Table VI. Apparent Helix Contents of β-Lactoglobulin A in Water–2-Chloroethanol Mixtures

2-Chloroethanol, vol %	Apparent per cent right handed α helix from		
	b_0	H_{193}	H_{225}
0	11	26	11
10	10	26	11
20	36	42	37
30	46	48	45
40	50	53	47
60	53	56	50
80	58	60	52
100	64	65	57

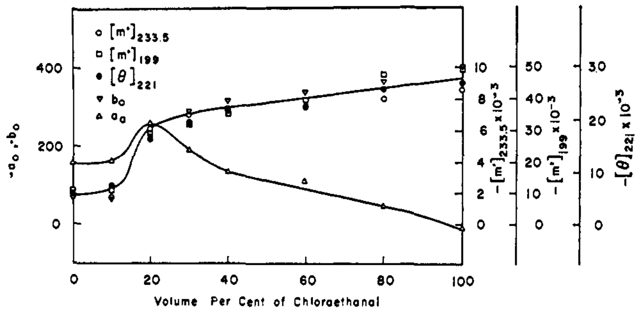

Figure 5. Dependence of a_0, b_0, $[m']_{233.5}$, $[m']_{199}$, and $[\theta]_{221}$ of β-lactoglobulin A on 2-chloroethanol concentration in the mixed solvents of water with 2-chloroethanol.

equation parameters.[57,58] The results are summarized in Table VI. We see that, by all criteria, the apparent contents of α helix increase sharply between 10 and 20% 2-chloroethanol. Above this solvent composition, a slow rise in a α helix contents continues, reaching a maximum of about 65% in pure 2-chloroethanol, in a manner similar to the earlier observations in acidic methanol.[6] Comparison of the H_{193} and H_{225} values obtained in the presence of 2-chloroethanol (Table VI) shows that, according to the criteria of Shechter and Blout,[57] the optical rotatory dispersion properties of β-lactoglobulin in 2-chloroethanol cannot be accounted for in terms of α-helical and unordered regions alone, but that another non-α-helical ordered structure persists. When the S–S bridges in β-lactoglobulin are broken by S-sulfonation, the H_{193} and H_{225} values obtained in methanol become 87 and 88, respectively, indicating the disappearance of the "third" structure; this suggests that there is in this protein a structurally stable region constrained by an S–S bridge. In the earlier study with methanol,[6] the conclusion had been reached that this stable region is rich in β structure. It is interesting to note that the large electrophoretically immobile tryptic peptide of β-lactoglobulin[59] gives an infrared spectrum in the amide I band region typical for an antiparallel-chain pleated-sheet structure.[56]

The dependence of the preferential binding of 2-chloroethanol to β-Lg A on the concentration of the former is very similar to that observed in the case of the water–chloroethanol–bovine serum albumin system.[60] It is, however, quite different from that found with other organic solvents, for example, with β-Lg A in ethylene glycol and methyl Cellosolve,[61] and bovine serum albumin in glycerol.[60] In addition, this concentration dependence of preferential interaction with solvent components does not seem to have any simple relation to the conformational change in β-Lg A induced by the same mixed solvents. Further investigations on the effect of this and other solvent components on several proteins are now in progress.

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(57) E. Shechter and E. R. Blout, *Proc. Natl. Acad. Sci. U. S.*, **51**, 695, 794 (1964).

(58) J. P. Carver, E. Shechter, and E. R. Blout, *J. Am. Chem. Soc.*, **88**, 2562 (1966).

(59) R. Townend, *Arch. Biochem. Biophys.*, **109**, 1 (1965).

(60) J. Stauff and K. N. Mehrotra, *Kolloid-Z.*, **176**, 1 (1961).

(61) H. Inoue and S. N. Timasheff, in preparation.

Communications to the Editor

Reactions of Nonrigid Systems Sensitized by Anthracene and Substituted Anthracenes[1]

Sir:

Evidence has been presented that anthracenes sensitize reactions of rigid systems by energy transfer from their second triplet states.[1] We wish now to report examples of T_2 energy transfer to nonrigid systems where the proposed "nonvertical" excitations[2] are more likely to occur.

