Triplet–Triplet Energy Transfer from the Second Triplet States of Anthracenes. Chemical Studies[1a]

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Abstract: The case for energy transfer from the T_2 state of anthracenes in sensitized reactions of several rigid and nonrigid systems is presented. By eliminating any significant contribution of energy transfer from alternative states (S_1, T_1, S_0), it is concluded that anthracenes can serve as a triplet sensitizer of energy 68–74 kcal/mol. These results eliminate the need for the postulatory concept of "nonvertical" energy transfer in explaining these apparent "endothermic" sensitized reactions. From Stern-Volmer plots, rate constants for internal conversion between T_2 and T_1 states were obtained, and the average lifetime of T_2 state was calculated. For 9,10-dibromoanthracene, τ_{T_2} is $(2.2 \pm 0.5) \times 10^{-10}$ sec.

It is commonly accepted that in a triplet–triplet exchange energy transfer process only the lowest triplet state of the donor is important.[1c] The reasons for this are probably twofold. First, because of the rapid internal conversion process among excited singlet states, the path of cascade generally bypasses the higher triplet states. Secondly, internal conversion between states of the triplet manifold has also been assumed to be too fast to allow a bimolecular energy transfer such as

$$^{D}T_2 + {}^{A}S_0 \rightarrow {}^{D}S_0 + {}^{A}T_1$$

Thus, a successful investigation of energy transfer from higher triplet states must first overcome these two problems: sparce population and short lifetimes.

Recent spectroscopic studies have established in some compounds (notably anthracene[2] and substituted anthracenes[3]) the existence of at least another triplet state, T_2, in addition to T_1, with energy less than that of S_1, the lowest excited singlet state.[4] In these compounds, intersystem crossing from S_1 proceeds by way of T_2, the second triplet state. Thus, the efficiency of populating T_2 in these compounds is the same as the quantum yield of intersystem crossing, which in the case of anthracene is 0.75.[5] Anthracene and substituted anthracenes, therefore, eliminate the population problem and were chosen for our studies. The expected short lifetimes of such a state rules out conventional spectroscopic approaches in studies of energy transfer. Therefore, our program was initiated with the adoption of indirect chemical approaches where the short-lived higher excited triplets are trapped by the fast energy-transfer processes, producing an acceptor triplet which undergoes a chemical transformation. Information related to properties of higher triplet states is then provided in terms of quantum yields of the reactions or product compositions. This paper reports results of our investigation.[6] Subsequently we have also found that under special conditions, spectroscopic studies of energy transfer from T_2 states are also possible. The results have been reported separately.[7]

Being aware of the hazards and ambiguities in such chemical spectroscopy (see Discussion), particularly in recognizing the presence of the "nonvertical" excitation theory in explaining results of such apparent "endothermic" sensitized reactions,[8] experimental evidence establishing the case for T_2 sensitization is also presented.[9]

Results

Anthracenes unsubstituted at the 9,10 positions dimerize efficiently upon irradiation.[10] Therefore, only in qualitative studies the parent and monosubstituted anthracenes are used as donors. For quantitative studies, the 9,10-disubstituted anthracenes were used. The acceptors are four rigid molecules which undergo clean unimolecular triplet-state reactions and several acyclic olefins representing nonrigid molecules. Results with other systems, *e.g.*, the stilbenes[11a] and acrylonitrile,[6b,11b] will be reported elsewhere in detail.

Quantum Yields of Reactions. The four rigid molecules are 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene (**1**),[12,13] its benzo analog **2**,[12,13] norbornadiene (**3**),[6a,14]

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[1] (a) The Role of Second Triplet States in Solution Photochemistry. IV. (b) Author to whom inquiries should be addressed: Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822. (c) For a recent review on the triplet–triplet energy transfer processes in solution see: F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

[2] R. E. Kellogg, *J. Chem. Phys.*, **44**, 411 (1966).

[3] R. G. Bennett and P. J. McCartin, *ibid.*, **44**, 1969 (1966).

[4] In recent phosphorescence excitation studies, Kearns, *et al.*, have identified low lying T_2 states in several other molecules. See, *e.g.*, D. R. Kearns and W. A. Case, *J. Am. Chem. Soc.*, **88**, 5087 (1966); A. P. Marchetti and D. R. Kearns, *ibid.*, **89**, 768 (1967). See also: S. D. Colson and E. R. Berstein, *J. Chem. Phys.*, **43**, 2661 (1965); D. M. Hanson and G. W. Robinson, *ibid.*, **43**, 4174 (1965).

[5] T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, 61, 620 (1965).

