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Electron Transfer Induced Isomerization of *cis,trans*- and *trans,trans*-1,4-Diphenyl-1,3-butadiene

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Abstract: Irradiation of *cis,trans*- or *trans,trans*-1,4-diphenyl-1,3-butadiene with 9,10-dicyanoanthracene as a sensitizer results in predominant cis,trans → trans,trans geometric isomerization in acetonitrile. A cation radical chain mechanism is proposed to be operative.

Photoinduced electron transfer (ET) often results in geometric isomerization of alkenes. For example, cis, trans isomerization of stilbenes by photoinduced ET has attracted considerable attention in recent years.[1] 1,4-Diphenyl-1,3-butadiene **1**, a vinylene analogue of stilbene, is also an interesting system. Hug and co-workers[2a] have observed cation radicals of the three isomers (*cc*-**1**, *ct*-**1**, and *tt*-**1**) by laser flash photolysis and found that cation radical *cc*-$\mathbf{1}^{\bullet+}$ undergoes relatively slow isomerization to *tt*-$\mathbf{1}^{\bullet+}$ with a lifetime of *ca.* 25 μs. However, little has been mentioned on the reactivity of the other isomers, *ct*-**1** and *tt*-**1**, particularly under steady-state photolysis conditions. It was not clear whether or not the isomerizations of *ct*-**1** and *tt*-**1** can be promoted by photoinduced ET. We investigated the 9,10-dicyanoanthracene (DCA)-sensitized photoreactions of *ct*-**1** and *tt*-**1** and observed predominant *ct*-**1** → *tt*-**1** isomerization.

The dienes *ct*-**1** and *tt*-**1** are good electron donors and their oxidation potentials (E_{ox}), +1.26 and +1.21 V *vs.* SCE, respectively, are low enough for ET from the dienes to singlet excited DCA (^{1}DCA*) in acetonitrile. Calculations by using the Weller equation[3] show that the free energy changes (ΔG) for the ET processes in acetonitrile are exothermic by –0.68 and –0.73 eV for *ct*-**1** and *tt*-**1**, respectively. In accord with this, DCA fluorescence can be efficiently quenched by **1** with near diffusion-controlled rate constants, k_q being 2.2×10^{10} and 2.5×10^{10} M^{-1} s^{-1} for *ct*-**1** and *tt*-**1**, respectively. Steady-state photolyses were carried out by using a 500-W xenon-mercury lamp equipped with a glass filter (λ > 410 nm). Irradiation of 2 ml acetonitrile solutions of *ct*-**1** and DCA for 15 minutes afforded a 2.5:97.5 steady-state mixture of *ct*-**1** and *tt*-**1**. In a similar manner the photoreaction with *tt*-**1** afforded essentially the same photostationary mixture (2.1:97.9) as that from *ct*-**1**. The ratios indicate *ct*-**1** → *tt*-**1** isomerization is predominant.[5]

Under the steady-state photolysis conditions the isomerization reaction is generally efficient and the quantum yield (Φ) for the isomerization of *ct*-**1** exceeds unity in acetonitrile (Table 1, Run 1–4). Photolysis with lower light intensity resulted in higher Φ (Run 4 *vs.* 2). In the presence of oxygen or 1.5×10^{-4} M of tetramethoxybenzene (TMB, E_{ox} = 0.75 V *vs.* SCE), Φ decreased significantly (Run 5–7 *vs.* 1, 2). Photogenerated $\mathbf{1}^{\bullet+}$ can be intercepted by reaction with molecular oxygen or by ET to TMB. These observations in conjunction with the results of quencher effects suggest a chain mechanism as shown in Scheme 1, which is analogous to the mechanism for the ET induced isomerization of stilbenes proposed earlier by Lewis *et al.*[1a] The mechanism involves i) formation of free *ct*-$\mathbf{1}^{\bullet+}$ (and DCA$^{\bullet-}$) as an initiation step, ii) unimolecular isomerization of *ct*-$\mathbf{1}^{\bullet+}$ to *tt*-$\mathbf{1}^{\bullet+}$ prevalently, and iii) regeneration of *ct*-$\mathbf{1}^{\bullet+}$ by hole transfer from *tt*-$\mathbf{1}^{\bullet+}$ to *ct*-**1**. The latter two processes compete with charge recombination processes (k_t and $k_{t'}$).

