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Mechanism of Charge-transfer Polymerization. III.[1] Flash Photolysis of *N*-Vinylcarbazole—Chloranil System

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Photochemical formation of transient *N*-vinylcarbazole cation and chloranil anion-radicals has been demonstrated by means of flash spectroscopy for the *N*-vinylcarbazole–chloranil–solvent systems. Identification and decay of the species formed by flash illumination are described.

The photochemical reaction of *N*-vinylcarbazole (VCZ) in the presence of an electron acceptor has currently been the subject of great interest. The reaction is complex involving cationic polymerization, cyclodimerization, and in certain cases radical polymerization or copolymerization with an electron-accepting monomer, the reaction course being strongly solvent dependent.[2] For example, in the system VCZ–chloranil(CA), cationic polymerization of VCZ occurs in benzene,[3] while in polar, basic solvents such as acetone, acetonitrile or methanol cyclodimerization of VCZ takes place to form *trans*-1,2-dicarbazylcyclobutane.[2,4] It has been postulated that the reaction proceeds *via* transient VCZ cation-radical formed by the photochemical electron transfer between the donor, VCZ, and an electron acceptor, and the reaction course is explained in terms of the dual reactivity, cationic and radical, of the VCZ cation-radical.[2] However, no direct evidence for the formation of ion-radical intermediates has so far been obtained.

The present study was undertaken to demonstrate the formation of VCZ cation and CA anion-radicals by means of flash spectroscopy for the VCZ–CA–

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solvent systems. We reported[5] on the flash photolysis of CA in various solvents, the results of which were utilized for the present analysis. Formation of VCZ cation and CA anion-radicals was confirmed and occurrence of the electron transfer in the photochemical reaction of VCZ in the presence of an electron acceptor has been verified for the first time.[6,7] VCZ cation-radical was confirmed by the radiolytic method established for the selective formation of ion-radicals.

Experimental

Materials. *N*-Vinylcarbazole (VCZ) (Nakarai Chemical Ltd., extra pure grade) was recrystallized twice from methanol, then twice from *n*-hexane and dried *in vacuo* for two or three days at room temperature, mp 65°C. Chloranil (CA) of reagent grade (Wako Pure Chemical Ind. Ltd.) was recrystallized from benzene, then passed through a column of freshly baked calcium carbonate using benzene as an eluent to remove acidic impurities,[8] and then recrystallized twice from benzene, followed by a fractional sublimation *in vacuo*. Acetone was refluxed with potassium permanganate for half a day, dried with calcium sulfate and distilled. Acetonitrile was refluxed over phosphorus pentoxide for 24 hr, distilled and then refluxed over anhydrous potassium carbonate and again distilled immediately before use. Methanol was refluxed with small amounts of sodium metal and distilled. Benzene was purified and dried in the usual way and distilled from sodium wire immediately before use. *sec*-Butyl chloride (*s*-BuCl) (Tokyo Chemical Ind. Co.) was used as received, purity being proved to be good enough for the radiolytic experiment.

Flash Spectroscopy. The concentration ranges of VCZ and CA were 2×10^{-4}—8×10^{-4}M and 1×10^{-4}—2×10^{-4}M, respectively. Freshly prepared solutions were evacuated at 10^{-5} mmHg by several freeze-pump-thaw cycles or bubbled with highly purified nitrogen gas for about 20 min to remove dissolved oxygen, and then poured into a cylindrical silica cell, 1.5 cm in diameter and 20 cm in length. The apparatus is almost the same as that described by Yamamoto *et al.*[9] The transient absorption spectra were obtained photographically with Fuji Neopan SSS film (ASA 200). A combined filter composed of a glass plate and a benzene solution of ethylcarbazole (2×10^{-4}M) was used to cut off the light of wavelength below 350 nm.

Absorption Spectroscopy of γ-Irradiated Rigid Solutions. *N*-Vinylcarbazole in *s*-BuCl was frozen at 77°K to a glassy rigid solution and γ-irradiated at the same temperature (total dose 1.6×10^{19} eV/g). The absorption appearing in the visible to near infrared region was measured with a Cary 14RI spectrophotometer. Further details of the experiment are described elsewhere.[10]

Results and Discussion

N-Vinylcarbazole forms a charge-transfer complex with CA in the ground state (λ_{CTmax} 506 nm, shoulder at 590 nm, in CCl_4). However, in the present experiment no donor-acceptor interaction in the ground state was observed because of the low concentration of the solutions, selective excitation of the acceptor, CA, thus being possible. Absorption of photoenergy by VCZ (*ca.* 2×10^{-4}M) was almost negligible in the wavelength region above 350 nm. When CA was selectively excited by the flash illumination (hν>350 nm) of a nitrogen-bubbled acetone solution containing 2×10^{-4}M VCZ and 1×10^{-4}M CA at room temperature, a transient absorption spectrum consisting of two band systems was obtained, one with a maximum at 446 nm and a shoulder at 421 nm, and the other a weak, broad band system in the region of wavelength longer than 550 nm (Fig. 1).

