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Effects of Sensitizer Spin Multiplicity on Electron-Transfer Initiated Isomerization of cis-Stilbene

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The excited singlet and triplet states of 2,4,6-triphenylpyrylium were quenched by cis- and trans-stilbene to generate their radical cations; however, isomerization of stilbene occurred through radical cations only when the triplet state of the sensitizer was quenched by the cis isomer.

Photoinduced electron-transfer reactions have received current interest, and many electron-transfer sensitizers have been used not only in synthetic but also in mechanistic studies.[1)] Isomerization of olefins is also induced by electron-transfer sensitizers such as 9,10-dicyanoanthracene (DCA)[2)] and duroquinone.[3)] A photostationary trans isomer composition as high as 96% was reported in 2,4,6-triphenylpyrylium-induced isomerization of stilbene;[4)] however, pyrylium salts are among rather less studied sensitizers,[5)] and the isomerization mechanism is far less explained.

We now wish to report that 2,4,6-triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$) acquires, in both excited singlet and triplet states, an electron from ground-state cis- (CS) and trans-stilbene (TS), but that the efficiency of electron transfer induced cis→trans isomerization is highly dependent upon the spin multiplicity of the sensitizer. We believe that TPP^+ is an appropriate sensitizer for the study on such multiplicity effects on chemical processes since coulombic forces inherent in oppositely charged species generated in electron transfer between neutral molecules can be neglected in TPP^+-induced electron transfer.

$TPP^+BF_4^-$ fluoresces efficiently in MeCN, the quantum yield (Φ_f) being determined to be 0.51 by using 9-cyanoanthracene (CNA) as a standard,[6)] and the lifetime (τ_S) to be 4.2 ns by single photon counting.[5)] The fluorescence was quenched by CS, TS, and azulene (Az) at nearly diffusion controlled rates (k_q^S, Table 1).

Laser flash photolysis (LFP) of TPP^+ (1.8×10^{-5} M, M = mol dm^{-3}) in MeCN with 406-nm laser pulses [excimer laser(XeCl, 308 nm)-pumped dye laser (DPS), 10-ns fwhm] resulted in a transient absorption with λ_{max} at 490 and 830 nm, which was reasonably assigned to the T-T absorption of TPP^+ on the basis of the fact that it was quenched by CNA accompanied by a rise-up of CNA T-T absorption (λ_{max} 440 nm).[7)] The triplet lifetime (τ_T) of TPP^+ was determined as 14 μs by monitoring the T-T absorption at 830 nm under argon. CS, TS, and Az also quenched the T-T absorption at almost diffusion controlled rates (k_q^T, Table 1).

The free energies (ΔG) of electron transfer from CS and TS to singlet and triplet TPP^+ are estimated to be highly exothermic in MeCN according to Weller's

Table 1. Physical and Kinetic Parameters for TPP^+, CS, TS, and Az

	E_S/eV	E_T/eV	E_{ox}/V	E_{red}/V	$k_q^S/M^{-1}s^{-1}$	$k_q^T/M^{-1}s^{-1}$	ΔG_S/eV	ΔG_T/eV
TPP^+	2.8	2.3		-0.35				
CS		2.5	1.59		2.3×10^{10}	1.3×10^{10}	-0.92	-0.42
TS		2.1	1.49		2.9×10^{10}	1.5×10^{10}	-1.02	-0.52
Az		1.7	0.95		5.5×10^{10}	1.9×10^{10}	-1.56	-1.06

equation (Eq. 1,[8] Table 1). Actually, on quenching of singlet or triplet TPP^+ by various concentrations of TS and Az, the corresponding pyryl radicals $TPP^{\cdot}$ (λ_{max} 550 nm) were formed as observed by LFP.

$$\Delta G_{S,T} = - E_{S,T}(A) - E_{red}(A) + E_{ox}(D) \quad (1)$$
$$\Phi_q^S = k_q^S\tau_S[CS]/(1+k_q^S\tau_S[CS]) \quad (2)$$
$$\Phi_q^T = \Phi_{isc}x\{1/(1+k_q^S\tau_S[CS])\}x\{k_q^T\tau_T[CS]/(1+k_q^T\tau_T[CS])\} \quad (3)$$

