© 1997 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 70, 2677—2683 (1997)

Photoinduced Picosecond Bimolecular Reaction between *trans*-Stilbene and Carbon Tetrachloride

Koichi Iwata* **and Hiro-o Hamaguchi**†

Advanced Research Institute of Science and Engineering, Waseda University, Okubo, Shinjuku-ku, Tokyo 169

†Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received June 30, 1997)

A new photochemical reaction has been found between *trans*-stilbene and carbon tetrachloride. In carbon tetrachloride, the first excited singlet (S_1) state of *trans*-stilbene decays with a time constant of 3.1±0.2 ps, a factor of ten or more faster than in alcohols and hydrocarbons. The mechanism of this anomalous lifetime shortening has been studied by using four time-resolved spectroscopies: sub-microsecond infrared, picosecond Raman, sub-picosecond visible absorption, and picosecond fluorescence. After photoexcitation to the S_1 state, a bimolecular reaction occurs between *trans*-stilbene and the solvent carbon tetrachloride to form a stilbene-Cl adduct and the trichloromethyl ($\cdot CCl_3$) radical. Then, the stilbene-Cl adduct and the $\cdot CCl_3$ radical are likely to react further in about 100 μs, following second-order reaction kinetics. The newly found photochemical reaction between *trans*-stilbene and carbon tetrachloride can serve well as a prototype for studying the microscopic mechanism of bimolecular reactions in solution.

When *trans*-stilbene is irradiated with ultraviolet light, it is excited to the first excited singlet (S_1) state. The formed S_1 *trans*-stilbene is believed to isomerize to the perpendicular configuration, which eventually relaxes to the *trans*- and *cis*-forms in the electronically ground state with equal probabilities.[1,2] Because the radiative lifetime of S_1 *trans*-stilbene is 1.7 ns,[3] the rate of the *trans*-perpendicular isomerization reaction can be readily calculated from the measured lifetime of the S_1 state. Thus, the S_1 lifetime has been thoroughly examined in various solvent environments. The reported values for the lifetime range from 30 ps to more than 150 ps in alcohols and alkanes of various chain lengths.[4,5] Until we reported on the anomalously short S_1 lifetime of 3.1±0.2 ps in carbon tetrachloride,[6] 32 ps in methanol[5] and 30 ps in acetonitrile[7] had been the shortest S_1 lifetimes ever observed.

It was first reported in 1953 that anthracene reacted with carbon tetrachloride when irradiated with light. From an elemental analysis of the reaction products, 9-chloro-10-trichloromethylanthracene was suggested as a final product.[8] Since then, similar photochemical reactions with carbon tetrachloride have been found for many aromatic compounds,[9] although such a reaction had not been known for *trans*-stilbene until recently.[6,10] It has been accepted that radical reactions are involved in many of these photochemical reactions. The decrease in the concentration of a radical scavenger (diphenylpicrylhydrazyl radical) upon photoirradiation was found for carbon tetrachloride solutions of naphthalene, anthracene, diphenylanthracene, phenanthrene, and perylene.[11,12] Some radical species must be present when these aromatic molecules are photoexcited in carbon tetrachloride. Hexachloroethane (CCl_3–CCl_3) was detected after the photoirradiation of anthracene,[13] pyrene and perylene,[14] and free-base tetraphenylporphin[15] in carbon tetrachloride. Hydrogen chloride (HCl) and chloroform ($CHCl_3$) were found among the photochemical reaction products between naphthalene and carbon tetrachloride in methanol solution.[16] The detection of these radical species strongly suggests the presence of the trichloromethyl ($\cdot CCl_3$) radical as a photochemical reaction intermediate between the aromatic molecules and carbon tetrachloride. To the best of our knowledge, however, there had been no direct spectroscopic observation of the $\cdot CCl_3$ radical as a key reaction intermediate.

This paper is a full account of our recent study on the photochemistry of *trans*-stilbene in the carbon tetrachloride solution. Parts of the study have been published in preliminary reports.[6,10] In this paper, we describe the determination of an anomalously short lifetime of *trans*-stilbene in carbon tetrachloride, the spectroscopic detection of the trichloromethyl ($\cdot CCl_3$) radical as a photochemical intermediate, and the details of the Cl atom transfer process.

