

## Direct Observation of the Rate for Cis→Trans and Trans→Cis Photoisomerization of Stilbene with Picosecond Laser Photolysis

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The rates for direct cis→trans and trans→cis photoisomerizations of stilbene in solution were measured with a newly developed monitor light source for picosecond laser photolysis in the UV region. The rate constant of the trans→cis isomerization is  $1.2 \times 10^{10} \text{ s}^{-1}$  in hexane at 295 K. The fluorescence decay rate constant of the  $S_1$  state of *trans*-stilbene has the same value. Thus, the decay of the  $S_1$  state is the rate limiting step and the lifetime of an intermediate perpendicular state ( $^1p$ ) has to be very short. The cis→trans isomerization is very fast and the half life of the excited *cis*-isomer is less than a few picosecond. These observations strongly indicate that the isomerization reaction proceeds through the potential surface of the singlet excited states.

Great attention has been paid to the mechanistic investigation of the cis-trans photoisomerization of olefinic compounds. Stilbene was chosen as one of the most prototypical molecules and studied in detail.<sup>1)</sup> Several mechanisms have been proposed in the last decades. Earlier workers considered that the molecule in the excited state could rotate freely about the central double bond making *cis*- and *trans*-stilbenes interchangeable. Lewis *et al.*, however, pointed out that the fluorescence of *trans*-stilbene was not observed when the non-fluorescent *cis*-isomer was excited.<sup>2)</sup> They proposed some energy dissipating levels among these excited states. Later, Förster suggested a mechanism according to which the isomerization proceeds through the lowest triplet state of each isomer.<sup>3)</sup> This mechanism was supported by the analysis of the absorption spectrum of stilbene which seemed to indicate that the  $S_1(^1B_u)$  state had a barrier high enough to make the state inaccessible for the photoisomerization.<sup>4)</sup> However, this triplet mechanism failed to explain why azulene quenched the singlet excited state efficiently by energy transfer and reduced the efficiency of isomerization as well. Thus Saltiel proposed a singlet mechanism.<sup>5)</sup> If stilbene is excited directly into the excited singlet state, it rotates about the central double bond to a perpendicular singlet intermediate ( $^1p$ ), from which both isomers are formed.

From a theoretical point of view, Orlandi and Siebrand pointed out that the second excited singlet state  $S_2(^1A_g)$  played an important role in the photo-conversion of stilbene.<sup>6)</sup> This  $S_2$  level, which is characterized by a double electron excitation, is strongly stabilized, if the molecule rotates about the central double bond. The optical excitation to the lowest singlet state is followed by a non-adiabatic crossing to the  $S_2$  potential surface, which has an energy minimum at the perpendicular ( $^1p$ ) state, and then by a deactivation onto the ground potential surface.

Because of the inherently fast nature of the reaction, several works were made with time-resolved measurements.<sup>7)</sup> The fluorescence lifetime and its temperature dependence,<sup>8–12)</sup> the dynamics of the  $S_n \leftarrow S_1$  absorption,<sup>13–16)</sup> and the two-photon absorption<sup>17,18)</sup> of stilbene were studied recently in order to investigate the photophysical and photochemical properties of its excited state. A few workers claimed to have observed a two-component decay of the excited singlet state by measuring either the fluorescence decay<sup>8,9)</sup>

or transient absorptions.<sup>13,14)</sup> They ascribed these observations to the equilibration between the  $S_1$  and  $^1p$  states before deactivation to the ground state. On the other hand, we and others observed only a single exponential decay of the  $S_1$  state by measuring the fluorescence decay,<sup>10,11)</sup> and the  $S_n \leftarrow S_1$  absorption.<sup>15,16)</sup> No other transient absorption was observable except the  $S_n \leftarrow S_1$  absorption of stilbene. Very recently we measured the time course of the cis→trans isomerization by the laser-induced fluorescence method with a picosecond double pulse, and pointed out that the  $^1p$  state has a very short lifetime of less than a few picosecond.<sup>19)</sup>

