Photoinduced Ternary Electron Transfer Reactions: a Novel Application to Electron Transfer Sensitization

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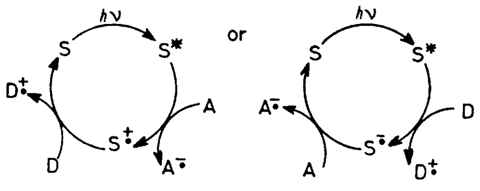
Summary Three examples of electron transfer sensitization in which aromatic hydrocarbons are photoexcited and recycled as electron carriers have been demonstrated.

Photosensitization by two successive electron transfer processes, as shown in Scheme 1, provides a new principle of electron transfer sensitization. This possibility has been pointed out based on the observation that photodecomposition of pyrene is almost completely inhibited in the presence of electron donors and acceptors.[1] The principle of a ternary electron-transfer system is not entirely new. The photocatalytic effect of azulene on the photoreduction of dyes by allylthiourea or ascorbic acid[2] falls into this category of reactions, the recycling component being azulene which is not a photoabsorber and, consequently, not a sensitizer. The mechanism of photodimerization of 1,2-diphenylcyclopropane-3-carboxylate sensitized by two acceptors[3] can be compared with the present systems on the assumption that the triplet state of the cyclopropane is produced from the relevant cation radical.



Scheme 1

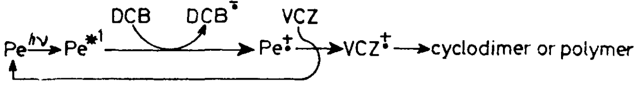
No attempt has been made to use the ternary electron-transfer systems as electron transfer sensitizers involving recycling of photoabsorbing species to induce ionic reactions. We now present three examples.

(i) The sensitization of photocyclodimerization and/or photopolymerization of *N*-vinylcarbazole (VCZ) in the presence of 1,4-dicyanobenzene (DCB) is known to proceed by a cation radical chain mechanism.[4] The results are given in Table 1. Irradiation at 435 nm is selectively absorbed by perylene (Pe). Although Pe could act as a photosensitizer even in the absence of DCB, the addition of DCB, which does not participate in photoabsorption, considerably enhances the product yield. The rapid photodecomposition of Pe in the presence of DCB is retarded in the ternary system VCZ–DCB–Pe in acetone as shown in the Figure. The overall sensitizer efficiency (*i.e.* product per consumed Pe) is over 8000. Similar results were obtained in methanol and acetonitrile in which the reaction is heterogeneous. These results indicate that the reaction proceeds as shown in Scheme 2.

TABLE 1. Sensitized photocyclodimerization of VCZ in acetone.[a]

Irradiation nm	Pe–VCZ–DCB	Pe–VCZ	VCZ–DCB	VCZ
435	**48**^{b}(**24**^{c})	**8**^{b}(**4**^{c})	0(0)	—
365	—	—	**30**^{b}(**21**^{c})	**30**^{b}(**5**^{c})

[a] Conditions: [VCZ] = 0·2 M, [Pe] = 2 × 2 × 10^{-5} M, [DCB] = 5 × 10^{-4} M, monochromatic irradiation for 16 min at room temperature. [b] Yield (%) of 1,2-dicarbazolylcyclobutane, aerated system. [c] Yield (%) of polyVCZ, evacuated system.