[6] Part of the results have been reported in two preliminary reports: (a) R. S. H. Liu and J. R. Edman, *J. Am. Chem. Soc.*, **90**, 213 (1968); (b) R. S. H. Liu and D. M. Gale, *ibid.*, **90**, 1897 (1968).

[7] R. S. H. Liu and R. E. Kellogg, *ibid.*, **91**, 250 (1969).

[8] (a) 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, *ibid.*, **86**, 3107 (1964); (b) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *ibid.*, **87**, 3406 (1965); (c) W. C. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4789 (1966); (d) A. Cox, P. de Mayo, and R. W. Yip, *ibid.*, **88**, 1043 (1966); (e) W. Dillion, *ibid.*, **89**, 2742 (1967); (f) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, **86**, 2532 (1964); (g) J. R. Fox and G. S. Hammond, *ibid.*, **86**, 4031 (1964); (h) C. Walling and M. J. Gibian, *ibid.*, **87**, 3413 (1965).

[9] Several reports on bimolecular reactions involving higher triplets have recently appeared in the literature: (a) N. C. Yang, R. Loschen, and D. Mitchell, *ibid.*, **89**, 5466 (1967); (b) P. de Mayo, J. P. Pete, and M. Tchir, *ibid.*, **89**, 5712 (1967); (c) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *ibid.*, **90**, 1657 (1968).

[10] See, *e.g.*, R. Calas and R. Lalande, *Bull. Soc. Chim. France*, 763, 766, 770 (1959).

[11] (a) R. S. H. Liu, *J. Am. Chem. Soc.*, **90**, 1899 (1968), and unpublished results of R. S. H. Liu; (b) D. M. Gale, unpublished results.

[12] R. S. H. Liu, *J. Am. Chem. Soc.*, **90**, 215 (1968).

[13] R. S. H. Liu and C. G. Krespan, *J. Org. Chem.*, in press.

[14] G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

Table I. Quantum Yields of Photosensitized Reaction of Compounds **1–4** and Isomerization of Piperylenes

		Quantum yield of reaction[b]					
						Piperylenes[d]	
Sensitizer	E_{T_1}[a]	**1**[c]	**2**	**3**	**4**	c → t	t → c
Xanthone	74.2	+	0.17	+	+	+	+
Acetophenone	73.6	0.9	0.16	0.26	0.49	+	+
Benzophenone	68.5	1.03	x	0.18	0.04	0.55 ± 0.01[g]	0.44 ± 0.10[g]
Michler's ketone	61.0	...	...	...	...	0.55 ± 0.01[g]	0.43 ± 0.10[g]
2-Acetonaphthone	59.3	0.037	...	...	x	+	+
9-Fluorenone	51[e]	0.0001	...	x	x	0.74	+
Benzanthrone	47.0	...	...	...	...	0.0084	...
Acridine	45.3	...	...	...	...	0.0054	...
Anthracene (An)	42.5[f]	+	+	+	+	+	+
9,10-Dibromo-An	40.2[f]	0.0081	x	+	+	0.042	0.032
9,10-Dichloro-An	40.2[f]	0.0035	...	...	+	0.0018	...
9,10-Dimethyl-An	?	0.0006	...	...	...	...	...
9-Bromo-10-methyl-An	?	0.0068	...	+	...	0.033	...

[a] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964), unless otherwise stated. [b] +, sensitized reaction observed; x, no reaction; ..., not run. [c] In *n*-hexane, concentration of **1** = 1.91 × 10^{-2} *M*. [d] In benzene, concentration of piperylene = 0.2 *M*. [e] K. Yoshikars and D. R. Kearns, *J. Chem. Phys.*, **45**, 1991 (1966). [f] Reference 21. [g] Reference 8a.

and benzonorbornadiene (**4**).[15] Their triplet-state reactions are shown in Figure 1. The nonrigid molecules are butadiene and piperylenes.

The quantum yields of rearrangements of compounds **1–4** and isomerization of piperylenes are shown in Table I. They are listed in decreasing order of the lowest triplet-state energy of the sensitizers. The values were obtained by glpc analyses of irradiated solutions of the acceptors with the sensitizer in either benzene or hexane at low conversions with 3660-Å light (with the exception of acetophenone and xanthone, where 3130-Å light was used).

