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Mechanism for Electron-Transfer Induced Isomerization of Stilbene as Studied by Magnetic Field Effects

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External magnetic field effects and laser flash photolysis were applied to elucidating the mechanism of dicyanoanthracene-sensitized isomerization of stilbene in acetonitrile, indicating that the stilbene cation radical is a key intermediate for isomerization. Sensitizer dependence of the isomerization efficiency is discussed in terms of the rate of back electron transfer in singlet radical pairs.

Direct observation of intermediates by laser flash photolysis (LFP) and measurements of magnetic field effects (MFE) upon reaction efficiency under steady illumination are useful tools for elucidating mechanisms for electron-transfer induced isomerization of aromatic olefins.[1)] For example, pyrene-sensitized isomerization of trans-stilbene (TS)[1a)] and photoisomerization of a naphthylethylene in the presence of electron acceptors[1b)] were proposed, on the basis of MFE study, as proceeding through olefin triplets generated by back electron transfer between initially produced ion radicals. Previously, we demonstrated that both excited singlets and triplets of triphenylpyrylium salt (TPP^+) were effectively quenched by cis-stilbene (CS), but only the triplets induced CS isomerization;[2)] the singlet ion radical pairs generated might decay by rapid back electron transfer. The singlet state of 9,10-dicyanoanthracene (DCA), on the contrary, has been reported to induce the CS isomerization with a cation radical chain mechanism; however, clear evidence has not been provided[3)] for the mechanisms particularly in the wide range of CS concentration. In order to clarify the effects of multiplicity and sensitizers on isomerization mechanisms, LFP and MFE studies were extended to DCA-sensitized isomerization of stilbenes.

Fluorescence of DCA was effectively quenched by CS and TS in acetonitrile (AN) with nearly diffusion controlled rates[4)] as already reported by others.[3,5)] The free energy changes ($\Delta G°$) associated with electron transfer from ground-state stilbenes to excited singlet DCA[6)] show that these processes are exothermic.[3)]

Quantum yields for DCA(3×10^{-4} M, M=mol dm^{-3})-sensitized isomerization of CS ($\phi_{c\rightarrow t}$) and TS ($\phi_{t\rightarrow c}$) in varying concentrations (0.001-0.1 M) were measured at low (<10%) conversion in degassed AN using monochromatic 405-nm irradiation. Their concentration dependence is depicted in Fig. 1, where the numbers on the abscissa ϕ_q^S indicate the quantum yields for quenching of DCA excited singlets by CS or TS. In Fig. 1 $\phi_{t\rightarrow c}$ is considerably low and almost constant [$(3-5)\times10^{-3}$] in the olefin concentration range employed. In cis→trans isomerization $\phi_{c\rightarrow t}$ increases slowly

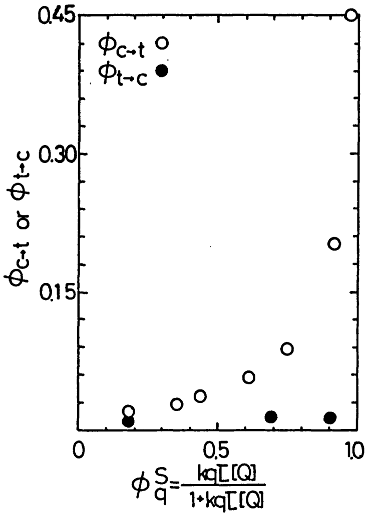

Fig. 1. Concentration Dependence of Isomerization Quantum Yields.

