Stilbene Dimer Radical Cations in the Radiolyses of Stilbenes and 1,2,3,4-Tetraphenylcyclobutanes

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The reaction of the stilbene radical cation formed by pulse radiolysis or γ-radiolyses is explained based on neutralization as well as the formation of a π-type stilbene dimer radical cation (π-$St_2^{+\bullet}$), converting to the σ-type $St_2^{+\bullet}$ (σ-$St_2^{+\bullet}$). The r-1,c-2,t-3,t-4-tetraphenylcyclobutane radical cation generated in a rigid matrix at 77 K which converted to σ-$St_2^{+\bullet}$ upon warming. Both r-1,c-2,t-3,t-4- and r-1,t-2,c-3,t-4-tetraphenylcyclobutane radical cations underwent photochemical cycloreversion to π-$St_2^{+\bullet}$ upon irradiation at wavelengths longer than 390 nm at 77 K, and converted to σ-$St_2^{+\bullet}$ upon warming. It is suggested that π-$St_2^{+\bullet}$ has overlapping arrangements of π-electrons, while σ-$St_2^{+\bullet}$ has radical and cation centers on the 1- and 4-positions of the C_4 linkage.

The formation of a dimer radical cation of an aromatic olefin, such as 1,1-diphenylethylene, is proposed in the reaction mechanism involving the radical cation produced by a photoinduced electron transfer.[1] However, a spectroscopic detection of the dimer radical cations has not yet been fully performed. This is probably attributed to a radical anion existing as a partner of an ion pair with the radical cation. On the other hand, associated and bonded dimer radical cations have been detected with absorption measurements in the pulse radiolysis of aromatic olefins, such as styrene derivatives and 1,1-diphenylethylene, at higher concentrations.[2]

It is well documented that stilbene (St) undergoes *cis–trans* isomerization in the singlet or triplet manifold upon direct irradiation and triplet sensitization, respectively.[3] Thermal isomerization of the *c*-St radical cation to the *t*-St radical cation occurs under photoinduced secondary electron-transfer conditions,[4] and the St dimer radical cation has been proposed as an intermediate.[5] The formation of a St dimer radical cation has also been reported regarding the irradiation of a mixture of *t*-St and 2,4,6-triphenylpyrylium tetrafluoroborate[6] and in the pulse radiolysis of *t*-St[7] in dichloromethane. It is recently assumed that a photochemical $c \rightarrow t$ one-way isomerization takes place in the laser-flash photolysis of the *c*-St radical cation formed by the pulse radiolysis of *c*-St in 1,2-dichloroethane[8a] or laser photolysis under a secondary electron transfer in acetonitrile.[8b]

In order to elucidate the reaction mechanism involving the St radical cation, we investigated pulse radiolyses of *c*-St and *t*-St in 1,2-dichloroethane (DCE) at room temperature and γ-radiolyses of *c*-St and *t*-St as well as r-1,c-2,t-3,t-4- and r-1,t-2,c-3,t-4-tetraphenylcyclobutanes (*t,c,t*-CB and *t,t,t*-CB respectively, the abbreviation being based on the stereochemistry of each neighboring phenyl group) in the rigid matrix of butyl chloride at 77 K. Particular attention was paid to the absorption measurements of the St dimer radical cations.

Experimental

Materials. *cis*- and *trans*-Stilbene (*c*-St and *t*-St) were purchased from Nacalai Tesque and Tokyo Kasei, and were purified by distillation and recrystallization from ethanol before use. GC analyses of the purified stilbenes showed purities higher than 99.5%. *t,c,t*-CB and *t,t,t*-CB were prepared photochemically by the irradiation of optically dense argon-saturated benzene (100 dm^3) solutions of *t*-St (13.5 g) in Pyrex flasks with a 500-W high-pressure mercury lamp for 5 d.[9] Separation was achieved by repeated recrystallization in ether-ethanol. GC analyses of the purified St and CB showed purities higher than 99.5%. DCE, used as a solvent, was distilled over calcium hydride. Butyl chloride was shaken with concentrated sulfuric acid, washed with water, dried over calcium chloride, and fractionally distilled.

Pulse Radiolysis. The pulse radiolysis of *c*-St or *t*-St (5×10^{-3} and 10^{-1} M, M=mol dm^{-3}) in DCE deoxygenated by bubbling with argon was carried out in a 1 cm×1 cm rectangular Suprasil cell at room temperature with the irradiation of an electron pulse from the linear accelerator of Osaka University. The energy was 28 MeV, the pulse width was selected to be 8 ns (single pulse), the dose was 0.7 kGy per pulse, and the diameter was approximately 0.4 cm. The probe beam was obtained from a 450-W Xe-lamp (Osram, XBO-450), sent into the sample solution with a perpendicular intersection of the electron beam, and focused to a monochromator (CVI Laser, Digikrom-

240). The output of the monochromator was monitored by a PMT (photomultiplier tube; Hamamatsu Photonix, R1417 or R2497). The signal from the PMT was recorded on a transient digitizer (Tektronix, 7912AD with plug-ins, 7A19 and 7B92A).

γ-Radiolysis. The γ-radiolysis of glassy rigid matrix of degassed butyl chloride solutions was carried out in 1.5-mm thick Suprasil cells cooled in liquid nitrogen at 77 K by a ^{60}Co γ source (dose, 4.5×10^6 Gy). The optical absorption spectra of the 77 K matrix were measured with a spectrophotometer (Hitachi 323) and a multichannel-photodetector (Otsuka Electronics, MCPD-100). After the irradiated sample at 77 K was placed in a pre-cooled quartz Dewar vessel, the absorption spectra were measured at 77 K. Warming of the irradiated sample was performed as follows. Immediately after the liquid nitrogen was removed from the vessel, the sample was again placed in the vessel and the absorption spectra were measured with the MCPD every 3 s for 3 m during an increase in temperature up to approximately 100 K, measured using a thermocouple. Since it took only 10 μs to measure each spectrum with the MPCD, the temperature was kept at constant while measuring the spectrum. Photoirradiation of solutions after γ-radiolysis was carried out in the vessel with a 150-W Xe-lamp through a glass filter (UV-39) at 77 K.

