ketone photoexcitation, is a more important initiation process than is $^1O_2$ generation. In addition, P-2, P-5, and P-7 do not quench $^1O_2$[26] yet do retard the photooxidation of PP-ketone.

Conclusions

Some PP photostabilizers can prevent the photolysis of ketonic substituents in solid PP by quenching excited states, and so retard photooxidation of the polymer sensitized by these macro ketones. The scission of excited ketonic groups to give radical products is probably prevented by collisional processes, rather than by long-range energy transfer, and quenching may be enhanced by chromophore-stabilizer association. There seems to be a fair correlation between the stabilization of ketone-substituted PP and the available data on the quenching of ketone photolysis in the liquid phase by these same compounds.

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Polymerization and Dimerization of Vinylcarbazole. II.[1] Relation between Reactive Intermediates and Final Products in Irradiated Benzonitrile Solutions

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ABSTRACT: Reactive intermediates involved in the reactions of dimerization or polymerization were directly observed by use of a pulse radiolysis technique. The relation between reactive intermediates and final products was studied in irradiated benzonitrile solutions of vinylcarbazole. The cyclodimer and polymer were found to be produced in the aerated and deaerated solutions irradiated, respectively. The initiating species of both the radiation-induced dimerization and polymerization was confirmed to be the cation radical of vinylcarbazole. The polymerization proceeds *via* a cationic process. The reaction of the radiation-induced cyclodimerization is a chain reaction as well as the photochemically induced cyclodimerization. The kinetic chain length was estimated to be several hundreds. Oxygen was concluded to play an important role in the formation of the cyclodimer after the production of the cation radical of vinylcarbazole.

Few attempts[1,3-7] to study reactive intermediates involved in a radiation-induced polymerization have been done by means of direct observations. The information about the reactive intermediates related to polymerization or dimerization of vinylcarbazole initiated by charge-transfer or photo-chemical reactions has been usually obtained from indirect observations except for a few cases.[1,8,9] The identification and behavior of some reactive intermediates involved in the irradiated benzonitrile solutions were reported in our previous paper.[1] Both the direct observations of the reactive intermediates and the product analysis for the same solutions were found to be necessary to elucidate the detailed mechanism of complicated reactions such as the dimerization and polymerization. The present paper deals mainly with the relation between the reactive intermediates and the final products.

I. Experimental Section

Materials. Vinylcarbazole, benzonitrile, and biphenyl were purified in a manner identical with that recently described.[1] Naphthalene was Tokyo Kasei's zone-refined reagent. Triethylamine, aniline, and dimethylaniline were distilled and water was triply distilled.

Pulse Irradiation. The method of pulse radiolysis has been described.[10] Only an outline of the equipment relevant to this work is presented here. A 2.5-2.8-Mev electron beam from a van de Graaff accelerator was used throughout. The pulse duration ranged from 0.5 to 2.0 μsec and peak currents were usually used in the range 120–200 mA.

Dosimetry. The mean radiation dose delivered to the solutions was determined by use of the ferrocyanide chemical dosimetry.[11] The molar extinction coefficient, $\epsilon(\mathrm{Fe(CN)_6}^{3-})$, at 420 nm was taken as 1000 M^{-1} cm^{-1} and $\mathrm{G(Fe(CN)_6}^{3-})$ as 3.2 molecules/100 ev.

Irradiation Cells. Rectangular irradiation cells made of Suprasil were used. Internal light path length was 4 cm.

Kinetic Spectroscopy. Light from a Ushio 150-W xenon lamp was focussed through the cell by a Suprasil quartz lens system. Grating monochromators, photomultipliers, and preamplifiers were placed behind blocks of lead.

Flow System. Since the products have an influence on the decay of the transient species in concentrated solutions, it was necessary to make the fresh solutions flow from a reservoir into the irradiation cell by use of a conventional slow-speed pump after each pulse in order to measure the exact decay and spectra of the transient species.

