Electron Transfer Sensitization. II. Photo-cyclodimerization and -polymerization of *N*-Vinylcarbazole[1)]

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Photoinduced ternary electron transfer reactions have been demonstrated in the system of perylene(Pe)-1,4-dicyanobenzene(DCB)-*N*-vinylcarbazole(VCZ) in acetone. Photoexcited perylene was recycled *via* two successive electron transfer reactions while VCZ-cyclodimer and/or -polymer were obtained in good yields. Quantum yields for VCZ-cyclodimer and -polymer formation were larger in the electron transfer sensitization system in comparison with the other reaction systems such as in the Pe–VCZ or the VCZ–DCB system. The photocatalytic effect of the electron transfer sensitization was clearly confirmed in the present system, by estimating the overall sensitizer efficiency as over 8000 although chain propagation steps of VCZ cation radical are involved in the present reaction processes.

The role of photosensitizer in photochemistry is unequivocally of primary importance. In the original meaning of photosensitizer(S), S is recycled by repeating photoabsorption and energy transfer to substrates.[2)] In view of utilizing low energy photons to initiate reactions *via* energy transfer processes, singlet sensitizers are by no means significant since the photoirradiation of sensitizers in a shorter wavelength region than the absorption of the substrates to be excited is required. Another category of photosensitization is the electron transfer sensitization consisting of at least two successive electron transfer processes. Although the number of examples are still limited, the most elegant example is the electron transport system in photosynthesis. It is consequently anticipated that the principle of the electron transfer sensitization will be widely applied to drive various one electron transfer redox reactions. Recently, some examples have been reported by several authors demonstrating such as dimerization of ethylenic compounds,[3)] photochemical addition of furans to electron-rich olefines,[4)] and photochemical cleavage of indene dimers,[5)] in addition to our preliminary report.[1)]

In the present article, we applied electron transfer sensitization to the Pe–DCB–VCZ system in polar media. Since VCZ cation radical is known to be the precursor of *trans*-1,2-di-9-carbazolylcyclobutane and the polymer,[6)] we expected that photo-cyclodimerization and/or -polymerization of VCZ were efficiently conducted in the electron transfer sensitization system while perylene was recycled as an electron carrier.

Experimental

Materials. Perylene (Tokyo Kasei, G. R. grade) was used without further purification. 1,4-Dicyanobenzene (Tokyo Kasei, G. R. grade) and *N*-vinylcarbazole (Koch Light Co.) were purified by several recrystallization from ethanol and hexane, respectively. Acetone was refluxed over $KMnO_4$ for several hours followed by drying over $MgSO_4$, and then distilled. Tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were dried over appropriate drying agents and then distilled before use.

Procedure. Absorption spectra were measured by a Hitachi Spectrophotometer EPS-III. The photoreactions were carried out in a quartz cell, under the conditions of monochromatic irradiation using a JASCO Spectroirradiator CRM-FA. After photoirradiation, the reaction mixture was evaporated to dryness under reduced pressure, and then 50 ml of methanol was added. The reaction mixture in methanol was stirred vigorously and insoluble precipitates were filtered off. The precipitates were dried *in vacuo* thoroughly and then weighed. The precipitates (VCZ-cyclodimer or -polymer) were analyzed by the usual accepted procedures (IR, mp, and NMR).[7)] The light intensities for quantum yield measurements were determined by a Hatchard-Parker actinometer.[8)]

Results and Discussion

Photodecomposition of Perylene. The absorption spectra of the reaction components are shown in Fig. 1. In the Pe–DCB–acetone system, perylene was photodecomposed readily when perylene was irradiated. However, if VCZ which did not participate in photoabsorption was added to the reaction system (*i.e.* Pe–DCB–VCZ system in acetone), photodecomposition of perylene was greatly retarded (Fig. 2a). The same phenomena have been observed in the systems of pyrene–diethyl terephthalate and of pyrene–diethyl terephthalate–*N,N*-dimethylaniline in polar media.[9)] Since photoinduced electron transfer processes in elec-

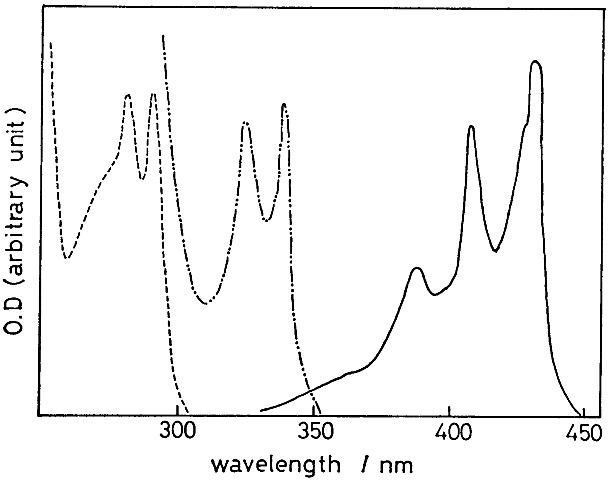


Fig. 1. Absorption spectrum in acetone.
Pe: (——), VCZ: (—‧‧—‧‧—), DCB: (----).

