CHEMISTRY LETTERS, pp. 149-152, 1994.

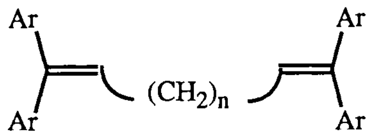
© 1994 The Chemical Society of Japan

Properties of Radical Cations Generated by the Pulse Radiolysis of 1,ω-Bis(diarylethenyl)alkanes. Trapping of Distonic 1,4-Radical Cation by Molecular Dioxygen

Toshiyuki TAMAI,[†] Kazuhiko MIZUNO,* Isao HASHIDA,[†] Yoshio OTSUJI,*
Akito ISHIDA,[††] and Setsuo TAKAMUKU*[††]
Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 593
[†]Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka 536
[††]The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567

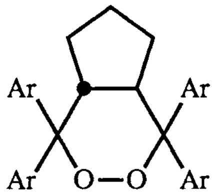
Physical and chemical properties of radical cations generated from $Ar_2C=CH(CH_2)_nCH=CAr_2$ ($Ar = 4\text{-}CH_3OC_6H_4$, $n = 2\text{-}4$) were studied by use of pulse radiolysis and γ-radiolysis techniques. When $n = 3$ and 4, 1,4-radical cations were formed via intramolecular cyclization of initially formed radical cations. The 1,4-radical cations were trapped by molecular dioxygen at the diarylalkylmethyl radical site, which suggests the "distonic" character of the species.

The photoinduced electron-transfer reaction of 1,1-diarylethenes in the presence of an electron acceptor in acetonitrile affords cyclodimers under inert gas atmosphere[1a,b)] and affords 1,2-dioxanes under oxygen atmosphere.[1b-e)] For these photoreactions, 1,4-radical cations have been proposed as a key intermediate, in which cationic and radical sites are seemed to be separated from each other (distonic radical cation[2)]). However, the physical and chemical properties of these distonic radical cations remain equivocal. We now report that 1,4-radical cations can be generated by the pulse radiolysis of 1,ω-bis(diarylethenyl)alkanes **1b**-**c** in 1,2-dichloroethane and also by the γ-radiolysis in a butyl chloride matrix at 77 K.[1e,3)] Measurements of transient absorption spectra provided unambiguous evidence supporting that the 1,4-radical cations are distonic radical cations and their radical sites can be trapped by molecular dioxygen.



1a-c

$Ar = 4\text{-}CH_3OC_6H_4$, **a**: $n = 2$; **b** : $n = 3$; **c** : $n = 4$



2b

$Ar_2C=CHCH_3$

3

The pulse radiolysis of 1,1,7,7-tetrakis(4-methoxyphenyl)-1,6-heptadiene (**1b**, 0.01 mol dm^{-3}) in 1,2-dichloroethane was carried out under argon at room temperature.[4)] Figure 1 shows time-resolved transient absorption spectra observed in the pulse radiolysis of **1b**. Two characteristic absorption bands were observed at λ_{max} 355 and 400 nm at 10 ns after the pulse irradiation. The 400 nm band decayed according to a pseudo-first-order kinetics. Decay of this band was accompanied by the rise of a new band at λ_{max} 485 nm and also by the rise of the 355 nm band. The rate constant for decay of the 400 nm band ($k = 1.0 \times 10^8\ s^{-1}$) was in fair

