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Mechanism for Isomerization of *cis*-Stilbene via Its Radical Cation as Investigated by Pulse Radiolysis. A Possible Role of a Dimeric Radical Cation as an Intermediate

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Synopsis. Pulse radiolysis of *cis*-stilbene was carried out and transient absorption spectra were measured in varying concentrations in dichloromethane under air at room temperature. Concentration dependence of the spectral change indicates that *cis*-stilbene radical cations isomerize to *trans*-stilbene radical cations through interaction with a neutral *cis*-stilbene molecule, probably by way of a σ-type dimeric radical cation.

Recently, it has been well recognized that irradiation of electron-accepting sensitizers like 9,10-dicyanoanthracene (DCA)$^{1,2)}$ and 2,4,6-triphenylpyrylium tetrafluoroborate ($TPP^+BF_4{}^-$)$^{3)}$ in polar solvents such as acetonitrile induces isomerization of *cis*-stilbene (CS) to *trans*-stilbene (TS) by way of a radical cation. The isomerization from *cis*-stilbene radical cation ($CS^{+\bullet}$) to *trans*-stilbene radical cation ($TS^{+\bullet}$) can take place either in a unimolecular way or in a bimolecular way through addition of $CS^{+\bullet}$ to CS giving a dimeric radical cation followed by elimination of $TS^{+\bullet}$. Actually, we directly observed a change of the transient absorption spectrum due to isomerization of the cis radical cations to the trans radical cations for 4,4′-dibromostilbene and 4,4′-dimethylstilbene in acetonitrile.$^{4)}$ Also, we observed the conversion of $CS^{+\bullet}$ to $TS^{+\bullet}$ in acetonitrile in the presence of salts such as lithium perchlorate and magnesium perchlorate,$^{5)}$ and $TPP^+BF_4{}^-$ induced the conversion of $CS^{+\bullet}$ to $TS^{+\bullet}$ in SDS micelles.$^{6)}$ Lewis et al. proposed participation of dimeric radical cations in the CS→TS isomerization in a high concentration of CS based on their results of stationary light irradiation with DCA as a sensitizer.$^{7)}$ The stability and the role of 1,4-radical cations were discussed by Takamuku et al. in cyclodimerization and cycloreversion of methoxystyrenes.$^{8)}$

The above situation has prompted us to investigate the role of the dimeric species particularly in high CS concentrations by means of pulse radiolysis. We have obtained clear evidence that $CS^{+\bullet}$ surely interacts with CS to afford $TS^{+\bullet}$.

Experimental

Materials. *cis*-Stilbene was purified by column chromatography on silica gel with hexane as an eluent and *trans*-stilbene was recrystallized from ethanol. Dichloromethane (Merck, Uvasol) was used as received.

Pulse Radiolysis. Pulse radiolysis measurements were carried out with an electron linac$^{9)}$ at the University of Tokyo. Solutions of *cis*- and *trans*-stilbene in dichloromethane were irradiated with a 28-MeV electron beam (pulse width, 2 ns) under air at room temperature, and time-dependent absorption spectra were recorded. The details of the pulse radiolysis system were reported elsewhere.$^{10)}$ A germanium photodiode detection system was used for measurements of a charge resonance (CR) band in the near-infrared region; the details of the system will be published in a due course.$^{11)}$

Results and Discussion

Pulse radiolysis of *cis*-stilbene (CS) in varying concentrations (10^{-3}—10^{-1} M, M=mol dm^{-3}) was carried out in aerated dichloromethane. Figure 1 depicts the transient absorption spectra observed at 5 and 155 ns after the pulse. Every absorption spectrum measured at 5 ns after the pulse exhibits an absorption maximum (λ_{max}) at 510 nm and this is safely assigned to $CS^{+\bullet}$.$^{12)}$ At 155 ns after the pulse, a new absorption band with a λ_{max} at 490 nm appears in addition to the absorption of $CS^{+\bullet}$ except in the most dilute solution ($[CS]=1\times10^{-3}$ M). This new band is reasonably assigned to *trans*-stilbene radical cation ($TS^{+\bullet}$).$^{12)}$ With increasing CS concentration the absorption band due to $TS^{+\bullet}$ at 155 ns becomes more intense than that due to $CS^{+\bullet}$.

