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Heavy-Atom Effects on the Spin-Forbidden Processes of Acenaphthylene[1]

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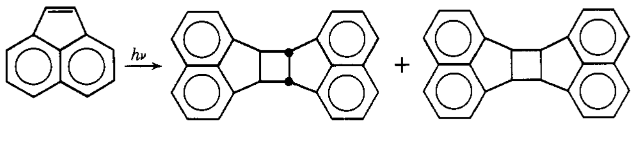
Abstract: The quantum yields of dimerization of acenaphthylene were measured at 365 nm as a function of ethyl iodide concentration, substrate concentration, and quencher concentration. The product distributions in each case were also determined. Ethyl iodide appears to have a considerable effect on $T_1 \leftarrow S_1$, thus leading to dimerization predominantly from the triplet state. A smaller but significant effect on $S_0 \leftarrow T_1$ also results from the presence of ethyl iodide producing a decrease in the dimerization efficiency at high concentrations of heavy-atom solvent. A mechanism consistent with the data has been proposed and the triplet rate constants for dimerization and the various modes of deactivation have been determined.

Although internal and external heavy-atom effects on photophysical processes have been extensively investigated using spectroscopic techniques,[2] relatively few photochemical studies have been reported.[3] The influence of heavy-atom solvents on the photodimerization of acenaphthylene was among the earliest of these studies.[3a-c] Somewhat later, heavy-atom effects on the cycloaddition of acenaphthylene to acrylonitrile,[3d] cyclopentadiene,[3e-g] and maleic anhydride[3h-k] were reported. The cycloaddition to maleic anhydride was of particular interest since the adduct was used as an intermediate in the synthesis of pleiadiene, thus providing the first example of a synthetic application of the heavy-atom effect. More recently. Plummer reported a detailed investigation of internal as well as external heavy-atom effects on the cycloaddition of acenaphthylene to cyclopentadiene.[3g]



In a preliminary report, we demonstrated that there is a practical limit to the amount of heavy-atom solvent enhancement one can obtain for a given photochemical reaction.[3l] This factor should be an important consideration in any synthetic application of the heavy-atom effect.

We now wish to report a detailed study illustrating the application of the heavy-atom effect in determining the rate constants for the various intercombinational nonradiative transitions of acenaphthylene. These rate constants, which are not accessible in light-atom solvents due to the complexity of the mechanism and the low efficiency of intersystem crossing from the first excited singlet to the first excited triplet, can be readily evaluated under the influence of heavy-atom perturbation. This study thus provides an important example of the utility of the heavy-atom effect in mechanistic photochemistry.

Results

A. Effect of Ethyl Iodide. As the concentration of ethyl iodide is increased from 0 to 10 mol %, a large increase in the quantum yield of dimerization results. Further increases in the ethyl iodide concentration, however, quench the dimerization although the quenching process appears to be considerably less sensitive to heavy-atom perturbation.[4] Throughout the concentration range of ethyl iodide in which quenching occurs, the reciprocal of the quantum yield is a linear function of the concentration of ethyl iodide (Figure 1).

The data further indicate that the product distribution is solvent dependent. In cyclohexane, for example, the major product is the cis dimer. When ethyl iodide is used as a cosolvent, the trans dimer becomes the major product although significant changes in the proportion of these dimers are observed with variations in the ethyl iodide concentration.[3l]

B. Concentration Effects. Figure 2 illustrates the effect of acenaphthylene concentration on the quantum yield of dimerization in the presence of ethyl iodide. A linear relationship between the reciprocal of the quantum yield and the reciprocal of the acenaphthylene concentration is observed.

The data in Tables I and II indicate that in the range of concentrations studied (0.04 to 0.12 *M*), the product distribution remains constant for a given concentration of ethyl iodide.

C. Quenching Studies. Figure 3 illustrates a Stern–Volmer plot of the quenching of acenaphthylene dimerization in 25 mol % ethyl iodide by ferrocene. At the maximum concentration of ferrocene used $(2 \times 10^{-4}\ M)$, approximately 70% of the dimerization is quenched. The relationship between $\Phi_D{}^0/\Phi_D$ and the ferrocene concentration re-

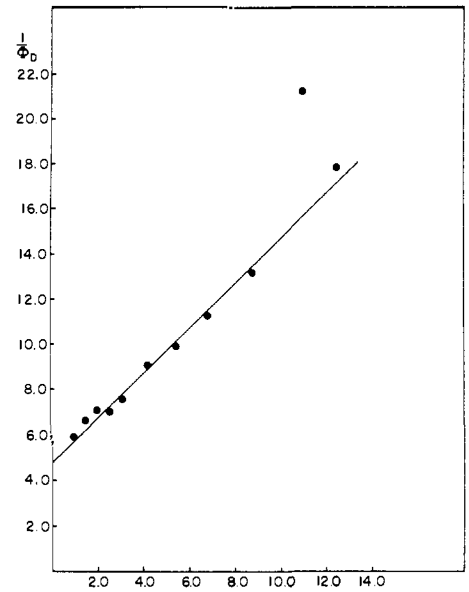


Figure 1. The dependence of $1/\Phi_D$ on the concentration of ethyl iodide.