The product composition of photosensitized dimerization of butadiene is known to vary with the triplet excitation energy of the sensitizer.[3] With anthracene and 9,10-dibromoanthracene (DBA), the dimer compositions are anomalous in that they agree with those of high-energy sensitizers (>60 kcal/mole).[3] The dimer compositions produced by many other anthracenes (Table I) are likewise anomalous, suggesting sensitization occurs by energy transfer from the T_2 states of the anthracenes.

The photoisomerization of 1,3-pentadiene (piperylene), for which the concept of nonvertical excitation

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(1) The Role of Second Triplet States in Solution Photochemistry. II. For the previous paper in this series, see R. S. H. Liu and J. R. Edman, *J. Am. Chem. Soc.*, **90**, 213 (1968).

(2) See, *e.g.*, G. S. Hammond, *Kagaku To Kogyo* (Tokyo), 18, 1464 (1965).

(3) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, 87, 3406 (1965), and previous papers in the series.

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

Sensitizer	E_T, kcal/mole[b] T_2	T_1	Per cent C_4
Anthracene	74.4	42.5	95, 84[c]
2-Methylanthracene	73.5	40.6	95
9-Methylanthracene	...	40.6	95
9-Methyl-10-chloroanthracene	...	...	92
9-Methyl-10-chloromethyl-anthracene	...	...	95
1,5-Dichloroanthracene	72.6	40.7	94
9,10-Dichloroanthracene	...	40.2	95
9,10-Dibromoanthracene	...	40.2	94, 97[c]
9,9′-Bianthryl	...	...	96

[a] Neat butadiene in Pyrex tubes irradiated around a 200-W Hanovia medium-pressure Hg lamp with Pyrex housing. [b] See literature quoted in ref 1. [c] Reference 3.

was also invoked,[4] was reinvestigated with emphasis on substituted anthracenes (Table II). The anthracenes fail to follow a monotonic decrease of quantum yield with sensitizer energy, suggesting that T_2 of anthracenes is, at least in part, responsible for the observed reaction. Lower values of quantum yields were obtained with double-sensitizer irradiation[1] in which selective population of the lowest triplet state of anthracene was partially achieved, indicating that the T_1 state is not important. The average lifetimes calculated[1] from the Stern–Volmer plots of the donor in the DBA-sensitized isomerization of the isomeric piperylenes are the same within experimental error ($1.1 \pm 0.3 \times 10^{-10}$, $1.5 \pm 0.2 \times 10^{-10}$ sec) and compare favorably with the less accurate value of 2×10^{-11} sec obtained previously.[1,5,6]

Table II. Quantum Yields of Photosensitized Isomerization of Piperylenes[a]

Sensitizer	$\Phi_{c\rightarrow t}$[b]	$\Phi_{c\rightarrow t}$[b]
Benzophenone	0.55 ± 0.01[c]	0.44 ± 0.01[c]
Michler's ketone	0.55 ± 0.01[c]	0.43 ± 0.01[c]
9-Fluorenone	0.74	
Benzanthrone	8.4×10^{-3}	
Acridine	5.4×10^{-3}	
9,10-Dichloroanthracene	1.8×10^{-2}	
9,10-Dibromoanthracene	4.2×10^{-2}	3.2×10^{-2}
9-Methyl-10-bromoanthracene	3.3×10^{-2}	
Benzanthrone (7×10^{-3} *M*) (90)[d] + DBA (1×10^{-3})	5.1×10^{-3}	
Benzanthrone (2.33×10^{-3}) (70[d]) + DBA (1×10^{-3})	1.21×10^{-2}	
Acridine (7×10^{-3}) (80)[d] + DBA (1×10^{-3})	1.82×10^{-2}	
Acridine (2.33×10^{-3}) (60)[d] + DBA (1×10^{-3})	3.08×10^{-2}	

[a] 0.2 *M* piperylene in benzene irradiated in a "merry-go-round" apparatus with Corning 0-52 and 7-60 filters. Michler's ketone sensitized reaction as standard. [b] Not corrected for sensitizer intersystem-crossing efficiency. [c] Reference 4. [d] Per cent of light absorbed by compound indicated.

