

triangle. If one were to keep the Co-carbyne bond at its initial distance of 1.87 Å<sup>12</sup> during this process, the individual pairs of Co atoms would be required to separate to 3.24 Å, appreciably beyond the normal bond length.<sup>12</sup> A more classical mechanistic alternative is shown in Scheme II and proceeds through 16- and 18-electron metal centers. Finally, the (superficial?) similarity of the topological changes associated with the deck shifts uncovered in this work to those occurring in carboranes<sup>13</sup> might be mechanistically significant.

(12) J. R. Fritch, K. P. C. Vollhardt, M. R. Thompson, and V. W. Day, *J. Am. Chem. Soc.*, **101**, 2768 (1979).

(13) See R. L. DeKock, T. P. Fehlner, C. E. Housecroft, T. V. Lubben, and K. Wade, *Inorg. Chem.*, **21**, 25 (1982), and references therein.

### Photosensitized Electron-Transfer Reactions. Interception of the Geminate Radical Ion Pair

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Photosensitized electron-transfer reactions such as dimerizations, nucleophilic additions, and rearrangements are usually carried out in polar solvents, which favor the formation of separated radical ions. Indeed, most of these reactions are likely to proceed via the out-of-cage, solvated radical ions.<sup>1</sup> Recently, however, we showed that, in the reaction of phenylacetylene sensitized by 2,6,9,10-tetracyanoanthracene (TCA), the geminate ion pair can be intercepted by a phenylacetylene or an alkylacetylene.<sup>2</sup> This reaction competes with the dissociation into separated ions and the energy-wasting, reverse electron transfer within the geminate pair. Reactions via the intercepted geminate pair may extend the diversity of photochemical electron-transfer reactions because of the difference in reactivities of these intermediates and those of the separated radical ions. Interception of the radical ion pair also offers the potential for increasing the quantum yield of product formation. In this study of the kinetics of the electron-transfer-photosensitized dimerization of 1,1-diphenylethylene (D), we found that interception of the geminate pair plays a central role in this reaction.

We have found<sup>3</sup> that electron-transfer sensitization of D leads to 2 + 2 cyclodimerization in competition with the well-known 2 + 4 cyclodimerization, first reported by Arnold (Scheme I).<sup>4</sup> The product distribution of this reaction is very dependent on the concentration of D, which suggests the involvement of different intermediates. The data presented below strongly support the mechanism outlined in Scheme II, in which the interception of the geminate radical ion pair by D forms a dimeric radical cation in cage with the sensitizer radical anion, S<sup>-</sup>. Reverse electron transfer produces the biradical  $\dot{D}-\dot{D}$ , which reacts differently from the dimeric radical cation,  $\dot{D}-D^+$ , formed from the separated D<sup>+</sup>. Two sensitizers were used in this study, 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA), which have reduction potentials (in CH<sub>3</sub>CN vs. SCE) of -0.89 and -0.45 V, respectively.

According to the proposed mechanism, the quantum yield for the formation of 1 and 2, corrected for incomplete interception

(1) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80 and references therein.

(2) Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* **1980**, 126.

(3) The formation of 1 or a mixture of 1 and 2 depends on the sensitizer used. With DCA as a sensitizer, 1 and 2 are formed in similar amounts. In this reaction the formation of 2, a dehydrodimer, is accompanied by an equal yield of *cis*- and *trans*-dihydrodicyanoanthracene. The details of this reaction will be given in another publication.

(4) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080.