The observed variation of quantum yields of reactions, for sensitizers other than anthracenes, are interpreted in terms of changes in the efficiencies in the energy-transfer step. Qualitatively, the latter depends upon the energy separation between the triplet states of the donor and the acceptor,[16] *i.e.*, at unit efficiency when E_T of the donor is greater than the acceptor's, proportionally reduced efficiencies when lower than the acceptor's.[8c,17] Following this line of reasoning, data in Table 1 lead to the assignment of the triplet-state energy of compound **1** between 62 and 68 kcal/mol, and those of compounds **2–4** about 69 kcal/mol or higher. These are useful numbers particularly in view of our failure to obtain such information more directly by taking S_0–T_1 absorption spectra in ethyl iodide.

Concentration Effects. With anthracenes as sensitizers, the quantum yields of reaction are found to depend upon the concentration of acceptor molecules. Results of concentration studies with compound **1** and piperylenes sensitized by 9,10-dibromoanthracene-h_8 and -d_8 are shown in Tables II and III.

Table II. Dependence of Quantum Yields[a] of Reaction of **1** Sensitized by 9,10-Dibromoanthracene-h_8 and -d_8 upon Concentration of **1**[b]

	Quantum yields (× 1000)	
Concn of **1** (*M*) × 100	With An-h_8	With An-d_8
2.72	10.4	10.2
2.18	8.0	8.6
1.77	6.6	6.8
1.495	5.6	5.6
1.36	5.0	5.1

[a] With 3660-Å light. [b] In *n*-hexane.

Table III. Dependence of Quantum Yield[a] of Isomerization of Piperylenes Sensitized by 9,10-Dibromoanthracene upon Concentration of Piperylene[b]

	Quantum yield (× 100)	
Piperylene concn, *M*	*trans* to *cis*	*cis* to *trans*
0.417	7.15	5.7
0.317	6.15	4.5
0.250	4.99	3.5
0.200	4.02	3.1
0.167	3.64	2.7
0.150	3.35	2.23
0.133	2.96	2.15
0.0667	1.67	1.16

[a] 3660-Å light. [b] In benzene.

Double Sensitizer Experiments. These experiments are designed to achieve conditions of selective excitation of T_1 of anthracene. Fluorenone is not effective in sensitizing the reaction of **1**, presumably because its triplet-state energy is too low. Therefore, fluorenone triplets, when present in a solution containing 9,10-dibromoanthracene (DBA) and compound **1**, can only transfer energy to the lowest triplet state of DBA, thus achieving a condition of selective excitation of DBA T_1. In practice, because of the broad absorption spectrum of anthracene, exclusive excitation of fluorenone is not possible. However, by adjusting the relative concentrations of fluorenone and DBA, light absorption predominantly by fluorenone can be accomplished. Results from such a study (Table IV) provide information as to the importance of DBA T_1 in the sensitized reaction of **1**. In the case of the piperylenes (Table V) because of their triplet-state energies being much lower[8a] benzanthrone or acridine,

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(15) J. R. Edman, *J. Am. Chem. Soc.*, **88**, 3454 (1966).

(16) Lifetimes of sensitizer triplets and other minor factors may also contribute to the difference in observed variation of quatum yield of reaction, but these contributions are expected to be small in comparison with that due to energy differences.

(17) K. Sanders and K. J. L. Backstrom, *Acta Chem. Scand.*, 16, 958 (1962).

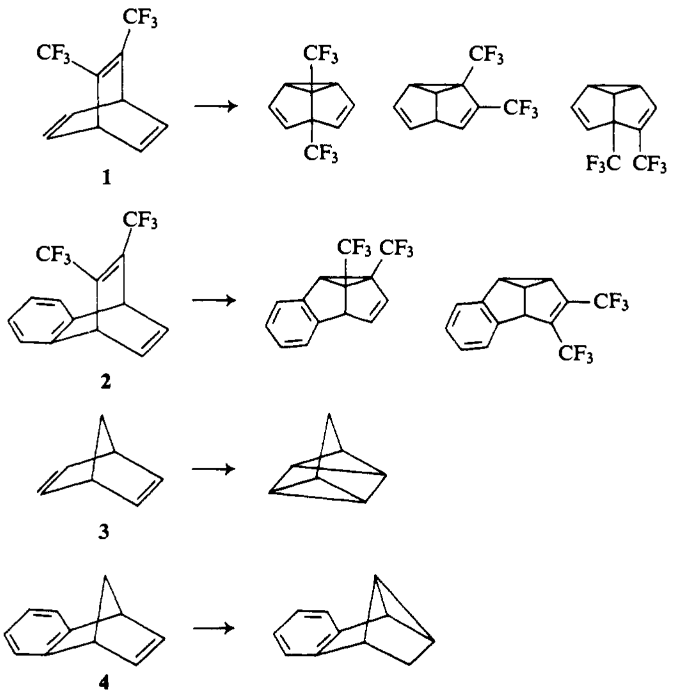

Figure 1. Photosensitized rearrangement reactions of compounds **1**–**4**.

