Laser Photolysis Studies on the Ionization of *N*-Vinylcarbazole and *N*-Ethylcarbazole in the Presence and Absence of Electron Acceptors[1]

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Formation of solvated ion radicals in the *N*-vinylcarbazole (VCZ)-and *N*-ethylcarbazole (ECZ)-electron acceptor systems in polar solvents has been studied by means of laser photolysis, transient photoconductivity and transient absorption measurements. Ion radical formation due to the encounter collision between an excited VCZ or ECZ and electron acceptor was confirmed directly. In the absence of electron acceptor, formation of cation radicals of carbazoles due to biphotonic process was observed in polar solvents. The $S_n \leftarrow S_1$ spectra of these molecules were observed both in polar and nonpolar solvents.

It was postulated that the photopolymerization of VCZ in the presence of electron acceptors is initiated by cation radicals formed by the electron transfer from VCZ molecules to acceptors in the excited state.[2] However, no direct experimental evidence has been given on the mechanism of cation radical formation.

We have shown the ion radical formation due to the encounter collision between an excited pyrene and *N,N*-dimethylaniline (DMA) and also between an excited anthracene and DMA in moderately and strongly polar solvents by means of laser photolysis, transient photoconductivity and absorption measurements.[3,4] We carried out analogous studies on VCZ, using 1,2,4,5-tetracyanobenzene (TCNB) and tetracyanoethylene (TCNE) as electron acceptors, and confirmed the formation of solvated cation radicals of VCZ and anion radicals of the acceptor due to the encounter collision between the excited VCZ and the ground state acceptor.

We also studied the photoionization of VCZ in polar solvents in the absence of the electron acceptor, since photopolymerization of VCZ can even thus be observed. The formation of VCZ cation radicals was found to be due to a biphotonic absorption process. $S_n \leftarrow S_1$ spectra of VCZ might be important for the elucidation of its excited state electronic structure.

We examined ECZ in detail for the purpose of comparison and obtained similar results to those of VCZ.

Experimental

The same Q-switched ruby laser as described previously[3,5] was used. The ion radicals produced were observed by measurement of the transient photocurrent and the transient absorption spectra induced by laser excitation, the methods for these measurements being the same as before. For examining the effect of exciting light intensity on the photocurrent, the intensity of the laser pulse was reduced by using neutral filters composed of wire gauzes. Relative values of the exciting intensity were monitored by measuring the intensity of light partially reflected by means of a beam splitter with a photomultiplier. The absolute value was determined by a ballistic thermopile TRG model 100 (Hadron). Measurements of fluorescence decay times were carried out by using a nitrogen gas laser.

TCNB was the same sample as used before and recrystallized from ethanol several times before use. TCNB was purified by repeated recrystallization from monochlorobenzene and sublimation in a vacuum. Solvents were Merck spectrograde and used without purification. Concentrations of VCZ and ECZ in solutions for the measurements were *ca.* 1.0×10^{-3} M, where the optical density of the solution at 347 nm was *ca.* unity. Concentrations of the electron acceptors in solutions for the laser photolysis were *ca.* 1.0×10^{-2} M. All solutions were deaerated by repeated freeze-pump-thaw cycles.

Results and Discussion

A. Formation and Annihilation Mechanisms of VCZ and ECZ Cation Radicals under the Presence of Electron Acceptors. The transient photocurrents of VCZ–TCNB–acetonitrile and ECZ–TCNE–methylene chloride systems are shown in Figs. 1 and 2, respectively. We see that the dissociated and solvated ion radicals are produced by excitation with 347 nm laser pulse, and vanish due to bimolecular recombination reaction. In a more concentrated solution, there arises a charge transfer (CT) absorption band near 570 nm due to complex formation. However, in the present case, the interaction of VCZ with TCNB in the ground state can be ignored, since no CT absorption is observed. The ion radicals (Figs. 1 and 2) might be formed by the encounter collision between excited carbazoles and

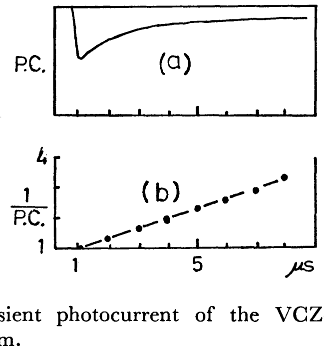

Fig. 1. Transient photocurrent of the VCZ-TCNB-acetonitrile system.
(a) The decay curve of photocurrents.
(b) The reciprocal of the photocurrent *vs.* time relation.

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[1] A preliminary report was published in *Chem. Lett.*, **1972**. 221.

[2] *Cf. e.g*, S. Tazuke, *Yuki Gosei Kagaku*, **27**, 15 (1969). *Adv. Polymer Sci.*, **6**, 321 (1969).

