The Photocycloaddition of *N*-Vinylcarbazole with 3-Cyanostyrene

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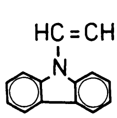
The photocycloaddition reaction of *N*-vinylcarbazole (VCZ) as an electron donor, with 3-cyanostyrene as an electron acceptor, was studied. In nonpolar solvents, two cyclobutanes of *cis*-1-(9-carbazolyl)-2-(3-cyanophenyl)-cyclobutane and *trans*-1-(9-carbazolyl)-2-(3-cyanophenyl)cyclobutane (in a ratio of 3 : 1) were obtained from an exciplex intermediate. The structure of cis cyclobutane seemed to originate from a sandwich conformation of the exciplex. In polar solvents, a photodissociation to free ion radicals was observed and *trans*-1,2-di(9-carbazolyl)cyclobutane was produced efficiently by means of a chain mechanism via a cation radical of VCZ. Transient intermediates were measured by means of nanosecond laser photolysis; the results supported the reaction scheme.

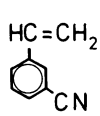
Previously, we reported on the photocycloaddition of 4-dimethylaminostyrene (DMASt) with 1-vinylpyrene (VP) and that with styrene (St).[1] In both systems, cyclobutanes were obtained as the main photoproducts in nonpolar solvents, and the stereochemistry of the cyclobutanes produced was explained by the reactivity of the exciplex intermediates. The long lifetime of the exciplex of DMASt with VP or the large pi system of VP allows a wide variety of conformations and leads to a trans-type cyclobutane, whereas in the reaction of DMASt with St, the short lifetime or the overlap of small pi rings limits the conformations of the exciplex and leads to a cis-type cyclobutane.

Here, we will report on the photocycloaddition reactions of *N*-vinylcarbazole (VCZ) with 3-cyanostyrene (CNSt). The photoirradiation of this system in nonpolar solvents gave mainly the cis-type cyclobutane, although an appreciable amount of trans-type cyclobutane formation was found simultaneously. From the results of the solvent effect on the photocycloaddition reaction and from the spectroscopic data, the reaction type of this VCZ-CNSt system is considered to be situated between those of the DMASt-VP and DMASt-St systems.

Experimental

Materials. *N*-Vinylcarbazole (VCZ, Tokyo Kasei Kogyo Co., Ltd.) was purified by recrystallization from ethanol and hexane. 3-Cyanostyrene (CNSt) was prepared from 3-cyanotoluene (Tokyo Kasei Kogyo Co., Ltd.),[2,3] and was purified by distillation under reduced pressure three times. Vinyl methyl terephthalate (VMTP) was synthesized by the ester-exchange reaction of vinyl acetate with the terephthalic acid monomethyl ester.


(VCZ)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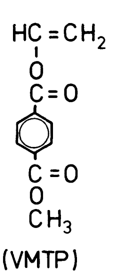
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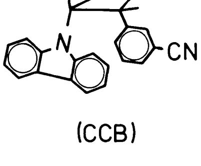
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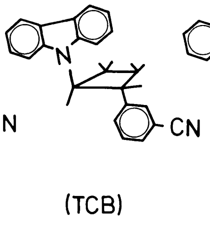
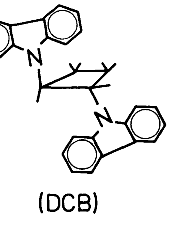

(TCB)


(DCB)

Benzene, diethyl ether, tetrahydrofuran (THF), methyl ethyl ketone (MEK), and acetone were dried and purified by distillation. *N*,*N*-Dimethylformamide (DMF) was dried and purified by distillation under reduced pressure. 2-Chlorobutane and 2-methyltetrahydrofuran (MTHF) for gamma-ray irradiation were dried by the use of molecular sieves and then distilled prior to use.

Photoreaction. A solution of VCZ (0.052 mol dm^{-3}) with CNSt (0.19 mol dm^{-3}) in benzene (2 ml) was degassed by repeated freeze-pump-thaw cycles in a Pyrex ampoule. The photoirradiation of the degassed ampoule was done by means of a 300-W high-pressure mercury lamp (Toshiba) fitted with a UV-33 filter (Toshiba) at 298 K: VCZ was selectively photoexcited in this system at 334 nm. After the evaporation of the benzene solvent, the photoproducts were analyzed by means of a gel-permeation chromatograph (Toyo Soda HLC-802UR) fitted with analytical columns eluting with THF. The quantity of products was determined by the use of a refractive index detector, where the refractive index for each compound was calibrated. The effect of thermal side reactions, which produced a small amount of a VCZ dimer or polymer in polar solvents, was corrected by the blank experiment in all cases.

