# More on the Second Triplet States of Anthracenes in Sensitized Reactions of Olefins. Evidence against the Singlet-Triplet Energy-Transfer Process[1]

Roger O. Campbell[2a] and R. S. H. Liu*[2b]

Contribution from the Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822. Received April 19, 1973

Abstract: Using the reaction of the dibromoanthracene-sensitized dimerization of cyclohexadiene, we obtained evidence separating processes of singlet quenching of donor and triplet formation of the acceptor, thus ruling out the applicability of the spin-forbidden energy-transfer process postulated by the Russian workers: $D(S_1) + A(S_0) \rightarrow D(S_0) + A(T_1)$. Additional information related to the second triplet states of several substituted anthracenes (9,10-dibromo-, -dichloro-, -diphenyl-, and 9-phenyl-) is also reported. Their average lifetimes are all very similar ($\sim 10^{-10}$ sec), and intersystem crossing efficiencies determined by the chemical T_2-sensitization method agree (with the exception of DPA) with reported values.

Since the appearance of our reports on the anthracene T_2-sensitized reactions of olefins,[3] Ermolaev and Sveshnikova, in a paper describing fluorescence quenching of anthracenes by naphthalene and other aromatic hydrocarbons, suggested an alternative explanation for our results.[4] That the fluorescence quenching efficiency is enhanced by heavy atom substitution on the donor (the respective quenching constants of 9,10-dipropyl-, 9,10-dichloro-, and 9,10-dibromoanthracene by naphthalene are $<10^7$, 2×10^7, and 5×10^8 M^{-1} sec^{-1}) led to their postulation that the quenching process is due to the following spin-forbidden energy-transfer process.

$$\text{Donor}(S_1) + \text{Acceptor}(S_0) \longrightarrow$$
$$\text{Donor}(S_0) + \text{Acceptor}(T_1)$$
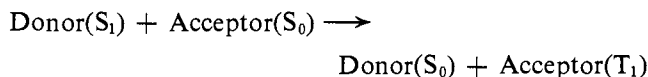
They further suggested that our sensitized reactions of acceptors in solution[3a,c] and phosphorescence of naphthalene in crystal[3b] are due to similar energy-transfer processes. On the other hand, several papers have also since appeared describing triplet-triplet energy transfer from higher triplet states of several other aromatic hydrocarbons which are populated by the two-photon excitation method.[5]

We noticed that Ermolaev's explanation of our anthracene-sensitized results failed to consider all the reported evidence; solution studies are usually performed in a concentration range where singlet quenching is not significant[3a,c] and 9,10-diphenylanthracene failed to sensitize phosphorescence of naphthalene as efficiently as anthracene.[3b] Nevertheless, we carried out additional definitive experiments to clarify this point. The results are reported below together with additional information on the higher excited states of anthracenes.

Results and Discussion

S_1 Quenching and T_2 Sensitization. The postulated spin-forbidden energy-transfer process demands that singlet quenching be accompanied by the formation of acceptor triplets. In the study by Ermolaev and Sveshnikova, triplet formation was not demonstrated but only inferred from other observations.[4] In fact, because of the possibility of a subsequent triplet-triplet energy-transfer process,[3b] demonstration of acceptor triplet formation in solution by spectroscopic methods will be difficult. Such complications, however, can be avoided by the use of acceptor systems capable of undergoing rapid chemical reactions. The system chosen for this study is 1,3-cyclohexadiene which is known to form characteristic triplet dimers at high efficiency[6] and also known to quench fluorescence of several aromatic hydrocarbons.[7]

Similar to Ermolaev's observation, we found that cyclohexadiene quenches fluorescence of various anthracenes with efficiencies increasing with the mass of substituents: quenching constants for 9,10-diphenyl-, 9,10-dichloro-, and 9,10-dibromoanthracene being 1.20, 1.35, and 2.06 $\times 10^6$ M^{-1} sec^{-1}, respectively. But, this enhancement of singlet quenching does not lead to increased triplet yield of cyclohexadiene. In fact, measurements of the quantum yield of dimers show a decrease in triplet yield in the concentration range where singlet quenching is most significant. The results are shown graphically in Figure 1 (solid line), expressed in reciprocals of quantum yield and diene concentration for ready Stern-Volmer analysis. In the low concentration region, the quantum yield of the reaction increases with an increase of diene concentration. The linear dependence of $1/\phi$ and $1/A$ is expected for a mechanism involving competing steps of energy transfer from anthracene T_2 and internal conversion from the same state.[8] (It has been established that in the concentration range for the current study cyclohexadiene triplet adds to form dimers at efficiency close to

(1) This is paper VII in the series "The Role of Second Triplet State in Solution Photochemistry;" for part VI see: K. S. Y. Lau, R. O. Campbell, and R. S. H. Liu, *Mol. Photochem.*, **4**, 315 (1972).

