CHEMISTRY LETTERS, pp. 221-224, 1972. Published by the Chemical Society of Japan

LASER PHOTOLYSIS STUDIES ON THE IONIZATION OF N-VINYLCARBAZOLE IN THE PRESENCE AND IN THE ABSENCE OF ELECTRON ACCEPTORS

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Formation of solvated ion radicals in the N-vinylcabazole (VCZ)-electorn acceptor system has been studied by means of the laser photolysis and transient photoconductivity as well as transient absorption measurments. Ion radical formation due to the encounter collision between an excited VCZ and electron acceptor has been established.

It has been postulated that the photo-polymerization 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.[1] However, there has been no direct experimental evidence for this mechanism of the cation radical formation.

On the other hand, we have already demonstrated clearly the ion radical formation due to the encounter collision between an excited pyrene and N,N-dimethylaniline in moderately and strongly polar solvents by means of the laser photolysis and transient photoconductivity as well as absorption measurements.[2] We have undertaken analogous studies in the case of VCZ-electron acceptor system, and we have confirmed unambiguously for the first time the formation of solvated cation radicals of VCZ and anion radicals for the acceptor due to the encounter collision between the excited VCZ and the acceptor.

We have examined also N-ethylcarbazole (ECZ) in detail for the purpose of comparison with VCZ.

We have used the same Q-switched ruby laser as described before.[2-3] The produced ion radicals were observed by measuring the photocurrent induced by laser excitation. Details of the photocurrent measurements are given elsewhere.[2] For examining the effect of the excitation light intensity on the photocurrent, the intensity of the laser pulse was reduced by using neutral filters composed of wire gauzes. Relateve values of the exciting light intensity were monitored by measuring with a photomultiplier the intensity of light partially reflected by means of a beam splitter. The absolute value of the exciting light intensity was determined by a ballistic thermopile TRG model 100 (Hadron). The transient absorption spectra of ions were observed by nsec flash photolysis method.[3] Measurements of

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fluorescence decay tims were carried out by using a nitrogen gas laser.[4)]

Tetracyanobenzene (TCNB) and tetracyanoethylene (TCNE), which do not show any absorption band at 347 nm, were used as electron acceptors. Both concentrations of VCZ and ECZ in solutions for the measurements were ca. 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. 10^{-2}M. All solutions were deaerated completely by repeated freeze-pump-thaw cycles.

The transient photocurrent of VCZ-TCNB-acetonitrile system is shown in Fig.1. The results in Fig.1 indicate that the ion radicals produced by the 347 nm excitation vanish due to the bimolecular recombination. In a more concentrated solution, there arises a charge transfer absorption band near 570 nm due to the complex formation. However, in the present case, the interaction of VCZ with TCNB in the ground state can be ignored, since no charge transfer absorption can be observed. Therefore, the ion radicals in Fig.1 may be formed by the encounter collision between excited VCZ and TCNB molecule. We have examined the effect of the TCNB addition on the fluorescence decay time of VCZ in acetonitrile solution. The rate constant of the quenching reaction has indicated clearly that the excited VCZ molecules make diffusion-controlled encounter collision with acceptor molecules.

The ion radical formation may be confirmed by the transient absorption measurements. The transient absorption spectra of VCZ-TCNB-acetonitrile system are shown in Fig.2. The decay of the optical absorption at 780 nm and the reciprocal of the absorbance vs. time relation are shown respectively in Fig.3a and b. 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 can be ascribed to the transition from the lowest excited singlet (S_1) to the higher excited singlet (S_n) state of VCZ, since its decay process is approximately the same as that of the fluorescence. 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 rather long life may be ascrined to the VCZ cation radical[5)] and that at ca. 460 nm to the TCNB anion radical.