instead of fluorenone, was used as the second sensitizer. Even so, the results are not clear-cut as in **1** because these low-energy sensitizers are still somewhat effective in sensitizing the reactions.[18]

Butadiene Dimerization. The product composition of photosensitized dimerization of butadiene[8b] has been reinvestigated with emphasis on substituted anthracenes as photosensitizers (Table VI). In the case of anthracene, our result of 95% cyclobutane dimers differs significantly from the published number of 84%.[8b] The difference appears due to a secondary photochemical reaction, *i.e.*, the composition becomes richer in cyclohexene dimer on prolonged irradiation, particularly after substantial consumption of anthracene through dimerization. Results in Table VI were obtained after short irradiation periods.

Fluorescene Quenching. The effect of compound 1, at concentrations comparable or slightly higher than those of reaction conditions, on the fluorescence of anthracene, both fluorescene yield (Table VII) and fluorescene lifetime (Table VIII), were investigated. The latter method has the advantage of not having to worry about internal filtering effect, although its sensitivity is much inferior when compared to intensity measurements. With norbornadiene, its effect on the fluorescence lifetime of anthracene was also examined. At concentrations up to 0.9 mol/l. in methylcyclohexane, no change on the radiative lifetime of anthracene singlets was observed.

Discussion

"Chemical spectroscopy," *i.e.*, the study of the excited-state properties of the donor molecules involved in a

Table IV. Comparison of Quantum Yields of Reaction of **1** from Single and Double Sensitizer Experiments[a]

Sensitizers (concn, *M*)	Concn of **1**	Quantum yield
9-Fluorenone (0.0167)	0.033	0.0001[b]
9,10-Dibromo-An (6.67 × 10^{-4})	0.033	0.0038
9-Fluorenone (0.0167) + 9,10-dibromo-An (6.67 × 10^{-4})[c]	0.033	0.002
9,10-Dibromo-An (2.00 × 10^{-3})	0.033	0.0037

[a] In *n*-hexane. [b] Limit of detection. [c] Approximately 80% light absorbed by fluorenone.

Table V. Comparison of Quantum Yields of Isomerization of *cis*-Piperylene in Single and Double Sensitizer Experiments[a]

Sensitizers (concn, *M*)[b]	% of light absorbed by DBA	Quantum yield
Benzanthrone	...	0.0084
Acridine	...	0.0054
DBA	100	0.042
Acridine (7 × 10^{-3} *M*) + DBA (1 × 10^{-3})	60	0.018
Acridine (2.33 × 10^{-3} *M*) + DBA (1 × 10^{-3})	80	0.031
Benzanthrone (7 × 10^{-3} *M*) + DBA (1 × 10^{-3})	70	0.0051
Benzanthrone (2.33 × 10^{-3} *M*) + DBA (1 × 10^{-3})	90	0.012

[a] In benzene. [b] Concentration of piperylene = 0.2 *M*.

Table VI. Butadiene Dimer Composition Sensitized by Anthracenes[a]

Sensitizer	E_T, kcal/mol[b] T_2	T_1	C_4, %
Anthracene	74.4	42.5	95, 84[d]
2-Methyl	73.5	40.6	95
9-Methyl	...	40.6	95
9-Methyl-10-chloro	...	...	92
9-Methyl-10-chloromethyl	...	...	95
1,5-Dichloro	72.6	40.7	94
9,10-Dichloro	...	40.2[c]	95
9,10-Dibromo	...	40.2[c]	94, 97[d]
9,9′-Bianthryl	...	...	96

[a] Pyrex tubes, unfiltered light. Neat butadiene. [b] References 2 and 3 unless otherwise stated. [c] Reference 21. [d] Reference 8b.

Table VII. Anthracene Fluorescence Yield in the Presence of Compound **1**

Concn of An,[a] *M*	Concn of **1**, *M*	Φ_f
6.67 × 10^{-4}	...	0.29[b]
6.67 × 10^{-4}	0.08	0.29
6.67 × 10^{-4}	0.53	0.28

[a] In cyclohexane. [b] Standard; see ref 5.

Table VIII. Fluorescence Lifetime of Anthracene in the Presence of Compound **1**[a]

[An], *M*	[**1**], *M*	η sec Not degassed	Degassed[b]
6.67 × 10^{-4}	0	4.7	5.8
6.67 × 10^{-4}	0.53	4.7	5.7
6.67 × 10^{-4}	0.08	4.7	5.8

[a] In cyclohexane. [b] Intermittent passage of N_2 through solution, until a constant reading is obtained.