[3] Y. Taniguchi, Y. Nishina, and N. Mataga, This Bulletin, **45**, 764 (1972).

[4] Y. Taniguchi and N. Mataga, *Chem. Phys. Lett.*, **13**, 596 (1972).

[5] H. Masuhara, N. Shimada, N. Tsujino, and N. Mataga, This Bulletin, **44**, 3310 (1971).

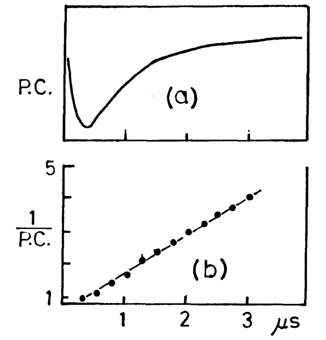

Fig. 2. Transient photocurrent of the ECZ-TCNE-methylene chloride system.
(a) The decay curve of photocurrent.
(b) The reciprocal of the photocurrent *vs.* time relation.

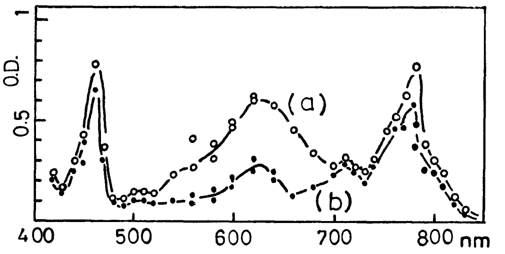

Fig. 3. Transient absorption spectra of VCZ-TCNB-acetonitrile system. The delay time from the laser pulse, (a) 0, (b) 200 ns.

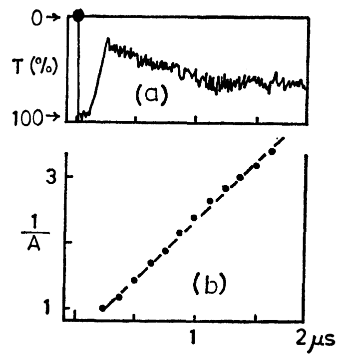

Fig. 4. The decay process of the absorption at 780 nm.
(a) The observed decay curve of the absorbance.
(b) The reciprocal of the absorbance *vs.* time relation.

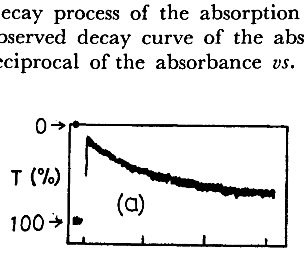

Fig. 5. The decay process of the absorption at 460 nm.
(a) The observed decay curve of the absorbance.
(b) The reciprocal of the absorbance *vs.* time relation.

acceptors. We examined the effect of the addition of acceptors on the fluorescence decay time and yield of VCZ in acetonitrile solution. The results can be reproduced by the simple Stern-Volmer equation, $\tau/\tau_0=1/(1+\tau_0 k[\mathrm{A}])$, from which k values were evaluated to be $1.5\times10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for VCZ–TCNB system and $1.3\times10^{10}\,\mathrm{M}^{-1}\mathrm{s}^{-1}$ for VCZ–TCNE system. These values of the rate constant of the quenching reaction indicate that the excited VCZ molecules make diffusion-controlled encounter collision with acceptor molecules. Analogous results were obtained by fluorescence yield measurements.

The ion radical formation can be confirmed also by transient absorption measurements. The transient absorption spectra of VCZ–TCNB–acetonitrile system are shown in Fig. 3. The decay of the optical absorption at 780 nm and the reciprocal of the absorbance *vs.* time relation are shown, respectively, in Figs. 4a and 4b, and the decay process at 460 nm in Figs. 5a and 5b. The absorbance *vs.* time relation at *ca.* 710 nm is similar to that at 780 nm. The decay curve of the absorption at *ca.* 620 nm consists of two components. The short lived component of the absorption at 540—680 nm may be ascribed to the transition from the lowest excited singlet (S_1) to the higher excited singlet (S_n) state of VCZ. The decay of the long lived component is the same as that at 780 nm. The transient absorption bands at 780, 710 and 620 nm with a rather long life may be ascribed to the VCZ cation radical since they are similar to those of the VCZ cation radical obtained by radiolysis at low temperatures.[7] The absorption band at *ca.* 460 nm can be ascribed to the TCNB anion radical. The results show that the ion radicals formed by the electron transfer from the excited VCZ to TCNB decay due to the bimolecular recombination reaction.