Experimental

Picosecond time-resolved Raman spectra were measured with the pump-probe method. *Trans*-stilbene was photoexcited to the S_1 state with the pump pulse of 294 nm and the Raman spectra of the S_1 state were measured with the probe pulse of 588 nm. The details of the apparatus have been published elsewhere.[17] In short, a mode-locked dye laser was synchronously pumped by the second harmonic of the pulse-compressed output of a cw mode-locked Nd : YAG laser (Spectra Physics 3800S, 532 nm, 82 MHz, 0.8 W). The output of the dye laser (Rhodamine 6G, 588 nm, 82 MHz) was amplified with a dye amplifier pumped by the second harmonic of the cw Nd : YAG regenerative amplifier output (Spectra Physics 3800RA, 532 nm, 2 kHz, 0.6—0.8 W). The amplified dye-laser output (588 nm, 2 kHz, 10—15 mW) was frequency doubled and the generated second harmonic (294 nm, 2 kHz, 1—4 mW) was used as the pump light. The remaining visible light (588 nm) was used as the probe. The probe light power was reduced to 0.1 mW to avoid the deformation of the observed Raman band shape under the strong laser light field. The time delay between the pump and probe pulses was regulated by a stepping-motor-controlled optical delay line. A carbon tetrachloride solution of *trans*-stilbene (2×10^{-3} mol dm^{-3}) was circulated through a flat nozzle and formed into a thin film at the sample point. The scattered Raman signal was analyzed with a single spectrograph (Instruments SA, HR320, 1800 grooves/mm) and detected with a liquid-nitrogen-cooled CCD detector (Princeton Instruments LN/CCD-1024 TKB). A narrow band optical rejection filter (Kaiser Optical Systems) was used to reject the unshifted excitation light. The spectral width of the probe light was 3.5 cm^{-1} and the slit width of the spectrograph was 200 μm (5.6 cm^{-1}).

Time-resolved infrared spectra were measured with a home-made spectrometer consisting of a dispersive infrared spectrometer, an MCT detector, an a.c.-coupled low-noise amplifier, and a digital oscilloscope.[18,19] A carbon tetrachloride solution of *trans*-stilbene (1.1×10^{-2} mol dm^{-3}) in an infrared flow-cell made of a pair of BaF_2 windows was photoexcited by the fourth harmonic of a diode-pumped cw Q-switched Nd : YLF laser (Spectra Physics TFR, 262 nm, 190 Hz, 20 μJ, 5 ns pulse width). The transmitted infrared light was analyzed with a dispersive spectrometer (Hitachi I-3000), detected with a liquid-nitrogen-cooled MCT detector (photoconductive type, New England Research Center MPC-14-2-B1), and amplified with an ultra-low-noise a.c.-coupled preamplifier (NF Electronic Instruments NF-218K, 50 Hz—100 MHz bandwidth, 55 dB gain). The intensity change of the infrared monitor light induced by the sample irradiation was recorded at each wavenumber while the grating angle was changed. The time-dependent intensity change was accumulated for approximately 4×10^4 pulses at every 4 cm^{-1}. After the wavenumber scanning was finished, the recorded set of time profiles was reconstructed into a set of the time-resolved spectra. At several spectral positions where the time dependence of the absorption change was of special interest, the time profiles were measured separately for 8×10^4 to 2×10^5 pulses. The sample solution was kept under an argon atmosphere to avoid the effect of oxygen.

For the time-resolved fluorescence measurements, the sample solution was irradiated with the same pump light as that used for the time-resolved Raman measurements (294 nm). The collected fluorescence signals were dispersed with an astigmatism corrected spectrograph (Chromex 500, 100 groove/mm) and detected with a streak camera (Hamamatsu C2909, modified).[20] Only the fluorescence component, whose polarization was 54.7 degrees (magic angle) to the excitation polarization, was collected for the measurement.

