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Mechanism of Charge-transfer Polymerization. X. Flash Photolysis of the *N*-Vinylcarbazole–Pyromellitic Dianhydride System

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The formation of transient *N*-vinylcarbazole cation-radical and pyromellitic dianhydride anion-radical was demonstrated for the *N*-vinylcarbazole-pyromellitic dianhydride-solvent system by means of flash spectroscopy. The transient decay process was found to be solvent-dependent. In 1,2-dichloroethane the decay of the anion-radical was of the first-order at initial stage ($t < 100$ μs), and the second-order kinetics ($t > 100$ μs) then followed. In acetonitrile the transient decay followed the second-order kinetics in the whole time region.

The photochemical reaction of *N*-vinylcarbazole (VCZ) in the presence of an electron acceptor is currently receiving great attention. The reaction involves cationic polymerization, radical polymerization or radical copolymerization with an electron-accepting monomer and cyclodimerization to give the *trans*-head-to-head cyclodimer, the reaction course being strongly solvent-dependent.[1] It has been postulated that these reactions are initiated by VCZ cation-radical formed by the photochemical electron transfer from VCZ to the electron acceptor, and the multi-reaction courses are explained in terms of the dual cationic and radical reactivity of the VCZ cation-radical.[1]

Recently, efforts have been made to elucidate the primary process of the above photochemical reactions. We demonstrated for the first time the formation of VCZ cation-radical and the anion-radical of the electron acceptor by means of flash spectroscopy for the VCZ–chloranil system in acetone, acetonitrile and methanol.[2] The formation of ion-radical species has since been confirmed successively for the VCZ–tetracyanobenzene[3] and VCZ–dimethyl terephthalate[4] systems by means of laser photolysis or conventional flash photolysis. However, only a few systems were studied as regards the photochemical primary process of the VCZ-electron acceptor system, not many studies being carried out on the effect of solvent on the transient decay.

As an extension of our studies on the photosensitized charge-transfer reaction of VCZ, we have investigated the flash photolysis for the VCZ–pyromellitic dianhydride (PMDA)–solvent system. 1,2-Dichloroethane and acetonitrile were selected as solvents: cationic polymerization of VCZ takes place in the former solvent, while the cyclodimerization of VCZ occurs in the latter solvent.[1] The transient absorption spectra and the transient decay process are described and discussed.

Experimental

Materials. *N*-Vinylcarbazole (VCZ) was purified and dried as described before.[2] Pyromellitic dianhydride (PMDA) (Wako Pure Chemical Ind., Ltd.) was recrystallized from anhydrous ethyl acetate and then sublimed twice *in vacuo*. 1,2-Dichloroethane was shaken with dilute aqueous sodium hydroxide, washed with water, dried over calcium chloride, refluxed with calcium hydride, and distilled immediately before use. Acetonitrile was refluxed over phosphorus pentoxide for more than 24 hr, distilled and then refluxed over anhydrous potassium carbonate and again distilled immediately before use.

Flash Spectroscopy. The concentrations of VCZ and PMDA for flash spectroscopy were mostly 3×10^{-4} M and 4×10^{-4} M, respectively. Freshly prepared solutions were degassed at 10^{-5} mmHg by means of several freeze-pump-thaw cycles and flashed at room temperature in a cylindrical silica cell with 20 cm path length and 1.5 cm diameter. The flash apparatus, a conventional one, was almost the same as that described by Yamamoto *et al.*[5] A stored electrical energy available for the flash was approximately 250 J, the half-duraction time of the flash being about 7 μs. The transient absorption spectra were photographed with a Narumi RM-23-I grating spectrograph with a Kodak high speed infrared film. A photoelectric recording system consisting of a R446 photomultiplier and a National type 501 oscilloscope was used. A filter solution composed of a glass plate and an aqueous solution of $NaNO_3$ (86 g in 500 ml solution) was inserted between the flash lamp and the reaction cell in order to ensure selective excitation of VCZ by the flash illumination (Fig. 1). In the case of the photoelectric recording of a transient decay, an aqueous solution of $CuSO_4\cdot5H_2O$ (80 g) and $NaNO_3$ (30 g) in 500 ml solution was used as a filter to obtain light of wavelength 330—620 nm. The electronic absorption spectra of the ground state molecule were taken with a Hitachi 124 spectrophotometer.