Results and Discussion

Pulse Radiolysis of *t*-St in DCE. It has been established by Yamamoto and co-workers that the *t*-St radical cation (t-St$^{+\bullet}$), showing an absorption maximum at 480 nm, is formed by pulse radiolysis in DCE at room temperature (Eq. 1), and decays via neutralization with Cl$^-$ formed from dissociative electron attachment to DCE (Eq. 2) at a rate constant of $k_\mathrm{N}=1.6\times10^{11}$ M^{-1} s^{-1} when the concentration of *t*-St is low (10^{-4} M):$^{10)}$

$$\mathrm{S} + \text{hole} \rightarrow \mathrm{S}^{+\bullet}, \tag{1}$$

$$\mathrm{S}^{+\bullet} + \mathrm{Cl}^- \rightarrow \text{neutral product}, \tag{2}$$

where S denotes *t*-St, *c*-St, *t*,*c*,*t*-CB, or *t*,*t*,*t*-CB. Tokumaru and co-workers have demonstrated that a bimolecular reaction of the *t*-St radical cation and *t*-St occurs to give the *t*-St dimer radical cation at a bimolecular rate constant (k_tt) of 3.4×10^8 M^{-1} s^{-1} (Eq. 3):

$$t\text{-St}^{+\bullet} + t\text{-St} \rightarrow \pi\text{-}(t\text{-St})_2{}^{+\bullet}, \tag{3}$$

even at a *t*-St concentration of 5×10^{-3} M. This was based on the pseudo-first-order decay of the transient absorption of the *t*-St radical cation and an absorption maximum shifting to a shorter wavelength of 480 nm in the pulse radiolysis of dichloromethane solutions of *t*-St at a high concentration of 10^{-1} M.$^{7)}$

We also carried out a pulse radiolysis of *t*-St in DCE (Figs. 1a and 1b), and found that the 480 nm absorption of the *t*-St radical cation decayed according to a pseudo-first-order rate equation, as shown in the insets of Fig. 1. The value of $k_\mathrm{tt}=3.9\times10^8$ M^{-1} s^{-1} was obtained from a plot of the observed rate constant (k_obs) and the concentration of *t*-St, which was essentially equivalent to that reported.$^{7)}$ The rate constants are summarized in Table 1. The absorption maximum shifted to 460—470 nm, and remained even 1 μs after the pulse at a high concentration of *t*-St (10^{-1} M).$^{7)}$ This result is reasonably explained by the formation of a π-type *t*-St dimer radical cation (π-(t-St)$_2{}^{+\bullet}$) from the *t*-St radical cation and *t*-St with an absorption maximum at 460—470 nm. The π-type *t*-St dimer radical cation is configurationally stable because of an overlapping of π-electrons between two benzene rings of the *t*-St radical cation and *t*-St. In other words, the *t*-St dimer radical cation is in equilibrium with the *t*-St radical cation and *t*-St (Eqs. 3 and 4):

$$\pi\text{-}(t\text{-St})_2{}^{+\bullet} \rightarrow t\text{-St}^{+\bullet} + t\text{-St}. \tag{4}$$

Pulse Radiolysis of *c*-St in DCE. Decay of the *c*-St radical cation has been analyzed by neutralization (Eq. 2) and the formation of the *c*-St dimer radical cation with $k_\mathrm{cc}=3.5\times10^8$ M^{-1} s^{-1} (Eq. 5);$^{7)}$

$$c\text{-St}^{+\bullet} + c\text{-St} \rightarrow \sigma\text{-St}_2{}^{+\bullet}. \tag{5}$$

Fast isomerization of the *c*-St radical cation to the *t*-St radical cation through a σ-type St dimer radical cation (σ-St$_2{}^{+\bullet}$) is proposed, since the *t*-St radical cation is detected even at 5 ns after the pulse. Pulse radiolyses of *c*-St in DCE were also carried out at 5×10^{-3} and 10^{-1} M (Figs. 1c and 1d, respectively), and $k_\mathrm{cc}=3.9\times10^8$ M^{-1} s^{-1} was obtained from a similar analysis of the transient absorption of the *c*-St radical cation with a maximum at 515 nm (Table 1). The absorption maximum of the *c*-St radical cation shifted to 480 nm of the *t*-St radical cation. Because no transient absorption of the *c*-St dimer radical cation was detected, the σ-type St dimer radical cation has a shorter lifetime than the duration of an electron pulse of 8 ns in DCE at room temperature, and rapidly decomposes into the thermodynamically stabler *t*-St radical cation and *t*-St (Eq. 6), as proposed:$^{7)}$

$$\sigma\text{-St}_2{}^{+\bullet} + \Delta E \rightarrow t\text{-St}^{+\bullet} + t\text{-St}. \tag{6}$$

γ-Radiolyses of *t*-St at 77 K. In order to elucidate the dimer radical cations, γ-radiolyses of *t*-St as well as *t*,*c*,*t*-CB and *t*,*t*,*t*-CB were carried out in rigid matrices of a glassy butyl chloride solution at 77 K. UV and visible absorption spectra were measured at both 77 K and upon warming. Since the rigid matrix was gradually softened during warming, reactions with structural changes can be allowed to occur.

The absorption of the *t*-St radical cation with a maximum at 485 nm$^{11)}$ was detected at 5×10^{-3} M of *t*-St, and collapsed upon warming (Fig. 2a). In addition to the absorption band, two broad absorption bands at around 400—470 and at 600—800 nm were detected at 10^{-1} M of *t*-St (Fig. 2b). The broad and strong absorption band at 600—800 nm comprised two peaks at 680 and 770 nm. The two broad absorption bands at around 400—470 and 600—800 nm collapsed, while two

