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Remarkable Enhancements of Isomerization and Oxidation of Radical Cations of Stilbene Derivatives Induced by Charge-Spin Separation

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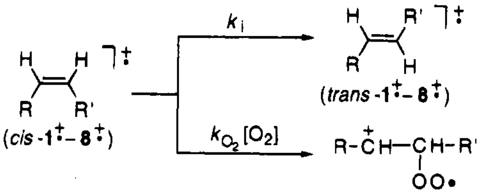
As typical reactions of radical cations of aromatic olefins, *cis* (*c*)–*trans* (*t*) isomerization, dimerization, and addition of a nucleophile are well-known.[1] However, factors which control the relative rates of these reactions are unclear. No unimolecular *c*–*t* isomerization occurs in stilbene radical cation (St$^{\bullet+}$),[2] while dimerization[3] of St$^{\bullet+}$ with St occurs with the rate constant of $k_d = (3.5–3.9) \times 10^8\ M^{-1}\ s^{-1}$ [3b,c] to yield a π-dimer radical cation (π-St$_2^{\bullet+}$) which converts to a σ-dimer radical cation (σ-St$_2^{\bullet+}$) decomposing to *t*-St$^{\bullet+}$ and St as final products.[3c] It is reported that *t*-St$^{\bullet+}$ reacts with superoxide molecule[4] at the rate constant of $k_{so} = 1.9 \times 10^9\ M^{-1}\ s^{-1}$ near to the diffusion rate constant,[4c] while *t*-St$^{\bullet+}$ has little reactivity toward O$_2$.[3a,4,5] On the other hand, we have found that both unimolecular *c*–*t* isomerization and oxidation of St$^{\bullet+}$ derivatives substituted with a *p*-methoxyl group (*p*-CH$_3$O), as an electron-donating substituent, proceed with the rate constants of $k_i = 4.5 \times 10^6–1.4 \times 10^7\ s^{-1}$ and $k_{O_2} = (1.2–4.5) \times 10^7\ M^{-1}\ s^{-1}$, respectively (Scheme 1). On the basis of the two types of reactions (*c*–*t* isomerization and oxidation) of eight St$^{\bullet+}$ derivatives (RCH=CHC$_6$H$_5$: **1**, R = C$_6$H$_5$; **2**, R = 4-CH$_3$C$_6$H$_4$; **3**, R = 4-CH$_3$OC$_6$H$_4$ (= An); **4**, R = 2,4-(CH$_3$O)$_2$C$_6$H$_3$; **5**, R = 3,4-(CH$_3$O)$_2$C$_6$H$_3$; **6**, R = 3,5-(CH$_3$O)$_2$C$_6$H$_3$; **7**, AnCH=C(CH$_3$)C$_6$H$_5$; **8**, AnCH=CHAn),[6] it is found that separation and localization of positive charge and an unpaired electron play an important role in increasing the reactivities and that the reactivities of radical cations in solution are explained in terms of distonic radical cations.[7,8]

Scheme 1



The reactions of radical cations **1**$^{\bullet+}$–**8**$^{\bullet+}$ were investigated using a pulse radiolysis technique in 1,2-dichloroethane (DCE) at room temperature.[9] The transient absorption spectra immediately after the electron pulse were assigned to *c*- and *t*-**1**$^{\bullet+}$–**8**$^{\bullet+}$ formed from the capture of the hole generated in the initiation step (Table 1). *c*- and *t*-**2**$^{\bullet+}$–**8**$^{\bullet+}$ show two typical absorption bands in the range of 400–600 and 700–1000 nm assigned to D$_2$ ← D$_0$ and D$_1$ ← D$_0$ transitions, respectively, similarly to **1**$^{\bullet+}$.[10] However, the absorption peaks of both shorter and longer wavelength bands of **3**$^{\bullet+}$–**5**$^{\bullet+}$ and **8**$^{\bullet+}$ shift to longer wavelengths with higher intensities than those of **1**$^{\bullet+}$ (Table 1). *c*-**6**$^{\bullet+}$ shows the absorption peak with extremely low intensity similar to that of 1,3-dimethoxybenzene radical cation.[11]