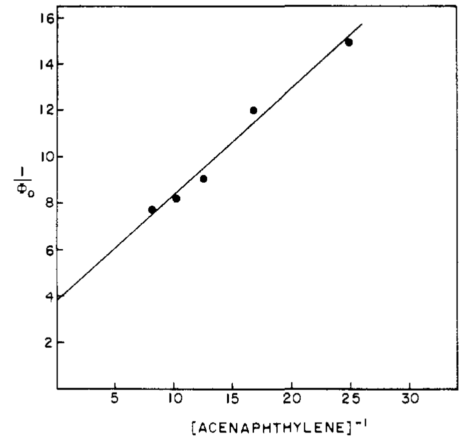


Figure 2. The dependence of $1/\Phi_D$ on the reciprocal of the concentration of acenaphthylene in 25 mol % ethyl iodide.

Table I. Dependence of Quantum Yields and Product Distributions on the Concentration of Acenaphthylene in 25 mol % Ethyl Iodide

[A], *M*	Φ_D	% cis	% trans
0.0403	0.067	17	83
0.0600	0.082	19	81
0.0800	0.11	21	79
0.1002	0.12	17	83
0.1205	0.13	19	81

mains linear throughout the concentration ranged used.

The data in Table III indicate that the product distribution does not vary as the ferrocene concentration is increased. The product distribution is also consistent with that given in Table I in which no quencher is present.

Discussion

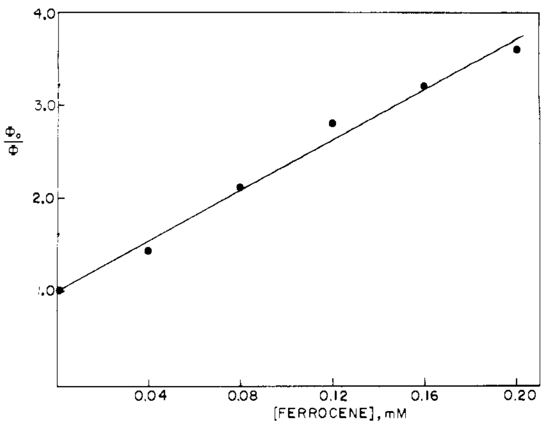


Figure 3. A Stern–Volmer plot of the dimerization of acenaphthylene as a function of the concentration of ferrocene in 25 mol % ethyl iodide.

Table II. Dependence of Quantum Yields and Product Distributions on the Concentration of Acenaphthylene in 30 mol % Ethyl Iodide

[A], *M*	Φ_D	% cis	% trans
0.0405	0.065	23	77
0.0600	0.090	21	79
0.0800	0.11	22	78
0.0998	0.13	20	80
0.1202	0.14	22	78

Table III. Quantum Yields and Product Distributions in the Presence of Ferrocene in 25 mol % Ethyl Iodide[a]

[Ferrocene]	Φ_D	% cis	% trans
0	0.139	19	81
4.0×10^{-5}	0.097	22	78
8.0×10^{-5}	0.067	18	82
1.2×10^{-4}	0.050	20	80
1.6×10^{-4}	0.044	20	80
2.0×10^{-4}	0.039	22	78

[a] Acenaphthylene concentration: 0.10 *M*.

A. Excited States. The dimerization of acenaphthylene can occur from either the first excited singlet state or the first excited triplet state.[5] Dimerization from the singlet has been shown to produce exclusively cis dimer.[5b] As a result, a singlet excimer has been proposed as a probable intermediate.[6] Dimerization from the triplet state produces both cis and trans dimer, although the latter has been the major product in all cases studied.[3c,5b,6] The relative importance of each excited state in the dimerization of acenaphthylene depends on the nature of the solvent.