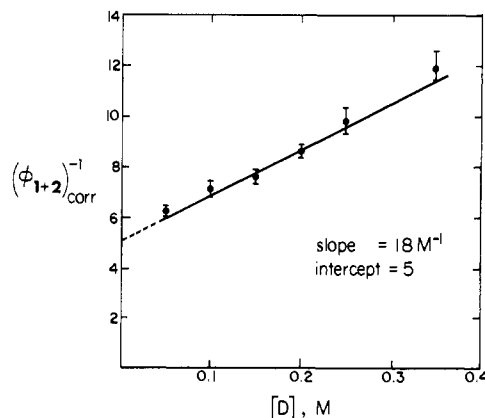
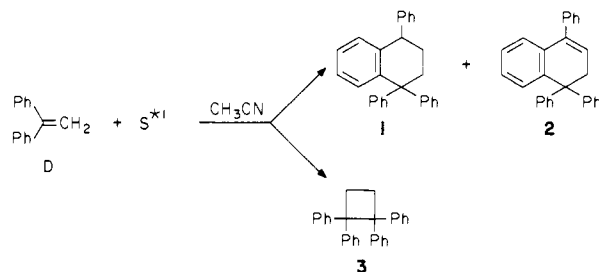
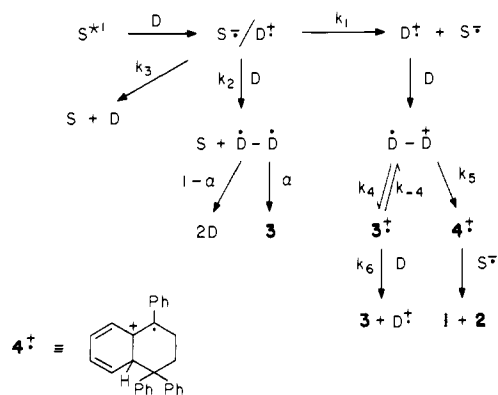


Figure 1. Plot of  $(\phi_{1+2})_{\text{corr}}^{-1}$  vs. [D]. The data were obtained from irradiation ( $\lambda \geq 405$  nm) of saturated solutions of DCA under N<sub>2</sub>.

#### Scheme I



#### Scheme II



of the excited sensitizer,<sup>5</sup>  $(\phi_{1+2})_{\text{corr}}$ , should decrease with increasing [D], as shown by eq 1.

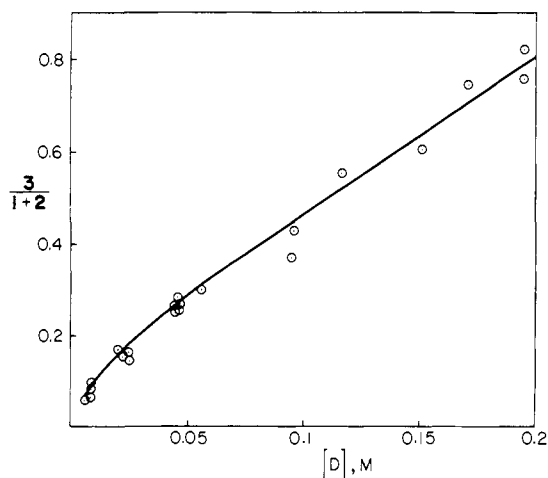
$$\frac{1}{(\phi_{1+2})_{\text{corr}}} = \frac{k_1 + k_3}{k_1} + \frac{k_2}{k_1}[D] \quad (1)$$

A plot of  $1/(\phi_{1+2})_{\text{corr}}$  vs. [D], with DCA as a sensitizer, has an intercept,  $(k_1 + k_3)/k_1$ , of 5 and a slope,  $k_2/k_1$ , of 18 M<sup>-1</sup> (Figure 1). A slight deviation from linearity at low [D] (<0.03 M) is probably due to other reactions of D<sup>+</sup> competing with the dimerization. With TCA as a sensitizer, the quantum yields are much lower,<sup>6</sup> i.e., the ratio  $k_3/k_1$  is higher, and the dependence of  $(\phi_{1+2})_{\text{corr}}$  on [D] is much less, as expected. For TCA,  $(k_1 + k_3)/k_1$  is ca. 28. These values show that, at low [D], the efficiency of formation of separated radical ions from the pair DCA<sup>-</sup>/D<sup>+</sup> is ca. 20% and from TCA<sup>-</sup>/D<sup>+</sup> is 3-4%.

An estimate of  $k_2$  can be obtained from the effect of quenchers on the quantum yields. Using the quencher 1,2,4-trimethoxy-

(5) The Stern-Volmer slopes for the quenching of the fluorescence of DCA and TCA by D in CH<sub>3</sub>CN are 310 and 130 M<sup>-1</sup>, respectively. The lifetimes of the singlet states of these compounds are 19.6 and 15.2 ns, respectively.