A common intermediate in all three reactions is clearly indicated. The photostationary state with DBA as sensitizer (% *trans* = 57)[7,8] falls well within the range for sensitizers of energy above 60 kcal/mole.[4]

The photosensitized dimerization[9] of acrylonitrile gives a mixture of *cis*- and *trans*-1,2-dicyanocyclobutanes. The ratio of the product isomers (Table III) varies slightly with the media but is independent of sensitizer, suggesting a common intermediate (triplet acrylonitrile) formed by triplet–triplet energy transfer. The efficiency of the reaction varies in a manner which can best be explained by T_2 sensitization from the anthracenes. Bromine radical has been rigorously excluded as a catalyst for the dimerization. Because of complete failure of fluorenone to sensitize the reaction, the double-sensitizer experiment clearly negates the involvement of T_1 of DBA.

Table III. Photosensitized Dimerization of Acrylonitrile (AN)[a]

Sensitizer	[AN], *M* (solvent)[a]	Dicyano-cyclo-butane (t/c)[b]	ΣΦ[c]
Xanthone	10 (B)	0.8	...
Acetophenone	Neat	0.82[d]	...
Triphenylene	Neat	0.82[d]	...
Benzophenone	Neat	0.84[d]	0.062
	10 (B)	0.8	...
	1.0 (B)	1.3	...
	0.3 (B)	2.33[d]	...
	10 (A)	0.8	...
	1.0 (A)	0.8	...
2-Acetonaphthone	Neat	None	<0.002[f]
1-Acetonaphthone	Neat	None	<0.002[f]
9-Fluorenone	Neat	None[d]	<0.002[f]
DBA	Neat	0.82[d]	0.078
	10 (B)	0.7	...
	1.0 (B)	1.2	...
	0.3 (B)	2.33[d]	...
	10 (A)	0.7	...
	1.0 (A)	0.7	...
(9-Fluorenone + DBA)[e]	Neat	...	0.01
9-Bromoanthracene	Neat	0.9	0.067

[a] Irradiated in Pyrex tubes in a "merry-go-round" apparatus with Dow-Corning 0-52 and 7-60 filters; solvent: benzene (B) or acetonitrile (A). [b] ~10% error, unless specified. [c] Benzophenone–benzhydrol actinometry. Analysis by gc on a silicone gum nitrile column at 175 or 200°. Values not corrected for intersystem-crossing efficiency. [d] Large-scale experiment with ir and nmr identification. [e] 1.67×10^{-2} *M* 9-fluorenone, 6.67×10^{-4} *M* DBA; *ca.* 80% of the light absorbed by 9-fluorenone. [f] Limit of detection.

Other examples[3,4,10] are known for which sensitization by anthracenes closely parallels that of "high-

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

(5) Part of the difference could be due to the choice of k_D, rate constant of diffusion, used in the calculations. Here, with benzene as solvent, k_D is assumed[6] to be 1.0×10^{10} l. mole^{-1} sec^{-1} as compared with 2.0×10^{10} l. mole^{-1} sec^{-1} in previous study in hexane.

(6) F. Wilkinson, *Advan. Photochem.*, 3, 248 (1964).

(7) The fact that DBA failed to produce a stationary state similar to thermal equilibrium distribution of the two isomers (84% *trans*[8]) clearly indicates that radicals resulting from photodissociation of DBA do not affect this reaction significantly.

(8) D. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, 87, 3311 (1965).

(9) (a) This reaction was discovered independently and reported: J. Runge and R. Kache, French Patent 1,470,282, issued to Veb. Chemische Werke Buna (Feb 17, 1967). (b) After this paper was submitted, another independent report appeared: S. Hosaka and S. Wakamatsu, *Tetrahedron Letters*, 219 (1968).

