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Transient Absorption in the Sensitized Photoisomerization of Stilbene

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The sensitized photoisomerization of stilbene was studied with nanosecond time-resolved absorption spectroscopy at room temperature. In non-viscous solvents (heptane, benzene, and ethanol), the transient spectrum does not depend upon a starting material being either *cis*- or *trans*-stilbene. The kinetic analysis of the transient spectrum due to stilbene shows that the observed spectrum consists of the T_n-T_1 absorption spectrum of *trans*-stilbene and that of twisted triplet (phantom triplet) stilbene. The lifetime of the twisted triplet stilbene is determined to be approximately 120 ns. In a viscous solvent (*t*-butyl alcohol), the transient behavior of triplet stilbene is dependent upon the starting materials being either *cis*- or *trans*-stilbene. The contribution of the twisted triplet stilbene to the transient spectrum is larger for the case starting from *cis*-stilbene than for the case starting from *trans*-stilbene.

In the reaction of *cis-trans* photoisomerization of stilbene, two possible mechanisms have been proposed mainly with the aid of the steady state method; (i) reaction occurs through the lowest triplet state (triplet mechanism), or (ii) through the lowest excited singlet state, S_1 (singlet mechanism). In both cases, the phantom singlet and triplet states with the twisted central double bond are possible intermediates in the course of the isomerization.[1–3] In searching these interesting species many attempts have been made without success by flash photolysis or laser photolysis.[4,5]

In the sensitized photoisomerization of stilbene, the reaction was found to occur through the triplet state of stilbene.[1] From the temperature dependence of quenching experiments, it was suggested that a small potential barrier existed between the triplet state of *trans*-stilbene and the phantom triplet state.[6,7] Very recently Benson and Williams[8] proposed a potential barrier from an experiment of the direct excitation to the triplet state by an argon-ion laser. The energy barriers obtained by direct and sensitized photoisomerization agree well with each other. From quenching experiments Saltiel *et al.*[9] estimated the effective lifetime of the triplet state of *trans*-stilbene to be of the order of 10^{-8} s in fluid solution.[10]

On the other hand, in the direct photoisomerization of stilbene, Saltiel and his coworkers[1,12] proposed the singlet mechanism on the basis of their quenching experiments. They further assumed that a phantom singlet state (^{1}p) is a possible intermediate of the reaction. Recently a decay of fluorescence consisting of two exponential decay components with the time constants of ≤ 0.2 and 1.4 ns at room temperature was reported by a photon-counting method.[13] The result was explained by a rapid equilibration of the population between S_1 and ^{1}p. Very recently, we investigated with a picosecond Nd^{3+}:YAG laser the temperature dependence of the fluorescence lifetime of *trans*-stilbene.[14] A smooth sigmoidal relation was obtained, quite similar to the temperature dependence of fluorescence quantum yields. Contrary to the photon-counting experiment the fluorescence had only one exponential decay component (0.11 ns) at room temperature and agreed with the S_1 lifetime estimated by a quenching experiment.[15] The results indicate that the back reaction to S_1 from the ^{1}p state does not contribute to the fluorescence decay, the ^{1}p state has a very short lifetime or the rate of back reaction is very slow.

In order to understand more clearly the *cis-trans* photoisomerization mechanism, it is necessary to elucidate the dynamical behavior of the reaction intermediate—^{1}p or ^{3}p. In the present work we examined the sensitized excitation of *cis*- and *trans*-stilbene to their triplet state and observed an absorption spectrum of a reaction intermediate by laser-flash time-resolved spectroscopy. The sensitized *cis-trans* isomerization mechanism and a role of the phantom triplet state were discussed on the basis of the observation of the transient absorption.