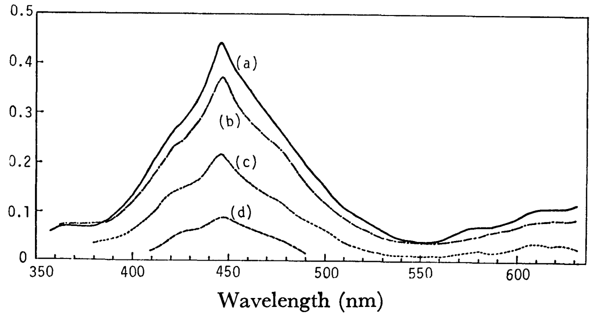

Fig. 1. The absorption spectra of transient species obtained by the flash photolysis of an acetone solution of VCZ (2×10^{-4} M) and CA (1×10^{-4} M). Delay time: (a) 3 μsec (b) 9 μsec (c) 26 μsec (d) 84 μsec. O. D. stands for the optical density.

The former was assigned to CA anion-radical from its identity with the spectrum of the chemically prepared CA anion-radical in acetone.[11] The latter was attributed to VCZ cation-radiacl as the most reasonable counterpart of the CA anion. Its intensity was found to decrease with increasing concentration of VCZ, which suggests the occurrence of the reaction of VCZ cation-radical formed with VCZ monomer. The assignment was substantiated by γ-irradiation of VCZ in *s*-BuCl at 77°K which is known to produce exclusively the solute cation.[10,12] The absorption spectrum of the VCZ cation observed for the irradiated frozen solution is shown in Fig. 2. The authenticity of the spectrum as due to VCZ cation would be supported by the fair agreement of the result of calculation shown by the sticks in Fig. 2. The result was obtained by using a computer program[13] for the SCF–MO calculation of open-shell molecules.[14] The absorption identified with the VCZ cation (Fig. 2) may be compared favorably with the absorption (Fig. 1) at wave-

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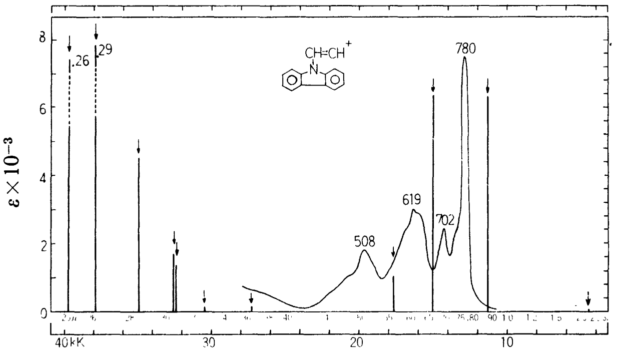


Fig. 2. The absorption spectrum of VCZ cation-radical produced by γ-ray irradiation of VCZ in *s*-BuCl matrix at 77°K. The sticks represent the theoretical spectrum obtained by an SCF-MO calculation for the cation. The left ordinate refers to the molar extinction coefficient of the experimental spectrum while the right refers to the oscillator strength of the theoretical spectrum. The numbers at peak are the wavelengths in unit of nm.

lengths longer than 550 nm (due to the limitation in the film, the absorption beyond 650 nm in Fig. 1 could not be measured).

