Electron Transfer Sensitization. III. A Kinetic Study of Oxidative Dye Formation from Leuco Crystal Violet

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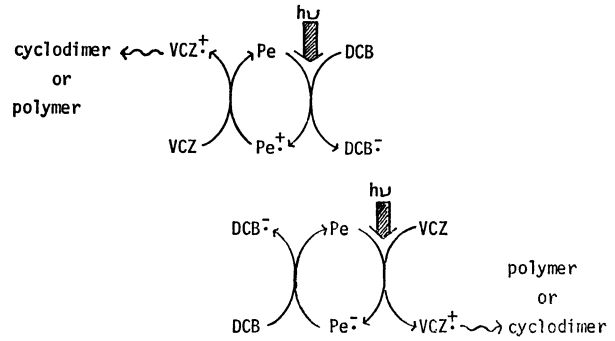
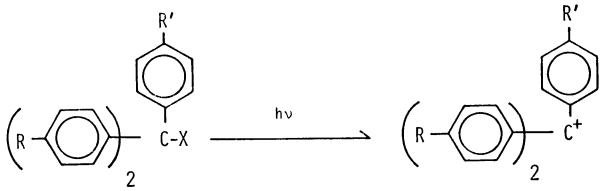
The action of electron transfer sensitization was quantitatively discussed by measuring photooxidative dye formation of leuco Crystal Violet (LCV) in the perylene(Pe)-1,4-dicyanobenzene(DCB)-LCV combination in polar media. Under the conditions of exclusive photoexcitation of perylene (λ_{ex} at 435 nm), the kinetic study revealed that the turn over number of perylene as a sensitizer was immeasurably large in the ternary system *in vacuo*. This is an indication that perylene is indeed recycled *via* two successive electron transfer processes. The turn over number decreased to 58 in air, probably due to instability of intermediate ion radicals. The quantum yield was larger for the ternary system than for the binary system(Pe–LCV) irradiated at 435 nm. Although the absolute quantum yield of photooxidation was in the order of 10^{-3} or less in both systems, the ternary electron transfer system was apparently advantageous since the efficiency of back electron transfer would be reduced when multiple electron transfer processes are linked. Furthermore, the concept of electron transfer sensitization enables spectral sensitization and utilization of low energy photons in singlet state photoredox reactions. Such systems would be considered as a model for the primary action of photosynthesis.

In the preceding articles, we have reported the electron transfer sensitization of Pe–DCB–*N*-vinylcarbazole(VCZ) system in polar media.[1] On selective irradiation of perylene, VCZ-cyclodimer and -polymer were obtained in good yields. Since the monomer cation radical is known to be the precursor of the VCZ-cyclodimer and -polymer,[2] we assumed the scheme described below. However, the formation of



VCZ-cyclodimer and -polymer involves chain propagation processes, and consequently the mean turn over number of perylene as a sensitizer could not be determined. In the present paper, we are presenting a kinetic study of oxidative dye formation from LCV sensitized by the electron transfer sensitizer (perylene).



(I) CRYSTAL VIOLET R=R'=NMe_2

(II) MALACHITE GREEN R=NMe_2, R'=H

(III) BRILLIANT GREEN R=NEt_2, R'=H

(IV) DOEBNER'S VIOLET R=NH_2, R'=Ph

X=H OR CN

Since the photoreactions of leuco triphenylmethane derivatives in the presence or the absence of an electron acceptor are well established,[3] quantitative information on the action of electron transfer sensitization is expected.

Experimental

Materials. Perylene(Aldrich) was used without further purification. 1,4-Dicyanobenzene and leuco Crystal Violet (both Tokyo Kasei, guaranteed reagent) were recrystallized from ethanol several times. 9-Cyanoanthracene (CNA) was prepared according to literature,[4] and was purified by column chromatography, followed by recrystallization from ethanol and finally sublimed *in vacuo* before use. Acetonitrile was refluxed over phosphorus pentaoxide for several hours and then distilled. Benzene, tetrahydrofuran (THF), and *N*,*N*-dimethylformamide (DMF) were dried over appropriate drying reagents (CaH_2, Na and $LiAlH_4$, and CaH_2, respectively) and then distilled. Acetone was treated over $KMnO_4$ and $MgSO_4$ successively, and then distilled.