II. Results and Discussion

Product Analysis. A colorless and needle-like crystal was produced in aerated benzonitrile solutions of vinylcarbazole irradiated with electrons or γ-rays. The molecular weight of the product was determined to be 386 by mass spectrometry. The results of the elemental analysis gave: C, 86.6; H, 5.8; N, 7.1. The ir, uv, and nmr spectra all corresponded to those of *trans*-1,2-dicarbazylcyclobutane previously reported.[12,13]

The cyclodimerization was inhibited by a cation scavenger such as triethylamine, aniline, or dimethylaniline and was not inhibited by oxygen which is an effective scavenger of anions and free radicals. The *G* value for the formation of the cyclodimer was proportional to the concentration of vinylcarbazole as shown in Figure 1, and about 300 in 1 *M* vinylcarbazole solutions.

A white amorphous compound was produced in deaerated benzonitrile solutions of vinylcarbazole irradiated. The ir, uv, and nmr spectra all corresponded to those of poly(vinylcarbazole) previously reported.[12,14] Since the formation of the polymer was inhibited by cation scavengers and was not inhibited by oxygen, this radiation-induced polymerization of vinylcarbazole is considered to take place *via* a cationic process.

Chain Reaction. *G* value for the formation of the dimer was of the order of several hundreds as Figure 1 shows and that of the vinylcarbazole cation which is the initiating species of the dimerization was 0.8 as previously reported.[1] These facts indicate that the reaction of this radiation-induced dimerization should be a chain reaction as shown in Scheme I and the kinetic chain length amounted to several hundreds.

Scheme I

$$\begin{array}{lllll}
\mathrm{S} & & \xrightarrow{\qquad\qquad} & \mathrm{S}^+, \mathrm{e}^-, \text{other products} & \\
\mathrm{S}^+ & + \mathrm{M} & \longrightarrow & \mathrm{S} & + \mathrm{M}^+ \\
\mathrm{M}^+ & + \mathrm{M} & \longrightarrow & \mathrm{M}_2^{\,+} & \\
\mathrm{M}_2^{\,+} & + \mathrm{M} & \longrightarrow & \mathrm{M}^+ & + \mathrm{M}_2 \\
\mathrm{M}^+ & + \mathrm{X}^- & \longrightarrow & \mathrm{M} & + \mathrm{X} \\
\mathrm{M}_2^{\,+} & + \mathrm{X}^- & \longrightarrow & \mathrm{M}_2 & + \mathrm{X}
\end{array}$$

where S, M, and M_2 are a benzonitrile, a monomer, and a dimer molecule, respectively. X may be O_2, because the electron affinity of O_2 is the strongest in this system.

As for the photochemically induced cyclodimerization,[15] quantum yields for the formation of the cyclodimer were less than 10. However, the kinetic chain length of this radiation-induced cyclodimerization amounted to several hundreds at the same concentration of vinylcarbazole. This difference may be mainly due to the fact that the quantum yield for the formation of the cation radical in the photochemically induced cyclodimerization is much less than unity.

Effects of Oxygen. As the concentration of oxygen decreased, the yield of the cyclodimer decreased and poly(vinylcarbazole) started to be produced in irradiated benzonitrile solutions of vinylcarbazole. As for the photochemically induced cyclodimerization, effects of oxygen on the cyclodimerization could be interpreted in terms that oxygen enabled the formation of the cation radical of vinylcarbazole.[15-17] However, the yield of the cation radical of vinylcarbazole by use of a pulse radiolysis technique was almost the same in both aerated and deaerated benzonitrile solutions but the cyclodimerization did not occur in the deaerated benzonitrile solutions. Consequently, oxygen was concluded to play an important role in the formation of the cyclodimer after the production of the cation radical of vinylcarbazole. An oxygen molecule may form a complex with the monomer cation or the dimer cation. This complexation may prevent the addition polymerization and promote the cyclization of a linear dimer cation to a cyclic dimer cation.