The reaction quantum yield of cycloadducts was determined by using a degassed 1-cm quartz cell where the light intensity at 335 nm was found to be 1.77×10^{-9} E s^{-1} by actinometry.[4,5]

Identification of Cycloadducts. A degassed solution of VCZ (0.4 g) with CNSt (1.0 g) in benzene (40 ml) was photoirradiated for 14 h by means of a 300-W high-pressure mercury lamp fitted with a Pyrex glass filter at 298 K.[1,6] Products were injected into a recycle gel-permeation chromatograph (Toyo Soda HLC-802R) fitted with TSK-GEL-G2000HG6 and TSK-GEL-G2000HG8 columns, with chloroform as the eluent. Recycling for four times gave enough separation of cycloadducts: The cis cycloadduct (CCB) had a larger retention time than the trans cycloadduct (TCB). Recrystallization from hexane gave 79 mg of CCB and 25 mg of TCB. The configuration of the two cycloadducts was determined by NMR (JOEL JNM-FX90Q) on the basis of the chemical shifts.[1,6,7] The positions of the protons were determined by means of ^{1}H homonuclear decoupling or selective proton decoupling ^{13}C NMR measurements.

***cis*-1-(9-Carbazolyl)-2-(3-cyanophenyl)cyclobutane (CCB):** Mp 100—101 °C; IR (KBr) 3075w, 2970w, 2290w, 2250s, 1597s, 1487vs, 1448vs, 1409w, 1335vs, 1320m, 1240m, 1224s, 1212m, 1189m, 1160m, 1123m, 1085w, 1031w, 1004w, 925w, 888w, 812s, 802s, 751vs, 722vs, 702w, 620w, 559w, 530w, 515w, and 482w cm^{-1}; ^{1}H NMR (90 MHz; $\mathrm{C_6D_6}$; $\mathrm{Me_4Si}$) δ=1.68—2.38 (3H, m, $\mathrm{H_{(c)}}$ and $\mathrm{H_{(e)}}$), 2.74—3.24 (1H, m, $\mathrm{H_{(d)}}$), 3.38—3.72 (1H, m, $\mathrm{H_{(b)}}$), 4.76—5.12 (1H, m, $\mathrm{H_{(a)}}$), 5.92—6.60 (4H, m, aromatic), and 7.00—7.98 (8H, m, aromatic); ^{1}H NMR (90 MHz; $\mathrm{CDCl_3}$; $\mathrm{Me_4Si}$) δ=2.16—3.04 (3H, m, $\mathrm{H_{(c)}}$ and $\mathrm{H_{(e)}}$), 3.22—3.72 (1H, m, $\mathrm{H_{(d)}}$), 3.96—4.36 (1H, m, $\mathrm{H_{(b)}}$), 5.34—5.72 (1H, m, $\mathrm{H_{(a)}}$), 6.60—7.24 (4H, m, aromatic), and 7.10—8.04 (8H, m, aromatic); MS (70 eV), *m/z* (rel intensity) 322 (10%, $\mathrm{M^+}$), 294 (7, $\mathrm{M^+{-}C_2H_4}$), 193 (100, $\mathrm{VCZ^+}$), and 129 (7, $\mathrm{CNSt^+}$).

Found: C, 85.9; H, 5.5; N, 8.5%. Calcd for $\mathrm{C_{23}H_{18}N_2}$: C, 85.7; H, 5.6; N, 8.7%.