On the other hand, pulse radiolysis of TS in a high concentration of 0.05 M afforded an absorption band with a λ_{max} at 490 nm attributable to $TS^{+\bullet}$ at 5 ns after the pulse; however, the λ_{max} was shifted to shorter wavelength of 480 nm at 155 ns after the pulse (Fig. 1f).

The time profiles of absorption observed at 520 nm on pulse radiolysis of CS in varying concentrations are illustrated in Fig. 2; the higher the CS concentration, the faster the decay of $CS^{+\bullet}$. The decay curves fit two components of the first- and second-order kinetics in comparable magnitudes.$^{13)}$ The second-order decay is certainly due to recombination of $CS^{+\bullet}$ with radical anions produced from the solvent or $O_2{}^{-\bullet}$.

The first-order decay rate constant (k_{obsd}) increases almost linearly with CS concentration as depicted in Fig. 3. This figure indicates that $CS^{+\bullet}$ interacts with CS with a rate constant (k_{cc}) of 3.5×10^8 M^{-1} s^{-1} as estimated from the slope of the plot. Likewise, on pulse radiolysis of TS in varying concentrations, the decay rate of the absorption of $TS^{+\bullet}$ at 490 nm increased with

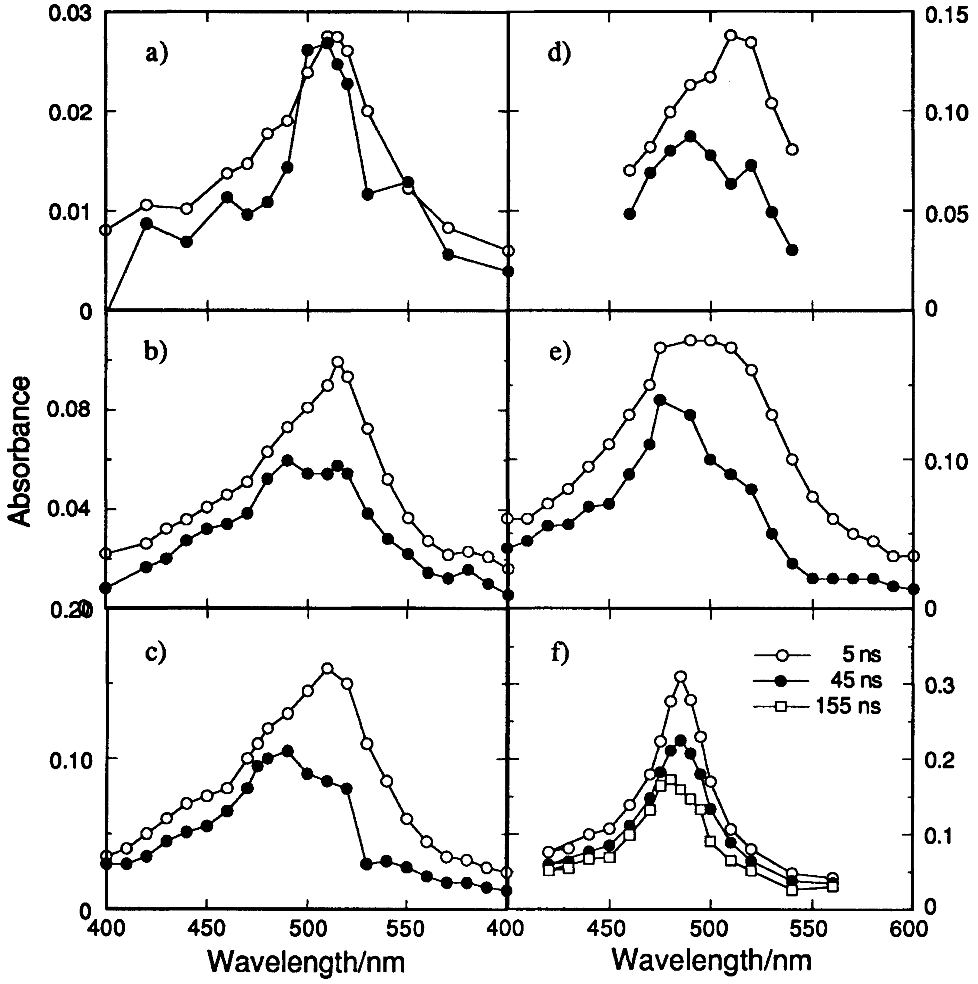

Fig. 1. Transient absorption spectra observed at 5 (○) and 155 ns (●) after pulse radiolysis of CS in varying concentrations in aerated CH_2Cl_2; a) [CS]=1 mM, b) [CS]=10 mM, c) [CS]=30 mM, d) [CS]=50 mM, e) [CS]=100 mM, f) [TS]=50 mM.