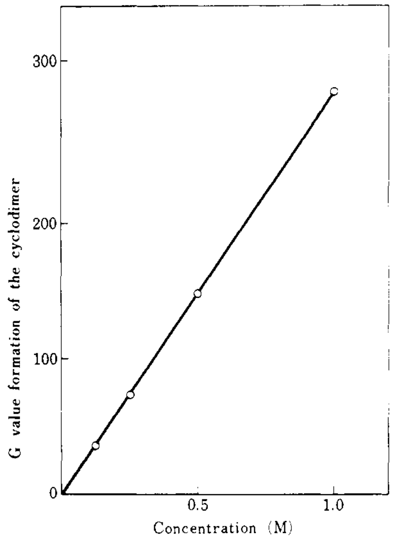

Figure 1. Dependence of *G* value for the formation of *trans*-1,2-dicarbazylcyclobutane on concentration of vinylcarbazole in the γ-irradiated benzonitrile solutions.

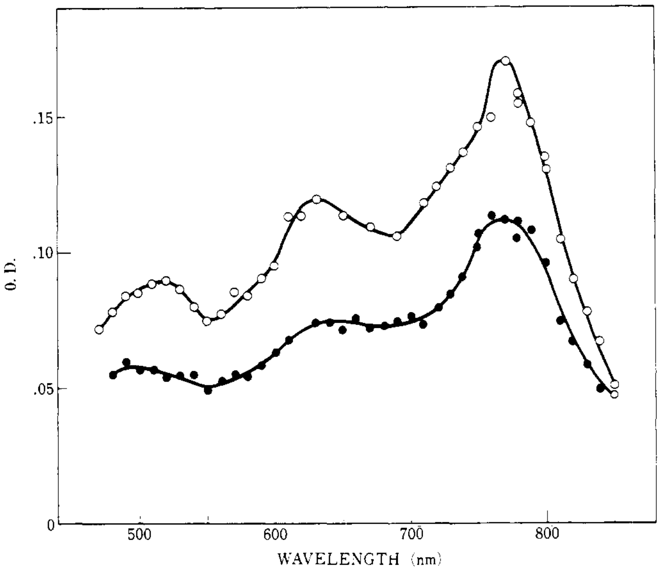

Figure 2. Absorption spectra observed for aerated benzonitrile solution of 0.003 *M* vinylcarbazole immediately (○) and at 1.6 μsec (●) after a pulse at room temperature.

Identification of Reactive Intermediates in the Aerated Solutions. The absorption spectra observed for the aerated benzonitrile solution of 0.003 *M* vinylcarbazole immediately and at 1.6 μsec after a pulse at room temperature are shown in Figure 2. The former spectrum with a sharp peak at 790 nm and other broad peaks at 700, 640, and 510 nm is in good agreement with the absorption spectrum of the vinylcarbazole cation observed for the γ-

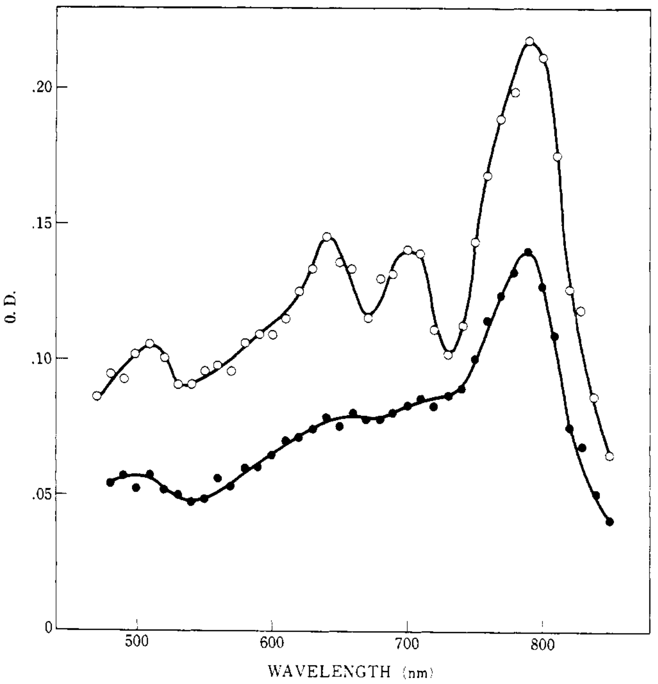

Figure 3. Absorption spectra observed for aerated benzonitrile solution of 1 *M* vinylcarbazole immediately (○) and at 1.6 μsec (●) after a pulse at room temperature.