(6) The quantum yield  $(\phi_{1+2})_{\text{corr}}$  at [D] = 0.1 is ca. 0.033 for TCA vs. 0.15 for DCA.



**Figure 2.** Plot of  $3/(1+2)$  (analyzed by NMR) vs.  $[D]$ . The data were obtained from irradiations ( $\lambda \geq 405$  nm) of saturated solutions of DCA or TCA under  $N_2$ . The concentration of D decreased by ca. 0.003 M during the irradiation. The points are placed at the average of the starting and final concentrations. The curve is calculated from  $3/(1+2) = 3.3[D] + 0.15[D]/([D] + 0.015)$ .

benzene, which has a lower oxidation potential than D, and correcting for its competing reaction with  $S^{*1}$ , we observed inefficient quenching of dimerization, which suggests that  $k_2$  is almost diffusion controlled (ca.  $10^{10} M^{-1} s^{-1}$ ). This means that  $k_1$  is  $5-6 \times 10^8 s^{-1}$ , which is well within the expected range.<sup>7</sup> Accordingly, the reaction constant for the reverse electron transfer,  $k_3$ , is  $\sim 2.2 \times 10^9 s^{-1}$  for  $DCA^-/D^{*+}$  and  $\sim 1.5 \times 10^{10} s^{-1}$  for  $TCA^-/D^{*+}$ .

According to the proposed mechanism, the ratio  $3/(1+2)$  should increase with  $[D]$ , as shown by eq 2,<sup>8</sup> and is likely to be

$$\frac{3}{1+2} = \frac{\alpha k_2}{k_1} [D] + \frac{k_4}{k_5 k_{-4}/k_6 + [D]} [D] \quad (2)$$

similar with DCA and TCA. Indeed, similar dependence of the ratio on  $[D]$  was obtained with both sensitizers (Figure 2).

The reversible formation of the cyclobutane radical cation,  $3^{*+}$ , and the proposed electron transfer from D to  $3^{*+}$  were incorporated into the mechanism in order to account for the deviation from linearity of the plot of  $3/(1+2)$  vs.  $[D]$  at low concentrations of D.<sup>9</sup> The data in Figure 2 fit a curve obtained by use of the following sets of constants in eq 2:  $\alpha k_2/k_1 = 3.3$ ;  $k_4/k_5 = 0.15$ ;  $k_{-4}/k_6 = 0.015$ . From the value of 3.3 for  $\alpha k_2/k_1$  and the ratio  $k_2/k_1$ , which was shown above to be ca. 18,  $\alpha$  is estimated to be 0.18.<sup>8</sup> In spite of this low efficiency for cyclization, the quantum yield of cyclobutane formation increases steadily with increasing  $[D]$  because interception of the geminate pair competes with the energy-wasting reverse electron transfer, which is the major reaction path for the geminate pair. From the ratio  $k_{-4}/k_6$ , which can have considerable error,  $k_{-4}$  can be estimated by assuming that  $k_6$  is diffusion controlled ( $1.5 \times 10^{10} M^{-1} s^{-1}$ ), i.e.,  $k_{-4}$  is  $2-3 \times 10^8 s^{-1}$ .

(7) Schulten, K.; Staerk, H.; Weller, A.; Werner, H. J.; Nickel, B. Z. *Phys. Chem. Wiesbaden* **1976**, *101*, 371. Weller, A. *Ibid.* **1982**, *130*, 129. See also ref 2.

(8)  $\alpha$  is the overall efficiency of dimerization via the intercepted geminate pair. The energy-wasting steps along this path are the cleavage of the biradical and/or reverse electron transfer in the intermediate  $S^-/D^{*+} \cdots D$ . The latter process is not shown in the scheme.

(9) The involvement of similar chain propagation steps is frequently encountered in cyclobutadimerization whenever the oxidation potential of the dimer is higher than that of the monomer.<sup>10</sup> The cyclobutane **3** does not quench the fluorescence of DCA, which shows that this condition applies for the present system. There are also several examples of reversible cyclizations<sup>11</sup> analogous to  $D-D^{*+} = 3^{*+}$ .

(10) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.