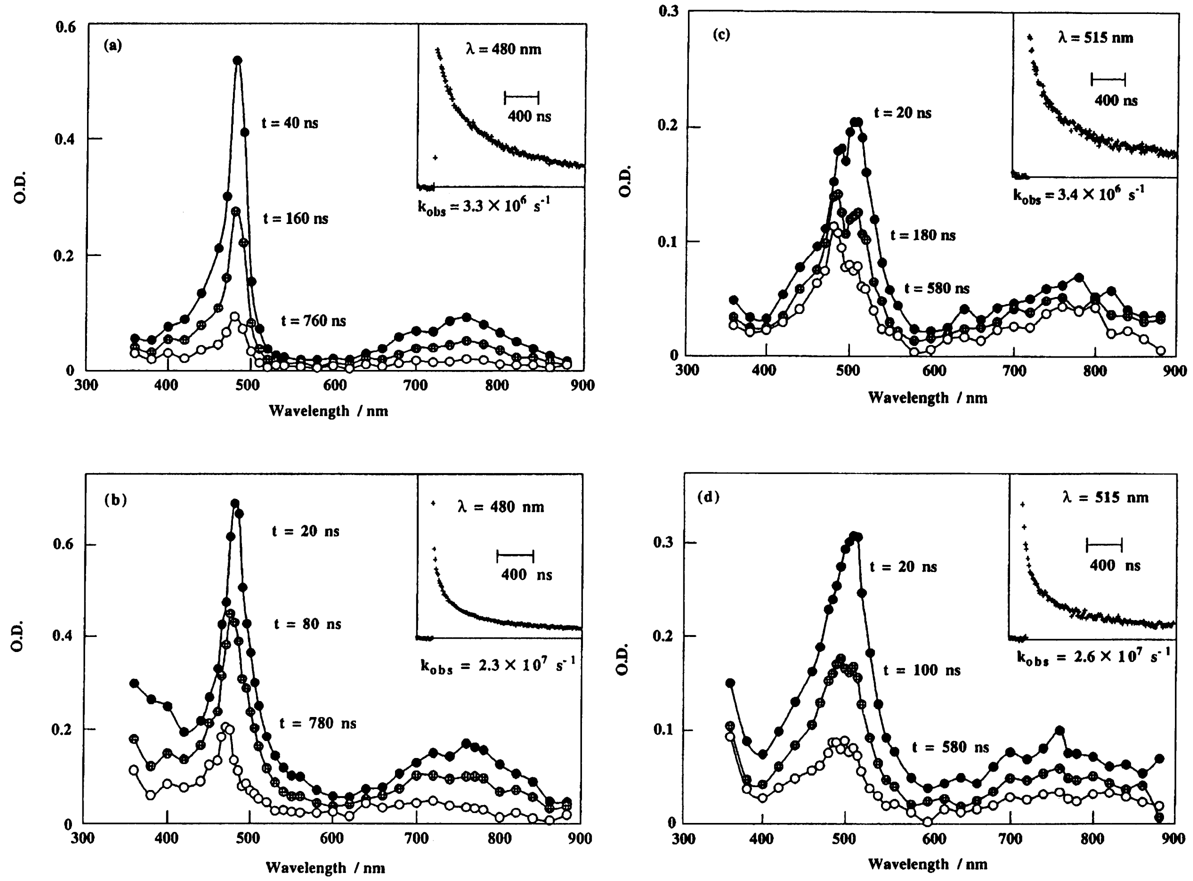


Fig. 1. Transient absorption spectra recorded after an electron pulse in the pulse radiolysis of an argon-saturated DCE solution of (a) *t*-St (5×10^{-3} M), (b) *t*-St (10^{-1} M), (c) *c*-St (5×10^{-3} M), and (d) *c*-St (10^{-1} M). Insets: kinetic traces illustrating the time profiles of the optical densities at 480 nm (a, b) and 515 nm (c, d) as a function of time after the electron pulse. Times after the pulse and the observed rate constant are mentioned inside.

Table 1. Summary of Reactions of *t*-St$^{+\bullet}$ and *c*-St$^{+\bullet}$ in Pulse Radiolyses of *t*-St and *c*-St in DCE at Room Temperature

St$^{+\bullet}$	Reaction	Equation	Rate constant/$\mathrm{M^{-1}\,s^{-1}}$
t-St$^{+\bullet}$	Neutralization	*t*-St$^{+\bullet}$+ Cl$^-$ → neutral product	$k_\mathrm{N}=1.6\times10^{11}$ [10]
	Dimerization	*t*-St$^{+\bullet}$+ *t*-St → π-(*t*-St)$_2$$^{+\bullet}$	$k_\mathrm{tt}=3.4\times10^{8}$, [7] 3.9×10^{8}
	Radical fission	π-(*t*-St)$_2$$^{+\bullet}$→ *t*-St$^{+\bullet}$+ *t*-St	—[a]
c-St$^{+\bullet}$	Dimerization	*c*-St$^{+\bullet}$+ *c*-St →σ-St$_2$$^{+\bullet}$	$k_\mathrm{cc}=3.5\times10^{8}$, [7] 3.9×10^{8}
	Radical fission	σ-St$_2$$^{+\bullet}$+ ΔE → *t*-St$^{+\bullet}$+ *t*-St	—[a]

a) Not determined.

new absorption bands at around 330—400 and 500—600 nm arose upon warming, as shown in Figs. 2b and 3. The 485 nm absorption band assigned to the *t*-St radical cation did not change. Since the 680 nm peak collapsed more rapidly than the 770 nm peak, it is considered that the 700—800 nm absorption band with the 770 nm peak also arose upon warming together with other two bands at around 330—400 and 500—600 nm. The formation of the 700—800 nm band is probably compensated by the collapse of the 600—800 nm absorption band. Thus, three different transient radical cations can be distinguished in rigid matrices of butyl chloride at 77 K as follows:

1. *t*-St radical cation showing absorption maximum at 485 nm,
2. radical cation A showing absorption bands at 400—470 and at 600—800 nm with a shorter lifetime than that of B,
3. radical cation B showing absorption bands at 330—400, 500—600, and 700—800 nm with a longer lifetime than that of A (vide infra).

Apparently, the collapse of A is related to the formation of B. Table 2 summarizes the transient species formed by the γ-radiolyses of *t*-St at 10^{-1} M as well as *t,c,t*-CB and *t,t,t*-CB at 5×10^{-3} M in rigid matrices of butyl chloride at 77 K.