Experimental

The details of a N_2-laser photolysis system[6] and a dye laser photolysis system[7] were reported elsewhere. We used a coaxial type N_2-laser (peak power at 337 nm, 100 kW; pulse duration, 7 ns FWHM) as an actinic light for the photolysis with 2-acetonaphthone as a sensitizer. Stilbene is not excited efficiently by a N_2-laser. For the photolysis with biacetyl, we used a dye-laser with POPOP which was excited by a travelling-wave type N_2-laser (peak power, 1 MW; pulse duration, 6 ns FWHM).

An analyzing light was monitored by means of a Hamamatsu R666 photomultiplier and the signal was fed either to a Tektronix 465 oscilloscope or to a Tektronix 561B sampling oscilloscope combined with a 3S1 dual-trace sampling unit and a 3T77A sampling sweep unit.

The signal from the photomultiplier was monitored and amplified with a 465 oscilloscope. The amplified output signal from the oscilloscope was divided into two halves with a Tektronix 874-TPD divider. One of the signals was connected to the channel A of the 3S1 unit, and the other was passed through a delay cable and put into the channel B of the 3S1 unit. The sampling time of the channel A was fixed manually at a suitable delay position of the absorption with an intensity of $I(t)$, while the channel B was set before the pulse irradiation with an intensity of $I(0)$ (Fig. 1). The recorder output signals of the A and B channels were divided with an operational amplifier. A time-resolved absorption spectrum was obtained by scanning the wavelength and recording $I(t)/I(0)$. By sampling $I(t)$ and $I(0)$ form the same laser shot, we measured $I(t)/I(0)$ quite accurately ir-

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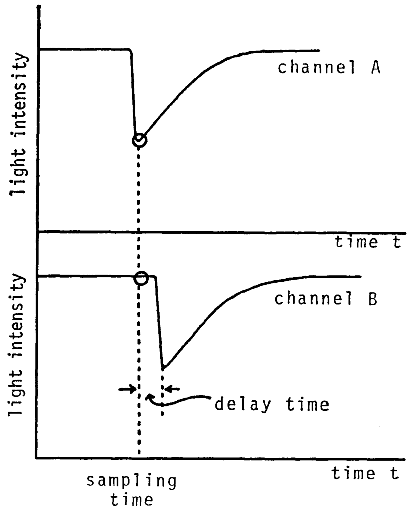


Fig. 1. The timing correlation of the absorption intensity at $t(I(t))$ and that at $t=0$ $(I(0))$. The former is fed into the channel A of the sampling oscilloscope and the latter into the channel B (see the text).

respective of considerable amplitude variation of the laser pulse. The $I(t)/I(0)$ values were later converted to the absorbance scale.

trans-Stilbene and 2-acetonaphthone were purified with alumina column chromatography. *cis*-Stilbene and biacetyl were purified by distillation. The purity of all the samples was checked with gas chromatography to be more than 99%. The sample was deaerated with nitrogen flow and a fresh sample was supplied for each run.

Gas chromatographic analysis showed that the *cis-trans* isomerization reaction was straightforward and no other reaction took place during the laser irradiation.

Results

Transient Spectra. We chose 2-acetonaphthone as a sensitizer of the photoisomerization since the energy of the triplet state (E_{T}) is 59.3 kcal/mol (the lowest triplet state in $\pi\pi^*$,[18]) just above the triplet state of *cis*-($E_{\mathrm{T}}=56.7$ kcal/mol) and *trans*-($E_{\mathrm{T}}=49$ kcal/mol) stilbenes. Figure 2 shows the time-resolved absorption spectra of *cis*-stilbene with 2-acetonaphthone in heptane at room temperature. We used heptane ($\eta=0.418$ cP; 20 °C) and benzene ($\eta=0.649$ cP; 20 °C) as nonpolar solvents and ethanol ($\eta=1.08$ cP; 25 °C) as a polar solvent. The absorption maxima, the shape of the absorption profile, and the time course of the absorption were found to be unaffected by the solvents so far as the viscosity is low. The "0 ns" spectrum (a spectrum observed just after the laser irradiation) has intense absorption bands at 424, 404, and 384 nm. These bands were assigned to the T_n-T_1 absorption of the sensitizer, 2-acetonaphthone, since the "0 ns" spectrum of 2-acetonaphthone in heptane gave the same spectrum. These bands decayed quickly and different absorption bands appeared about 70 ns after the laser pulse, irrespective of the starting materials being either *cis*- or *trans*-stilbene. The lifetime of this species was 110± 10 ns. This transient absorption spectrum was also observed in an additional experiment using biacetyl (the lowest triplet state is $n\pi^*$, $E_{\mathrm{T}}=56.3$ kcal/mol[19]) as triplet sensitizer. We excited biacetyl with a dye-laser at 428 nm. Again the main spectral features in the region of 345—390 nm and the lifetimes were identical irrespective of the starting isomers. As described later, this transient absorption is due to a mixture of the triplet state of *trans*-stilbene and the phantom triplet.