Laser-flash spectroscopy is a powerful method for studying the time course of photochemical reactions. In the picosecond range, several methods have been used for generating and detecting the monitoring light. A picosecond continuum light,<sup>20)</sup> a flash lamp,<sup>21,22)</sup> and a laser-induced dye emission<sup>15)</sup> were combined with a vidicon camera, a photodiode array, or a picosecond streak camera. The picosecond continuum light has been used most widely, because it covers a rather wide spectral region and does not cause problems due to time jitter. However, it also has disadvantages, because it requires many laser shots in order to study the time profiles of transient species. Besides, it is usually difficult to generate UV light. The flash lamp technique has a large time jitter even with especially designed electric circuits. Using the laser-induced dye emission it is difficult to generate UV light. We developed a new simple method which does not require any special techniques using a jitter-free laser-induced Xe flash lamp and a streak camera. The spectrum of the monitoring light is continuous from the UV to the near IR region. By this method the time- and the wavelength-dependence of a transient can be resolved by one laser shot.

In this paper, we report the direct measurement of the reaction rates of both cis→trans and trans→cis isomerizations of stilbene with picosecond flash photolyses. We will show that the rate of trans→cis isomerization is limited by the  $S_1$  lifetime of *trans*-stilbene and also that the rate of cis→trans isomerization is very high and the lifetime of the  $^1p$  state is very short.

### Experimental

The experimental set-up is shown in Fig. 1. The actinic light source of the photolysis system was the fourth harmonic

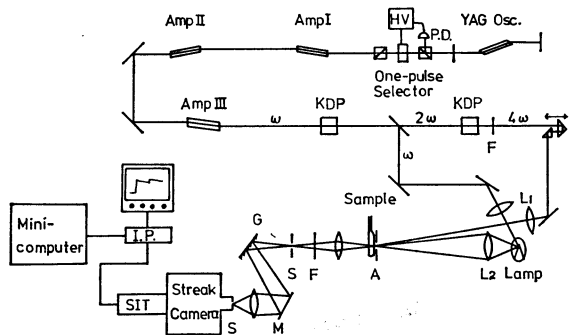


Fig. 1. Schematic diagram of apparatus employed for picosecond photolysis in the UV region.

(266 nm,  $\approx 2$  mJ) of a passively mode-locked Nd:YAG laser. A single pulse of the YAG laser was selected from the pulse train by a Pockels cell and was amplified in three stages with YAG amplifiers. The pulse width (FWHM) of the fourth harmonic was 11 ps. It was measured with a Hamamatsu streak camera/microcomputer system (C979 and C1000).

The analytic light was generated by focussing the fundamental laser beam onto the electrode of a high pressure Xe flash lamp (Xenon N722C). The break down occurred at the focal point of the laser beam at the electrode surface. An intense light emitted from this point was used as a monitoring light. No voltage was supplied on the electrodes. By this technique, the monitoring light was synchronized accurately with the actinic laser flash without any time jitter. The spectrum was similar to the Xe lamp and was continuous from the UV to the near IR region. The actinic laser and the monitoring light were focussed through an aperture onto the sample cell with lenses  $L_1$  and  $L_2$  (cf. Fig. 1), respectively. The monitoring light passed through the sample cell and a monochromator was detected by a streak camera.<sup>23)</sup> The time delay between the start of the monitoring light and the actinic light was about 200 ps. The monochromator consisted of a Bausch & Lomb grating, G, (300 grooves/mm, 300 nm blaze wavelength), a mirror, M, and a pair of slits, S. We kept the wavelength resolution of the monochromator and the time resolution of the streak camera low in order to obtain a better signal/noise ratio. The wavelength resolution was about 10 nm at 254 nm and 313 nm. This was checked with a low pressure Hg lamp. The time resolution of this system was about 30 ps.

*trans*-Stilbene was purified by zone-refining and sublimation in the dark. *cis*-Stilbene was purified by means of high-speed liquid chromatography (Waters model 440). The content of *trans*-stilbene in the *cis*-isomer was less than one part in 500. The concentration of *cis*- or *trans*-stilbene was  $1 \times 10^{-4}$  M (1 M = 1 mol dm<sup>-3</sup>) in hexane.