π-Type *t*-St Dimer Radical Cation. The π-type *t*-St dimer radical cation was found to show an

Table 2. Transient Species Formed by γ-Radiolyses of *t*-St at 10^{-1} M[a] as Well as *t*,*c*,*t*-CB and *t*,*t*,*t*-CB at 5×10^{-3} M in Rigid Matrices of Butyl Chloride at 77 K

Transient species	Precursor	Method[b]	Absorption region or peaks/nm	Fate[c]	Assignment
t-St$^{+\bullet}$	—	—	485, 650—850 (weak)	—	—
t,*c*,*t*-CB$^{+\bullet}$	—	—	360—800 (broad)	—	—
t,*t*,*t*-CB$^{+\bullet}$	—	—	400—670 (broad)	—	—
A	*t*-St$^{+\bullet}$+ *t*-St	$h\nu$	400—470, 680—800	B	π-(*t*-St)$_2^{+\bullet}$
B	A	Warming	370, 550, 770	*t*-St$^{+\bullet}$+ *t*-St	σ-St$_2^{+\bullet}$
C	*t*,*c*,*t*-CB$^{+\bullet}$	$h\nu$	400—470, 680—800	D	π-(*t*-St)$_2^{+\bullet}$
D	*t*,*c*,*t*-CB$^{+\bullet}$, C	Warming	350, 550, 780	*t*-St$^{+\bullet}$+ *t*-St	σ-St$_2^{+\bullet}$
E	*t*,*t*,*t*-CB$^{+\bullet}$	$h\nu$	480	F	*t*-St$^{+\bullet}$/*t*-St pair
F	E	Warming	370, 550, 770	*t*-St$^{+\bullet}$+ *t*-St	σ-St$_2^{+\bullet}$

a) M=mol dm^{-3}. b) Method to form the transient species from the precursor, where warming and $h\nu$ denote warming of rigid matrices of butyl chloride and photoirradiation at the wavelength longer than 390 nm respectively. See the experimental section in detail. c) Thermal products of the transient species.

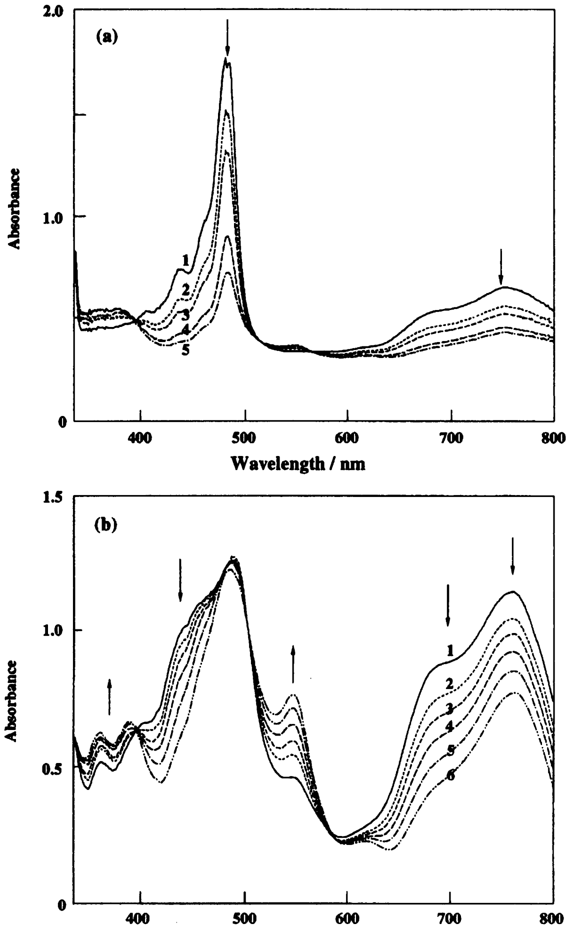


Fig. 2. Absorption spectral changes recorded immediately (1) after γ-radiolyses of (a) *t*-St (5×10^{-3} M) and (b) *t*-St (10^{-1} M) in degassed butyl chloride matrices at 77 K and after warming (in the order of 2, 3, 4, 5, and 6). Arrows show increase or decrease of the peak upon warming. See the experimental section in detail.

absorption maximum at 460—470 nm in the pulse radiolysis of *t*-St at 10^{-1} M at room temperature (Eq. 3 and Fig. 1b). The π-type dimer radical cation of 1,1-diphenylethylene shows absorption maxima at 395 and 1000—1200 nm in dichloromethane.[2g] The π-type *t*-St dimer radical cation shows an absorption band in the longer wavelength region than 1200 nm with an extremely low intensity compared to the 460—470 nm band in the pulse radiolysis of *t*-St in dichloromethane at room temperature.[7] The dimer radical cations of polycyclic aromatic hydrocarbons in solution at room temperature exhibit a charge resonance band in the near-infrared region with an intensity comparable with or several tenths of those of the shorter wavelength band due to monomeric radical cations.[12] Therefore, the weak absorption band in the wavelength region longer than 1200 nm has been assigned to a monomeric *t*-St radical cation or some π-type *t*-St dimer radical cation having an overlapping arrangement.[7]

Radical cation A is assigned to the π-type *t*-St dimer radical cation on the basis of the experimental results as well as the reported results described above. The 400—470 nm absorption band in a rigid matrix at 77 K is consistent with the 460—470 nm absorption band of the π-type *t*-St dimer radical cation at room temperature.[7] However, the 600—800 nm absorption band detected in a rigid matrix at 77 K shifted to shorter wavelengths compared with the charge resonance band of the dimer radical cations at 1200 nm,[7] and had an intensity comparable with those of the 400—470 nm absorption (Fig. 2b). The difference in the wavelength and the relative intensity of the charge resonance band at 600—800 nm at 77 K, compared with the 1200 nm band at room temperature, can probably be attributed to a difference between the rigid matrix at 77 K and the solution at room temperature. The π-type *t*-St dimer radical cation can take various structures with overlapping of π-electrons between two benzene rings of stilbene, which is easier in a rigid matrix because of the shorter distance than in solution. Therefore, the intensity of the charge resonance band at 600—800 nm in a rigid matrix at 77 K is larger than that in solution at room temperature. The π-type *t*-St dimer radical cation can take thermodynamically the most stable structure with overlapping arrangements in solution at room temperature. On the other hand, the π-type *t*-St dimer radical cation can take various structures with different overlapping arrangements in a rigid matrix at 77 K. It is suggested that the charge-resonance band of the π-type *t*-St dimer radical cation shifts to longer wavelength with a large π-electron interaction and a larger delocalization of the π-electrons. Therefore, the *t*-St dimer radical cation exhibits the charge resonance band in the considerably shorter-wavelength region of 600—800 nm in rigid matrices of butyl chloride at 77 K.

