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A Pulse Radiolysis Study of the Formation of Dimer Radical Cations of Aromatic Olefins

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The formation of dimer radical cations of several aromatic olefins has been studied by the pulse radiolysis technique. The aromatic olefins examined are 2-vinylnaphthalene (VN), 2-(1-propenyl)naphthalene (PN), 4-vinylbiphenyl (VBP), *trans,trans*-1,4-diphenyl-1,3-butadiene (1,4-DPB), and *s-trans*-2,3-diphenyl-1,3-butadiene (2,3-DPB). The formation of dimer radical cations were observed with all of them except 1,4-DPB, although it was very limited with VBP. Two types of dimer radical cations, bonded and associated ones, are formed with VN, whereas only the associated dimer radical cation is formed with PN. The influence of the aromatic substituents on the formation of the dimer radical cations is described.

It has been well-established that the radical cations of aromatic and olefinic hydrocarbons react with neutral parent molecules to form dimer radical cations.[1,2] The structure of the dimer radical cations has been described as a sandwich structure. The dimerization of radical cations has also been studied for styrene derivatives.[3] The pulse radiolysis studies have revealed the formation of two types of dimer radical cations, bonded and associated ones. In the present study, the pulse radiolysis of several aromatic olefins, such as 2-vinylnaphthalene, 2-(1-propenyl)-naphthalene, 4-vinylbiphenyl, *trans,trans*-1,4-diphenyl-1,3-butadiene, and *s-trans*-2,3-diphenyl-1,3-butadiene, has been carried out in 1,2-dichloroethane solution in order to see the influence of the aromatic substituents on the formation of the dimer radical cations.

Experimental

1,2-Dichloroethane was washed three times with an aqueous solution of sodium hydroxide and water and then distilled over calcium hydride. The middle fraction was stored under vacuum over calcium hydride. 2-Vinylnaphthalene and 4-vinylbiphenyl (both Aldrich) were chromatographed on alumina using hexane as an eluent and then recrystallized. 2-(1-Propenyl)naphthalene was prepared from 2-naphthaldehyde by the Wittig procedure[4] and chromatographed on silica gel using hexane. *s-trans*-2,3-Diphenyl-1,3-butadiene was prepared by the literature procedure.[5] *trans,trans*-1,4-Diphenyl-1,3-butadiene (Aldrich) was recrystallized from hexane. n-Bu$_4$NPF$_6$ (n-Bu, butyl) used as an additive was prepared from n-Bu$_4$NBr and KPF$_6$ and twice recrystallized from a water–methanol mixture. The samples for pulse radiolysis were prepared in a high vacuum operation and sealed into Suprasil cells of 10-mm optical path length.

The pulse radiolysis was carried out with an L-band linear accelerator. The pulse width was 8 ns. The analytical light source was a 450-W xenon pulse lamp (OPG-450, Osram). The detection system consisted of a monochromator (Nikon G-250), a photomultiplier (Hamamatsu-TV R928), and a programmable digitizer (Tektronix 7912 AD). The experiments were done at room temperature kept at ca. 22 °C.

Results and Discussion

The pulse radiolysis of the aromatic olefins in 1,2-dichloroethane results in the formation of the radical cations. They decay by neutralization with Cl$^-$, which is a product of electron attachment to the solvent. When the monomer radical cations react with the parent neutral molecules to form the dimer radical cations, the dimerization reaction competes with the neutralization reaction to exhibit concentration dependence. The following reaction scheme has proposed for the formation of the dimer radical cations of styrene derivatives[3]

$$\mathrm{S(solvent)} \rightsquigarrow \mathrm{S}^{\dot{+}} + \mathrm{e}^- \tag{1}$$

$$\mathrm{S}^{\dot{+}} + \mathrm{M(monomer)} \longrightarrow \mathrm{S} + \mathrm{M}^{\dot{+}} \tag{2}$$

$$\mathrm{S}^{\dot{+}} + \mathrm{M}_2 \longrightarrow \mathrm{S} + (\mathrm{M}_2)^{\dot{+}} \tag{3}$$

$$\mathrm{S}^{\dot{+}} + \mathrm{M}_2 \longrightarrow \mathrm{S} + \mathrm{M}\text{-}\mathrm{M}^{\dot{+}} \tag{4}$$

