CHEMISTRY LETTERS, pp. 1371-1374, 1994.

Isomerization Behavior of Halostilbene Radical Cations in the Excited States.
Two-Color Photochemistry of Stilbene Derivatives

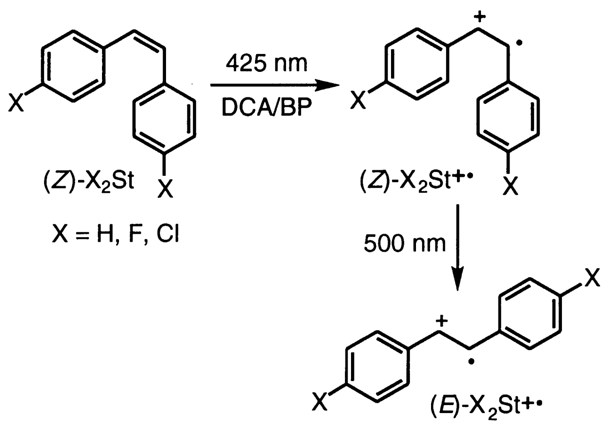
Yasunao KURIYAMA,* Fumiko HASHIMOTO, Masahiro TSUCHIYA,
Hirochika SAKURAGI,* and Katsumi TOKUMARU*
Department of Chemistry, University of Tsukuba, Tsukuba 305

Two-color laser excitation of (*Z*)-4,4'-dichlorostilbene and (*Z*)-4,4'-difluorostilbene with 425- and 500-nm laser pulses in acetonitrile containing 9,10-dicyanoanthracene and biphenyl exhibited a spectral change indicating a rapid conversion of the *Z*-radical cations in the excited state to the corresponding *E*-radical cations in a one-way fashion. The efficiencies of isomerization were determined and the isomerization energy surfaces were discussed.

Isomerization of olefin radical cations has attracted current interest.$^{1-4)}$ (*Z*)-Stilbene isomerizes through radical cations under steady irradiation in the presence of electron-accepting sensitizers; however, direct observation of the isomerization by transient spectroscopy is achieved only in the presence of salts which retard back electron transfer to the radical cations.$^{3b)}$ Isomerization of stilbene radical cations in the excited state has been reported to proceed in a *Z*→*E* one-way fashion,$^{5)}$ and the potential energy surfaces for isomerization have been discussed on the basis of MO calculations.$^{5c,6)}$ In order to determine experimentally the energy surfaces for isomerization in the excited state we employed two-color laser excitation$^{7)}$ of stilbene derivatives in double-sensitized electron transfer systems.$^{3)}$

9,10-Dicyanoanthracene (DCA, 5×10^{-5} mol dm^{-3}) was excited with 425-nm laser$^{8)}$ in the presence of biphenyl (BP, 0.1 mol dm^{-3}) as a primary electron donor$^{9)}$ and a *Z*- or *E*-isomer of olefins (1×10^{-3} mol dm^{-3}) in acetonitrile at 23 °C under air. As reported for (*Z*)-stilbene ((*Z*)-St) and (*E*)-stilbene ((*E*)-St),$^{1b,3a)}$ (*Z*)-4,4'-dichlorostilbene ((*Z*)-Cl_2St) and (*E*)-4,4'-dichlorostilbene ((*E*)-Cl_2St) gave the transient absorption spectra (Fig. 1; λ_{max} 530 and 505 nm for the *Z*- and *E*-isomers, respectively) due to the corresponding radical cations with a configuration of the starting isomer, and no clear spectral changes indicating *Z*→*E* conversion of the radical cations were observed in the time range of the experiment (100 μs), during which the spectra decayed with second-order kinetics through a probable recombination with $O_2^{-\cdot}$. (*Z*)-4,4'-difluorostilbene ((*Z*)-F_2St) and (*E*)-4,4'-difluorostilbene ((*E*)-F_2St) exhibited similar behavior under the similar conditions (λ_{max} 510 and 480 nm for the *Z*- and *E*-isomers, respectively). Thus, the spectroscopic behavior of these halostilbenes is very similar to that of stilbene itself, but contrasted with that of 4,4'-dibromostilbene (Br_2St); the Z-isomer radical cations of the latter isomerize in the range of microseconds.$^{3a)}$

In spite of this behavior, steady irradiation of acetonitrile solutions of the *Z*-isomers of the halostilbenes in the presence of DCA and BP afforded the corresponding *E*-isomers. The quantum yields for *Z*→*E* isomerization through radical cations were determined at ambient temperature with 366-nm light to be 0.09 for F_2St and



Scheme 1.