σ-Type St Dimer Radical Cation. Since the π-type *t*-St dimer radical cation (A) converted to radical cation B upon warming (Figs. 2 and 3), radical cation B is assigned to a σ-type St dimer radical cation (Eq. 7),

$$\pi\text{-}(t\text{-St})_2{}^{+\bullet} + \Delta E \rightarrow \sigma\text{-St}_2{}^{+\bullet} \qquad (7)$$

If radical cation B is assigned to the σ-type St dimer radical cation, the formation of absorption bands at 330—400, 500—600, and 700—800 nm is expected along with a disappearance of radical cation A (vide infra). A failure to observe the formation of the 700—800 nm band for the σ-type St dimer radical cation is due to a compensation of the large absorption band at 600—800 nm for the π-type *t*-St dimer radical cation with a shorter lifetime than that of the σ-type St dimer radical cation. Since the collapse of the 770 nm peak was slower than that of the 680 nm peak upon warming in the order of 1—4, the formation of the 770 nm band is clearly suggested.

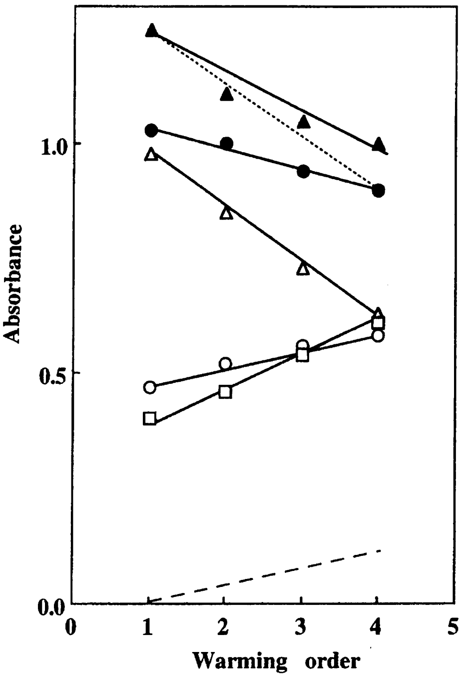


Fig. 3. Plots of absorbances at 370 (○), 430 (●), 550 (□), 680 (△), and 770 nm (▲) vs warming order obtained from Fig. 2(b) in γ-radiolysis of *t*-St (10^{-1} M) in degassed butyl chloride matrix at 77 K. When a dotted line was calculated as a change at 770 nm similarly to the collapse of the 680 nm peak, a broken line was obtained by subtraction of the calculated (dotted) line from the experimental (solid) line (▲) at 770 nm.

The collapse of the 770 nm peak was calculated as a dotted line similarly to that of the 680 nm peak for the π-type *t*-St dimer radical cation. Since the difference between the dotted line and the experimental line with solid triangles is due to the formation of the σ-type St dimer radical cation, subtraction of the dotted line from the experimental line provided a broken line for the formation of σ-type *t*-St dimer radical cation upon warming in the order of 1—4 (Fig. 3). The difference spectrum between the spectra immediately after γ-radiolysis (no. 1) and after warming clearly indicates the collapse of absorption bands at 400—470 and 600—800 nm and the formation of absorption bands at around 330—400 and 500—600 nm (Fig. 4), where A is the absorbance and $\Delta A = A_{\text{No. 1}} - A_{\text{No. 3}}$. Assuming the formation of the σ-type *t*-St dimer radical cation along with a disappearance of the π-type *t*-St dimer radical cation, as shown in Figs. 2 and 3, the difference spectrum was calculated, and depicts the collapse of the π-type *t*-St dimer radical cation as a broken line with two peaks at 680 and 770 nm and the formation of the σ-type *t*-St dimer radical cation as a dotted line with a peak at 770 nm in the region of 600—800 nm (Fig. 4). The σ-type St dimer radical cation rapidly decomposes into the thermodynamically stabler *t*-St radical cation and *t*-St upon warming (Eq. 6).

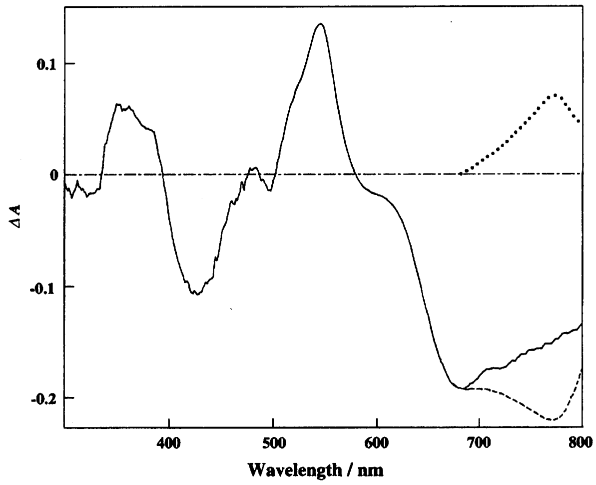


Fig. 4. Difference spectra between the spectra immediately after γ-radiolysis and after warming ($\Delta A = A_{\text{No. 1}} - A_{\text{No. 3}}$) obtained from Fig. 2b in γ-radiolysis of *t*-St (10^{-1} M) in degassed butyl chloride matrix at 77 K. When an absorption of a dotted line forms at 700—800 nm, the corresponding collapse spectrum is shown as a broken line.