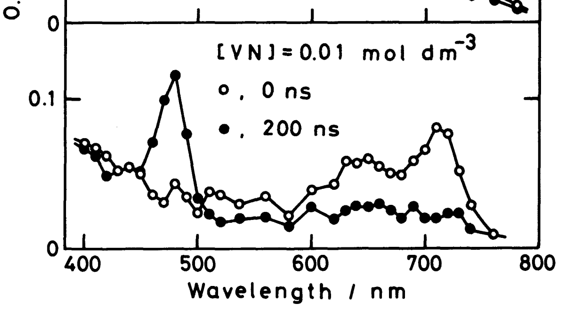

Fig. 1. Transient absorption spectra for 0.1 and 0.01 mol dm^{-3} 2-vinylnaphthalene (VN) solutions.

$$\mathrm{M}^{\dot{+}} + \mathrm{M} \rightleftharpoons (\mathrm{M_2})^{\dot{+}} \tag{5}$$

$$\mathrm{M}^{\dot{+}} + \mathrm{M} \longrightarrow \mathrm{M\text{-}M}^{\dot{+}} \tag{6}$$

$$(\mathrm{M_2})^{\dot{+}} \longrightarrow \mathrm{M\text{-}M}^{\dot{+}} \tag{7}$$

where $\mathrm{M\text{-}M}^{\dot{+}}$ and $(\mathrm{M_2})^{\dot{+}}$ are the bonded and associated dimer radical cations, respectively, and $\mathrm{M_2}$ is a molecular aggregate, which has been proposed to account for the rapid formation of the dimer radical cations.

2-Vinylnaphthalene (VN). Figure 1 shows the transient absorption spectra for 0.1 and 0.01 mol $\mathrm{dm^{-3}}$ VN solutions. The absorption bands at around 480, 630, and 710 nm are assigned to $\mathrm{M\text{-}M}^{\dot{+}}$, $(\mathrm{M_2})^{\dot{+}}$, and $\mathrm{M}^{\dot{+}}$, respectively, based on the following observations. The 480-nm band increases slowly with time after the pulse, whereas the 630- and 710-nm bands continue to decrease as a function of time. The relative absorption intensities of the 480- and 630-nm bands increase when the VN concentration is increased from 0.01 to 0.1 mol $\mathrm{dm^{-3}}$.

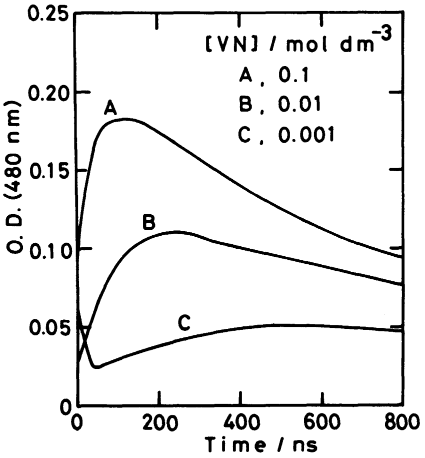

Fig. 2. Changes in optical density at 480 nm for 2-vinylnaphthalene (VN) solutions.

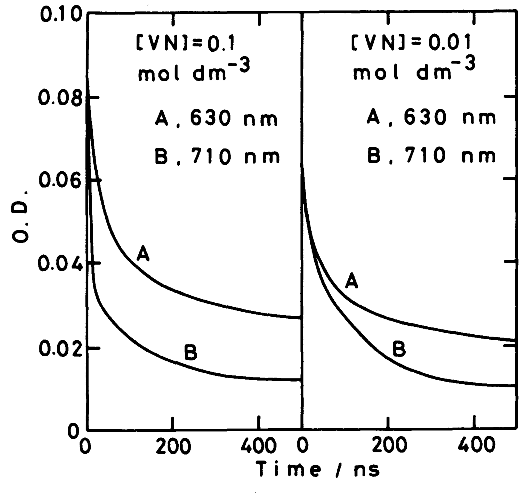

Fig. 3. Changes in optical densities at 630 and 710 nm for 2-vinylnaphthalene (VN) solutions.