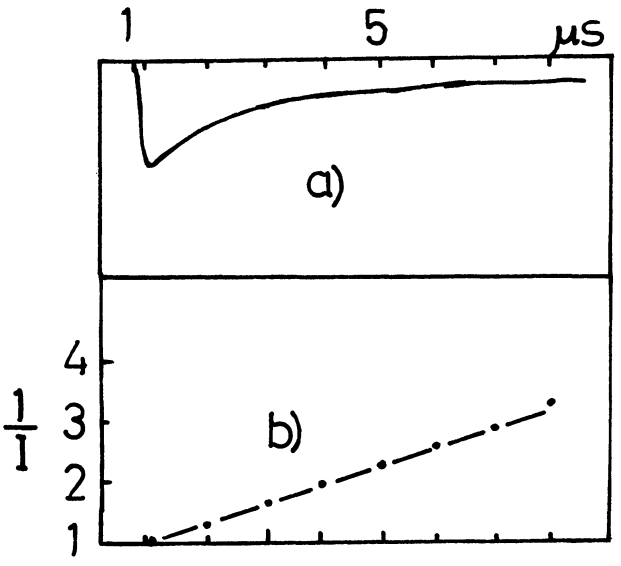

Fig.1. Transient photocurrent of the VCZ-TCNB-acetonitrile system.
(a) The decay curve of photocurrents.
(b) The reciprocal of the photocurrent vs. time relation.

Since the exciting light pulse in the present work is fairly strong, it may be possible that the ionization of VCZ due to the double photon absorption occurs. In order to examine this problem, we have investigated the effect of the exciting intensity on the peak

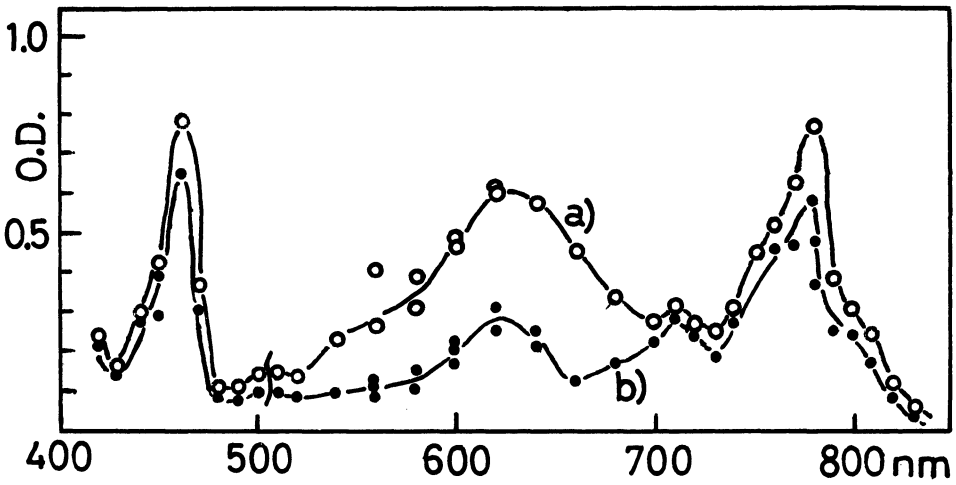

Fig.2. Transient absorption spectra. The delay time from the laser pulse, (a) 0, (b) 200 nsec.

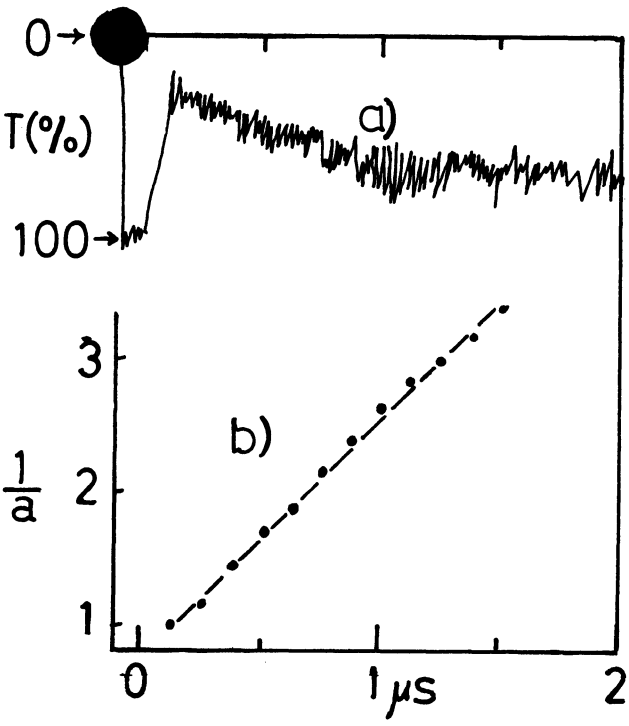

Fig.3. The decay process of the absorption at 780 nm.