Time-resolved visible absorption spectra were measured with a spectrometer based on a home-made mode-locked Ti : sapphire laser and a Ti : sapphire regenerative amplifier (Clark-MXR CPA-1).[21] The third harmonic of the amplified output (266 nm, 1 kHz) was used as the pump light. The amplifier output was also focused into a water cell where a white-light continuum was generated. The spectral deformation caused by the group-velocity dispersion in the white-light continuum was corrected by using the measured chirp structure.[22] The cross-correlation times between the pump and probe pulses were approximately 0.5 ps for the spectral region used in this study. For recording the decay kinetics of the S_n–S_1 absorption at a single wavelength, the output pulse from the synchronously pumped mode-locked dye laser used for the picosecond time-resolved Raman measurement was compressed for achieving a better time resolution. A single-mode optical fiber (New Port, F-SPV, 10 m) and a pair of gratings (Spectrogon, type PC, 2400 groove/mm) were used for this purpose. The compressed pulses (588 nm) were amplified with the dye amplifier and frequency doubled to produce the pump light (294 nm). The intensity of the probe light (588 nm) after the sample was recorded as a function of the time delay between the pump and probe pulses.[6] Because the S_1–S_0 transition moment and the S_n–S_1 transition moment are parallel to each other,[23] the angle between the pump and probe polarizations were set to be the magic angle. The cross-correlation time between the pump and probe pulses was 1.7 ps.

Carbon tetrachloride (Dotite, Spectrasol or Wako Chemicals, HPLC grade) and *trans*-stilbene (Wako Chemicals) were used as received.

Results and Discussion

Lifetime Shortening of S_1 *trans*-Stilbene in Carbon Tetrachloride. A carbon tetrachloride solution of *trans*-stilbene was photoirradiated with a Xe flashlamp at room temperature and the induced change in the UV absorption spectrum was monitored as a function of the irradiation time. The obtained spectral change was compared with the change in the heptane solution, in which *trans*-stilbene was converted to a *trans–cis* mixture. The results are shown in Fig. 1. In the heptane solution (Fig. 1A), an absorption band of *trans*-stilbene at 300 nm is decreased while the band of *cis*-stilbene is increased at 250 nm as the irradiation time increases. There is a clear isosbestic point at 265 nm. This spectral change

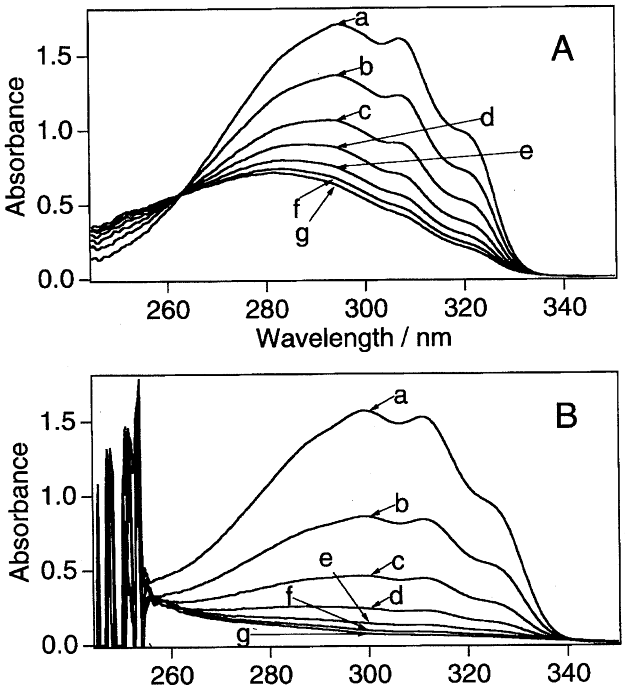

Fig. 1. Change of the UV absorption spectra of *trans*-stilbene in (A) heptane and (B) carbon tetrachloride solutions under the steady state photoirradiation. The spectra (a) before the irradiation and after (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min, (f) 25 min, and (g) 30 min of the irradiation are shown.

illustrates the ordinary *trans–cis* photoisomerization process of stilbene under steady-state photoirradiation. Unlike in heptane, however, there is no *trans–cis* photoisomerization process observed in carbon tetrachloride (Fig. 1B). Although the absorption band from the *trans*-form is decreased, no band of the *cis*-form shows a concomitant increase. From this steady-state irradiation experiment, it is concluded that *trans*-stilbene is not isomerized to the *cis*-form, but is simply decomposed upon photoexcitation in the carbon tetrachloride solution.

