Lifetimes and Transient Phenomena of Stilbene Radical Cations in the Second Excited Doublet State

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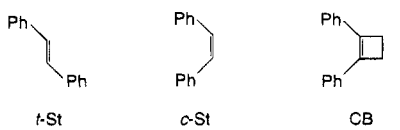
Radical cations of *cis*- and *trans*-stilbene (*c*-St$^{\bullet+}$, *t*-St$^{\bullet+}$) and of 1,2-diphenylcyclo-1-butene (CB$^{\bullet+}$) in the second excited doublet state (D_2) have been generated using sequential pulse radiolysis−laser flash photolysis, and their lifetimes have been measured using selective hole transfer quenching with anisole. In the deactivation of the D_2 state of *c*-St$^{\bullet+}$, the internal conversion competes with the isomerization to *t*-St$^{\bullet+}$ in a quantum yield of 0.49 ± 0.12 and conversion to another product as a minor process, whereas the D_2 states of *t*-St$^{\bullet+}$ and CB$^{\bullet+}$ are only deactivated via internal conversion. Lifetimes of the *t*-St$^{\bullet+}$ and *c*-St$^{\bullet+}$ D_2 states are estimated to be approximately 240 and 120 ps, respectively, while that of the CB$^{\bullet+}$ D_2 state is approximately 380 ps. The shorter lifetime of the *c*-St$^{\bullet+}$ D_2 state is attributed to isomerization and conversion to another product via twisting about the central C=C double bond. The analogous process in CB is severely hindered by structural constraints. The transient phenomena of the D_2 states of *c*-St$^{\bullet+}$, *t*-St$^{\bullet+}$, and CB$^{\bullet+}$ are compared in terms of thier lifetimes, structures, energies, and reaction processes.

Introduction

The photoexcitation of radical cations and anions increases their electron acceptor and donor characteristics, respectively, because an electron is promoted from a low-energy molecular orbital to a higher-energy molecular orbital.[1−3] Electron transfer reactions that are catalyzed by photoexcited radical ions have been studied at electrode surfaces[4,5] and in solution.[6−14] However, the nature of this excited-state electron transfer is not clear because only a small number of studies on the radical ions in the excited state have been completed. The excited states of the radical ions are usually nonluminescent in solution, although weak luminescences of thermally stable radical ions such as the anthraquinone radical anion and *N*-methylphenothiazine radical cation have been reported at 470−580 nm[15,16] and at 600 nm,[12] respectively. Fox and co-workers have recently reported the weak luminescence of two substituted triarylamine radical cations with luminescence peaks at 790 and 803 nm and with the luminescence quantum yield of approximately 10^{-5}, while the other thermally stable radical ions investigated were nonluminescent.[14] They have concluded that the internal conversion from the lowest excited doublet state (D_1) to the ground doublet state (D_0) proceeds as the primary deactivation pathway for D_1 of the radical anions due to the small energy gaps between the D_1 and D_0 states.

It is well-known that *cis* (*c*)−*trans* (*t*) isomerization of stilbene (St) occurs via twisting about the central C=C double bond in the singlet or triplet excited states upon irradiation with UV light.[17] Lewis and co-workers have reported that the stilbene radical cation (St$^{\bullet+}$) does undergo thermal *c* → *t* one-way isomerization via the stilbene dimer radical cation as an intermediate.[18] On the other hand, it is assumed that the photochemical *c* → *t* one-way isomerization of *c*-St$^{\bullet+}$ to *t*-St$^{\bullet+}$ occurs in rigid solid matrices at 77 K[19] and in solution at room temperature on the basis of the laser flash photolysis of *c*-St$^{\bullet+}$ formed using pulse radiolysis in 1,2-dichloroethane[20] or secondary electron transfer in acetonitrile.[21] The photochemical *c* → *t* isomerization has been reported to take place in the second excited doublet state (D_2) but not in the D_1 state of *c*-St$^{\bullet+}$.[20] It is supposed that the energy of the D_2 state is rapidly lowered by twisting from *c*-St$^{\bullet+}$ to *t*-St$^{\bullet+}$ with no minimum at the 90° twisted geometry.[20] On the other hand, it has been reported that the D_2 state exhibits minimum and maximum energies at the 40° and 90° twisted geometries, respectively, against the planar structure (0° twisted geometry) of *c*-St$^{\bullet+}$ in the D_2 state, on the basis of the MO calculations.[22] Because the D_2, D_1, and D_0 states closely lie at the 40° twisted geometry, it is assumed that the D_2 state of *c*-St$^{\bullet+}$ is stabilized by twisting and avoidably crosses with the D_1 state, which leads to the D_0 state of *t*-St$^{\bullet+}$ via an allowed crossing.[21,22]

Characterizations of the St$^{\bullet+}$ D_2 state are necessary in order to elucidate the isomerization mechanism. Because the St$^{\bullet+}$ D_2 state is nonluminescent, the lifetimes must be determined using other experiments such as quenching of the excitation energy or quenching of the hole (hole transfer quenching). Because the St$^{\bullet+}$ D_2 state has a higher oxidation potential than the St$^{\bullet+}$ D_0 state,[1−3] the hole transfer occurs from the St$^{\bullet+}$ D_2 state to an appropriate quencher. In this article, we have identified the selective hole transfer quenching of the St$^{\bullet+}$ D_2 state using anisole (A) and estimated the lifetimes of the St$^{\bullet+}$ D_2 states as well as the 1,2-diphenylcyclo-1-butene radical cation (CB$^{\bullet+}$) as a structurally constrained derivative of *c*-St using a pulse radiolysis−laser flash photolysis combined method.[20,23−25]



Experimental Section

Materials. *c*-St and *t*-St were purchased from Aldrich and Tokyo Kasei and purified by distillation and recrystallization from ethanol before use. Analyses of the purified St using GC showed the purities to be higher than 99.5%. 1,2-Diphenylcyclo-1-butene (CB) was prepared from the acid-catalyzed dehydration of 1-(α-hydroxybenzyl)-1-phenylcyclopropane. 1-Benzoyl-1-phenylcyclopropane was prepared from a reaction of

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benzyl phenyl ketone with 1,2-dibromoethane in the presence of aqueous sodium hydroxide−benzyltriethylammonium chloride according to the literature[26] and then reduced to 1-(α-hydroxybenzyl)-1-phenylcyclopropane by sodium borohydride in methanol. The CB was purified by recrystallization from ethanol: mp 51−52° (lit.[27] mp 51.5−52.5°).

Anisole and *p*-methylanisole were purchased from Tokyo Kasei and were purified by distillation before use. Analyses using GC showed the purities to be higher than 99.5%.