For comparison with the VCZ-CA system the absorption spectrum obtained by the flash illumination of CA only in acetone solution is shown in Fig. 3. It should be noted that no pure absorption of CA anion-radical was obtained in this case. The *T-T′* absorption of CA appeared in the region 450—550 nm at the delay time of 3 μsec and faded away mostly at 17 μsec, and the bands at *ca.* 440 nm and *ca.* 370 nm which persisted after disappearence of *T-T′* absorption were regarded as due to the mixture of CA semiquinone radical and CA anion-radical.[5] The absorption spectra of CA semiquinone radical and CA anion-radical are similar, but the semiquinone radical has a second band at λ_{max} 357—375 nm,[5] while the anion-radical has none in this region. The absorption spectrum of CA semiquinone radical has been obtained by the flash photolysis of CA in tetrahydrofuran as a result of hydrogen abstraction reaction from the solvent by the excited CA, showing a band at λ_{max} 437 nm with a shoulder at 414 nm and a band at λ_{max} 375 nm.[5] Although a very weak, broad band system was also observed beyond 550 nm even with CA only in acetone solution, it decayed at nearly the same rate as for the triplet state of CA and was assigned to the charge-transfer band between the solvent as a donor and triplet CA as an acceptor. The same phenomenon was found in a benzene solution.[5]

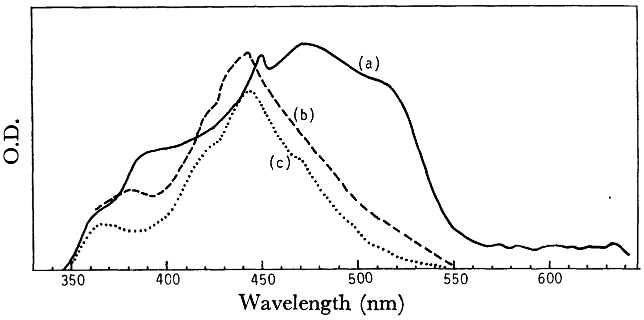


Fig. 3. The absorption spectra of transient species obtained by the flash photolysis of CA (2.3×10^{-4} M) in acetone. Delay time: (a) 3 μsec (b) 17 μsec (c) 56 μsec.

Chloranil anion-radical formed in an acetone solution of VCZ and CA decayed at a diffusion-controlled rate (Fig. 4). A rate constant $k=2.1\times10^{10}\text{M}^{-1}\text{sec}^{-1}$ was obtained by using the molar extinction coefficient $\varepsilon=9\times10^3$ reported for CA anion-radical at its abosrption.[10]

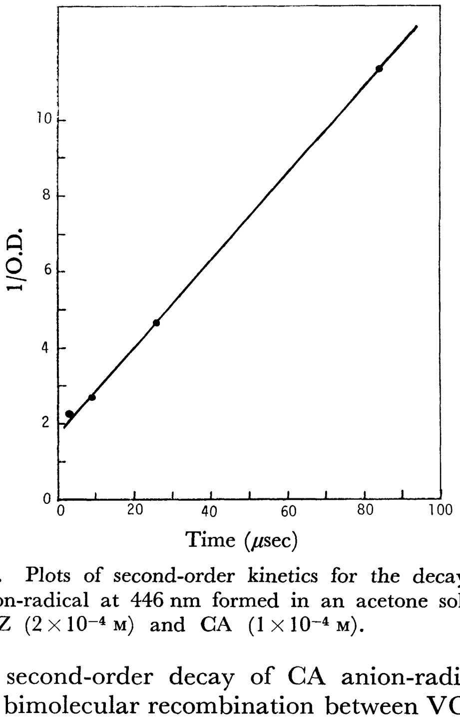
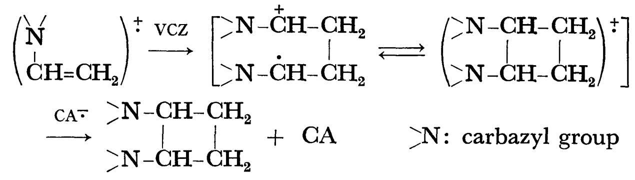


Fig. 4. Plots of second-order kinetics for the decay of CA anion-radical at 446 nm formed in an acetone solution of VCZ (2×10^{-4} M) and CA (1×10^{-4} M).

The second-order decay of CA anion-radical indicates a bimolecular recombination between VCZ cation and CA anion-radicals and/or between VCZ dimer cation-radical and CA anion-radical, which is consistent with the proposed mechanism for the cyclodimerization of VCZ,[2,4] if the reaction proceeds under the conditions of the present flash photolysis as in the preparatory scale reaction.