Results and Discussion

The VCZ–PMDA system forms a charge-transfer complex in the ground state, showing a charge-transfer absorption band (CT band) with a maximum at 490 nm (for the 1st CT band) in 1,2-dichloroethane. In the present flash photolysis, however, the donor-acceptor interaction in the ground state was negligible because of the low concentration of the solution (*ca.* 10^{-4} M order). Selective excitation of VCZ was possible as shown in Fig. 1.

Transient Spectra Obtained for the VCZ–PMDA–Acetonitrile System. The cyclodimerization of VCZ takes place to give *trans*-1,2-(9-dicarbazolyl)cyclobutane. The reaction mechanism is explained in terms of the intermediacy of VCZ cation radical formed by

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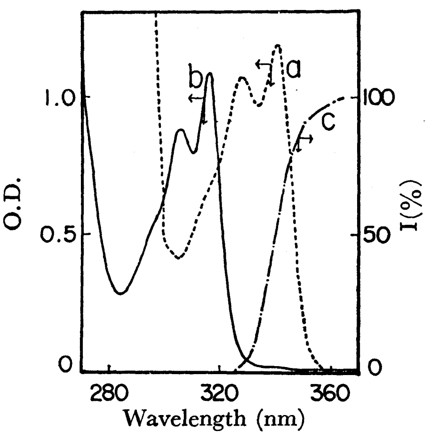


Fig. 1. The electronic absorption spectra of VCZ and PMDA in 1,2-dichloroethane and the transmittance of the filter solution used for the flash photolysis. (a) VCZ(3×10^{-4} M) (b) PMDA(4×10^{-4} M) (c) filter solution ($NaNO_3$ 86 g in 500 ml aqueous solution)

the photochemical electron transfer from VCZ to PMDA.[1] Flash excitation of VCZ in this system gave rise to a transient absorption spectrum consisting of two band systems, one in the wavelength region 550—700 nm with maxima at 665 and 615 nm, and the other in the wavelength region 700—850 nm with a maximum at 780 nm (Fig. 2). The former was identified as the PMDA anion-radical by comparison with the spectrum of the chemically prepared PMDA anion-radical.[6] The latter was assigned to the VCZ cation-radical by comparison with the spectrum of the authentic VCZ cation-radical generated by γ-ray irradiation in *sec*-butyl chloride glass at 77 K.[2] The absorption band of the VCZ cation-radical seems to more or less overlap with the absorption band of the PMDA anion-radical especially in the wavelength region around 615 nm. The transient absorption weakened more rapidly at around 615 nm than at 665 nm (Figs. 2 and 3). No transient absorption was obtained by the flash excitation of VCZ alone in acetonitrile. This indicates that the electron transfer occurred from the excited VCZ to PMDA to produce the VCZ cation-radical and the PMDA anion-radical.

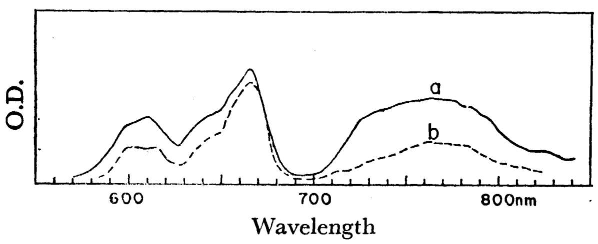


Fig. 2. The transient absorption spectra obtained by the flash photolysis for the VCZ(3×10^{-4} M)–PMDA (4×10^{-4} M)–acetonitrile system at room temperature. Delay time after flash excitation: (a) 4 μs (b) 59 μsec.