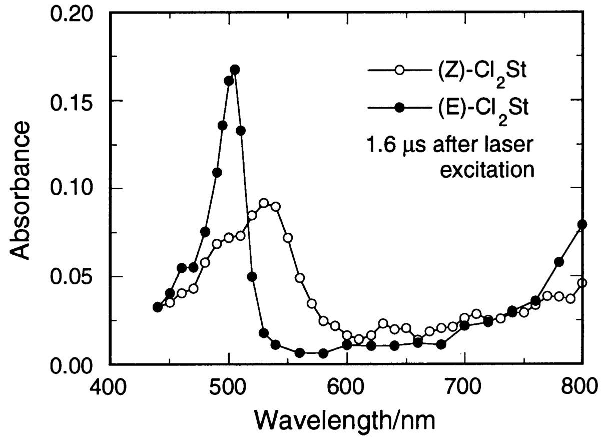


Fig. 1. Transient absorption spectra observed on 425-nm laser excitation of DCA in the presence of biphenyl and (*E*)- or (*Z*)-Cl_2St in acetonitrile.

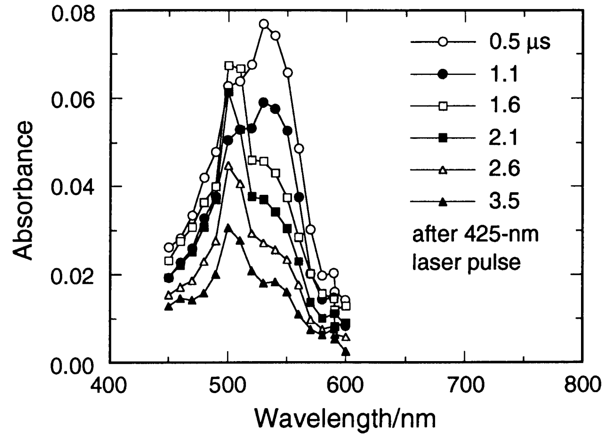


Fig. 2. Transient absorption spectra observed on 425-nm laser excitation of the DCA/BP/(Z)-Cl_2St system in acetonitrile followed by a 500-nm laser pulse at 1.5 μs after the first laser pulse.

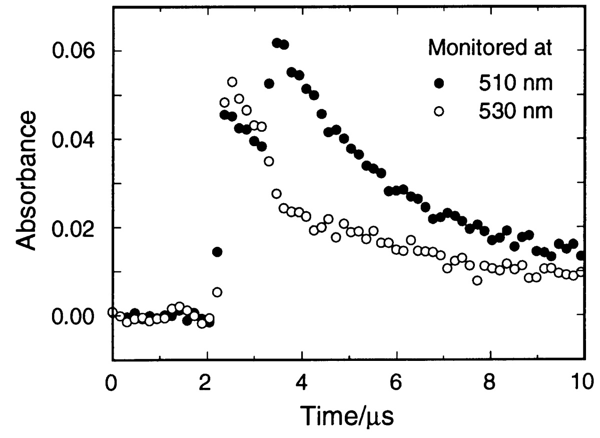


Fig. 3. Time profiles of the transient absorption monitored at 510 and 530 nm on 425-nm laser excitation of the DCA/BP/(Z)-Cl_2St system in acetonitrile followed by a 500-nm laser pulse at 1 μs after the first laser pulse.

0.50 for Cl_2St in comparison with 0.12 for St[10)] and 0.72 for Br_2St.[10)] The effect of substituent can be understood in terms of acceleration of the *Z*→*E* conversion of the radical cations by reduction of the electron density on the unsaturated linkage.[3a)]

Two-color laser excitation of the DCA/BP/(Z)-Cl_2St system was made with a 425-nm laser pulse followed by a 500-nm laser pulse with 1–2 μs delay.[11)] The 500-nm laser excites (*Z*)-$Cl_2St^{+\cdot}$ to the upper excited state, as seen in Fig. 1. The observed transient absorption spectra and time profiles monitored around the absorption maxima of the radical cations of both isomers are shown in Figs. 2 and 3, respectively. Figure 2 shows that immediately after the second laser pulse the spectrum profile changes markedly, and this can be ascribed to a rapid conversion of (*Z*)-$Cl_2St^{+\cdot}$ to (*E*)-$Cl_2St^{+\cdot}$ on excitation. Since (*Z*)-$Cl_2St^{+\cdot}$ have a lower and a higher molar extinction coefficient than those of (*E*)-$Cl_2St^{+\cdot}$ at 510 and 530, respectively, the gain and loss in absorbance at these wavelengths, as seen in Fig. 3, correspond to the quantities of isomerization. These figures indicate that the conversion is completed within some hundreds of nanoseconds.