## Results

Figure 2 shows the UV absorption spectra of *cis*- and *trans*-stilbenes.<sup>24)</sup> The molar extinction coefficients of *cis*- and *trans*-stilbenes above 240 nm are markedly different from each other except for the isosbestic point around 266 nm. By inducing the *trans*→*cis* or *cis*→*trans* isomerization the transmission of the monitoring light was, therefore, expected to change strongly by the formation of the reaction products.

Figure 3 shows the observed time-dependent transmission change after excitation of *cis*- or *trans*-stilbene

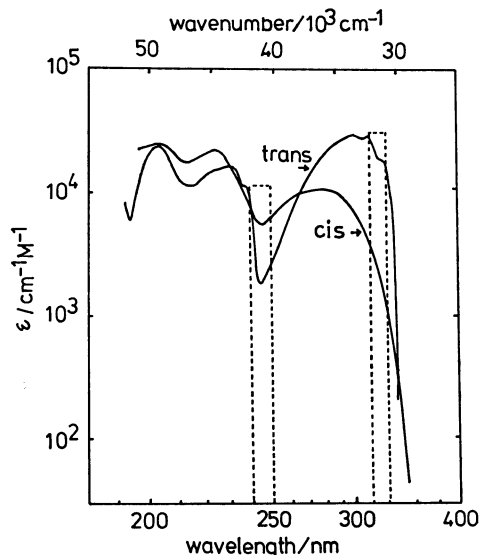


Fig. 2. UV absorption spectra of *cis*- and *trans*-stilbenes reproduced from 22. The transmission change was observed in two broken line regions.

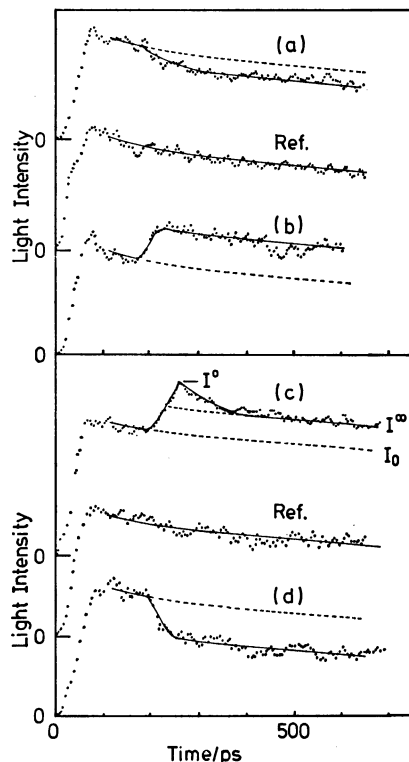


Fig. 3. Time dependent transmission change; (a) and (b) were observed at 240–250 nm upon excitation of solutions of *trans*-stilbene (a) and *cis*-stilbene (b) respectively. (c) and (d) were observed at 310–320 nm when solutions of *trans*-stilbene (c) and *cis*-stilbene (d) were excited respectively. Broken curves represent the reference light profile (ref.) at each wavelength region. The data represent the average of 5–10 shots.

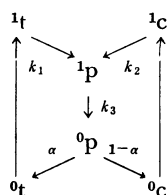
by a picosecond laser flash. At 240–250 nm the molar extinction coefficient of *cis*-stilbene is larger than that of *trans*-stilbene (Fig. 2). Therefore, the transmission will decrease if *trans*→*cis* and increase

if *cis*→*trans* isomerization occurs. Flashing a solution of *trans*-stilbene one observes a decrease in the transmission which reaches a final value after about 80 ps (Fig. 3(a)). For the *cis*→*trans* isomerization (Fig. 3(b)), the transmission increases rapidly within the resolution time of the apparatus by flashing a solution of *cis*-stilbene.