Transient Spectra Obtained for the VCZ–PMDA–1,2-Dichloroethane System. The cationic polymerization of VCZ occurs in preparatory scale reactions of this system. It has been proposed to be initiated by the VCZ cation-radical.[1] The formation of the transient VCZ cation-radical and PMDA anion-radical was likewise demonstrated by flash photolysis. The transient absorption spectra obtained by flash illumination are similar to those obtained in acetonitrile (Fig. 3). Confirmation of the occurrence of the electron transfer from VCZ to PMDA to produce the VCZ cation-radical and the PMDA anion-radical in acetonitrile and in 1,2-dichloroethane by means of flash spectroscopy provided direct evidence for the intermediacy of the VCZ cation-radical proposed for the photocyclodimerization and cationic photopolymerization of VCZ.

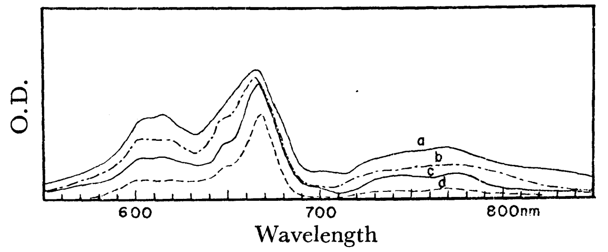


Fig. 3. The transient absorption spectra obtained by the flash photolysis for the VCZ(3×10^{-4} M)–PMDA (4×10^{-4} M)–1,2-dichloroethane system at room temperature. Delay time after flash excitation: (a) 3 μs (b) 23 μs (c) 53 μs (d) 105 μs.

Transient Spectra Obtained for the VCZ–1,2-Dichloroethane System. *N*-Vinylcarbazole generally undergoes radical polymerization by direct irradiation in the UV light in a high vacuum system in various solvents such as tetrahydrofuran, acetone, acetonitrile, *N*,*N*-dimethylformamide or dimethyl sulfoxide, the polymerization being suggested to be initiated by the excited triplet state of VCZ.[7,8] However, cationic photopolymerization of VCZ takes place in dichloromethane or in 1,2-dichloroethane even in the absence of an electron acceptor.[8] It has been suggested that the solvent, dichloromethane or 1,2-dichloroethane acts as an electron acceptor to the excited VCZ, the electron transfer occurring in these solvents from the excited VCZ to the solvent to produce the transient VCZ cation-radical which initiates the cationic polymerization of VCZ.[9] When VCZ alone was flash illuminated in 1,2-dichloroethane at room temperature, a transient absorption spectrum assignable to the VCZ cation-radical was obtained (Fig. 4), whereas no transient absorption was obtained in tetrahydrofuran, acetonitrile or *N*,*N*-dimethylformamide.[10] The results of flash photolysis support the mechanism of the VCZ cation-

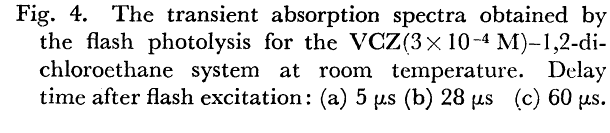
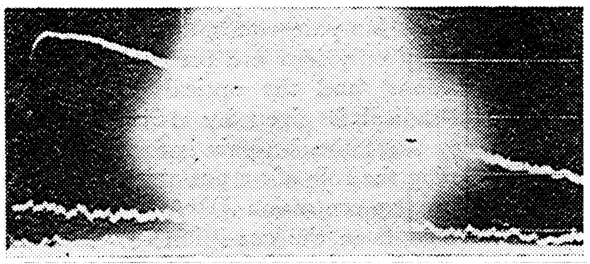


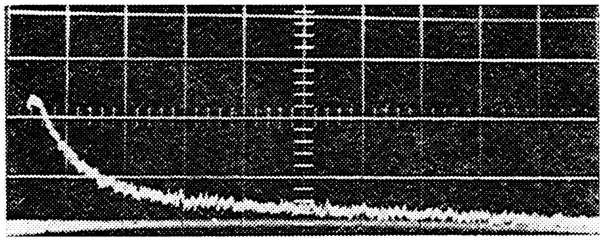
Fig. 4. The transient absorption spectra obtained by the flash photolysis for the VCZ(3×10^{-4} M)–1,2-dichloroethane system at room temperature. Delay time after flash excitation: (a) 5 μs (b) 28 μs (c) 60 μs.

radical initiation for the cationic photopolymerization of VCZ in 1,2-dichloroethane or in dichloromethane in the absence of an added electron acceptor.