(2) (a) NDEA predoctoral trainee, 1970–1973; (b) Alfred P. Sloan Research Fellow, 1970–1972.

(3) (a) R. S. H. Liu and J. R. Edman, *J. Amer. Chem. Soc.*, **90**, 213 (1968); (b) R. S. H. Liu and R. E. Kellogg, *ibid.*, **91**, 250 (1969); (c) R. S. H. Liu and J. R. Edman, *ibid.*, **91**, 1492 (1969).

(4) V. L. Ermolaev and E. B. Sveshnikova, *Opt. Spectrosc. (USSR)*, **29**, 324 (1970).

(5) (a) M. V. Alfimov, I. G. Batekha, and V. A. Smirov, *Dokl. Akad. Nauk SSSR*, **185**, 626 (1969); (b) M. V. Alfimov, I. G. Batekha, Yu. B. Sheck, and V. I. Gerko, *Spectrochim. Acta, Part A*, **27**, 329 (1971).

(6) D. Valentine, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5202 (1964); G. S. Vesley and G. S. Hammond, manuscript in preparation.

(7) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968).

(8) For a complete reaction scheme and the Stern–Volmer equation see ref 3c.

unity.)[6] Singlet quenching becomes a dominant process (dotted line) when diene concentration exceeds ~0.5 M. But instead of increasing product yield it leads to a rapid decrease of dimer yield upon further increase of diene concentrations.[9] Therefore, it is clear that singlet quenching and triplet sensitization in this system are two independent processes, thus clearly ruling out the applicability of the Ermolaev energy-transfer process.

It should be noted that many other cases of singlet quenching leading to reduction of triplet reaction of acceptors are known in the literature, for example, the first definitive study by Stephenson and Hammond on quenching of naphthalene fluorescence by dienes[7] and in other reports.[10] Although it is tempting to conclude from these results, combined with the present results, that the spin-forbidden energy-transfer process is generally not an important one in sensitized reactions in solution, they are clearly not sufficient to rule out its possible occurrence in selected systems under properly chosen conditions. In fact, in several recent spectroscopic studies of energy-transfer processes in solids, including cases with donors without low-lying second triplet states, the formation of acceptor triplets is again attributed to such a spin-forbidden process (in fact coined as intermolecular intersystem crossing).[11] In one case, the rate for such a process was determined and indeed, in agreement with a spin-forbidden process, it is very slow ($\sim 10^5$ M^{-1} sec^{-1}).[11b]

T_2 of Substituted Anthracenes. Using the chemical kinetic approach we determined the average lifetime of the second triplet state of 9,10-dibromoanthracene (DBA): 2.2×10^{-10} sec.[3c] We have now extended similar studies to several other anthracenes, 9,10-dichloro- (DCA), 9,10-diphenyl- (DPA), and 9-phenyl- (PA), using geometric isomerization reaction of *trans*-1,3-pentadiene (*t*-P)[3c] and the internal cycloaddition reaction of *endo*-dicyclopentadienone (EDP)[12] for monitoring the transfer process.
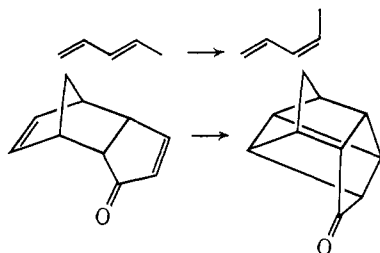
Product yields are analyzed by the use of the Stern–Volmer equation derived from schemes similar to the one reported previously.[3c] Thus, from values of the slope of lines in plots of reciprocals of quantum yields of products *vs.* reciprocal of acceptor concentrations, rate constants of internal conversion ($T_2 \rightarrow T_1$) of
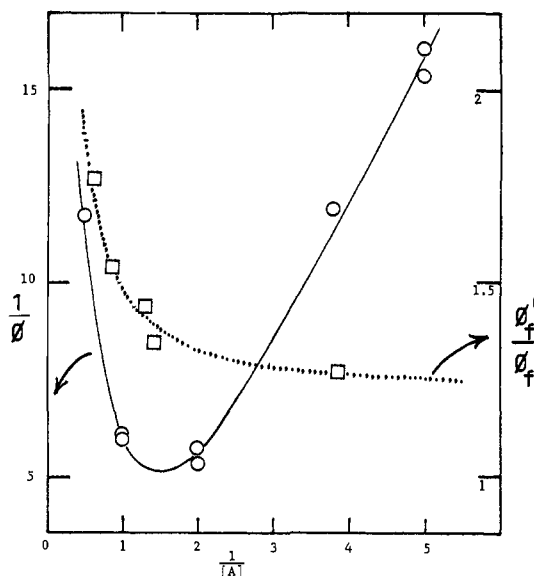