1,2-Dichloroethane (DCE) that was used as a solvent was distilled over calcium hydride. Solutions were freshly prepared in a 1 cm × 1 cm rectangular Suprasil cell before irradiation and were deoxygenated by bubbling with argon through a capillary for 10 min.

Pulse Radiolysis−Laser Flash Photolysis Combined Method. A solution containing *c*-St or *t*-St in DCE (5 mM) was irradiated with an electron pulse and sequentially with a laser flash at a delay time of 10 ns to 1 μs after the electron pulse at room temperature. An electron pulse was obtained from a L-band linear accelerator provided by Osaka University. The energy was 28 MeV, the pulse width was selected as 8 ns (single pulse), the dose was 0.7 kGy pulse^{-1}, and the diameter was approximately 0.4 cm. A flash at 532 nm was obtained using the second-harmonic oscillation from a Nd:YAG laser (Quantel Model Brilliant), which was operated by a large current pulsed-power supply, which was synchronized with the electron pulse. The single laser flash has a diameter of 0.5 cm, 5 ns duration, 100 mJ pulse^{-1}, and an incident photon number of 1.4×10^{18} pulse^{-1} cm^{-2} that was measured using a pyroelectric power meter (Gentec ED-500). The laser beam was sent in the opposite direction of the electron beam through the sample solution. The laser beam intersected the electron beam at an angle of about 20°. An almost collinear arrangement was used, such that the narrow laser beam passed through the central part of the irradiated volume. The probe beam was obtained from a 450 W Xe-lamp (Osram, XBO-450), which was also operated by a large current pulsed-power supply that was synchronized with the electron pulse. The probe beam was passed through an iris with a diameter of 0.2 cm and sent into the sample solution with a perpendicular intersection of the electron and laser beams. Additionally, the probe beam was closely arranged to the entrance side of the laser beam. The probe beam was then focused to a computer-controlled monochromator (CVI Laser, Digikrom-240) with two lenses and four mirrors. The output of the monochromator was monitored using a PMT (photomultiplier tube; Hamamatsu Photonix, R1417 or R2497). The signal from the PMT was recorded on a transient digitizer (Tektronix, 7912AD with plug-ins, 7A19 and 7B92A). The total system control was completed with a microcomputer (Sharp, X-68000), which was connected to all measurement components with a GP-IB interface. The data processing was completed using Igor on a Macintosh computer. To avoid pyrolysis of the sample solution by the probe beam, a suitable cutoff filter was used. An irradiation cell was placed in the beam of the linear accelerator and in front of the beam port at a distance of approximately 15 cm.

The pulse radiolysis−flash photolysis combined method at low temperatures over the range of 140−300 K was performed in the cell that was mounted in a variable-temperature liquid-nitrogen cryostat (Oxford DN1704).

Lifetime Measurements. In order to determine the lifetimes (τ_c and τ_t) of the D_2 states of *c*-St$^{\bullet+}$ and *t*-St$^{\bullet+}$ (*c*-St$^{\bullet+}$* and *t*-St$^{\bullet+}$*), we investigated the hole transfer quenching of St$^{\bullet+}$* using anisole (A);

$$St^{\bullet+}* + A \rightarrow St + A^{\bullet+} \quad (1)$$

where the asterisk denotes the second excitation from the D_0 state to the D_2 state. An analogous study has been reported for the hole transfer quenching of the *trans,trans,trans*-1,6-diphenyl-1,3,5-hexatriene radical cation (DPH$^{\bullet+}$) in the excited states using biphenyl.[13] The quenching of St$^{\bullet+}$* can be induced using a hole transfer quencher, which performs as a hole acceptor for St$^{\bullet+}$* but not for the St$^{\bullet+}$ D_0 state. The hole donor ability of St$^{\bullet+}$* is higher than that of the St$^{\bullet+}$ D_0 state because of the excitation energy of the St$^{\bullet+}$*. When the oxidation potential (E^{ox}) of a molecule is lower than those of *c*-St and *t*-St ($E_{p/2}^{ox}$ = 1.25 and 1.14 V vs Ag/Ag$^+$ in acetonitrile, respectively), the molecule works as a hole acceptor of St$^{\bullet+}$.

Because the $E_{p/2}^{ox}$ = 1.76 V[28] of A is 0.5−0.6 V greater than the $E_{p/2}^{ox}$ of *c*-St and *t*-St, A does not perform as a hole acceptor of the St$^{\bullet+}$ D_0 states. The reduction potentials of St$^{\bullet+}$* are expected to be approximately 2.3 V greater than those of the St$^{\bullet+}$ D_0 states because of the excitation energy of 50−53 kcal mol^{-1}, if the energy remains in St$^{\bullet+}$*. The hole transfer from St$^{\bullet+}$* to A with the rate constant of k_A (eq 1) is considerably exergonic; therefore, it proceeds at the diffusion-controlled rate in DCE, $k_A = k_{diff} = 7.8 \times 10^9$ M^{-1} s^{-1}, as discussed below. Free energy changes (ΔG) associated with the hole transfer can be calculated to be −38 kcal mol^{-1} for *c*-St$^{\bullet+}$* and −39 kcal mol^{-1} for *t*-St$^{\bullet+}$* using the Rehm−Weller equation,[29] where the Coulombic attraction energy is 0 in the process. If the D_1 state of St$^{\bullet+}$ would be formed by fast relaxation of St$^{\bullet+}$*, the hole transfer from the St$^{\bullet+}$ D_1 state, with an excitation energy of approximately 38 kcal mol^{-1}, to A occurs at the diffusion-controlled rate because ΔG = −25 kcal mol^{-1}. Consequently, $k_A\tau_c$ and $k_A\tau_t$ are obtained from the linear Stern−Volmer plots for *c*-St$^{\bullet+}$* and *t*-St$^{\bullet+}$* quenching using A (eq 1), respectively, and τ_c and τ_t are calculated with the assumption that $k_A = k_{diff}$ = 7.8×10^9 M^{-1} s^{-1}.