(10) (a) R. S. H. Liu, *J. Am. Chem. Soc.*, **90**, 1899 (1968); (b) J. R. Fox and G. S. Hammond, *ibid.*, **86**, 4031 (1964); (c) C. Walling and M. J. Gibian, *ibid.*, 87, 3413 (1965); (d) A. Cox, P. deMayo, and R. W. Yip, *ibid.*, 88, 4789 (1966); (e) W. L. Dilling, *ibid.*, 89, 2742 (1967); (f) E. F. Ullman and W. A. Henderson, Jr., *ibid.*, **89**, 4390 (1967).

energy" sensitizers. For these cases, involvement of T_2 states should be considered.

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9,10-Dichloroanthracene-Sensitized Isomerization of Stilbenes. The Question of Energy Transfer between Intimately Associated Molecular Pairs[1]

Sir:

The situation existing between the donor–acceptor pair, following transfer from the second triplet state of the donor,[1] appears ideal for further rapid "reversible" energy transfer.

$$\mathrm{D_{T_2} + A_{S_0} \longrightarrow D_{S_0} + A_{T_1} \longrightarrow D_{T_1} + A_{S_0}}$$

Normally, the second transfer would only be reflected in the reduction of quantum yield of the reaction of $\mathrm{A_{T_1}}$; thus its importance is experimentally difficult to determine. However, in stilbenes such quenching is expected to affect their photostationary-state (pss) compositions significantly.[2] We therefore studied this isomerization reaction sensitized by 9,10-dichloroanthracene (DCA = A).

The results can be successfully accounted for by the following scheme in which *only the DCA molecule in the T_2 state acts as donor.*

Excitation

$$\mathrm{A \xrightarrow{h\nu} A_{S_1} \longrightarrow A_{T_2}}$$

Fate of T_2

$$\mathrm{A_{T_2} + t \xrightarrow{k_1} \overline{A + t^*}} \qquad (1)$$

$$\mathrm{A_{T_2} + c \xrightarrow{k_2} \overline{A + t^*}} \qquad (2)$$

$$\mathrm{A_{T_2} \xrightarrow{k_d} A_{T_1}}$$

Fate of $\mathrm{\overline{A + t^*}}$

$$\mathrm{\overline{A + t^*} \xrightarrow{k_3} \overline{A_{T_1} + t} \longrightarrow A_{T_1} + t} \qquad (3)$$

$$\mathrm{\overline{A + t^*} \xrightarrow{k_4} A + t^*} \qquad (4)$$

Fate of t*

$$\mathrm{t^* \xrightarrow{k_5} t} \qquad (5)$$

$$\mathrm{t^* \xrightarrow{k_6} c} \qquad (6)$$

$$\mathrm{t^* + A \xrightarrow{k_7} A_{T_1} + t} \qquad (7)$$

Fate of $\mathrm{A_{T_1}}$

$$\mathrm{A_{T_1} \xrightarrow{k_d'} A}$$

Equation 7 differs from 3 by being diffusive in nature.[3]