Figures 2 and 3 show the concentration dependence of the formation and decay of the 480-, 630-, and 710-nm bands. The formation rate of the 480-nm band increases with increasing VN concentration (Fig. 2). The decay rate of the 710-nm band is higher at the higher VN concentration, whereas that of 630-nm band is independent of the VN concentration (Fig. 3). These findings are consistent with the assignment described above.

As has previously been reported, the addition of *n*-$\mathrm{Bu_4NPF_6}$ results in the stabilization of radiolytically produced cations toward neutralization through the ion-pair formation of the cations with $\mathrm{PF_6}^-$.6) The formation and decay behaviors of the 480-, 630-, and 710-nm bands are apparently affected by the addition of the salt, demonstrating that the light absorbing species are ionic. When 5 mmol $\mathrm{dm^{-3}}$ *n*-$\mathrm{Bu_4NPF_6}$ was added to the 0.01 mol $\mathrm{dm^{-3}}$ VN solution, the decay rates of the 630- and 710-nm bands are decreased and the formation of the 480-nm band is enhanced. Figure 4 shows the salt effect for the 480- and 710-nm bands; the effect on the 630-nm decay is similar to that of the 710-nm decay. This is consistent with the view that $\mathrm{M\text{-}M}^{\dot{+}}$ is formed from $\mathrm{M}^{\dot{+}}$ and $(\mathrm{M_2})^{\dot{+}}$.

The formation of $(\mathrm{M_2})^{\dot{+}}$ seems to be completed within the pulse width, 8 ns, even at the lower VN concentration (Fig.3). An explanation for this observation is that $(\mathrm{M_2})^{\dot{+}}$ is formed via Reaction 3, which involves the molecular aggregate, $\mathrm{M_2}$, and has the same order of rate constant as Reaction 2. However, we cannot rule out the possibility that the rate constant for the formation of $(\mathrm{M_2})^{\dot{+}}$ from $\mathrm{M}^{\dot{+}}$, the forward reaction of 5, is as large as $10^{11}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$. When 0.1 mol $\mathrm{dm^{-3}}$ naphthalene was added to the 0.01 mol $\mathrm{dm^{-3}}$ VN solution, the decay of the absorption due to the naphthalene dimer radical cation (λ_{max},

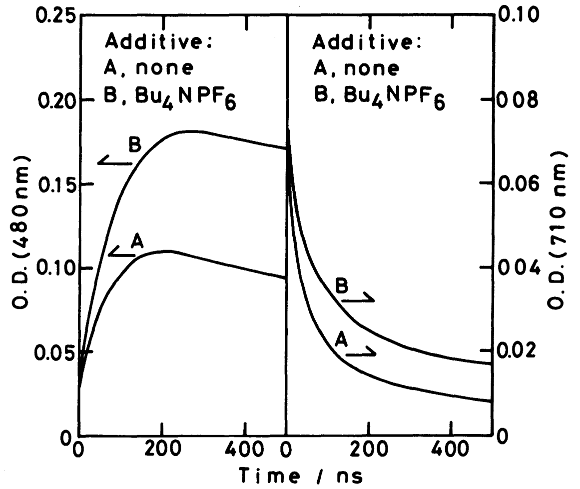

Fig. 4. Changes in optical densities at 480 and 710 nm in the absence and presence of 5 mmol $\mathrm{dm^{-3}}$ *n*-$\mathrm{Bu_4NPF_6}$ for 0.01 mol $\mathrm{dm^{-3}}$ 2-vinylnaphalene solution.

570 nm) was accompanied by the formation of the M-M^{+} band without appearance of the M^{+} and $(M_2)^{+}$ bands. This may be accounted for by the occurrence of the following reaction involving M_2

$$(\mathrm{Naph})_2^{+} + M_2 \longrightarrow 2\mathrm{Naph} + \mathrm{M\text{-}M}^{+} \quad (8)$$

where $(\mathrm{Naph})_2^{+}$ denotes the naphthalene dimer radical cation.

