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MECHANISM OF CHARGE-TRANSFER POLYMERIZATION: DETECTION OF ION-RADICAL INTERMEDIATES IN THE PHOTOSENSITIZED REACTION OF N-VINYLCARBAZOLE IN THE PRESENCE OF p-CHLORANIL

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Formation of transient ion-radicals in the photosensitized reaction of N-vinylcarbazole with p-chloranil as an acceptor has been demonstrated for the first time by means of flash spectroscopy.

The photosensitized reaction of N-vinylcarbazole(VCZ) in the presence of an electron acceptor has currently received much attention. Typically, in the system of VCZ-p-chloranil (p-CA) cationic polymerization of VCZ proceeds in benzene,[1] while in polar, basic solvents such as acetone, acetonitrile or methanol, cyclodimerization of VCZ takes place to form trans-1,2-dicarbazylcyclobutane.[2,3] It has been postulated that these reactions proceed via transitory VCZ cation-radical($VCZ^{+\cdot}$) formed by the photochemical electron transfer between the donor and the acceptor. However, no direct evidence for the formation of the ion-radicals has been obtained to date.

We have now demonstrated the formation of transient ion-radicals for the first time in the system of VCZ-p-CA in polar solvents by means of flash spectroscopy. In the present experiment formation of the charge-transfer complex in the ground state was negligible because of the low concentration of solutions. When p-CA was selectively excited by the flash illumination ($h\nu > 350$ nm) of an oxygen-free acetone solution containing 2×10^{-4}M VCZ and 1×10^{-4}M p-CA with combined filters of a glass plate and a benzene solution of ethylcarbazole(2×10^{-3}M) at room temperature, a transient absorption spectrum was obtained, which consisted of a band with a maximum at 446 nm and a shoulder at 421 nm, and a weak, broad band in the wavelength longer than 550 nm as shown in the Fig. The former band was assigned to p-CA anion-radical(p-$CA^{-\cdot}$) from identity with the spectrum of the chemically produced p-$CA^{-\cdot}$ in acetone[4] or in THF.[5] The decay of p-$CA^{-\cdot}$ followed the second-order kinetics with a rate constant $k=2.1\times10^{10}$ $M.^{-1}sec.^{-1}$,

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which was estimated by using the molar extinction coefficient value $\varepsilon = 9\times10^3$ reported for p-CA$^{\overline{\bullet}}$ at the maximum.[4] The latter band observed in the longer wavelength was attributed to VCZ$^{\overset{+}{\bullet}}$,[6] the intensity of which decreased with the increasing concentration of VCZ. Almost identical absorption spectrum was obtained by the flash illumination of an acetonitrile solution of VCZ (2×10^{-4}M) and p-CA(1×10^{-4}M). In methanol, formation of the semiquinone radical of p-CA was observed in addition to p-CA$^{\overline{\bullet}}$ and VCZ$^{\overset{+}{\bullet}}$, the former being formed by the protonation of p-CA$^{\overline{\bullet}}$. The acid-base equilibrium between the semiquinone radical and the semiquinone anion in methanol has been established in the flash photolysis of duroquinone[7] or p-CA.[5] For the analysis of the present absorption spectra flash photolysis of p-CA alone was examined in detail.[5] The facts that the pure absorption spectrum of p-CA$^{\overline{\bullet}}$ was not obtained with p-CA alone and that the band observed in the wavelength longer than 550 nm attributable to VCZ$^{\overset{+}{\bullet}}$ was not observed in the absence of VCZ in acetonitrile and in methanol[8] confirm that the electron transfer did occur between VCZ and the excited p-CA.

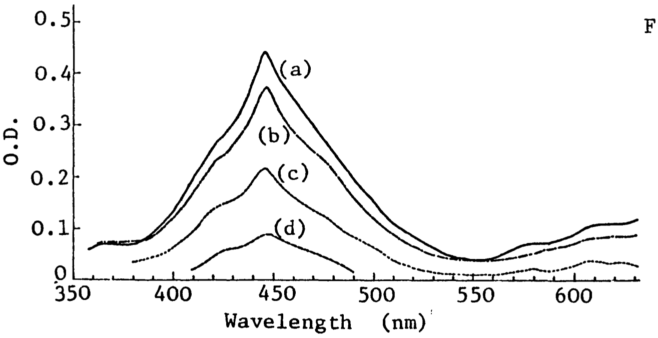

Fig. Transient absorption spectra obtained by flash illumination of VCZ(2×10^{-4}M) and p-CA(1×10^{-4}M) in oxygen-free acetone.
Cell length: 20 cm. Delay time: (a) 3 μsec. (b) 9 μsec. (c) 26 μsec. (d) 84 μsec.

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6. We are grateful to Dr.Shida(The Institute of Physical and Chemical Research, Tokyo,Japan) who was kind enough to provide us with an authentic spectrum of VCZ$^{\overset{+}{\bullet}}$ produced by γ-ray irradiation of VCZ in sec-butyl chloride matrix at 77°K. The spectrum was more resolved than that obtained in the present flash photolysis, covering almost whole visible region with maxima at 508, 619, 702, and 780 nm.
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8. In acetone a weak, broad band was observed even in the wavelength beyond 550 nm by the flash illumination of p-CA alone, which decayed at nearly the same rate as T←T′ absorption of p-CA and was assigned to the charge-transfer band between the solvent as a donor and the triplet p-CA as an acceptor.[5]

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