The opposite transmission changes should be observed in the 310–320 nm wavelength region, because in this case the molar extinction coefficient of *trans*-stilbene is larger than that of *cis*-stilbene (Fig. 2). Indeed, when *cis*-stilbene is excited and the *cis*→*trans* isomerization takes place, the transmission decreases (Fig. 3(d)), and it increases due to the *trans*→*cis* isomerization when *trans*-stilbene is excited (Fig. 3(c)). Since in the 310–320 nm region the molar extinction coefficient is about 10 times greater than that in the 240–250 nm region (*cf.* Fig. 2) ground state depletion becomes important and causes a more complicated time behaviour of the transmission change compared with that observed in the 240–250 nm region.

### Discussion

When stilbene is excited with a 266 nm laser flash, the excited singlet state is populated, from which the isomerization takes place with a characteristic rate constant. The most probable mechanism of the *cis*-*trans* photoisomerization of stilbene is shown in Scheme 1:



Scheme 1.

where t is the *trans* and c the *cis* isomer, 1 and 0 denote the excited singlet state and the ground state, respectively, p is the perpendicular state of stilbene, and the *k*'s are rate constants. The change of transmission with time,  $\Delta(I/I_0)$ , is represented as follows:

$$\Delta(I/I_0) = 10^{-(\epsilon_t(-\Delta c) + \epsilon_t[\cdot^0t] + \epsilon_c[\cdot^0c])l} \quad (1)$$

$$[\cdot^0t] = \alpha k_3 \frac{k\Delta c}{k_3 - k} \left( \frac{e^{-k_3 t}}{k_3} - \frac{e^{-kt}}{k} \right) + \alpha \Delta c$$

$$[\cdot^0c] = (1-\alpha)k_3 \frac{k\Delta c}{k_3 - k} \left( \frac{e^{-k_3 t}}{k_3} - \frac{e^{-kt}}{k} \right) + (1-\alpha)\Delta c$$

$$k = k_1 \text{ or } k_2$$

where  $\epsilon_t$  and  $\epsilon_c$  are the molar extinction coefficients of *trans*- and *cis*-stilbene, respectively, *l* is the optical path length,  $I_0$  is the reference light intensity,  $\epsilon_s$  is the extinction coefficient of the starting material (*cis* or *trans* isomer), and  $\Delta c$  is the concentration of the excited singlet state of stilbene at  $t=0$ . From both excited singlet states of *trans*- and *cis*-stilbenes an intermediate state,  $^1p$ , is produced in which the two phenyl rings are perpendicular to each other. With a characteristic branching factor  $\alpha$  the  $^1p$  state decays into

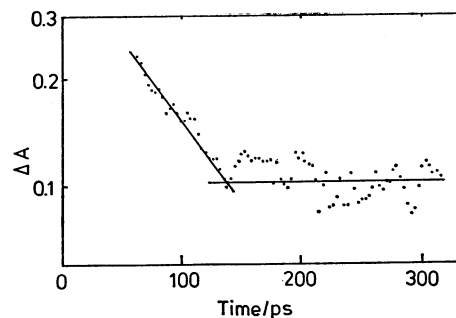


Fig. 4. Logarithmic plot of absorbance change ( $\Delta A$ ) taken from Fig. 3(c).

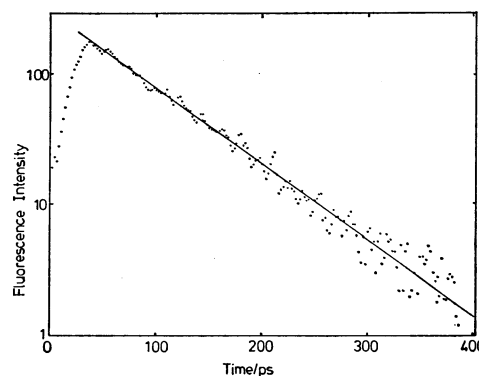


Fig. 5. Logarithmic plot of a fluorescence decay curve of *trans*-stilbene in hexane at 295 K.