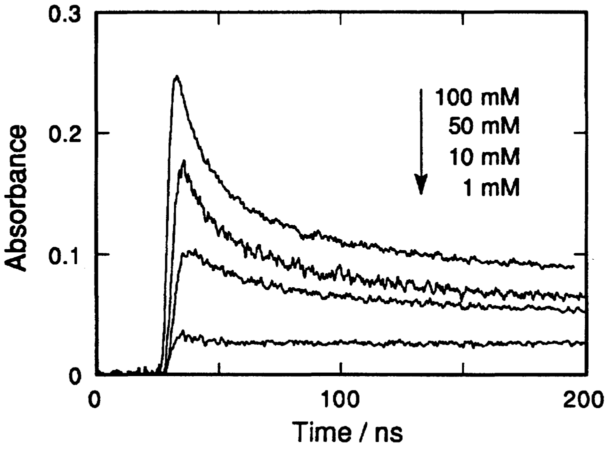

Fig. 2. Time profiles of $CS^{+\bullet}$ monitored at 520 nm on pulse radiolysis of CS in varying concentrations in CH_2Cl_2.

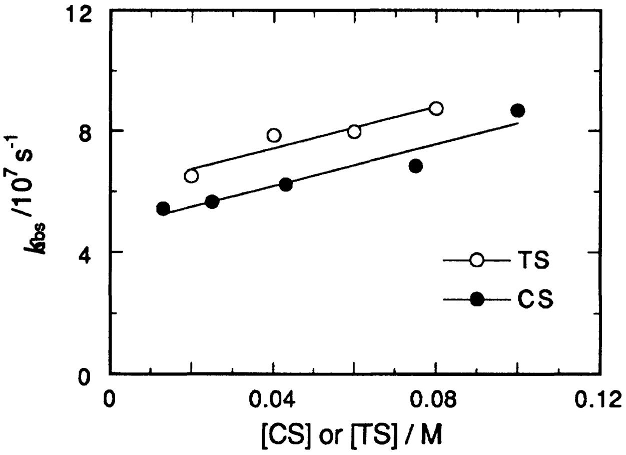

Fig. 3. Plots of first-order decay rate constants of stilbene radical cations against stilbene concentration.

TS concentration, and the results were analyzed in a similar manner. The obtained first-order rate constants are plotted against [TS] in Fig. 3 to give a rate constant (k_{tt}) of 3.4×10^8 M^{-1} s^{-1} for the interaction between $TS^{+\bullet}$ and TS.

$$CS^{+\bullet} + CS \xrightarrow{k_{cc}} {}^{+}CS\ CS^{\bullet}$$
$$TS^{+\bullet} + TS \xrightarrow{k_{tt}} {}^{+}TS\ TS^{\bullet}$$

The above rate constants, k_{cc} and k_{tt}, are essentially identical with 3.9×10^{8} $M^{-1}\,s^{-1}$ for both k_{cc} and k_{tt} recently measured by Takamuku's group.[14] The present rate constants are much higher than those estimated by Lewis et al. by indirect procedures, 8×10^{6} $M^{-1}\,s^{-1}$ and 3×10^{6} $M^{-1}\,s^{-1}$ for k_{cc} and k_{tt} in acetonitrile, respectively.[7] Also, the present k_{tt} value is higher than the value of 2×10^{7} $M^{-1}\,s^{-1}$ obtained from 408-nm laser excitation of $TPP^{+}BF_4^{-}$ in the presence of TS in varying concentrations in dichloromethane.[15]