Procedure of Photoreactions. Photoreactions in air were carried out in a Teflon capped quartz cell (optical length 1 cm). Degassed samples were prepared by several freeze-pump-thaw cycles and then sealed off at the constriction of a Pyrex branch of a quartz cell. Monochromatic light source was obtained by a JASCO Spectroirradiator CRM-FA equipped with a 2-kW xenon lamp. Absorption and fluorescence spectroscopy were made by a Shimadzu UV-200S spectrophotometer and a Hitachi MPF-4 spectrofluorometer, respectively. For fluorescence quenching experiments, samples were thoroughly deaerated by argon bubbling. Light intensity for the quantum yield measurements were determined by a Hatchard-Parker actinometer (0.15 mol dm^{-3} potassium trioxalatoferrate(III) in a 0.1 mol dm^{-3} aqueous sulfuric acid solution).[5]

Results and Discussion

Oxidative Dye Formation of LCV and Photodecomposition of Perylene. Figure 1 shows the absorption spectra of the components in this electron transfer sensitization system in acetonitrile. Perylene is an electron transfer sensitizer (a photoabsorber), DCB and CNA are electron acceptors, and LCV is an electron donor. It

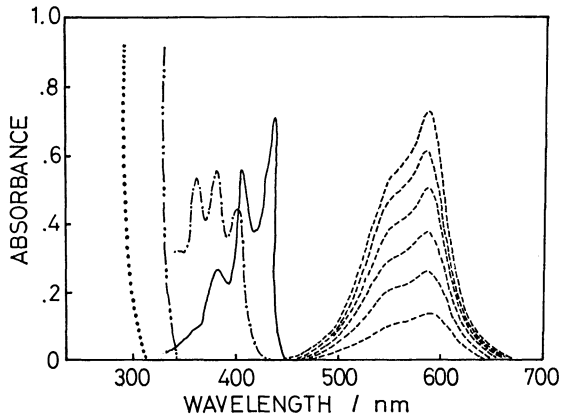


Fig. 1. Absorption spectrum of the components for the present reaction system in acetonitrile.
[Pe]$=1.7\times10^{-5}$ mol dm^{-3} (——); [CNA]$=1.0\times10^{-3}$ mol dm^{-3} (—·—·—); [DCB]$=1.0\times10^{-3}$ mol dm^{-3} (·····), [LCV]$=1.0\times10^{-3}$ mol dm^{-3} (—··—··—); CV^+ (----).

is clear from these spectra that LCV and DCB have no absorption at the absorption maximum of perylene (435 nm). CNA is also transparent at 435 nm under our experimental conditions ([CNA]$=1\times10^{-4}$ mol dm^{-3}) as manifested by the fact that the fluorescence from CNA on excitation at 435 nm is not observed at all. Hence, the selective excitation of perylene is attained in this system.

On excitation of perylene in the Pe–CNA–LCV system, the development of violet color showing an absorption maximum around 590 nm was observed. This new absorption band is identical to that observed upon direct excitation of LCV. Since LCV is easily photooxidized to give its violet colored carbonium ion, and the spectrum in Fig. 1 agrees with the reported one,[6] we identified the violet species as Crystal Violet cation (CV^+) which is one of the triphenylmethane dyes ($\lambda_{max}=590$ nm, $\varepsilon=1.1\times10^5$ dm^3 mol^{-1} cm^{-1}).[7] The dye was stable within the time scale of our experimental conditions. As the absorption intensity at 590 nm due to the dye formation increases, the absorption around 435 nm also increases and the conditions of selective excitation of perylene are no longer sustained. However, since the extinction coefficient around 435 nm is negligibly small compared with the value at 590 nm and also with the value for perylene, the inner filter effect due to the increase in the absorption at 435 nm is negligible if the dye absorbance at 590 nm is less than 0.8.

Figure 2 shows the time conversion curves of the dye formation in the Pe–CNA–LCV and the Pe–LCV systems in acetonitrile. It is obvious that the rate of the dye formation is faster in the ternary system than in the binary one, and the reactions seem to be favored in air than *in vacuo*. The photodecomposition of perylene shown in Fig. 3 indicated that the fast decomposition of perylene in the aerated system of Pe–CNA was retarded by the addition of LCV which did not concern with the light absorption. In a similar manner, the fast decomposition of perylene in the Pe–LCV system was completely inhibited in

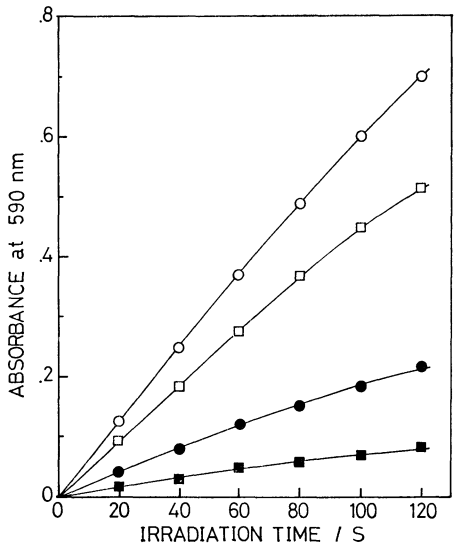


Fig. 2. Time conversion curves for the dye formation under various conditions.
Pe–CNA–LCV; (○; in air, ●: *in vacuo*), Pe–LCV; (□: in air, ■: *in vacuo*), [Pe]$=1.7\times10^{-5}$ mol dm^{-3}, [CNA]$=$[LCV]$=1.0\times10^{-3}$ mol dm^{-3} in acetonitrile.

