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PHOTOPOLYMERIZATION OF N-VINYLCARBAZOLE IN WHICH EDA COMPLEX IS INVOLVED: PHOTOIONIZATION OF N-VINYLCARBAZOLE IN THE PRESENCE OF ELECTRON ACCEPTORS

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Photochemical formation of VCZ cation radical and electron acceptor anion radical has been demonstrated by means of flash spectroscopy for the VCZ-electron acceptor systems where exciplex emission can be observed. The ion radicals are produced by one photonic process and they decay by bimolecular recombination.

Recently photoionization of N-vinylcarbazole (VCZ) in the presence of various acceptors has been studied by means of flash photolysis$^{1,2)}$ to elucidate the photopolymerization mechanism. We have been also investigating the photopolymerization of VCZ where EDA complex is involved in the reaction mechanism of photopolymerization. As for the photopolymerization systems, two typical schemes can be considered. The case (1): an initiating species is produced photochemically by excitation of a charge transfer complex formed between VCZ and an acceptor in the ground state. An example of this system is VCZ-2,4,7-trinitrofluorenone whose system is polymerized photochemically by cationic mechanism in a polar solvent, nitrobenzene.$^{3)}$ The case (2): photochemically excited VCZ interacts with an acceptor within the lifetime of the excited state and an initiating species is produced. For example the VCZ-dimethyl terephthalate system exhibits exciplex emission in non-polar solvents and is photopolymerized by radical mechanism in a polar DMF solvent.$^{4)}$

In the course of the investigation in detail of the latter system (2), it has been found that VCZ cation radical and acceptor anion radical are produced photochemically. Measurement of ion radical formation was carried out by means of flash spectroscopy. Flash photolysis was made at room temperature by using a jacketed quartz cell (100 mm long, 10 mm in diameter). Dimethyl terephthalate acceptor solution is filled in the outer jacket to excite only the VCZ donor. Input energy was 150 J and the half value of duration time for the photolysis flash was about 16 μsec. Electron acceptors described in this report are methyl benzoate (MB), dimethyl terephthalate (DMTP), trimethyl trimesate (TMT), tetramethyl pyromellitate (TMP), benzene pentacarboxylic acid pentamethylester (PMB), and hexamethyl mellitate (HMM). Behaviors of the other derivatives, $C_6H_4(COOCH_3)_2$(1,2-, 1,3), $C_6H_3(COOCH_3)_3$ (1,2,3-, 1,2,4-), $C_6H_2(COOCH_3)_4$(1,2,3,4-, 1,2,3,5-) are almost the same as those of the above electron acceptors. Acetonitrile was used as a solvent for all these experiments. All the samples were deaerated.

Addition of the above acceptors to the VCZ solution quenched the normal fluorescence of VCZ and gave a new emission band around 480-530 nm. The new emission band is ascribed to an exciplex formed between VCZ and an acceptor since the excitation spectrum of the new emission agreed closely with the VCZ absorption spectrum and no charge transfer absorption band was observed for all the VCZ-acceptor systems even at low temperatures, e.g., at 77°K in 2-methyltetrahydrofuran. The fluorescence quenching of VCZ followed the Stern-Volmer equation. The excited singlet lifetime of VCZ, τ_0 was measured to be 9.8 nsec by the phase method. Quenching constant, k_q of the VCZ fluorescence for each acceptor, and relative intensity and λ_{max} of the exciplex emission are shown in Table 1. $k_q(\mathrm{DMTP}) \simeq k_q(\mathrm{TMP}) \gtrsim k_q(\mathrm{PMB}) \simeq k_q(\mathrm{TMT}) > k_q(\mathrm{HMM}) > k_q(\mathrm{MB})$. DMTP and TMT acceptors give the strongest exciplex emission. λ_{max} of the exciplex emission is at around 480-530 nm.