In order to gain insight into the mechanism, we undertook laser flash photolysis experiments.[6] Fig. 1 (a) shows the transient absorption spectra at 200 ns after the pulsed laser excitation of the *ct*-**1**–DCA and *tt*-**1**–DCA systems in acetonitrile. These transients from *ct*-**1** and *tt*-**1** are readily assigned as being due to the corresponding cation radicals, *ct*-$\mathbf{1}^{\bullet+}$ and *tt*-$\mathbf{1}^{\bullet+}$. Indeed their shape and maxima (543 and 530 nm for *ct*-$\mathbf{1}^{\bullet+}$ and *tt*-$\mathbf{1}^{\bullet+}$, respectively) well compare with those reported previously.[2a,4,7] Similar but more intense transient spectra were obtained with 0.1 M of biphenyl as a co-sensitizer[1d,g] (Fig. 1 (b)). In the presence of biphenyl the ratio of the intensities of the transient absorption maxima of *ct*-$\mathbf{1}^{\bullet+}$ and *tt*-$\mathbf{1}^{\bullet+}$ at zero time corresponds to the ratio of extinction coefficients (ε) of *ct*-$\mathbf{1}^{\bullet+}$ and *tt*-$\mathbf{1}^{\bullet+}$. By using ε of *tt*-$\mathbf{1}^{\bullet+}$ (6.8×10^4 M^{-1} cm^{-1} at 530 nm),[4c] ε of *ct*-$\mathbf{1}^{\bullet+}$ was determined to be 2.6×10^4 M^{-1} cm^{-1} at 543 nm. Either with or without biphenyl, both transients due to *ct*-$\mathbf{1}^{\bullet+}$ and *tt*-$\mathbf{1}^{\bullet+}$ decayed with second order kinetics and the rate constants, k_t and $k_{t'}$ in Scheme 1, were determined to be near diffusion-controlled values, 2–3 × 10^{10} M^{-1} s^{-1}.

As shown in Fig. 1 (c), spectral change of *ct*-$\mathbf{1}^{\bullet+}$ could be visualized when the time-resolved spectra obtained with biphenyl were normarized at the isosbestic point, 550 nm. Slight blue-shifting and increase in the intensity of the spectra at 1 μs and 10 μs are most likely due to *ct*-$\mathbf{1}^{\bullet+} \rightarrow$ *tt*-$\mathbf{1}^{\bullet+}$ conversion. Based on ε of *tt*-$\mathbf{1}^{\bullet+}$ we estimated that 6% of *ct*-$\mathbf{1}^{\bullet+}$ isomeraized to *tt*-$\mathbf{1}^{\bullet+}$ in 10 μs, which corresponds to the rate constant (k_i) of *ca.* 6×10^3 s^{-1}. Spectral change of *ct*-$\mathbf{1}^{\bullet+}$ without biphenyl was obscure because of the quality of the

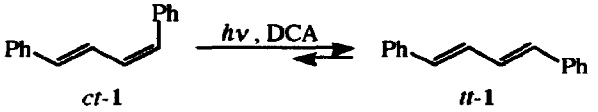
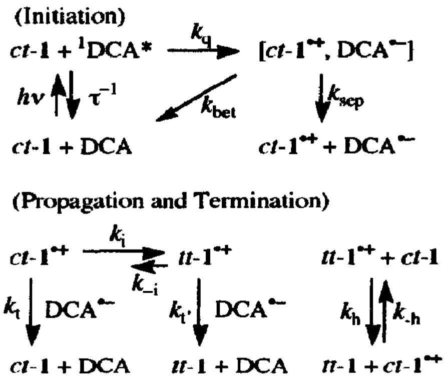


Table 1. Effects of Light Intensity (*I*) and Additives on the Quantum Yield (Φ) of the DCA-sensitized Photoisomerization of *ct*-**1** in Acetonitrile [a)]

Run	[*ct*-**1**] / 10^{-3} M	*I* / 10^9 einstein s^{-1}	Additive	Φ
1	4.52	3.75	none	1.4
2	17.7	3.75	none	3.1
3	47.7	3.21	none	6.6
4	17.7	0.328	none	8.6
5	4.52	3.75	O_2, 1 atm	0.53
6	17.7	3.75	O_2, 1 atm	1.7
7	4.52	3.75	TMB, 0.15 mM	0.36

a) Solutions of *ct*-**1** and DCA (3×10^{-4} M) were photolyzed by using a 150-W Xe lamp equipped with a monochromator (λ 420 nm). Photolysates were analyzed by HPLC.

Scheme 1



$$f_{\mathrm{sep}} = \frac{k_{\mathrm{sep}}}{k_{\mathrm{sep}} + k_{\mathrm{bet}}} \quad \text{--- (1)}$$

$$n = \frac{\Phi}{f_{\mathrm{et}} \times f_{\mathrm{sep}}} \quad \text{--- (2)}$$

$$f_{\mathrm{et}} = \frac{k_q[ct\text{-}1]}{\tau^{-1} + k_q[ct\text{-}1]} \quad \text{--- (3)}$$

spectra, which is due to the fact that the efficiency for separation (f_{sep}) (eq. (1)) of the photogenerated ion pair[*ct*-**1**$^{\bullet+}$, DCA$^{\bullet-}$] is low. Recently, we have determined f_{sep} of the photogenerated ion pair [*tt*-**1**$^{\bullet+}$, DCA$^{\bullet-}$] to be 0.11.[4c] By using ε values and the ratio of the extrapolated intensities at zero time of *ct*-**1**$^{\bullet+}$ and *tt*-**1**$^{\bullet+}$, f_{sep} for [*ct*-**1**$^{\bullet+}$, DCA$^{\bullet-}$] can be evaluated to be 0.08.