Decay of the Transient Species. The transient decay followed by the photoelectric recording method was found to be solvent-dependent. In 1,2-dichloroethane, the decay of the PMDA anion-radical was of first-order at an initial stage ($t<100$ μs), followed by the second-order kinetics ($t>100$ μs). In contrast, the transient decay in acetonitrile followed the second-order kinetics for all the time intervals ($t>20$ μs). The oscilloscope traces for the decay of the PMDA anion-radical measured at the wavelength of the absorption maximum, 668 nm in 1,2-dichloroethane and 665 nm in acetonitrile, are shown in Figs. 5(a) and (b), and 6(a) and (b), respectively. The first-order and second-

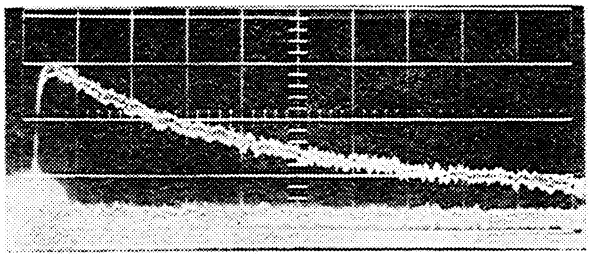


20 μs/div.

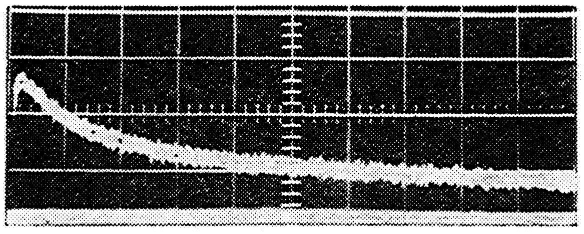


200 μs/div.

Fig. 5 (a) and (b). The oscilloscope traces for the decay of the transient PMDA anion-radical measured at 668 nm in 1,2-dichloroethane at around 20 °C. [VCZ] $=3\times10^{-4}$ M, [PMDA]$=4\times10^{-4}$ M. The vertical scale is 0.02 V/div.



50 μs/div.



200 μs/div.

Fig. 6 (a) and (b). The oscilloscope traces for the decay of the transient PMDA anion-radical measured at 665 nm in acetonitrile at around 20 °C. [VCZ]$=3\times10^{-4}$ M, [PMDA]$=4\times10^{-4}$ M. The vertical scale is 0.02 V/div.

TABLE 1. RATE CONSTANTS FOR THE DECAY OF THE TRANSIENT PMDA ANION-RADICAL PRODUCED IN THE VCZ–PMDA–SOLVENT SYSTEM AT AROUND 20 °C

Solvent	Wavelength (nm) measured	Rate constant
1,2-Dichloroethane	668	1.3×10^{4} s^{-1} ($t<100$ μs)
		$7.8\times\varepsilon_{A^-}\times10^{5}$ M^{-1} s^{-1} ($t>100$μs)
Acetonitrile	665	$1.4\sim3.1\times\varepsilon_{A^-}\times10^{5}$ M^{-1} s^{-1} (in all the time region measured, $t>20$ μs)

ε_{A^-} represents the molar extinction coefficient of the PMDA anion-radiacl at each wavelength.

