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Effects of Salt on Isomerization of Stilbene Cation Radicals. Direct Observation of their Cis→Trans Conversion[#]

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Unimolecular cis→trans conversion of stilbene cation radicals generated from 9,10-dicyanoanthracene-biphenyl co-sensitization under air was directly observed in the presence of salt such as $LiClO_4$ in acetonitrile, and the activation parameters of this process were determined by means of transient spectroscopy. It is proposed that the salt reduces the rate of charge recombination between the olefin cation radical and the resulting superoxide anion by complexing with the latter anion.

The efficiency of unimolecular cis→trans conversion of cation radicals of stilbene derivatives depends upon the substituents on the phenyl rings, and the cation radicals of *cis*-4,4'-dibromo-, *cis*-4,4'-dimethyl-, and *cis*-4,4'-dimethoxystilbene were, when generated by secondary electron transfer, converted unimolecularly to those of the corresponding *trans*-stilbenes in high quantum yields at ambient temperature.[1] However, the cation radicals of stilbene itself have been reported not to undergo cis→trans conversion in the 100 μs range.[2] Herein, we wish to report the effects of salt which reduce the rate of charge recombination to make it possible to determine the rate for unimolecular cis→trans conversion of stilbene cation radicals by transient spectroscopy.[3]

On pulsed laser excitation at 406 nm under double sensitization conditions with 9,10-dicyanoanthracene (DCA, 5×10^{-5} mol dm^{-3}) and biphenyl (BP, 0.1 mol dm^{-3}) as a primary electron donor in acetonitrile at 23 °C under air,[1] *cis*-stilbene exhibited transient absorption spectra shown in Fig. 1a. This technique prevents the back electron transfer to the olefin cation radical from $DCA^{-\cdot}$ since $DCA^{-\cdot}$ and $BP^{+\cdot}$ generated from the primary electron transfer between the excited DCA and BP react with oxygen and the olefin, respectively, to afford DCA ($+O_2^{-\cdot}$)[4] and the olefin cation radical. The spectra (λ_{max}=505 nm) in Fig. 1a are due to *cis*-stilbene cation radicals (c-$St^{+\cdot}$) with the original configuration, and no clear spectral changes indicating cis→trans conversion of the cation radicals were observed in the time scale of the experiment (100 μs), as already reported.[1,2] The cation radicals decayed with second-order kinetics through recombination with $O_2^{-\cdot}$.

Figure 1b depicts transient absorption spectra observed on similar laser excitation of *cis*-stilbene in the presence of $LiClO_4$ (3×10^{-3} mol dm^{-3}), showing that the decrease in c-$St^{+\cdot}$ absorption intensity is accompanied by appearance of the absorption due to *trans*-stilbene cation radicals (t-$St^{+\cdot}$, λ_{max}=475 nm) at 6.3 μs after laser excitation (cf. Fig. 2a). In the presence of the salt, the decay kinetics of the absorption monitored at 510 nm is comprised of two first-order components due to c-$St^{+\cdot}$ disappearance ($k_1=3.5\times10^5$ s^{-1}) and probably due to

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[#] Dedicated to Professor Emeritus Osamu Simamura, The University of Tokyo, for the occasion of his 80th birthday.

