November, 1985] © *1985 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 58, 3369—3370 (1985)* 3369

Formation of α-Methylstyrene Dimer Radical Cations *via* Molecular Aggregates Studied by Pulse Radiolysis

Yukio Yamamoto,* Yukio Chikai, and Koichiro Hayashi
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567

(Received May 30, 1985)

Synopsis. Pulse radiolysis of α-methylstyrene was carried out in 1,2-dichloroethane, and the effect of additives on the formation of the dimer radical cations was investigated. In the presence of excess amounts of hexenes and biphenyl, the dimer radical cations are suggested to be formed *via* molecular aggregates by charge-transfer reactions.

The initiation processes of the radiation-induced cationic polymerization of styrene derivatives have been studied by pulse radiolysis methods.[1–4] Monomer and dimer radical cations and propagating cations have been detected as transient species responsible for the cationic polymerization. The monomer radical cations are quite short-lived, and the mechanistic details have been obtained by the pulse radiolysis at low temperature, −165 °C, in a mixture of isopentane and butyl chloride.[3] The following reaction scheme has been proposed for styrene and α-methylstyrene (MS):

$$\text{S(solvent)} \rightsquigarrow \text{S}^{\dot{+}} + \text{e} \quad (1)$$

$$\text{S}^{\dot{+}} + \text{M(monomer)} \longrightarrow \text{S} + \text{M}^{\dot{+}} \quad (2)$$

$$\text{S}^{\dot{+}} + \text{M}_2 \longrightarrow \text{S} + (\text{M}_2)^{\dot{+}} \quad (3)$$

$$\text{S}^{\dot{+}} + \text{M}_2 \longrightarrow \text{S} + \text{M-M}^{\dot{+}} \quad (4)$$

$$\text{M}^{\dot{+}} + \text{M} \rightleftarrows (\text{M}_2)^{\dot{+}} \quad (5)$$

$$\text{M}^{\dot{+}} + \text{M} \longrightarrow \text{M-M}^{\dot{+}} \quad (6)$$

$$(\text{M}_2)^{\dot{+}} \longrightarrow \text{M-M}^{\dot{+}} \quad (7)$$

$$\text{M-M}^{\dot{+}} + \text{M} \longrightarrow \cdot\text{M-M-M-M}^{+} \quad (8)$$

where $\text{M-M}^{\dot{+}}$ and $(\text{M}_2)^{\dot{+}}$ are the bonded and associated dimer radical cations, respectively. The formation of the dimer radical cations *via* molecular aggregates, M_2, has been proposed to account for their rapid formation during pulse irradiation.[2,3] The existence of the molecular aggregates, however, has been ruled out by another research group.[4] In the present study, the pulse radiolysis of MS was carried out in 1,2-dichloroethane at room temperature (*ca.* 22 °C) by using 8 ns electron pulses. The effect of additives on the formation of the dimer radical cations was examined in order to investigate the contribution of such neutral molecular aggregates.

Experimental

MS and 1,2-dichloroethane (Wako Chemicals) were successively washed three times with an aqueous solution of NaOH and with distilled water and then distilled over CaH_2. The middle fractions were stored under vacuum over CaH_2. Cyclohexene and 1-hexene (Wako Chemicals) were distilled over CaH_2 and stored under vacuum. Zone-refined biphenyl (BP) (Tokyo Kasei) was used without further purification. Bu_4NPF_6 (Bu, butyl) was prepared from Bu_4NBr and KPF_6 and twice recrystallized from a water–methanol mixture. The samples for the pulse radiolysis were prepared in a high vacuum operation and sealed into Suprasil cells of 10-mm optical path length. The pulse radiolysis techniques employed in this laboratory have been described elsewhere.[5]

Results and Discussion

The transient absorption spectra of MS in 1,2-dichloroethane are shown in Fig. 1. According to the literature,[3] the absorption band at 470 nm is assigned to the bonded dimer radical cations, although the possibility of a contribution of another type of dimer radical cations, associated ones, to the absorption still remains.[2] In this paper, the dimer radical cations having the 470-nm band are tentatively represented by $\text{M-M}^{\dot{+}}$, and their formation processes are discussed.