Product analyses and quenching studies indicate that in light-atom solvents, dimerization occurs from both excited states.[6] Dimerization from the singlet state is a relatively inefficient process in all solvent systems that have been studied. For example, the quantum efficiency of singlet dimerization for acenaphthylene (0.10 *M*) in cyclohexane is approximately 0.3%.[7] Based on studies previously undertaken in this laboratory, comparable results are obtained with other light-atom solvents such as benzene and methanol.[6] Oxygen quenching studies indicate that even in heavy-atom solvents, singlet dimerization occurs with an efficiency no greater than 1%.[8] Dimerization from the triplet state in light-atom solvents is also inefficient. The amount of triplet-derived dimer, however, depends not only on the fraction of triplet molecules which undergo dimerization, but also on the efficiency of intersystem crossing from the singlet to the triplet state. It is the low quantum yield of this latter process in light-atom solvents that limits triplet-derived dimer, thus making singlet dimerization competitive with triplet dimerization.

In heavy-atom solvents, dimerization occurs predominantly from the triplet state. This has been attributed to a large increase in the rate of intersystem crossing leading to the triplet and to the high efficiency of dimerization from the triplet state.[3a–c,l] In 10 mol % ethyl iodide, for example, more than 90% of the dimerization occurs through the triplet.[8] Comparable results have been obtained with solvents containing bromine at concentrations of 100 mol %.[3c] It appears therefore that dimerization from the singlet is negligible when sufficient heavy-atom perturbation is present.

Sensitized dimerization studies have been used to suggest that the lowest triplet state of acenaphthylene is 43 to 45 kcal/mol above the ground state.[6] However, attempts to observe the triplet state spectroscopically have thus far been unsuccessful.[5a,6] As a check on the sensitized studies, we have performed semiempirical limited configuration interaction (LCI-SCF) calculations of the Pariser-Parr-Pople type on acenaphthylene. The singlet state parameters used were $U_c = 11.42$ eV, $\gamma_{cc} = 10.84$ eV, and $\beta_{cc} = -2.318$ eV; the triplet state parameters[9] used were $U_c = 11.42$ eV, $\gamma_{cc} = 8.2$ eV, and $\beta_{cc} = -2.5$ eV. Two-center electronic repulsion integrals ($\gamma_{\mu\nu}$) were calculated *via* the Mataga-Nishimoto[10] relation and the LCI treatment used only singly excited configurations. Some indication of the reliability of Zahradnik's[9] parameters can be obtained from the recently determined[11] second and third triplet levels of benzene. As can be seen from Table IV, the calculated and observed triplet energies for benzene are in good agreement. Using the triplet parameters, the lowest triplet state of acenaphthylene is calculated to have an energy of 2.005 eV (46.24 kcal/mol), which is also in reasonable agreement with the observed value obtained in the sensitized dimerization studies.

Table IV. Calculated and Experimental Singlet–Singlet and Singlet–Triplet Transitions for Benzene[a]

	$S_X \leftarrow S_0$			$T_X \leftarrow S_0$	
Transition (X)	Electron scattering[o]	Optical	Theory	Electron scattering[b]	Theory
1	5.0	4.74	4.76	3.95	3.92
2	6.2	6.02	6.05	4.75	4.67
3	6.9	6.85	6.79	5.60	5.12

[a] All values in eV. [b] Reference 11.

B. Intersystem Crossing. Heavy-atom solvents have been shown to have a large influence on the transition $T_1 \leftarrow S_1$ in acenaphthylene.[3a-g] Since heavy-atom perturbation may affect any transition between states of different multiplicity,[21] we have undertaken a more thorough investigation of the influence of heavy-atom solvents on the photochemistry of acenaphthylene.

We recently reported that the quantum efficiency of dimerization can be reduced when sufficiently large concentrations of ethyl iodide are employed.[31] We have attributed this quenching effect to an increase in the rate of intersystem crossing from the triplet to the ground state. The fact that this process is considerably less sensitive to heavy-atom perturbation than $T_1 \leftarrow S_1$ can be understood by considering the transition probability, *P*, for a nonradiative intercombinational transition, as given in eq 1[12]

$$P \propto \sum_{i,j} \langle \theta_{S_i} \theta_{T_j} \rangle^2 \langle \Phi_S | H_{SO} | \Phi_T \rangle^2 \qquad (1)$$

where θ_{S_i} and θ_{T_j} are the vibrational wave functions belonging to the singlet and triplet electronic wave functions Φ_S and Φ_T. For simple model systems, the spin-orbit Hamiltonian, H_{SO}, has the following form

$$H_{SO} \propto \xi(L \cdot S) \qquad (2)$$

where *L* and *S* are the orbital and spin angular momentum operators and ξ is the spin-orbit coupling parameter[13] which increases with increasing atomic weight of the heavy atom. From eq 1 and 2, it is obvious that the transition probability is directly proportional to ξ^2. The transition probability is also inversely related to the energy difference between the singlet and triplet states involved. Both the vibrational and electronic factors in eq 1 decrease as $|E_S - E_T|$ increases, thus decreasing the probability of the transition. Since the energy difference between S_0 and T_1 is considerably larger than that between S_1 and T_1, it is not surprising that $S_0 \leftarrow T_1$ is far less sensitive to heavy-atom perturbation.