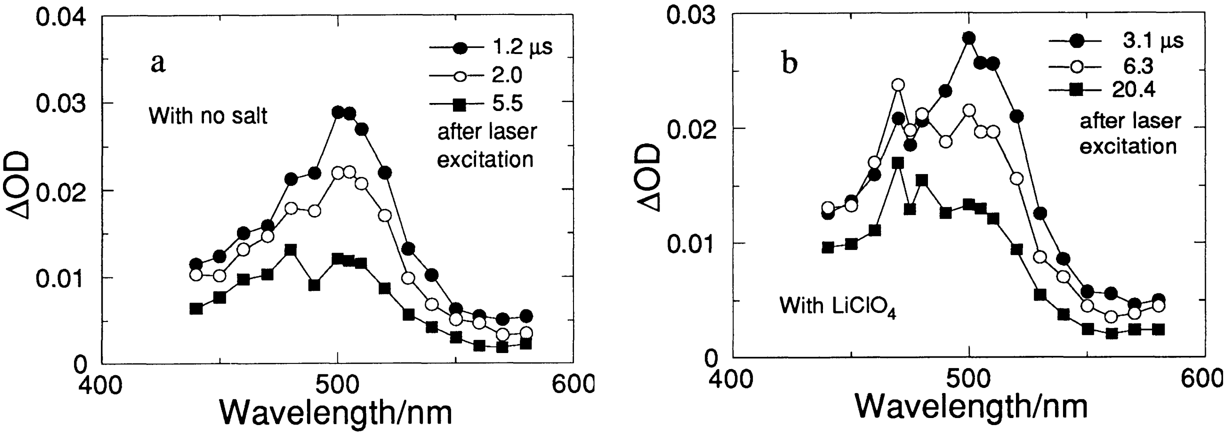

Fig. 1. Transient absorption spectra observed on 406-nm laser excitation of DCA with BP and *c*-St in the absence (a) and presence of $LiClO_4$ (b) in acetonitrile.

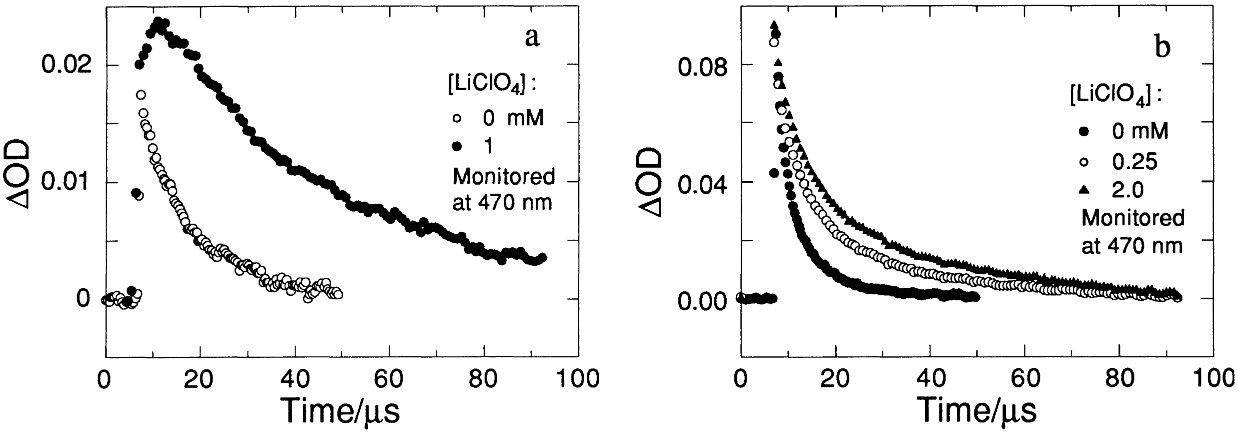

Fig. 2. Time profiles of *c*-St (a) and *t*-St cation radicals (b) in the absence and presence of $LiClO_4$ (M=mol dm^{-3})

(apparently first-order) recombination of the resulting $t\text{-St}^{+\cdot}$ with $O_2^{-\cdot}$ which might be in equilibrium with $Li^+O_2^{-\cdot}$ ($k_1'=2.5\times10^4$ s^{-1}).5-9) The rise of $t\text{-St}^{+\cdot}$ absorption gave $k_1=3.1\times10^5$ s^{-1}, and the resulting $t\text{-St}^{+\cdot}$ decayed with an apparent first-order rate constant, $k_1'=2.7\times10^4$ s^{-1}, as monitored at 470 nm. The decay component of $c\text{-St}^{+\cdot}$ might consist of unimolecular $c\text{-St}^{+\cdot}\rightarrow t\text{-St}^{+\cdot}$ conversion and charge recombination of $c\text{-St}^{+\cdot}$ with $O_2^{-\cdot}$. The superoxide anion appears to form a stable complex, $Li^+O_2^{-\cdot}$,10) preventing a rapid reverse electron transfer to the stilbene cation radicals, and thus the cis→trans conversion can be detected. An interaction of the cation radicals with perchlorate anion is assumed not to be important since the spectra of the cation radicals are not affected by addition of the salt. Similar salt effects were observed in use of $NaClO_4$, Et_4NClO_4, and $Mg(ClO_4)_2$.11)