The pulse radiolysis of A itself in DCE provided radical cations of anisole and the anisole dimer (A$^{\bullet+}$ and $A_2^{\bullet+}$ denoted by Q$^{\bullet+}$), which absorb at around 350 and 450−700 nm and are stable in the time scale of 1 μs.[30] A broad transient absorption spectrum composed of the absorption bands of Q$^{\bullet+}$ and St$^{\bullet+}$ was observed in the pulse radiolysis of *c*-St or *t*-St in the presence of excess A (molar ratios of A and St, 40−220) in which Q$^{\bullet+}$ was initially generated in a major yield together with St$^{\bullet+}$ in a minor yield. The hole transfer from Q$^{\bullet+}$ to St then proceeded,

$$Q^{\bullet+} + St \rightarrow St^{\bullet+} + Q \quad (2)$$

to give St$^{\bullet+}$ with 1.0×10^{-5} M, which was approximately 70% of 1.5×10^{-5} M of St$^{\bullet+}$ after the electron pulse in the absence of A. The rate constant for the hole transfer was evaluated to be 7.8×10^9 M^{-1} s^{-1} from the rise of OD_{480} after the electron pulse (for example Figure 1b, *vide infra*) and found to be equivalent to k_{diff} because of the highly exergonic process.[31]

Disappearance of *t*-St$^{\bullet+}$. In the irradiation of *t*-St$^{\bullet+}$ in the presence of A, Q$^{\bullet+}$ also exists. The $|\Delta OD_\lambda|$ shown in Figure 1b is represented as

$$|\Delta OD_\lambda| = (\epsilon_\lambda^t[t\text{-St}^{\bullet+}]_{disapp} + \epsilon_\lambda^Q[Q^{\bullet+}]_{disapp})l \quad (3)$$

where OD_λ, $|\Delta OD_\lambda|$, ϵ_λ^t ($\epsilon_{480}^t = 6.5 \times 10^4$ M^{-1} cm^{-1} in DCE[32]), ϵ_λ^Q, $[t\text{-St}^{\bullet+}]_{disapp}$, $[Q^{\bullet+}]_{disapp}$, and l denote the optical density at λ nm, the differences of OD_λ before and after the laser flash, the molar absorption coefficients of *t*-St$^{\bullet+}$ and Q$^{\bullet+}$ at λ nm, the molar concentrations of *t*-St$^{\bullet+}$ and Q$^{\bullet+}$ that immediately disappeared after the laser flash, and the optical path length of

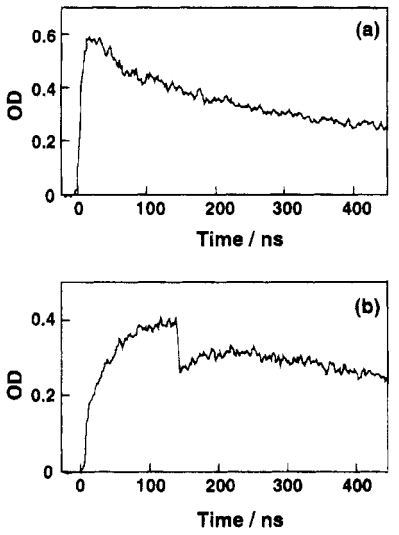


Figure 1. Kinetic traces illustrating the time profile of OD_{480} as a function of time in the pulse radiolysis–laser flash photolysis experiment of *t*-St (5×10^{-3} M) in the absence (a) and presence (b) of A (1 M) in Ar-saturated DCE.

0.4 cm, respectively. Because ϵ_λ^Q and $[Q^{\bullet+}]_{disapp}$ were measured during a separate experiment of $Q^{\bullet+}$ itself under the same conditions, $[t\text{-St}^{\bullet+}]_{disapp}$ was obtained.

Disappearance of *c*-St$^{\bullet+}$ and Formation of *t*-St$^{\bullet+}$. In the irradiation of *c*-St$^{\bullet+}$ in the absence of A, the concentrations of *c*-St$^{\bullet+}$ that immediately disappeared ($[c\text{-St}^{\bullet+}]_{disapp}$) and *t*-St$^{\bullet+}$ formed ($[t\text{-St}^{\bullet+}]_{form}$) after the laser flash were calculated using

$$|\Delta OD_\lambda| = (\epsilon_\lambda^c[c\text{-St}^{\bullet+}]_{disapp} - \epsilon_\lambda^t[t\text{-St}^{\bullet+}]_{form})l \qquad (4)$$

where ϵ_λ^c, $[c\text{-St}^{\bullet+}]_{disapp}$, and $[t\text{-St}^{\bullet+}]_{form}$ denote the absorption molar coefficients of *c*-St$^{\bullet+}$ at λ nm, the molar concentration of *c*-St$^{\bullet+}$ that immediately disappeared, and the molar concentration of *t*-St$^{\bullet+}$ formed after the laser flash. $\epsilon_{515}^c = 1.8 \times 10^4$, $\epsilon_{515}^t = 6.5 \times 10^3$, and $\epsilon_{480}^c = 1.3 \times 10^4$ M^{-1} cm^{-1} were determined from the absorption spectra on the basis of $\epsilon_{480}^t = 6.5 \times 10^4$ M^{-1} cm^{-1}.[32]

In the irradiation of *c*-St$^{\bullet+}$ in the presence of A, $|\Delta OD_\lambda^A|$ is represented by

$$|\Delta OD_\lambda^A| = |(\epsilon_\lambda^c[c\text{-St}^{\bullet+}]_{disapp}^A - \epsilon_\lambda^t[t\text{-St}^{\bullet+}]_{form}^A + \epsilon_\lambda^Q[Q^{\bullet+}]_{disapp})l| \qquad (5)$$

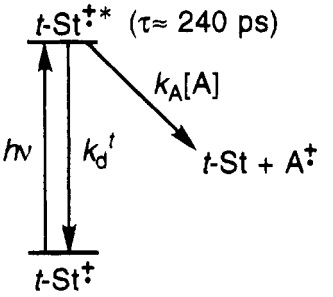
instead of eq 4, where $[c\text{-St}^{\bullet+}]_{disapp}^A$ and $[t\text{-St}^{\bullet+}]_{form}^A$ represent the concentrations of *c*-St$^{\bullet+}$ that disappeared and *t*-St$^{\bullet+}$ formed in the presence of A.

Oxidation Potential Measurements. The half-wave oxidation potentials ($E_{p/2}^{ox}$) of 0.01 M samples were measured with a cyclic voltametry equipped with a potentiostat (Hokuto HA-104) and a function generator (Hokuto HB-107A) in which the reference electrode of $Ag/AgNO_3$, the working electrode of the platinum disk, the pair of platinum wire electrodes, and supporting electrolyte of 0.1 M tetraethylammonium tetrafluoroborate in acetonitrile were used.