Since the efficiency of the initiation step is not so high, chain length must be long. Chain length *n* at early stage of the reaction can be evaluated by using eq. (2). For example, Φ of 3.1 at 17.7 mM of *ct*-**1** (Table 1, run 2) results in calculated *n* of 44. Therefore, isomerization and hole transfer processes must be much more efficient than the termination steps. In other words, both k_i and k_h must be larger than k_t[DCA$^{\bullet-}$] and $k_{t'}$[DCA$^{\bullet-}$], which are dependent on the concentration of DCA$^{\bullet-}$. Under the laser flash photolysis conditions, where [DCA$^{\bullet-}$] can be in the order of 10^{-5} M or higher, k_t[DCA$^{\bullet-}$] and $k_{t'}$[DCA$^{\bullet-}$] are expected to be as large as 2–3 × 10^5 s^{-1}. In fact only 6% of *ct*- to *tt*-**1** conversion was observed in the 10 μs time scale. On the other hand, k_t[DCA$^{\bullet-}$] and $k_{t'}$[DCA$^{\bullet-}$] should become as small as 2 to 3 s^{-1} because [DCA$^{\bullet-}$] would be as low as *ca.* 10^{-10} M under the steady-state photolysis conditions. Under the circumstances k_i of *ca.* 6 × 10^3 s^{-1} is indeed high enough to exceed the termination steps. Hole transfer from *tt*-**1**$^{\bullet+}$ to *ct*-**1** may efficiently proceed particularly when the concentration of *ct*-**1** is high, since the oxidation potential of *ct*-**1** is higher than that of *tt*-**1** by only 0.05 eV in acetonitrile. There exist a number of experimental precedents and theoretical support for such an endothermic ET reaction to proceed with considerable efficiency.[8] It is reasonable that the ET reaction with endothermicity of 0.05 eV may proceed with rate constant of 10^8–10^9 M^{-1} s^{-1}.

Recently Lewis *et al.*[1g] proposed an alternative mechanism for the ET induced isomerization of *cis*-stilbene involving the formation of dimer cation radicals of stilbene as a key process. The dimer cation radicals may revert with loss of the stereochemistry to give *trans*-stilbene and *trans*-stilbene$^{\bullet+}$. The mechanism readily account for the observation that the quantum yields are greater than unity while unimolecular isomerization of *cis*-stilbene$^{\bullet+}$ to *trans*-stilbene$^{\bullet+}$ does not occur on the 10 μs time scale.[1d,9] However, the experimental evidence for such a σ-type dimer formation has been inconclusive.[1g,10] Although a mechanism involving similar dimer cation radical (**1**)$_2^{\bullet+}$ is fascinating for the present case, we have not been able to observe the dimer formation in the flash photolysis experiments with **1**. Moreover no indication for the formation of dimer cation radical has been obtained by a pulse radiolysis study with *tt*-**1**.[11] Thus a mechanism involving dimer cation radical cannot be a principal route for the present isomerization.

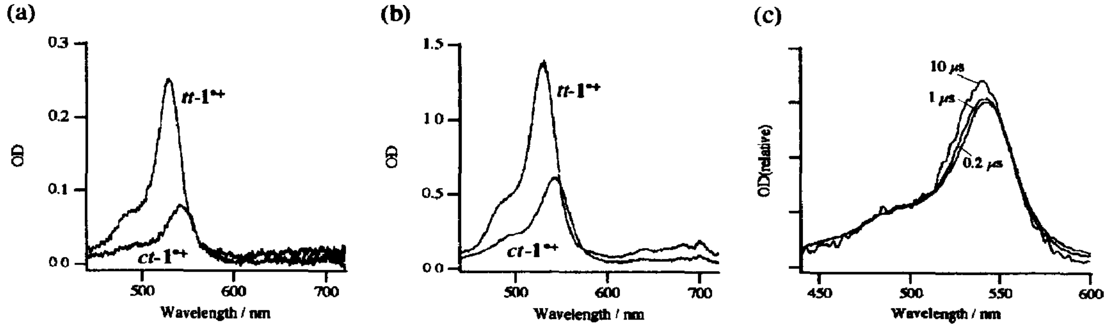


Fig. 1 Transient absorption spectra of *ct*-**1**$^{\bullet+}$ and *tt*-**1**$^{\bullet+}$ in N$_2$-saturated acetonitrile obtained by laser flash photolyses: (a) from *ct*-**1** (10 mM) and *tt*-**1** (10 mM) with DCA (0.3 mM), and (b) from *ct*-**1** (0.82 mM) and *tt*-**1** (0.86 mM) with DCA (0.3 mM) and biphenyl (0.1 M) at 200 ns after excitation. (c) Transient spectra of *ct*-**1**$^{\bullet+}$ normalized at 550 nm.