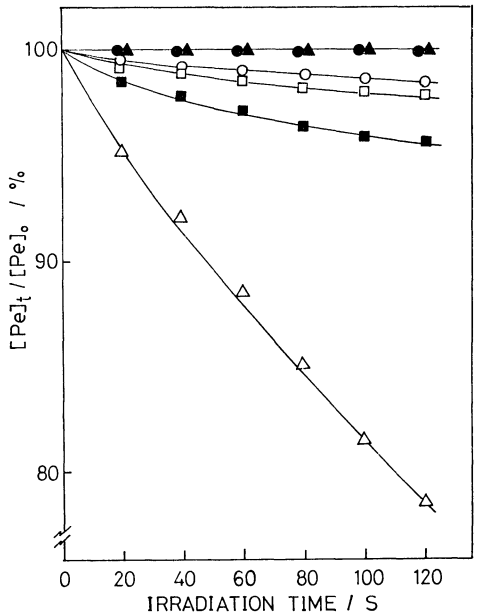


Fig. 3. Photodecomposition of perylene.
Perpendicular axis is a relative concentration of perylene(%).
Pe–CNA–LCV (○: in air, ●: *in vacuo*), Pe–LCV (□: in air, ■: *in vacuo*), Pe–CNA (△: in air, ▲: *in vacuo*).
The reaction conditions are same as Fig. 2.

the ternary system *in vacuo*. The same results were also obtained using DCB as an electron acceptor instead of CNA.

Proposed Mechanism. Either energy transfer or electron transfer should be responsible for the primary processes. However, energy transfer mechanism is excluded because the energy of the excited state of perylene is lower than the energy of LCV or the acceptors either in the excited singlet or the triplet state (see Table 1). On the other hand, the negative free

TABLE 1. EXCITED SINGLET AND TRIPLET ENERGIES, AND REDOX POTENTIALS

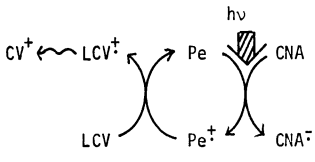
	$\Delta E_{0\cdot0}$ Singlet (kJ/mol)	$\Delta E_{0\cdot0}$ Triplet (kJ/mol)	$E(A/A^-)$[a] (V)	$E(D^+/D)$[a] (V)	ΔG[b] (kJ/mol)
Pe	275.3[c]	146.9[c]	−1.65[g]	0.85[g]	—
DCB	412.5[c]	295.0[c]	−1.64[i]	—	−40.6
CNA	297.1[d]	175.7[e]	−1.58[j]	—	−46.4
LCV	376.6[d]	309.6[f]	—	0.74[k]	−50.2

a) A half-wave potential (*versus* S.C.E. in acetonitrile). b) Calculated from Eq. 1. ΔG values for the electron transfer reactions between Pe*[1] and an electron acceptor or an electron donor. c) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York (1973), Sec. 1. d) Estimated from the onset of UV absorption. e) J. B. Birks, "Organic Molecular Photophysics," Wiley Interscience (1975), Vol. 2, Chap. 9. f) The value for leuco Ethyl Crystal Violet complied with MacLachlan, Ref. 6. g) See Ref. 8. h) E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963). i) See Ref. 8. j) J. Eriksen and C. S. Foote, *J. Phys. Chem.*, **82**, 2659 (1978). k) F. D. Saeva and G. R. Olin, *J. Chem. Soc., Chem. Commun.*, **1976**, 943.

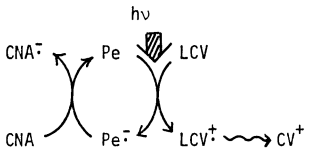
energy change (ΔG listed in Table 1) for the electron transfer between the excited singlet state of perylene (Pe*[1]) and LCV or the electron acceptors (CNA and DCB), calculated from Eq. 1,[8] indicate that electron transfer from Pe*[1] to the electron acceptor or from

$$\Delta G = E(D^+/D) - E(A/A^-) - e^2/\varepsilon r - \Delta E_{0\cdot0} \quad (1)$$

LCV to Pe*[1] is the primary key step for the subsequent reactions. Consequently, we assumed the following ion radical mediated reaction schemes. In Scheme 1, electron transfer takes place between



Scheme 1.



Scheme 2.

Pe*[1] and CNA in the first step, and then in the second, an electron is transferred from LCV to perylene cation radical to bring about the recovery of perylene molecule. On the other hand, Scheme 2 indicates that the first electron transfer occurs between Pe*[1] and LCV, and then the second electron transfer occurs between perylene anion radical and CNA. Since Schomburg *et al.* have also reported such electron transfer reactions in the system of pyrene–*N*,*N*-dimethylaniline–DCB in acetonitrile,[9] and the free energy change for the electron transfer between Pe*[1]–LCV or Pe*[1]–CNA (or DCB) has a negative value,[10] we considered that these schemes are plausible. Furthermore, by assuming these schemes, the retardation or the inhibition of perylene decomposition in the ternary system compared with the binary one is well interpreted.