2-(1-Propenyl)naphthalene (PN). Figure 5 shows the transient absorption spectra for 0.1 and 0.01 mol dm^{-3} PN solutions. No slow increase in absorption after the pulse is observed over the whole wavelength range measured, indicating that M-M^{+} is not formed in contrast to the case of VN described above. This is similar to the results previously reported for *α,β*-disubstituted olefins such as *trans-β*-methylstyrene and 1,2-dihydronaphthalene.[3c,d] Similar to the case of VN, the absorption bands due to M^{+} and $(M_2)^{+}$ may be located at around 710 and 650 nm, respectively. The absorption band at around 430 nm is assigned to $(M_2)^{+}$ as well as the 710-nm band since these bands have constant relative intensities and the same decay rate.

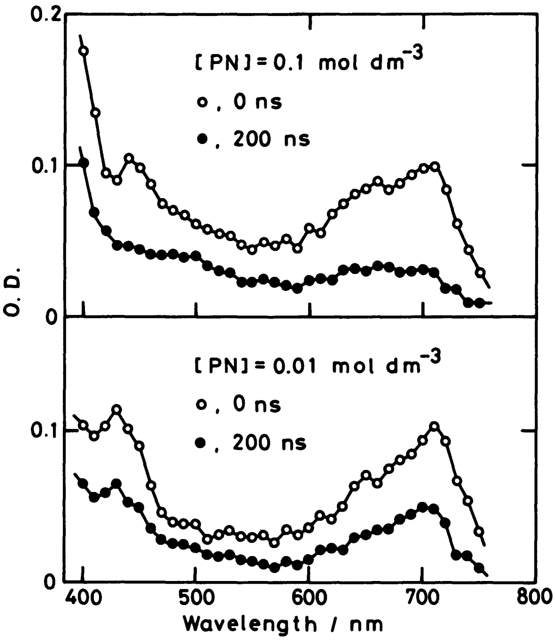

Fig. 5. Transient absorption spectra for 0.1 and 0.01 mol dm^{-3} 2-(1-propenyl)naphthalene (PN) solutions.

4-Vinylbiphenyl (VBP). Figure 6 shows the transient absorption spectra for 0.1 and 0.01 mol dm^{-3} VBP solutions. The absorption bands at around 410 nm and above 710 nm are assigned to M^{+}.[7] The decay rates of these bands are identical and increase with increasing VBP concentration. The small absorption band at around 560 nm increases slowly with time after the pulse at 0.01 mol dm^{-3}, whereas it continues to decrease with time at 0.1 mol dm^{-3}. The slow formation is enhanced by the addition of 5 mmol dm^{-3} n-Bu_4NPF_6. This band may be due to M-M^{+}. It can be said that the formation of M-M^{+} is limited for VBP since it is unlikely that the extinction coefficient of M-M^{+} of VBP is much smaller than those of styrene and *α*-methylstyrene.

***s-trans*-2,3-Diphenyl-1,3-butadiene (2,3-DPB).** Figure 7 shows the transient absorption spectra for a 0.01 mol dm^{-3} 2,3-DPB solution. The absorption bands at around 460 and 700 nm increase slowly with time after the pulse. The slow formation is enhanced by the addition of 5 mmol dm^{-3} n-Bu_4NPF_6. These bands may be due to M-M^{+}. The absorption band at around 460 nm is observed even at a low concentration, 1 mmol dm^{-3}, and at the end of the pulse. Therefore, it is considered that M^{+} also has an absorption band at this wavelength region. The slow increase in the absorption may be attributed to a difference in

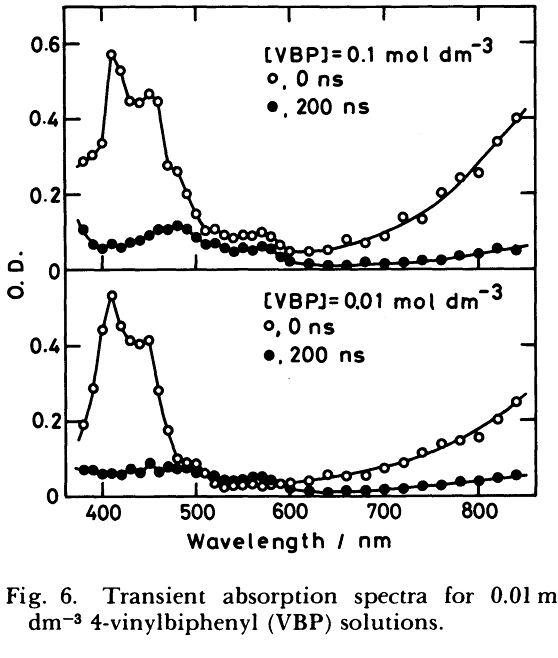

Fig. 6. Transient absorption spectra for 0.01 mol dm^{-3} 4-vinylbiphenyl (VBP) solutions.