The reduced contribution of the second-order component in decay kinetics was clearly demonstrated by change in the time profile of $t\text{-St}^{+\cdot}$ generated from *t*-St in the presence of the salt. Figure 2b depicts the decay profiles of $t\text{-St}^{+\cdot}$ monitored around the peak wavelength (470 nm) in the presence of varying concentrations of $LiClO_4$. In the absence of the salt the decay fits to second-order kinetics; however, in its presence the decay is single-exponential and the first-order rate constant decreases linearly with increasing salt concentration. Under argon atmosphere the salt also affected the decay profile of $t\text{-St}^{+\cdot}$; the second-order decay profile in the absence of salt was changed to the first-order decay by addition of the salt, but it is to a lower extent than that under air at a given concentration of salt. In the absence of oxygen metallic ions might interact with DCA anion radicals.[8)]

We propose a mechanism for the present salt-affected isomerization of *cis*-stilbene as shown in Scheme 1. In Scheme 1 the doubly sensitized electron transfer with DCA and BP from *c*-St affords $DCA^{-\cdot}$ and $c\text{-}St^{+\cdot}$ (processes 1 and 2). Under air $DCA^{-\cdot}$ transfers an electron to molecular oxygen to generate $O_2^{-\cdot}$, which is in equilibrium with $M^+O_2^{-\cdot}$ in the presence of salt, M^+X^- (processes 3 and 4). $c\text{-}St^{+\cdot}$ disappears through the reverse electron transfer with $O_2^{-\cdot}$ (process 6) or is converted to $t\text{-}St^{+\cdot}$ (process 5), which also disappears through reverse electron transfer with $O_2^{-\cdot}$ (process 7). For the bimolecular disappearance processes 6 and 7 of stilbene cation radicals, the usual second-order kinetics cannot hold because of involvement of process 4.

$$^1DCA^* + BP \rightarrow DCA^{-\cdot} + BP^{+\cdot} \qquad (1)$$
$$BP^{+\cdot} + c\text{-}St \rightarrow BP + c\text{-}St^{+\cdot} \qquad (2)$$
$$DCA^{-\cdot} + O_2 \rightarrow DCA + O_2^{-\cdot} \qquad (3)$$
$$O_2^{-\cdot} + M^+ \rightleftarrows M^+O_2^{-\cdot} \qquad (4)$$
$$c\text{-}St^{+\cdot} \rightarrow t\text{-}St^{+\cdot} \qquad (5)$$
$$c\text{-}St^{+\cdot} + O_2^{-\cdot} \rightarrow c\text{-}St + O_2 \qquad (6)$$
$$t\text{-}St^{+\cdot} + O_2^{-\cdot} \rightarrow t\text{-}St + O_2 \qquad (7)$$

Scheme 1.

trans-4,4'-Dibromostilbene (*t*-BrSt) cation radicals generated similarly under air disappeared according to the second-order kinetics in the absence of salt, but decayed single-exponentially in the presence of $LiClO_4$ (1×10^{-3} mol dm^{-3}). Previously, we directly observed unimolecular cis→trans conversion of $BrSt^{+\cdot}$ under the double sensitization conditions, and determined the activation parameters for this process.[1)] The 540-nm band of $c\text{-}BrSt^{+\cdot}$ decayed with bicomponent kinetics of the first ($k_{c\rightarrow t}=3\times10^5$ s^{-1} for cis→trans conversion) and second-order ($k_2/\varepsilon\approx10^8$ cm s^{-1} for reverse electron transfer), and was accompanied by a rise of 520-nm band of $t\text{-}BrSt^{+\cdot}$, which decayed with second-order kinetics ($k_2/\varepsilon\approx2\times10^6$ cm s^{-1}). Behavior of the transient absorptions in the presence of salt ($[LiClO_4]=1\times10^{-3}$ mol dm^{-3}) was very similar to that of stilbene; $c\text{-}BrSt^{+\cdot}$ from *c*-BrSt decayed with bicomponent first-order kinetics ($k_1=3\times10^5$ s^{-1} and $k_1'= 4\times10^4$ s^{-1}), and $t\text{-}BrSt^{+\cdot}$ from *t*-BrSt with one component first-order kinetics ($k_1'= 3\times10^4$ s^{-1}). The first-order decay rate constant of $t\text{-}BrSt^{+\cdot}$ decreases linearly with increasing salt concentration under air, and under argon atmosphere its decay (6.6×10^4 s^{-1}) was faster than under air (2.9×10^4 s^{-1}).