SCHEME 2

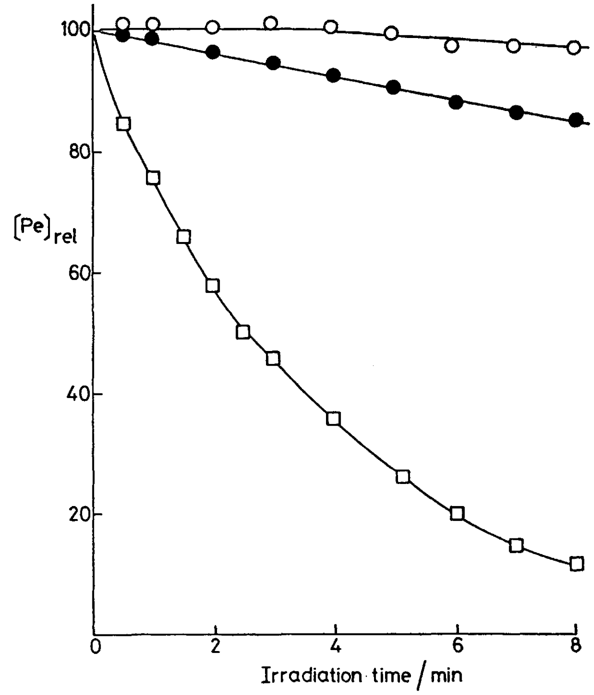


FIGURE. Photodecomposition of perylene: [Pe] = 2 × 10^{-5} M in acetone, aerated system; irradiation at 435 nm. ○, [VCZ] = 0·2 M; □, [DCB] = 5 × 10^{-4} M; ●, [VCZ] = 0·2 M, [DCB] = 5 × 10^{-4} M.

(ii) Irradiation of the *NN*-diethylaniline (DEA) (2 × 10^{-2}M)–CBr_4 (5 × 10^{-2}M)–MeCN system at 435 nm sensitized by Pe (2 × 10^{-5}M) results in immediate colour development showing maximum absorption at *ca.* 630 nm. When any one of the three components, Pe, CBr_4, and DEA, is omitted, no colour-developing reaction occurs. The direct excitation of the DEA–CBr_4 system at 285 nm produces similar blue-green colouration showing maximum absorption at *ca.* 630 nm. The fast photodecomposition of Pe in the presence of CBr_4 is also retarded when DEA is added. The formation of a triarylmethane dye by the photoinduced electron-transfer process[5] is thus catalysed by Pe.

(iii) In photopolymerization of the acrylonitrile (AN)–styrene (S)–pyrene (Py)–*NN*-dimethylaniline (DMA)–dimethylformamide (DMF) system on irradiation at >300 nm *in vacuo* (Table 2), the photoenergy is mostly absorbed by Py and the anion radicals of Py produced by electron transfer from DMA are responsible for initiating polymerization. The copolymer composition analysis indicates the participation of anionic propagation to some extent when both Py and DMA are present. When either Py or DMA is omitted, slow polymerization is still observed. However, the contribution of anionic propagation is negligible indicating different reaction mechanisms. The use of anthracene in the place of Py gave comparable results.

TABLE 2. Sensitized photopolymerization of AN–S in DMF.[a]

	Py–DMA	Py	DMA
Polymer yield (%)	9·5	2·9	5·4
AN–(AN+S) (%) in polymer[b]	55·4	44·3	46.9

[a] Conditions: [Py] = 8 × 10^{-4} M, [DMA] = 4 × 10^{-3} M, AN–S (1:1) 1 ml per 5 ml solution. Irradiation by a 300 W high pressure Hg lamp through a Pyrex filter for 1·5 h at room temperature. Polymer is not formed in the absence of Py and/or DMA. [b] The composition calculated for radical copolymerization [r_{AN} = 0·04, r_S = 0·04 (G.E. Ham, 'Copolymerization,' Interscience, New York, 1964, p. 778)] is 42·6%.

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[1] S. Tazuke and K. Sato, *J. Phys. Chem.*, 1976, **80**, 1727.

[2] M. Hafner, U. Steiner, S. Schreiner, and H. E. A. Kramer, *Z. phys. Chem.*, 1973, **86**, 220; U. Steiner, M. Hafner, S. Schreiner, and H. E. A. Kramer, *Photochem.* and *Photobiol.*, 1974, **19**, 119.

[3] S. Farid and K. A. Brown, *J.C.S. Chem. Comm.*, 1976, 564.

[4] A. Ledwith, 'Exciplex,' eds. M. Gordon and E. R. Ware, Academic Press, New York, 1975, p. 209; Y. Shirota, K. Tada, M. Shimizu, S. Kusabayashi, and H. Mikawa, *Chem. Comm.*, 1970, 1110.

[5] J. Kosar, 'Light-Sensitive Systems,' Wiley, New York, 1965, Ch. 8.