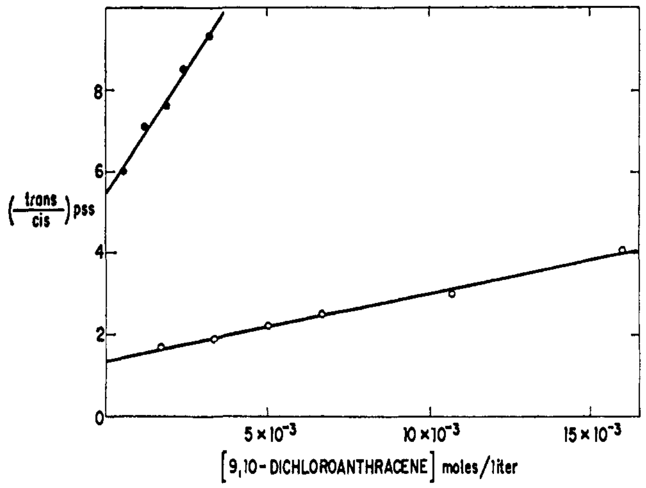

Figure 1. Photostationary-state composition of stilbenes (0.05 *M*) sensitized by 9,10-dichloroanthracene in benzene (○) and 1-propanol (●), irradiated at 26° in a "merry-go-round" apparatus, equipped with a 550-W Hanovia Hg lamp and Corning 0-51 filter.

By assuming a steady-state concentration of the intimately associated molecular pairs, $\mathrm{\overline{A_{T_1} + t}}$, one arrives at an equation relating photostationary-state composition and concentration of DCA.

$$\frac{[\mathrm{t}]_\mathrm{s}}{[\mathrm{c}]_\mathrm{s}} = \frac{k_2}{k_1 k_6}\left(\frac{1}{1 - b}\right)(k_6 b + k_5 + k_7[\mathrm{A}]) \qquad (8)$$

where $b = k_3/(k_3 + k_4)$.

A plot of the isomer ratio at photostationary states, $[\mathrm{t}]_\mathrm{s}/[\mathrm{c}]_\mathrm{s}$, in benzene as solvent (○) (Figure 1) *vs.* DCA concentration gives an excellent linear correlation. The photostationary-state compositions are invariably richer in *trans;* this trend has not been observed previously.[2] The importance of "cage" quenching (eq 3) is evident. The constant *b*, a measure of the extent of t* quenched by the intimately associated anthracene molecule, can be calculated from the intercept with the added assumption that $k_1 = k_2$ and k_5/k_6 (the decay ratio) = 0.67.[2] The value for k_5/k_6 was obtained from the stationary-state composition produced by benzophenone.[4] In benzene $b = 0.28$. In addition, $k_2k_7/k_1k_6 = k_7/k_6$, obtained from the intercept and slope, is a measure of diffusive quenching. The calculated value of 120 ± 12 l./mole agrees well with values from similar studies with azulene as quencher (110–160 l./mole).[2] This result indicates that the quenching constants (k_7) in both cases are the same, and since $E_{\mathrm{T_1}}$ of DCA (40.2 kcal/mole) is much higher than that of azulene (31–39 kcal/mole),[5] it could only imply that they both approach k_D, the rate of diffusion.

The proposed scheme is further substantitated by the following observations. Results of parallel studies (Figure 1) in 1-propanol (●), a more viscous solvent (1.92 cP as compared with 0.616 cP for benzene), give a much larger value for the intercept indicating more molecular-pair quenching (calculated $b = 0.74$).[6]

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[1] The Role of Second Triplet States in Solution Photochemistry. III. For the previous papers in this series, see R. S. H. Liu and J. R. Edman, *J. Am. Chem. Soc.*, **90**, 213 (1968); R. S. H. Liu and D. M. Gale, *ibid.*, **90**, 1897 (1968).

[2] For the effect of a similar type of diffusive quenching uniquely shown in stilbene, *e.g.*, by azulene, see 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**, 3197 (1964).

[3] We have observed a dependence of photostationary-state composition upon the concentration of stilbene. Evidently the present scheme does not accommodate such a dependence. The variation is, however, small over a wide range of stilbene concentration. In order to retain simplicity of the present scheme, and further, considering that the results presented here were carried out at a constant concentration of stilbene, no additional steps were introduced to account for this dependence.

[4] Although the exact T_2 energy level of DCA cannot be determined spectroscopically (see R. G. Bennett and P. J. McCartin, *J. Chem. Phys.*, **44**, 1969 (1966)), based on chemical evidence, we believe its energy is between 68 and 70 kcal/mole.

[5] A. A. Lamola, W. G. Herkstroeter, J. C. Dalton, and G. S. Hammond, *ibid.*, **42**, 1715 (1967).