Table 1. Quencihg constant, k_q, and relative intensity and λ_{max} of the exciplex emission

Acceptors	$k_q \times 10^8$ (l/mole·sec)	Exciplex emission	
		Relative intensity	λ_{max}
MB	8	-	
DMTP	96	+++	∼ 480 nm
TMT	73	+++	∼ 480 nm
TMP	98	++	520-530 nm
PMB	75	+	∼ 530 nm
HMM	65	+	

Solvent: toluene, at room temperature

Absorption spectra of intermediates observed by flash spectroscopy are shown in Figs. 1(b), 2, 3(b), and 4(b). Figs. 1(a)5), 3(a), and 4(a) show the absorption spectra of acceptor anion radicals which were produced from acceptors by sodium reduction in a THF solvent under high vacuum. Absorption spectra of the anion radicals were taken immediately after contacting the acceptor solutions to sodium mirror. It is clear from the identity of two absorption spectra that the bands around 530 nm in the absorption spectra of the intermediates are assigned to the anion radicals of the electron acceptors. Absorption peaks around 780 nm can be ascribed to VCZ cation radical.1) As for methyl benzoate whose accepting power is weak, photochemical ion radical formation was scarcely observed in the present measurements. For some acceptors, e.g., PMB, 1,3-$C_6H_4(COOCH_3)_2$, photoionization of the VCZ-acceptor systems was detected, but new absorption peaks appeared too in addition to the ion radical ones mentioned above. These new absorption peaks seem to be due to succeeding intermediates formed from the ion radicals in so short interval in comparison with light flash duration. Light intensity dependence of anion radical or cation radical production is shown in Fig. 5. The slope is about one. This means that these ion radicals are produced by one photon, not by two photon excitation. For typical VCZ-acceptor system, the decay of acceptor anion radicals followed the second-order kinetics. Therefore anion radicals seem to be neutralized by the recombination with VCZ cation radical. The rise and fall profile of anion radical absorption shows that the rate of anion radical production is much faster than the rise time of light flash.

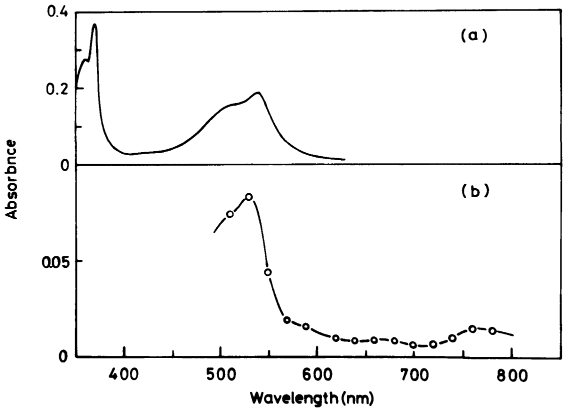

Fig. 1. (a) The absorption spectrum of DMTP anion radical produced by sodium reduction in THF.

(b) The absorption spectrum of transient species obtained by the flash photolysis of VCZ(5x10^{-3}M)-DMTP(1x10^{-2}M) in acetonitrile. 100 μsec.

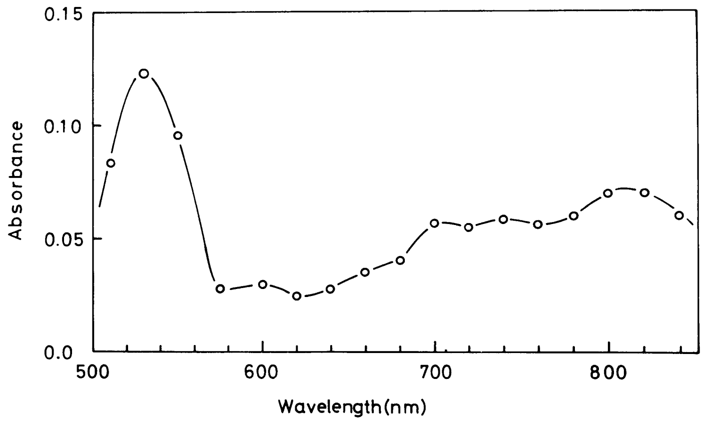

Fig. 2. The absorption spectrum of transient species obtained by the flash photolysis of VCZ(5x10^{-3}M)-TMT(1x10^{-2}M) in acetonitrile. 100 μsec.