The photoionization of VCZ in the presence of TCNB was also examined for the tetrahydrofurane (THF) solution, the results being shown in Figs. 6 and 7. They are similar to those in the case of acetonitrile solution, except that the amount of produced ions is considerably smaller. We observed both dissociated ion radical

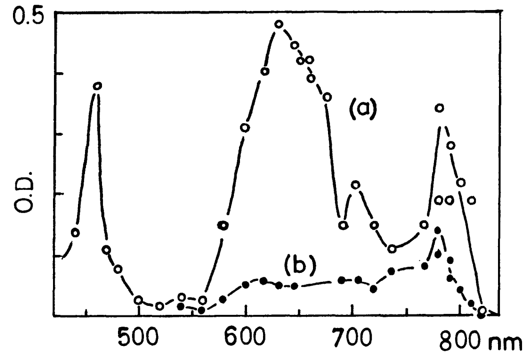

Fig. 6. Transient absorption spectra of VCZ-TCNB-THF system. The delay time from the laser pulse, (a) 0, (b) 500 ns.

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6) N. Nakashima, N. Mataga, F. Ushio, and C. Yamanaka, *Z. Phys. Chem.*, *N. F.*, **79**, 150 (1972).

7) Y. Shirota, K. Kawai, N. Yamamoto, K. Tada, T. Shida, H. Mikawa, and H. Tsubomura, This Bulletin, **45**, 2683 (1972).

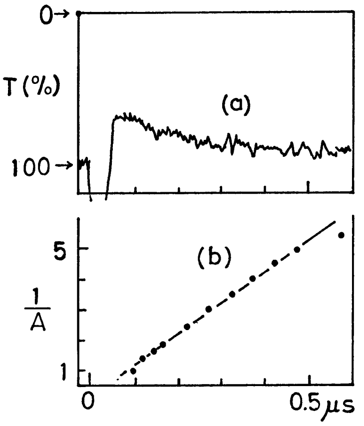

Fig. 7. The decay process of the absorption at 765 nm. The same system as in Fig. 6.
(a) The observed decay curve of the absorbance.
(b) The reciprocal of the absorbance *vs.* time relation.

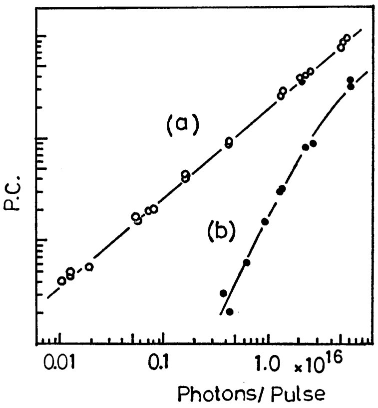

Fig. 8. The effect of the exciting light intensity on the peak photocurrent.
(a) VCZ-TCNB-acetonitrile system.
(b) VCZ-acetonitrile system.

formation and fluorescent exciplex formation in the case of pyrene–*N*,*N*-dimethylaniline–THF system, but no fluorescent exciplex formation was observed in the present case. This was the same also in the case of ECZ–TCNB system.

It is possible that ionization of VCZ or ECZ due to double photon absorption occurs since the exciting light pulse we used is fairly strong. For the sake of confirmation we investigated the effect of exciting light intensity on the peak photocurrent, the results of which are given in Fig. 8. We see that the ionization is a one-photon process in the case of the VCZ–TCNB–acetonitrile system.

We can conclude that the photoionization process of the VCZ–acceptor system is the encounter collision between the excited VCZ and the acceptor molecule followed by one electron transfer from the excited VCZ to the acceptor leading to the dissociation into ions.

The results might be of some interest for the elucidation of the CT photopolymerization mechanisms. Only a very small part of the dissociated ion radicals which have escaped deactivation due to recombination might initiate the polymerization.

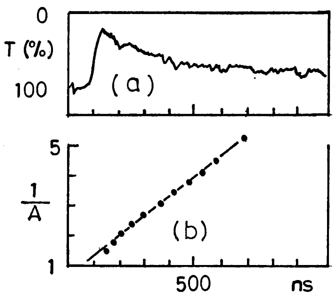

Fig. 9. The decay process of the absorption at 720 nm in the case of VCZ-acetonitrile system.
(a) The observed decay curve of the absorbance.
(b) The reciprocal of the absorbance *vs.* time relation.

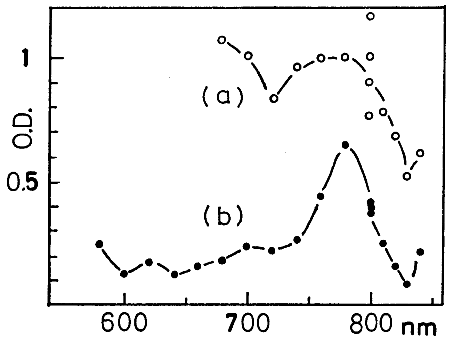

Fig. 10. Transient absorption spectra of ECZ-methanol system. The delay time from the laser pulse. (a) 0, (b) 100 ns.