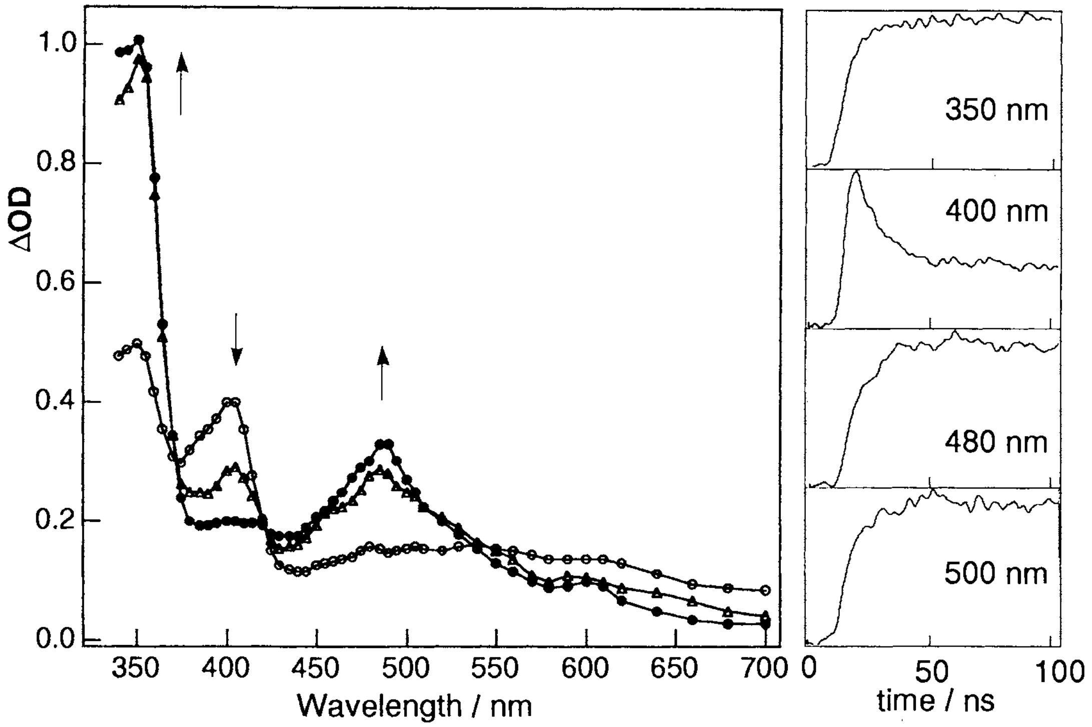


Fig. 1. Transient absorption spectra obtained at 10 ns (–○–), 20 ns (-△-), and 50 ns (-●-) after 8 ns pulse irradiation of **1b** (0.01 mol dm^{-3}) under argon in 1,2-dichloroethane at room temperature and time dependent profiles monitored at 350, 400, 480, and 500 nm.