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[18] The picture with piperylenes was also muddied by possible involvement of cisoid and transoid dienes.[8b] The results are, however, qualitatively meaningful.

Table IX. Comparison of Quantum Yields of Reaction of **1** and Fluorescence, Triplet Yields, and Fluorescence Lifetimes of Substituted Anthracenes

Anthracene	Φ_f	$\Phi_{ic}{}^d$	$\Phi_{reaction} \times 10^4$
9,10-Dibromo	0.10[a]	(0.90)	81
9,10-Dichloro	0.56[b]	0.48[b]	35
9,10-Dimethyl	0.81[c]	(0.19)	6

[a] Reference 24. [b] Reference 3. [c] W. H. Melhuish, *N. Z. J. Sci. Tech.*, **37B**, 142 (1955). [d] Values in parentheses are $1 - \Phi_f$.

Table X. Fluorescence Lifetime of Anthracenes[a]

	η sec	
Compd (concn, *M*)	Not degassed	Degassed[b]
Me_2-An (2×10^{-4})	8.8	16.2
Cl_2-An (2×10^{-4})	7.3	9.0
Br_2-An (2×10^{-4})	1.7	1.8

[a] Incyclohexane. [b] Values obtained after repeated passage of N_2 through solution.

triplet–triplet energy-transfer process by examination of the chemical changes of the acceptor molecules, has proven a useful technique particularly in cases where spectroscopic approaches are not applicable. There is, however, an inherent weakness in this method, *i.e.*, interpretation of the results is frequently muddied by the possible involvement of other excited states of the donor molecule, which are unavoidably involved in the cycle of activation and deactivation. For example, the study of the donor triplet state is complicated by initial population of the corresponding excited singlet state. With this thought in mind, we shall first present evidence that the observed anthracene-sensitized reactions do not result from energy transfer from some other state but must result from energy transfer from T_2.

The second intense absorption band in anthracene, due to transition to ${}^1B_{3u}{}^+$ state, is much higher energy than that to S_1 (${}^1B_{2u}{}^+$); therefore, 3660-Å light used in this study only excites anthracene to S_1. Intersystem crossing ($\Phi_{ic} = 0.75$)[5] populates T_2, which undergoes rapid internal conversion to T_1 (Figure 2).[2] To establish the case of T_2 energy transfer, it is necessary to eliminate the possible involvement of S_0, S_1, and T_1. The evidence is presented in the following paragraphs with the 9,10-dibromoanthracene (DBA)[19] sensitized reaction of **1** studied in most detail.

Evidence against S_0 (Ground-State Complex). The uv spectrum of DBA in benzene was compared with that of DBA in the presence of compound **1** (concentrations up to 0.09 *M*). No difference was observed, indicating the absence of ground-state complex. Further, the quantum yield of the reaction of **1** sensitized by DBA was found not to depend upon the concentration of DBA within the range of investigation (Table IV).

Evidence against S_1, the Lowest Excited Singlet. The quantum yields of rearrangement of **1** sensitized by three substituted anthracenes are reproduced in Table IX together with their fluorescence, triplet yields, and fluorescence lifetimes. It is obvious that quantum yields of reaction qualitatively parallel intersystem crossing efficiencies of the anthracenes but not with fluorescence yields. The results also cannot be explained by the difference in the fluorescence lifetimes of the corresponding anthracene (Table X).

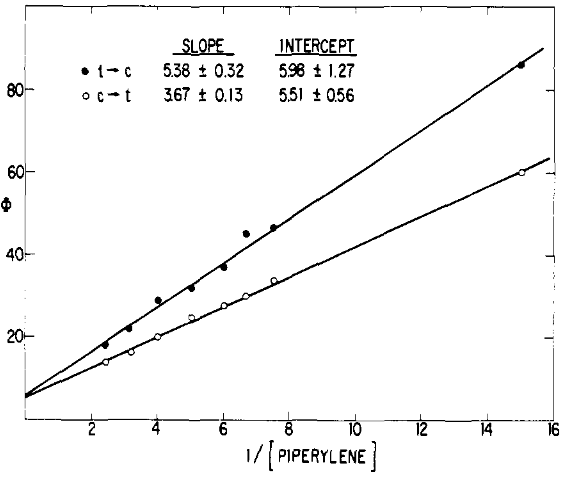

Figure 2. The energy diagram of anthracene (based on Kellogg[2]).

