phenyldiphenylmethylamine from photoreduction of benzophenone phenylimine.[18] Reaction of triphenylmethyl azide with tri-*n*-butyltin hydride in the dark gave 3-5% triphenylmethylamine, so that the net yield in the photolysis was 5-7%.

A solution of 0.17 g (0.06 mol) of triphenylmethyl azide in 10 ml of *sec*-butyl mercaptan was photolyzed for 48 hr with the Hanovia medium-pressure lamp. Analysis of the reaction mixture by glpc showed 3-4% yield of material with the same retention time as triphenylmethylamine.

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[18] M. Fisher, *Tetrahedron Letters*, 5273 (1966).

Sensitized Photolysis of Organic Azides. A Possible Case of Nonclassical Energy Transfer[1]

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Abstract: Quantum yields for nitrogen evolution were determined in sensitized photolyses of several alkyl azides, phenyl azide, and ethyl azidoformate. Determination of the quantum yield as a function of azide concentration, along with data from the literature on the sensitizers, permitted the calculation of rates of triplet energy transfer from sensitizers to azide. These rates were closely similar for any given sensitizer with *n*-hexyl, cyclohexyl, and isobutyl azides, but were larger for phenyl azide and smaller for ethyl azidoformate. The energy transfer to the alkyl azides approaches the diffusion-controlled rate only as the sensitizer triplet energy approaches 75-80 kcal/mol, suggesting a triplet energy in this range for the azides. Sensitizers with lower triplet energies are considerably more effective than expected for a classical endothermic energy transfer. It is suggested that the energy transfer is accompanied by bending of the N-N-N bond angle from its normal 180°, resulting in a "nonspectroscopic" triplet. Extended Hückel theory calculations on methyl azide support the hypothesis that the molecule is more stable with a bent than a linear configuration of the azide group in the first excited state.

Recently we reported that the loss of nitrogen and rearrangement to benzophenone phenylimines of triarylmethyl azides could be effected by various triplet sensitizers.[3] Sensitizers as low in triplet energy as pyrene (48.7 kcal/mol) gave appreciable reaction, which led us to suggest that the triplet energy of the azide was below 48 kcal/mol. Efforts to confirm this estimate by emission studies failed when no emission spectrum could be observed from the azide in a 3-methylpentane glass at 77°K. Attempts to observe singlet-triplet absorption in ethyl iodide solution[4] also failed.

In the absence of confirming evidence, our estimate of the triplet energy remained a nagging problem. It requires a very large difference between the lowest triplet and lowest singlet, for the latter is in the vicinity of 100 kcal/mol for alkyl azides.[5] Consequently, we sought other means of determining the triplet energies of the azides.

Determination of the rate of energy transfer as a function of the triplet energy of the sensitizer seemed a promising approach. As long as the triplet energy of the sensitizer is greater than that of the acceptor, the energy transfer should occur at the diffusion-controlled rate. When the triplet energy of the sensitizer becomes less than that of the acceptor the rate of energy transfer falls very rapidly, for the energy deficiency must be supplied as a thermal activation energy.[6] By determining the region in which the fall off begins, then, one can estimate the triplet energy of the acceptor within a few kcalories/mole.

Because we lacked the equipment for determining the rate of energy transfer by flash spectroscopy,[6] we chose an indirect method. Degassed solutions of sensitizer and azide, prepared so that the sensitizer absorbed >99% of the incident light, were photolyzed, and the quantum yield of nitrogen evolution determined as a function of azide concentration. A plot of $1/\phi$ *vs.* $1/[A]$ was found to be linear. This, and our other experimental observations are accommodated by the following mechanism, where S = sensitizer, S_1^* = singlet excited sensitizer, S_3^* = triplet excited sensitizer, A = azide, and A_3^* = triplet excited azide.

$$S \xrightarrow{h\nu} S_1^* \tag{1}$$

$$S_1^* \xrightarrow{\text{ISC}} S_3^* \tag{2}$$

$$S_3^* \xrightarrow{k_d} S \tag{3}$$

$$S_3^* + A \xrightarrow{k_q} A_3^* + S \tag{4}$$

$$A_3^* \xrightarrow{k_p} \text{products} \tag{5}$$

$$A_3^* \xrightarrow{k_o} A \tag{6}$$

The over-all quantum yield of azide decomposition may then be expressed as follows.

$$\frac{1}{\phi} = \frac{1}{\phi_{ST}}\left(1 + \frac{k_d}{k_q[A]}\right)\frac{k_o + k_p}{k_p} \tag{7}$$

Here ϕ_{ST} is the quantum yield for intersystem crossing

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] National Science Foundation Trainee, 1966-1967. Eastman Kodak Scientific Award, 1967.