At the higher concentration, 0.1 mol dm^{-3} (Fig. 1 (A)), the formation of $\text{M-M}^{\dot{+}}$ seems to be almost completed within the pulse duration, 8 ns, and the 470-nm band decreases as a function of time. The absorption bands at 350 and 690 nm assigned to the monomer radical cations, $\text{M}^{\dot{+}}$, are negligible even at the end of the pulse. The absorption below 400 nm with a relatively slow decay rate is attributed to

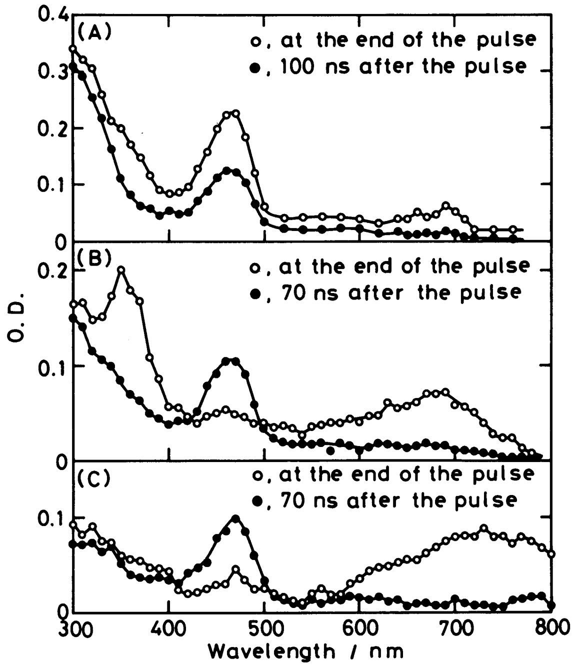

Fig. 1. Transient absorption spectra of MS solutions: (A) [MS]=0.1 mol dm^{-3}; (B) [MS]=0.01 mol dm^{-3}; and (C) [MS]=0.01 mol dm^{-3} in the presence of 0.5 mol dm^{-3} cyclohexene.

radical species such as benzyl-type radicals. The formation of the associated dimer radical cations having absorption bands at 620 and 1600 nm seems to be less important at room temperature than at −165 °C.[3]

At the low MS concentration, 0.01 mol dm^{-3} (Fig. 1 (B)), a rapid decay of the absorption due to M† can be seen, and the 470-nm band increases after the pulse. The absorption of M–M† attained a maximum at 70 ns. The effect of $\mathrm{Bu_4NPF_6}$ was examined in order to establish the formation of M–M† from M†. As has been reported,[6,7] the addition of $\mathrm{Bu_4NPF_6}$ results in the stabilization of radical cations toward neutralization through ion-pair formation. When 5×10^{-3} mol dm^{-3} $\mathrm{Bu_4NPF_6}$ was added to the 0.01 mol dm^{-3} MS solution, the formation of M–M† was enhanced, and the decay of M† became slightly slower. Therefore, the enhancement of the M–M† formation is attributable to the stabilization of M† toward neutralization with Cl^{-}, the product of dissociative electron capture by the solvent. That is to say, the growth of the 470-nm band is a result of the reaction of M† taking place in competition with the neutralization.

In the 0.01 mol dm^{-3} MS solution containing 0.5 mol dm^{-3} cyclohexene (Fig. 1 (C)), the 470-nm band increases after the pulse similarly to that in the solution not containing cyclohexene. However, no absorption peak is observed at 350 nm. The result can be explained by assuming that M–M† is formed *via* the MS molecular aggregates by the charge-transfer reaction probably from the cyclohexene dimer radical cations.[8] A similar result was obtained for the 0.01 mol dm^{-3} MS solution containing 0.5 mol dm^{-3} 1-hexene.

When 0.1 mol dm^{-3} BP was added to the 0.01 mol dm^{-3} MS solution, the transient absorption spectrum obtained at the end of the pulse was similar to that of the BP solution not containing MS. The absorption bands at 370 and 680 nm are assigned to BP†, although the former band includes the absorption by the triplet excited state of BP. As the absorption of BP† decayed, the 470-nm band appeared, whereas no absorption peak due to M† was observed at any stage after the pulse. It was demonstrated that the decay of BP† is accelerated in the presence of added MS resulting in the direct formation of M–M†. The result may be explained by the occurrence of the charge-transfer from BP† to the MS molecular aggregates.

From the results presented above, it seems likely that the MS molecular aggregates exist and contribute to the formation of M–M†. Clearly further investigation is required to reveal the nature of the molecular aggregates.

References

1) H. Yoshida, M. Noda, and M. Irie, *Polymer J.*, **2**, 359 (1971).

2) K. Hayashi, M. Irie, D. Lindenau, and W. Schnabel, *Eur. Polym. J.*, **13**, 925 (1977).

3) S. Egusa, Y. Tabata, S. Arai, A. Kira, and M. Imamura, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 729 (1978).

4) O. Brede, J. Bös, W. Helmstreit, and R. Mehnert, *Radiat. Phys. Chem.*, **19**, 1 (1982).

5) Y. Yamamoto, S. Nishida, K. Yabe, K. Hayashi, S. Takeda, and K. Tsumori, *J. Phys. Chem.*, **88**, 2368 (1984).

6) S. Mah, Y. Yamamoto, and K. Hayashi, *J. Phys. Chem.*, **87**, 297 (1983).

7) S. Mah, Y. Yamamoto, and K. Hayashi, *Radiat. Phys. Chem.*, **23**, 137 (1984).

8) B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, **65**, 2576 (1969).