Organic and Biological Chemistry

The Sensitized Photolysis of Acyclic Azo Compounds. Singlet Energy Transfer

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Abstract: Azomethane is decomposed by direct photolysis in hexane and in toluene with quantum yields of 0.15 and 0.088, and with cage effects (ethane–nitrogen product ratio) of 68 and 76%, respectively. Sensitized photolysis is observed with phenanthrene, triphenylene, pyrene, anthracene, and acetone, with cage effects indistinguishable from those in direct photolysis. Thioxanthone gave a 9% lower cage effect than direct photolysis. With benzophenone, benzanthrone, and acridine the quantum yields were only of the order of magnitude attributable to some direct light absorption by the azomethane. In the case of azo-2-methyl-2-propane, sensitized photolysis is observed with six sensitizers, listed in Table III, with four aromatic ketones failing to show appreciable sensitized decomposition of the azo compound. Azo-2-methyl-2-propane quenches the fluorescence of five aromatic hydrocarbons with Stern–Volmer slopes from 6.6 for perylene to 435 for phenanthrene. The highest quantum yield for sensitized decomposition is equal to that for direct photolysis at the same substrate composition, 0.02 *M*. Efficient triplet quenchers do not affect the sensitized photolysis. Selective irradiation of benzophenone (triplet energy (E_T) = 68.5 kcal) in the presence of azo-2-methyl-2-propane and excess triphenylene (E_T = 66.6 kcal) results in no nitrogen formation. The quantum yield of decomposition of azo-2-methyl-2-propane sensitized by triphenylene increases with increasing substrate concentration to a limit of 0.40, equal to that of direct photolysis under the same conditions. These results are interpreted as meaning that the azo compounds efficiently accept energy from π,π^* excited singlets of sensitizers. Possible sequences of states leading to the *cis,trans* isomerization and decomposition of azo compounds are discussed. The exceptionally easy transfer of singlet energy to azo compounds accounts for previous failures to observe spin correlation in radical pairs from azo sources.

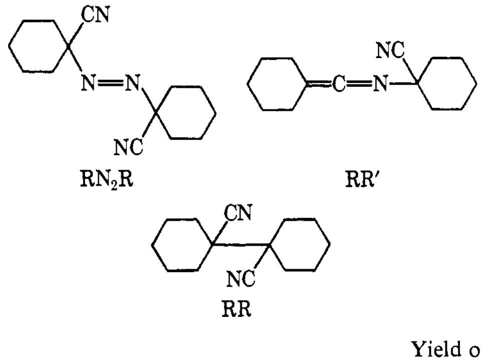
Because thermolysis of azoalkanes occurs in some cases at moderate temperatures, certain azo

$$RN{=}NR \longrightarrow 2R\cdot + N_2$$

compounds have found wide application as free-radical initiators.[1] Most of the azoalkanes are also unstable toward ultraviolet irradiation and the photolysis of the lower members of the series has been extensively studied in the gas phase over the last 30 years.[2] Recently there has been renewed interest not only in the photolysis of the azoalkanes in the gas phase[3,4] but also in their use in solution as sources of radical pairs of different multiplicity.[5–13] It is assumed that a directly irradiated azo compound decomposes from a singlet excited state and produces radicals with antiparallel electron spins while triplet-sensitized photolysis leads to parallel spins. When the subsequent behavior of the radicals depends upon their multiplicity, we shall say that the system shows a spin correlation effect.

An example is a report by Fox and Hammond[13] which indicated that a spin correlation effect could be observed when a pair of cyanocyclohexyl radicals R· ·R in a solvent cage was produced from a ketenimine RR′ but not from the corresponding azo compound RN_2R (*cf.* Scheme I).

Scheme I



	Yield of RR, %
$RR' \xrightarrow{h\nu} [R\downarrow \quad \uparrow R] \longrightarrow RR$	24.1
$RR' \xrightarrow{\text{sens}^{*3}} [R\uparrow \quad \uparrow R] \longrightarrow RR$	8.3
$RN_2R \xrightarrow{h\nu} [R\uparrow \quad N_2 \quad \downarrow R] \longrightarrow RR$	19.9
$RN_2R \xrightarrow{\text{sens}^{*3}} [R\uparrow \quad N_2 \quad \uparrow R] \longrightarrow RR$	17.7

Nelsen and Bartlett,[12] working with azocumene (**1**), also observed that the cage effect was apparently

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[1] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 129.

[2] R. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.*, **87**, 1847 (1965), and references cited therein.

[3] S. Collier, D. Slater, and J. Calvert, *Photochem. Photobiol.*, 7, 737 (1968).

[4] B. Solomon, T. Thomas, and C. Steel, *J. Amer. Chem. Soc.*, **90**, 2249 (1968).

[5] S. Andrews and A. C. Day, *J. Chem. Soc. B*, 1271 (1968).

[6] E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **89**, 7133 (1967); **91**, 6766 (1969).

[7] P. Scheiner, *ibid.*, **88**, 4759 (1966); **90**, 988 (1968).

[8] H. Kato, *Chem. Commun.*, 496 (1968).

[9] P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968).

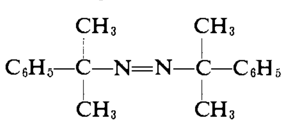
[10] P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).

[11] M. Szwarc, unpublished results on perfluoroazomethane.

[12] S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 143 (1966).

[13] J. R. Fox and G. S. Hammond, *ibid.*, **86**, 4031 (1964).

independent of the singlet or triplet nature of the precursor of the radical pair from an azo compound.



$$\begin{array}{ccccccc} & CH_3 & & & CH_3 & \\ & | & & & | & \\ C_6H_5- & C & -N{=}N- & & C & -C_6H_5 \\ & | & & & | & \\ & CH_3 & & & CH_3 & \end{array}$$

1

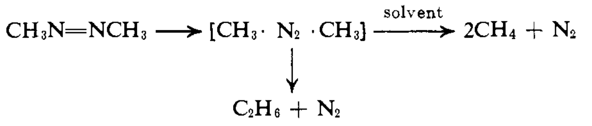
These authors concluded that spin inversion must in general be faster than diffusion. Fox and Hammond attributed the lack of spin correlation from their azo compound to a special damping effect of the intervening nitrogen molecule on the interaction between the electron spins in the freshly formed radical pair. Neither explanation was correct, as will be shown in the present paper.