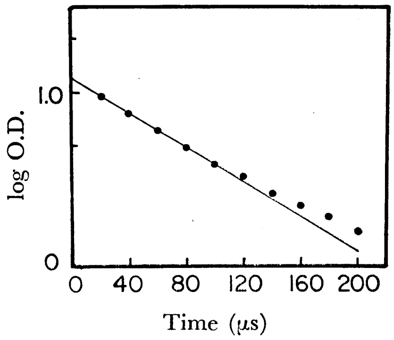


Fig. 7. The first-order plots for the decay of the transient PMDA anion-radical shown in Fig. 5(a) (in 1,2-dichloroethane).

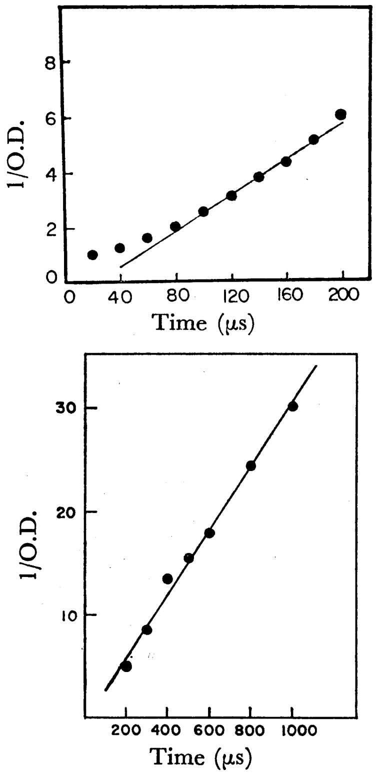


Fig. 8 (a) and (b). The second-order plots for the decay of the transient PMDA anion-radical shown in Figs. 5 (a) and (b), respectively (in 1,2-dichloroethane).

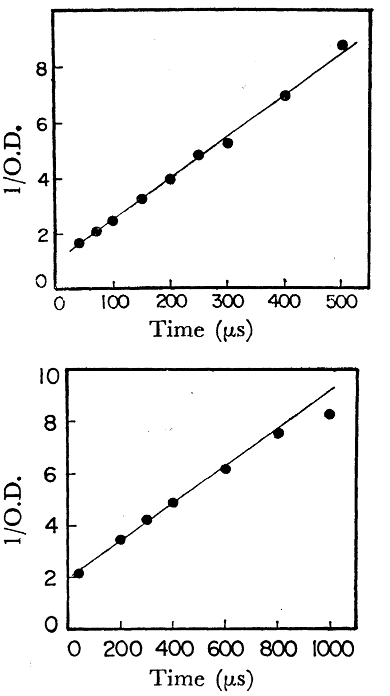


Fig. 9 (a) and (b). The second-order plots for the decay of the transient PMDA anion-radical shown in Figs. 6 (a) and (b), respectively (in acetonitrile).

order plots for the transient decay in 1,2-dichloroethane are shown in Figs. 7, and 8(a) and (b), respectively. The second-order plots for the transient decay in acetonitrile are shown in Fig. 9(a) and (b). Rate constants for the decay of the PMDA anion-radical obtained in each solvent are summarized in Table 1. Since the molar extinction coefficient of the absorption of the PMDA anion-radical is estimated to be at least 10000 at the wavelength of its absorption maximum,[6] it is indicated that the second-order decay occurred at a diffusion-controlled rate in each solvent. A similar transient decay has been observed for the triphenylene-PMDA system.[6]

The transient decay behaviors observed in the present systems can be explained by essentially the same kinetic treatment as described for the triphenylene–PMDA system. It is suggested that in acetonitrile possessing a high dielectric constant (37 at 20 °C) formation of the free ions are predominant by flash excitation, while in less polar 1,2-dichloroethane (dielectric constant: 10.37 at 25 °C) the ion pair is produced predominantly. The initial first-order decay followed by the final second-order decay process of the PMDA anion-radical in 1,2-dichloroethane is rationalized in terms of the initial very fast decay of the ion-pair, followed by the slower decay of the free ions. The photochemical primary process is given as in the following scheme of reactions.