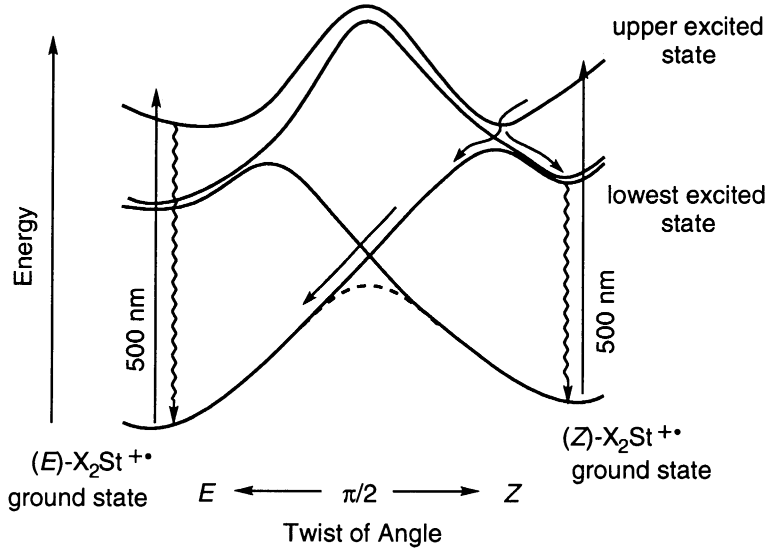


Fig. 4. Energy Surfaces for Isomerization from the Upper Excited State.

On two-color laser excitation under the similar conditions, (*Z*)-F_2St and (*Z*)-St showed spectral changes and time profiles very similar to those of (*Z*)-Cl_2St. The efficiencies for *Z*→*E* conversion of the radical cations were evaluated to be 0.41, 0.37, and 0.37 for (*Z*)-St$^{+\cdot}$, (*Z*)-F_2St$^{+\cdot}$, and (*Z*)-Cl_2St$^{+\cdot}$, respectively. The value for (*Z*)-St$^{+\cdot}$ is in agreement with that from pulse radiolysis-laser photolysis experiments.[5d)] The present results indicate that the isomerization efficiency is not influenced by the halogen substituents in this series. On the contrary, the *E*-isomers of St, F_2St, and Cl_2St exhibited no clear spectral change on the second laser pulse in the two-color laser excitation. Thus, the isomerization of the present stilbene radical cations proceeds in the *Z*→*E* one-way fashion, as reported previously for stilbene itself.[5)]

Two-color laser excitation of (*Z*)-Cl_2St was attempted in various temperatures under otherwise similar conditions. However, the quantum efficiency of isomerization of (*Z*)-Cl_2St$^{+\cdot}$ was almost constant in the range of 10–53 °C, indicating that the *Z*→*E* conversion process of the excited radical cations has no activation barrier in contrast with the corresponding process in the ground state.[3)]

Use of a 740-nm laser pulse, which excites (*Z*)-Cl_2St$^{+\cdot}$ to the first excited state, as the second excitation light in the two-color laser photolysis exhibited no clear gain in absorbance at 510 nm (quantum efficiency of isomerization < 0.05) at ambient temperature.[11)] Consequently, the lowest excited state of (*Z*)-Cl_2St$^{+\cdot}$ is not effective in collapse to (*E*)-Cl_2St$^{+\cdot}$, as reported for stilbene.[5d)]

The efficient *Z*→*E* conversion from the upper excited state is consistent with the results of MO calculations;[6d)] the upper excited state (mainly of the SOMO→LUMO excited configuration)[6d)] of the *Z* form crosses avoidedly with the lowest excited state which leads to the ground-state *E* form through an allowed crossing. The route involves no activation barriers (Fig. 4). In the lowest excited state, however, the twisting involving some activation barrier could not compete with a rapid decay to the ground state.

The authors thank the Ministry of Education, Science and Culture for the partial support of this work by a Grant-in-Aid for Specially Promoted Research No. 03101004 (K.T. and H.S.) and also thank The University of Tsukuba for the President's Special Grant for Education and Research (K.T.).