photocurrent, the results of which are indicated in Fig.4. In the case of the VCZ-TCNB-acetonitrile system, one can see clearly that the ionization is an one-photon process. Therefore, the most predominant process leading to the photoionization in this case appears to be the encounter collision between the excited VCZ and the TCNB molecules followed by one electron transfer from the excited VCZ to TCNB. We have confirmed that the laser induced photoconductivity of the pure solvent can be neglected. However, the photocurrent of VCZ-solvent two-component system was not negligible compared with that of the three-component system. We have confirmed the formation of VCZ cation radicals by the transient absorption measurements in the case of the VCZ-acetonitrile two-component system. One can see in Fig.4 that the ionization of VCZ-acetonitrile two-component system is mainly due to the double photon absorption.

We have examined in detail the systems which contain ECZ instead of VCZ. The results of the studies on the ECZ solutions were quite similar to those on the VCZ

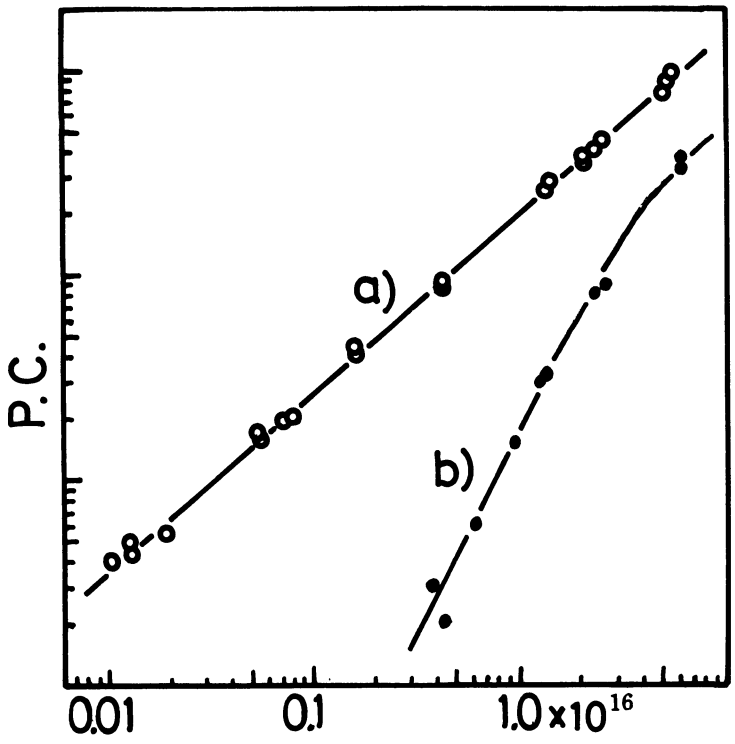

Fig.4. The effect of the exciting light intensity on the peak photocurrent.
(a) VCZ-TCNB-acetonitrile system.
(b) VCZ-acetonitrile system.

solutions. Namely, not only the ion radical formation processes but also thier decay processes due to the recombination in the case of the ECZ solutions are quite similar to those of the VCZ solutions, respectively. The above result might be of some interest from the viewpoint of elucidating the CT photopolmerization mechanisms. According to it, only a very small part of the dissociated ion radicals which have escaped the deactivation due to the recombination might initiate the polmerization.

Acknowledgement

The authors wish to express their thanks to Dr.S. Tazuke of Kyoto University for the offer of VCZ and ECZ samples and for valuable discussions.

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(Received January 20, 1972)