The present results indicate that the stilbene radical cation, irrespective of $CS^{+\bullet}$ or $TS^{+\bullet}$, interacts with a stilbene molcule to give probably a dimeric radical cation species. Particularly, the dimeric species arising from $CS^{+\bullet}$ and CS undergoes configurational change to the thermodynamically stabler trans geometry to afford $TS^{+\bullet}$, therefore accomplishing the isomerization.[16] On the other hand, the dimeric species from $TS^{+\bullet}$ and TS is configurationally stable and in equilibrium with $TS^{+\bullet}$, exhibiting an absorption with the λ_{max} at 480 nm instead of 490 nm for $TS^{+\bullet}$

The proportions of $TS^{+\bullet}$ to the total concentration of radical cations ($[TS^{+\bullet}]/([CS^{+\bullet}]+[TS^{+\bullet}])$) resulting from the pulse radiolysis were calculated from the transient spectra using the molar extinction coefficients (ε) of $CS^{+\bullet}$ and $TS^{+\bullet}$,[7] 15000 and 3500 $cm^{-1}\,M^{-1}$ at 520 nm, and 9900 and 58000 $cm^{-1}\,M^{-1}$ at 470 nm, respectively. Figure 4 depicts the time profiles of $[TS^{+\bullet}]/([CS^{+\bullet}]+[TS^{+\bullet}])$ in CS concentrations of 0.075 and 0.1 M. As Fig. 4 shows, $CS^{+\bullet}$ is quickly converted to $TS^{+\bullet}$ with 100—200 ns, and the rate increases with increasing CS concentration to give finally $TS^{+\bullet}$ in 10—15% of the total stilbene radical cations. The above time constant corresponds to the reciprocal of the pseudo-first-order rate constant obtained from k_{cc} multiplied by [CS]. It means that $CS^{+\bullet}$ interacts with CS to give a dimeric radical cation, which must be too short-lived to be actually detected, however.

In order to get insight into the structure of the dimeric species, we measured the near-infrared absorption on pulse radiolysis of TS and CS, since the dimeric radical cations of polycyclic aromatic hydrocarbon moieties exhibit a charge resonance (CR) band in the near-infrared region.[17] The observed absorption spectra are shown in Fig. 5. $TS^{+\bullet}$ exhibits an absorption hand in the longer wavelengh region than 1200 nm; however, its intensity is extremely low compared to the absorption around 490 nm and the decay rate increases with increasing TS concentration in a similar way to that of the shorter-wavelength band due to the monomeric radical cations. This is in contrast to the features of CR bands of polycyclic aromatics in which the CR band intensity is comparable with, or several tenths of those of the shorter wavelength bands.[17] These observations indicate that the longer-wavelength band is due to monomeric $TS^{+\bullet}$ or some π-type dimeric radical cations having an overlapping arrangement. The slight shift of the λ_{max} from 490 nm for monomeric $TS^{+\bullet}$ to 480 nm in the present radiolysis as well as the similar shift observed in TPP^{+} photosensitization might be attributed to the π-type structure of the dimeric species form TS.

On the contrary, CS showed no absorption band at the near-infrared region. The conversion of $CS^{+\bullet}$ to $TS^{+\bullet}$ within 100—200 ns and the failure of observation of any absoption attributable to a dimeric species suggest that interaction of $CS^{+\bullet}$ with CS give a σ-type species,[8] which rapidly undergoes internal rotation and subsequent elimination of $TS^{+\bullet}$ and $CS^{+\bullet}$ in a ratio of 10 : 90—15 : 85 (Chart 1).