The mechanism of Crystal Violet dye formation from LCV cation radical has been reported by MacLachlan for the system of leuco Ethyl Crystal Violet–carbon tetrachloride, based on ESR and flash photolysis study, as follows;[6]

$$LCV^+ \overset{K}{\rightleftharpoons} CV\cdot + H^+ \quad (2)$$

$$LCV^+ + CV\cdot \xrightarrow{k_r} LCV + CV^+ \quad (3)$$

where K denotes the equilibrium constant

$$K = [CV\cdot][H^+]/[LCV^+].$$

The dye is yielded by disproportionation between LCV cation radical and Crystal Violet radical (CV·) which is formed by the equilibrium Eq. 2. The participation of equilibrium is supported by the results from the temperature effects on the dye formation. The Arrehnius plots and the activation energies are shown in Fig. 4 and Table 2, respectively. The activa-

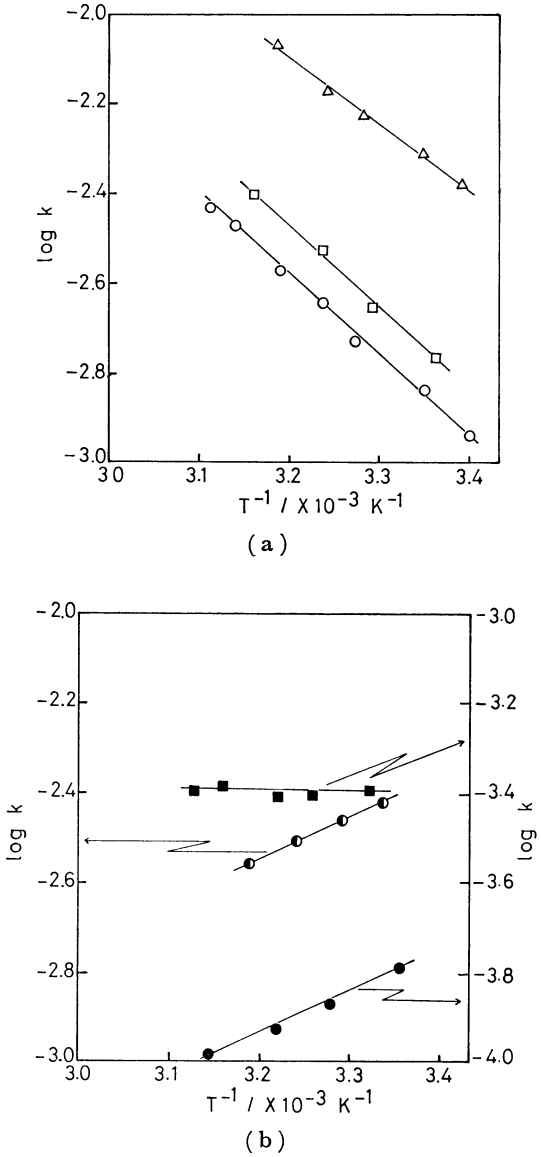


Fig. 4. Arrehnius plots for the dye formation.
a) In air, ○: Pe–LCV–DCB, □: Pe–LCV, △: LCV.
b) ●: Pe–LCV–DCB (*in vacuo*), ■: Pe–LCV (*in vacuo*), ◐: Pe–LCV–DCB (under CO_2 atmosphere). The reaction conditions are shown in Table 2.

Table 2. Activation energies for the dye formation

Atmosphere	Activation energy (kJ/mol)		
	Pe-LCV-DCB[a]	Pe-LCV[a]	LCV[b]
Air[c]	33.9	37.2	31.4
Vacuum[d]	−18.0	1.7	
CO_2[e]	−13.8		

Irradiated at a) 435 nm, or b) 304 nm in acetonitrile. ([Pe] = 1.8×10^{-5} mol dm^{-3}, [LCV] = [DCB] = 1×10^{-3} mol dm^{-3}). c) Air saturated solution. d) Degassed by several freeze-pump-thaw cycles. e) Degassed by several freeze-pump-thaw cycles, and then CO_2 gas was introduced to atmospheric pressure.

tion energies for the dye formation were +33.5 kJ/mol under aerated conditions, while the nearly zero or slightly negative temperature dependence was observed *in vacuo*. We consider that such temperature dependence indicates the participation of equilibrium Eq. 2 in the dye formation, corresponding the positive and the negative (or zero) temperature dependence, for the forward and the backward reactions in the equilibrium, respectively.