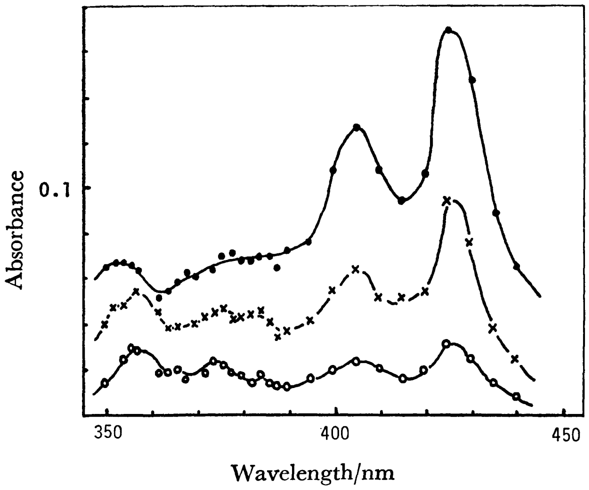


Fig. 2. Time-resolved absorption spectra of the 2-acetonaphthone-stilbene system in heptane: —●—, immediately after; —×—, 30 ns after; —○—, 70 ns after a laser pulse reached its maximum intensity.

The Rate of Triplet Energy Transfer from 2-Acetonaphthone to cis- *or* trans-*Stilbene.* In order to elucidate the mechanism of sensitization processes of the triplet state of *trans*-stilbene and twisted stilbene, we examined the first order decay rate of the 2-acetonaphthone triplet state as a function of the concentration of *cis*- or *trans*-stilbene. Figure 3 shows the Stern-Volmer relationship observed by the T_n-T_1 absorption at 430 nm in heptane. The plots give a straight line with a slope of $8.9\times10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ for *trans*-stilbene and $5.2\times10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ for *cis*-stilbene at room temperature.

*Transient Absorption in a Viscous Solvent (*t*-Butyl Alcohol).* The transient absorption of *cis*- or *trans*-stilbene in *t*-butyl alcohol with 2-acetonaphthone as a sensitizer has two components; the T_n-T_1 absorption of the sensitizer,