C. Proposed Mechanism. The following mechanism is consistent with all of the experimental observations

$$\begin{array}{lll}
 & \text{Rate} & \\
A + h\nu \longrightarrow {}^1A & Ia & (3) \\
{}^1A \xrightarrow{k_{1c}} A & k_{1c}[{}^1A] & (4) \\
{}^1A + A \xrightarrow{k_0} {}^1(A\cdots A) & k_0[{}^1A][A] & (5) \\
{}^1(A\cdots A) \xrightarrow{k_1} A_2 \text{ (cis)} & k_1[{}^1(A\cdots A)] & (6) \\
{}^1(A\cdots A) \xrightarrow{k_r} 2A & k_r[{}^1(A\cdots A)] & (7) \\
{}^1A \xrightarrow{k_{1sc}} {}^3A & k_{1sc}[{}^1A] & (8) \\
{}^1A + HA \xrightarrow{k_{1sc}'} {}^3A + HA & k_{1sc}'[{}^1A][HA] & (9) \\
{}^3A + A \xrightarrow{k_2} A_2 \text{ (cis and trans)} & k_2[{}^3A][A] & (10) \\
{}^3A + A \xrightarrow{k_{cq}} 2A & k_{cq}[{}^3A][A] & (11) \\
{}^3A + HA \xrightarrow{k_{1sc}''} A + HA & k_{1sc}''[{}^3A][HA] & (12) \\
{}^3A + Q \xrightarrow{k_q} A + Q & k_q[{}^3A][Q] & (13) \\
{}^3A \xrightarrow{k_d} A & k_d[{}^3A] & (14)
\end{array}$$

where A = acenaphthylene, ^{1}(A···A) = singlet excimer, A_2 = acenaphthylene dimer, HA = ethyl iodide, and Q = ferrocene. By application of the steady-state approximation, one obtains the quantum yield of dimerization, Φ_D.

$$\Phi_D = \left\{\frac{k_0[A]}{k_{1c} + k_{1sc} + k_0[A] + k_{1sc}'[HA]}\right\}\left\{\frac{k_1}{k_1 + k_r}\right\} + \left\{\frac{k_{1sc} + k_{1sc}'[HA]}{k_{1c} + k_{1sc} + k_0[A] + k_{1sc}'[HA]}\right\} \times \left\{\frac{k_2[A]}{k_2[A] + k_{cq}[A] + k_{1sc}''[HA] + k_q[Q] + k_d}\right\} \qquad (15)$$

The first term in this expression represents the quantum yield of dimerization from the singlet state, $^1\Phi_D$, and the second term represents the quantum yield from the triplet state, $^3\Phi_D$. Although eq 15 appears rather complex, several assumptions can be made which simplify this equation considerably. As previously stated, singlet dimerization is negligible in the presence of heavy-atom solvents. We will therefore completely ignore the first term in (15) in subsequent calculations. We also assume that the first factor in the second term of (15), which is the quantum yield of intersystem crossing, Φ_{isc}, is equal to 1 for concentrations of ethyl iodide greater than 10 mol %.[14] Having made these assumptions, one obtains the following simplified expression for Φ_D.

$$\Phi_D = \frac{k_2[A]}{k_2[A] + k_{cq}[A] + k_{1sc}''[HA] + k_q[Q] + k_d} \qquad (16)$$

It is immediately obvious from eq 16 that $1/\Phi_D$ is a linear function of both [HA] (eq 17) and 1/[A] (eq 18). Equation 17 is the analytical expression for the plot illustrated in Figure 1. The plot illustrated in Figure 2 is represented by eq 18.

$$\frac{1}{\Phi_D} = \frac{(k_2 + k_{cq})[A] + k_d + k_q[Q]}{k_2[A]} + \frac{k_{isc}''}{k_2[A]}[HA] \quad (17)$$

$$\frac{1}{\Phi_D} = \frac{k_2 + k_{cq}}{k_2} + \frac{k_{isc}''[HA] + k_d + k_q[Q]}{k_2}\frac{1}{[A]} \quad (18)$$

D. Rate Constants. The linearity of the Stern–Volmer plot in Figure 3, represented by eq 19, is a further indication that only one excited state is involved in the dimerization when sufficiently large concentrations of heavy-atom solvent are used. Assuming that the quenching of the acenaphthylene triplet is diffusion controlled, one can obtain an estimate of k_q from eq 20. From the slope of the Stern–Volmer plot and the value of k_q, an estimate of τ, the triplet lifetime, can be determined. The value of k_2, the rate constant for dimerization from the triplet, can then be calculated according to eq 21.