One hypothesis considered was that bicumyl could possibly be formed in a triplet state, thus requiring no spin inversion from an energetic triplet radical pair. This consideration prompted the study of azomethane, which yields a radical with a minimum of spin delocalization and a cage product, ethane, having no low-lying triplet state. Azomethane, despite the high diffusion rate of the methyl radical, is known to have high cage effects in solution.[14]

In the work with azomethane and azo-2-methyl-2-propane (**5**) to be described here, many facts were encountered which were at variance with the usual view that photosensitized reactions generally proceed through triplet energy transfer. Finally, a consistent picture of the behavior of azoalkanes required the conclusion that they are rapid acceptors of singlet energy even from sensitizers with efficient intersystem crossing. Thus the previous experiments designed to produce triplet radical pairs from azoalkanes were in fact only producing singlet radical pairs by an alternative route.

Results

Sensitized Photolysis of Azomethane (2). Azomethane was first prepared in 1909 by Thiele[15] and has since been extensively studied in the gas phase.[2] Kodama[14] carried out an elegant study of the photolysis of azomethane in several solvents at various temperatures. Under conditions of complete scavenging, the ethane/nitrogen ratio is a measure of the cage effect. As shown by Kodama, nearly any hydrogen-containing solvent is sufficient to scavenge all free methyl radicals. Our experiments consisted of determining the product composition from direct and sensitized photolysis of azomethane in hydrocarbon solvents. A spin correlation effect would be manifested by a decrease in the ethane/nitrogen ratio under triplet photosensitization. From the results which are shown in Table I, it is apparent that with the possible exception of thioxanthone, which will be discussed later, no spin correlation effect is seen. The methane yield can, of course, be decreased if methyl radicals add to the sensitizer. Since the quantum yields of direct photolysis of azomethane in hexane and in toluene are only 0.15 and 0.088, respectively, and the quantum yields of the sensitized photolyses are still less, it is necessary to take account of the absorbancies of the components of the solutions of Table II in order to decide to what extent sensitization is actually occurring. The results indicate that there is sensitization in the cases of acetone, triphenylene, phenanthrene, pyrene, and anthracene, but little or none in the case of benzophenone.



$$\begin{array}{ccc} CH_3N{=}NCH_3 \longrightarrow & [CH_3\cdot\ N_2\ \cdot CH_3] & \xrightarrow{\text{solvent}} 2CH_4 + N_2 \\ & \downarrow & \\ & C_2H_6 + N_2 & \end{array}$$

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Table I. Photolysis of 0.02 *M* Azomethane

Sensitizer	CH_4/N_2, %	C_2H_6/N_2, %	Product balance, %
	In Hexane at 20°		
None	58.3	68.5	97.6
None	55.4	67.9	95.6
Phenanthrene	52.0	66.0	92.0
Pyrene	50.4	69.4	94.6
Benzophenone	53.5	66.4	93.1
Acetone-d_6	53.8	66.4	93.3
	In Toluene at 20°		
None	37.8	75.9	94.8
Anthracene	22.7	76.1	87.4
Triphenylene	34.5	76.2	94.7
Thioxanthone	42.6	66.9	88.2
Thioxanthone	42.8	67.1	88.5

Examination of the data in Table II reveals the same anomalous pattern which Fox and Hammond[13] observed several years ago for photosensitized ethyl azoisobutyrate decomposition. In particular, some sensitizers with a low triplet energy give higher quantum yields than others with higher lying triplet states. Furthermore, sensitizers whose triplet state ought to be too low to transfer energy to the azo group cause moderately efficient decomposition. Similar results were obtained by Nelsen,[16] who found that anthracene and 1,2-benzanthracene (E_T = 42.6 and 47 kcal, respectively) would decompose azocumene with moderate efficiency.

At the outset of this work, the triplet energy levels of azo compounds were entirely unknown because they have never been observed to phosphoresce.[2,3] Theoretical estimates, however, suggested that the n–π^* singlet–triplet splitting (E_{S-T}) ought to be in the region of 15–20 kcal,[13,17–19] which would place the n–π^* triplet of acyclic aliphatic azo compounds above 50 kcal. Recently one of us[20] estimated the triplet energy of compound **3** as 59.3–61 kcal and Calvert[3] estimated the triplet level of **4** as 53 ± 3 kcal. The efficiency of low-energy sensitizers could then be rationalized as due to nonvertical energy transfer, in analogy with stilbene.[21] The term "nonvertical" means that the shape of the acceptor molecule undergoes a change during the transfer process to a new form representing an energy minimum for the excited state. Since azo compounds are known to undergo *cis–trans* isomerization photochemically,[22,23] geometric changes must occur in the excited state.

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(14) S. Kodama, *Bull. Chem. Soc. Jap.*, **35**, 652 (1962).

(15) J. Thiele, *Chem. Ber.*, **42**, 2575 (1909).

(16) S. F. Nelsen, Ph.D. Thesis, Harvard University, 1965.

(17) D. R. Kearns, *J. Phys. Chem.*, **69**, 1062 (1965).

(18) R. Ake, personal communication, 1966.

(19) The n–π^* S–T splitting in *trans*-diimide has recently been calculated as 21 kcal; *cf.* M. Robin, R. Hart, and M. Kuebler, *J. Amer. Chem. Soc.*, **89**, 1564 (1967).

(20) P. S. Engel, *ibid.*, **89**, 5031 (1967).

(21) G. S. Hammond, *et al.*, *ibid.*, **86**, 3197 (1964).

(22) R. F. Hutton and C. Steel, *ibid.*, **86**, 745 (1964).

(23) E. Fischer, *ibid.*, **90**, 796 (1968), and previous papers.

Table II. Photolysis of 0.02 *M* Azomethane at 20°

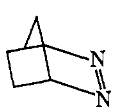
Sensitizer	Concn, *M*	E_T,[a] kcal mol^{-1}	k_1,[b] sec^{-1} × 10^{-3}	$\phi_{i.c.}$[c]	Solvent	ϕ_{N_2}[d]
None					Hexane	0.15
None					Toluene	0.088
Anthracene	0.050	42.6	2.7	0.70	Toluene	0.012
Acridine	0.022	45.3	2.5		Toluene	0.0008
Benzanthrone	0.021	47	0.73		Toluene	0.0005
Pyrene	0.058	48.7	0.65	0.27,[e] 0.38[f]	Hexane	0.044
Phenanthrene	0.050	62.2	9.0	0.76,[h] 0.80[e]	Hexane	0.084
Thioxanthone	0.016	65.5	13	1.0[k]	Toluene	0.0020
Triphenylene	0.050	66.6	1.6	0.96,[h] 0.89[e]	Toluene	0.066
Benzophenone	0.200	68.5	530[g]	1.0[h]	Hexane	0.0087
Acetone-d_6	0.68	80[j]	1050[i]	1.0[j]	Hexane	0.037

[a] Sensitizer triplet energy: W. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966); J. Calvert and J. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 298. [b] Rate constant for decay of sensitizer triplet (see Herkstroeter and Hammond in footnote *a*). [c] Intersystem crossing efficiency. [d] Uncorrected for direct photolysis. [e] Value in ethanol: C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, **62**, 2785 (1966). [f] Value in ethanol: A. Horrocks, *et al.*, *ibid.*, **62**, 3393 (1966). [g] H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960). [h] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 86. [i] P. J. Wagner, *J. Amer. Chem. Soc.*, **88**, 5672 (1966). [j] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966). [k] F. Lewis and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **90**, 7033 (1968).