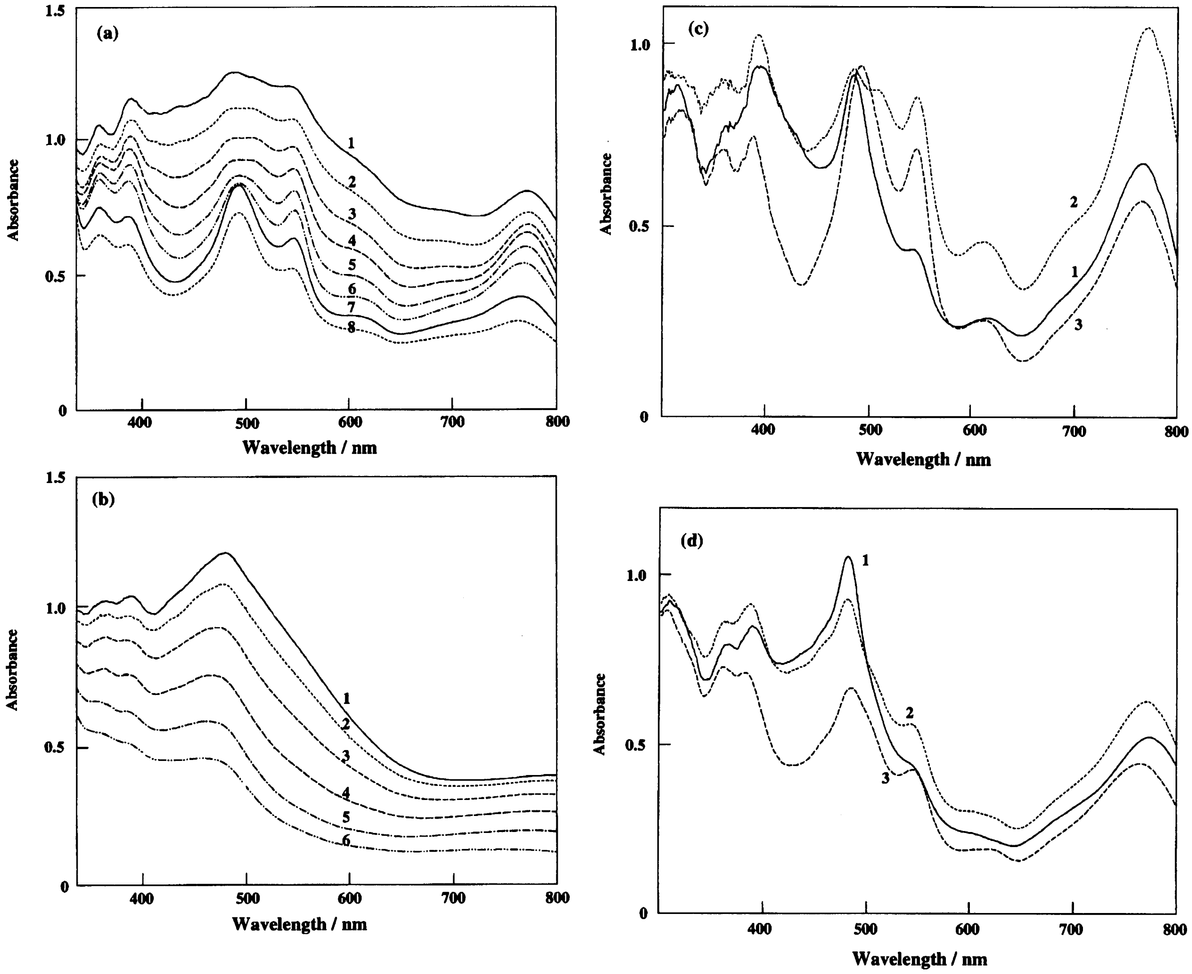


Fig. 5. Absorption spectral changes recorded immediately (1) after γ-radiolyses of (a) *t,c,t*-CB and (b) *t,t,t*-CB in degassed butyl chloride matrices at 77 K and after warming (in the order of 2, 3, 4, 5, 6, 7, and 8), or after γ-radiolyses and subsequent photoirradiation of (c) *t,c,t*-CB and (d) *t,t,t*-CB at wavelengths longer than 390 nm (1) and after warming (in the order of 2 and 3). Concentration of CB, 5×10^{-3} M.

The two absorption bands at around 370 and 500 nm are characteristics for an acyclic 1,4-bis(4-methoxyphenyl)butane-1,4-diyl radical cation.[12] The σ-type dimer radical cations of 1,1-diphenylethylene[2g] and α-methylstyrene[2d] show absorption maxima at 435 and 465 nm, respectively, in dichloromethane. Various bis(methoxyphenyl)methyl cations and radicals show absorption maxima at 440—500 and 330—350 nm, respectively, depending on the substituents on the methyl carbon,[14] while the methoxybenzyl cations and radicals show absorption maxima at 310—360 and 290—300 nm, respectively, depending on the substituents on the benzyl carbon.[15] These results are consistent with the absorption bands at around 330—400 and 500—600 nm with peaks at 370 and 550 nm for the σ-type St dimer radical cation, although an additional charge-resonance absorption band was detected at around 700—800 (peak at 770) nm in rigid matrices of butyl chloride at 77 K (Fig. 4).

Relatively large shifts of the absorption bands were observed between the π-type and the σ-type *t*-St dimer radical cations, and softening of the rigid matrix upon warming is necessary to form the σ-type *t*-St dimer radical cation. Therefore, an acyclic linear structure having both a radical and a cation on 1- and 4-positions of C_4 linkage is assumed to a stable structure of the σ-type St dimer radical cation. The interaction between the charge and the electron exists in the acyclic linear structure to show the charge-resonance band at 770 nm.

γ-Radiolyses of *c*-St at 77 K. γ-Radiolyses of the rigid matrix of butyl chloride containing *c*-St were also carried out at 77 K. However, the measured absorption spectrum was not assigned to the *c*-St radical cation, but to the *t*-St radical cation. It is considered that the photochemical isomerization of the *c*-St radical cation to the *t*-St radical cation occurs quantitatively upon irradiation of monitor light from the multichannel-photodetector, and, therefore, the *c*-St radical cation could not be detected even at 77 K by a multichannel photodetector. According to the results of pulse radiolyses of *c*-St and *t*-St as well as a γ-radiolysis of *t*-St in a butyl chloride matrix at 77 K, it is suggested that the *c*-St radical cation reacts with *c*-St to provide the *c*-St dimer radical cation, which is probably of the σ-type, similar to species B, and rapidly decomposes to the thermodynamically stable *t*-St radical cation and *t*-St.