$$\Phi_D{}^0/\Phi_D = 1 + k_q\tau[Q] \quad (19)$$

$$k_q \doteq 8RT/3000\eta \quad (20)$$

$$(\Phi_D{}^0/\tau)(1/[A]) = k_2 \quad (21)$$

Using this value of k_2, along with the slopes and intercepts of the plots in Figures 1 and 2, one can now calculate k_{cq}, the rate constant for concentration quenching, k_d, the rate constant for unimolecular decay, and k_{isc}'', the rate constant for quenching by the heavy-atom solvent. k_{cq} was evaluated by substituting the value of k_2 into the analytical expression for the intercept given in eq 18 and setting this intercept equal to 3.4.[15] k_d was obtained in a similar manner by setting the intercept given in eq 17 equal to 4.8 and by substituting k_2, k_{cq}, and [A] into this expression. k_q[Q] was set equal to zero since no quencher was present. k_{isc}'' was calculated by substituting the values of k_2 and [A] into the expression for the slope (eq 17) which was set equal to 1.02. The results of these calculations are presented in Table V.

In order to compare each of the triplet processes, it is helpful to compute the actual rates or relative efficiencies of these processes. The relative efficiencies for concentration quenching and intersystem crossing from the triplet to the ground state are given by eq 22 and 23, respectively. Using

$$\Phi_{cq} = \frac{k_{cq}[A]}{k_2[A] + k_{cq}[A] + k_d + k_{isc}''[HA] + k_q[Q]} \quad (22)$$

$$\Phi_{ST} = \frac{k_d + k_{isc}''[HA]}{k_2[A] + k_{cq}[A] + k_d + k_{isc}''[HA] + k_q[Q]} \quad (23)$$

the calculated rate constants, Φ_{cq} and Φ_{ST} may be evaluated for a given concentration of acenaphthylene and heavy-atom solvent. Several values for these relative efficiencies are presented in Table V.

One will note that in 100 mol % cyclohexane, concentration quenching is the predominant energy wasting process. Even in the absence of heavy-atom solvent, however, intersystem crossing to the ground state is quite significant. As the concentration of ethyl iodide is increased, Φ_{ST} increases, reaching a maximum value of 0.81 in 100 mol % ethyl iodide. Thus at high concentrations of heavy-atom solvent, intersystem crossing becomes the major process leading to depopulation of the triplet state.

Table V. Evaluation of Data

	EtI Dependence		
Slope, M^{-1}		1.02 ± 0.03	
Intercept		4.8 ± 0.2	
Correlation coefficient		0.997	
	Concentration Dependence		
Mol % EtI	25	30	
Slope, M^{-1}	0.46 ± 0.02	0.49 ± 0.01	
Intercept	3.8 ± 0.4	3.0 ± 0.1	
Correlation coefficient	0.992	0.999	
	Ferrocene Dependence		
Slope, M^{-1}		13,600 ± 600	
Intercept		1.00 ± 0.07	
Correlation coefficient		0.995	
	Triplet Lifetime and Rate Constants		
τ	2.15×10^{-6} sec		
k_2	$6.58 \times 10^{5}\ M^{-1}\ \text{sec}^{-1}$		
k_{cq}	$1.58 \times 10^{6}\ M^{-1}\ \text{sec}^{-1}$		
k_d	$9.20 \times 10^{4}\ \text{sec}^{-1}$		
k_{isc}''	$6.71 \times 10^{4}\ M^{-1}\ \text{sec}^{-1}$		
	Relative Triplet Efficiencies[a]		
[EtI], M	0	1.0	12.4
Φ_D	0.21	0.17	0.06
Φ_{cq}	0.50	0.41	0.14
Φ_{ST}	0.29	0.42	0.81

[a] These values were calculated using an acenaphthylene concentration of 0.10 M.

E. Products. Our results indicate that although the product distribution is significantly affected by the ethyl iodide concentration, it is relatively independent of acenaphthylene concentration and of the presence of quencher. The influence of ethyl iodide on the proportion of cis and trans dimer is probably due to the change in solvent polarity resulting from variations in ethyl iodide concentration. Hartmann, Hartmann, and Schenck have shown that when the dimerization of acenapthylene occurs from the triplet state, increasing solvent polarity results in an increasing proportion of cis dimer.[5b] This solvent effect has been attributed to increased stabilization of the transition state leading to the cis dimer (dipoles parallel) relative to that leading to the trans dimer (dipoles opposed) as the polarity of the solvent is increased.[5b,6,16]

The insensitivity of the product distribution to variations in acenaphthylene concentration and quencher concentration is consistent with the proposed mechanism. The lack of concentration dependence rules out the possibility of significant dimerization from the singlet state as previous studies have shown that concentration effects are quite important when dimerization occurs from both states.[6] The invariance of product distribution to variations in ferrocene concentration is further evidence for the intermediacy of a single excited state since it is unlikely that the two excited states, which lead to different product ratios, would be quenched at the same rate.