The rate constants of unimolecular *c*–*t* isomerization (k_i) were calculated from the formation of *t*-**1**$^{\bullet+}$–**8**$^{\bullet+}$ bands at the absorption peaks of D$_2$ (λ_{max}) at 5 mM of *c*-**1**–**8** where unimolecular *c*–*t* isomerization was little affected by dimerization of *c*-**1**$^{\bullet+}$–**8**$^{\bullet+}$ and *c*-**1**–**8** (Table 1). The rate constants of dimerization (k_d) were measured from the dependence of the decay of **1**$^{\bullet+}$–**8**$^{\bullet+}$ bands at λ_{max} on the concentration of **1**–**8** (5–100 mM), while the rate constants of oxidation (k_{O_2}) were obtained from the dependence of the decay of *c*- and *t*-**1**$^{\bullet+}$–**8**$^{\bullet+}$ bands on the concentration of O$_2$ (2–14 mM). These rate constants thus obtained are summarized in Table 1.

Unimolecular *c*–*t* isomerization was observed in *c*-**3**$^{\bullet+}$–**5**$^{\bullet+}$ and *c*-**8**$^{\bullet+}$ with *p*-CH$_3$O ($k_i = 4.5 \times 10^6–1.4 \times 10^7\ s^{-1}$), but not in *c*-**1**$^{\bullet+}$, *c*-**2**$^{\bullet+}$, and *c*-**6**$^{\bullet+}$ without *p*-CH$_3$O. No isomerization or $k_i < 10^6\ s^{-1}$ was observed in *c*-**7**$^{\bullet+}$ with *p*-CH$_3$O and a methyl substitution on the olefinic carbon. The oxidation with O$_2$ was also observed in *t*-**3**$^{\bullet+}$–**5**$^{\bullet+}$ and *t*-**7**$^{\bullet+}$ with *p*-CH$_3$O ($k_{O_2} = (1.2–4.5) \times 10^7\ M^{-1}\ s^{-1}$), but not in *c*-**1**$^{\bullet+}$, *c*-**2**$^{\bullet+}$, and *c*-**6**$^{\bullet+}$ without *p*-CH$_3$O. No oxidation or $k_{O_2} < 10^6\ M^{-1}\ s^{-1}$ was observed in *t*-**8**$^{\bullet+}$ with two *p*-CH$_3$O. The dimerization was observed in **1**$^{\bullet+}$–**3**$^{\bullet+}$ and *t*-**6**$^{\bullet+}$ ($k_d = (2.0–4.3) \times 10^8\ M^{-1}\ s^{-1}$).[12] Since the dimerization occurs even in **3**$^{\bullet+}$ with the large k_d value but not in **4**$^{\bullet+}$, **5**$^{\bullet+}$, and **7**$^{\bullet+}$, it is suggested that the dimerization involves initial formation of a π-complex with overlapping of two benzene rings and that the π-complex formation

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(1) (a) Fox, M. A., Chanon, M., Eds. *Photoinduced Electron Transfer*; Elsevier: Amsterdam, The Netherlands, 1988. (b) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Deckker: New York, 1983; Vol. 6, pp 233–326. (c) Lewis, F. D. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, The Netherlands, 1988; Part C, Chapter 4. (d) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233. (e) Parker, V. D. *Acc. Chem. Res.* **1984**, *17*, 243. (f) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79. (g) Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1994**, *116*, 6895 and references cited therein.

(2) (a) Lewis, F. D.; Bedell, A. M.; Dykstra, R. E.; Elbert, J. E.; Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 8055 and references cited therein. (b) Kuriyama, Y.; Arai, T.; Sakuragi, H.; Tokumaru, K. *Chem. Phys. Lett.* **1990**, *173*, 253.

(3) (a) Lewis, F. D.; Petisce, J. R.; Oxman, J. D.; Nepras, M. J. *J. Am. Chem. Soc.* **1985**, *107*, 203. (b) Kuriyama, Y.; Sakuragi, H.; Tokumaru, K.; Yoshida, Y.; Tagawa, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1852 and references cited therein. (c) Tojo, S.; Morishima, K.; Ishida, A.; Majima, T.; Takamuku, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 958.