The lack of quenching effect of compound **1** and norbornadiene on the fluorescence yield (Table VII) and lifetime (Table VIII) of anthracene further substantiates the point that anthracene S_1 is not involved in these reactions. It should be noted that our negative results with norbornadiene do not necessarily contradict recent observations of the compound and related systems by Murov, Cole, and Hammond.[20] In fact, their quenching constant indicates that the concentration of norbornadiene used in our study was probably too low for definitive detection of quenching on our instrument.

Evidence against T_1, the Lowest Triplet. The lowest triplet-state energy of DBA (40.2 kcal/mol)[21] or other substituted anthracenes is much lower than the corresponding triplet-state energy of **1** or the other acceptors used in this study. Thus, they would not be expected to be efficient sensitizers. However, energy considerations are not sufficient to rule out T_1 as possible triplet energy donors, for the concept of "nonvertical" excitation advanced by Hammond and coworkers[22] was designed especially to explain cases of "endothermic" energy transfer. Using rigid molecules **1–4** as acceptors is one way to render the concept of "nonvertical" excitation inapplicable, *i.e.*, due to geometric restriction, no low-energy pathway of excitation involving twisting of the double bond is available. However, other "nonvertical" low-energy pathways can be envisioned. To seek unequivocal evidence against T_1, double sensitizer experiments were designed to achieve selective excitation of the T_1 state of DBA. Results show (Table IV) that under selective excitation of T_1, quantum yields lower than in the corresponding sample when DBA alone was used as sensitizer were obtained. Since the intersystem

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(19) DBA does not show a well-resolved 0–0 band in its triplet–triplet absorption spectrum; therefore, its T_2 level can only be deduced from chemical information. Based on its behavior in sensitizing the reactions of compounds **1–4**, its T_2 level must be 68–72 kcal/mol above the ground state.

(20) S. L. Murov, R. S. Cole, and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 2957 (1968).

(21) S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964).

(22) For a recent discussion of the topic see: P. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1967).

Table XI. Calculation of k_{ic} from the Stern–Volmer Plots

Acceptor	k_{ic}/k_t, mol/l. sec	$(k_t)_{exptl} \times 10^9$, l./mol	$(k_D)_{calcd}$, l./mol	$k_{ic}{}^a \times 10^9$, sec^{-1}	$\tau_{T_2} \times 10^{-10}$, sec
cis-Piperylene	0.67 ± 0.09	6.2[b]	1.0×10^{10}	4.2 ± 0.6 (6.7 ± 0.9)	2.4 ± 0.4 (1.11 ± 0.15)
trans-Piperylene	0.90 ± 0.24	6.2[b]	1.0×10^{10}	5.6 ± 1.5 (9.0 ± 2.4)	1.8 ± 0.5 (1.49 ± 0.40)
1	2.4	3[c]	2.0×10^{10}	10 (50)	1 (0.2)

[a] Upper, from experimental value of k_t; lower, in parentheses, from calculated value for k_D. [b] Reference 8c. [c] Reference 1b, p 259.

crossing efficiency in 9-fluorenone ($\Phi_{ic} = 0.93$)[23a] is higher than that of DBA ($\Phi_{ic} \sim 0.90$),[23b] these results can only be interpreted to mean that T_1 of DBA is not involved in the sensitized reaction, at least not to a significant extent.

The Second Triplet State of DBA. Energy transfer from T_2 remains the only plausible explanation. The logical sequence for a T_2-sensitized reaction is[24]

$$^DS_0 \xrightarrow{h\nu} {}^DS_1$$

$$^DS_1 \rightarrow {}^DT_2 \qquad \text{efficiency} = a$$

$$^DT_2 \xrightarrow{k_{ic}} {}^DT_1 \rightarrow {}^DS_0$$

$$^DT_2 + {}^AS_0 \xrightarrow{k_t} {}^DS_0 + {}^AT_1$$

$$^AT_1 \rightarrow \text{products} \qquad \text{efficiency} = b$$

where D = donor (sensitizer); A = acceptor. The following Stern–Volmer expression is obtained

$$\frac{1}{\Phi} = \frac{1}{ab}\left(1 + \frac{k_{ic}}{k_t}\frac{1}{[\mathrm{A}]}\right)$$

The results with DBA sensitizing the reaction of three acceptors are shown graphically in Figures 3 and 4. The ratio k_{ic}/k_t can be calculated from the slope and the intercept of the plots. With the knowledge of k_t from independent studies, k_{ic}, a rate constant of internal conversion between excited states, can be calculated. Before proceeding further, however, a word about the absolute value of k_t is necessary.