Many of the short-lived intermediate species in photochemical reactions can be characterized by their absorption in the visible region. A carbon tetrachloride solution of *trans*-stilbene was photoexcited with the 266 nm light and the time-resolved absorption spectra were recorded for the 440 to 650 nm region. The results are shown in Fig. 2. At around 580 nm, a transient absorption band appears at time 0 within the time resolution of the present apparatus, and decays in a few picoseconds. The spectral band shape agrees with that for the S_n–S_1 absorption of *trans*-stilbene which we observe in the other solvents. However, the lifetime of the observed transient absorption, a few picoseconds, is quite different from those in other solvents. In all of the solvents reported thus far, the lifetime of S_1 *trans*-stilbene is 30 ps or longer.[4,5,7] The lifetime of S_1 *trans*-stilbene in carbon tetrachloride is shorter than the ordinary values by a factor of ten or more.

The short-lived transient species that gives the absorption band at 580 nm was identified unambiguously as the S_1 state of *trans*-stilbene by its Raman spectrum. The time-resolved Raman spectra were measured with the pump wavelength of 294 nm and the probe wavelength of 588 nm. This probe light was in a strong resonance with the observed S_n–S_1 transition at around 580 nm. The obtained time-resolved Raman spectra are shown in Fig. 3. In the figure, the recorded time-resolved Raman spectra for the 1650 to 1000 cm^{-1} ("finger print") region are shown with time delays of 0 to 15 ps. No Raman band from carbon tetrachloride is observed in this spectral region. The observed Raman spectra agree completely with the spectrum of S_1 *trans*-stilbene already established in the other solvents.[24—29] There is no doubt that the transient species that gives the 580 nm absorption band in Fig. 1 is the S_1 state of *trans*-stilbene. The intensities of the observed Raman bands decrease within a few picoseconds as the transient absorption band at 580 nm does.

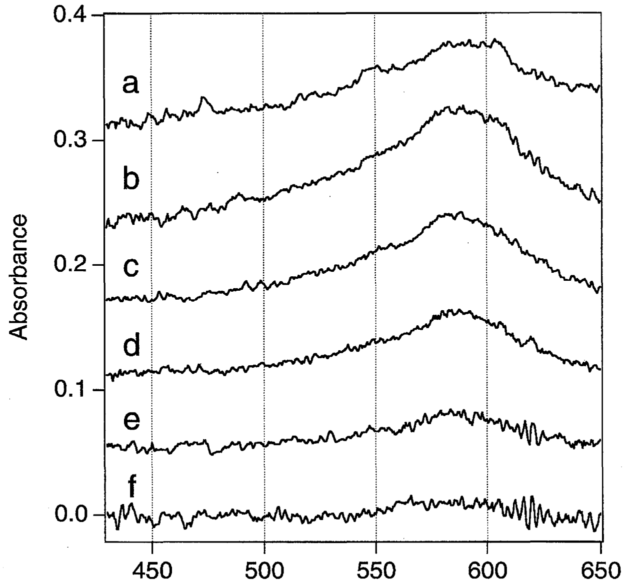

Fig. 2. Time-resolved absorption spectra of *trans*-stilbene in carbon tetrachloride after (a) 0 ps, (b) 1 ps, (c) 2 ps, (d) 3 ps, (e) 5 ps, and (f) 7 ps of the photoexcitation. The rise and decay of the S_n–S_1 absorption band are recorded.

More detailed decay kinetics of the S_1 state of *trans*-stilbene can be obtained by monitoring the S_n–S_1 absorption intensity at a fixed probe wavelength. The time dependence of the S_n–S_1 absorption was monitored at 588 nm while the sample was photoexcited at 294 nm. The cross-correlation time between the pump and probe pulses was 1.7 ps. The observed S_n–S_1 time profile is shown in Fig. 4. The error bars in the figure were estimated from ten independent measurements. The absorption rises at time 0 without a delay and decays within a few picoseconds. The observed data points were fitted with a model function, a convolution between a single exponential decay function and a Gaussian instrumental response function. The best-fitted model function is shown with a solid curve in Fig. 4. The fitted model function agrees with the observed time dependence well. The obtained decay rate constant is $0.32 \pm 0.02\ \mathrm{ps}^{-1}$. The lifetime