Results and Discussion

It is well established that *c*-St$^{\bullet+}$ and *t*-St$^{\bullet+}$ are selectively generated in pulse radiolyses of *c*-St and *t*-St in DCE at room temperature and show absorption bands at 420–580 and 700–850 nm assigned to $D_2 \leftarrow D_0$ and $D_1 \leftarrow D_0$ transitions, respectively, and absorption maxima (λ_{max}) at 515 and 780 for *c*-St$^{\bullet+}$ and 480 and 760 nm for *t*-St$^{\bullet+}$.[20,33,34] The excitation of

SCHEME 1



St$^{\bullet+}$ at 532 nm generates the St$^{\bullet+}$ D_2 states (St$^{\bullet+}$*) with excitation energies of 50 and 53 kcal mol^{-1} for *c*-St$^{\bullet+}$* and *t*-St$^{\bullet+}$*, respectively, that were calculated from the red edges of the absorption bands at 420–580 nm. The asterisk denotes the second excitation from the D_0 state to the D_2 state.

Lifetime and Transient Phenomena of *t*-St$^{\bullet+}$*. The irradiation of *t*-St$^{\bullet+}$ with a laser flash at 532 nm exhibited no change in the transient absorption spectra and time profiles of OD_{480} where *t*-St$^{\bullet+}$ shows an absorption peak (Figure 1a). Therefore, *t*-St$^{\bullet+}$* does not isomerize to the D_0 state of *c*-St$^{\bullet+}$ with the irradiation but decays to the D_0 state of *t*-St$^{\bullet+}$ with the rate constant of internal conversion of *t*-St$^{\bullet+}$* (k_d^t) (Scheme 1).

The irradiation of *t*-St$^{\bullet+}$ in the presence of anisole (A) caused a decrease in the OD_{480} immediately after the flash (Figure 1b). The $|\Delta OD_{480}|$ increased with an increasing concentration of A ([A]). It is obvious that *t*-St$^{\bullet+}$* is quenched by A via hole transfer quenching to give *t*-St and A$^{\bullet+}$ with the bimolecular rate constant of k_A (Scheme 1). The rise of OD_{480} after the laser flash corresponds to the hole transfer from A$^{\bullet+}$ to *t*-St to yield A and *t*-St$^{\bullet+}$ (eq 2),[33] which occurs at the rate constant of 7.8×10^9 M^{-1} s^{-1}, which is equivalent to k_{diff} in DCE.

The chemical yield of $[t\text{-St}^{\bullet+}]_{disapp}$ (Y_{-t}) in the presence of A is represented by

$$Y_{-t} = \frac{[t\text{-St}^{\bullet+}]_{disapp}}{[t\text{-St}^{\bullet+}]_0} = \frac{I_0 k_A[A]}{\tau_t^{-1} + k_A[A]} \qquad (6)$$

where $[t\text{-St}^{\bullet+}]_0 = 1.0 \times 10^{-5}$ M and $[t\text{-St}^{\bullet+}]_{disapp}$ are the molar concentrations of *t*-St$^{\bullet+}$ before irradiation of the laser flash and *t*-St$^{\bullet+}$ that immediately disappeared after the laser flash, I_0 is the efficiency of formation of *t*-St$^{\bullet+}$*, and τ_t^{-1} is the reciprocal of the lifetime of *t*-St$^{\bullet+}$* and defined as $\tau_t^{-1} = k_d^t$. According to eq 6, the Stern–Volmer plots of Y_{-t}^{-1} vs $[A]^{-1}$ produced a linear line with an intercept of I_0^{-1} and a slope of $I_0^{-1}k_A^{-1}\tau_t^{-1}$ (Figure 2). Consequently, $I_0 = 0.36$ is obtained, while τ_t and k_d^t were calculated to be approximately 240 ± 50 ps and $(4.1 \pm 1.1) \times 10^9$ s^{-1}, respectively, on the basis that $k_A = k_{diff} = 7.8 \times 10^9$ M^{-1} s^{-1}, as discussed below.

It is known that the electron transfer rate between the donor and acceptor molecules increases with a decrease in the viscosity and an increase in the polarizability of the medium.[35,36] The addition of A up to 2 M may influence the hole transfer from St$^{\bullet+}$* to A due to the changing solvent properties such as the viscosity and the polarizability.[37] Because a radical cation and a neutral molecule are reactants and products, the interaction between the radical cation and solvent is not influenced in the hole transfer from St$^{\bullet+}$* to A. The rate constant of 7.8×10^9 M^{-1} s^{-1} that was equivalent to k_{diff} in DCE was observed in the hole transfer from A$^{\bullet+}$ to *t*-St to yield A and *t*-St$^{\bullet+}$ with a large exothermicity. The absorption spectrum of St$^{\bullet+}$ in the presence of 2 M A is identical to that in the absence of A, which indicates that there is no significant interaction between St$^{\bullet+}$ and A. Moreover, it is reported that solvent effects on the

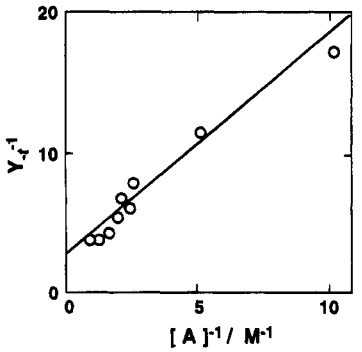


Figure 2. Plots of Y_{-t}^{-1} vs $[A]^{-1}$ in the irradiation of t-St$^{\bullet+}$ in the presence of A.

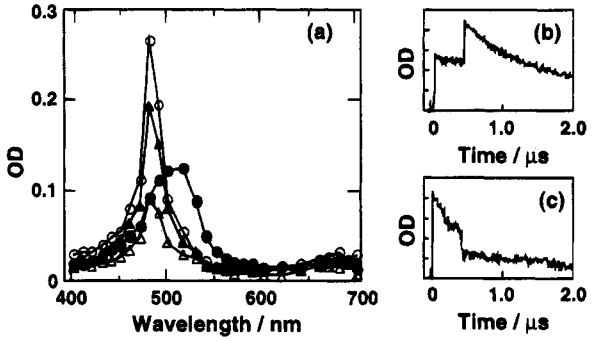


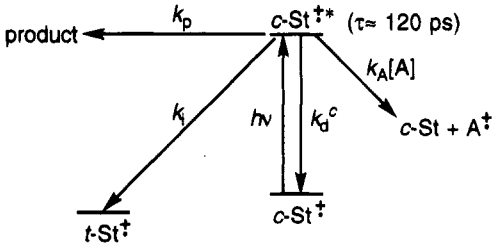
Figure 3. Transient absorption spectra recorded before the laser flash (○) and immediately after (●) and 200 ns (△) and 1 μs (▲) after the laser flash in the pulse radiolysis–laser flash photolysis experiment of c-St (5×10^{-3} M) in Ar-saturated DCE (a). Kinetic traces illustrating the time profiles of OD_{480} (b) and OD_{515} (c) as a function of time after the electron pulse.