***trans*-1-(9-Carbazolyl)-2-(3-cyanophenyl)cyclobutane (TCB):** Mp 51—52 °C; IR (KBr) 3140w, 2940w, 2250s, 1628w, 1600s, 1489vs, 1454vs, 1335vs, 1238m, 1224s, 1211m, 1158s, 1124m, 1081w, 1030w, 1005w, 931w, 892w, 842w, 826w, 801m, 751vs, 724vs, 690m, 664m, 620w, 565w, 530w, 504w, and 418w cm^{-1}; ^{1}H NMR (90 MHz; $\mathrm{C_6D_6}$; $\mathrm{Me_4Si}$) δ=1.38—2.20 (3H, m, $\mathrm{H_{(c)}}$ and $\mathrm{H_{(d)}}$), 2.46—3.02 (1H, m, $\mathrm{H_{(e)}}$) 3.96—4.30 (1H, m, $\mathrm{H_{(b)}}$), 4.48—4.84 (1H, m, $\mathrm{H_{(a)}}$), 6.40—7.00 (4H, m, aromatic), and 6.96—8.12 (8H, m, aromatic); ^{1}H NMR (90 MHz; $\mathrm{CDCl_3}$; $\mathrm{Me_4Si}$) δ=1.92—2.78 (3H, m, $\mathrm{H_{(c)}}$ and $\mathrm{H_{(d)}}$), 2.92—3.46 (1H, m, $\mathrm{H_{(e)}}$), 4.54—4.92 (1H, m, $\mathrm{H_{(b)}}$), 5.00—5.36 (1H, m, $\mathrm{H_{(a)}}$), and 7.08—8.22 (12H, m, aromatic); MS (70 eV), *m/z* (rel intensity) 322 (36%, $\mathrm{M^+}$), 294 (1, $\mathrm{M^+{-}C_2H_4}$), 193 (100, $\mathrm{VCZ^+}$), and 129 (8, $\mathrm{CNSt^+}$).

Found: C, 85.7; H, 5.7; N, 8.8%. Calcd for $\mathrm{C_{23}H_{18}N_2}$: C, 85.7; H, 5.6; N, 8.7%.

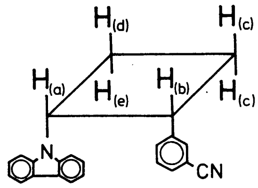
Spectroscopic Measurements. All measurements of the absorption and emission spectra and of the lifetime were made on the samples in a degassed 1-cm quartz cell at 298 K. The absorption spectra were measured by means of a UV-200S (Shimadzu) spectrophotometer. The emission spectra were obtained by the use of an RF-501 (Shimadzu) spectrofluorophotometer. The emission quantum yield was determined relative to that of quinine sulfate in sulfuric acid.[8] The lifetime of the emission was measured by the single-photon counting method (PRA, Inc.).

The transient absorption was obtained by the use of a nanosecond ruby laser photolysis apparatus which has been described elsewhere.[9] The exciting 347-nm light pulse had a pulse energy of 10 mJ and a pulse duration of 14 ns.

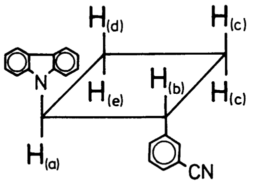
The reference spectra of $\mathrm{VCZ}^{+\cdot}$ and $\mathrm{CNSt}^{-\cdot}$ were measured by means of gamma-ray irradiation at 77 K in 2-chlorobutane and MTHF respectively.[10]

Results and Discussion

Emission Analysis. The fluorescence of VCZ (emission lifetime=10.4 ns in a benzene solvent) was quenched by the addition of CNSt in the degassed solvents. The rate constants of fluorescence quenching (k_q) were determined, by means of the Stern-Volmer plots at 298 K, to be 3.1×10^8 and $2.9\times10^9\,\mathrm{M^{-1}\,s^{-1}}$ in nonpolar benzene and polar *N,N*-dimethylformamide (DMF) solvents respectively; the value of k_q in benzene is rather small when it is compared with a diffusion-controlled rate constant (ca. $1\times10^{10}\,\mathrm{M^{-1}\,s^{-1}}$ in benzene). This fluorescence quenching is considered to occur via an electron-transfer reaction from $^1\mathrm{VCZ}^*$ to CNSt; energy-transfer quenching can be excluded by considering their energy levels. In this case, the free energy change of electron-transfer quenching is estimated by Weller's equation[11] to be ca. 5 kcal mol^{-1} exothermic.



(CCB)



(TCB)

A weak and structureless emission was observed at around 470 nm in a nonpolar benzene solvent when the VCZ fluorescence was quenched by CNSt; the quantum yield of this new emission was ca. 0.01, and the lifetime was 10.7 ns, under these experimental conditions. This new emission is ascribed to the exciplex emission as it disappears in polar solvents, where photodissociation to free-ion radicals competes with exciplex formation from a transient ionic complex.[12]