[3] F. D. Lewis and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **89**, 645 (1967).

[4] M. Kasha and S. P. McGlynn, *Ann. Rev. Phys. Chem.*, 7, 403 (1956).

[5] W. D. Closson and H. B. Gray, *J. Am. Chem. Soc.*, **85**, 290 (1963).

[6] W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

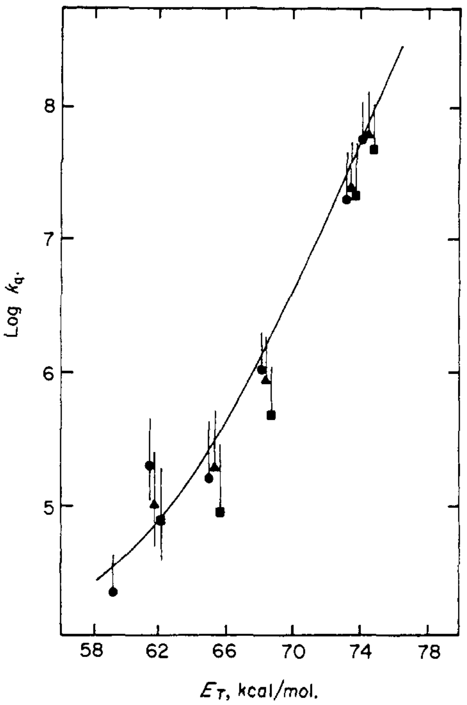

Figure 1. Plot of log k_q (rate constant for triplet energy transfer) *vs.* E_T (triplet energy of sensitizer): ●, hexyl azide; ■, cyclohexyl azide; ▲, isobutyl azide. Points for identical sensitizers with different substrates are displaced slightly along abscissa for clarity.

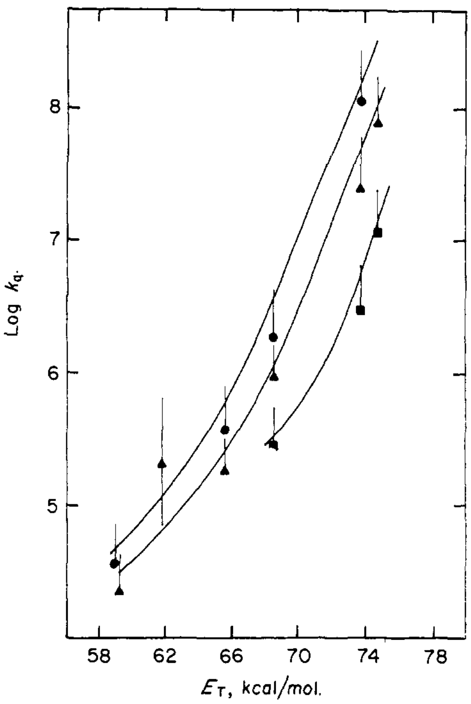

Figure 2. Plot of log k_q (rate constant for triplet energy transfer) *vs.* E_T (triplet energy of sensitizer): ●, phenyl azide; ▲, hexyl azide; ■, ethyl azidoformate.

of the sensitizer. These were either known[7] or readily determined for our sensitizers so that the slope and intercept of a plot of $1/\phi$ *vs.* $1/[A]$ permitted calculation of the ratios k_d/k_q and $(k_o + k_p)/k_p$. Since the k_d values are also known,[6] the treatment gives k_q, the rate constant of the energy-transfer step.

In order to ascertain whether there was a significant effect of structure on the rate of energy transfer, we performed experiments on three simple alkyl azides where the alkyl groups were isobutyl, *n*-hexyl, and cyclohexyl. Attempts to study the rate of energy transfer to triphenylmethyl azide, the compound we had previously used[3] were complicated by the appearance of triphenylmethyl radical,[8] which functioned as an internal filter and made the results of quantum yield determinations unreliable. We also studied briefly phenyl azide and ethyl azidoformate. The relatively small changes in rate of energy transfer even with these compounds in which the azide is directly conjugated with unsaturated linkages make it very likely that triphenylmethyl azide has a triplet energy close to that of our alkyl azides. The results of the energy transfer experiments are given in Table I and in Figures 1 and 2. The curve drawn through the experimental points in Figure 1 assumes that the results are *minimum* values for k_q, since any impurities in solvent or sensitizer would raise the apparent k_d. From the reported[6] errors in k_d, errors in k_q of 0.3–0.5 log units were estimated. Confirmation that our reagents, solvents, and sensitizers were of satisfactory purity and our techniques sound came from control experiments on rates of energy transfer to *trans*-stilbene, which were within experimental error of those reported[6] from flash spectroscopic measurements.