The kinetic observation in an acetone solution may be explained in terms of the following scheme of reactions.

$$\text{VCZ} + \text{CA} \xrightarrow{h\nu} \text{VCZ}^{+\cdot} + \text{CA}^{-\cdot} \tag{1}$$

$$\text{VCZ}^{+\cdot} + \text{CA}^{-\cdot} \xrightarrow{k_1} \text{VCZ} + \text{CA} \tag{2}$$

$$\text{VCZ}^{+\cdot} + \text{VCZ} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{VCZ}_2^{+\cdot} \tag{3}$$

$$\text{VCZ}_2^{+\cdot} + \text{CA}^{-\cdot} \xrightarrow{k_3} \text{VCZ}_2 + \text{CA} \tag{4}$$

The rate equation of the decay of CA anion-radical is

$$-\text{d}[\text{CA}^{-\cdot}]/\text{d}t = k_1[\text{CA}^{-\cdot}]\{[\text{VCZ}^{+\cdot}]+(k_3/k_1)[\text{VCZ}_2^{+\cdot}]\}, \tag{5}$$

where

$$[\text{VCZ}^{+\cdot}] + [\text{VCZ}_2^{+\cdot}] = [\text{CA}^{-\cdot}] \tag{6}$$

$$[\mathrm{VCZ}_2{}^{\dot{+}}]/[\mathrm{VCZ}^{\dot{+}}][\mathrm{VCZ}] = k_2/k_{-2} = K \tag{7}$$

Substituting Eqs. (6) and (7) into (5) we obtain

$$\begin{aligned} -\mathrm{d}[\mathrm{CA}^{\dot{-}}]/\mathrm{d}t &= k_1[\mathrm{CA}^{\dot{-}}]^2\left\{\frac{1+(k_3/k_1)K[\mathrm{VCZ}]}{1+K[\mathrm{VCZ}]}\right\} \\ &= k_1C[\mathrm{CA}^{\dot{-}}]^2, \qquad (8) \\ &([\mathrm{CA}^{\dot{-}}]\ll[\mathrm{VCZ}]) \quad C\text{: constant} \end{aligned}$$

which is the second-order decay equation. The following rate equation is derived from the above scheme of reactions where the process k_{-2} is not considered in Eq. (3), if the rate constant k_1 is assumed to be equal to k_3.

$$-\mathrm{d}[\mathrm{CA}^{\dot{-}}]/\mathrm{d}t = k_1[\mathrm{CA}^{\dot{-}}]^2 \tag{9}$$

If the absorption at longer wavelengths in Fig. 1 is due to the VCZ cation, it should be observed irrespective of solvent. When acetonitrile was used in place of acetone, the solution of VCZ (2.5×10^{-4}M) and CA (1×10^{-4}M) gave the spectrum shown in Fig. 5 which is similar to Fig. 1 and may be interpreted in terms of the formation of VCZ cation and CA anion-radicals. In contrast to the solution containing the two solutes CA only in acetonitrile showed the absorption shown in Fig. 6. This can be attributed to *T-T′* absorption of CA and the absorption mainly due to the semiquinone radical. No absorption appeared at the wavelength longer than 550 nm.

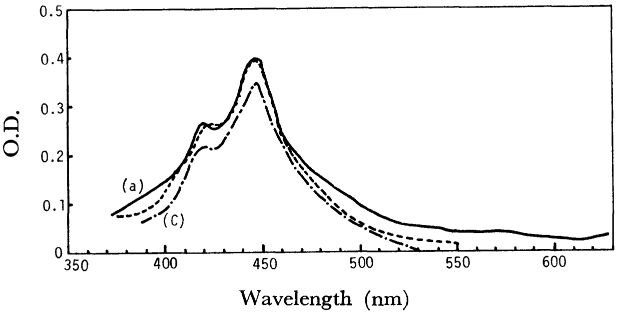


Fig. 5. The absorption spectra of transient species obtained by the flash photolysis of an acetonitrile solution of VCZ (2.5×10^{-4} M) and CA (1×10^{-4} M). Delay time: (a) 4 μsec, (b) 9 μsec, (c) 250 μsec.

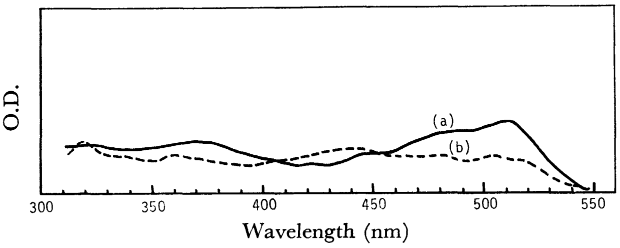
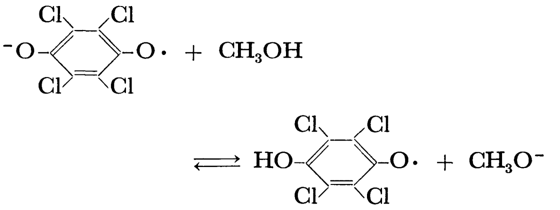
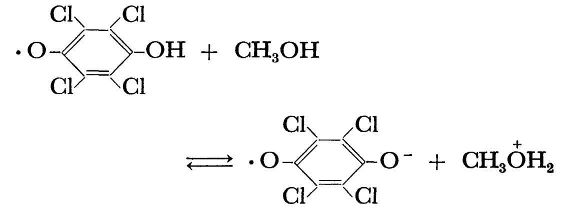