(4) (a) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083. (b) Yamashita, T.; Tsurusako, T.; Nakamura, N.; Yasuda, M.; Shima, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 857. (c) Tsuchiya, M.; Ebbesen, T. W.; Nishimura, Y.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1987**, 2121. (d) Konuma, S.; Aihara, S.; Kuriyama, Y.; Misawa, H.; Akaba, R.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1991**, 1897.

(5) Tokumaru and his co-workers proposed that the oxidation depends on the structures of olefins, since the rate constant of k_{O_2} varied in the wide range, $k_{O_2} = 1.3 \times 10^6$, 7.2×10^5, and $2.6 \times 10^8\ M^{-1}\ s^{-1}$ for *t*-**1**$^{\bullet+}$, *t*-**8**$^{\bullet+}$, and radical cation of (*E*)-2,3-diphenyl-2-butene, respectively, in laser flash photolysis of the olefin and 9-cyanoanthracene in DMSO.[4c]

(6) *c*- and *t*-**2**–**6** were prepared by the Wittig reaction.

(7) (a) Yates, B. F.; Bouma, W. J.; Radom, L. *Tetrahedron* **1986**, *22*, 6225 and references cited therein. (b) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123. (c) Stirk, K. M.; Kiminkinen, L. K. M.; Kenttämaa, H. I. *Chem. Rev.* **1992**, *92*, 1649.

(8) Tojo, S.; Toki, S.; Takamuku, S. *J. Org. Chem.* **1991**, *56*, 6240.

(9) The sample solutions was irradiated with an 8-ns pulse of 28 MeV electrons.[3c]

(10) Shida, T.; Hamill, W. *J. Chem. Phys.* **1966**, *44*, 2375.

(11) Takamuku, S.; Komitsu, S.; Toki, S. *Radiat. Phys. Chem.* **1989**, *34*, 553.

(12) The dimerization was also observed in *t*-**8**$^{\bullet+}$ on the basis of electrochemical measurements, although $k_d = (3.4–5) \times 10^3\ M^{-1}\ s^{-1}$ was too small to be observed under the present conditions in this study. Steckhan, E. *J. Am. Chem. Soc.* **1978**, *100*, 3526. Burgbacher, G.; Schaefer, H. J. *J. Am. Chem. Soc.* **1979**, *101*, 7590.

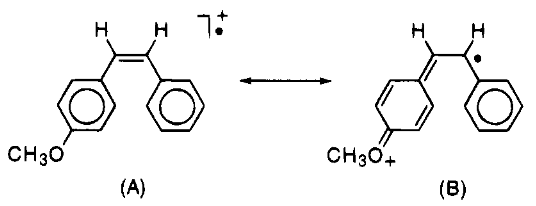
0022-3263/95/1960-4684$09.00/0

Table 1. Absorption Peak of D_2 of $\mathbf{1}^{\bullet+}$–$\mathbf{8}^{\bullet+}$ in DCE and Rate Constants for the Reactions of $\mathbf{1}^{\bullet+}$–$\mathbf{8}^{\bullet+}$ in Pulse Radiolyses in DCE at Room Temperature[a]

	cis(*c*)					*trans* (*t*)			
stilbene	λ_{max}/nm	ϵ_λ/M^{-1} cm^{-1}	k_i/s^{-1}	k_d/M^{-1} s^{-1}	k_{O_2}/M^{-1} s^{-1}	λ_{max}/nm	ϵ_λ/M^{-1} cm^{-1}	k_d/M^{-1} s^{-1}	k_{O_2}/M^{-1} s^{-1}
$\mathbf{1}^{\bullet+}$	515	18 000	*b*	3.9×10^8	*c*	480	65 000	3.9×10^8	*c*
$\mathbf{2}^{\bullet+}$	520	30 900	*b*	3.4×10^8	*c*	490	80 900	4.3×10^8	*c*
$\mathbf{3}^{\bullet+}$	530	13 200	4.5×10^6	2.0×10^8	*d*	470, 500	39 200, 74 800	3.0×10^8	4.5×10^7
$\mathbf{4}^{\bullet+}$	530	*d*	1.3×10^7	*d*	*d*	480	10 5000	*c*	4.0×10^7
$\mathbf{5}^{\bullet+}$	540	*d*	1.4×10^7	*d*	*d*	480	84 600	*c*	1.2×10^7
$\mathbf{6}^{\bullet+}$	520	3270	*b*	*d*	*c*	460, 510	24 500, 20 800	3.4×10^8	*c*
$\mathbf{7}^{\bullet+}$	450, 500	8820, 9710	*b*	*d*	2.5×10^7	440, 490	18 400, 29 400	*c*	2.8×10^7
$\mathbf{8}^{\bullet+}$	500, 570	*d*	5.5×10^6	*d*	*c*	480, 540	33 100, 76 000	*c*	*c*