None of the sensitizers gives energy transfer at the diffusion-controlled rate ($k_q \cong 10^9$ l. mol^{-1} sec^{-1}) so that the triplet energies of the alkyl azides must be in excess of the 74.4 kcal/mol for cyclopropyl phenyl ketone, the highest energy sensitizer. Extrapolation of the lines in Figures 1 and 2 to log k_q = 9 suggests

Table I. Rates of Triplet Quenching by Organic Azides

Sensitizer[a]	Acceptor, R in RN_3	10^5k_q, l. mol^{-1} sec^{-1}	$(k_o + k_p)/k_p$[b]
Phenanthrene	*i*-Bu	0.20	1.1 ± 0.2
Thioxanthone		1.6	5.0 ± 1.0
Benzophenone		10.0	3.5 ± 0.5
Acetophenone		190.0	1.6 ± 0.3
Cyclopropyl phenyl ketone		540.0	1.2 ± 0.2
β-Acetonaphthone	*n*-C_6H_{13}	0.22	15.0 ± 2.5
Phenanthrene		2.1	1.2 ± 0.3
Thioxanthone		2.1	3.4 ± 0.5
Benzophenone		10.0	2.3 ± 0.3
Acetophenone		250.0	1.8 ± 0.4
Cyclopropyl phenyl ketone		630.0	1.0 ± 0.2
Phenanthrene	*c*-C_6H_{11}	1.4	1.0 ± 0.2
Thioxanthone		0.79	5.0 ± 1.0
Benzophenone		4.8	3.5 ± 0.2
Acetophenone		290.0	1.9 ± 0.2
Cyclopropyl phenyl ketone		470.0	1.4 ± 0.2
β-Acetonaphthone	C_6H_5	0.26	3.0 ± 1.2
Thioxanthone		3.3	2.3 ± 0.4
Benzophenone		14.0	2.0 ± 0.2
Acetophenone		1100.0	1.8 ± 0.4
Benzophenone	EtO_2C	3.0	36.0 ± 5.0
Acetophenone		31.0	18.0 ± 6.0
Cyclopropyl phenyl ketone		120.0	12.0 ± 8.0

[a] See Table III for data on the sensitizers used in these calculations. [b] Ratio of total azide molecules sensitized to those undergoing loss of nitrogen.

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(7) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43, 2129 (1965).

(8) F. D. Lewis and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, 90, 3828 (1968).

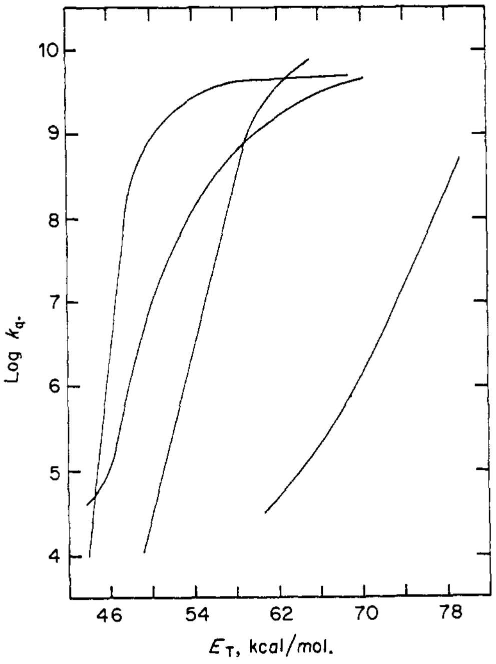

Figure 3. Plot of log k_q (rate constant for triplet energy transfer) *vs.* E_T (triplet energy of sensitizer). Left to right: *trans*-stilbene (ref 6), *cis*-1,2-diphenylpropene (ref 6), biacetyl (ref 11), hexyl azide (this work).

that the triplet energies of the azides all lie in the range of 75–80 kcal/mol. The alkyl azides are estimated to lie at 77–78 kcal/mol, phenyl azide a little lower at about 75 kcal/mol, and ethyl azidoformate a little higher at about 79 kcal/mol. There is evidently very little dependence of triplet energy on structure. Furthermore, these triplet energies are entirely reasonable in comparison to lowest singlets in the vicinity of 100 kcal/mol.[5] The low-intensity transition of alkyl azides around 2870 Å is considered to be a forbidden π, π^* transition, and singlet–triplet splittings of 20–30 kcal/mol are common in the π, π^* transitions of polycyclic aromatic hydrocarbons.[7]

While the alkyl azides all have the same triplet energies within experimental error, phenyl azide is distinctly lower and ethyl azidoformate distinctly higher. The long-wavelength absorption for phenyl azide is at longer[9] and for ethyl azidoformate at shorter[10] wavelengths than for simple alkyl azides. If one makes the assumption that the triplet energies are shifted in the same direction as the singlet energies, the observed results are entirely reasonable.