Conclusions

On pulse radiolysis of CS and TS in aerated dichlo-

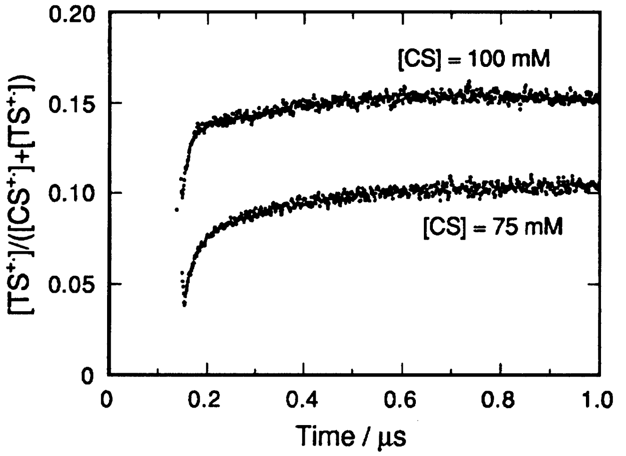

Fig. 4. Time profile of $TS^{+\bullet}$ proportion to the total radical cation concentration ($[TS^{+\bullet}]/([CS^{+\bullet}]+[TS^{+\bullet}])$) on pulse radiolysis of CS in CH_2Cl_2.

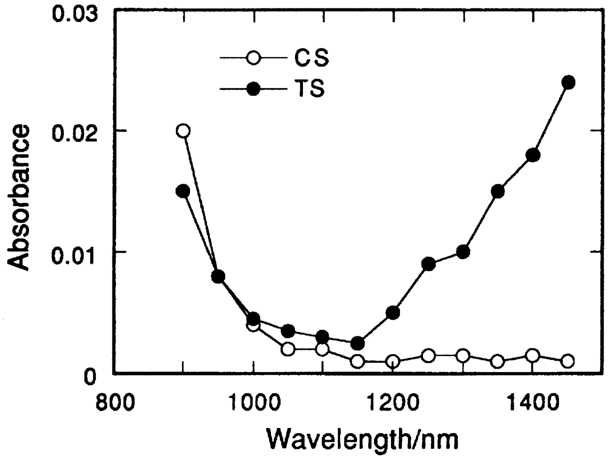

Fig. 5. Transient absorption spectra in the near-infrared region observed at 5 ns after pulse radiolysis of CS (0.2 M) and TS (0.3 M) in CH_2Cl_2.

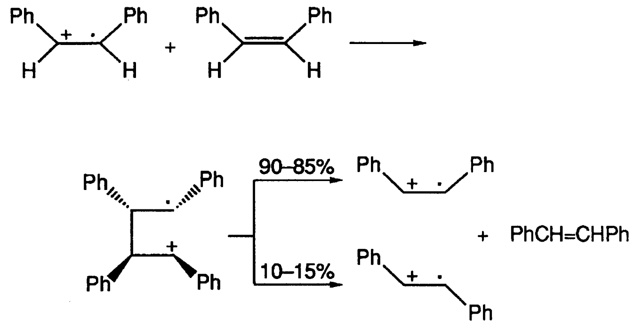

Chart 1.

romethane at ambient temperature, the resulting CS$^{+\bullet}$ (λ_{max}=520 nm) interacts with CS with a rate constant of 3.5×10^{8} $M^{-1}\,s^{-1}$, and TS$^{+\bullet}$ (λ_{max}=490 nm) interacts with TS with a rate constant of 3.4×10^{8} $M^{-1}\,s^{-1}$ shifting its λ_{max} to 480 nm within 150 ns. CS$^{+\bullet}$ isomerizes to TS$^{+\bullet}$ within 100—200 ns; the isomerization is proposed to proceed through addition of CS$^{+\bullet}$ to CS giving a short-lived dimeric radical cation species, which finally affords TS$^{+\bullet}$ and CS$^{+\bullet}$ in a ratio of 10 : 90—15 : 85. On the other hand, TS$^{+\bullet}$ gives a dimeric species (λ_{max}=480 nm) which does not participate in isomerization. Therefore, it is sure that in high CS concentrations, CS$^{+\bullet}$ undergoes isomerization to TS$^{+\bullet}$ through the interaction with CS.

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