(11) Ledwith, A. *J. Chem. Soc. C* **1970**, 2508. Evans, T. R.; Wake, R. W.; Jaenicke, O. In "The Exciplex"; Gordon, M.; Ware, W. R., Eds.; Academic Press: New York, 1975; p 345. Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5265 and references therein.

Strong support for the proposed mechanism of interception of the geminate radical ion pair was obtained by irradiation in the presence of biphenyl (BP). Electron transfer to  $TCA^{*1}$  from both D and BP is exothermic and proceeds, as judged by fluorescence quenching, at the diffusion-controlled rate. Thus, both compounds compete for the excited sensitizer. BP has higher oxidation potential than D, so electron transfer from D to  $BP^{*+}$ , being exothermic, should be an efficient reaction leading to  $D^{*+}$ . Since this process circumvents the geminate pair  $S^-/D^{*+}$  and leads directly to  $D^{*+}$ , the ratio  $3/(1+2)$  would be expected to decrease with increasing  $[BP]$  and to level off at a value corresponding to the products formed from the out-of-cage reactions.

The results agree well with this prediction. For example, the ratio  $3/(1+2)$  at  $[D] = 0.05$  M decreases from ca. 0.29 in the absence of BP to ca. 0.23 at 0.05 M, 0.20 at 0.1 M, and 0.15 at 0.4 M BP.<sup>12</sup>

The data presented here show that the interception of the geminate pair leads to the biradical  $D-D$ , which cyclizes predominantly or exclusively to the cyclobutane, whereas the radical cation  $D-D^{*+}$ , from the out-of-cage reaction, undergoes 1,4- and 1,6-cyclization in the ratio of only 0.15:1.0.<sup>13</sup> This study has also shown that the reaction constant for the reverse electron transfer in the geminate radical ion pair seems to decrease with increasing energy content stored in the radical ion pair, i.e., with increasing exothermicity of the reaction. We are evaluating this phenomenon in related reactions and also the structure of the interceptable geminate pair. These points will be discussed in a future publication.

**Acknowledgment.** We thank Professor Jack Kampmeier of the University of Rochester for helpful discussions.

**Registry No.** 1, 41977-31-5; 2, 72805-46-0; 3, 84537-61-1; D, 530-48-3.

(12) The efficiency of ion separation from the pair  $TCA^-/BP^{*+}$  is ca. 1.6 times higher than that of the  $TCA^-/D^{*+}$  pair, as judged by an increase in  $\phi_{1+2}$  with increasing  $[BP]/[D]$ .

(13) In the electron-transfer-sensitized photooxygenation of D, the biradical  $D-D$  and the radical cation  $D-D^{*+}$  are intercepted by  $O_2$  forming 3,3,6,6-tetra-phenyl-1,2-dioxane.<sup>14</sup>

(14) This dioxane was reported first by Haynes: Haynes, R. K.; Probert, M. K. S.; Wilmot, J. D. *Aust. J. Chem.* **1978**, *31*, 1737.

### Aggregation of the Bacteriochlorophylls c, d, and e. Models for the Antenna Chlorophylls of Green and Brown Photosynthetic Bacteria

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Chlorophylls and bacteriochlorophylls function *in vivo* as antenna and phototraps that harvest light and provide the source of chemical oxidants and reductants that drive the biochemistry of photosynthetic organisms.<sup>1</sup> The visible absorption spectra of (bacterio)chlorophylls *in vivo* are often significantly red shifted relative to those of monomeric species *in vitro*.<sup>2</sup> A considerable

(1) (a) Clayton, R. K.; Sistrom, W. R., Eds. "The Photosynthetic Bacteria"; Plenum Press: New York, 1978. (b) Govindjee, Ed. "Bioenergetics of Photosynthesis"; Academic Press: New York, 1975. (c) Olson, J. M.; Hind, G. *Brookhaven Symp. Biol.* **1976**, *28*.

(2) Katz, J. J.; Norris, J. R.; Shipman, L. L., ref 1c, pp 15-66. Cogdell, R. J.; Thornber, J. P. *Ciba Found. Symp.* **1979**, *61*, 61-79. Thornber, J. P.; Trospen, T. L.; Strouse, C. E., ref 1a, pp 133-160.