For triplet–triplet energy transfer, it is usually assumed that when the triplet-state energy of the donor is 3 kcal/mol or more than that of the acceptor, the transfer process is diffusion controlled.[1c] However, experimental results from several laboratories show that the measured exothermic energy-transfer rate constants are invariably five to ten times the calculated diffusion rate constants.[1c,8c,17] The situation is summarized in a recent paper by Wagner.[25] In our situation undoubtedly we are dealing with a case of exothermic energy transfer. In view of the noted discrepancy, experimentally determined exothermic energy-transfer rate constants are used for k_t in our calculation of k_{ic}. However, values of k_{ic}, calculated from theoretical diffusion rate constants, are also shown in Table XI for comparison.

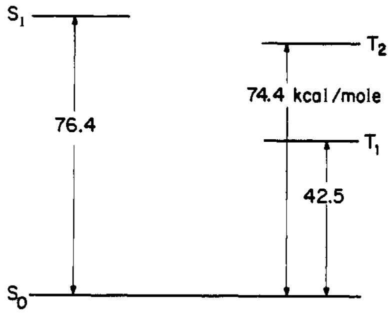

Figure 3. Stern–Volmer plot of DBA-sensitized reaction of **1**.

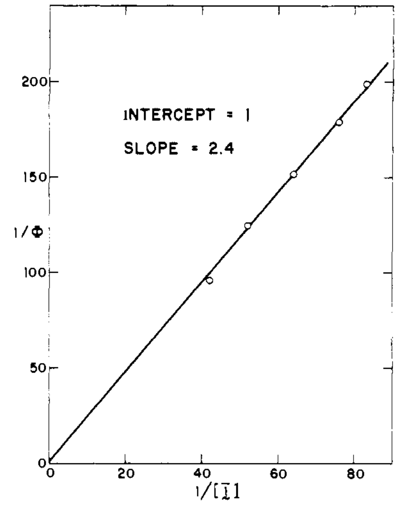

Figure 4. Stern–Volmer plots of DBA-sensitized isomerization of piperylenes.

Values of k_{ic} and τ_{T_2} obtained with the piperylenes are, within experimental error, the same as expected for a common triplet donor. Results for compound **1** are less accurate mainly because of difficulties in making accurate product analyses; however, qualitatively, the calculated values are the same as in the piperylene cases. We, therefore, conclude that the average lifetime for the second triplet state of 9,10-dibromoanthracene is $2.2 \pm 0.5 \times 10^{-10}$ sec, a value significantly higher than that commonly assumed for higher excited states.[1c]

The long lifetime of the second triplet state of DBA is expected from the uniquely large energy separation between T_1 and T_2 of the anthracenes. An analogous

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(23) (a) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965); (b) W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).

(24) The "reversible" energy-transfer step:

$$^AT_1 + {}^DS_0 \rightarrow {}^AS_0 + {}^DT_1$$

is not considered important, thus not included in the scheme because the lifetime of the lowest triplet state of all compounds used in this study is apparently too short to undergo such bimolecular reversible energy transfer in that in the case of piperylenes. no azulene and sensitizer concentration effect were observed,[8a] and in the case of rigid molecules, no dependence of quantum yield of reaction upon sensitizer concentration was observed (Table IV). In fact, stilbene triplet is the only case in the literature where such a "reversible" transfer step has been shown to be competitively important with the associated unimolecular reaction.[8a,11a]

(25) P. Wagner and I. Kochevar, *J. Am. Chem. Soc.*, **90**, 2232 (1968).

case of such energy separation, but among states of the singlet manifold, is the well-documented case of azulene,[26,27] which emits exclusively from S_2 with a radiative lifetime of 1.4 nsec.[28] The long lifetime of azulene S_2 has been well considered and explained by several recent theories on radiationless transitions.[29–31a] Since these theories do not distinguish between internal conversion processes among singlet states or triplet states, parallel arguments can be offered on the long lifetime of DBA T_2.[31b]

The unexpectedly long lifetime of the T_2 state suggests possible detection of such T_2 energy transfer process by direct spectroscopic means. Indeed, in recent studies of triplet–triplet energy transfer from anthracene to naphthalene in mixed crystal systems, the observed emission is only consistent with a scheme involving a crucial step of energy transfer from the T_2 state of anthracene.[7]

Deuterium substitution has proved a useful technique to slow down the nonradiative deactivation processes, thus increasing the lifetime of an excited state.[32] However, our experiment with DBA-d_8 shows the lifetime of T_2 of DBA is not significantly dependent upon isotopic substitution (Table II). This negative result was not expected. In fact, the magnitude of the T_1, T_2 energy gap would suggest an increase of a factor of approximately two on the T_2 lifetime upon deuterium substitution.[33] Presently we cannot offer an explanation for this result. We note, however, similar negative results in the literature.[34]