Table III. Photolysis of Azo-2-methyl-2-propane at 20°

Sensitizer	Sens concn, *M* × 10^2	E_T,[a] kcal mol^{-1}	E_S,[b] kcal mol^{-1}	**5** concn, *M* × 10^2	λ, mμ	Direct[c] *hν*, %	Φ_{N_2}[d]
None				2.2	366	100	0.46
Acetone	75	80[e]	80,[f] 85[e]	2.02	313	1.03	0.072
Acetophenone	11	73.6	79	2.04	313	0.83	0.012
p-Methoxyacetophenone	5.15	71.5	80	2.0	313	0.54	0.015
Benzophenone	5.0	68.5	76.5[h]	2.06	366	7.4	0.020
Benzophenone	5.0	68.5	76.5[h]	1.06	313	0.63	0.013
Benzophenone	5.3	68.5	76.5[h]	2.07	366	7.0	0.048[j]
Triphenylene	5.0	66.6	83.5[i]	2.0	313	0.14	0.39
Triphenylene	5.0	66.6	83.5[i]	2.0	313	0.14	0.42
Thioxanthone	1.05	65.5	76	2.04	366	0.46	0.014
Phenanthrene	5.0	62.2	83.0[i]	2.15	313	0.46	0.46
Pyrene	5.0	48.7	77.0	1.8	366	3.2	0.18
Anthracene	1.35	42.6	75.5[i]	2.07	366	0.94	0.058
Anthracene	1.38	42.6	75.5[i]	2.0	366	0.89	0.062
9,10-Diphenylanthracene	0.54	<42	73.0	2.02	366	0.55	0.27
9,10-Diphenylanthracene	0.55	<42	73.0	1.92	366	0.51	0.25
Perylene	0.605	37 ± 5[g]	65.0	2.03	366	1.12	0.025

[a] See Table II, footnote *a*. [b] Singlet energy estimated from the long-wavelength limit of the uv absorption unless otherwise noted. [c] Per cent of light absorbed directly by the azo compound calculated from the extinction coefficient of sensitizer and **5** at the wavelength of irradiation. [d] Not corrected for simultaneous direct photolysis. [e] See Table II, footnote *j*. [f] W. A. Noyes, *Chem. Rev.*, **56**, 49 (1956). [g] C. A. Parker and T. A. Joyce, *Chem. Commun.*, 108 (1966). [h] See Table II, footnote *h*, p 48. [i] See Table II, Calvert and Pitts in footnte *a*, p 254. [j] At 70.5 ± 1°.



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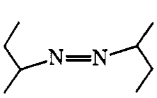

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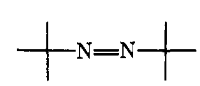

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A difficulty with the nonvertical transfer hypothesis, however, is that despite its intersystem crossing yield of unity, benzophenone behaves as a relatively poor sensitizer for azo compounds. Its triplet energy is certainly high enough (E_T = 68 kcal) to transfer energy to azo compounds and despite its short lifetime, nearly all of the benzophenone triplets produced under our conditions should transfer before decay (see later). This anomaly indicated that in order to rationalize the quantum yield data, some explanation besides nonvertical energy transfer was needed.

Sensitized Photolysis of Azo-2-methyl-2-propane. Evidence for Singlet Sensitization. Further mechanistic investigations were carried out with the more convenient substrate, azo-2-methyl-2-propane (**5**). Since it has no α hydrogens, there is no possibility of tautomer formation.[24] Another important reason for this choice is that the only noncondensable gas produced is nitrogen, which greatly simplified the product analysis. The quantum yields of nitrogen evolution were measured with a variety of sensitizers; the results are shown in Table III. The confused pattern seen for azomethane and for ethyl azoisobutyrate is evident here also.

Examination of the data in Tables II and III reveals that nearly all the efficient photosensitizers are aromatic hydrocarbons. Since these species have much longer singlet lifetimes[25] than ketones, it became attractive to consider singlet- rather than triplet-sensitized decomposition. Coupled with the postulate that triplet-sensitized decomposition does not occur (see below), this leads to a completely consistent picture.

To ascertain whether hydrocarbon singlets were involved, we examined the effect of added **5** upon the

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(24) C. Overberger, *Rec. Chem. Progr.*, **21**, 21 (1960).

(25) I. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965.

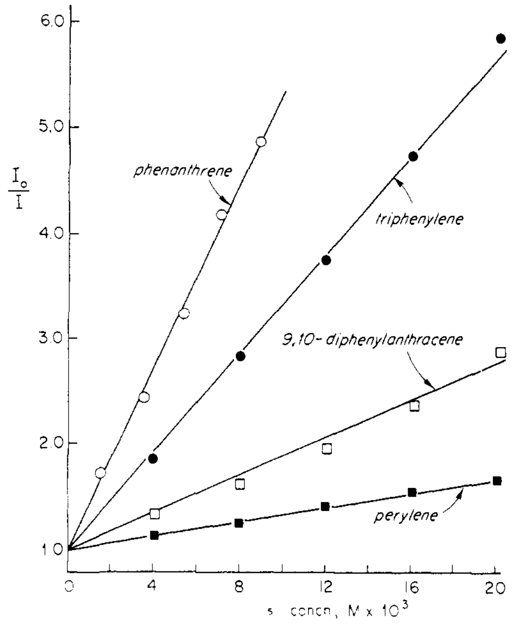

Figure 1. Quenching of sensitizer fluorescence by azo-2-methyl-2-propane (**5**). For perylene, the quencher concentration was five times that shown.

fluorescence intensity of pyrene and anthracene. In fact we observed a decrease much greater than that calculated if radiation were only absorbed by the azo compound. That fluorescence quenching was extremely efficient was confirmed in the case of triphenylene by following the decrease in singlet lifetime. In Figure 1 are shown Stern–Volmer plots for quenching of fluorescence from several hydrocarbons by **5** while Table IV tabulates the quantative results.