[a] The absorption peaks of D_2 (λ_{max}) of $\mathbf{1}^{\bullet+}$–$\mathbf{8}^{\bullet+}$ in DCE. The molar absorption coefficients (ϵ_λ) were estimated from the optical density at λ nm and the optical length of 1 cm with assumption of concentration of 8×10^{-6} M for $\mathbf{2}^{\bullet+}$–$\mathbf{8}^{\bullet+}$ which was measured for *t*-$\mathbf{1}^{\bullet+}$ on the basis of $\epsilon_{480} = 6.5 \times 10^4$ M^{-1} cm^{-1} in DCE. k_i, calculated from the formation of $t^{\bullet+}$ at 5 mM of *c*-**1**–**8**; k_d, measured from the dependence of the decay of $\mathbf{1}^{\bullet+}$–$\mathbf{8}^{\bullet+}$ on the concentration of **1**–**8**; k_{O_2}, obtained from the dependence of the decay of $c^{\bullet+}$ or $t^{\bullet+}$ on the concentration of O_2. [b] $k_i < 10^6$ s^{-1} since the formation of $t^{\bullet+}$ was not observed. [c] k_d and $k_{O_2} < 10^6$ M^{-1} s^{-1} since no dependence of decay of $c^{\bullet+}$ or $t^{\bullet+}$ on the concentration of *c*, *t*, or O_2. [d] Not determined.

Scheme 2



is inhibited by steric hindrance of substituents on benzene rings and olefinic carbons.

On the basis of these experimental results of k_i and k_{O_2} it is clearly shown that *p*-CH_3O as an electron-donating substituent on the benzene ring changes remarkably the reactivities of $\mathbf{1}^{\bullet+}$–$\mathbf{8}^{\bullet+}$. It is considered that a resonance structure (B) as shown in Scheme 2 for *c*-$\mathbf{3}^{\bullet+}$ contributes to the electronic states of $\mathbf{3}^{\bullet+}$–$\mathbf{5}^{\bullet+}$, $\mathbf{7}^{\bullet+}$, and $\mathbf{8}^{\bullet+}$ with *p*-CH_3O. Positive charge is more localized on oxygen of *p*-CH_3O, while the unpaired electron density is more localized on the olefinic β-carbon in $\mathbf{3}^{\bullet+}$–$\mathbf{5}^{\bullet+}$, $\mathbf{7}^{\bullet+}$, and $\mathbf{8}^{\bullet+}$ with *p*-CH_3O (charge-spin separation) than in $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ without *p*-CH_3O. Alternatively, oxygen of *p*-CH_3O and the olefinic β-carbon participate considerably to SOMO of $\mathbf{3}^{\bullet+}$–$\mathbf{5}^{\bullet+}$, $\mathbf{7}^{\bullet+}$, and $\mathbf{8}^{\bullet+}$. Since the energy barrier for the unimolecular *c*–*t* isomerizations decreases with increasing the single bond character in the central C=C double bond, the reactivity of the isomerization increases in $\mathbf{3}^{\bullet+}$–$\mathbf{5}^{\bullet+}$, $\mathbf{7}^{\bullet+}$, and $\mathbf{8}^{\bullet+}$. Since unpaired electron density is localized on the olefinic β-carbon, the reactivity of the oxidation increases in $\mathbf{3}^{\bullet+}$–$\mathbf{5}^{\bullet+}$, $\mathbf{7}^{\bullet+}$, and $\mathbf{8}^{\bullet+}$. Consequently, *p*-CH_3O in $\mathbf{3}^{\bullet+}$–$\mathbf{5}^{\bullet+}$, $\mathbf{7}^{\bullet+}$, and $\mathbf{8}^{\bullet+}$ causes enhancement of the reactivity due to the charge-spin separation, like distonic radical cations carrying spatially separated positive charge and an unpaired electron.