F. Summary and Conclusions. Although the transition $T_1 \leftarrow S_1$ appears to be the intercombinational process most sensitive to heavy-atom perturbation, sufficiently large concentrations of heavy-atom solvent can have a significant influence on $S_0 \leftarrow T_1$. At concentrations of ethyl iodide greater than 1.0 M, intersystem crossing from the triplet to the ground state becomes the predominant mode of deactivation. The efficiency of dimerization from the triplet state even at high concentrations of ethyl iodide, however, is considerably greater than that of singlet dimerization in light-atom solvents. As a result, moderate concentrations of heavy-atom solvent can produce dramatic increases in the total quantum yield of dimerization. In light-atom solvents such as cyclohexane in which Φ_{isc} for $T_1 \leftarrow S_1$ is very small, dimerization occurs from both excited states. In heavy-atom solvents of sufficient concentration to increase Φ_{isc} for $T_1 \leftarrow S_1$ to ~100%, dimerization occurs almost exclusively from the triplet state.

This work illustrates the application of the heavy-atom effect in elucidating the mechanism of a photochemical reaction. Virtually all of the rate constants and quantum yields that have been discussed would have been inaccessible in light-atom solvents due to the importance of both excited states and the low efficiency of $T_1 \leftarrow S_1$ in the absence of heavy-atom perturbation. Thus the heavy-atom effect may prove to be an important tool to future investigators in mechanistic as well as synthetic studies.

Experimental Section

Materials. Acenaphthylene (K & K Laboratories, Inc., Tech), mp 86.5-87.5°, was purified by recrystallization of the picrate complex from benzene.[5b] Following decomposition of the picrate by treatment with concentrated NH_4OH, the acenaphthylene was twice recrystallized from 95% ethanol and sublimed at 50° (0.01 Torr), mp 92-93° (lit.[5a] mp 92-93°). Ethyl iodide (Eastman Kodak) was distilled at 72° on a column (46 × 2 cm) packed with glass helices. Ferrocene (Alfa Inorganics) was recrystallized once from hexane, mp 173-175°. Eastman spectograde cyclohexane was used without further purification.

Irradiation Procedure. Irradiations were performed on a merry-go-round apparatus using a 450-W Hanovia medium-pressure mercury arc lamp in a water-cooled Hanovia Vycor immersion vessel. A combination of Corning CS-0-52 and CS-7-37 filters was used which produced a narrow band around 365 nm. Irradiation times varied from 8 to 40 hr depending on the quantum yields of the samples. Each sample was degassed with five freeze–pump–thaw cycles and sealed before irradiation. The irradiation vessels consisted of 10-ml Pyrex test tubes, each containing 2.8 ml of solution. The incident light intensity was periodically measured by actinometry with ferrioxalate. At the concentrations (≥ 0.04 *M*) of acenaphthylene used, virtually all of the light was absorbed.

Quantum Yields of Dimerization. The optical densities of the irradiated and corresponding unirradiated acenaphthylene solutions were measured at 340 nm using a Cary Model 14 spectrophotometer. Since the acenaphthylene dimers do not absorb at 340 nm, the difference in the optical densities of these solutions is a direct measure of the amount of dimer formed.

The irradiated solutions were prepared for analysis in the following manner. Each solution was carefully transferred to a volumetric flask and diluted to 100 ml with cyclohexane. From each of these solutions, an appropriate aliquot (≤ 1.25 ml) was further diluted to yield a $\sim 10^{-4}$ *M* solution for spectral analysis.

Product Distribution. Solutions of pure cis and pure trans dimers in cyclohexane were prepared and the molar absorptivities at 314 and 284 nm for each were determined: cis, $\epsilon_{314} = 1.78 \times 10^4\ M^{-1}\ cm^{-1}$ and $\epsilon_{284} = 1.02 \times 10^4\ M^{-1}\ cm^{-1}$; trans, $\epsilon_{314} = 3.93 \times 10^3\ M^{-1}\ cm^{-1}$ and $\epsilon_{284} = 1.18 \times 10^4\ M^{-1}\ cm^{-1}$. The composition of the product dimer mixtures was determined by measuring the optical densities of cyclohexane solutions of these dimers at 314 and 284 nm. From these optical densities and the corresponding molar absorptivities, the concentrations of the cis and trans dimers were calculated.