Table IV. Photochemical Parameters for Sensitized Decomposition of Azo-2-methyl-2-propane (**5**)

Sensitizer	E_S,[a] kcal mol^{-1}	τ_S,[b] nsec	M[d]	k_q,[e] $\times 10^{-9}$	Φ_{N_2}[g]
Phenanthrene	83.0	56[c]	435	7.6	0.46
Triphenylene	83.5	36.6	227	6.2	0.40
Triphenylene	83.5	26.4		5.6[f]	0.40
Anthracene	75.5	4.9	100	20	0.06
9,10-Diphenyl-anthracene	73.0	9.35	80	8.5	0.26
Perylene	65.0	6.4	6.6	1.0	0.025

[a] Sensitizer singlet energy, see Table III. [b] Singlet lifetime from ref 25 unless otherwise noted. [c] C. Amata, M. Burton, W. Helman, P. Ludwig, and S. Rodemeyer, *J. Chem. Phys.*, **48**, 2374 (1968). [d] Slope of Stern–Volmer plot. [e] Rate of fluorescence quenching, $k_q = M/\tau_S$. [f] We thank Dr. C. Wamser for determining this value by fluorescence lifetime quenching. [g] Quantum yield for sensitized photolysis; *cf.* Table III.

The fact that **5** quenches fluorescence does not alone establish that decomposition is sensitized by hydrocarbon singlets. However, if it is assumed that **5** does not enhance intersystem crossing in hydrocarbons, one can show for the case of triphenylene that at least part of the observed decomposition is singlet sensitized. A Stern–Volmer treatment of the mechanism in Scheme II

Scheme II

$$\mathrm{S} \xrightarrow{I} \mathrm{S}^{*1}$$

$$\mathrm{S}^{*1} \xrightarrow{k_{i.c.}} \mathrm{S}^{*3}$$

$$\mathrm{S}^{*1} \xrightarrow{k_f} \mathrm{S} + h\nu$$

$$\mathrm{Q} + \mathrm{S}^{*1} \xrightarrow{k_q} \mathrm{S} + \mathrm{Q}$$

predicts that

$$\frac{\Phi_f^0}{\Phi_f} = 1 + \frac{k_q[\mathrm{Q}]}{k_{i.c.} + k_f} = \frac{\Phi_{i.c.}^0}{\Phi_{i.c.}}$$

where Φ_f is the quantum yield of fluorescence (which is proportional to the emitted light intensity), $\Phi_{i.c.}$ is the intersystem crossing yield, and the superscript 0 indicates no added azo compound (Q). At 0.02 *M* **5**, $\Phi_f^0/\Phi_f = 5.5$ so that $\Phi_{i.c.} = 0.18\Phi_{i.c.}^0$. From the literature value[26,27] of $\Phi_{i.c.}^0$ (0.95), we calculate that $\Phi_{i.c.} = 0.17$ under these conditions. Since the experimental quantum yield of nitrogen is 0.41, at least part of the decomposition must occur *via* the singlet.

Additional evidence was sought for the singlet mechanism by studying the rates of sensitized decomposition in the presence of high concentrations of a known triplet quencher. Triphenylene was chosen as the sensitizer because of its high efficiency for azo compound photolysis and because of its use in previous spin correlation studies.[12,13] Piperylene is an ideal quencher for this purpose since (a) it does not absorb light at the wavelength of irradiation, (b) its triplet energy (E_T = 58.8 kcal)[21] lies considerably below that of triphenylene so that triplet quenching should be diffusion controlled,[28] and (c) it does not affect the singlet state of triphenylene.[29]

The data in Table V show clearly that addition of 0.1 *M* piperylene does not lower the quantum yield of the triphenylene-sensitized photolysis of **5**. Outside of the explanation that decomposition is singlet sensitized, the only other possibility is that the piperylene triplet efficiently transfers energy to **5** which in turn decomposes. If this were so, then producing piperylene triplets by benzophenone sensitization ought to result in as high a quantum yield as by triphenylene. From Table V it is seen that this is not the case, although piperylene appears to increase the quantum yield slightly over that with benzophenone and **5** only. Even if piperylene triplets indeed have an appreciable rate of energy transfer to **5**, it is too small by an order of magnitude to provide an escape from the conclusion that triphenylene is behaving here as a singlet sensitizer.

A complexity in the pattern of energy transfer is revealed by the effect of concentration of azo-2-methyl-2-propane on the quantum yield of its decomposition sensitized by triphenylene. A combination of the data of Figure 1 and Table V allows the construction of Figure 2, showing the disposal of the excitation energy of

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(26) See Table II, footnote *e*.

(27) See Table II, footnote *h*.

(28) Triplet energy transfer to isoprene (E_T = 60 kcal) is diffusion controlled; see A. J. Fry, R. S. Liu, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4781 (1966).

(29) Dienes are known to quench some hydrocarbon singlet states;[30] however, we found that 0.25 *M* piperylene does not affect the fluorescence of triphenylene.

(30) L. M. Stephenson, D. G. Whitten, and G. S. Hammond, "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, Ltd., London, 1967, p 35.

Table V. Photolysis of **5** with 0.05 *M* Sensitizer in Toluene at 20°

Sensitizer[a]	**5** concn, $M \times 10^2$	Direct[b] $h\nu$, %	Φ_{N_2}[c]
Triphenylene	2.0	0.14	0.39
Triphenylene	2.0	0.14	0.42
Triphenylene	2.0	0.14	0.44[d]
Triphenylene	2.0	0.14	0.37[d]
Benzophenone	2.08	7.4	0.046[d]
Benzophenone	1.99	7.1	0.045[d]
Benzophenone	2.06	7.4	0.020
Triphenylene	1.13	0.082	0.36
Triphenylene	1.04	0.075	0.38
Triphenylene	0.535	0.039	0.22
Triphenylene	0.475	0.034	0.18
Triphenylene	0.350	0.024	0.103
Triphenylene	0.24	0.017	0.054
Benzophenone	1.04	3.9	0.019[e]
Benzophenone	1.20	4.4	0.033[f]

[a] Triphenylene was irradiated at 313 mμ and benzophenone at 366 mμ. [b] Per cent light absorbed directly by the azo compound calculated from the extinction coefficients. [c] Uncorrected for direct photolysis. [d] 0.10 *M* mixed piperylene added. [e] 0.10 *M* triphenylene added. [f] 0.089 *M* triphenylene added.