Product analyses were performed in γ-radiolyses of *c*-**3**–**5** in Ar- or O_2-saturated DCE at room temperature.[13] *t*-**3**–**5** were formed in high yields in γ-radiolyses of *c*-**3**–**5** in Ar-saturated DCE, and 4-methoxybenzyl phenyl ketone was regioselectively formed in γ-radiolysis of *t*-**3** in O_2-saturated DCE, although the details will be published elsewhere. These results are consistent with the order of k_i and k_{O_2} and the charge-spin separation induced by *p*-CH_3O in $\mathbf{3}^{\bullet+}$–$\mathbf{5}^{\bullet+}$, $\mathbf{7}^{\bullet+}$, and $\mathbf{8}^{\bullet+}$.

The unimolecular *c*–*t* isomerization of *c*-$\mathbf{7}^{\bullet+}$ or oxidation of *t*-$\mathbf{8}^{\bullet+}$ did not occur, although both $\mathbf{7}^{\bullet+}$ and $\mathbf{8}^{\bullet+}$ have *p*-CH_3O. These are possibly explained in terms of steric hindrance for the twisting and spin density on the olefinic carbon, respectively. Methyl substitution on the olefinic carbon in *c*-$\mathbf{7}^{\bullet+}$ provides more steric hindrance for the twisting about the C=C double bond than in *c*-$\mathbf{3}^{\bullet+}$. The density of unpaired electron on the olefinic carbon in $\mathbf{8}^{\bullet+}$ with two symmetrical *p*-CH_3O is lower than in $\mathbf{3}^{\bullet+}$. The unimolecular *c*–*t* isomerization or the oxidation of *c*-$\mathbf{6}^{\bullet+}$ did not occur. It should be noted that *c*-$\mathbf{6}^{\bullet+}$ has the absorption peak at 520 nm with extremely low intensity similar to that of 1,3-dimethoxybenzene radical cation. These results may be interpreted by a twisted structure with the 3,5-dimethoxyphenyl ring rotating against the C=C double bond, since a structure (B) is not possible in *c*-$\mathbf{6}^{\bullet+}$ having *m*-CH_3O.

Tokumaru and his co-workers reported $k_i = 3 \times 10^5$ s^{-1} for radical cations of *c*-4,4′-dibromostilbene (*c*-$\mathbf{9}^{\bullet+}$) and *c*-4,4′-dimethylstilbene (*c*-$\mathbf{10}^{\bullet+}$) and $k_i > 3 \times 10^5$ s^{-1} for *c*-$\mathbf{8}^{\bullet+}$ [2b] and proposed that *c*–*t* isomerization might be accelerated by reduction of the electron density on the unsaturated linkage induced by the substituents on the basis of lower coupling constants of the α-H of *t*-**9** and *t*-**10** having *p*-substituents than that of *t*-**1** itself in ESR studies.[14] They also proposed that the oxidation depends on the structures of olefins, since the k_{O_2} values varied in the over a wide range.[4c,d] The k_i values for *c*-$\mathbf{3}^{\bullet+}$–$\mathbf{5}^{\bullet+}$ and *c*-$\mathbf{8}^{\bullet+}$ are 1 or 2 orders larger than those for *c*-$\mathbf{9}^{\bullet+}$ and *c*-$\mathbf{10}^{\bullet+}$ [2b] as shown in Table 1. Remarkable enhancements of the isomerization by *p*-CH_3O are explained by charge-spin separation in *c*-$\mathbf{3}^{\bullet+}$–$\mathbf{5}^{\bullet+}$ and *c*-$\mathbf{8}^{\bullet+}$.

The present work is the first example to clarify that the reactivities of stilbene radical cations are controlled predominantly by charge-spin separation induced by *p*-CH_3O, and it is suggested that distonic radical cations can be acceptable to explain reactivities of radical cations even in solution.

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[13] γ-Radiolyses of the sample solutions were performed by a ^{60}Co γ source; concentration of substrate, 10 mM.[3c]

(14) Bonazzola, L.; Michaut, J.-P.; Roncin, J.; Misawa, H.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 347.