irradiated butyl chloride solution at 77 K as previously reported.[1] These facts indicate that the vinylcarbazole cation is a major intermediate at least immediately after a pulse. As time proceeds, the width around the sharp peak becomes broader and the other peaks become obscure. These facts are suggestive that spectrum of a new transient species is not different greatly from that of the vinylcarbazole cation. In the solution of 1 *M* vinylcarbazole, the observed spectrum did not change clearly with time as shown in Figure 3. In comparison with the spectra for the dilute solution, the total shape is similar to that observed at 1.6 μsec after a pulse, although the wavelength of the sharp peak is observed to shift from 790 to 770 nm. Figure 4 shows the absorption spectrum observed for the aerated benzonitrile solution of 5 m*M* *trans*-1,2-dicarbazylcyclobutane immediately after a pulse at room temperature. This spectrum may be ascribed to be a dimer cation, because it was removed by the cation scavengers and was not removed by oxygen. It should be noted that the wavelength of the peak was 770 nm, and there were no other peaks except for a small shoulder at 740 nm which might be involved within the limit of the experimental error. The absorption spectra shown in Figure 3 was similar to that of the dimer cation shown in Figure 4.

Reactive intermediates which have absorption in the visible region are probably a monomer cation and a dimer cation, judging from their spectra and the reaction product as mentioned before. A contribution of each intermediate to the observed spectra may depend on the concentration of vinylcarbazole and on the time when the spectra were determined after a pulse. In a dilute solution, a dimer cation will be produced as time proceeds. In a concentrated solution, however, both cations may coexist even immediately after a pulse.

Kinetic behavior of both cations will be reported in a succeeding paper.

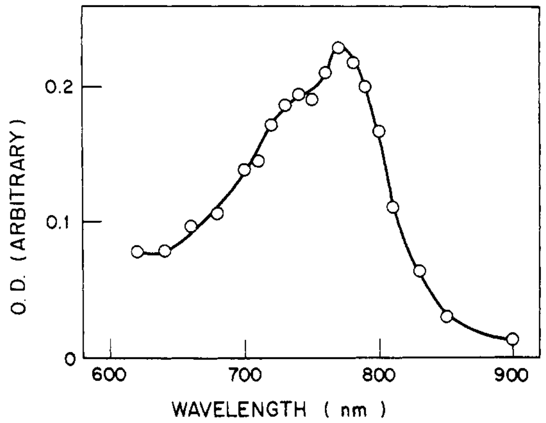

Figure 4. The absorption spectrum observed for aerated benzonitrile solution of 5 m*M* *trans*-1,2-dicarbazylcyclobutane immediately after a pulse at room temperature.

Identification of Reactive Intermediates in the Deaerated Solutions. The absorption spectra in a longer wavelength region observed for deaerated benzonitrile solutions of vinylcarbazole irradiated with electron pulses were similar to those observed for the aerated solutions and were removed by the cation scavengers. The absorption spectrum observed for the dilute benzonitrile solutions immediately after a pulse was similar to that due to the cation radical of vinylcarbazole shown in Figure 2.

Our previous paper[1] reported the absorption spectra in a shorter wavelength region observed for the deaerated solutions. The cation scavengers did not remove these spectra but inhibited the polymerization. These spectra may not be directly related to the polymerization. The identification of the broad absorption spectrum observed for the deaerated pure benzonitrile previously reported has not yet been done but it may be ascribed to an aggregated anion,[18] that is, $(C_6H_5CN)_n^-$.

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