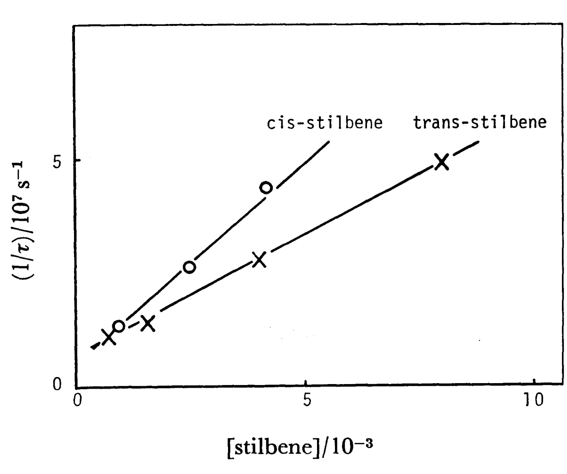
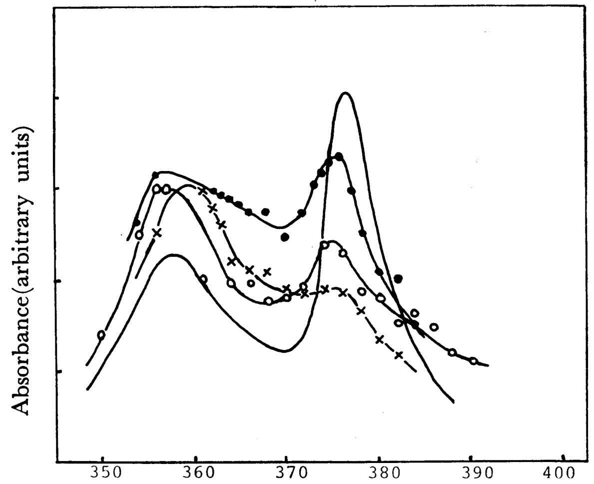


Fig. 3. The first-order decay rate of the 2-acetonaphthone triplet quenched by *cis*- and *trans*-stilbenes in heptane at room temperature.



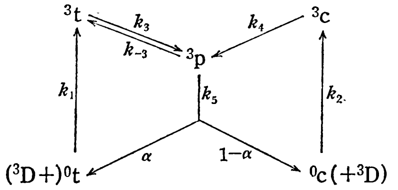
Wavelength/nm

Fig. 4. Transient absorption of stilbene: —○—, *trans*-stilbene in non-viscous solvent; —●—, *trans*-stilbene in viscous solvent; —×—, *cis*-stilbene in viscous solvent; ——, the T_n-T_1 absorption spectrum of *trans*-stilbene at 77 K from Ref. 26.

2-acetonaphthone, which promptly decays, and the absorption due to the mixture of the triplet *trans*-stilbene and the phantom triplet. The time-resolved absorption spectrum of the long-lived species measured 60 ns after the laser irradiation is shown in Fig. 4. In a viscous solvent, contrary to the behavior in non-viscous solvents, the profiles of the transient absorption spectra were different for *cis*- and *trans*-stilbenes. The decay time of the long lived species was 120±10 ns and 80±10 ns for *cis*- and *trans*-stilbenes, respectively.

Discussion

Reaction Paths. The simplest mechanism which accounts for various observations of the sensitized photoisomerization of stilbene with a triplet donor (^{3}D) is shown as follows:[1,20]



In the above diagram, t, c, and p stand for the *trans*-, *cis*-, and twisted stilbene, respectively. The superscripts 0 and 3 indicate the ground state and the lowest triplet state. The fraction of ^{3}p decaying to the transoid ground state is given by α. *k*'s are the corresponding rate constants.

Recent theoretical studies show that the σ-π excited configuration mixing plays an important role in photochemical rearrengements involving rotation around double bonds. The results of an *ab initio* calculation for ethylene[21] show that the potential energy curve of the triplet state changes smoothly with an absolute minimum at $\theta=90°$, and stays always above the ground state potential. Thus there is no crossing. 1,3,5-Hexatriene, with the simplest π bond system in both sides of the central double bond, behaves in the same manner as ethylene for twisting the central double bond.[21] For styrene, Bruni *et al.*[22] discussed the predominant nature of the lowest triplet state was ethylenic, and showed a similar behavior as ethylene for twisting. In all cases, the main configuration of the lowest triplet state is the ethylenic π system, and becomes more and more localized in the ethylenic π bond during the internal rotation. We consider the same discussion is applicable to the potential surface of stilbene,[23–25] and a potential crossing between the ground and triplet state at $\theta=90°$ is not accounted.