The apparent quantum yields for TPP^+-sensitized cis→trans isomerization ($\Phi_{c\rightarrow t}$) of CS were measured in varying [CS] (9.4×10^{-4}-8.4×10^{-2} M) on steady irradiation at 405 nm using potassium tris(oxalato)ferrate(III) actinometry. Under these conditions the quantum yields for quenching of singlet (Φ_q^S, Eq. 2) and triplet TPP^+ (Φ_q^T, Eq. 3) varied from 0.083 to 0.89 and from 0.45 to 0.054, respectively, where it is assumed that deactivation of TPP^+ singlets in the absence of quencher is due to fluorescence emission and intersystem crossing, i.e., $\Phi_{isc} + \Phi_f = 1$. Interestingly $\Phi_{c\rightarrow t}$ increased with decreasing [CS] (i.e., with increasing Φ_q^T), indicating that the isomerization takes place more efficiently in triplet quenching than in singlet quenching. Figure 1 indicates a linear relationship between $\Phi_{c\rightarrow t}$ and Φ_q^T and extrapolation to $\Phi_q^T = 0$ and 1 gives 0.003 and 0.11, respectively, as the limiting $\Phi_{c\rightarrow t}$ values. This means that the c→t isomerization results from interaction with triplet TPP^+, but not from that with singlet TPP^+.

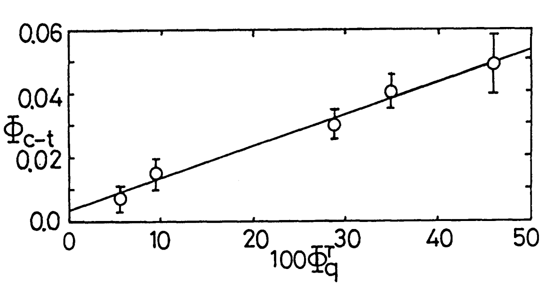


Fig. 1. Isomerization Quantum Yields of CS in Varying Quantum Yields of Triplet TPP^+ Quenching.

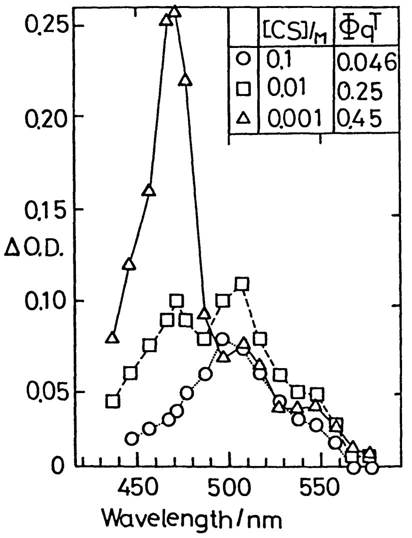
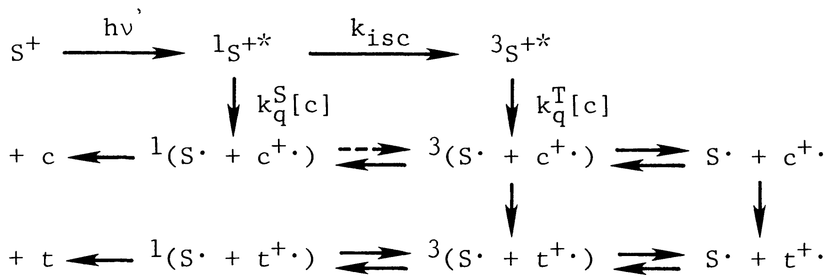


Fig. 2. Transient Absorption Spectra on TPP^+-Sensitized Excitation of CS in Varying Concentrations.



Scheme 1.

On LFP of TPP^+ in the presence of varying [CS] (0.001-0.1 M), the transient absorption ascribable to $TS^{+\cdot}$ (λ_{max} 475 nm) and $CS^{+\cdot}$ (λ_{max} 515 nm) was observed in varying intensities accompanied by the $TPP\cdot$ absorption of almost constant intensity immediately (ca. 1 μs) after laser excitation (Fig. 2). (LFP of TPP^+ with TS under similar conditions exhibited only the transient absorption due to $TS^{+\cdot}$ and $TPP\cdot$.) Under these conditions Φ_q^S and Φ_q^T varied from 0.088 to 0.91 and from 0.45 to 0.046, respectively. The CS concentration dependence of the $TS^{+\cdot}$ yield, as estimated from the transient absorption intensity, is in qualitative agreement with the concentration dependence of $\Phi_{c\rightarrow t}$. These results also indicate that the efficiency of c→t isomerization is associated with the multiplicity of sensitizer.