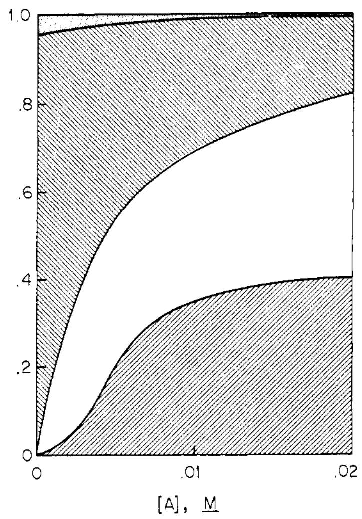
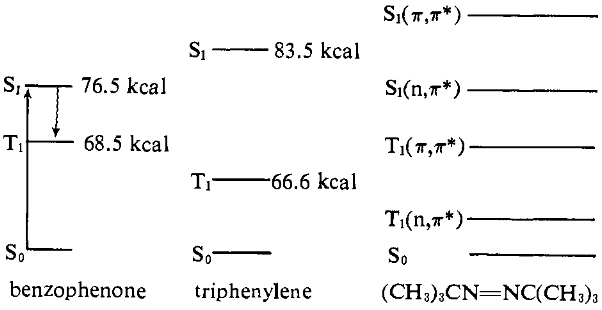


Figure 2. Disposal of excitation energy by singlet excited triphenylene in the presence of azo-2-methyl-2-propane (**5**) [A]: dotted area, fluorescence; upper diagonal area, triphenylene deactivated otherwise than by energy transfer to **5**; blank area, quenched by **5** without formation of N_2; lower diagonal area, quenched by **5** with formation of N_2.

the singlet excited triphenylene as a function of the azo compound concentration. At low azo concentrations about 5% of this energy appears as fluorescence, while 95% of the excited triphenylene crosses to triplet. The quenching of the fluorescence (Figure 1) provides an index to the competition between energy transfer to **5** and all other modes of deactivation. However, the quantum yield of excited **5** deduced in this way is not the same as the quantum yield of nitrogen, which lags behind it by a factor decreasing as the concentration of azo compound increases. The fraction of excited azo compound that decomposes amounts to about half at the highest azo compound concentrations, but is less than one-sixth at 0.0024 *M* azo-2-methyl-2-propane. The excited azo compound apparently follows a branching path after its excitation, the path leading to decomposition being of higher order in azo compound than that leading to unchanged ground state. Possible interpretations are discussed below.

A fourth type of experiment which points toward involvement of sensitizer singlets is one using a mixture of two sensitizers whose energy levels are shown in Scheme III. Benzophenone is selectively irradiated and instantly[31] crosses to triplet. Its energy is transferred to triphenylene whose triplets should then sensitize decomposition of **5**, if indeed it is the triplet which decomposes. From Table V it is seen that generating triphenylene triplets by benzophenone sensitization results in virtually no decomposition. If triphenylene triplets really are produced here, we may conclude that they do not cause decomposition of azo compound and that upon direct irradiation, triphenylene acts through its singlet.

Scheme III



Wagner[32] has shown that triphenylene quenches the benzophenone–benzhydrol photoreduction with a Stern–Volmer slope of 360, and we have obtained a similar value. Triphenylene is not quite as good a quencher for benzophenone triplets as **5**; however, the concentrations have been arranged in favor of triphenylene being the major acceptor of triplet energy in the mixed sensitizer experiment.

One further result from Table III deserves comment since it offers support for the singlet energy transfer hypothesis, namely 9,10-diphenylanthracene is a rather efficient sensitizer. In view of the fact that its fluorescence quantum yield[25] is 1.0, energy transfer must involve the singlet state.

Ketone Sensitizers. The reason for the low quantum yield with benzophenone could be (a) that the lifetime of the benzophenone triplet is too short, (b) the benzophenone has a lower triplet energy than the azo compounds, or (c) that the azo triplet does not decompose. The short lifetime of the benzophenone triplet[33] alone is not enough to explain its low quantum yield. At an azo concentration of 0.02 *M*, the pseudo-first-order rate constant for diffusion-controlled energy transfer would be about $0.02 \times 10^{10} = 2 \times 10^8$ sec^{-1}. The rate of benzophenone triplet decay[34] is 5.3×10^5 sec^{-1}. Therefore 99.7% of the triplets should transfer energy before they decay

$$\frac{2 \times 10^8}{2 \times 10^8 + 5.3 \times 10^5} = 0.997$$

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(31) The lifetime of benzophenone singlet is less than 2×10^{-10} sec; see W. Moore, G. Hammond, and R. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

(32) P. Wagner, *ibid.*, **89**, 2920 (1967).

(33) H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **16**, 958 (1962).

(34) J. Heicklen and N. Cohen, *Advan. Photochem.*, **5**, 264 (1968).

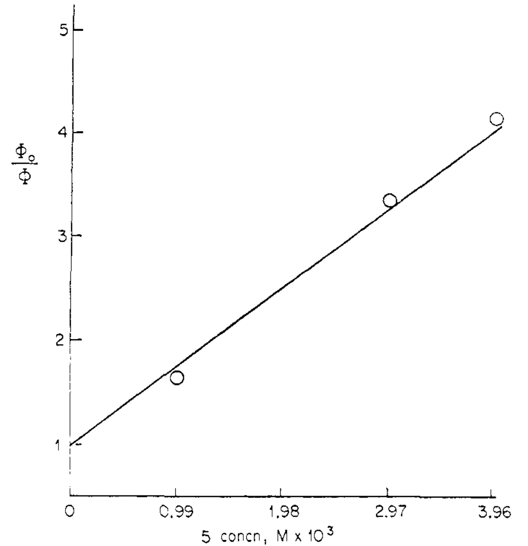

Figure 3. Quenching of the benzophenone-benzhydrol photoreduction by azo-2-methyl-2-propane (**5**).

Possibility b is ruled out since we have found that **5** quenches the benzophenone-benzhydrol photoreduction[35] with moderate efficiency. The Stern-Volmer slope in Figure 3 is 760. Azo-2-methyl-2-propane (**5**) was also used as a quencher of biacetyl phosphorescence in hexane solution at room temperature with the results shown in Figure 4. The calculated rate of energy transfer is 3.3×10^8 which means that some triplet state of **5** must lie below the triplet level of biacetyl ($E_T = 54.9$ kcal). Since decomposition does not follow energy transfer, we looked for other reactions which the azo compound might undergo.

The other known photoreaction of acyclic azo compounds besides decomposition into free radicals is *cis-trans* isomerization.[22,23] Steel[22] discovered that direct irradiation of *trans*-azomethane causes isomerization to *cis* and that this change is manifested by an enhancement of the absorbance in the ultraviolet spectrum and a shift to longer wavelength. When we followed the benzophenone-sensitized photolysis of azomethane by uv spectroscopy, the curves in Figure 5 were obtained. In this experiment, azo compound and solvent were distilled away from the solid sensitizer so that the latter would not interfere with the azo compound spectrum. Figure 5 strongly suggests that benzophenone sensitizes *cis-trans* isomerization of azomethane; we estimate the quantum yield to be greater than 0.4.