A striking feature of our results is revealed in Figure 3, which compares the relationship between log k and sensitizer triplet energy for hexyl azide, *cis*-1,2-diphenylpropene,[6] *trans*-stilbene,[6] and biacetyl.[11] The last two compounds show the rapid fall off expected when the energy transfer becomes endothermic. In fact, the steep portion of the curve for *trans*-stilbene has just the slope predicted from this assumption (eq 8).[6] In contrast, the slopes for hexyl azide and *cis*-1,2-diphenylpropene are much less steep, indicating that the low-energy sensitizers are much more effective than they should be. Such behavior has been called "nonclassical" energy transfer by Hammond and his coworkers.[6,12]

$$\frac{\Delta \log k}{\Delta E_T} = -\frac{1}{2.303RT} \tag{8}$$

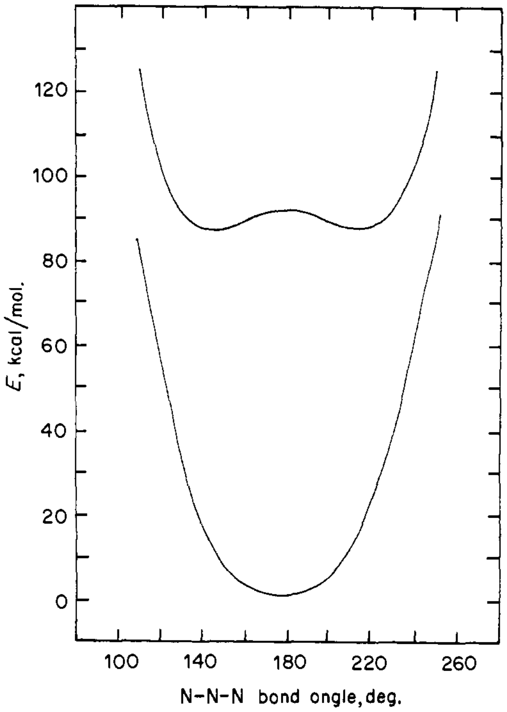

Figure 4. Plot of energy *vs.* N–N–N bond angle for methyl azide as determined by extended Hückel calculations: lower curve, ground state; upper curve, first excited state.

In olefin isomerization, energy transfer to a nonspectroscopic or "phantom" triplet state of the acceptor has been invoked to explain this behavior.[6,12] It is assumed that twisting about the carbon–carbon double bond can accompany the energy transfer, giving a species of lower energy than the spectroscopic triplet, which must have the same geometry as the ground state by the Franck–Condon principle. The phenomenon is presumably prominent with *cis*-1,2-diphenylpropene because twisting relieves steric interactions between the *cis*-phenyl groups, but not with *trans*-stilbene because strain is negligible in the planar conformation.

Alkyl azides in their ground states possess a linear arrangement of the three nitrogen atoms,[13] but Roberts[14] has concluded from simple molecular orbital calculations that the energy difference between the linear and bent configurations is not large. It seemed conceivable to us that the bent configuration might even be more stable in the first excited state, and we undertook extended Hückel calculations on methyl azide to test this hypothesis. The computer program was essentially that described by Hoffmann.[15] While the method has the disadvantage of not distinguishing between singlet and triplet excited states, it has been shown to do well at predicting geometry.[16] While

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(9) A. Reiser, G. Bowes, and R. J. Horne, *Trans. Faraday Soc.*, **62**, 3162 (1966).

(10) W. Lwowski and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **87**, 1947 (1965).

(11) K. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964).

(12) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

(13) R. L. Livingston and C. N. R. Rao, *J. Phys. Chem.*, **64**, 756 (1960).

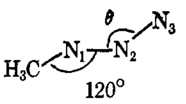
(14) J. D. Roberts, *Chem. Ber.*, **94**, 273 (1961).

(15) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(16) L. C. Allen and J. D. Russell, *ibid.*, **46**, 1029 (1967).

we cannot be sure that it will predict accurately the geometry of excited states, we shall assume in the absence of evidence to the contrary that it gives a qualitatively acceptable picture of the dependence of energy on geometry for the ground and first excited triplet states of methyl azide.