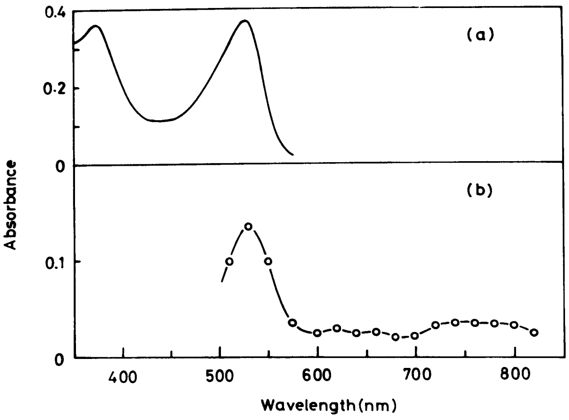

Fig. 3. (a) The absorption spectrum of TMP anion radical produced by sodium reduction in THF.

(b) The absorption spectrum of transient species obtained by the flash photolysis of VCZ(5x10^{-3}M)-TMP(1x10^{-2}M) in acetonitrile. 100 μsec.

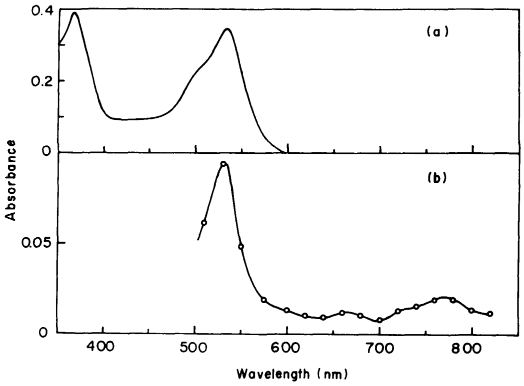

Fig. 4. (a) The absorption spectrum of HMM anion radical produced by sodium reduction in THF.

(b) The absorption spectrum of transient species obtained by the flash photolysis of VCZ(5×10^{-3}M)-HMM(1×10^{-2}M) in acetonitrile. 100 μsec.

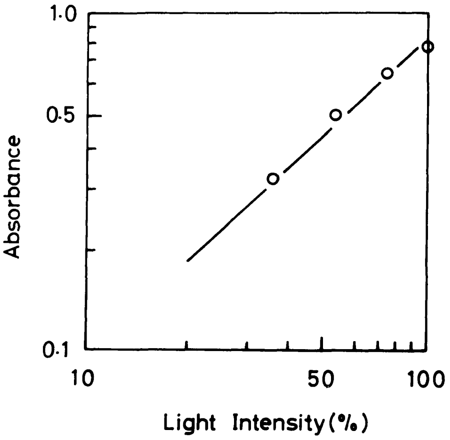

Fig. 5. Light intensity dependence of anion radical concentration (absorbance at 530 nm) produced by flash illumination. VCZ(5×10^{-3}M)-TMP(1×10^{-2}M)

Even without electron donor (VCZ), these electron acceptors are photoionized to show acceptor anion radical absorption spectra when these electron acceptors are excited directly by light flash in acetonitrile solvent.6) But this kind of direct ion radical formation is negligibly small in the above experiments since the outer jacket is filled with an acceptor solution and moreover the absorbance of VCZ is overwhelmingly large.

Further investigation on photochemical ion radical formation, especially the mechanism of ion radical formation is in progress and will be reported at a later date.

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5) The absorption spectrum of DMTP anion radical has been already reported by T.Kowata, M.Koizumi, Bull, Chem. Soc. Japan, 42, 3352 (1969) and the spectrum obtained by us agreed closely with that obtained by them.

6) To be published.

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