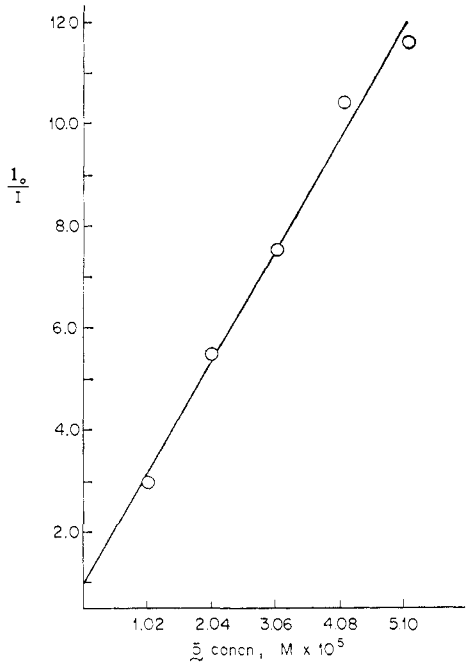

Figure 4. Quenching of phosphorescence of biacetyl by azo-2-methyl-2-propane (**5**).

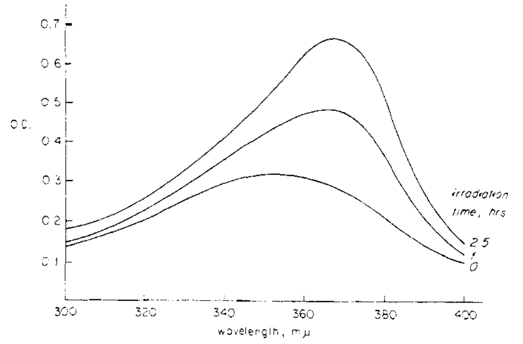

Figure 5. *cis-trans* isomerization of azomethane, sensitized by benzophenone.

Discussion

We have presented five lines of evidence that decomposition of azo compounds can be sensitized by hydrocarbon singlets: (1) **5** is capable of efficiently quenching the fluorescence of several hydrocarbons; (2) addition of 0.1 *M* piperylene does not alter the quantum yield of the triphenylene-sensitized decomposition of **5**; (3) the efficiency of triphenylene-sensitized decomposition falls markedly at lower concentrations of **5**; (4) producing triphenylene triplets by benzophenone sensitization results in virtually no azo decomposition; (5) using 9,10-diphenylanthracene whose fluorescence quantum yield is 1.0 leads to quite efficient decomposition. It seems appropriate now to consider what the mechanism of the singlet interaction is.

It has been recognized for over 30 years that many substances will quench sensitizer fluorescence[36] but only in some instances does the quenching initiate any chemical change. As a result of several recent investigations, the known cases can now be divided into five categories: (1) quenching by paramagnetic species such as oxygen and nitric oxide,[34] (2) quenching by heavy atoms,[37] (3) charge-transfer complex formation,[38] (4) exciplex formation,[30,39] (5) direct intermolecular energy transfer, whether of the diffusion-controlled type[40] or by the long-range Förster mechanism.[41]

In considering the mechanism of our singlet-sensitized decomposition we can exclude from further con-

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(35) G. S. Hammond and P. S. Leermakers, *J. Phys. Chem.*, 66, 1148 (1962).

(36) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience, New York, N. Y., 1949, p 328.

(37) W. Ware and J. Novros, *J. Phys. Chem.*, 70, 3246 (1966).

(38) H. Leonhardt and A. Weller in "Luminescence of Organic and Inorganic Materials," H. Kallman and G. Spruch, Ed., Wiley, New York, N. Y., 1962, p 74.

(39) S. Murov and G. Hammond, *J. Phys. Chem.*, 72, 3797 (1968).

(40) J. T. Dubois and M. Cox, *J. Chem. Phys.*, **38**, 2536 (1963).

(41) Th. Förster, *Discuss. Faraday Soc.*, 27, 7 (1959).

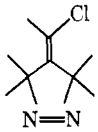
sideration categories 1 and 2 since there are no paramagnetic species or heavy atoms involved. Furthermore quenching by such species generally leads to no photochemical reaction.[42]

Weller[38] and Ware[37] have advocated mechanism 3 for quenching of perylene singlet by amines. The evidence in this case was a pronounced effect of solvent polarity on quenching rate and observation of the spectrum of the perylene radical anion. Charge-transfer interactions are unlikely in the present work, however, since azo compounds are considerably less basic than amines and since nonpolar solvents have been used exclusively. The good charge-transfer donor, triethylamine, is only 0.1% as effective as **5** as a quencher of triphenylene fluorescence in isooctane; moreover, changing the solvent to acetonitrile results in a dramatic increase in the rate for triethylamine, while for **5** the rate is unchanged.

Mechanism 4 has been proposed where fluorescence quenching occurs in the absence of heavy atoms, paramagnetic species, or a low-lying singlet state of the acceptor.[30,39,43] Exciplexes may decay with[39,44] or without[30,36,45] chemical change. Unlike the cases requiring exciplex formation, **5** has a singlet state eligible to receive the energy of the sensitizer.

Förster-type energy transfer is rendered unlikely by the forbidden nature of the $n-\pi^*$ transition in azoalkanes; therefore, we consider that the hydrocarbon-sensitized decomposition of **5** proceeds *via* direct intermolecular singlet energy transfer.

Despite the number of ways in which singlet states can play a role in photochemistry, examples of simple singlet sensitization have been scarce. Zimmerman and Swenton[46] found that naphthalene singlet sensitizes the photorearrangement of a dienone. deMayo and coworkers[47] reported that acenaphthene sensitizes cyclopentenone dimerization *via* the singlet. Andrews and Day[5] have recently reported that singlet-sensitized decomposition of **6** is possible while singlet-sensitized decomposition of **3** has been postulated in three cases.[4,6,48] A case closely analogous to that of the azo compounds is the very recent observation of Lewis and Dalton[49] that alkyl azides undergo singlet-sensitized decomposition.



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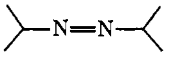
Triplet Energy Transfer to Azo Compounds. The fact that **5** quenches the benzophenone–benzhydrol photoreduction and the phosphorescence of biacetyl is evidence that it has a triplet state lying below 55 kcal. Using 1 μsec for the triplet lifetime of benzophenone[50] and 660 μsec for that of biacetyl,[33] we obtained quenching rate constants of 7.6×10^8 M^{-1} sec^{-1} and 3.3×10^8 M^{-1} sec^{-1}, respectively. Direct measurement by kinetic spectroscopy[51,52] shows that **5** quenches triphenylene triplets with a rate constant of 7.7×10^8 M^{-1} sec^{-1}. All of these rates are less than diffusion controlled. Calvert,[3] on the other hand, found that **4** quenches biacetyl phosphorescence at a rate of 5×10^9 M^{-1} sec^{-1}. It is therefore tempting to suggest that energy transfer to **5** is slow because of steric hindrance. One other case like this has been reported,[53] namely, the sensitized isomerization of stilbene with sterically hindered benzophenones.