B. Photoionization of VCZ and ECZ in the Absence of Electron Acceptors. In the photoionization of VCZ and ECZ in polar solvents in the absence of electron acceptors, the formation of their cation radicals was confirmed by transient absorption and transient photoconductivity measurements. The decay process of the absorption of VCZ cation radical in acetonitrile solution is shown in Fig. 9 and the transient absorption spectra of ECZ–methanol system in Fig. 10.

The photocurrent in two-component system is similar to that of three-component systems, but in the former it is due to solvated cation radicals and solvated electrons.

We have confirmed that ionization is mainly due to the double photon process. The result in the case of VCZ–acetonitrile two-component system is shown in Fig. 8.

C. $S_n \leftarrow S_1$ Absorption Spectra of VCZ and ECZ. In order to examine the $S_n \leftarrow S_1$ transitions of VCZ and

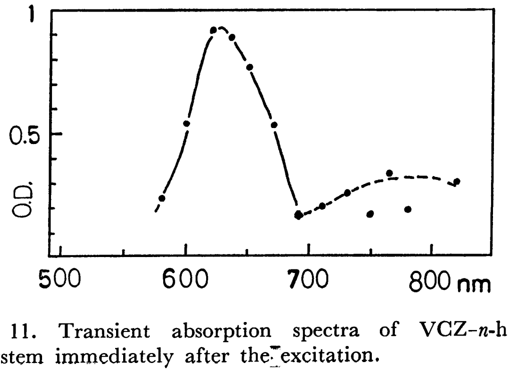

Fig. 11. Transient absorption spectra of VCZ-*n*-hexane system immediately after the excitation.

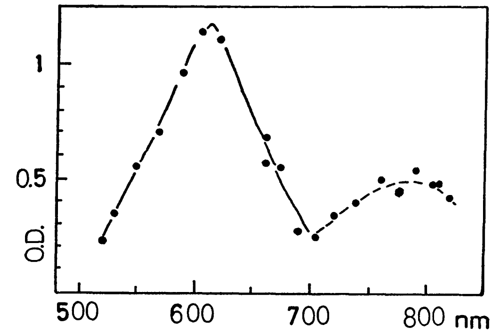

Fig. 12. Transient absorption spectra of ECZ-*n*-hexane system immediately after the excitation.

ECZ in detail, we carried out the laser photolysis and transient absorption measurements in n-hexane solution of these molecules, in order to avoid the formation of ion radicals.

The transient absorption spectra of VCZ-*n*-hexane and ECZ-*n*-hexane systems are shown in Figs. 11 and 12, respectively. The rise and decay curves of the transient absorption and the fluorescence of VCZ-*n*-hexane system are shown in Fig. 13. We can conclude that the observed transient absorption spectra are due to the $S_n \leftarrow S_1$ transitions, since the decay process of absorption is approximately the same as that of the fluorescence.

It might be of interest to note that the 620 nm band in the $S_n \leftarrow S_1$ spectra is similar to the absorption band of biphenyl anion. According to theoretical calculations on the electronic structures of carbazole[8,9] and VCZ[9], a considerable amount of charge transfer from nitrogen to the biphenyl part occurs in the S_1 state. Thus, the structure of these molecules in the equilibrium S_1 state might be highly polar where the biphenyl part is negatively charged, giving rise to $S_n \leftarrow S_1$ spectra similar to the absorption band of biphenyl anion. On the other hand, the wavelengths of the absorption bands in the $S_n \leftarrow S_1$ spectra are similar to those in the absorption spectra of cation radicals of VCZ and ECZ. Similarity of the $S_n \leftarrow S_1$ spectra of a molecule to those of its cation radical may be understood at least qualitatively on the basis of simple MO theory.

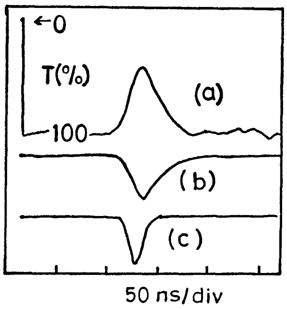

Fig. 13. The rise and decay curves of the transient absorption and fluorescence of VCZ-*n*-hexane system.
(a) Absorption at 620 nm.
(b) Fluorescence at 370 nm.
(c) Exciting laser pulse.

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[8] N. Mataga, Y. Torihashi, and K. Ezumi, *Theoret. Chim. Acta*, **2**, 158 (1964).

[9] K. Nishimoto, Private communication.