Figure 1. Quantum yield of the dibromoanthracene-sensitized dimerization of 1,3-cyclohexadiene (O) and the relative quantum yield of fluorescence of DBA in the presence of the diene ($\square$).

anthracenes are calculated and from the intercept values the reciprocals of relative intersystem crossing efficiencies (1/a). These values are listed in Table I.

Table I. Average Lifetimes of T_2 States and Intersystem Crossing Efficiencies of Substituted Anthracenes

Donor	Acceptor	$k_{ic} \times$ 10^{-9},[a] sec^{-1}	$\tau_{T_2} \times$ 10^{10}, sec	Rel 1/a[b]
PA	*t*-P	Reaction		
	EDP	3.5	2.9	1.6 (1.5)[c]
PA-d_{10}	EDP	3.3	3.1	1.2
DCA	*t*-P	1.8	5.6	
	EDP	3.3	3.0	1.7 (1.7)[d]
DBA	*t*-P	4.9	2.0	
	EDP	5.1	2.0	1.0 (1.0)[d]
DPA	EDP	4.8	2.1	1.6 (4.0)[e]

[a] k_{ic} = slope/k_t = slope/k_D = slope/(5×10^9). [b] Ratio of intercept values; DBA as standard. [c] A. R. Horrocks, T. Medinger, and F. Wilkinson, *Photochem. Photobiol.*, **6**, 21 (1967). [d] See ref 3c. [e] W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).

There is little difference between the values of average T_2 lifetimes of the four substituted anthracenes. This result is perhaps not surprising because the energy gaps between T_1–T_2 states are not expected to differ significantly. For parent anthracene this value is reported to be 31.9 kcal/mol.[13] Similar values for the substituted anthracenes are not known but can be estimated from the energy of S_1[14] and T_1[15] states and their spectroscopic[16] and chemical behavior:[3c] ~30, 31, 30, and 30 kcal/mol for DBA, DCA, DPA, and PA. The relative reciprocal intersystem crossing efficiency values obtained in this way with DBA as standard (Table I) match well, in the cases of DCA and PA,

(9) A similar curve was obtained in studies of the benzanthracene T_1-sensitized dimerization of 1,3-cyclohexadiene: G. S. Vesley, Ph.D. Thesis, submitted to California Institute of Technology, 1966; G. S. Vesley and G. S. Hammond, presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(10) See, *e.g.*, P. S. Engel and B. M. Monroe, *Advan. Photochem.*, **8**, 245 (1971).

(11) (a) G. Vaubel, *Chem. Phys. Lett.*, **9**, 51 (1971); (b) H. Zimmerman, D. Stehlile, and K. H. Hausser, *ibid.*, **11**, 496 (1971); (c) G. Vaubel and H. Baessler, *ibid.*, **11**, 613 (1971).

(12) Ring closure by direct irradiation is known: R. C. Colson, J. Hudec, and R. O. Williams, *Tetrahedron Lett.*, 29 (1960); W. L. Dilling, *Chem. Rev.*, **66**, 384 (1966); we found the reaction also proceeds under triplet-sensitization conditions.

(13) R. E. Kellogg, *J. Chem. Phys.*, **44**, 441 (1966).

(14) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1971.

(15) (a) S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964); (b) $E(T_1)$ for PA = 41.6 kcal/mol: R. O. Campbell, unpublished results.

(16) R. G. Bennett and P. J. McCartin, *J. Chem. Phys.*, **44**, 1969 (1966).

with values calculated from reported absolute quantum yields of these compounds (in parentheses in Table I). The value for DPA deviates significantly from that reported. There are several possible causes for this increased triplet yield, and the case is being studied in more detail.[17]

We noted previously that deuteration at outer rings as in perdeuterio-DBA failed to give an enhancement of T_2 lifetime.[3c] The result with PA-d_{10} now shows that deuteration at C_{10} also does not have a significant effect on the T_2 lifetime. There is, however, a definite increase in its intersystem crossing efficiency.