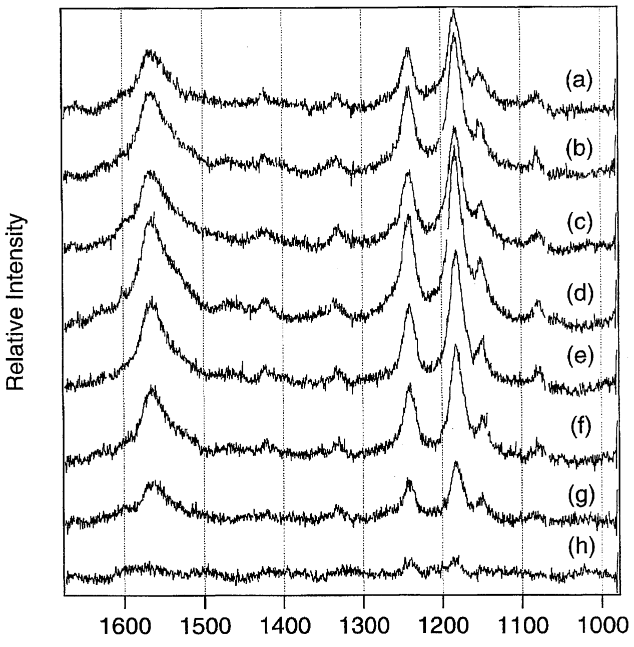

Fig. 3. Time-resolved Raman spectra of *trans*-stilbene in carbon tetrachloride after (a) 0 ps, (b) 1 ps, (c) 2 ps, (d) 3 ps, (e) 5 ps, (f) 7 ps, (g) 10 ps, and (h) 15 ps of the photoexcitation. All the observed bands are form the S_1 state of *trans*-stilbene. The pump and probe wavelengths are 294 and 588 nm.

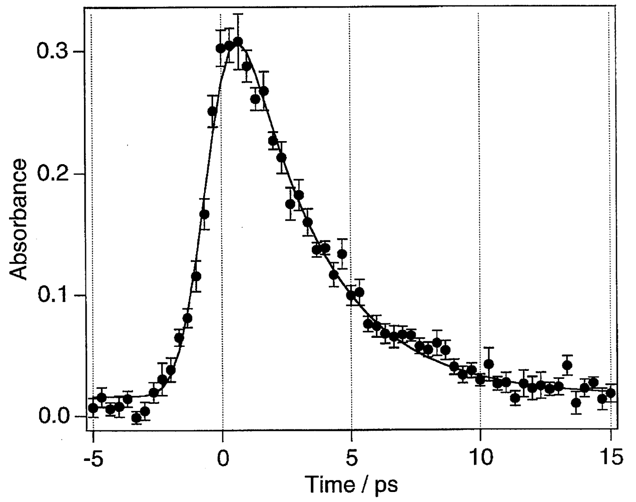

Fig. 4. The time dependent change of the S_n–S_1 absorption intensity of *trans*-stilbene in carbon tetrachloride measured at 588 nm. The sample was photoexcited at 294 nm. The best fitted model function is also shown in a solid curve.

of the S_1 state of *trans*-stilbene in carbon tetrachloride is therefore determined to be 3.1±0.2 ps at room temperature.

The S_1 lifetime of *trans*-stilbene in carbon tetrachloride was studied further with time-resolved fluorescence spectroscopy. From the recorded two-dimensional streak images of the time-resolved fluorescence spectra, the fluorescence decay profiles of *trans*-stilbene were reconstructed for the chloroform (Fig. 5(a)) and carbon tetrachloride (Fig. 5(b)) solutions. The fluorescence lifetime in chloroform is 49 ps, which is within the normal range of the stilbene fluorescence lifetimes. In carbon tetrachloride solution, the fluorescence lifetime is again as short as 3.5 ps. The S_1 lifetimes obtained from the S_n–S_1 absorption and fluorescence agree with each other within the experimental uncertainties. From the observed difference of the fluorescence lifetimes in carbon tetrachloride and in chloroform, we think that the S_1 lifetime shortening in carbon tetrachloride is not the result of acceleration of the S_1–T_1 intersystem crossing by the external heavy atom effect. With the use of the streak camera, the fluorescence decay curve was measured much more easily than the S_n–S_1 absorption profile. In a separate publication, time-resolved fluorescence spectroscopy was used to monitor the temperature dependence of the S_1 lifetime to examine if a reaction occurring in 3 ps could be regarded as being diffusion-controlled.[30)]