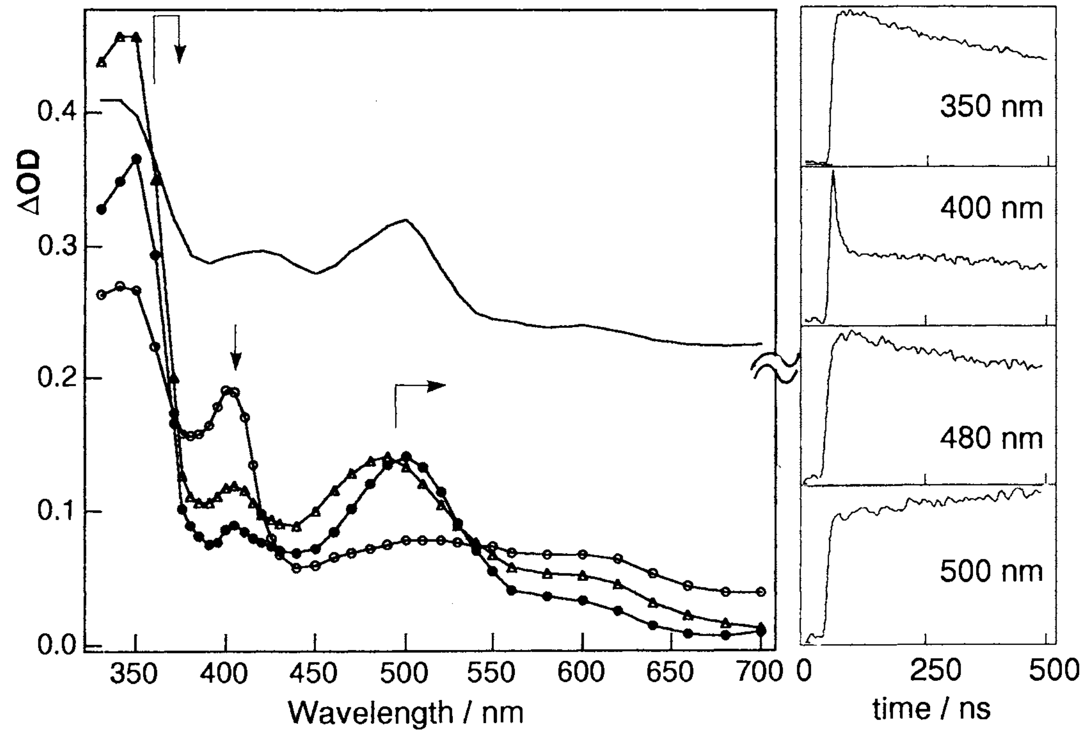


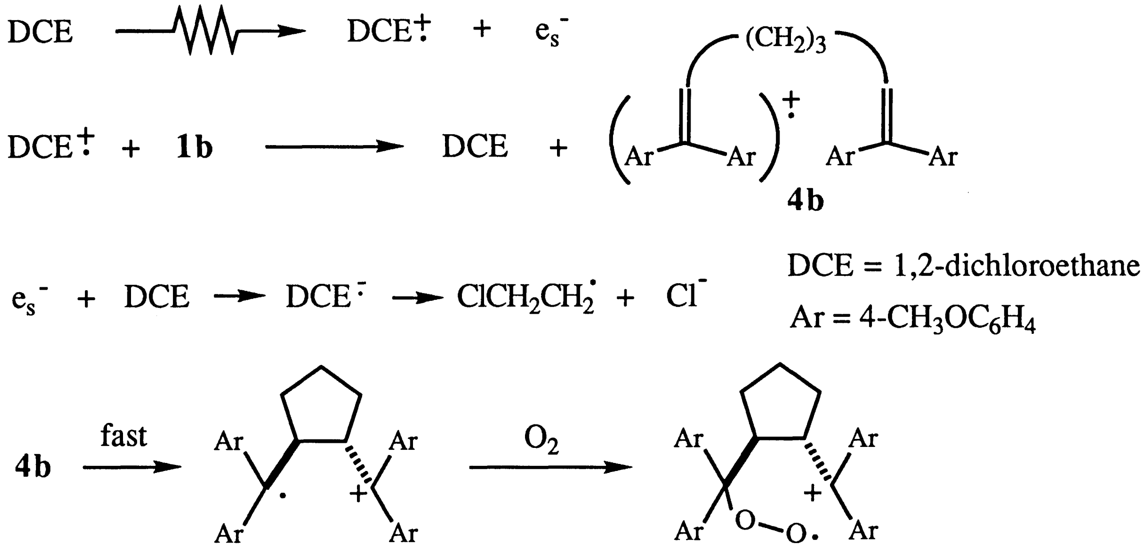
Fig. 2. Transient absorption spectra obtained at various times after 8 ns pulse irradiation of **1b** (0.01mol dm^{-3}) under oxygen and **2b** (0.01 mol dm^{-3}) under argon in 1,2-dichloroethane at room temperature (–○– : 10 ns after the pulse for **1b**; –△– : 30 ns after the pulse for **1b**; –●– : 350 ns after the pulse for **1b**; ——— : 400 ns after the pulse for **2b**) and time dependent profiles for **1b** monitored at 350, 400, 480, and 500 nm.

agreement with that for the rise of the 485 nm band (k = 1.2 x 10^8 s^{-1}). The rate of the rise of the 485 nm band was independent of the concentration of **1b**. Similar spectral changes were observed when the γ-radiolysis of **1b** was carried out in a butyl chloride matrix (0.01 mol dm^{-3}) at 77 K.4) These results suggest that the spectral changes in the pulse radiolysis and the γ-radiolysis are caused by a successive conversion: radical cation **4b** → 1,4-radical cation **5b** (Scheme 1). Comparison of the spectra observed in the pulse radiolysis of **1b** with those of the reference compound **3** (vide infra) and analogous alkenes1e,3) indicates that the absorption at 400 nm can be assigned to radical cation **4b**, the absorptions at 485 and 355 nm to radical cation **5b**.

Molecular dioxygen caused a remarkable change in the transient absorption spectra. Figure 2 shows transient absorption spectra observed in the pulse radiolysis of **1b** in 1,2-dichloroethane under oxygen atmosphere. The 400 nm band decayed similarly to the pulse radiolysis of **1b** under argon. The rise of the 355 nm and 485 nm bands was observed after the pulse irradiation. Then, both the bands decayed gradually, accompanying the appearance of a new band at λ_{max} 500 nm. Plots of the rate constants for decay of the 355 nm band and the 485 nm band against the concentration of molecular dioxygen gave straight lines. The slopes of these two lines were approximately equal. These results indicate that the species associated with the 355 and 485 nm bands are quenched by molecular dioxygen according to a first-order kinetics,5) but the species associated with the 400 nm band is not quenched appreciably. The 500 nm and 355 nm bands were also observed in transient absorption spectra obtained in the pulse radiolysis of the dioxane **2b**6b) (0.01 mol dm^{-3}) in 1,2-dichloroethane under argon. All the above results can be explained by assuming that the diarylalkylmethyl radical site of **5b** is trapped by molecular dioxygen to form the oxygenated radical cation **6b** (Scheme 1). Noteworthy is here that besides the disappearance of the 355 nm band due to the diarylalkylmethyl radical moiety of **5b**, the absorption due to the diarylalkylmethyl cation moiety is sifted from 485 nm to 500 nm by the conversion of **5b** into **6b**. This is apparently ascribed to the change in interaction between the cation and radical moieties of **5b** and **6b**.