Photoproduct Formation. The selective photoexcitation (Hg lamp, UV-33 filter) of VCZ (0.052 mol dm^{-3}) in the presence of CNSt (0.19 mol dm^{-3}) in a degassed benzene solvent produced two cyclobutanes: *cis*-1-(9-carbazolyl)-2-(3-cyanophenyl)cyclobutane (CCB) and *trans*-1-(9-carbazolyl)-2-(3-cyanophenyl)cyclobutane (TCB). The quantum yields of the cyclobutane formation were determined by actinometry to be 0.28 and 0.10 for CCB and TCB respectively under the complete quenching of $^1\mathrm{VCZ}^*$ by CNSt. In this system, the yield of the cis-type cyclobutane formation was three times larger than that of the trans-type, and the other side reactions gave only a small yield of the by-products. A small amount of a polymer was also produced by photoirradiation, but the initiating species of the polymer was negligible, judging from the estimate based on the molecular weight of the polymer (ca. 10^4). As a control, the following experiments were carried out: the photoirradiation of VCZ (0.052 mol dm^{-3}) in the absence of CNSt in benzene produced the polymer and a very small amount of *trans*-1,2-di(9-carbazolyl)cyclobutane (DCB), while the photoirradiation of CNSt (0.19 mol dm^{-3}), which has no light absorption at 334 nm, in the absence of VCZ produced no photoproduct. The thermal reaction produced only a small amount of a copolymer, the contribution of which was corrected for in all experiments.

Figure 1 shows the time-conversion plots of the photoproducts. Here, the yield of the photoproducts was calculated on the basis of the total amount of VCZ. The formation of CCB and TCB is proportional to the

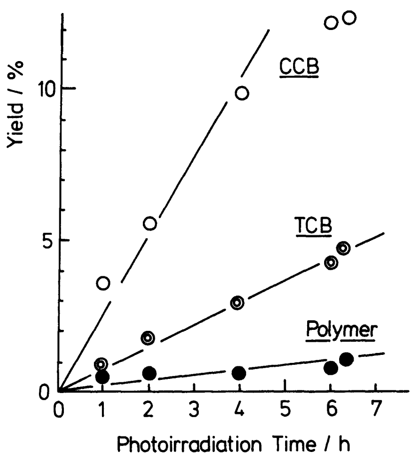


Fig. 1. Time-conversion plots of photoproducts. VCZ (0.052 mol dm^{-3}) was photoirradiated in the presence of CNSt (0.19 mol dm^{-3}) in benzene at 298 K.

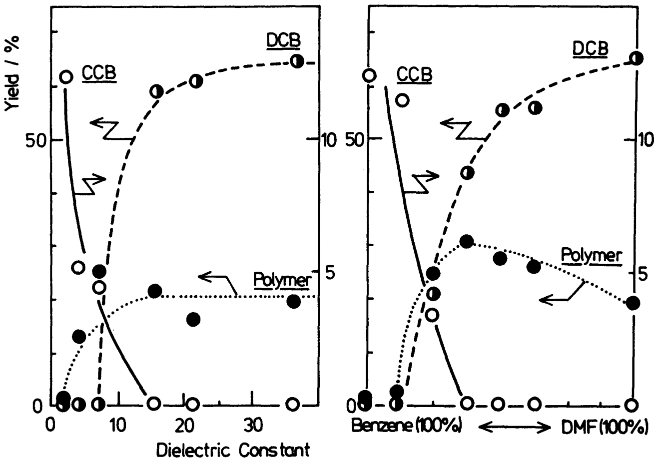


Fig. 2. Effects of solvent polarity on the distribution of photoproducts. Solvents used in the left figure were benzene, diethyl ether, tetrahydrofuran, methyl ethyl ketone, acetone, and *N*,*N*-dimethylformamide. A mixed solvent of benzene and *N*,*N*-dimethylformamide was used in the right figure. VCZ (0.052 mol dm^{-3}) was photoirradiated in the presence of CNSt (0.19 mol dm^{-3}) at 298 K for 320 min. The yield of TCB, which was not plotted in this figure, was ca. 1/3 of CCB in every solvent.

irradiation time, though the yield of CCB reaches the saturation point after a long irradiation time (>4 h). The effect of cis-trans isomerization on the photoproduct distribution is neglected, since the photoisomerization rates from CCB to TCB and from TCB to CCB were slow enough under these experimental conditions.