electron transfer processes will be observed only when $\Delta G > -10$ kcal mol^{-1}.[29,36] If so, the solvent effects do not appear upon hole transfer from St$^{\bullet+}$* to A with a large exothermicity of $\Delta G = -25$ kcal mol^{-1}. This, together with a linear Stern–Volmer plot for the hole transfer over the range 0.05–2 M A, suggests that the hole transfer from St$^{\bullet+}$* to A occurs at k_{diff} in DCE.[38]

On the other hand, it is found that electron transfer rates at a higher concentration of quencher are greater relative to that measured at a lower concentration in the electron transfer quenching of triplet benzophenone using several amines at 1 M[36,39] as well as singlet excited t-St using fumaronitrile at 1–5 M.[40] Similarly, it may be considered that the hole transfer from St$^{\bullet+}$* to A in the first solvent shell occurs much faster than the diffusion-controlled rate because a large fraction of St$^{\bullet+}$* should have an A within the first solvent shell at the higher concentration of A.[41] In addition to diffusion-controlled electron transfer, long-range electron transfer between an excited molecule and a quencher in the outer solvent shells contributes in several cases.[42] These possibilities cannot be eliminated in the hole transfer from St$^{\bullet+}$* to A. However, no evidence was obtained for the hole transfer occurring faster than the diffusion-controlled rate. At present, k_{diff} in DCE should be assumed for k_A.[43]

Lifetime and Transient Phenomena of c-St$^{\bullet+}$*. Contrary to t-St$^{\bullet+}$*, $c \rightarrow t$ one-way isomerization of c-St$^{\bullet+}$* to t-St$^{\bullet+}$ was observed within a laser flash. The analogous results have been reported by Ebbesen[20] and Tokumaru and his co-workers.[21] Figure 3 shows the transient spectral changes and the time profiles of OD at 515 and 480 nm, where c-St$^{\bullet+}$ and t-St$^{\bullet+}$ show the absorption peaks, respectively.[28] The concentrations of $[c\text{-St}^{\bullet+}]_{disapp} = 1.2 \times 10^{-5}$ M and $[t\text{-St}^{\bullet+}]_{form} = 8.9 \times 10^{-6}$ M that were calculated from eq 4 demonstrate that the photochemical conversion of c-St$^{\bullet+}$ per flash is approximately (80 ± 15)%

SCHEME 2



on the basis of concentrations of c-St$^{\bullet+}$ before irradiation of the laser flash ($[c\text{-St}^{\bullet+}]_0 = 1.5 \times 10^{-5}$ M), that the chemical yield of t-St$^{\bullet+}$ from the D_2 state of c-St$^{\bullet+}$ is approximately (75 ± 15)% per flash, and that isomerization of c-St$^{\bullet+}$ to t-St$^{\bullet+}$ proceeds as the main process. Because only the decay of c-St$^{\bullet+}$ and formation of t-St$^{\bullet+}$ were observed in Figure 3, the remaining (25 ± 15)% of c-St$^{\bullet+}$ that disappeared is considered to convert to c-St, t-St, or a radical cation as a product showing little or weak absorption obscured by the strong absorption bands of t-St$^{\bullet+}$ and c-St$^{\bullet+}$ over the range 400–700 nm. An electrocyclic product such as dihydrophenanthrene is assumed as an intermediate of phenanthrene that is formed as an oxidation product in the photolysis of c-St.[44]

The number of laser photons absorbed by c-St$^{\bullet+}$ that were generated in the pulse radiolysis was 3.0×10^{-5} Einstein L^{-1} from $OD_{532} = 0.13$ for c-St$^{\bullet+}$ for the laser beam path (1.0 cm) using an actinometry of T–T absorption of zinc tetraphenylporphyrin at 470 nm in cyclohexane ($\epsilon_T\phi_T = 50\,000$ M^{-1} cm^{-1} at 470 nm).[20] The quantum yield of photochemical $c \rightarrow t$ isomerization of c-St$^{\bullet+}$ to t-St$^{\bullet+}$ was then determined to be 0.65 ± 0.15 from c-St$^{\bullet+}$ that disappeared (ϕ_{-c}) and 0.49 ± 0.12 from t-St$^{\bullet+}$ formed (ϕ_t). Taking into account ϕ_{-c} and ϕ_t as well as the conversion of (80 ± 15)% for c-St$^{\bullet+}$ per laser flash, c-St$^{\bullet+}$* isomerizes to t-St$^{\bullet+}$ at (49 ± 12)%, converts to other products at (16 ± 4)%, and deactivates to c-St$^{\bullet+}$ at (35 ± 8)% yield.

The quantum yield was found to be almost constant at various numbers of laser photons that were absorbed by c-St$^{\bullet+}$ over the range 3.0×10^{-6} to 3.0×10^{-5} Einstein L^{-1}. This result excludes the two photon processes as well as sequential processes of products that are primarily formed with consecutive photoabsorption during a laser flash. The quantum yield was almost constant at various temperatures over the range 140–300 K ($\phi_{-c} = 0.65 \pm 0.20$ and $\phi_t = 0.49 \pm 0.15$).

In order to determine τ_c, the irradiation of c-St$^{\bullet+}$ was completed in the presence of A. The transient phenomena of c-St$^{\bullet+}$* that involved the isomerization and hole transfer quenching of c-St$^{\bullet+}$* using A are shown in Scheme 2. The Stern–Volmer equations for ϕ_t and ϕ_{-c} are represented in

$$\frac{\phi_t}{\phi_t^{A}} = 1 + k_A\tau_c[A] \tag{7}$$

$$\frac{\phi_{-c}}{\phi_{-c}^{A}} = \frac{k_i + k_p}{k_i + k_p + k_d^{c}}\left(1 + \frac{k_d^{c}}{k_i + k_p + k_A[A]}\right) \tag{8}$$

respectively, where ϕ_t^A, ϕ_{-c}^A, k_i, k_p, and k_d^c denote the quantum yields of c-St$^{\bullet+}$ that disappeared and t-St$^{\bullet+}$ formed in the presence of A, and the rate constants of isomerization of c-St$^{\bullet+}$* to t-St$^{\bullet+}$, conversion of c-St$^{\bullet+}$* to another product, and internal conversion of c-St$^{\bullet+}$* with the definition of $k_i + k_p + k_d^c = \tau_c^{-1}$. According to eq 7, the Stern–Volmer plots of ϕ_t/ϕ_t^A vs [A] gave a linear line with an intercept of 1.0 and a slope of $k_A\tau_c$ (Figure 4). The value of τ_c was calculated to be