Fig. 6. The absorption spectra of transient species obtained by the flash photolysis of CA (1.4×10^{-4} M) in acetonitrile. Delay time: (a) 3 μsec. (b) 26 μsec.

The transient absorption spectrum obtained in methanol is shown in Fig. 7. In methanol the spectrum in the region 400—500 nm differs somewhat in shape from that observed in acetone or in acetonitrile, showing two bands at $\lambda_{\max}$ 426 and 451 nm. The absorption attributable to VCZ cation-radical appeared at a wavelength longer than 550 nm. The absorption bands in the region 400—500 nm are almost the same as those obtained by the flash photolysis of CA only in methanl and interpreted as an admixture of the absorption of CA anion-radical and CA semiquinone radical. The semiquinone radical is suggested to be formed by the protonation of the anion-radical initially formed.



In the flash photolysis of CA only in methanol the spectrum obtained is composed of the *T-T′* absorption, the absorption of the semiquinone radical and of the anion-radical. No absorption appeared at a wavelength longer than 550 nm (Fig. 8). In this case the initially formed semiquinone radical by the hydrogen abstraction reaction of the excited CA from the solvent dissociates into the anion-radical and is in equilibrium with the latter species.



The acid-base equilibrium between the semiquinone radical and the anion-radical (semiquinone anion) in

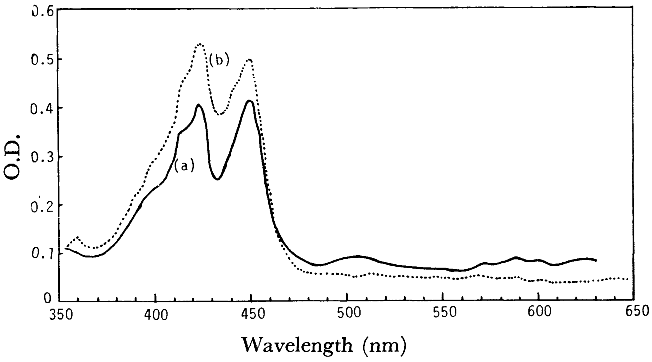


Fig. 7. The absorption spectra of transient species obtained by the flash photolysis of a methanol solution of VCZ (2×10^{-4} M) and CA (1×10^{-4} M). Delay time: (a) 3 μsec (b) 8.5 μsec.

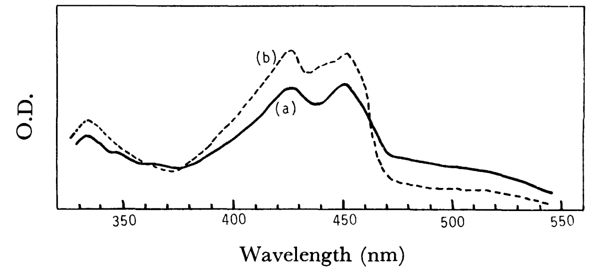


Fig. 8. The absorption spectra of transient species obtained by the flash photolysis of CA (1.8×10^{-4} M) in methanol. Delay time: (a) 3 μsec (b) 16 μsec.

methanol has also been shown by Bridge and Porter[15] in the flash photolysis of duroquinone.

Noticeably, CA anion-radical formed in acetonitrile or in methanol persisted for a much longer time than in acetone under comparable conditions. Details are not available at present and further studies are needed with respect to this point. Flash photolysis of the system VCZ–CA was also carried out in benzene solution, but the absorption bands obtained were very low in intensity and no definite conclusions were reached.

Transient CA anion and VCZ cation-radicals were detected in the VCZ–CA–solvent systmes by selective excitation of the acceptor, while in the absence of VCZ no pure absorption of CA anion-radical was obtained. This confirms the fact that photochemical electron transfer took place between VCZ and the excited CA in polar solvents. This seems to be the first example to demonstrate the occurrence of electron transfer in the photochemical reaction of VCZ in the presence of an electron acceptor.

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