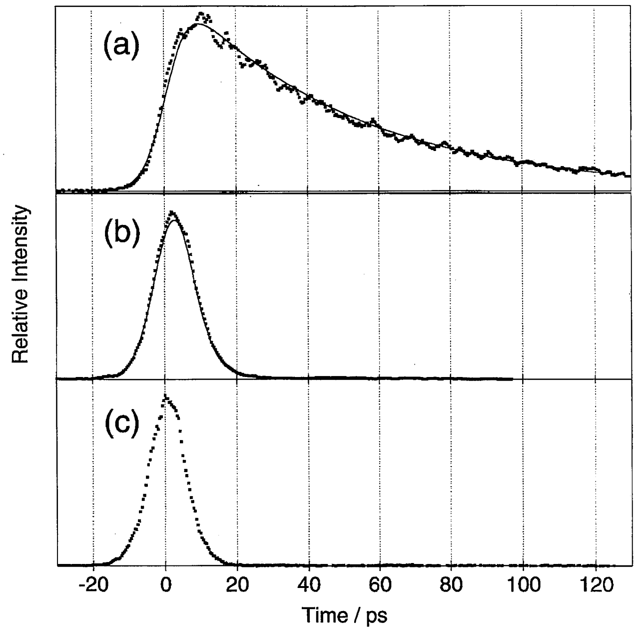

Fig. 5. Fluorescence decay profiles of *trans*-stilbene in (a) chloroform and (b) carton tetrachloride solutions. The instrumental response function (c) is also shown.

It is now clear that the photogenerated S_1 state of *trans*-stilbene has a lifetime of 3.1±0.2 ps in carbon tetrachloride. Because we observe no *cis*-form generation in the steady-state photoirradiation experiment (Fig. 1), and because the *trans*-form is decomposed, the lifetime of 3.1 ps represents the time required for S_1 *trans*-stilbene to react and to form products which have no (or very small) absorption in the near-UV region. In a room-temperature carbon tetrachloride solution, molecules can move 0.1 to 0.2 nm in 3 ps by diffusion motion. The only available molecule for S_1 *trans*-stilbene to react is the solvent carbon tetrachloride. The distance of 0.1 to 0.2 nm is by far smaller than the average distance between two stilbene molecules (10 nm for the 2×10^{-3} mol dm^{-3} solution), and there is no evidence that indicates the formation of *trans*-stilbene dimers in carbon tetrachloride in the absorption or fluorescence spectrum. It is most likely that S_1 *trans*-stilbene reacts with the solvent carbon tetrachloride in 3.1±0.2 ps after photoexcitation.

It is possible that *trans*-stilbene reacts with carbon tetrachloride in the vibrationally excited state of the electronically ground (S_0) state, and not in the S_1 state. In this case, the observed S_1 lifetime of 3.1±0.2 ps does not represent the bimolecular reaction rate. It simply means that S_1 *trans*-stilbene relaxes to the ground state without reacting with carbon tetrachloride or isomerizing to the *cis*-form. The bimolecular reaction with carbon tetrachloride should start in a vibrationally excited state after the internal conversion. However, it is difficult to explain the reason why the internal conversion to the ground state is so fast only in carbon tetrachloride. Usual intermolecular interactions can not explain the internal conversion to the ground state in 3 ps. The external heavy atom effect is not the reason, either, because the observed fluorescence lifetime in chloroform was 49 ps (Fig. 5, see above). We think it most likely that *trans*-stilbene reacts with carbon tetrachloride in the S_1 state. Observation of the generation kinetics of the $\cdot CCl_3$ radical infrared band (896 cm^{-1}) will clarify this point.

Detection of the $\cdot CCl_3$ Radical. The newly found photochemical reaction between *trans*-stilbene and carbon tetrachloride was studied further with time-resolved infrared spectroscopy. A carbon tetrachloride solution of *trans*-stilbene was photoexcited with the 262 nm pump pulse and the induced change was monitored with the infrared spectra. The results are shown in Fig. 6 in the form of difference spectra.