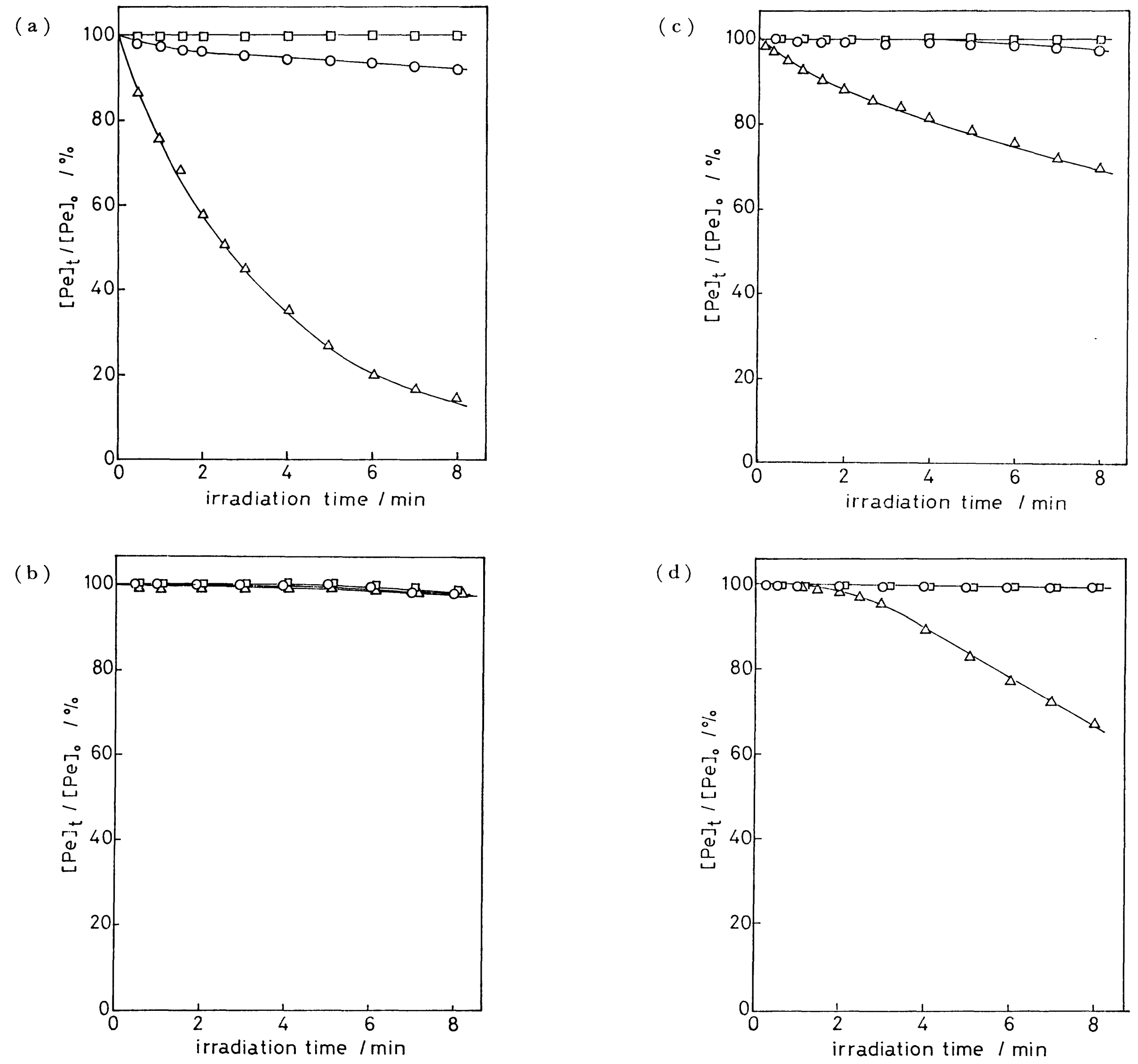
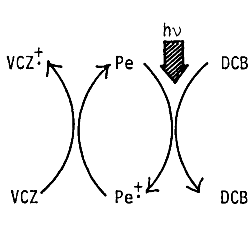
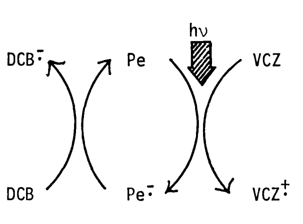