The irradiated solutions were prepared for dimer analysis in the following manner. Each solution was first evaporated to dryness on a rotary evaporator. The resulting mixture of acenaphthylene and dimers was then carefully transferred with a small amount of ether to a sublimer cavity. After evaporation of the ether, the mixture was sublimed at 50° (0.01 Torr) to remove unreacted acenapthylene. The residue was dissolved in enough cyclohexane to yield a $\sim 5 \times 10^{-5}$ *M* solution for spectral analysis.

Preparative Irradiations. Solutions containing 15.2 g of acenaphthylene in 150 ml of *n*-propyl bromide and 150 ml of cyclohexane, respectively, were irradiated preparatively for 15 hr with a 450-W Hanovia medium-pressure mercury arc lamp in a water-cooled Hanovia Vycor immersion vessel fitted with a uranium glass filter sleeve to absorb all radiation of wavelengths shorter than 325 nm. The water-cooled arc was immersed in the reaction vessel which was magnetically stirred and continuously flushed with purified nitrogen. After irradiation, the insoluble dimer product was collected by filtration.

Isolation of Acenaphthylene Dimers. A. Trans Dimer. A 5.0-g sample of mixed dimer obtained from the irradiation of acenaphthylene in *n*-propyl bromide was placed in a Buchner funnel with a fritted disk and washed with 400 ml of hot cyclohexane. The material remaining in the funnel was then dissolved in benzene, treated with Norit, and recrystallized, yielding 0.77 g of white needle-like crystals: mp 300-301° (lit.[17] mp 306-307°), nmr (CCl_4) δ 7.3-7.7 (m, 12 H), 4.0 (s, 4 H). The uv absorption spectrum of this material was identical with that obtained by Livingston and Wei[5a] for the trans dimer of acenaphthylene.

B. Cis Dimer. A 5.0-g sample of mixed dimer obtained from the irradiation of acenaphthylene in cyclohexane was placed in a Buchner funnel with a fritted disk and washed with 500 ml of hot cyclohexane. The cyclohexane solution was concentrated until dimer began to precipitate. The solution was then filtered and again concentrated. This process was repeated three times. The material remaining in solution was treated with Norit and recrystallized, yielding 0.59 g of white prisms: mp 231.5-233.5° (lit.[17] mp 232-234°); nmr (CCl_4) δ 6.8-7.2 (m, 12 H), 4.75 (s, 4 H). The uv absorption spectrum of this material was identical with that obtained by Livingston and Wei[5a] for the cis dimer of acenaphthylene.

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References and Notes

(1) Photochemical Reactions XII. For part XI, see D. O. Cowan and R. P. DeToma, submitted for publication.

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(4) At high concentrations of ethyl iodide, a small amount of light is absorbed by the heavy-atom solvent (<5% at 100 mol % ethyl iodide). Since prolonged irradiation of ethyl iodide results in partial decomposition, the following experiment was done to determine the effect of these decomposition products on the quantum yield. Solutions of acenaphthylene (0.10 *M*) in 50 mol % ethyl iodide were irradiated for periods of 23.9, 44.2, and 65.9 hr. The quantum yields obtained for these irradiation periods were 0.10, 0.093, and 0.084, respectively. These results indicate that only a small amount of "quenching" occurs even after extensive irradiation. Furthermore, the observed decrease in quantum yield with increasing irradiation time cannot be due entirely to triplet quenching, but must result, at least partially, from a decrease in substrate concentration (~15% in 66 hr). We therefore conclude that ethyl iodide decomposition products are not responsible for the observed decrease in Φ_D at high concentrations of heavy-atom solvent.

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(7) This value was estimated from the product distribution and quantum yield of dimerization of acenaphthylene in cyclohexane.[3l] It is assumed that triplet acenaphthylene in cyclohexane produces a dimer mixture containing 70% trans dimer and 30% cis dimer.[6] The quantum yield of dimerization of acenaphthylene (0.10 *M*) in oxygen-saturated cyclohex-

ane was found to be 0.005. Since most of the acenaphthylene triplet species is quenched in the presence of oxygen, this experiment establishes the maximum singlet dimerization efficiency of acenaphthylene at 0.5%.

(8) The quantum yield of dimerization of acenaphthylene (0.10 *M*) in oxygen-saturated 10 mol % ethyl iodide was found to be 0.01. This experiment both establishes the maximum singlet dimerization efficiency and demonstrates that more than 90% of the dimerization in this solvent occurs from the triplet state.

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(15) Since the two concentration dependence intercepts given in Table V should be equal, the experimental values were averaged.