From Figure 5, it appears that benzophenone efficiently sensitizes *cis,trans* isomerization of azomethane. Although it is tempting to speculate that triplet energy transfer always results in *cis,trans* isomerization of azo compounds, recent work shows that this is not true.[54] Using benzophenone and benzene as a sensitizer for azoisopropane (**7**) isomerization, Steel and coworkers[54] found the quantum yield of *cis*-isomer formation to be only 0.06. In the still more sterically hindered compound, azo-2-methyl-2-propane, it has recently been shown[55] that the *cis* form decomposes to nitrogen even at room temperature. Since energy transfer from benzophenone did not result in nitrogen formation, no isomerization could have occurred. Apparently there exists a barrier to isomerization of the triplet in more hindered azo compounds.



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The observation of *cis,trans* isomerization in the benzophenone-sensitized photolysis of azomethane has a rather subtle implication regarding the quantum yield data given in Table II. During irradiation, the absorbance of azomethane increases so that it competes better for light with sensitizer. Thus we believe that all of the observed decomposition was due to direct photolysis in the case of benzophenone.

Coupled with the result that azo compounds accept triplet energy from benzophenone and biacetyl, the data of Tables II and III imply that the lowest triplet state of azomethane and of azo-2-methyl-2-propane does not undergo homolysis. Steel has obtained a similar result for **7**.[54] This important conclusion can probably be generalized to include all acyclic azo compounds but not cyclic ones.[56]

It will be noted that the quantum yield for the 9,10-diphenylanthracene-sensitized photolysis of **5** is higher than that for acetophenone sensitization. Since the triplet energy of the latter is higher than the singlet energy of 9,10-diphenylanthracene, the triplet state produced by ketone sensitizers must not lie on the de-

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(42) A notable exception to this statement is the chemically active singlet state produced by energy transfer from triplet sensitizers to molecular oxygen; *cf.* K. Kawauka, A. Kahn, and D. Kearns, *J. Chem. Phys.*, **46**, 1842 (1967).

(43) L. A. Singer and G. Davis, *J. Amer. Chem. Soc.*, **89**, 158 (1967).

(44) R. S. Cooke and G. S. Hammond, *ibid.*, **90**, 2958 (1968).

(45) Fluorescence occurs from rigid cyclic azo compounds, but not from acyclic ones such as we are discussing here.

(46) H. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967).

(47) P. deMayo, J. P. Pete, and M. Tchir, *ibid.*, **89**, 5712 (1967).

(48) P. D. Bartlett and P. S. Engel, *ibid.*, **90**, 2960 (1968).

(49) F. D. Lewis and C. Dalton, *ibid.*, **91**, 5260 (1969).

(50) T. S. Godfrey, J. W. Hilpern, and G. Porter, *Chem. Phys. Lett.*, **1**, 490 (1967).

(51) See Table II, Herkstroeter and Hammond in footnote *a*.

(52) We thank Dr. C. Wamser for determining this value.

(53) W. Herkstroeter, L. Jones, and G. Hammond, *J. Amer. Chem. Soc.*, **88**, 4777 (1966).

(54) I. Abram, G. Milne, B. Solomon, and C. Steel, *ibid.*, **91**, 1220 (1969).

(55) T. Mill and R. Stringham, *Tetrahedron Lett.*, 1853 (1969).

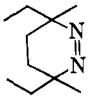
(56) P. S. Engel, *J. Amer. Chem. Soc.*, **89**, 4731 (1967); **91**, 6903 (1969).

composition pathway of singlet **5**. This is of interest since recent reports[3,54] suggest that azo decomposition proceeds through *some* triplet state; in particular, the π,π^* state is postulated to lead to decomposition while sensitization produces the n,π^* state.

Acetone is a sensitizer which deserves special mention since it does not behave like our other ketone sensitizers. Perdeuterioacetone was used because its triplet lifetime is longer than that of the hydrogen compound[57] and because it was important to be able to distinguish methane arising in acetone photolysis from that formed in decomposition of azomethane. Rebbert and Ausloos[2] and also Calvert[3] have shown that acetone sensitizes gas phase azo decompositions. From Tables II and III, it is apparent that acetone is also capable of sensitizing azo decomposition in solution to some extent.

Two explanations for the efficiency of acetone come to mind: production of an azo triplet capable of decomposition, and sensitization by acetone singlet. Calvert[3] found that in the gas phase **4** quenches phosphorescence of both acetone and biacetyl but is decomposed only by the former. This was taken as evidence of an activation energy to decomposition of triplet **4**. Since acetone is the highest energy triplet sensitizer which we used, it could be the only one high enough to overcome an activation energy for decomposition of our azo compounds. The second explanation, however, is equally possible since, unlike the aromatic ketones but like the aromatic hydrocarbons, acetone emits fluorescence. Rebbert and Ausloos[2] reported that azomethane does not quench this fluorescence and this alone would argue against sensitization by acetone singlet. However, since low azo concentrations were used in that work[2] and since the lifetime of the acetone singlet is short[58] quenching probably would not have been seen. The fact that energy transfer would be exothermic leads us to believe that azo compounds will quench acetone singlets but the actual experiment is complicated by the high azo concentrations necessary to observe quenching, the overlap of the azo absorption spectrum with the fluorescence of acetone,[57] the low fluorescence yield of acetone, and the recently discovered excimer emission from acetone.[59] Thioxanthone is the only sensitizer which shows a smaller ethane yield than in direct azomethane photolysis. This result is surprising since we had anticipated that, as with benzophenone, the only decomposition would be due to light absorbed directly by azomethane. The high methane yield is consistent with a true spin correlation effect; however, since the product balance is somewhat low, we hesitate to rule out experimental problems as the explanation.

On the other hand, Bartlett and Porter[9] observed a spin correlation effect using thioxanthone and the cyclic azo compound **8**.



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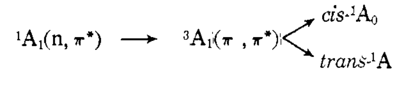
With postulates that acyclic azo compounds undergo little if any triplet-sensitized decomposition and that aromatic hydrocarbons can cause singlet-sensitized decomposition, the observed quantum yields in Tables II and III are understandable. The behavior of acyclic azo compounds contrasts sharply with that of cyclic ones where triplet-sensitized decomposition is well documented.[5-9,56] The most important conclusion to be drawn from the present work concerns our attempts and those of others[10-13] to observe spin correlation effects in acyclic azo compound decompositions. Fox and Hammond[13] used triphenylene as their sensitizer for decomposition of azo-1-cyanocyclohexane, Nelsen and Bartlett[12] used triphenylene and pyrene for azocumene decompositions, and Szwarc[11] used phenanthrene for perfluoroazomethane. Since all these materials are good singlet sensitizers, it now appears that in each case only singlet radical pairs have been observed.