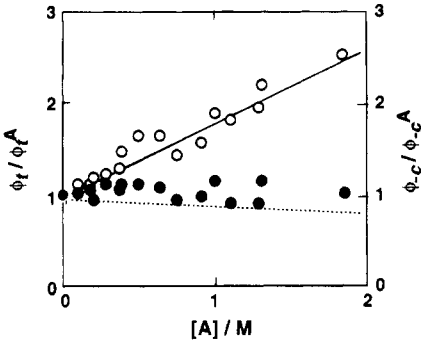


Figure 4. Plots of ϕ_t/ϕ_t^A (○) and ϕ_{-c}/ϕ_{-c}^A (●) vs [A] in the irradiation of *c*-St$^{\bullet+}$ in the presence of A. The solid line for the plot of ϕ_t/ϕ_t^A vs [A] was calculated using the least-squares method, while the broken line for the plot of ϕ_{-c}/ϕ_{-c}^A vs [A] was calculated using eq 8 with $k_i = 4.1 \times 10^9$ s^{-1}, $k_d^c = 2.9 \times 10^9$ s^{-1}, $k_p = 1.3 \times 10^9$ s^{-1}, and $k_A = k_{diff} = 7.8 \times 10^9$ M^{-1} s^{-1}.

approximately 120 ± 30 ps and found to be one-half of τ_t, and k_A was assumed to be equal to $k_{diff} = 7.8 \times 10^9$ M^{-1} s^{-1}. Because the ratios of $(k_i + k_p)/k_d^c = 1.9$ and $k_i/k_p = 3.1$ are estimated from $\phi_{-c} = 0.65 \pm 0.15$ and $\phi_t = 0.49 \pm 0.12$, k_i, k_p, and k_d^c are determined to be $(4.1 \pm 1.0) \times 10^9$, $(1.3 \pm 0.3) \times 10^9$, and $(2.9 \pm 0.7) \times 10^9$ s^{-1}, respectively. Therefore, the Stern–Volmer plot of ϕ_{-c}/ϕ_{-c}^A vs [A] was calculated from eq 8 with the values of k_i, k_p, and k_d^c and found to be almost consistent with the experimental plots within experimental error (Figure 4).

It should be mentioned that excitation of *c*-St$^{\bullet+}$ and deactivation of *c*-St$^{\bullet+}$* repeat during a laser flash because of the shorter τ_c than 5 ns duration of the laser flash. In other words, *c*-St$^{\bullet+}$ regenerated via deactivation of *c*-St$^{\bullet+}$* is re-excited to *c*-St$^{\bullet+}$*, which affords isomerization and conversion to another product within a laser flash (5 ns). Thus, it is proposed that $\phi_{-c} = 0.65 \pm 0.15$ is less than the conversion of *c*-St$^{\bullet+}$ per flash (80% ± 15%). On the other hand, it is suggested that the sequential processes of *t*-St$^{\bullet+}$ and the other product that were initially formed do not considerably participate during a laser flash, because the quantum yields (ϕ_t and ϕ_{-c}) are independent of the number of laser photons absorbed by *c*-St$^{\bullet+}$. The smaller value of $\epsilon_{532}^t = 6.3 \times 10^3$ M^{-1} cm^{-1} than $\epsilon_{532}^c = 1.1 \times 10^4$ M^{-1} cm^{-1} at the laser wavelength shows that *c*-St$^{\bullet+}$ is predominantly excited and the participation of consecutive excitation of *t*-St$^{\bullet+}$ that was formed with isomerization is negligibly small especially at lower conversions. Because τ_c is shorter than τ_t, the hole transfer quenching of *t*-St$^{\bullet+}$* using A could not participate in the irradiation of *c*-St$^{\bullet+}$.

Lifetime and Transient Phenomena of CB$^{\bullet+}$*. The measurement of the lifetime of the D_2 state with the hole transfer quenching was examined for the D_2 state of 1,2-diphenylcyclo-1-butene radical cation (CB$^{\bullet+}$*). Because CB has a rigid planar structure with the *c*-St chromophore structually constrained by the cyclobutene ring and is stable for geometrical isomerizations, CB$^{\bullet+}$ is expected to have the same rigid planar structure as CB. Pulse radiolysis in a DCE solution of CB produces CB$^{\bullet+}$, which shows absorption bands at 420–560 and 700–850 nm that are assigned to $D_2 \leftarrow D_0$ and $D_1 \leftarrow D_0$ transitions, respectively, as the absorption bands of *t*-St$^{\bullet+}$ and *c*-St$^{\bullet+}$.[20,33,34] The excitation of CB$^{\bullet+}$ at 532 nm generates CB$^{\bullet+}$* with an excitation energy of 51 kcal mol^{-1}, which is determined from the red edges of the band at $\lambda_{max} = 490$ nm. However, the irradiation of CB$^{\bullet+}$ with a laser flash at 532 nm exhibited no change in the transient absorption spectra and the time profiles of OD_{480} (Figure 5a). Therefore, CB$^{\bullet+}$* is deactivated to the D_0 state of CB$^{\bullet+}$ within the laser flash, which is similar to *t*-St$^{\bullet+}$* (Scheme 1).

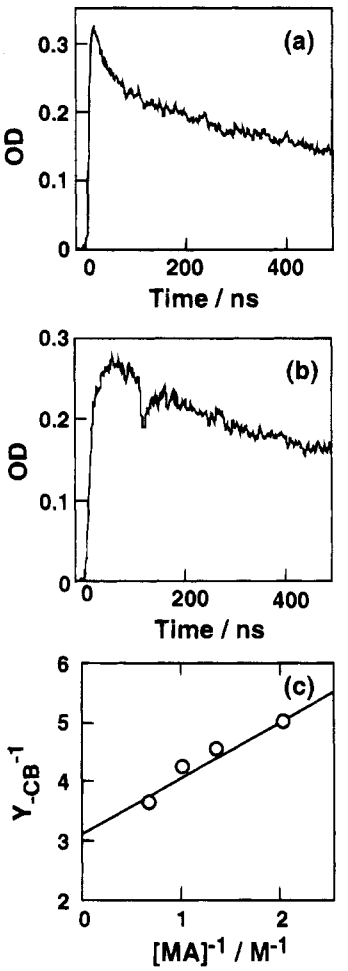
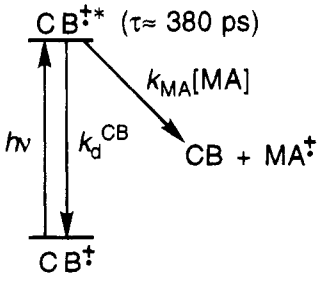


Figure 5. Kinetic traces illustrating the time profile of OD_{480} as a function of time in the pulse radiolysis–laser flash photolysis experiment of CB (1×10^{-2} M) in the absence (a) and presence (b) of MA (1 M) in Ar-saturated DCE. Plots of the reciprocal of the chemical yield of CB that disappeared (Y_{-CB}^{-1}) vs $[A]^{-1}$ (c).