Using 2-acetonaphthone as a sensitizer, the excitation rate constants k_1 and k_2 in heptane were obtained from the slope of the Stern-Volmer plots to be 8.9×10^9 and $5.2\times10^9\ \mathrm{M^{-1}\,s^{-1}}$, respectively. Considering the effect of the viscosity (η(benzene)/η(heptane) $=1.5$—1.6) on the bimolecular rate constants in benzene, these values become 5.6×10^9 and $3.2\times10^9\ \mathrm{M^{-1}\,s^{-1}}$, respectively. These are in good agreement with the values ($5.0\times10^9\ \mathrm{M^{-1}\,s^{-1}}$ for k_1, and $3.4\times10^9\ \mathrm{M^{-1}\,s^{-1}}$ for k_2) obtained by Herkstroeter and Hammond[4] with conventional flash photolysis.

Kinetic Analysis of Observed Absorption. Let us analyze the observed absorption from the kinetic point of view based upon the reaction scheme in the previous section.

For the excitation of *trans*-stilbene,

$$\mathrm{d}[^3\mathrm{t}]/\mathrm{d}t = k_1[^0\mathrm{t}][^3\mathrm{D}] + k_{-3}[^3\mathrm{p}] - k_3[^3\mathrm{t}], \tag{1}$$

$$\mathrm{d}[^3\mathrm{p}]/\mathrm{d}t = k_3[^3\mathrm{t}] - (k_{-3}+k_5)[^3\mathrm{p}]. \tag{2}$$

For the excitation of *cis*-stilbene,

$$\mathrm{d}[^3\mathrm{t}]/\mathrm{d}t = k_{-3}[^3\mathrm{p}] - k_3[^3\mathrm{t}], \tag{3}$$

$$\mathrm{d}[^3\mathrm{p}]/\mathrm{d}t = k_4[^3\mathrm{c}] + k_3[^3\mathrm{t}] - (k_{-3}+k_5)[^3\mathrm{p}]. \tag{4}$$

The differential equations are solved approximately as follows (see Appendix):

For the excitation of *trans*-stilbene,

$$[^3\mathrm{p}]_\mathrm{t} = k_3[^3\mathrm{D}_0](\mathrm{e}^{-\lambda_1 t}-\mathrm{e}^{-\lambda_2 t})/a, \tag{5}$$

$$[^3\mathrm{t}]_\mathrm{t} = [^3\mathrm{D}_0]\{(d-\lambda_1)\mathrm{e}^{-\lambda_1 t}+(\lambda_2-d)\mathrm{e}^{-\lambda_2 t}\}/a. \tag{6}$$

For the excitation of *cis*-stilbene,

$$[^3\mathrm{p}]_\mathrm{c} = [^3\mathrm{D}_0]\{(k_3-\lambda_1)\mathrm{e}^{-\lambda_1 t}+(\lambda_2-k_3)\mathrm{e}^{-\lambda_2 t}\}/a, \tag{7}$$

$$[^3\mathrm{t}]_\mathrm{c} = k_{-3}[^3\mathrm{D}_0](\mathrm{e}^{-\lambda_1 t}-\mathrm{e}^{-\lambda_2 t})/a. \tag{8}$$

Here

$$\lambda_{1,2} = \frac{1}{2}[(k_3+k_{-3}+k_5)\mp\{(k_3+k_{-3}+k_5)^2-4k_3k_5\}^{1/2}], \tag{9}$$

$$a = \lambda_2 - \lambda_1. \tag{9'}$$

The ratio of [^{3}t] to [^{3}p] at time t is given as follows:

$$\left(\frac{[^3\mathrm{t}]}{[^3\mathrm{p}]}\right)_\mathrm{t} = \frac{(d-\lambda_1)\mathrm{e}^{-\lambda_1 t}+(\lambda_2-d)\mathrm{e}^{-\lambda_2 t}}{k_3(\mathrm{e}^{-\lambda_1 t}-\mathrm{e}^{-\lambda_2 t})}, \tag{10}$$

$$\left(\frac{[^3\mathrm{t}]}{[^3\mathrm{p}]}\right)_\mathrm{c} = \frac{k_{-3}(\mathrm{e}^{-\lambda_1 t}-\mathrm{e}^{-\lambda_2 t})}{(k_3-\lambda_1)\mathrm{e}^{-\lambda_1 t}+(\lambda_2-k_3)\mathrm{e}^{-\lambda_2 t}}. \tag{11}$$

Here $d=k_{-3}+k_5$.