If singlet energy is directly transferred from sensitizer to azo compound, the problem remains of tracing the transformations which lead in part to deactivation and in part to decomposition of the azo compound. The study of the quantum yield of decomposition of azo-2-methyl-2-propane sensitized by triphenylene, together with the fluorescence quenching of triphenylene, shows the nature of this problem as illustrated in Figure 2, constructed on the assumption that when triphenylene fluorescence is partially quenched, a proportional part of the excited triphenylene is replaced by excited singlet azo compound, and all the rest of the absorbed energy appears as triphenylene triplets. If singlet excited azo compound decomposes unimolecularly, this scheme predicts that the nitrogen quantum yield (the bottom curve in Figure 2) ought to be directly proportional to the yield of excited azo singlets (the middle curve). Instead the fraction of azo singlets which eventually give nitrogen appears to decrease at lower azo concentrations. When the reciprocal of the nitrogen quantum yield is plotted against the reciprocal square of the concentration of azo compound, a reasonably straight line is obtained. These observations are consistent with a variety of mechanisms, none of which, however, is completely satisfactory.

Singlet quenching, for example, could lead to an excimer which, upon collision with another azo molecule, decomposes to one or two molecules of nitrogen. One would feel more ready to invoke an *ad hoc* excimer if there were any indication in the uv or fluorescence spectrum of interaction between the molecules concerned.

Another mechanism is suggested by the recent report of Steel and coworkers,[54] who have proposed that azo-2-propane (**7**) photochemistry takes the course



$$^1A_1(n,\pi^*) \longrightarrow {}^3A_1(\pi,\pi^*) \left< \begin{matrix} cis\text{-}^1A_0 \\ trans\text{-}^1A_0 \end{matrix} \right.$$

In the case of **5**, rapid thermolysis of the *cis* isomer might be the source of nitrogen.[55] Consistent with this hypothesis is the fact that the quantum yield of nitrogen (0.46) is equal within experimental error to the quantum yield of *cis–trans* isomerization (0.5 for **7** and for **5**[60]). The quantum yield of sensitized photolysis of **5** approaches 0.46 with long-lived singlet sensitizers at the

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[57] See Table II, footnote *j*.

[58] F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).

[59] A. Testa, *J. Amer. Chem. Soc.*, **90**, 6245 (1968). See, however, G. D. Renkes and F. S. Wettack, *ibid.*, **91**, 7514 (1969).

[60] T. Mill and R. Stringham, unpublished data.

highest concentration of **5** used. These facts are consistent with the view that direct and sensitized photolyses of **5** proceed through the same excited state.

The above scheme places two intermediates on the decomposition pathway of excited singlet **5** and thereby presents a number of explanations for the anomalous behavior discussed above. The second-order dependence of nitrogen quantum yield on concentration of **5** can be explained if we may assume that the $^3\pi,\pi^*$ state lives long enough[61] to undergo triplet–triplet annihilation with formation of an unstable upper excited state. This, however, would predict a strong dependence of quantum yield on light intensity which, in preliminary experiments, was not observed. Furthermore, the direct photolysis of azocumene is not subject to quenching by di-*t*-butyl nitroxide, despite the fact that this free radical is expected to be a good quencher of triplets.[43]

Another explanation which has been considered is that the increasing yield of triphenylene triplets at lower azo concentration somehow destroys *cis*-**5** without production of nitrogen. Further experiments, such as the effect of temperature on the quantum yield of the triphenylene-sensitized decomposition of **5**, will be required to establish the mechanism fully.

Experimental Section

Materials. Most sensitizers were purified as described previously.[56] Acetone-d_6 from Merck Sharp & Dohme was used without further purification. *p*-Methoxyacetophenone was MCB practical grade and was vacuum distilled before use. 9,10-Diphenylanthracene was prepared by Dr. B. Kaski and showed a fluorescence spectrum in agreement with that reported.[25] Aldrich perylene was zone refined on a microscale and the lightest colored material was taken for use. Aldrich acridine was chromatographed on alumina and recrystallized from aqueous ethanol, mp 110.4–111.6°. Benzanthrone from Eastman was dissolved in methylene chloride and filtered through alumina. After drying in a vacuum desiccator, it melted at 173.3–174.4°. Solvents were subjected to the same modes of purification as previously described.[56]

Azomethane was prepared by heating its cuprous chloride complex[62] according to Jahn.[63] The compound was purified by repeated distillation through a tower containing a mixture of calcium chloride, barium oxide, and soda lime. It was stored in red glass ampoules at −25°. Azo-2-methyl-2-propane (**5**) was prepared by the IF_5 oxidation of *t*-butylamine according to Stevens.[64] It was purified by preparative vpc on a 20-ft column of 5% tetra(hydroxyethyl)ethylenediamine and 15% tetraethylenepentamine on 60–80 mesh Chromosorb W. The column was operated at 60° and the injector temperature was 120°.

A more convenient method for the preparation of **5** was found to be that of Stowell.[65] The material thus prepared was subjected to spinning band distillation.

Azomethane Product Analysis. Photolysis and quantum yield determinations were carried out as previously described.[56] Because fractionation of the product gases was necessary and because analysis was sensitive to small amounts of residual gas in the solvent, determining the product composition from azomethane photolysis was considerably more difficult than when nitrogen was the only gas formed.

In order to remove carbon dioxide present in the solvents used for azomethane photolysis, they were repeatedly distilled under vacuum. Portions (20 cc) of the solvent were sealed under vacuum in storage tubes equipped with break-seals. After photolysis, the cell was opened to a series of 4 traps at −78, −78, −160, and −196°, respectively. The contents of the cell were distilled from trap to trap as a Töpler pump collected the gas. The first fraction, consisting of methane and nitrogen, was analyzed by combustion over a hot platinum wire.[66] The −196° trap was then warmed to −160° to vaporize the ethane, which was determined volumetrically in a gas buret. Mass spectrometry of the two fractions showed them to be uncontaminated by one another.

Luminescence Quenching. Fluorescence quenching was done on an Aminco fluorimeter while quenching of biacetyl phosphorescence was carried out on a Hitachi MPF-2A spectrofluorimeter.

Acknowledgment. We thank the National Science Foundation for predoctoral fellowships to P. S. E. The work was assisted by grants from the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund administered by the American Chemical Society.

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[61] In order for the quantum yield to be 0.46, it can be calculated that at the light intensities used in this work, the π,π^* triplet would have to live for 0.10 sec.

(62) Diels and Koll, *Ann.*, **443**, 269 (1925).
(63) F. P. Jahn, *J. Amer. Chem. Soc.*, **59**, 1761 (1937).
(64) T. E. Stevens, *J. Org. Chem.*, 26, 2531 (1961).
(65) J. Stowell, *ibid.*, **32**, 2360 (1967).
(66) L. Nash, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 505 (196).