$$\mathrm{D} \xrightarrow{h\nu} \mathrm{D}^*$$

$$\mathrm{D}^* + \mathrm{A} \xrightarrow{k_1} \mathrm{D}^+\mathrm{A}^- \text{ or } \mathrm{D}^+ + \mathrm{A}^-$$

$$\mathrm{D}^+\mathrm{A}^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{D}^+ + \mathrm{A}^-$$

$$\mathrm{D}^+\mathrm{A}^- \xrightarrow{k_3} \mathrm{D} + \mathrm{A}$$

$$(\mathrm{D}^+ + \mathrm{D} \rightsquigarrow \text{Cyclodimer or Polymer})$$

The optical density of the absorption of the PMDA anion-radical is given by $\Delta D = \varepsilon_{\mathrm{A}^-}[\mathrm{A}^-] + \varepsilon_{\mathrm{D}^+\mathrm{A}^-}[\mathrm{D}^+\mathrm{A}^-]$, where $\varepsilon_{\mathrm{A}^-}$ and $\varepsilon_{\mathrm{D}^+\mathrm{A}^-}$ represent the molar extinction coefficients of the free ion and the ion-pair, respectively. In 1,2-dichloroethane the ion-pair $\mathrm{D}^+\mathrm{A}^-$ is the predominant species, thus $\Delta D \simeq \varepsilon_{\mathrm{D}^+\mathrm{A}^-}[\mathrm{D}^+\mathrm{A}^-]$. Since the decay of $\mathrm{D}^+\mathrm{A}^-$ is very fast, $k_3 \gg k_2$ holds and the k_2 and k_{-2} terms can be neglected in the above scheme of reactions, and time-dependent behavior of the change in the optical density of the PMDA anion-radical in the initial decay stage would be given by $-\mathrm{d}\Delta D/\mathrm{d}t = k_3 \Delta D$. When the ion-pair concentration rapidly decreases, essentially only ions are present (although in low concentrations) and the optical density of the PMDA anion-radical is given by $\Delta D \simeq \varepsilon_{\mathrm{A}^-}[\mathrm{A}^-]$. In the final decay stage the ion-pair is formed from D^+ and A^-, assuming the role of an unstable intermediate. The steady-state concentration $[\mathrm{D}^+\mathrm{A}^-] = k_{-2}/(k_2+k_3) \cdot [\mathrm{A}^-]^2$ is obtained from the condition $\mathrm{d}[\mathrm{D}^+\mathrm{A}^-]/\mathrm{d}t = 0$. Since $k_3 \gg k_2$, the decay equation becomes $-\mathrm{d}\Delta D/\mathrm{d}t = (k_{-2}/\varepsilon_{\mathrm{A}^-})(\Delta D)^2$. On the other hand, free ions are the predominant species in acetonitrile. Thus $\Delta D \simeq \varepsilon_{\mathrm{A}^-} \cdot [\mathrm{A}^-]$. The ion-pair equilibrium seems to be established very rapidly (within 20 μs) in acetonitrile. It is reasonable to assume that $k_2 \gg k_3$, *viz.*, the ion-pair equilibrium is maintained during the decay process. In this case the concentration of $\mathrm{D}^+\mathrm{A}^-$ would also be negligibly small. The second-order decay equation $-\mathrm{d}\Delta D/\mathrm{d}t = k_3(k_{-2}/k_2)(\Delta D)^2/\varepsilon_{\mathrm{A}^-}$ is then obtained in acetonitrile. The first-order and the second-order rate constants for the decay of PMDA anion-radical in 1,2-dichloroethane and in acetonitrile (Table 1) represent k_3, k_{-2}, and $k_3(k_{-2}/k_2)$, respectively, in the above scheme of reactions (the absolute values of k_2, k_{-2}, and k_3 may differ with solvent).

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9) The lifetime of VCZ phosphorescence decreased appreciably with the addition of dichloroethane, but not that of VCZ fluorescence.[8]

10) Photoionization of VCZ by a double-photon process was not observed in the present flash photolysis.