The rate constants and activation parameters for the cis→trans conversion of $St^{+\cdot}$ and $BrSt^{+\cdot}$ were determined from the decay profiles of cis cation radicals in the temperature range of 4.6–68.4 °C by assuming that the cis and trans cation radicals undergo charge recombination with $O_2^{-\cdot}$ with the same rate constant ($k_1=k_{c\rightarrow t}+k_1'$). The results are summarized in Table 1. This table also summarizes the data similarly obtained for 4,4'-dimethylstilbene (MeSt). In Table 1 the activation energies for cis→trans conversion in the presence of the salt are very similar among the cis cation radicals employed, but seem to decrease in the order of $c\text{-}St^{+\cdot} > c\text{-}BrSt^{+\cdot} > c\text{-}MeSt^{+\cdot}$. Also, the salt seems not to affect so much the rate of cis→trans conversion, as observed, for example, in $c\text{-}MeSt^{+\cdot}$ ($E_a=3.3\pm0.5$ kcal mol^{-1}, $\log (A/\text{s}^{-1})=9\pm2$ in the absence of salt).

The salt effects in electron transfer reactions have been reported on quantum yield, reaction rate, selectivity, intermediate lifetime, etc. In the present case, the lifetime of intermediate cation radicals is lengthened by inhibition of reverse electron transfer, and as a result, their cis→trans conversion can be directly detected by the spectroscopic techniques.

Table 1. Kinetic parameters of cis→trans conversion[a)]

Cation radical	$k_{c\to t}/s^{-1}$ b)	E_a/kcal mol^{-1}	log (A/s^{-1})
c-St$^{+\cdot}$	3.0×10^5	4.3±0.8	8.7±0.6
c-BrSt$^{+\cdot}$	2.6×10^5	4.2±0.7	8.6±0.5
c-MeSt$^{+\cdot}$	3.1×10^5	3.4±0.6	8.4±0.4

a) In the presence of $LiClO_4$ in 1×10^{-3} mol dm^{-3}. b) At 19 °C.

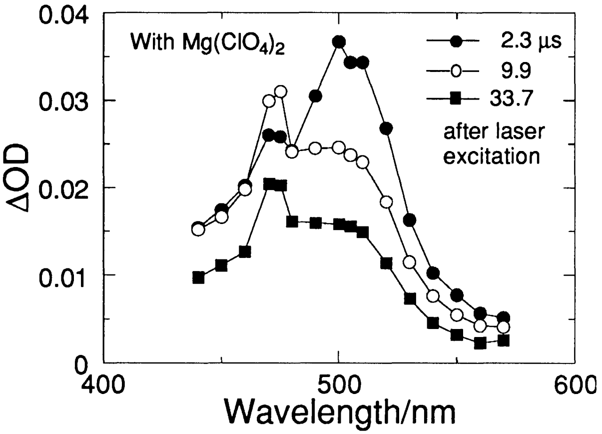

Fig. 3. Transient absorption spectra observed on 406-nm laser excitation of DCA with BP and c-St in the presence of $Mg(ClO_4)_2$ in acetonitrile.

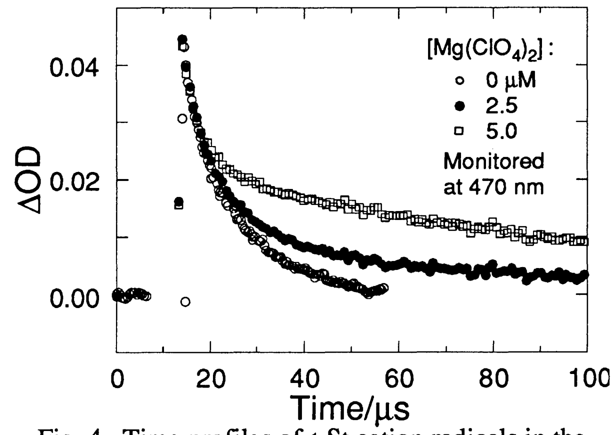

Fig. 4. Time profiles of t-St cation radicals in the absence and presence of $Mg(ClO_4)_2$.

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11) Transient absorption spectra observed on similar laser excitation of *cis*-stilbene in the presence of $Mg(ClO_4)_2$ (5×10^{-3} mol dm^{-3}) and time profiles of *trans*-stilbene cation radicals in the presence of $Mg(ClO_4)_2$ are depicted in Figs. 3 and 4, respectively.

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