$^0t$  and  $^0c$ . The factor  $\alpha$  determines mainly the isomerization quantum yields  $\phi_t$  and  $\phi_c$ .

***Trans*→*cis* Isomerization.** The lifetime of the lowest excited singlet state of *trans*-stilbene is about 75 ps, and the lifetime of the  $^1p$  state is very short (less than a few picoseconds<sup>19</sup>), *i.e.*  $k_1 \ll k_3$  and from Eq. 1, we obtain a simpler expression (2) for the absorbance change

$$\Delta A = \log(\Delta(I_0/I)) = [\epsilon_t(-\Delta c) + \epsilon_t \Delta c \alpha (1 - e^{-k_1 t}) + \epsilon_c \Delta c (1 - \alpha) (1 - e^{-k_1 t})]l \quad (2)$$

In the wavelength region 240–250 nm, the molar extinction coefficient of *trans*-stilbene is smaller than that of *cis*-stilbene. Therefore, one can neglect the terms containing  $\epsilon_t \Delta c l$  and  $\epsilon_c \Delta c \alpha l$ , because these are smaller than  $\epsilon_c \Delta c (1 - \alpha) l$ . Then we obtain Eq. 3 for the absorbance change caused by the formation of the *cis* isomer:

$$\Delta A = \epsilon_c \Delta c (1 - \alpha) (1 - e^{-k_1 t})l \quad (3)$$

In this equation, the change of absorbance with time depends only on the rate constant  $k_1$  of the *trans*→*cis* isomerization. In agreement with this the observed rise time was  $85 \pm 10$  ps (*cf.* Fig. 3(a)).

At 310–320 nm, the molar extinction coefficient of *trans*-stilbene is very large ( $\approx 3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ ) (*cf.* Fig. 2), thus the ground-state depletion contributes significantly to the observed transmission change. For this reason, the observed rise of the transmission is very fast, followed by a slower decrease to a constant value. A logarithmic plot of the latter transmission change shows that it decays exponentially with a lifetime of  $85 \pm 10$  ps (Fig. 4), which corresponds to

the decay of the excited singlet state of *trans*-stilbene (Fig. 5). The constant part of the depletion did not recover even 5000 ps after the laser excitation. It is due to an increase in concentration of the *cis* isomer which has a much smaller molar extinction coefficient than *trans*-stilbene.

The absorbance change at  $t=0$  caused by the excitation of *trans*-stilbene (cf. Eq. 2) is given by

$$\Delta A^0 = \epsilon_t(-\Delta c)l, \quad (4)$$

provided there is no  $S_n \leftarrow S_1$  absorption in this region. After infinite time, the (permanent) decrease caused by the formation of *cis*-stilbene is

$$\Delta A^\infty = \epsilon_t(-\Delta c\alpha)l. \quad (5)$$

In Eq. 5, we neglected the term containing  $\epsilon_c\Delta c(1-\alpha)l$ , because its value is one order of magnitude smaller than the one containing  $\epsilon_t\Delta c\alpha l$  in this wavelength region. Combining Eqs. 4 and 5, we obtain Eq. 6 for the branching ratio  $(1-\alpha)/\alpha$ :

$$\frac{\Delta A^0 - \Delta A^\infty}{\Delta A^\infty} = \frac{1-\alpha}{\alpha}. \quad (6)$$

The fluorescence process was neglected in the derivation, because of the small fluorescence quantum yield ( $\phi_f=0.038^{25}$ ). From the analysis of Fig. 4, we obtained for  $\Delta A^0=0.23$  and for  $\Delta A^\infty=0.10$  and the corrected branching ratio yielded  $(1-\alpha)/\alpha \approx 1.3$ . This ratio is also determined by a photostationary method as  $(1-\alpha)/\alpha=1.4^{1,26}$ . These two values are in good agreement.