Kinetics. The reaction Schemes 1 and 2, and the CV^+ dye formation processes from LCV cation radical lead to kinetic expressions as follows.

$$Pe \xrightarrow{I} Pe^{*1} \quad (4)$$

$$Pe^{*1} \xrightarrow{\tau^{-1}} Pe \text{ or } Pe^{*3} \quad (5)$$

Equation 5 expresses the sum of the decay processes of the excited singlet state of perylene by internal conversion to the ground state (rate constant: k_d), radiative decay (k_f), and intersystem crossing (k_{isc}) to the excited triplet state (Pe^{*3}). In the presence of an electron acceptor or LCV, we take the non-electron transfer quenching processes into account (Eqs. 6 and 7). The elementary reactions in the schemes are

$$Pe^{*1} + A \xrightarrow{k_{qa}} Pe + A \quad (6)$$

$$Pe^{*1} + LCV \xrightarrow{k_{qd}} Pe + LCV \quad (7)$$

expressed as below (Eqs. 8—11). The quantum yield

Scheme 1

$$Pe^{*1} + A \xrightarrow{k_1} Pe^{+\cdot} + A^{-\cdot} \quad (8)$$

$$Pe^{+\cdot} + LCV \xrightarrow{k_2} Pe + LCV^{+\cdot} \quad (9)$$

Scheme 2

$$Pe^{*1} + LCV \xrightarrow{k_3} Pe^{-\cdot} + LCV^{+\cdot} \quad (10)$$

$$Pe^{-\cdot} + A \xrightarrow{k_4} Pe + A^{-\cdot} \quad (11)$$

of the CV^+ dye formation (ϕ_{CV}) is expressed as Eq. 12.

$$\phi_{CV} = \frac{k_r[LCV^{+\cdot}][CV\cdot]}{I}, \quad (12)$$

where I indicates the absorbed photoenergy. Now assuming the stationary concentration for Pe^{*1}, CV radical, LCV cation radical, and perylene cation radical, we obtained the Stern-Volmer equation for the dye formation (Eq. 13).

$$\phi_{CV} = Z\left(1+\frac{k_{qa}[A]+k_{qd}[LCV]}{k_1[A]+k_3[LCV]}+\frac{1}{\tau(k_1[A]+k_3[LCV])}\right), \quad (13)$$

where

$$Z = ([H^+]+Kk_r)/K.$$

Varying the concentration of DCB or LCV (1.0×10^{-3}—1.0×10^{-4} mol dm^{-3}) while keeping the concentration of LCV or DCB constant at 1.0×10^{-4} mol dm^{-3}, respectively, the change in ϕ_{CV} was spectroscopically determined and presented in a form of Stern-Volmer plot in Fig. 5. It is shown that the slopes depend upon the concentration of DCB or LCV. Under two extreme conditions, namely [DCB] $\gg$[LCV] and [DCB]$\ll$[LCV], Eq. 13 can be simplified as Eqs. 14 and 15, respectively.

$$\phi_{CV} = Z\left(1+\frac{k_{qa}}{k_1}+\frac{1}{\tau k_1[DCB]}\right) \quad (14)$$

$$\phi_{CV} = Z\left(1+\frac{k_{qd}}{k_3}+\frac{1}{\tau k_3[LCV]}\right) \quad (15)$$

The concentration dependent terms in Eqs. 14 and 15 correspond to the initial slopes in Fig. 5 (*i.e.* the high concentration limits of DCB and LCV, respectively) and Eq. 13 to the low concentration region. Consequently, the slopes in the high concentration regions give the values $Z/\tau k_1$ and $Z/\tau k_3$ relevant to the electron transfer processes Eqs. 8 and 10, respectively. From the ratio of these slopes, we obtained k_1/k_3=2.5. Namely, the electron transfer between Pe^{*1} and DCB is faster than that between Pe^{*1} and LCV. These results suggest that the perylene cation radical intermediate mechanism (Scheme 1) is more plausible, although Scheme 2 participates to a lesser extent.

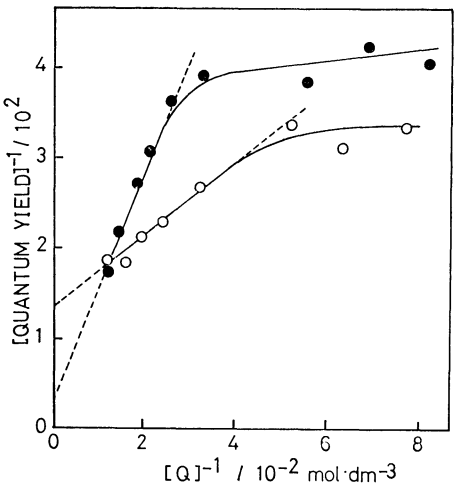


Fig. 5. Stern-Volmer plots for the dye formation. The concentration of perylene was fixed at constant (2×10^{-5} mol dm^{-3}), while the concentration of DCB (○) or LCV (●) was varied from 1×10^{-3} mol dm^{-3}—1×10^{-4} mol dm^{-3}. The reactions were carried out under air saturated conditions at 23.0 °C. Irradiation at 435 nm.