The dependence of energy on the N–N–N bond angle (θ in I) is given in Figure 4 for the ground state and first excited state. The minimum lies at θ = 180° for the ground state, as expected,[13] but the excited state possesses two minima at about 140 and 220°, the former being slightly lower in energy. That the transoid configuration was also slightly more stable than configurations with the methyl group out of the N_1–N_2–N_3 plane was shown by a further set of calculations. The transoid configuration with θ = 140° is some 4.8 kcal/mol stabler than the linear configuration of the first excited state. If energy transfer from a sensitizer is accompanied by bending of the N_1–N_2–N_3 angle, the unexpected efficiency of the low-energy sensitizers is at least qualitatively explicable.



I

A number of possible ambiguities come to mind. Energy transfer from the second triplet state (T_2) of the donor might be involved. Anthracene, for which there is evidence of involvement of T_2 in energy transfer[17] was used as a sensitizer in our earlier work with triarylmethyl azides.[3] Although we had reported slight sensitization by anthracene,[3] it now appears to be completely ineffective as a sensitizer for alkyl azides when direct excitation of the azide is blocked by proper filtering. Furthermore, most of our sensitizers are carbonyl compounds with small energy differences between S_1 and T_1 so that T_2 is undoubtedly *above* S_1 for them, unlike anthracene. Consequently, production of T_2 from S_1 would be endothermic and therefore inefficient. The high energy of T_2 would make it much shorter lived than T_2 from anthracene.

Energy transfer from S_1 of the sensitizer should also be considered. Indeed, there is evidence in the form of fluorescence quenching by alkyl azides that this may be occurring with one of our sensitizers, phenanthrene.[18] Our results contain internal evidence as well that there is something unusual about phenanthrene, for the k_q values are distinctly above the curves defined by the other sensitizers in Figures 1 and 2, and the values of $(k_o + k_p)/k_p$ (Table I) are out of line with those for other low-energy sensitizers.

The chemical consequences of the quenching of phenanthrene fluorescence by azides remain to be explored. Recent evidence suggests that quenching of naphthalene fluorescence involves transfer of vibrational rather than electronic energy.[19] If that is the case in our work, decomposition of the vibrationally excited azide probably does not ensue, for the phenanthrene-sensitized rearrangement of diphenyl(*p*-dimethylaminophenyl)methyl azide shows no discrimination between phenyl and substituted phenyl, contrary to the expectation for a thermal rearrangement.[3]

For the remainder of our sensitizers, with the possible exception of β-acetonaphthone, singlet energy transfer seems unlikely. All of our sensitizers have S_1 states well below S_1 for alkyl azides,[5,7] and rapid intersystem crossing by these carbonyl compounds make their S_1 states very short lived. Benzophenone, for example, undergoes intersystem crossing at a rate of *ca.* 10^{10} sec^{-1}.[20] This would require $k_q > 10^{11}$ l. mol^{-1} sec^{-1} for the endothermic energy transfer from singlet benzophenone.

While nonclassical triplet energy transfer as described by Hammond[6,12] is perhaps the simplest explanation of our results, it is worthwhile to consider other ways of accounting for the effectiveness of low-energy sensitizers. The following discussion is based upon ideas advanced by Liu.[21] First, one must keep in mind that, although most of the ground-state azide molecules will be in their lowest vibrational states, some will be in higher states. The band at 666 cm^{-1} in the infrared spectrum of methyl azide[22] has been assigned to the in-plane bend of the azide group, from which the zero-point energy is 0.9 kcal/mol and the energy of the first vibrationally excited state is 2.9 kcal/mol. Though only a few per cent of the molecules will be in this state, and even less in higher vibrational states, energy transfer to these molecules will still be exothermic when energy transfer to molecules in the zero level is endothermic. Consequently, it is not unreasonable to expect significant contributions to the total process of energy transfer which involve acceptor molecules in the first or even higher vibrationally excited levels.

As long as one considers only the simple classical picture in which linear ground-state azide is excited to linear triplet azide, incorporating the above picture does not lower the energy required for excitation to the triplet state nearly enough to account for our results. However, transitions can also occur *vertically* from bent azide to bent triplet. Because the vibrational wave functions have larger values near the turning points for vibrationally excited than for zero-level species, these vertical transitions should also be more probable from the vibrationally excited states. In addition, the greater amplitude of vibration in the vibrationally excited states will put the turning point more nearly directly under the minima in the triplet-state potential energy curve (see Figure 4).

Whether this explanation can account quantitatively for the results remains uncertain, though it is clear that simultaneous raising of the ground-state and lowering of the excited-state energy will do better than either alone. It also has the advantage of not violating the Franck–Condon principle, and can still be considered a "classical" explanation. One could also, of course, invoke "nonclassical" transitions from excited vibrational levels of the ground state, so that the same energetic advantage could be incorporated into the Hammond[6,12] mechanism. The difference between the two

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[17] R. S. H. Liu and J. R. Edman, *J. Am. Chem. Soc.*, 90, 213 (1968).