γ-Radiolyses of *t,c,t*-CB at 77 K. CB can serve as a model compound for the St dimer radical cations, since the CB radical cation is expected to decompose into a π-type *t*-St dimer radical cation, a σ-type St dimer radical cation, or a *t*-St radical cation plus *t*-St. Absorption spectral measurements of the radical cation of *t,c,t*-CB were performed by a γ-radiolysis of the rigid matrix of glassy butyl chloride solutions of *t,c,t*-CB (5×10^{-3} M) at 77 K. A broad absorption spectrum of the *t,c,t*-CB radical cation was detected at 77 K at 360—800 nm with weak peaks at 370, 390, 485, 550, and 780 nm, which changed to have clear peaks at 370, 485, 550, and 780 nm upon warming (Fig. 5a). The photoirradiation of the *t,c,t*-CB radical cation at 77 K using a Xe lamp at wavelengths over 390 nm gave absorption bands at 400—470, 470—500, and 680—800 nm (Fig. 5c). Warming this sample caused a large increase of the peak at around 350, 550, and 780 nm. The difference spectrum was obtained by subtracting the spectra after photoirradiation and warming; it clearly indicated the collapse of the absorption bands at 400—470 and 470—500 nm and the formation of absorption peaks at 350, 550, and 780 nm (Fig. 6a), although the collapse of the 680—800 nm band was compensated by the formation of the 780 nm band.

Thus, four different transient radical cations can be distinguished in rigid matrices of butyl chloride at 77 K, as follows (Table 2):

1. *t,c,t*-CB radical cation showing a broad absorption band at 360—800 nm;
2. *t*-St radical cation showing an absorption band at 470—500 nm;
3. radical cation C formed from a photochemical reaction of the *t,c,t*-CB radical cation, showing absorption bands at 400—470 and 680—800 nm and a shorter lifetime than that of D; and
4. radical cation D formed from a thermal reaction of the *t,c,t*-CB radical cation or C, showing absorption peaks at 350, 550, and 780 nm with longer lifetimes than that of C.

Apparently, the collapse of C is related to the formation of D. On the basis of the absorption bands and the lifetimes, radical cations C and D are assigned to π- and σ-type *t*-St dimer radical cations, respectively. Radical cations C and D are essentially equivalent to A and B, respectively, whereas various overlapping of π-electrons between two benzene rings are involved in A compared with in C. Consequently, the *t,c,t*-CB radical cation converts to the σ-type St dimer radical cation upon warming (Eq. 8),

$$t,c,t\text{-CB}^{+\bullet} + \Delta E \rightarrow \sigma\text{-St}_2{}^{+\bullet} \qquad (8)$$

Photoirradiation of the *t,c,t*-CB radical cation at 77 K causes cycloreversion into the π-type *t*-St dimer radical cation (Eq. 9),

$$t,c,t\text{-CB}^{+\bullet} + h\nu \rightarrow \pi\text{-}(t\text{-St})_2{}^{+\bullet}, \qquad (9)$$

which converts to the σ-type St dimer radical cation upon warming (Eq. 7).

γ-Radiolyses of *t,t,t*-CB at 77 K. Absorption spectral measurements of radical cations of *t,t,t*-CB were also carried out by the γ-radiolysis of glassy butyl chloride solutions of *t,t,t*-CB (5×10^{-3} M) at 77 K. The broad absorption spectrum of the *t,t,t*-CB radical cation was measured at 77 K at 400—670 nm with a maximum at around 480 nm; it collapsed without any particular spectral change upon warming (Fig. 5b). However, the spectrum changed to have clear peaks at 485 and 780 nm upon photoirradiation at 77 K using a Xe lamp (Fig. 5d). The absorption spectrum then changed to have a clear peak at 550 nm upon warming. The difference spectrum, obtained by subtracting the spectra both before and after warming, clearly indi-

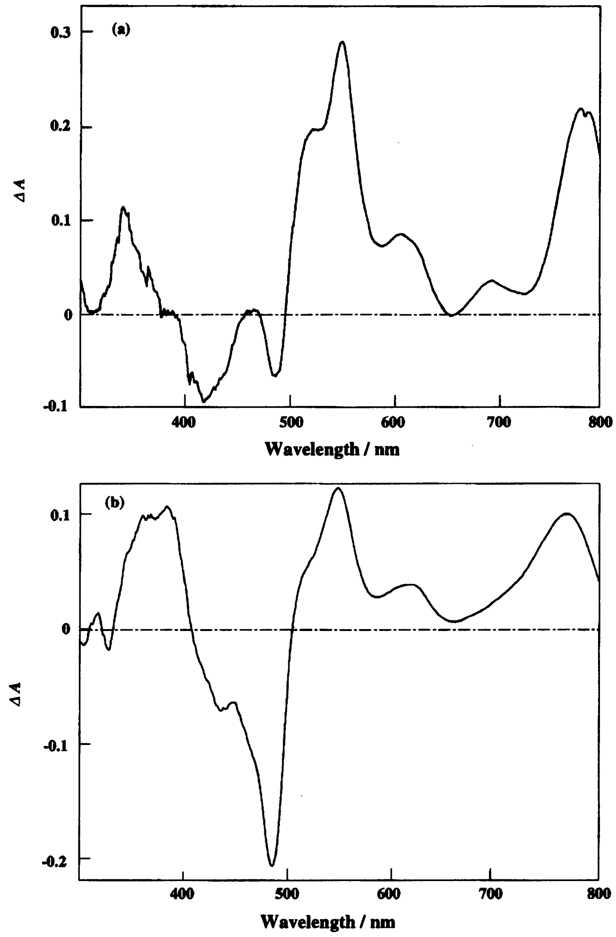
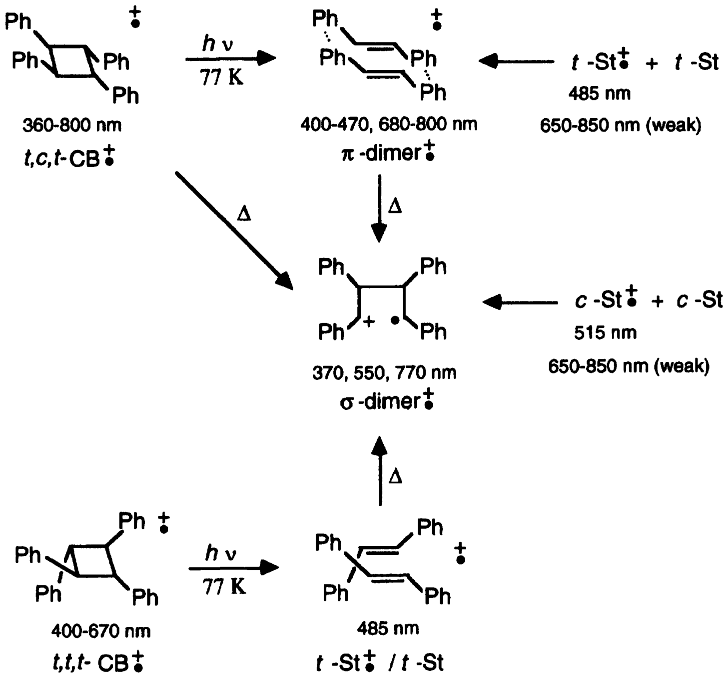