When $[Q]^{-1}$ in Fig. 5 increases, the assumptions on which the deviation of Eqs. 14 and 15 is based are no longer valid. Under the conditions of [LCV] $=1\times10^{-4}$ mol dm^{-3}, [DCB] being variable, Eq 13 indicates that ϕ_{CV}^{-1} should approach a constant value of $Z\left(1+\frac{k_{qd}}{k_3}+\frac{1}{\tau k_3[LCV]}\right)$ at the low concentration limit of DCB. Similarly, when [LCV] is variable, [DCB] being fixed, the limiting ϕ_{CV}^{-1} at [LCV]$\rightarrow$0 corresponds to $Z\left(1+\frac{k_{qa}}{k_1}+\frac{1}{\tau k_1[DCB]}\right)$. Deviation of Stern-Volmer plots in Fig. 5 with decreasing the quencher concentration is the manifestation of these.

The value of k_1/k_3 can be also estimated from the fluorescence quenching experiments of Pe*[1] as shown in Fig. 6. Since quenching of fluorescence in electron donor-acceptor systems in polar media is known to proceed *via* electron transfer process,[11] the Stern-Volmer quenching constants, K_q(DCB) and K_q(LCV), determined for DCB and LCV, respectively, will represent the relative rate of the electron transfer processes (Eqs. 8 and 10). The ratio of K_q therefore provides the value of k_1/k_3,

$$K_q(DCB)/K_q(LCV) = k_1/k_3 = 2.7.$$

Good agreement of the values obtained by reaction kinetic analysis and fluorescence quenching study strongly supports the validity of the present kinetic treatments.

It is worth noting that the electron transfer between Pe*[1] and DCB is faster than that between Pe*[1] and LCV, whereas, the values of ϕ_{CV} obtained by extraporating [LCV] to the infinite concentration, [DCB] being kept constant, is larger than the value at the infinite concentration of DCB with a fixed [LCV]. The difference between the ϕ_{CV} values is explained by the fact that two successible electron transfer processes (Eqs. 8 and 9) are necessary for the dye formation in the latter case, whereas the dye is formed directly by single electron transfer reaction (Eq. 10) in the former case. In other words, fast electron transfer between Pe*[1] and DCB does not necessarily bring about an increase in the quantum yield by Scheme 1, since another electron transfer between perylene cation radical and LCV is necessary. If the second electron transfer is slow, the overall quantum yield turns to be smaller, probably due to competing back electron transfer processes, Eqs. 16, 17, and 18. The back

$$Pe^{+\cdot} + DCB^{-\cdot} \longrightarrow Pe + DCB \quad (16)$$

$$LCV^{+\cdot} + DCB^{-\cdot} \longrightarrow LCV + DCB \quad (17)$$

$$LCV^{+\cdot} + Pe^{-\cdot} \longrightarrow LCV + Pe \quad (18)$$

electron transfer processes involving perylene cation radical (Eq. 16) would be more efficient than those involving LCV cation radical since LCV cation radical dissociates to CV radical. For the reaction to proceed by Scheme 1 at high DCB concentration, Eq. 9 has to compete with Eq. 16 at a fixed LCV concentration at 1×10^{-4} mol dm^{-3}. Apparently, the efficiency of reaction by Scheme 1 at infinite concentration of LCV is higher than that by Scheme 1 at infinite concentration of DCB in which the overall effciency is reduced by the ion recombination (Eq. 16) and also by the limited probability of Eq. 9 to occur within the lifetime of perylene cation radical at [LCV] $=1\times10^{-4}$ mol dm^{-3}. These discussions, however, could not be expressed by a kinetic treatment. Including these back electron transfer processes in the kinetic expression, the rate equation is far too complicated to be graphically presented. As a compromise, all factors reducing overall efficiency are attributed to Eqs. 6 and 7 in our present kinetic treatment. Phenomenalogically, participation of Eq. 16 is equivalent to increasing k_{qa} in Eq. 6.

Quantum Yield Measurements. The quantum yields for the dye formation (ϕ_{CV}) and perylene photodecomposition (ϕ_{Pe}) were measured in various conditions and shown in Table 3. The values of f in Table 3 confirm the turn over number of perylene by Scheme 1 or Scheme 2. In fact, the f value is about 58 in air and immeasurably large *in vacuo* in the ternary system. The finding that perylene is recycled even

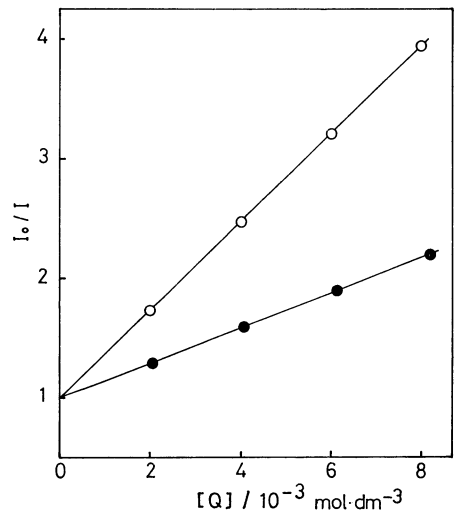


Fig. 6. Fluorescence quenching of perylene.
Quencher ○: DCB, ●: LCV, ([Pe]$=2\times10^{-5}$ mol dm^{-3} in acetonitrile).