Solvent Effects. This photocycloaddition reaction of VCZ with CNSt was found to be greatly affected by the solvent polarity. In a polar DMF solvent, no CCB and TCB could be found; a large amount of the VCZ cyclobutane dimer (DCB) was produced instead of these cycloadducts. The photodimerization of VCZ in polar solvents was extensively studied by Ledwith,[13] who found that the dimerization proceeds by means of a chain mechanism via the cation radical of VCZ. In DMF, the participation of the chain mechanism is obvious, as the quantum yield of DCB formation was much larger than unity. The effect of solvent polarity on the photoreaction of VCZ with CNSt is demonstrated in Fig. 2. The left half of Fig. 2 shows the effect of the solvent polarity on the photoreaction in six different solvents, while the right half shows the results in mixed solvents of benzene and DMF. The results of these two experiments are in fairly good agreement. In nonpolar solvents, the cycloadditions are the main reactions, and the dimerization and polymerization are negligible. However, with an increase in the solvent polarity, the yield of the DCB by means of a chain mechanism increases greatly, and the cycloadduct formation is suppressed. This tendency is the same as that we reported previously.[1] In nonpolar solvents, photocycloaddition via an exciplex is dominant, while in polar solvents, the photodissociation of the exciplex to free-ion radicals becomes predominant, and the free-ion radicals so produced lead to product formation. In the photoreaction system of VCZ with CNSt in polar solvents, the dimerization occurs via an ion-radical intermediate, and the reaction is amplified by a chain mechanism.

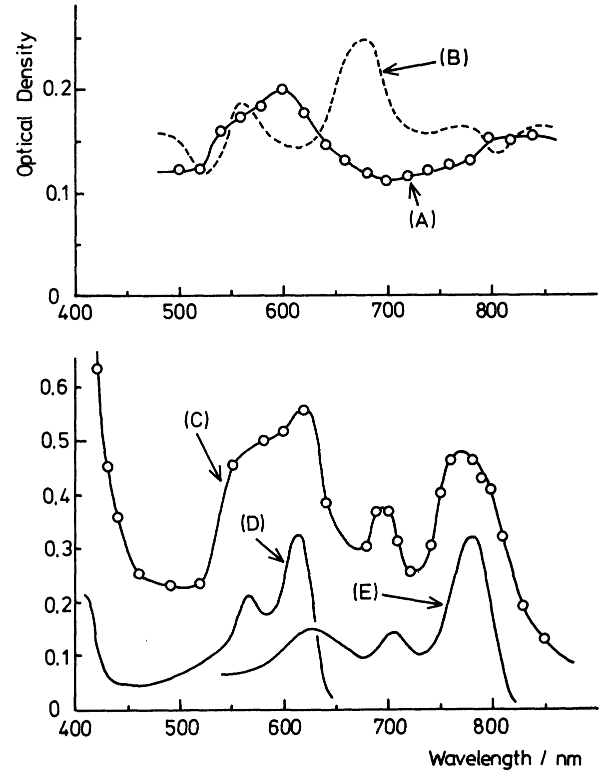
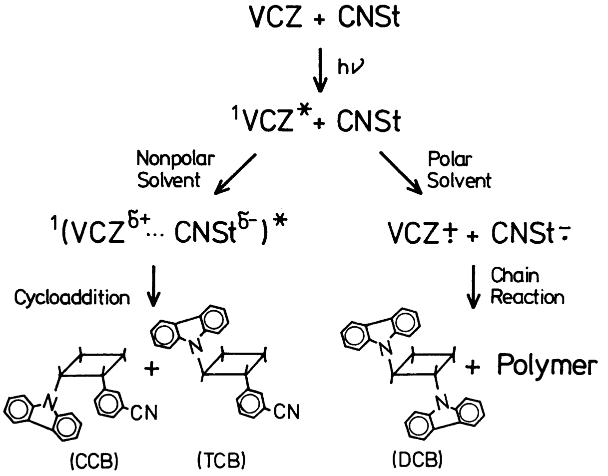


Fig. 3. Transient absorption spectra of VCZ (OD$_{347}$=1.2) with CNSt (1.1 mol dm^{-3}) measured by ns laser photolysis. Spectra were obtained in benzene at 20 ns (A) or in *N*,*N*-dimethylformamide at 50 ns (C) after excitation. Transient absorption spectrum of VCZ (B) without CNSt was obtained in benzene at 20 ns after excitation as a reference of the spectrum (A). Reference absorption spectra of ion radicals CNSt$^{\overline{\cdot}}$ (D) and VCZ^{+} (E) were obtained by gamma-ray irradiation in rigid matrices at 77 K.