References

1) a) F. D. Lewis, J. R. Petisce, J. D. Oxman, and M. J. Nepras, *J. Am. Chem. Soc.*, **107**, 203 (1985); b) F. D. Lewis, R. E. Dykstra, I. R. Gould, and S. Farid, *J. Phys. Chem.*, **92**, 7042 (1988).

2) Y. Kuriyama, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Lett.*, **1988**, 1193; Y. Kuriyama, T. Arai, H. Sakuragi, and K. Tokumaru, *ibid.*, **1989**, 251; K. Tokumaru, Y. Kuriyama, T. Arai, I. K. Lednev, R. Akaba, and H. Sakuragi, "Photochemical Processes in Organized Molecular Systems," ed by K. Honda, Elsevier (1991), p. 199; I. K. Lednev, M. V. Alfimov, Y. Kuriyama, T. Arai, H. Sakuragi, and K. Tokumaru, *J. Photochem. Photobiol. A: Chem.*, **63**, 201 (1992); Y. Kuriyama, H. Sakuragi, K. Tokumaru, Y. Yoshida, and S. Tagawa, *Bull. Chem. Soc. Jpn.*, **66**, 1852 (1993); B. W. Zhang, Y. Kuriyama, Y. Cao, and K. Tokumaru, *ibid.*, **66**, 1859 (1993).

3) a) Y. Kuriyama, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **173**, 253 (1990); b) Y. Kuriyama, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Lett.*, **1992**, 879.

4) S. Takamuku, "Frontier of Highly Efficient Photochemical Processes," Ministry of Education, Science and Culture, Kyoto (1989), p. 75; K. Morishima, S. Tojo, A. Ishida, and S. Takamuku, Presented at Symposium on Radiation Chemistry, Osaka, Oct. 1991, Abstract p. 61; S. Takamuku, Y. Okamoto, A. Ishida, and S. Tojo, "Annual Report 1992," Radiation Laboratory, The Institute of Scientific and Industrial Research, Osaka University (1992), p. 43.

5) a) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2375 (1966); b) V. A. Sazhnikov, M. Rakhmatov, and M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, **241**, 1378 (1978); V. A. Sazhnikov, M. Rakhmatov, and M. V. Alfimov, *Chem. Phys. Lett.*, **71**, 33 (1980); c) H. Suzuki, K. Koyano, T. Shida, and A. Kira, *Bull. Chem. Soc. Jpn.*, **55**, 3690 (1982); H. Suzuki, K. Ogawa, T. Shida, and A. Kira, *ibid.*, **56**, 66 (1983); d) T. W. Ebbesen, *J. Phys. Chem.*, **92**, 4581 (1988).

6) a) E. Haselbach, U. Klemm, R. Gschwind, T. Bally, L. Chassort, and S. Nitsche, *Helv. Chim Acta*, **65**, 2464, (1982); b) R. W. Bigelow, *Chem. Phys. Lett.*, **117**, 22 (1985); c) O. Kikuchi, T. Oshiyama, O. Takahashi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **65**, 2267 (1992); d) T. Oshiyama, O. Takahashi, K. Morihashi, O. Kikuchi, and K. Tokumaru, *ibid.*, **66**, 1622 (1993).

7) For example, J. C. Scaiano, L. J. Johnston, W. G. McGimpsey, and D. Weir, *Acc. Chem. Res.*, **21**, 22 (1988); L. J. Johnston, *Chem. Rev.*, **93**, 251 (1993).

8) Laser flash photolyses were performed with an excimer laser (Lambda Physik LPX-100, XeCl, 308 nm, 10-ns fwhm)-pumped dye laser (Lambda Physik FL-3002) exciting at 425 nm (Stilbene 3, 3–4 mJ/pulse) and a pulsed xenon arc (Wacom KXL-151, 150 W) as a monitoring light source.

9) This technique prevents the back electron transfer to the olefin radical cation 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 ($+O_2^{-\cdot}$) and the olefin radical cation.

10) Previously we reported the values of 0.04 and 0.80 for (*Z*)-St and (*Z*)-Br_2St, respectively, with light of wavelength longer than 400 nm from a xenon lamp; Ref. 3a.

11) The 500-nm and 740-nm laser pulses were supplied from an excimer laser (Lambda Physik EMG101, XeCl, 308 nm, 10-ns fwhm)-pumped dye laser (Lambda Physik FL-1000; dye: Coumarin 307, 2–3 mJ/pulse for 500-nm laser and Oxazine 725, 2–3 mJ/pulse for 740-nm laser).

(Received March 28, 1994)