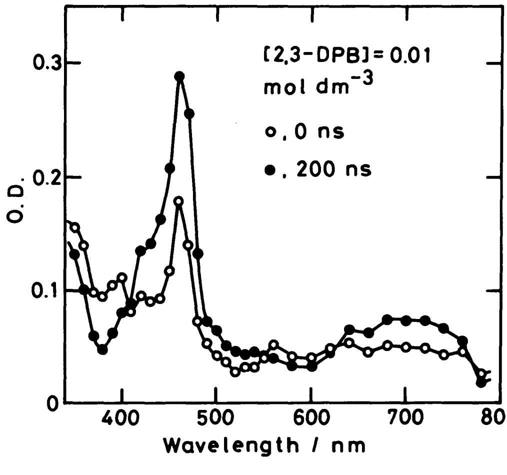

Fig. 7. Transient absorption spectra for 0.01 mol dm^{-3} *s-trans*-2,3-diphenyl-1,3-butadiene (2,3-DPB) solution.

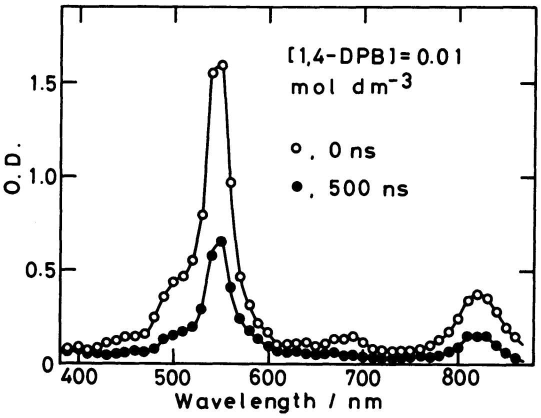

Fig. 8. Transient absorption spectra for 0.01 mol dm^{-3} *trans,trans*-1,4-diphenyl-1,3-butadiene (1,4-DPB) solution.

extinction coefficient between $\mathrm{M}^{\dot{+}}$ and $\mathrm{M\text{-}M}^{\dot{+}}$.

***trans,trans*-1,4-Diphenyl-1,3-butadiene (1,4-DPB).** Figure 8 shows the transient absorption spectra for a 0.01 mol dm^{-3} 1,4-DPB solution. The spectral shape is independent of the solute concentration and does not change during the decay after the pulse. The decay of the absorption obeys the second-order kinetics, indicating that the decay is due exclusively to neutralization with Cl^-. The absorption bands at around 550 and 820 nm are assigned to $\mathrm{M}^{\dot{+}}$.[7] It is suggested that 1,4-DPB forms neither $\mathrm{M\text{-}M}^{\dot{+}}$ nor $(\mathrm{M}_2)^{\dot{+}}$ in contrast with *trans*-stilbene, which has been reported to form $(\mathrm{M}_2)^{\dot{+}}$.[1k,8,9]

Associated Dimer Radical Cation, $(\mathrm{M}_2)^{\dot{+}}$. The dimer radical cations, whose formation is completed within the pulse duration, are assigned to $(\mathrm{M}_2)^{\dot{+}}$ having a sandwich structure. Its formation was observed with VN and PN but not with the other aromatic olefins. It has previously been reported that the formation of $(\mathrm{M}_2)^{\dot{+}}$ is not important for α-methylstyrene under the same conditions as the present study.[3f] It has also been reported that the formation of $(\mathrm{M}_2)^{\dot{+}}$ of styrene derivatives is a special low-temperature phenomenon.[3e] Therefore, it can be said that the 2-naphthyl group is largely responsible for the formation of $(\mathrm{M}_2)^{\dot{+}}$. When a solution of 0.1 mol dm^{-3} naphthalene in 1,2-dichloroethane was pulse irradiated, no absorption due to $\mathrm{M}^{\dot{+}}$ ($\lambda_{\max}$, 710 nm) was observed even at the end of the pulse, indicating that all of $\mathrm{M}^{\dot{+}}$ is converted into $(\mathrm{M}_2)^{\dot{+}}$ ($\lambda_{\max}$, 570 nm). On the other hand, the $\mathrm{M}^{\dot{+}}$ bands are clearly observed with the 0.1 mol dm^{-3} VN and PN solutions under the same conditions (Figs. 1 and 5). These results indicate that the vinyl and 1-propenyl substitutions of naphthalene result in a decrease in association constant for Reaction 5. This is attributed to steric hindrance since the substituents are not coplanar to the naphthyl group.