[18] F. D. Lewis and C. Dalton, unpublished work done at Columbia University.

[19] S. L. Murov, R. S. Cole, and G. S. Hammond, *J. Am. Chem. Soc.*, 90, 2957 (1968); L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, **88**, 3665 (1966).

[20] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 75.

[21] R. S. H. Liu, private communication.

[22] F. A. Miller and D. Bassi, *Spectrochem. Acta*, **19**, 565 (1963).

is sufficiently subtle that it is hard to see how one might distinguish them experimentally.

The ratio $(k_o + k_p)/k_p$ given in the last column of Table I deserves comment. It represents the total number of excited azide molecules divided by the number that decompose to give nitrogen, and (except with phenanthrene) approaches unity only with the highest-energy sensitizers. In fact, a plot of log $((k_o + k_p)/k_p)$ *vs.* E_T (sensitizer) for the alkyl azides is roughly linear, and extrapolates to zero at 75–80 kcal/mol. Perhaps the bent configurations of the excited state in Figure 4 simply occupy depressions in a potential-energy surface which elsewhere is dissociative. Excitation with a low-energy sensitizer then would raise the azide molecule only to one of the depressions, from which an activation energy would be required for dissociation. Excitation with a high-energy sensitizer, however, could raise the azide molecule to a dissociative region of the potential-energy surface. Whatever the correct explanation, this observation provides further evidence that the species produced by low-energy sensitizers differs in some way from the "normal" triplet.

Experimental Section

Preparation of Alkyl Azides. Alkyl halides were treated with sodium azide in methyl or butyl Carbitol by the procedure of Lieber.[23] The starting material for ethyl azide was ethyl sulfate. Ethyl, propyl, and butyl azides were collected by direct distillation from the reaction mixture. All products were better than 98% pure (glpc analysis) and were stable for several months when stored in the dark at 5°. Their properties are recorded in Table II.

Table II. Properties of Alkyl Azides

R in RN_3	Yield, %	Bp, °C (mm) Obsd	Bp, °C (mm) Lit.[a]	$n^{26}D$
Ethyl	65	48–49 (760)	47–49 (760)[b]	
n-Propyl	30	34–35 (90)	58 (357)	
n-Butyl		50–51 (100)	71 (225)	
Isobutyl	86	47 (100)	43 (100)	1.4251
n-Hexyl	87	85 (63)	85 (63)	1.4282
Cyclohexyl	59	77–78 (30)	72 (30)	1.4661

[a] Reference 22 except where otherwise noted. [b] W. Pritzkow and D. Timm, *J. Prakt. Chem.*, **32**, 178 (1966).

Phenyl azide was prepared in 52% yield by the method of Lindsay and Allen.[24] It had bp 50° (5 mm), $n^{26}D$ 1.5572 (lit.[24] 49–50° (5 mm)).

Ethyl azidoformate was prepared by the method of Lwowski and Mattingly.[10] It had bp 41–43° (34 mm), $n^{26}D$ 1.4165 (lit.[10] 39–41° (30 mm)).

Solvent and Sensitizers. Benzene was spectro grade refluxed twice over fresh phosphorus pentoxide and fractionated, the middle 70% being retained. β-Acetonaphthone (Matheson Coleman and Bell) was chromatographed on alumina and recrystallized several times from petroleum ether. Acetophenone (Eastman White Label) was recrystallized once from ethanol–water at 8° and twice from petroleum ether (bp 30–60°), and then distilled. It had bp 76° (10 mm). Cyclopropyl phenyl ketone (Aldrich) was redistilled prior to each use. It had bp 83° (0.5 mm). Phenanthrene (Reilly) was treated with maleic anhydride to remove anthracene, chromatographed on alumina, and recrystallized twice from ethanol. Thioxanthone (K and K) was chromatographed on alumina, recrystallized twice from ethanol, and sublimed under vacuum. Benzophenone (Eastman While Label) was recrystallized four times from ethanol.

Preparation of Samples for Photolysis. All photolyses were run in benzene solution at ambient temperature. Photolysis tubes were made of 15-mm o.d. Pyrex tubing and equipped with stopcocks. Tubes were thoroughly cleaned and rinsed repeatedly with distilled water and stopcocks greased with Dow-Corning high-vacuum silicone grease prior to each use. Degassing was performed on a small manifold equipped with a McLeod gauge and manometer and connected to a mechanical pump capable of achieving *ca.* 10^{-4} torr. Solutions were frozen in liquid nitrogen for 20 min, and evacuated for 15 min. The stopcock was then closed and the tube thawed with warm water. The cycle was repeated until no further pressure change was noted on opening the frozen tubes to the manifold (usually three times). The stopcocks were closed and the solutions either photolyzed immediately or frozen and stored in the dark.