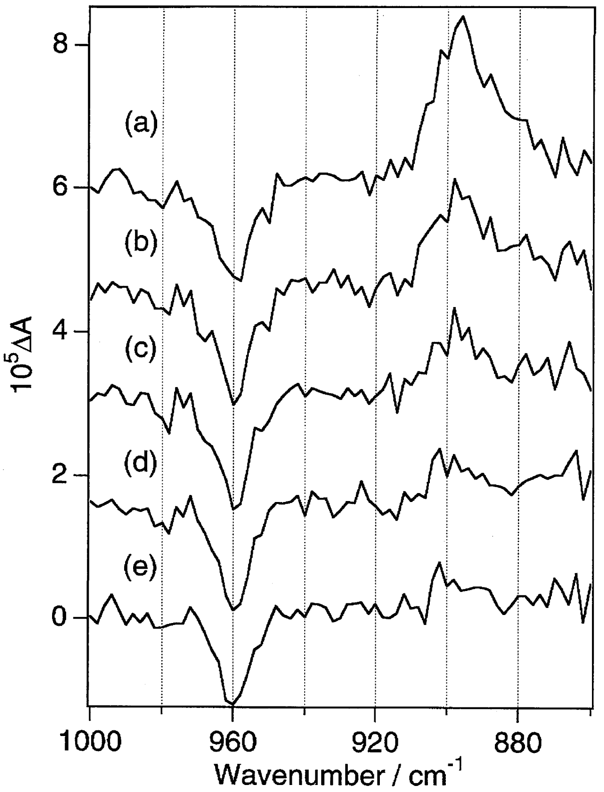

Fig. 6. Time-resolved infrared spectra of *trans*-stilbene in carbon tetrachloride after (a) 0—50 μs, (b) 50—100 μs, (c) 100—150 μs, (d) 150—200 μs, and (e) 200—250 μs of the photoexcitation. The upward peak represents the generation of a transient species while the downward peak represents the depletion of the ground state parent molecule.

A positive (upward) peak represents the increase in absorption, meaning the presence of a newly formed molecular species that shows infrared absorption there. On the contrary, a negative (downward) peak represents the decrease in absorption, resulting from the depletion of a parent molecule that has an infrared absorption band there. In this case, the parent molecule, *trans*-stilbene, has a strong infrared band at 960 cm^{-1} (CH out-of-plane bend). The negative band at 960 cm^{-1} in Fig. 6 means that the ground state of *trans*-stilbene is depleted at time 0 and that it is not recovered even after 200 μs (Fig. 6e). The upward peak at 896 cm^{-1} indicates the presence of the newly generated transient species. This transient species is formed at time 0 and decays completely after 200 μs. It has been known that the $\cdot CCl_3$ radical trapped in low-temperature matrices shows a strong infrared absorption at 898 cm^{-1} in argon[31)] or at 902 cm^{-1} in nitrogen.[32)] Because the detected transient species also has an infrared band at 896 cm^{-1}, this photogenerated species has been identified as the $\cdot CCl_3$ radical.

The formation of the $\cdot CCl_3$ radical is consistent with the reported experimental results indicating the involvement of the $\cdot CCl_3$ radical in the photochemical reactions between the aromatic compounds and carbon tetrachloride.[11—16,33)] We believe, however, that this is the first direct detection of the $\cdot CCl_3$ radical as a reaction intermediate in this series of photochemical reactions.

The time profiles of the observed transient infrared band intensities were recorded at 960 cm^{-1} (Fig. 7a) and at 896 cm^{-1} (Fig. 7b). Figure 7a shows that the population of the reactant stilbene molecule is depleted at time 0 and does not recover later (the slow recovery from the depletion recorded in the figure is caused by the circulation of the sample solution). This is consistent with the conclusion obtained in the previous section. Upon photoirradiation, *trans*-stilbene is decomposed by reacting with carbon tetrachloride. The population of the ground-state *trans*-stilbene is depleted and is not recovered until the reaction products are replaced with the fresh sample by circulation.