Transient Spectra. The transient species in this photoreaction were studied by means of ns ruby-laser-photolysis measurements. The upper half of Fig. 3 shows the transient absorption spectra obtained in benzene 20 ns after excitation at 298 K. The photoexcitation of VCZ in the presence of CNSt (1.1 mol dm^{-3}) by means of a laser pulse (347 nm, 14 ns) gave Spectrum (A). This absorption spectrum is different from the S–S absorption of VCZ which was obtained by the reference sample without CNSt and which is shown by Spectrum (B). The lifetime of the transient species of Spectrum (A) agreed well with that of the exciplex emission, and the absorption bands are broad. Therefore, this transient absorption is considered to originate from the exciplex of VCZ with CNSt. No transient absorption which has a longer lifetime could be found except that of ^{3}VCZ*. On the other hand, in DMF, the formation of free-ion radicals was observed, as is shown in the lower half of Fig. 3. Spectrum (C) was obtained by the photoexcitation of VCZ with CNSt in DMF. The transient species found in this spectrum are ascribed to CNSt$^{-\cdot}$ and VCZ$^{+\cdot}$ by reference to the (D) and (E) absorption spectra. The lifetimes of these ion radicals were longer than a micro second, and these ion radicals are considered to be solvated free-ion radicals. The free VCZ$^{+\cdot}$ leads to DCB formation by means of a chain reaction.

The Reaction Mechanism. The scheme summarizes the photochemical reaction mechanism. In nonpolar solvents, two cycloadducts, CCB and TCB, are produced by the photoirradiation of VCZ with CNSt. Three times as much of the cis-type cyclobutane (CCB) is obtained as the trans-type cyclobutane (TCB). In a previous report,[1] we discussed the relationship between the reactivity of the exciplex intermediates and the stereochemistry of the cycloadduct products. The pair of 4-dimethylaminostyrene (DMASt) and 1-vinylpyrene (VP) gave an emissive exciplex whose lifetime was 55 ns in benzene. The long lifetime or the large pi ring of VP allows for a wide variety of exciplex conformations, which in turn leads to a trans-type cyclobutane formation. On the other hand, the photoreaction of DMASt with styrene (St) produces cis-type cyclobutane by means of the short lifetime or the small overlap of pi rings in the exciplex intermediate. Hence, the conformational distribution of the exciplex intermediate was concluded to allow the formation of trans-type cyclobutane. In the present study of the VCZ–CNSt system, the cis-type cyclobutane, which reflects the sandwich structure of the exciplex intermediate, was the main product, but an appreciable amount of the trans-type cyclobutane was also obtained simultaneously. The exciplex lifetime of this system is rather short (10.7 ns), and the pi ring of carbazole is not as large as that of pyrene. The reactivity of this exciplex is considered to be situated between those of the DMASt–VP and DMASt–St systems. On the other hand, in polar solvents, the photodissociation of the exciplex to VCZ$^{+\cdot}$ and CNSt$^{-\cdot}$ becomes a dominant reaction process, and DCB is mainly produced by a chain mechanism of VCZ via VCZ$^{+\cdot}$ as the intermediate; the chain reaction via VCZ$^{+\cdot}$ amplifies the reaction yield. The anion radical of CNSt is considered to be neutralized by the recombination with VCZ$^{+\cdot}$ or DCB$^{+\cdot}$. Hence, the reactivities of the ion radical and exciplex can be clearly distinguished.[14–21]



Scheme

To understand the reactivity of the cycloaddition reactions via the exciplex, the VCZ–VMTP system was also examined. The diffusion-controlled quenching of ^{1}VCZ* by VMTP in benzene produced an emissive exciplex (lifetime=49 ns). The free-energy change of the electron transfer from VCZ to VMTP is estimated to be 14-kcal mol^{-1} exothermic by the use of Weller's equation.[11] The photoirradiation of this system, however, produced only a polymer with a very small amount of DCB; no cyclobutane formation between VCZ and VMTP could be detected. It seems that the cyclobutane formation between two vinyl groups of aromatic vinyl monomers requires the pi conjugation of the vinyl group to the aromatic ring in the exciplex state.

Conclusion

The photoexcitation of VCZ with CNSt in nonpolar solvents produced two cycloadducts of CCB and TCB via an exciplex intermediate. In this system, the yield of cis cyclobutane CCB was three times higher than that of the trans-type TCB. The structure of CCB originated from the sandwich conformation of the exciplex. The formation of trans cyclobutane TCB is considered to be due to the looseness of the exciplex conformation. In polar solvents, the photodissociation of the exciplex to free VCZ$^{+\cdot}$ and CNSt$^{-\cdot}$ occurred. The VCZ$^{+\cdot}$ thus produced gave DCB efficiently by means of a chain mechanism, and the products of the exciplex reaction and the ion radical reaction were clearly differentiated.

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