SCHEME 3



The irradiation of CB$^{\bullet+}$ in the presence of A caused a decrease in the absorption bands immediately after the flash. Similarly, the irradiation of CB$^{\bullet+}$ in the presence of *p*-methylanisole (MA) also caused a decrease in OD_{480} immediately after the flash (Figure 5b). Because MA$^{\bullet+}$ shows no absorption above the range 400–700 nm,[30] the decrease in OD_{480} ($|\Delta OD_{480}|$) is due to the decrease in CB$^{\bullet+}$. The $|\Delta OD_{480}|$ increased with an increasing [MA]. It is obvious that CB$^{\bullet+}$* is quenched by MA via hole transfer quenching to give CB and MA$^{\bullet+}$ (Scheme 3).

In the presence of MA, MA$^{\bullet+}$ is initially generated immediately after the electron pulse[30] and is followed by the formation of CB$^{\bullet+}$ via hole transfer from MA$^{\bullet+}$ to CB. The increase in the OD_{480} after the laser flash also corresponds to the formation of CB$^{\bullet+}$ via hole transfer from MA$^{\bullet+}$ to CB. The rate constant for the hole transfer (k_{MA}) was evaluated to be

TABLE 1: Properties of Radical Cations in the D_2 State: Lifetime, Rate Constants for Internal Conversion (k_d), $c-t$ Isomerization (k_i), and Product Formation (k_p), and Excitation Energy

radical cations in D_2	t-St$^{\bullet+}$*	c-St$^{\bullet+}$*	CB$^{\bullet+}$*
lifetime (ps)	240 ± 50	120 ± 30	380 ± 30
k_d (s^{-1})	(4.1 ± 1.1) × 10^9	(2.9 ± 0.7) × 10^9	(2.6 ± 0.2) × 10^9
k_i (s^{-1})	0	(4.1 ± 1.0) × 10^9	0
k_p (s^{-1})	0	(1.3 ± 0.3) × 10^9	0
excitation energy (kcal mol^{-1})	53	50	51

7.8×10^9 M^{-1} s^{-1} from the increases in the OD_{480} (Figure 5b) and equivalent to k_{diff} because of the highly exergonic process.[31]

The Stern−Volmer equation for the chemical yield of CB$^{\bullet+}$ that disappeared (Y_{-CB}) in the presence of MA is represented by an equation similar to eq 6, because CB$^{\bullet+}$* decays to the D_0 state of CB$^{\bullet+}$ or is quenched using MA via the hole transfer quenching within a laser flash. From the Stern−Volmer plots of $Y_{-CB}{}^{-1}$ vs $[MA]^{-1}$ (Figure 5c), the lifetime of CB$^{\bullet+}$* (τ_{CB}) and the rate constant of internal conversion of CB$^{\bullet+}$* ($k_d{}^{CB}$) were calculated to be 380 ± 30 ps and (2.6 ± 0.2) × 10^9 s^{-1}, respectively, and k_{MA} was assumed to be equal to the diffusion-controlled rate constant of $k_{diff} = 7.8 \times 10^9$ M^{-1} s^{-1}, as previously discussed. Consequently, it is summarized that τ_{CB} is longer than τ_c and τ_t, whereas $k_d{}^{CB}$ is comparable with $k_d{}^c$ and $k_d{}^t$ (Table 1).

Comparison of Lifetimes of c-St$^{\bullet+}$*, t-St$^{\bullet+}$*, and CB$^{\bullet+}$*. Similar to most radical cations in the excited state, c-St$^{\bullet+}$*, t-St$^{\bullet+}$*, and CB$^{\bullet+}$* are nonluminescent. Isomerization of c-St$^{\bullet+}$* to t-St$^{\bullet+}$, which proceeds via twisting about the central C=C double bond as a main process as well as conversion to another product as a minor process, competes with the internal conversion of c-St$^{\bullet+}$*. However, t-St$^{\bullet+}$* and CB$^{\bullet+}$* are deactivated to the D_0 state without any other reactions. Although t-St$^{\bullet+}$* could slightly twist about the C=C double bond, it does not isomerize to c-St$^{\bullet+}$. The twisting about the C=C double bond is faster in c-St$^{\bullet+}$* than in t-St$^{\bullet+}$* due to the interactions between the phenyl groups of c-St. Because twisting about the C=C double bond is severely hindered by structural constraints in CB, CB is unable to change its initial planar rigid structure. Both CB$^{\bullet+}$* and the D_0 state of CB$^{\bullet+}$ probably have the rigid planar structure. The energy levels of c-St$^{\bullet+}$*, t-St$^{\bullet+}$*, and CB$^{\bullet+}$* are assumed to be almost equivalent because of the similar $E_{p/2}{}^{ox}$ values for c-St, t-St, and CB as well as the similar excitation energies of c-St$^{\bullet+}$*, t-St$^{\bullet+}$*, and CB$^{\bullet+}$* (Table 1). It is suggested that c-St$^{\bullet+}$*, t-St$^{\bullet+}$*, and CB$^{\bullet+}$* exist in potential minima and that the order $\tau_c < \tau_t < \tau_{CB}$ (Table 1) is attributed to the isomerization and conversion to another product via twisting about the central C=C double bond only in c-St$^{\bullet+}$*. It is clear that twisting is favorable in c-St$^{\bullet+}$*, slightly favorable in t-St$^{\bullet+}$*, but not at all in CB$^{\bullet+}$*.

The lifetime of the *trans,trans,trans*-1,6-diphenyl-1,3,5-hexatriene radical cation (DPH$^{\bullet+}$) in the excited state has been estimated to be longer than 430 ps from the hole transfer quenching by biphenyl[13] and is on the same order of magnitude as but longer than τ_t, τ_c, and τ_{CB} in the range 120−380 ps (Table 1). The difference is probably related to the structural change between DPH$^{\bullet+}$ in the D_0 states and DPH$^{\bullet+}$ in the excited states and the slower internal conversion and $t \rightarrow c$ isomerization of DPH$^{\bullet+}$ in the excited state than those of c-St$^{\bullet+}$*, t-St$^{\bullet+}$*, and CB$^{\bullet+}$*.