Product Composition from Sensitized Reactions. In several photosensitized reactions, the product composition varies with the triplet-state energy of the sensitizer. Thus, for piperylenes, sensitizers of energy above 60 kcal/mol produce photostationary states containing 54–59% *trans* isomer, and with lower energy sensitizers, the photostationary states become proportionally richer in *trans*.[8a] On prolonged irradiation, the stationary state of piperylenes sensitized by DBA was established. The value 59 ± 1% *trans* agrees well with that of a high energy sensitizer.[35,36]

The dimer composition of butadiene also varies with the triplet energy of sensitizers, such that sensitizers of energy above 60 kcal/mol give predominantly cyclobutane dimers (92–97%).[8b] The dimer composition obtained with anthracene sensitizers (Table VI) again agrees with donors of energies above 60 kcal/mol. Parallel results were also observed in dimerization of isoprene[8b] and acrylonitrile,[6b,11b] and in photosensitized isomerization of stilbenes.[11a] The last case, however, is further complicated by reverse energy transfer from stilbene triplet to the neighboring ground-state anthracene.[11a] The system is still presently under investigation.

Comments on Anthracene-Sensitized Reactions. Many reactions, including isomerizations,[8a] cycloadditions,[8b,e] and photodecompositions,[8f–h] are reportedly sensitized by anthracene T_1. Several of these cases have been taken as circumstantial evidence for "nonvertical" excitations involving T_1 of anthracenes. Among these are piperylene[8a] and butadiene,[8b] which we have now shown more consistent with T_2 sensitization. Further, recent reports have shown that quenching of anthracene S_1 could also result in chemical transformations of the acceptor.[20,37] In view of these findings, we question whether any of the reported observations are due to T_1 sensitization. Certainly, the results of anthracene-sensitized reactions do not represent anomalous cases of triplet energy-transfer processes, and in these cases the postulation of "nonvertical" excitation processes appears unnecessary.

Experimental Section

Materials. Preparation and reactions of compounds **1**, **2**,[13] and **4**[15] are described elsewhere. Norbornadiene (Shell Chemical) was distilled before use. Butadiene (Matheson Coleman and Bell) and *cis*- and *trans*-piperylenes (Chemical Sample Co.) were used without further purification. Anthracene (Eastman, synthetic grade) was recrystallized from toluene, mp 217–218°; 9,10-dichloro-An (Aldrich) recrystallized from toluene, mp 209–211°; 9,10-dibromo-An, prepared according to the procedure of Heilbron, *et al.*,[38] was recrystallized from xylene. Anthracene-d_{10} (Merck Sharp and Dohme), 9,10-dimethyl-An, and 9-methyl-An (Aldrich) were used as supplied. 9,10-Dibromo-An-d_8 was prepared by reaction of anthracene-d_{10} with bromine,[38] then recrystallized from toluene. Analysis by mass spectrometry indicates a sample containing 12% d_7h_1 isomer. 9-Bromo-10-methyl was prepared by reaction of 9-bromo-10-lithio-An with methyl iodide[39] and 9-chloro-10-methyl-An from the corresponding chlorolithio-An.[39] Purification procedures for other sensitizers have been described.[8a]

Quantum Yields. Sample preparation procedure and irradiation apparatus have been described in the literature.[8a,b] Corning 0-52 and 7-37 filter plates were used for isolation of the 3660-Å band. The Michler's ketone sensitized reaction of myrcene (φ = 0.023)[40] was used for calibration of light intensity. With acetophenone and xanthone as sensitizers, two irradiation procedures were used; first isolation of 3130 Å by combination of filter solutions (intensity considerably reduced),[41] or using a Pyrex well and unfiltered light, with the light intensity calibrated by the myrcene reaction sensitized by the same sensitizer of the same concentration (samples in quartz tubes). All samples were irradiated at 25° to approximately 10% conversion.

Analysis Procedures. Gas chromatography was used for analyses of all irradiated samples. Conditions for analyses for product mixtures from compounds **1**, **2**,[13] **4**,[15] butadiene,[8b] and piperylenes[8a] are known. For norbornadiene, **3**, a 4-ft 15% silicone gum column (50°) was used. For the piperylenes, quanta loss due to back isomerization were corrected;[23] and for other acceptors the averaged values of initial and final concentraions were used for calculations.

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