Lamps, Filters, and Actinometry. Photolyses at 3650 Å utilized a Hanovia 679A medium-pressure mercury lamp with Corning filters 7-54 and 0-52. When phenanthrene and cyclopropyl phenyl ketone were used as sensitizers irradiation was in a Rayonet type RS reactor, and light in the range 3000–3200 Å was obtained by using the "3000 Å" lamps and Pyrex filters (density 2.0 at 2967 Å). Actinometry at 3650 Å utilized either a uranyl oxalate[25] or a *trans*-stilbene-benzophenone[12] actinometer. In the latter method, a benzene solution containing 0.05 *M* benzophenone and 0.05 *M* *trans*-stilbene is degassed and photolyzed and the fraction of *cis*-stilbene determined by glpc on a 5 ft × 0.125 in. column of 3% Apiezon L on Chromosorb G operating at 200°. The observed fraction, β, is corrected for back reaction by eq 9, where α is the

$$\beta' = \alpha \ln (\alpha/(\alpha - \beta)) \qquad (9)$$

fraction of *cis*-stilbene at the photostationary state (0.59). The light intensity is then given by

$$I = [\beta'(\text{moles of } cis\text{-stilbene})N]/(0.45t) \qquad (10)$$

where *N* is Avogadro's number, 0.45 is the quantum yield for the *trans–cis* isomerization, and *t* is the time. The uranyl oxalate actinometer was used for the photolyses at 3000–3200 Å. Lamp intensities varied little after a warm-up period of 15–20 min. Equal illumination of samples and actinometers was assured by a homemade "merry-go-round" apparatus.[12]

Photolysis Procedure. Quantum yields for nitrogen evolution were determined by measuring the nitrogen evolved from degassed solution in Pyrex tubes of known volume equipped with high-vacuum stopcocks. After photolysis for a specified time, the solution was slowly frozen with liquid nitrogen from the bottom up so as to expel dissolved nitrogen. The tube was then opened into a vacuum line of known volume and the pressure change observed on a U-tube manometer. The moles of nitrogen evolved were calculated from the ideal gas law assuming the gas to be at ambient temperature (the chilled volume was negligible compared to the total volume of the system). It was previously established that nitrogen evolution followed a first-order rate law to at least 20% of reaction, and conversions were kept well under this figure in the quantum yield determinations. Concentrations of sensitizer were chosen so that the sensitizer absorbed more than 99% of the incident light, and at least four azide concentrations in the range 0.02–0.2 *M* were used with each sensitizer. Higher sensitizer concentrations were used with phenyl azide to prevent interference by the azobenzene formed in the photolysis.

Quenching rates were calculated from plots of $1/\phi$ *vs.* 1/[azide]. The value of the azide concentration in any given run was the *average* over the extent of reaction in that run, *i.e.*, 90% of initial concentration for a reaction that consumed 20% of the azide. Quantum yields for intersystem crossing were either those of Lamola and Hammond,[7] or were determined as described below. Rate constants for decay of sensitizer triplets (k_d) were those of Herkstroeter and Hammond[6] or DeBoer and Hardham.[26] The quenching rates so obtained were assumed to be minimum values because of possible impurities in the solvent or sensitizer. Maximum rates were calculated assuming maximum error in the sensitizer triplet decay rates as reported by Herkstroeter.[27] Since the error in k_d for phenanthrene is considerably greater than for the other sensitizers, the calculated k_q was considered an average value

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[23] E. Lieber, T. S. Chao, and C. N. R. Rao, *J. Org. Chem.*, **22**, 238 (1957).

[24] R. O. Lindsay and C. F. H. Allen, *Org. Syn.*, **22**, 96 (1942).

[25] G. S. Forbes and W. G. Leighton, *J. Am. Chem. Soc.*, **52**, 3192 (1930).

[26] C. DeBoer and W. Hardham, Ph.D. Theses, California Institute of Technology, 1965.

[27] W. G. Herkstroeter, Ph.D. Thesis, California Institute of Technology, 1965.

and error bars drawn on both sides (Figure 1) to reflect the error in k_d. The sensitizers and their triplet energies, rates of deactivation (k_d), and quantum yields for intersystem crossing are listed in Table III.