Bonded Dimer Radical Cation, $\mathrm{M\text{-}M}^{\dot{+}}$. The dimer radical cation is characterized by a slow formation. The covalently bonded dimer is considered to be responsible for the initiation of cationic polymerization and to have a head-to-head linkage.[3c,d] The formation of $\mathrm{M\text{-}M}^{\dot{+}}$ may be a characteristic feature for polymerizable olefins. It was observed with VN, VBP, and 2,3-DPB but not with the α,β-disubstituted olefins, PN and 1,4-DPB, whose head-to-head addition is sterically hindered.

The formation of $\mathrm{M\text{-}M}^{\dot{+}}$ of VBP is very limited. When solutions of biphenyl in 1,2-dichloroethane was pulse irradiated, no dimer radical cation was formed in contrast to naphthalene. It is suggested that the formation of $\mathrm{M\text{-}M}^{\dot{+}}$ largely depends on the association propensity of the aromatic substituents as well as that of $(\mathrm{M}_2)^{\dot{+}}$.

Pulse radiolysis of the binary systems consisting of VN and VBP, α-methylstyrene and VBP, α-methylstyrene and 1,4-DPB, and 2,3-DPB and 1,4-DPB was also examined. No result demonstrating the formation of mixed dimer radical cation complexes was obtained.

Conclusion

The formation of dimer radical cations was studied for several aromatic olefins such as 2-vinylnaphthalene (VN), 2-(1-propenyl)naphthalene (PN), 4-vinylbiphenyl (VBP), *trans,trans*-1,4-diphenyl-1,3-butadiene (1,4-DPB), and *s-trans*-2,3-diphenyl-1,3-butadiene (2,3-DPB). The formation of associated dimer radical cations, $(\mathrm{M}_2)^{\dot{+}}$, is important only for VN and PN. This is attributed to the large association propensity of the naphthyl group. The association constants for the formation of $(\mathrm{M}_2)^{\dot{+}}$ of VN and PN (Reaction 5) are smaller than that of naphthalene because of steric hindrance due to the substituents. Bonded dimer radical cations, $\mathrm{M\text{-}M}^{\dot{+}}$, are formed with VN, VBP, and 2,3-DPB, although the formation is limited with VBP. The α,β-disubstituted olefins, PN and 1,4-DPB, give no $\mathrm{M\text{-}M}^{\dot{+}}$. The formation of $\mathrm{M\text{-}M}^{\dot{+}}$ via $\mathrm{M}^{\dot{+}}$ and $(\mathrm{M}_2)^{\dot{+}}$ (Reactions 6 and 7) was demonstrated by the effect of n-$\mathrm{Bu_4NPF_6}$ added to the VN solution. No direct evidence was obtained for the formation of $(\mathrm{M}_2)^{\dot{+}}$ and $\mathrm{M\text{-}M}^{\dot{+}}$ via molecular aggregates, M_2 (Reactions 3 and 4). However, it was proposed that $\mathrm{M\text{-}M}^{\dot{+}}$ of VN is formed via M_2 in the presence of an excess amount of naphthalene (Reaction 8).

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9) We have also observed that the decay of the *trans*-stilbene radical cation in 1,2-dichloroethane is accompanied by a shift of the absorption peak from 480 to 475 nm, which is attributable to the formation of $(\mathrm{M_2})^{\dot{+}}$. The spectral shift was observed at a high concentration, 0.1 mol dm^{-3}, but not at a low concentration, 3 mmol dm^{-3}.