In such non-viscous solvents as heptane, the observed new transient species has a nearly single exponential decay. The decay rate of ^{3}p and ^{3}t are both approximated by the same λ_1. Therefore λ_1 should correspond to the observed long decay time ($\approx$110 ns). Since $\lambda_2 \gg \lambda_1$, the terms including $e^{-\lambda_2 t}$ can safely be disregarded in Eqs. 10 and 11.

$$\frac{([^3\mathrm{t}]/[^3\mathrm{p}])_\mathrm{t}}{([^3\mathrm{t}]/[^3\mathrm{p}])_\mathrm{c}} = \frac{(d-\lambda_1)(k_3-\lambda_1)}{k_3k_{-3}} = 1 \tag{12}$$

This means that the transient absorption spectrum observed with the non-viscous solution is independent of the starting material being either *cis*- or *trans*-stilbene. The spectrum in the wavelength region, 345—390 nm, is quite similar to the T_n-T_1 absorption spectrum of *trans*-stilbene reported by Herkstroeter and McClure in solid solution at 77 K[26] (see Fig. 4). The spectrum is the absorption of ^{3}t, since the isomerization does not take place at 77 K. However, at shorter wavelengths, our spectrum has distinctly higher intensity. Subtracting the ^{3}t absorption from the transient absorption observed with the non-viscous solution, we have a new absorption band at $\approx$360 nm. The band is assigned to the intermediate between ^{3}t and the isomerization product, namely ^{3}p. The band at $\approx$360 nm becomes more predominant in the viscous solution.

The behavior of the transient species in a viscous solvent is dependent upon the starting materials as is shown in Fig. 4. The rotation is hindered in a viscous solvent. Since the forward rate constant k_3 is about nine times smaller in *t*-butyl alcohol than in benzene at room temperature[15], it is difficult to ignore the contribution of $e^{-\lambda_2 t}$ in the viscous solution. Thus we obtain much more complicated relation than Eq. 12,

$$\frac{([^3\mathrm{t}]/[^3\mathrm{p}])_\mathrm{t}}{([^3\mathrm{t}]/[^3\mathrm{p}])_\mathrm{c}} \approx \frac{e^{-2\lambda_1 t}+e^{-2\lambda_2 t}+e^{-(\lambda_1+\lambda_2)t}\{(k_3-\lambda_1)^2+(\lambda_2-k_3)^2\}/k_3k_{-3}}{e^{-2\lambda_1 t}+e^{-2\lambda_2 t}-2e^{-(\lambda_1+\lambda_2)t}} > 1. \tag{13}$$

This relation shows that the concentration of ^{3}p relative to that of ^{3}t increases for the reaction from the *cis* isomer compared with the reaction from the *trans* isomer: in other words, the spectrum of the phantom triplet is more predominant in the transient spectrum from *cis*-stilbene than in that from *trans*-stilbene. This is consistent with the observation shown in Fig. 4 supporting the assignment of the 360 nm band to ^{3}p. We can see from Fig. 4 that the intensity ratio of the 360 nm band to the 376 nm band in the viscous solution is much larger in the transient spectrum from *cis*-stilbene than in that from the *trans*-stilbene.

In a viscous solvent the transient absorption decays differently depending upon the starting material. Exciting *trans*-stilbene, the lifetime is 80 ns at room temperature and this decay process (represented by λ_2) is considered to be from ^{3}t since the transient absorption spectrum mainly consists of the T_n-T_1 absorption spectrum. Exciting *cis*-stilbene, the transient absorption spectrum decays with the lifetime of 120 ns and is mainly due to ^{3}p, the decay process being controlled by λ_1.