The fluorescence lifetime of *trans*-stilbene at room temperature was  $75 \pm 5$  ps in hexane as shown in Fig. 5. The observed absorbance change is caused by the isomerization of *trans*→*cis* reaction with a rise time of  $85 \pm 10$  ps. These observations lead us to the conclusion that the photoisomerization of *trans*-stilbene is determined by the lifetime of the excited singlet state of *trans*-stilbene. Therefore, the lifetime of the perpendicular singlet state ( $^1p$ ), which is considered as the reaction intermediate, must be very short. The above observations are consistent with the other results in the investigations of stilbene: i) In picosecond flash experiments one observes only the  $S_n \leftarrow S_1$  absorption of *cis*- or *trans*-stilbene.<sup>15,16</sup> ii) The fluorescence decay of *trans*-stilbene shows strictly first order kinetics between 77 K and 333 K.<sup>10,11</sup> In the theoretical analysis of the potential surface,<sup>27</sup> the perpendicular state has nearly the same energy as the  $S_1$  state of *trans*-stilbene and the energy barrier between the excited singlet state of *trans*-stilbene and the  $^1p$  state is about 14 kJ/mol. Therefore, it may be energetically possible that an equilibrium exists between these two states. However, judging from a single exponential decay of the fluorescence of *trans*-stilbene, no equilibrium between  $S_1$  of *trans*-stilbene and the perpendicular state  $^1p$  exists. This means that the lifetime of  $^1p$  must be very short. iii) The fluorescence lifetime and the fluorescence quantum yield increase exactly with the same factor when the temperature is lowered from 330 K to 77 K. Moreover, in the same temperature range the *trans*→*cis* isomerization quantum yield decreases correspondingly.<sup>10</sup> That is to say, the isomerization is an ac-

tivated process and the fluorescence lifetime becomes shorter by the increasing rate of the chemical reaction. iv) The activation energy determined from the temperature dependence of the isomerization reaction (10.5 kJ/mol<sup>28</sup>) is in good agreement with that calculated from the temperature dependence of the fluorescence quantum yield<sup>4,28</sup> and the fluorescence lifetime.<sup>10</sup>

**Cis→trans Isomerization.** The risetime of the transmission change is very fast for the *cis*→*trans* isomerization at both wavelength regions (Figs. 3(b) and (d)). The lifetime of the excited singlet state of *cis*-stilbene was observed to be 7 ps.<sup>14</sup> If the isomerization rate is limited by the lifetime of the excited singlet state of *cis*-stilbene, the observed risetime of the formation of *trans*-stilbene is limited by the time resolution of our flash apparatus. We already reported the rate constant of the *cis*→*trans* reaction determined by the laser-induced fluorescence method with a picosecond double pulse.<sup>19</sup> This isomerization rate constant was greater than  $10^{11}$  s<sup>-1</sup>. Therefore, it may be concluded that the decay of the excited singlet state of *cis*-stilbene is the rate determining step in the *cis*→*trans* isomerization reaction.

Thus the isomerization process of stilbene in solution can be described as follows: By excitation of stilbene into a higher vibrational state of the  $S_1(^1B_u)$  state, the excess energy dissipated to the surrounding solvent by the vibrational relaxation. Then rotation about the central double bond with transfer to the  $S_2(^1A_g)$  perpendicular state takes place. This process is the rate determining step. In the case of the *trans*→*cis* isomerization it has an activation energy of 14 kJ/mol. No energy barrier has ever been observed for the isomerization of *cis*-stilbene. The optical excitation probably leads to the maximum of the potential surface, since the ground state of *cis*-stilbene is already twisted considerably ( $\approx 40^\circ$ ) about the central double bond by steric hindrance.<sup>29</sup> After excitation a quick rotation occurs from the strongly mixed state between  $S_1(\text{cis})$  and  $S_2$  to the  $S_2(\text{perpendicular})$  state across a perhaps very low energy barrier. The perpendicular state interacts strongly with the ground perpendicular  $S_0(^1A_g)$  state, so that the internal conversion is very rapid. Finally the vibrational relaxation of the perpendicular  $S_0(^1A_g)$  state to the *cis* or *trans* configuration takes place ( $\alpha$  in Scheme 1).

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