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Mechanisms of Photochemical Reactions in Solution. LXXIX.[1] Production of Triplets in the Quenching of the Fluorescent State of Naphthalene by an Unsaturated Hydrocarbon

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Abstract: The fluorescence of naphthalene is quenched by *trans*-β-ethylstyrene. Counter experiments using *cis*-piperylene as a monitor show that triplets are produced as a part of the process of quenching the excited states. The triplet yield varies in different solvents and in all cases studied is smaller than the triplet yield when naphthalene decays without the assistance of a perturbing quencher. In the absence of piperylene there is a significant amount of isomerization of the quencher even when it is present in sufficiently high concentration to quench all of the excited singlets of naphthalene, an indication that triplets of either the quencher, the quenchee, or both are produced. Little isomerization of β-ethylstyrene is observed in the presence of piperylene (0.066–0.198 *M*). We believe that a singlet exciplex is formed and decays rapidly to give either both molecules in their ground states or to give naphthalene triplets and β-ethylstyrene in its ground singlet state.

Several groups have studied the quenching of fluorescence of naphthalene and other aromatic hydrocarbons by conjugated dienes.[2-7] Models to account for the quenching include two features: formation of an exciplex from the quencher and the fluorescent species, and rapid nonradiative decay of the exciplex. There has been a good deal of speculation as to the mechanisms of intermolecular interaction which leads to binding in the exciplex.[4-6] The mechanism of nonradiative decay has been discussed less and is not an easily studied phenomenon although it seems likely that some vibrational modes in the quencher must serve as especially efficient energy sinks in the internal conversion process. We now report a study of quenching of naphthalene fluorescence by a hydrocarbon, *trans*-β-ethylstyrene, in which the decay process leads to formation of naphthalene triplets in substantial yield.

Results

The fluorescence of naphthalene is quenched by *trans*-β-ethylstyrene with moderate efficiency. Series of quenching measurements with varying concentrations of quencher were carried out in four different solvents. Plots of $\Phi_F{}^0/\Phi_F$ were linear. The results are summarized in Table I.

Introduction of *cis*-piperylene (1,3-pentadiene) into the solutions led to isomerization of the diene to the *trans* isomer, indicating formation of triplets having sufficient excitation energy to transfer energy to the diene. Since naphthalene is a well-known triplet sensitizer for diene isomerization,[8,9] the reaction was to be expected in unquenched solutions. Addition of β-ethylstyrene reduced the triplet yield as expected, but *the limits approached at high concentrations of the quencher were nonzero.* The quenching act itself must produce some triplets.[10] We assume the following to be the mechanism for sensitized isomerization and quenching.

$$\mathrm{N} \xrightarrow{h\nu} {}^1\mathrm{N} \qquad (1)$$

$$ {}^1\mathrm{N} \xrightarrow{k_f} \mathrm{N} + h\nu' \qquad (2)$$

$$ {}^1\mathrm{N} \xrightarrow{k_1} {}^3\mathrm{N} \qquad (3)$$

$$ {}^1\mathrm{N} + trans\text{-}\mathrm{E} \xrightarrow{k_2} \alpha{}^3\mathrm{N} + (1 - \alpha)\mathrm{N} + trans\text{-}\mathrm{E} \qquad (4)$$

$$ {}^1\mathrm{N} + cis\text{-}\mathrm{P} \xrightarrow{k_q} \mathrm{N} + cis\text{-}\mathrm{P} \qquad (5)$$

$$ {}^3\mathrm{N} + cis\text{-}\mathrm{P} \xrightarrow{k_q'} \beta{}^3\mathrm{P} + (1 - \beta)cis\text{-}\mathrm{P} + \mathrm{N} \qquad (6)$$

$$ {}^3\mathrm{N} \xrightarrow{k_3} \mathrm{N} \qquad (7)$$

$$ {}^3\mathrm{P} \longrightarrow \gamma trans\text{-}\mathrm{P} + (1 - \gamma)cis\text{-}\mathrm{P} \qquad (8)$$

N = naphthalene, E = β-ethylstyrene, P = piperylene

We have omitted nonradiative decay of excited naphthalene singlets to the ground state since that process is known to be relatively unimportant.[11] The yield of naphthalene triplets is determined by the intersystem crossing efficiency for naphthalene singlets in the absences of quenchers [$\Phi_{ISC} = k_1/(k_1 + k_f)$] and α, the efficiency of triplet production in the quenching of naphthalene singlets by β-ethylstyrene. We measured relative fluorescence intensities: (1) in the absence of any quencher (F^0), (2) in a series of solutions containing varying concentrations of β-ethylstyrene but no piperylene (F'), and (3) in a series of solutions containing vary-