Fig. 2. Photodecomposition of perylene in various solvents. Perpendicular axis is a relative concentration of perylene(%).
Pe–VCZ–DCB: (○), Pe–VCZ: (□), Pe–DCB: (△), [Pe]=5×10^{-5} mol dm^{-3}, [VCZ]=0.2 mol dm^{-3}, [DCB]=5×10^{-4} mol dm^{-3}, irradiated at 435 nm in aerated conditions. a) In acetone, b) in THF, c) in DMF, d) inDMSO.

tron donor-acceptor systems in polar media are well established,[10] the results were interpreted by assuming two successive electron transfer reactions. In the present reaction system (Pe–DCB–VCZ), the reaction schemes are given as below. Namely, the successive electron transfer between perylene anion radical or cation radical and DCB or VCZ, respectively, brings about the recovery of perylene molecule, and then the photodecomposition of perylene is suppressed. In other words, perylene is recycled *via* two successive electron transfer reactions, and consequently perylene acts as an electron carrier. These mechanisms are called as "electron transfer sensitization" being contrasted to the conventional energy transfer sensitization.



Scheme 1.



Scheme 2.

The free energy change for the electron transfer between the excited singlet state of perylene (Pe^{*1}) and DCB or VCZ, calculated from Eq. 1 (E(D$^+$/D) and E(A/A$^-$) are oxidation potential of an electron donor and reduction potential of an electron acceptor, respectively. $e^2/\varepsilon r$ is the Coulombic term and $\Delta E_{0\text{-}0}$ is the 0.0-band energy for the photoexcited species(Pe)),[11] is −38.5 or +5.9 kJ/mol, respectively.

$$\Delta G = E(\mathrm{D^+/D}) - E(\mathrm{A/A^-}) - e^2/\varepsilon r - \Delta E_{0\text{-}0} \qquad (1)$$

These values suggest that the electron transfer between Pe^{*1} and DCB proceeds with a nearly diffusion controlled rate whereas that between Pe^{*1} and VCZ is a rather slow process ($\approx 10^8$ dm^3 mol^{-1} s^{-1}); as being expected from the results reported by D. Rehm and A. Weller.[12] Consequently, Scheme 1 is considered as the main reaction path with a minor contribution of Scheme 2.

In the Pe–DCB system, the rapid photodecomposition of perylene is attributed to unstable perylene cation radical which is formed by the electron transfer between Pe^{*1} and DCB. On the other hand, the result that perylene is scarcely photodecomposed in the course of photoirradiation in the Pe–VCZ system requires some comments. We consider that the electron transfer between Pe^{*1} and VCZ occurs to produce perylene anion radical, since perylene is a weak but definite sensitizer for photoreactions of VCZ as shown in the next section. However, under aerobic conditions, perylene anion radical will be oxidized by oxygen to reproduce perylene molecule as shown below.

$$Pe^{\cdot-} + O_2 \longrightarrow Pe + O_2^{\cdot-} \qquad (2)$$

The elctron transfer from perylene anion radical to oxygen is a highly exothermic process so that we consider that the reaction in Eq. 2 occurs efficiently.[13]

The photodecomposition of perylene was also studied in THF, DMF, and DMSO (Figs. 2b, 2c, and 2d, respectively). Similar to the case in acetone, the fast photodecomposition of perylene in the Pe–DCB system was retarded or inhibited by the addition of VCZ. However, perylene was hardly photodecomposed in THF in the Pe–DCB system. Taking into account that the photodecomposition of perylene is induced by the electron transfer between Pe^{*1} and DCB or VCZ, solvent polarity is suggested to be of primary importance. The finding that the free ion yield in photo-induced electron transfer reactions in electron donor-acceptor systems is nearly zero in a low polarity solvent such as THF would explain the stability of perylene in THF even in the presence of DCB.[14] On the other hand, the fact that the free ion is produced efficiently in polar solvents such as acetone, DMF, and DMSO, is in good agreement with the present results.[14]

Photo-cyclodimerization and -polymerization of VCZ. Since VCZ cation radical is known as the precursor of VCZ-cyclodimer and -polymer,[6] it is expected that VCZ-cyclodimer and/or -polymer are produced by irradiating the present ternary system. Indeed, photoirradiation leads to the formation of VCZ-cyclodimer and/or -polymer. Quantum yields for VCZ-cyclodimerization and -polymerization under various conditions are listed in Table 1. In the Table, the quantum yields over 1.0 indicate that the cyclodimerization or -polymerization of VCZ involves chain propagation processes which have been discussed by Ledwith in detail.[6] The mechanisms are as follows. The reaction path of VCZ cation radical as function of atmosphere and solvent is identical with the previous results.[15]