The ratios of $[^3\mathrm{t}]/[^3\mathrm{p}]$ in heptane and *t*-butyl alcohol are estimated by taking the most reliable rate constants.[1,3] With the aid of Eqs. 10 and 11, these values *ca.* 50 ns after the laser irradiation are calculated and given in Table 1. We can see that in a viscous solvent $[^3\mathrm{t}]/[^3\mathrm{p}]$ is greatly different for *cis*- and *trans*-stilbenes.

TABLE 1. VISCOSITY DEPENDENCE OF $[^3\mathrm{t}]/[^3\mathrm{p}]$

Solvent		Heptane (non-viscous solv.)	*t*-Butyl alcohol (viscous solv.)
Viscosity(cP)	η	0.40	3.88
Rate constants (s^{-1})	k_3	10^8	1.3×10^7
	k_{-3}	10^7	1.3×10^6
	k_5	10^7	10^7
	λ_1	0.9×10^7	7.95×10^6
	λ_2	1.11×10^7	1.64×10^7
$([^3\mathrm{t}]/[^3\mathrm{p}])_\mathrm{t}$		0.12	1.4
$([^3\mathrm{t}]/[^3\mathrm{p}])_\mathrm{c}$		0.12	0.06

The initial concentrations of ^{0}t and ^{0}c are 0.1 M.

Appendix

The exact solution of linear differential equations 1, 2, 3, and 4 is as follows:
for the excitation of *trans*-stilbene,

$$[^3\mathrm{p}]_\mathrm{t} = k_3k_1[^0\mathrm{t}][^3\mathrm{D}_0]\left\{\frac{e^{-\lambda_1 t}}{ab}+\frac{e^{-\lambda_2 t}}{ac}+\frac{e^{-k_1[^0\mathrm{t}]t}}{bc}\right\}, \tag{A1}$$

$$[^3\mathrm{t}]_\mathrm{t} = k_1[^0\mathrm{t}][^3\mathrm{D}_0] \times\left\{\frac{d-\lambda_1}{ab}e^{-\lambda_1 t}-\frac{\lambda_2-d}{ac}e^{-\lambda_2 t}-\frac{k_1[^0\mathrm{t}]-d}{bc}e^{-k_1[^0\mathrm{t}]t}\right\}, \tag{A2}$$

for the excitation of *cis*-stilbene,

$$[^3\mathrm{p}]_\mathrm{c} = k_2[^0\mathrm{c}][^3\mathrm{D}_0] \times\left\{\frac{k_3-\lambda_1}{ab'}e^{-\lambda_1 t}-\frac{\lambda_2-k_3}{ac'}e^{-\lambda_2 t}-\frac{k_3-k_2[^0\mathrm{c}]}{b'c'}e^{-k_2[^0\mathrm{c}]t}\right\}, \tag{A3}$$

$$[^3\mathrm{t}]_\mathrm{c} = k_{-3}k_2[^0\mathrm{c}][^3\mathrm{D}_0]\left\{\frac{e^{-\lambda_1 t}}{ab'}+\frac{e^{-\lambda_2 t}}{ac'}+\frac{e^{-k_2[^0\mathrm{c}]t}}{b'c'}\right\}, \tag{A4}$$

where

$$\lambda_{1,2} = \frac{1}{2}[(k_3+k_{-3}+k_5)\mp\{(k_3+k_{-3}+k_5)^2-4k_3k_5\}^{1/2}],$$

$a = \lambda_2 - \lambda_1,$

$b = k_1[^0\mathrm{t}] - \lambda_1,$ $\quad b' = k_2[^0\mathrm{c}] - \lambda_1,$

$c = \lambda_2 - k_1[^0\mathrm{t}],$ $\quad c' = \lambda_2 - k_2[^0\mathrm{c}],$

$d = k_{-3} + k_5.$

$[^0\mathrm{c}]$, $[^0\mathrm{t}]$, and $[^3\mathrm{D}_0]$ are the initial concentration of *cis*-stilbene, *trans*-stilbene, and sensitizer, respectively. Under our experimental conditions, we can make the concentrations of ^{0}t and ^{0}c high enough to have $k_1[^0\mathrm{t}]$ and $k_2[^0\mathrm{c}] \gg \lambda_1, \lambda_2$. The equations A1 to A4 are able to be approximated as Eqs. 5 to 8.