TABLE 3. QUANTUM YIELDS FOR THE DYE FORMATION AND PERYLENE DECOMPOSITION

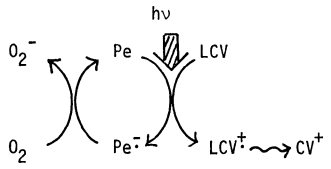
	In air			*In vacuo*		
	ϕ_{CV} / 10^{-3}	ϕ_{Pe} / 10^{-3}	f[b]	ϕ_{CV} / 10^{-3}	ϕ_{Pe} / 10^{-3}	f[b]
Pe-DCB-LCV	4.4	0.15	58	3.9	~0	c)
Pe-LCV	3.0	0.42	14	0.3	1.2	0.5
Pe-DCB	—	20.8	—	—	0.3	—
LCV-DCB	0	—	—	—	—	—
LCV-DCB[a]	4.3	—	—	0.9	—	—
LCV	0	—	—	—	—	—
LCV[a]	1.2	—	—	0.1	—	—

Irradiated at absorption maximum of perylene(435 nm) at 23.0 °C ([Pe]$=2\times10^{-5}$ mol dm^{-3}, [DCB]$=$[LCV]$=2\times10^{-3}$ mol dm^{-3} in acetonitrile). a) Irradiated on LCV directly at 304 nm. b) Turn over number of perylene as an electron carrier, which is defined as $f=2\times\phi_{CV}/\phi_{Pe}$. c) Immeasurably large.

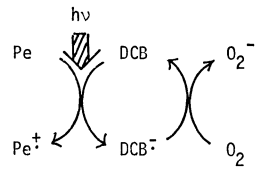
in the Pe–LCV system (f=14) in air requires comments. In this system, O_2 will act as an electron acceptor so that Pe anion radical formed by Eq. 10 will be oxidized to reproduce the Pe molecule by Eq. 19. Although the detection of superoxide ion (O_2^-)

$$Pe^{\cdot-} + O_2 \longrightarrow Pe + O_2^- \quad (19)$$

was not carried out, the participation of O_2 is confirmed by the facts that perylene is not recycled *in vacuo* (f=0.5) and Eq. 19 is a highly exothermic process ($\Delta G = -100.4$ kJ/mol).[12] Recently, the similar electron transfer reaction between O_2 and 9,10-dicyanoanthracene anion radical has been reported as an elementary process of non-singlet oxygen photooxygenation of alkenes or sulfides *via* superoxide ion.[13] We conclude that the electron transfer sensitization is also attained in this system, O_2 being an electron acceptor, as described below (Scheme 3).



Scheme 3.



Scheme 4.

In a similar manner, a large quantum yield of perylene photodecomposition in Pe–DCB system in air is understandable by assuming Scheme 4, where DCB acts as an electron carrier instead of perylene. DCB anion radical is reproduced by the electron transfer from DCB anion radical to O_2 ($\Delta G = -100.4$ kJ/mol),[12] whereas perylene cation radical must escape from the cycle to decompose. Although the product analysis has not been carried out, perylene cation radical will be decomposed by oxygenation with superoxide ion as Eriksen *et al.* have reported.[13] The participation of oxygen (superoxide ion) in the perylene decomposition is confirmed by the difference in quantum yields of perylene photodecomposition in air and *in vacuo* (ϕ_{Pe} (in air) $= 20.8 \times 10^{-3}$ and ϕ_{Pe} (*in vacuo*) $= 0.3 \times 10^{-3}$, in Table 3).

The larger quantum yield of dye formation in air relative to the value *in vacuo* will be also explained by assuming the participation of superoxide ion. Superoxide ions produced by the electron transfer from acceptor anion radicals to O_2 reduce the proton concentration according to Eq. 20 and consequently

$$H^+ + O_2^{\cdot-} \longrightarrow HO_2\cdot \quad (20)$$

shift the equilibrium (Eq. 2) towards right to increase the quantum yield of dye formation. Such assumption is supported by the fact that the activation energy for the dye formation in air has a positive value whereas the rate of the dye formation *in vacuo* shows negative dependence on temperature. The negative temperature dependence of the rate is explainable only by considering equilibrium in the course of the dye formation.

In comparison with the unimolecular photodissociation of Crystal Violet leuconitrile (X=CN) to the dye which proceeds with a quantum yield close to unity,[3] the quantum yields given in Table 3 are very much smaller. ϕ_{CV} in the LCV–DCB system on direct irradiation of LCV at 304 nm is almost the same as the values in the ternary system in air. The quantum yields of these electron transfer sensitization systems are small in general, because the presence of back electron transfer between ion radicals diminishes the efficiency. The merit of electron transfer sensitization is to shift the effective absorption wavelength towards longer wavelength regions in comparison with the direct excitation of a redox pair. Singlet state sensitization by means of energy transfer is obviously impossible. The same principles of electron transfer sensitization will be applicable to redox reactions in which the excited triplet state participates.