In the Pe sensitized systems (Pe–DCB–VCZ, Pe–VCZ) in acetone, VCZ-cyclodimer and -polymer were formed efficiently in air and *in vacuo*, respectively. The quantum yield is larger by a factor of ≈ 6 in the Pe–DCB–VCZ system than in the Pe–VCZ system

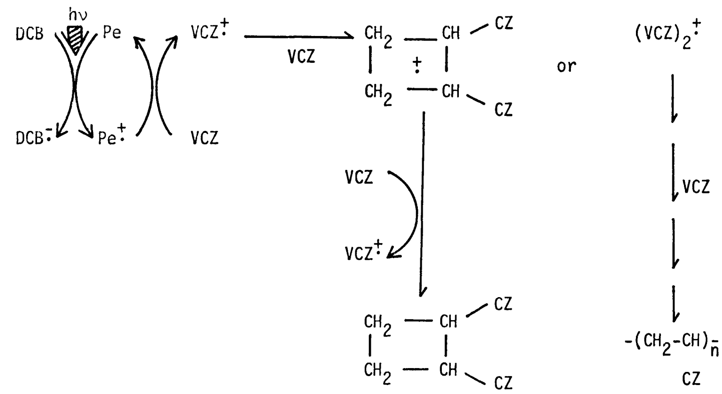


Table 1. Quantum yields for VCZ-cyclodimer and -polymer formation

Solvent	hν nm	Quantum yield in air (*in vacuo*) Pe-VCZ-DCB	Pe-VCZ	VCZ-DCB	VCZ
Acetone	435	4.5[a] (2.3)	0.75[a] (0.38)	0 (0)	——
	365	——	——	2.57[a] (1.80)	2.57[a] (0.43)
THF	435	0 (0)	0 (0)	0 (0)	——
	365	——	——	≈0 (≈0)	≈0 (0.08)
DMF	435	0 (0)	0 (0)	0 (0)	——
	365	——	——	0.27 (0.18)	0.36 (0.09)
DMSO	435	≈0 (0.1)	≈0 (0.9)	0 (0)	——
	365	——	——	2.10 (1.00)	1.71 (0.52)

Conditions; [Pe] $= 2\times10^{-5}$ mol dm^{-3}, [VCZ] $= 0.2$ mol dm^{-3}, monochromatic irradiation for 16 min at room temperature. a) 1,2-*trans*-Di-9-carbazolylcyclobutane, others are poly(*N*-vinylcarbazole).

either in air or *in vacuo*. Furthermore, in comparison with the quantum yield in the VCZ–DCB system or the system containing VCZ alone, the ternary system is twice as efficient as the others. The finding that the quantum yield is the highest in the ternary system indicates the suppression of the back electron transfer between ion radicals resulting in an increase in the steady state concentration of VCZ cation radical. Namely, an electron is transffered from VCZ to DCB by perylene and consequently, charge separation is most efficient in the ternary system, which brings about high quantum yields of cyclodimerization and/or -polymerization of VCZ. These results reveal the usefulness of the electron transfer sensitization system in respect of, i) the enhancement of quantum yield, and ii) the utilization of low enrgy photons. In the electron transfer sensitization system in air, we estimated the overall sensitizer efficiency which is defined as "product per consumed perylene," to be over 8000, although the mechanisms for VCZ-cyclodimer and -polymer formation involve chain propagation processes described above. Consequently, we conclude that the sensitizer (perylene) is reproduced *via* two successive electron transfer reactions, which is the same conclusion obtained in the previous section.

In THF, since the free ion yield in electron donor-acceptor systems is nearly zero, the absence of cyclodimerization or -polymerization of VCZ is quite reasonable. However, the features of the reactions in DMF and DMSO are more complicated. In perylene sensitized systems, VCZ-polymer was scarcely produced,[16] whereas the polymer was formed in the system of VCZ–DCB and of VCZ alone by irradiating VCZ. The reasons for these results are unclear at the present time. However, since it has been reported that viscous solvents such as DMF and DMSO promote geminate recombination of the ion radical pair,[17] we consider that the back electron transfer between perylene cation radical and DCB anion radical will suppress the polymerization or cyclodimerization from VCZ cation radical.

Conclusion

Although the quantitative information on the electron transfer sensitization was not obtained, it is concluded that perylene acts as an electron carrier to induce the cation radical initiated cyclodimerization and -polymerization of VCZ. The quantum yields for VCZ-cyclodimer and -polymer formation were enhanced in the presence of electron transfer sensitizer in comparison with other systems in which VCZ was directly excited. Furthermore, the effective absorption wavelength can be extended to longer wavelength region by the use of electron transfer sensitizer. The electron transfer sensitization is a useful tool for photo-redox reactions in general. Quantitative discussions on further examples of the electron transfer sensitization systems will be reported in near future.[18]

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