It should be noted again that the τ values (Table 1) are calculated from $k_A\tau$ assuming that $k_A = k_{diff}$ in DCE, because of several experimental results such as the linear Stern−Volmer plots over the range 0.05−2 MA (Figures 2 and 4). However, the hole transfer quenching in the first solvent shell may occur at a rate greater than the diffusion-controlled rate at high concentration,[36,39,40] while the long-range hole transfer may occur from St$^{\bullet+}$* to A in the outer solvent shell.[42] If so, τ values could be shorter. It is necessary to directly determine τ and k_A from the transient phenomena of radical cations in the excited state. Therefore, questions on the rate of hole transfer from St$^{\bullet+}$* are open for discussion.

Comparison of Transient Phenomena of c-St$^{\bullet+}$*, t-St$^{\bullet+}$*, and CB$^{\bullet+}$*. The transient phenomena of c-St$^{\bullet+}$*, t-St$^{\bullet+}$*, and CB$^{\bullet+}$* are considerably different from those of c-St, t-St, and CB in the singlet excited states (S_1) with excitation energies of approximately 85 kcal mol^{-1}. Twisting about the C=C double bond brings S_1 of c-St and t-St to a geometry that is favorable for radiationless conversion to S_0. Interactions between the phenyl groups of c-St provide the molecule with an inherent torque and tendency to twist about the C=C double bond faster than for t-St.[45] Therefore, the fluorescence quantum yield of 8 × 10^{-5} for c-St in S_1[46a] is significantly small compared with 0.035−0.038[46b] or 0.040[46c] for t-St in S_1 in hexane. On the other hand, S_1 of CB decays to S_0 via fluorescent transition with a quantum yield of 1.0 because of the planar rigid structure even in S_1.[47] Because the $S_1 \rightarrow S_0$ transitions occur much faster than the $D_2 \rightarrow D_0$ transitions, the lifetimes of 1.0[46a,48] and 70−83 ps[46c,49] for c-St and t-St in S_1 are much shorter than τ_t, τ_c, and τ_{CB} listed in Table 1. It is clearly suggested that the transient phenomena of radical cations in the D_2 state cannot be assumed on the basis of those of neutral molecules in S_1. It is necessary to obtain the direct data of radical cations in the excited states in order to elucidate the transient phenomena.

Judging from $\tau_c \approx 120$ ps and $\tau_t \approx 240$ ps together with the above discussion, a diabatic process is proposed for the isomerization of c-St$^{\bullet+}$* to t-St$^{\bullet+}$. Tokumaru and co-workers have proposed the analogous process in which c-St$^{\bullet+}$* avoidably crosses with the D_1 state of c-St$^{\bullet+}$, followed by an allowed crossing to the D_0 state of t-St$^{\bullet+}$ at the 40° twisted geometry against a planar c-St$^{\bullet+}$* where the D_2, D_1, and D_0 states closely lie, on the basis of MO calculations.[21,22] Because the quantum yield of isomerization did not depend on temperatures over the range 140−300 K ($\phi_{-c} = 0.65 \pm 0.20$ and $\phi_t = 0.49 \pm 0.15$), an adiabatic isomerization of c-St$^{\bullet+}$* to t-St$^{\bullet+}$* could be supposed. If so, c-St$^{\bullet+}$* has such a shallow potential minimum that isomerization proceeds much faster than internal conversion ($k_i > k_d{}^c$) with a quantum yield of 1.0, and the energy level of St$^{\bullet+}$* is lowered by the twisting of the C=C double bond from c-St$^{\bullet+}$* to t-St$^{\bullet+}$* with no minimum at a twisted geometry, as proposed by Ebbesen.[20] However, $\phi_{-c} = 0.65 \pm 0.15$, $\phi_t = 0.49 \pm 0.12$, $k_i = (4.1 \pm 1.0) \times 10^9$ s^{-1}, $k_p = (1.3 \pm 0.3) \times 10^9$ s^{-1}, and $k_d{}^c = (2.9 \pm 0.7) \times 10^9$ s^{-1} and the energy levels of c-St$^{\bullet+}$* and t-St$^{\bullet+}$* are almost equivalent because of the similar values of $E_{p/2}{}^{ox}$ for c-St and t-St as well as the similar excitation energies of c-St$^{\bullet+}$* and t-St$^{\bullet+}$*.

The barrier for the twisting of c-St$^{\bullet+}$* is estimated to be 0.32 kcal mol^{-1}, if the k_i values are assumed to be 5.3 × 10^9 s^{-1} for the largest limit and 2.9 × 10^9 s^{-1} for the smallest limit at 300 and 140 K, respectively, on the basis of the error limits (±30%) for ϕ and k_i. This suggests that c-St$^{\bullet+}$* is stabilized by twisting at a shallow potential minimum and that conversion to another product can compete with isomerization. Consequently, the diabatic isomerization from c-St$^{\bullet+}$* to t-St$^{\bullet+}$ as shown in Scheme 2 is strongly expected to take place via an avoidable crossing from the D_2 state of c-St$^{\bullet+}$* to the D_1 state, and then to the D_0 state of t-St$^{\bullet+}$ with a small barrier.

Conclusions

We have found that A and MA act as selective hole quenchers for $St^{\bullet+}$* and $CB^{\bullet+}$* via hole transfer quenching. The τ_c and τ_t are estimated to be approximately 120 and 240 ps, respectively, which are shorter than 380 ps of $CB^{\bullet+}$* (Table 1). The order $\tau_c < \tau_t < \tau_{CB}$ is attributed to the isomerization via twisting about the central C=C double bond only in c-$St^{\bullet+}$*, because twisting is favorable in c-$St^{\bullet+}$*, slightly favorable in t-$St^{\bullet+}$*, but not at all in $CB^{\bullet+}$*. It is also suggested that diabatic isomerization from c-$St^{\bullet+}$* to t-$St^{\bullet+}$ proceeds via an avoidable crossing of the D_2, D_1, and D_0 states. This method to determine the lifetimes of radical cations in the excited states, with the rate constant of the hole transfer to be assumed equal to k_{diff}, can be essentially applied to any radical cations and even to nonreactive radical cations, although it is necessary to find an appropriate molecule as a selective hole quencher. Moreover, the lifetimes of the radical cations in the excited state must be longer than about 50 ps, because the concentration of A is 2 M at the maximum to keep the solvent property.

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