Pulse radiolyses of a homologous series of compounds **1a** and **1c**, and also a reference compound **3** were conducted in a similar manner. For **1c**, very similar spectral changes to those for **1b** were observed. However, in the cases of **1a** and **3**, absorption bands in 400 nm region decayed more slowly (k = 3.8 x 10^6 s^{-1} for **1a** and k = 4.0 x 10^6 s^{-1} for **3**) than the corresponding absorption band for **1b**. New absorption bands appeared at λ_{max} 520 nm for **1a** and at λ_{max} 510 nm for **3** with slower rates. Intensities of these new bands were weaker than the corresponding bands for **1b** and **1c**. These results indicate that the chemical behavior of the reactive species generated by the pulse radiolysis of **1a-c** is affected by the methylene chain length of the compounds.

The proposed mechanism for the major pathways of the pulse radiolysis reaction of 1,1-diarylethene derivatives is given in Scheme 1. In the case of **1b**, the radical cation **4b** is formed via a one-electron oxidation by a radical cation of 1,2-dichloroethane, $DCE^{+\cdot}$; it is known that $DCE^{+\cdot}$ is generated as a primary reactive species in the γ-radiolysis in 1,2-dichloroethane.7) It should be noted that in **4b**, the radical cation center is localized on one of the diarylethenyl moieties and the other diarylethenyl moiety exists in close proximity to the radical cation center. Intramolecular cyclization of radical cation **4b** affords distonic 1,4-radical cation **5b**. The attack of molecular dioxygen on the radical site of **5b** affords **6b**. Molecular dioxygen does not attack a delocalized radical cation such as **4b**. The distonic 1,4-radical cation is also formed from **1c**. In the cases of **1a** and **3**, such a distonic radical cation is not formed. A molecular model shows that a severe steric strain would exist in 1,4-radical cations of **1a** and **3**, if they are formed. The destabilization in 1,4-radical cations caused by a steric strain accounts for the experimental facts that cyclodimers are not formed in photoinduced electron-transfer reactions of 2-substituted 1,1-diarylalkenes.[2a,6)]



4b **5b** **6b**

Scheme 1.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

1) a) R. A. Neunteufel and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 4080 (1973); T. Majima, C. Pac, and H. Sakurai, *ibid.*, **103** , 4499 (1981); b) S. L. Mattes and S. Farid, *J. Am. Chem. Soc.*, **108**, 7356 (1986); c) R. K. Haynes, M. K. S. Probert, and I. D. Wilmot, *Aust. J. Chem.*, **31**, 1737 (1978); d) K. Gollnick and A. Schnatterer, *Tetrahedron Lett.*, **25**, 185 (1984); e) M. Kojima, A. Ishida, and S. Takamuku, *Chem. Lett.*, **1993**, 979.

2) a) S. Tojo, S. Toki, and S. Takamuku, *J. Org. Chem.*, **56**, 6240 (1991); b) B. F. Yates, W. J. Bouma, and L. Radom, *J. Am. Chem. Soc.*, **106**, 5805 (1984); S. Hammerum, *Mass Spctrom. Rev.*, **7**, 123 (1988).

3) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 4372 (1966); O. Brede, J. Bos, W. Helmstreit, and R. Mehnert., *Radiat. Phys. Chem.*, **19**, 1 (1982); R. A. McClelland, V. M. Kanagasabapathy, and S. Steenken, *J. Am. Chem. Soc.*, **110**, 6913 (1988).

4) Pulse radiolysis was carried out by irradiation of electron beam (28 MeV, 8 ns) from the L-band linear accelerator at Osaka university in a Suprasil cell. γ-Irradiation in a matrix at 77 K was carried out with a ^{60}Co source (2.6 x 10^{14} Bq, dose rate 6.3 x 10^2 Gy/h) in a Suprasil cell.

5) The rate constants for the reaction of O_2 with the species associated with the 355 and 485 nm bands were unable to evaluated, because absolute concentrations of O_2 in the solutions could not be determined.

6) a) K. Mizuno, I. Nakanishi, N. Ichinose, and Y. Otsuji, *Chem. Lett.*, **1989**, 1095; b) T. Tamai, K. Mizuno, I. Hashida, and Y. Otsuji, *Tetrahedron Lett.*, **34**, 2641 (1993).

7) T. Shida, E. Haselbach, and T. Bally, *Acc. Chem. Res.*, **17**, 180 (1984).

(Received September 30, 1993)