Solvent Effects. The solvent effects on the dye formation are shown in Table 4. The free ion yields determined by the laser photolysis of electron donor-acceptor (EDA) systems are nearly zero in low polarity solvents. The threshold of the solvent polarity to promote photo-ionic dissociation of EDA systems *via* electron transfer seems to be around ≈ 10, which is confirmed by transient spectroscopy or photocurrent

Table 4. Solvent effect

	Solvent properties			$\phi_{CV}/10^{-3}$			
		DN	AN	Pe-LCV-DCB[a]	Pe-LCV[a]	LCV-DCB	LCV
Benzene	$\varepsilon=2.28$, $\eta=0.60$	0.1	8.2	0	0	≈ 0[b]	≈ 0[b]
THF	$\varepsilon=7.58$, $\eta=0.46$	20.0	8.0	0	0	≈ 0[b]	≈ 0[b]
Acetone	$\varepsilon=20.0$, $\eta=0.30$	17.0	12.5	1.8	3.1	1.9[c]	2.3[c]
CH_3CN	$\varepsilon=37.5$, $\eta=0.33$	14.1	19.3	4.4	3.0	4.3[b]	1.2[b]
DMF	$\varepsilon=36.7$, $\eta=0.80$	26.6	16.0	2.1	1.6	2.7[c]	1.0[c]

Irradiated under air saturated solution at 23.0 °C ([Pe] $= 2 \times 10^{-5}$ mol dm^{-3}, [DCB] = [LCV] $= 2 \times 10^{-3}$ mol dm^{-3}). ε and η indicate solvent polarity and solvent viscosity, respectively. Irradiation wavelength is as follows, a) 435 nm(Pe), b) 304 nm(LCV), c) 334 nm(LCV).

measurement in the pyrene–*N*,*N*-dimethylaniline system.[14] As anticipated from the preceeding discussions, the electron transfer between EDA pairs is an essential requirement for the dye formation. Consequently, the present results that ϕ_{CV} is nearly zero in benzene or THF whereas the efficient dye formation takes place in acetone, acetonitrile, and DMF are well understandable. Furthermore, the largest ϕ_{CV} in acetonitrile is in agreement with the finding that the relative free ion yield is the largest in this solvent. In addition to solvent polarity, solvent viscosity seems to influence the efficiency of the dye formation. While DMF is as polar as acetonitrile, the value of ϕ_{CV} in DMF is about half of that in acetonitrile. This difference would be attributed to the high viscosity of DMF. Recently, Schulten and Schulten have reported that ion radical recombination processes are largely affected by solvent viscosity.[16] Namely, viscous solvent like DMF, compared with acetonitrile, will promote the back electron transfer reactions between the ion radicals in geminate ion pair which will diminish the dye formation yield. Furthermore, since carbonium ions are stable and cationic reactions are favored in the solvent having a high acceptor number(AN) and a low donor number(DN) as Gutmann has suggested,[17] the high DN of DMF is also unfavorable factor for the formation of Crystal Violet cation dye.

In contrast to the case in acetonitrile or DMF, the electron transfer sensitization was not achieved in acetone, in which the ϕ_{CV} value was smaller in the ternary system than in the binary one. For electron transfer sensitization to be effective, highly polar solvent and sufficient lifetime of free ion are required. To satisfy these conditions, acetone is neither polar enough nor sufficiently electrophilic to stabilize the cations. The finding that ϕ_{CV} of Pe–LCV system in acetone is comparable to that in acetonitrile whereas the efficiency of the dye formation in the ternary system is low in acetone would indicate the participation of Scheme 1 to be inefficient. This is understandable since perylene cation radical intermediate will be unstable in acetone. From these discussions, it is a reasonable consequence that Crystal Violet dye cation formes efficiently in acetonitrile, having high polarity and low viscosity as well as having the highest AN and the lowest DN among the solvents examined.

Conclusion

On the basis of a kinetic investigation, we have shown that LCV is oxidized to Crystal Violet dye cation *via* electron transfer sensitization mechanism. Under a limited conditions, the turn over number of perylene used as the primary photoabsorber is measurably large. From the view point of singlet state sensitization, the principle of spectral sensitization of redox reactions *via* singlet state has been established. Furthermore, these systems can be considered as a kinetic model for the electron transport system in photosynthesis, which have been also reported by the present authors demonstrating the photoreduction of carbon dioxide to oxalic acid or formic acid using water as a hydrogen source,[18] or the primary action of chlorophyll using polymer bound or micellar electron transfer sensitizers to facilitate energy migration among the chromophores like in antena pigments.[19]

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