Table III. Data on Sensitizers

Sensitizer	E_T,[a] kcal/mol	ϕ_{ST}[d]	$10^4 k_d$,[g] sec^{-1}
β-Acetonaphthone	59.3	0.84	0.33 ± 0.03
Phenanthrene	61.8[b]	0.76	0.90 ± 0.08
Thioxanthone	65.5	1.0[e]	1.3 ± 0.1
Benzophenone	68.5	1.0	5.0 ± 2.0[f]
Acetophenone	73.6	1.0	100.0 ± 200.0[f]
Cyclopropyl phenyl ketone	74.4[c]	1.0	500.0 ± 200.0[f]

[a] Except where otherwise noted, from W. G. Herkstroeter, A. A. Lamola, and G. F. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964). [b] E. Clar and M. Zander, *Chem. Ber.*, **89**, 749 (1956). [c] Reference 25. [d] Reference 7 except where otherwise noted. [e] This research. [f] Reference 25. [g] Reference 6 except where otherwise noted.

Control Experiments on Quenching Rates. To test the validity of our methods and the purities of our sensitizers and solvents, we determined quenching rates for a number of sensitizer triplets by *trans*-stilbene, and compared the results with those of Herkstroeter and Hammond.[6] The procedure was identical with that above, except that the quantum yield of *cis*-stilbene was determined by glpc. The rates obtained were: anthracene, 2.3 × 10^5 M^{-1} sec^{-1} (lit.[6] 1.1 × 10^5); acridine, 1.6 × 10^6 (lit.[6] 5.8 × 10^6); and 1,2-benzanthracene, 7.1 × 10^7 (lit.[6] 3.3 × 10^8). The error in all three cases is less than that reported[26] for k_d of the sensitizer.

Intersystem Crossing Ratios. The method of Lamola and Hammond,[7] was used to determine intersystem crossing ratios (ϕ_{ST}) for several sensitizers. The values obtained were 1,2-benzanthracene, 0.87 ± 0.05; pyrene, 0.10 ± 0.05; and thioxanthone, 1.00 ± 0.05.

Molecular Orbital Calculations. The extended Hückel theory program described by Hoffmann[15] was adapted for use on our IBM 7074 computer. Bond lengths in methyl azide were those determined by Livingston and Rao.[13] Values for the Slater exponents were: hydrogen, 1.00; carbon, 1.625; nitrogen, 1.95.[28] Valence-state ionization potentials were those of Skinner and Pritchard.[29] In one series of calculations the $N_1N_2N_3$ bond angle (θ) was varied from 110 to 250° keeping other bond lengths and bond angles constant. In another, θ was held constant at 140° and the effect of varying the $MeN_1N_2N_3$ dihedral angle determined (Me and N_3 had been kept coplanar in the first series of calculations).

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Photocycloaddition of Thiocarbonyl Compounds to Olefins. The Reaction of Thiobenzophenone with Styrene and Substituted Styrenes

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Abstract: Thiobenzophenone reacts with styrene, on irradiation with ultraviolet or visible light to give 2,2,3,3,5-pentaphenyl-1,4-dithiane. The mechanism of this reaction has been studied kinetically. It is shown that the reaction proceeds through the addition of the n → π* triplet state of thiobenzophenone, which behaves like a thiyl radical, to styrene. The characteristic difference between the photocycloaddition of thiobenzophenone affording 1,4-dithianes and that of benzophenone to give oxetanes is discussed in terms of the reactivities of carbon radicals toward a thiocarbonyl sulfur and a carbonyl oxygen. The high reactivity of the intermediate composite radical toward the thioketone leads to 1,4-dithianes from thiobenzophenone. It is suggested that the use of photoexcited thiobenzophenone as a model of thiyl radicals simplifies the study of the addition reactions of thiyl radicals to olefins. From this viewpoint, the relative rates of the addition reactions of thiobenzophenone with unsubstituted and various *para*- and *meta*-substituted styrenes have been examined. Based on the absence of a substituent effect, it is proposed that the sulfur atom β to the radical center stabilizes it by forming a sulfur-bridged radical. The stabilizing effect of this type is strong enough to overshadow the effects of substituents in styrenes.

Photocycloaddition reactions of ketones to olefins to give oxetanes are well documented.[1] On the other hand, little is known[2-4] about the photochemistry of thioketones. A recent study on the photocycloaddition reactions of thiobenzophenone with various olefins, by irradiation with a high-pressure mercury lamp, has shown that the only isolable products are 1,4-dithianes.[5] Thus, reactions of thiobenzophenone with cyclohexene, 2,3-dihydropyran, ethyl vinyl ether, and styrene afford 3,3,4,4-tetraphenyl-2,5-dithiabicyclo[4.4.0]decane (I), 3,3,4,4-tetraphenyl-7-oxa-2,5-dithiabicyclo[4.4.0]decane (II), 2,2,3,3-tetraphenyl-5-ethoxy-1,4-dithiane (III), and 2,2,3,3,5-pentaphenyl-1,4-dithiane (IV), respectively. We have found that the same

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