Experimental Section

Fluorescence Quenching. Fluorescence spectra was recorded on a Hitachi Perkin-Elmer MPF-2 spectrometer. Quenching constants were determined from Stern-Volmer plots of relative fluorescence intensities (ϕ_f^0/ϕ_f) vs. quencher concentrations. Results of

a representative case of the DBA–cyclohexadiene system are shown in Table II.

Quantum Yield Measurements. Degassed samples were prepared in the usual manner[3c] and irradiated in a "merry-go-round" apparatus.[18] Conditions of irradiation and glc conditions for product analysis for each system are shown in Chart I. In the last case in Chart I only relative quantum yields were determined. They are shown in Table III.

Chart I

	Irrad wave-length, Å	Glc conditions for analysis	Actinometer
Cyclohexadiene	3600	10 ft 30% PEG column 130° (monomer) 230° (dimer)	$Ph_2C{=}O$ + cis-P
Pentadiene (P)	3600	25 ft 15% TCEP at 40°	$Ph_2C{=}O$ + cis-P
endo-Dicyclo-pentadiene	3800	6 ft 15% FFAP at 190°	None

Table II.[a-c] Fluorescence Quenching of 9,10-Dibromoanthracene by 1,3-Cyclohexadiene (Relative Intensity Units)

[Q], M	ϕ_f^0/ϕ_f
0.00	1.00
0.021	1.18
0.031	1.21
0.063	1.22
0.105	1.25
0.262	1.31
0.704	1.36
0.784	1.46
1.060	1.56
1.150	1.66
1.410	1.77

[a] Excitation wavelength, 3600 Å. [b] [DBA] = 1.07×10^{-3} M. [c] Solvent was benzene.

Table III. Relative Quantum Yields of T_2 Energy Transfer with Dicyclopentadienone[a]

[EDP], M	Product concn,[b] M			
	DBA	DCA	PA	DPA
0.0363	0.0133	0.0164	0.0171	0.0134
0.0726	0.0336	0.0302	0.0354	0.0295
0.1452	0.0534	0.0582	0.0666	0.0514
0.4356	0.1394	0.1254	0.1537	0.1336
1.163	0.2045	0.1737	0.1864	0.1765

[a] [DBA] = 1.18×10^{-3} M; [PA] = 9.90×10^{-4} M; [DCA] = 1.15×10^{-3} M; [DPA] = 1.24×10^{-3} M. [b] All samples irradiated for 16.6 days in a M-G-R quantum yield apparatus with Corning 0-51 and 7-60 filter plates.

(17) An interesting but speculative explanation to the cause of increased intersystem crossing in DPA is the existence of the $S_1 \rightleftarrows T_2$ equilibrium. In the absence of triplet acceptors fluorescence, $S_1 \rightarrow S_0$ is the predominant process, and with a high concentration of acceptors transfer from T_2 becomes competitive resulting in a higher "intersystem crossing value."

(18) F. G. Moses, R. S. H. Liu, and B. Monroe, *Mol. Photochem.*, 2, 245 (1969).

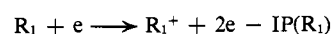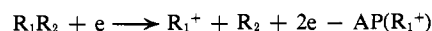# Heats of Formation of Free Radicals by Mass Spectrometry

D. K. Sen Sharma and J. L. Franklin*

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. Received May 21, 1973

Abstract: The appearance potentials and translational energies at onset of CH_3^+ from several hydrocarbons and amines have been determined by electron impact in a sector field mass spectrometer. The translational energy was determined by the deflection method and the total excess energy was computed from it. Very good agreement of the heats of formation of ethynyl, propargyl, allyl, amino, methylamino, and dimethylamino radicals with previous determinations was obtained. Reasonable values were also obtained for the dimethyl allyl, dimethyl propargyl, and CH_2NH_2 radicals, but there were no previous values to which ours could be compared. Results for two more complex radicals appear to be somewhat in error, possibly because of the large correction factor resulting from the large number of vibrational modes.

B ond strengths or free radical heats of formation have often been obtained by determining the appearance potential of an ion formed in a known process and independently measuring the ionization potential of the radical. The bond strength is then taken as the difference between the two measurements. Thus

$$R_1R_2 + e \longrightarrow R_1^+ + R_2 + 2e - AP(R_1^+)$$

$$R_1 + e \longrightarrow R_1^+ + 2e - IP(R_1)$$

$$AP(R_1^+) - IP(R_1) = D(R_1-R_2)$$