In the presence of Az, which has an oxidation potential of 0.95 V to be able to transfer an electron to $CS^{+\cdot}$ and $TS^{+\cdot}$, $\Phi_{c\rightarrow t}$ decreased with increasing [Az] (0-9.5×10^{-5} M) and reached a nearly constant value, as shown in Fig. 3, where [CS] = 4.2×10^{-3} M. At this [CS], $\Phi_q^S = 0.29$ and $\Phi_q^T = 0.35$. In the presence of less than 10^{-4} M of Az, more than 98% of triplet TPP^+ is quenched by CS, and, accordingly, a main role of Az must be played in quenching of $CS^{+\cdot}$ and $TS^{+\cdot}$.

On the basis of these results we propose isomerization processes shown in Scheme 1, where $S^+ = TPP^+$, t = TS, and c = CS. In this scheme, quenching of the sensitizer singlets ($^1S^{+*}$) by CS (c) affords the singlet pairs of $S\cdot$ and $c^{+\cdot}$, which undergo rapid back electron transfer to recover the starting S^+ and c without undergoing in-cage $c^{+\cdot}\rightarrow t^{+\cdot}$ isomerization. On the other hand, the triplet pairs of the same components generated from quenching of the sensitizer triplets ($^3S^{+*}$) can convert to the triplet $S\cdot + t^{+\cdot}$ ($TS^{+\cdot}$) 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 $c^{+\cdot}$ also isomerizes to $t^{+\cdot}$, which accepts subsequently an electron from $S\cdot$ to afford t (TS) finally. Formation of the sensitizer or olefin triplets through back electron transfer in the triplet pairs is improbable because of its endothermicity. Energy transfer from triplet TPP^+ plays no important role in the c→t isomerization, since the energy transfer is exothermic to TS, but endothermic to CS (Table 1). The fraction of $\Phi_{c\rightarrow t}$ unquenchable by Az reflects the in-cage isomerization of the triplet pairs.

The photostationary [c]/[t] ratio in the present isomerization was found to be 15/85 independent of the CS concentration. This value is significantly lower than that reported for DCA sensitization, 1.2/98.8.[2b] The difference may be due to participation of an energy transfer mechanism, particularly to contribution of triplet t→c isomerization at the photostationary state in the present case.

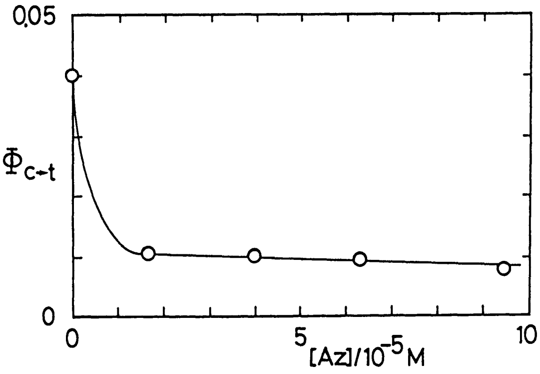


Fig. 3. Isomerization Quantum Yields of CS in the Presence of Azulene.

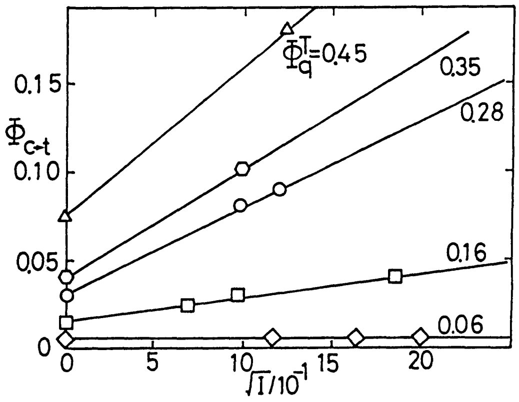


Fig. 4. Effect of $LiBF_4$ on CS Isomerization.

The isomerization quantum yield $\Phi_{c\to t}$ increased on addition of a salt, $LiBF_4$. Figure 4 shows the dependence of $\Phi_{c\to t}$ in varying [CS] on the ionic strength (I) of the salt in solution. The lower the CS concentration, the more effective the salt effect. Salts do not usually influence the rate for separation or recombination of paired neutral radicals. The origin of this salt effect is not clear, but the present result suggests that the salt affects the separation of the triplet radical pairs of neutral and charged species or accelerates the $CS^{+\cdot}\to TS^{+\cdot}$ isomerization.

The effect of spin multiplicity on electron transfer reactions has been discussed as one of the most important factors in particular from the viewpoint of charge separation. The present work was able to abstract only such effect by using the sensitizer which induces electron transfer in both excited singlet and triplet states.

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