Fig. 6. Difference spectra between spectra after photoirradiation and after warming ($\Delta A = A_{\mathrm{No.\,1}} - A_{\mathrm{No.\,2}}$), obtained from Fig. 5c in γ-radiolysis of *t,c,t*-CB (a) and from Fig. 5d in γ-radiolysis of *t,t,t*-CB (b) in degassed butyl chloride matrices at 77 K.



Scheme 1. Reaction mechanism involving St radical cations and St dimer radical cations on the basis of pulse radiolyses at room temperature and γ-radiolyses at 77 K.

cates the collapse of the absorption peak at 485 nm and the formation of absorption bands at around 370, 550, and 770 nm (Fig. 6b). Thus, four different transient radical cations can be distinguished in rigid matrices of butyl chloride at 77 K as follows (Table 2):

1. the *t*,*t*,*t*-CB radical cation showing a broad absorption band at 400—670 nm;
2. the *t*-St radical cation showing an absorption band at 485 nm;
3. species E formed from photochemical reaction of the *t*,*t*,*t*-CB radical cation, showing an absorption band at 480 nm and a shorter lifetime than that of F; and
4. radical cation F formed from a thermal reaction of E, showing absorption peaks at 370, 550, and 770 nm with longer lifetime than that of E.

Apparently, the collapse of E is related to the formation of F. On the basis of the absorption bands and lifetimes, species E and F are assigned to a *t*-St radical cation/*t*-St pair and the σ-type *t*-St dimer radical cation, respectively. Radical cation F is essentially equivalent to B and D.

Therefore, the *t*,*t*,*t*-CB radical cation is rather stable at 77 K, and does not convert thermally to a π-type nor a σ-type St dimer radical cation. Photoirradiation of the *t*,*t*,*t*-CB radical cation at 77 K causes cycloreversion into the *t*-St radical cation/*t*-St pair (Eq. 10), which converts to the σ-type St dimer radical cation upon warming (Eq. 11):

$$t,t,t\text{-CB}^{+\bullet} + h\nu \rightarrow t\text{-St}^{+\bullet}/t\text{-St}, \qquad (10)$$

$$t\text{-St}^{+\bullet}/t\text{-St} + \Delta E \rightarrow \sigma\text{-St}_2{}^{+\bullet}. \qquad (11)$$

On account of no overlapping of π-electrons between two benzene rings in the *t*-St radical cation/*t*-St pair, it is anticipated that the pair has the same absorption as does the *t*-St monomer radical cation.

Assignments of St Dimer Radical Cations. The π- and σ-type St dimer radical cations have been found by absorption measurements in rigid matrices of butyl chloride at 77 K. Radical cations A and C are assigned to π-type *t*-St dimer radical cations with overlapping arrangements of the π-electrons between two benzene rings, while radical cations B, D, and F are to the σ-type St dimer radical cation. Species E is assigned to the *t*-St radical cation/*t*-St pair showing the same absorption band as that of the *t*-St monomer radical cation, due to no overlapping of π-electrons between two benzene rings in the *t*-St radical cation/*t*-St pair in rigid matrices at 77 K. It is suggested that the π-type *t*-St dimer radical cations take various overlapping arrangements in rigid matrices of butyl chloride at 77 K and exhibit a large charge resonance band at shorter wavelengths of 680—800 nm than those of other dimer radical cations reported.[12)] On the basis of the experimental results and spectral data reported, it is suggested that the σ-type St dimer radical cation has an acyclic linear structure having both a radical and a cation on the 1- and 4-positions of the C_4 linkage, as discussed above. Although the *c*-St dimer radical cation was not detected, the bimolecular reaction of the *c*-St radical cations and *c*-St gives a σ-type St dimer radical cation (Eq. 5), being the same as those (B,D, and F) generated from cycloreversion of CB radical cations (Eqs. 7, 8, 9, 10, and 11) or association of the *t*-St radical cations and *t*-St (Eqs. 3 and 7), and which decomposes rapidly into thermodynamically stable *t*-St radical cation and *t*-St at room temperature (Scheme 1).

Conclusions

It is concluded that not only the St monomer radical cation, but also π- and σ-type St dimer radical cations, are formed as key intermediates in radiolyses of *c*-St, *t*-St, *t,c,t*-CB, and *t,t,t*-CB in DCE at room temperature and glassy butyl chloride at 77 K. Fast isomerization of the *c*-St radical cation to the *t*-St radical cation proceeds through a σ-type St dimer radical cation. On the basis of a spectroscopic measurements of the π- and σ-type St dimer radical cations, it is suggested that the π-type *t*-St dimer radical cation has overlapping arrangements of π-electrons between two benzene rings, while the σ-type St dimer radical cation has a linear structure having both radical and cation on 1- and 4-positions of C_4 linkage.

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