References

1) J. Saltiel, J. T. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, *Org. Photochem.*, **3**, 1 (1973).

2) J. Saltiel, J. T. D'Agostino, W. G. Herkstroeter, G. Saint-Ruf, and N. P. Buu-Hoï, *J. Am. Chem. Soc.*, **95**, 2543 (1973).

3) J. Saltiel and B. Thomas, *J. Am. Chem. Soc.*, **96**, 5660 (1974).

4) W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

5) D. V. Bent and D. Schulte-Frohlinde, *J. Phys. Chem.*, **78**, 446 (1974).

6) J. Saltiel and J. T. D'Agostino, *J. Am. Chem. Soc.*, **94**, 6445 (1972).

7) J. Saltiel, D. W. L. Chang, E. D. Megarity, A. D. Rousseau, P. T. Shannon, B. Thomas, and A. K. Uriarte, *Pure Appl. Chem.*, **41**, 559 (1975).

8) R. Benson and D. F. Williams, *J. Phys. Chem.*, **81**, 215 (1977).

9) J. Saltiel, *J. Am. Chem. Soc.*, **90**, 6394 (1968).

10) Dainton *et al.*[11] measured the transient absorption in pulse radiolysis of *trans*-stilbene, its lifetime being about 110 ns at room temperature. Their assignment of this transient species is not clear.

11) F. S. Dainton, E. A. Robinson, and G. A. Salmon, *J. Phys. Chem.*, **76**, 3897 (1972).

12) J. Saltiel, *J. Am. Chem. Soc.*, **89**, 1036 (1967).

13) D. J. S. Birch and J. B. Birks, *Chem. Phys. Lett.*, **38**, 432 (1976).

14) M. Sumitani, N. Nakashima, K. Yoshihara, and S. Nagakura, *Chem. Phys. Lett.*, **51**, 183 (1977).

15) J. Saltiel and E. D. Megarity, *J. Am. Chem. Soc.*, **94**, 2742 (1972).

16) K. Yoshihara, M. Sumitani, K. Nishi, I. Yokoyama, and S. Nagakura, *Oyo Butsuri*, **43**, 335 (1974).

17) M. Sumitani, S. Nagakura, and K. Yoshihara, *Bull. Chem. Soc. Jpn.*, **49**, 2995 (1976).

18) G. F. Vesly and B. A. Prichard, *Mol. Photochem.*, **5**, 355 (1973).

19) M. Almgren, *Photochem. Photobiol.*, **6**, 829 (1967).

20) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshow, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

21) S. Iwata, private communication.

22) M. C. Bruni, F. Momicchioli, I. Baraldi, and J. Langlet, *Chem. Phys. Lett.*, **36**, 484 (1975).

23) Recently, Benson and Williams[8] proposed a potential curve of the triplet state which crosses that of the ground state and has an energy hump at about $\theta \approx 90°$. In order to account for their experimental results, it may be reasonable to adopt a potential curve proposed by Ting and McClure,[23,24] with two energy humps in both side of the potential minimum at $\theta \approx 90°$.

24) C. H. Ting and D. S. McClure, *J. Chinese Chem. Soc. (Taipei)*, **18**, 95 (1971).

25) We thank Dr. W. Siebrand, NRC Canada for pointing out this possibility.

26) W. G. Herkstroeter and D. S. McClure, *J. Am. Chem. Soc.*, **90**, 4522 (1968).