. Triphenylene (K & K) was chromatographed on alumina, recrystallized twice from ethanol, and zone refined. Phenanthrene (Reilly) was treated with maleic anhydride to remove anthracene, chromatographed on alumina, recrystallized twice from ethanol, and zone refined. Pyrene (Carbide and Carbon) was recrystallized twice from ethanol and sublimed under vacuum. 1,2-Benzanthracene (Aldrich) was recrystallized from ethanol, chromatographed on alumina, recrystallized twice from ethanol, and sublimed under vacuum. Benzophenone (Eastman White Label) was recrystallized four times from ethanol.

Fluorescence Quenching Studies. Benzene solutions of the sensitizers containing varying amounts of azide were degassed four times using an oil diffusion pump and sealed under vacuum in 10-mm Pyrex tubes. Fluorescence spectra were measured on an Aminco-Bowman spectrofluorometer at room temperature. Excitation wavelengths and sensitizer concentrations, given in Table I, were chosen such that the absorbance of the solution was approximately 1.0 at the excitation wavelength. Relative fluorescence intensities were determined by measuring the peak heights for the maxima. The fluorescence lifetimes were measured by the single photon counting technique using either a nitrogen or deuterium flash lamp for excitation and a 0.25-m Jarrel Ash monochromator to isolate the fluorescence emission.[19] Lifetimes were determined either by a statistical average of repeated half-life determinations or by a computer fit to an exponential decay curve. Absorption spectra were taken on a Cary 14 or a Cary 15 spectrophotometer. All solutions were checked for competitive absorption by the hexyl azide at the wavelength of excitation.

Quantum Yields. Degassed benzene solutions of 0.03 M phenanthrene or 0.06 M benzophenone containing 0.02 M hexyl azide and varying amounts of piperylene were irradiated in parallel on a merry-go round apparatus. A 450-W Hanovia medium-pressure lamp was used with a potassium chromate filter solution to isolate the 3130-Å irradiation. All the light is absorbed by the sensitizers. Uranyl oxalate actinometers were irradiated simultaneously. Azide solutions were analyzed for disappearance of azide by gas chromatography using *m*-xylene as an internal standard. Analyses were performed on a Hewlett-Packard 5750 dual column gas chromatograph using a 5 ft × $^1/_8$ in. column of 5% Carbowax 20M on Chromosorb G.

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(19) For a description of apparatus, see T. Tao, *Biopolymers*, in press.