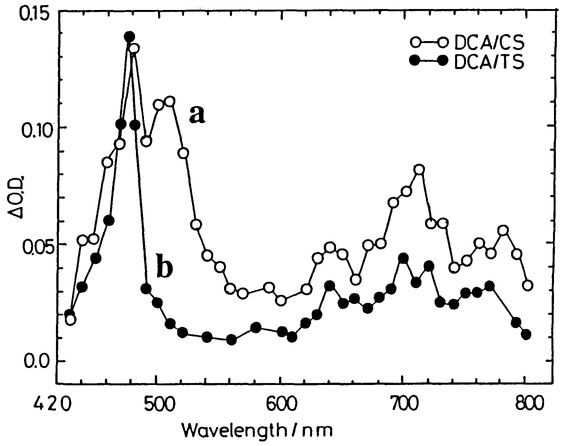

Fig. 2. Transient Absorption Spectra Observed on Laser Flash Photolysis of DCA in the Presence of CS (a) and TS (b) in AN.

with increasing ϕ_q^S in the lower concentration range and rapidly increases in the higher concentration range where ϕ_q^S approaches unity. The behavior of $\phi_{t\to c}$ and $\phi_{c\to t}$ in the higher olefin concentrations is in good agreement with that reported by Lewis (0.05-0.2 M).[3] In the lower concentrations, however, $\phi_{c\to t}$ depends linearly on ϕ_q^S, i.e., $\phi_{c\to t}/\phi_q^S$ is almost constant (ca. 0.02), indicating that DCA excited singlets are responsible for the isomerization.

The photostationary state isomer ratios [([t]/[c])$_s$] determined on DCA sensitization with 405-nm light were as high as ca. 98/2 independent of the stilbene concentrations ranging from 0.001 to 0.1 M. This value is close to that reported for the cation radical chain isomerization, 98.8/1.2.[3] The high value for ([t]/[c])$_s$ in the present reaction suggests isomerization of stilbenes in the form of cation radicals.

In order to confirm this mechanism some attempts were made to observe directly intermediates by LFP[9] and to measure MFE on the isomerization quantum yield. Figure 2 shows typical transient absorption spectra observed in LFP of DCA (9.5×10^{-5} M) with CS (0.05 M, Fig. 2a) and TS (0.043 M, Fig. 2b) in deaerated AN with 406-nm laser pulses (10-nm fwhm).[2,10] The transient absorption in Fig. 2b decayed by second order kinetics and is assigned mainly to TS cation radicals (λ_{max} 475 nm)[11] and DCA anion radicals (600-800 nm).[12] The transient absorption in Fig. 2a is assumed to be due to $DCA^{-\cdot}$ (600-800 nm), $CS^{+\cdot}$ (λ_{max} 515 nm),[11] and $TS^{+\cdot}$ (λ_{max} 475 nm). In neither case any excited triplet intermediates could be detected. The formation of $TS^{+\cdot}$ immediately (ca. 3 μs) after laser excitation of CS supports the above mechanism in which the isomerization takes place in cation radicals ($CS^{+\cdot}\to TS^{+\cdot}$) within ion radical pairs or in free ion radicals. This behavior is similar to that in TPP^+ triplet sensitization.[2]

Thus, quenching of the sensitizer singlets ($^1S^*$) by CS affords the singlet pairs of $S^{-\cdot}$ and $CS^{+\cdot}$, which undergo intersystem crossing to the triplet pairs in competition with rapid back electron transfer to recover the starting S and CS. The triplet pairs can convert to $S^{-\cdot}/TS^{+\cdot}$ pairs (in-cage isomerization) or escape out of the cage to give the free ion radicals in competition with intersystem crossing to the singlet pairs. The free $CS^{+\cdot}$ also isomerizes to $TS^{+\cdot}$, which accepts subsequently an electron from $S^{-\cdot}$ to afford TS finally.