Further studies of the photoisomerization are in progress. We thank the Ministry of Education, Science, and Culture (Grant No. 03403005 and 03303001) for financial support.

References and Notes

1 a) Lewis, F. D.; Petisce, J. R.; Oxman, J. D.; Nepras, M. J. *J. Am. Chem. Soc.* **1985**, *107*, 203. b) Tanimoto, Y.; Takayama, M.; Shima, S.; Itoh, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3641. c) Kuriyama, Y; Arai, T; Sakuragi, H; Tokumaru, K. *Chem. Lett.* **1988**, 1193. d) Lewis, F. D.; Dykstra, R. E.; Gould, I. R.; Farid, S. *J. Phys. Chem.* **1988**, *92*, 7042. e) Kuriyama, Y; Arai, T; Sakuragi, H; Tokumaru, K. *Chem. Lett.* **1989**, 251. f) Kuriyama, Y; Arai, T; Sakuragi, H; Tokumaru, K. *Chem. Phys. Lett.* **1990**, *173*, 253. g) Lewis, F. D.; Bedell, A. M.; Dykstra, R. E.; Elbert, J. E.; Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 8055. h) Kuriyama, Y; Arai, T; Sakuragi, H; Tokumaru, K. *Chem. Lett.* **1992**, 879.

2 a) Hug, S. J.; Yee, W. A.; Kliger, D. S. *Chem. Phys. Lett.* **1990**, *168*, 385. b) Yee, W. A.; Hug, S. J.; Kliger, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 2164.

3 Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834.

4 a) Takahashi, Y.; Wakamatsu, K; Kikuchi, K.; Miyashi, T. *J. Phys. Org. Chem.* **1990**, *3*, 509. b) Kikuchi, K.; Takahashi, Y.; Hoshi, M.; Niwa, T.; Katagiri, T.; Miyashi, T. *J. Phys. Chem.* **1991**, *95*, 2378. c) Kikuchi, K.; Takahashi, Y.; Koike, K.; Wakamatsu, K; Ikeda, H.; Miyashi, T. *Z. Phys. Chem. (München)* **1990**, *167*, 2378. d) Kikuchi, K.; Hoshi, M.; Niwa, T.; Takahashi, Y.; Miyashi, T. *J. Phys. Chem.* **1991**, *95*, 38.

5 DCA-sensitized photolyses of *ct*-**1** or *tt*-**1** in benzene also resulted in prevailing *cis*- to *trans*-**1** isomerization and afforded a photostationary mixture consisting of 5% of *ct*-**1** and 95% of *tt*-**1**. The quantum yields for the isomerization of *ct*-**1** were 5 to 10 lower than those in acetonitrile. Exciplex emission was observed for *ct*-**1** and *tt*-**1** in benzene. Since the emission maxima of the exciplexes of *ct*-**1** (561 nm) and *tt*-**1** (572 nm) are different, fast cis → trans isomerization within the exciplex manifold is unlikely. A possible mechanism in benzene would involve triplet state isomerization. Formation of ^{3}DCA* was observed by laser flash photolyses of the *ct*-**1**–DCA and *tt*-**1**–DCA systems.

6 An excimer-laser pumped dye laser (420 nm) was used for measurement.

7 Shida, T. *Electronic Absorption Spectra of Radical Ions;* Elsevier: Amsterdam, 1988; p 130.

8 a) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987. b) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

9 Recently Tokumaru *et al.*[1h] succeeded in observing *cis*- to *trans*-stilbene$^{\bullet+}$ isomerization directly by laser flash photolyis of *cis*-stilbene–DCA system with salt and biphenyl. The rate constant, 3.0×10^5 s^{-1} at 19 °C, is high enough to exceed the rate of termination due to recombination of *cis*-stilbene$^{\bullet+}$ with DCA$^{\bullet-}$ under the steady-state photolysis conditions. In this context the formation of dimer cation radical proposed by Lewis *et al.* may not be a necessary alternative for the isomerization of *cis*-stilbene.

10 Formation of (π-type) *trans*-stilbene dimer cation radical has been suggested in the radiolysis studies of *trans*-stilbene. Kira, A; Arai, S.; Imamura, M. *J. Phys. Chem.* **1972**, *76*, 1119; Robinson, E. A.; Salmon, G. A. *J. Phys. Chem.* **1987**, *82*, 382.

11 Chikai, Y.; Yamamoto, Y.; Hayashi, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2281.

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