If the triplet pairs play an important role in the CS isomerization, the external magnetic field might affect the isomerization efficiency. DCA (3.7×10^{-4} M) and CS (9.7×10^{-4} M) were irradiated in deaerated AN at ambient temperature with filtered light ($\lambda \geq 400$ nm) in applied magnetic fields (0-500 G) of an electromagnet. The isomerization yields $[\phi_{c \to t}(H)/\phi_{c \to t}(0)]$ at various applied magnetic fields relative to that at the zero magnetic field strength were plotted in Fig. 3a. Figure 3a shows that the relative yield is reduced at the field strengths lower than 300 G and reached a nearly constant value (ca. 0.65) at the higher strength region. A similar MFE was observed on irradiation of DCA (3.7×10^{-4} M) and TS (1.0×10^{-3} M). The isomerization yield decreased similarly and was saturated at a nearly constant value $[\phi_{t \to c}(H)/\phi_{t \to c}(0)$ = ca. 0.82, Fig. 3b]. However, the effect is smaller than that observed in the CS isomerization.

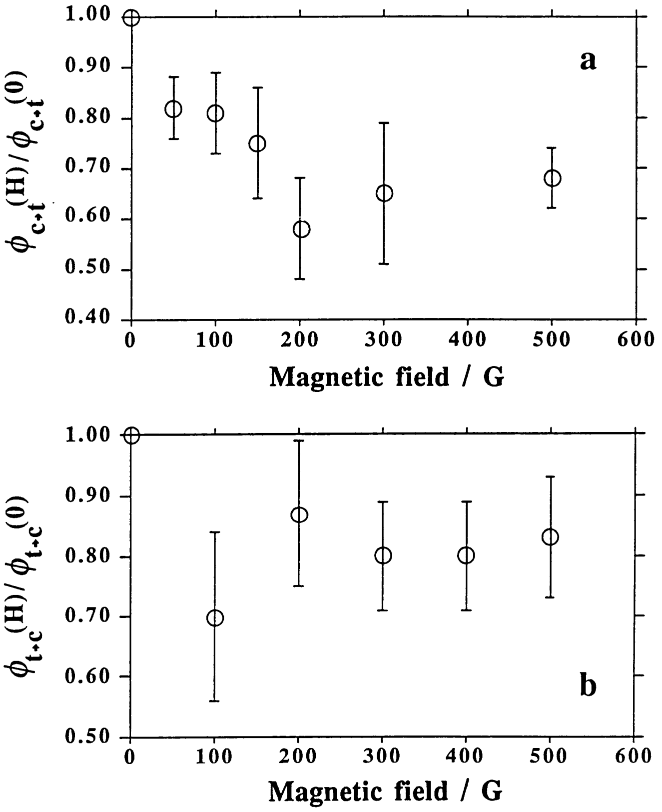

Fig. 3. Magnetic Field Effect on Quantum Yields for Isomerization of CS (a) and TS (b).

The observed MFE is interpreted in terms of the hyperfine interaction in ion radical pairs.[1b,13)] The intersystem crossing between singlet S_0 and triplet T_+, T_- states induced by the hyperfine interaction is appreciably diminished in the presence of the high magnetic fields thereby attenuating the quantum yields of the triplet radical ion pairs, the key intermediate.[19)]

As mentioned above, TPP^+ singlets do not induce the isomerization. The big difference between TPP^+ and DCA in sensitization efficiency can be ascribed to the rates of back electron transfers in the singlet ion radical pairs. The free energy changes for these processes are estimated as -1.9 and -2.6 eV for $TPP^{\cdot}/CS^{+\cdot}$ and $DCA^{-\cdot}/CS^{+\cdot}$ pairs, respectively. Recently, the bell-shaped energy gap dependence of the back electron transfer rate has been established,[20)] and the above values for energy gap are in the so-called inverted region; for $DCA^{-\cdot}/CS^{+\cdot}$ pairs the rate is much reduced than for $TPP^{\cdot}/CS^{+\cdot}$ pairs, though the two systems might show different energy gap dependence (charge recombination and charge shift).[20)] Therefore, this situation leads to more efficient sensitization with DCA singlets than that with TPP^+ singlets. Further studies on the sensitizer dependence of isomerization efficiency will be reported in due course.

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