The $\cdot CCl_3$ radical is also formed at time 0 (Fig. 7b). The decay curve of the $\cdot CCl_3$ radical under an argon atmosphere is well explained by using second-order decay kinetics (solid curve),

$$[\cdot CCl_3] = [\cdot CCl_3]_0/(1 + [\cdot CCl_3]k_2t). \qquad (1)$$

In Eq. 1, k_2 is the second order rate constant and $[\cdot CCl_3]_0$ is the concentration of the $\cdot CCl_3$ radical at time 0. The

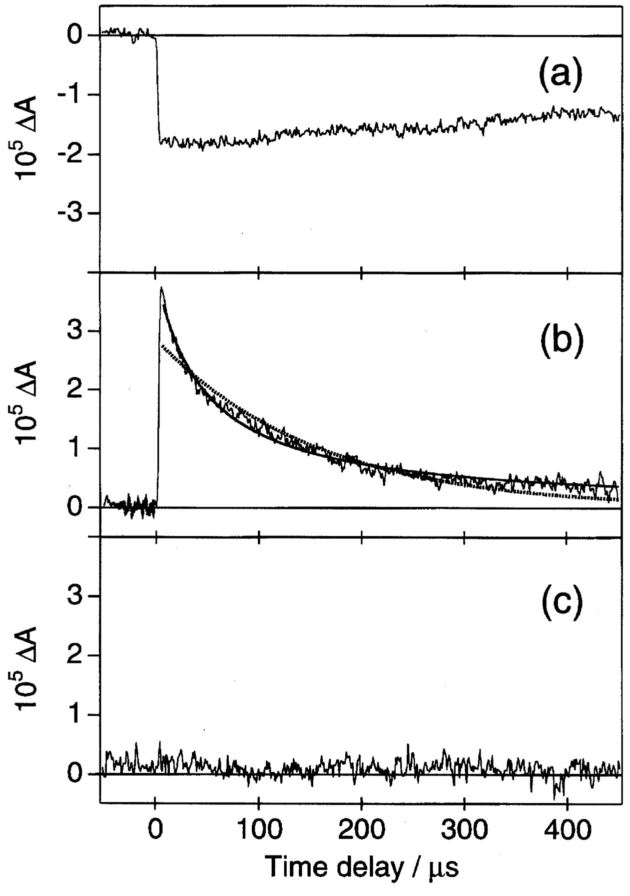

Fig. 7. Time profiles of the infrared absorption of *trans*-stilbene in carbon tetrachloride at (a) 960 cm^{-1} and (b) at 896 cm^{-1}. The profile (a) represents the depletion of the ground state *trans*-stilbene while the profile (b) shows the rise and decay of the $\cdot CCl_3$ radical. No infrared absorption change was observed at 896 cm^{-1} when pure carbon tetrachloride was photoirradiated (c).

agreement between the observed time profile and the first-order decay kinetics (single exponential decay function, dotted curve) is poor. Based on the observation that the decay profile of the $\cdot CCl_3$ radical follows second-order kinetics, there are two possible molecular species with which the $\cdot CCl_3$ radical reacts. One is another $\cdot CCl_3$ radical and the other is the stilbene-Cl adduct. In the first case, if the $\cdot CCl_3$ radical reacts with another $\cdot CCl_3$ radical, hexachloroethane (CCl_3–CCl_3) should be produced. Unfortunately, hexachloroethane does not have a strong infrared band between 4000 and 800 cm^{-1}. We will not be able to detect the rise of the infrared bands from hexachloroethane, even if it is formed. In the second case, if the $\cdot CCl_3$ radical reacts with the stilbene-Cl adduct, the concentration of the two species should be always equal, because they are formed in a single reaction. The decay kinetics of the $\cdot CCl_3$ radical, once again, should follow second-order kinetics. The reaction product between the $\cdot CCl_3$ radical and the stilbene-Cl adduct should have infrared bands between 4000 and 800 cm^{-1}. Thus far, however, we have not observed new infrared bands that rise as the 896 cm^{-1} band from the $\cdot CCl_3$ radical decays within the limit of the detection sensitivity. In the photochemical reaction between anthracene and carbon tetrachloride, we found that most of the generated $\cdot CCl_3$ radicals reacted with the anthracene-Cl adduct in 30—40 μs.[34] No evidence for the $\cdot CCl_3$ dimerization reaction was found within the sensitivity of the experimental apparatus. Therefore, we think that the reaction rate between the two $\cdot CCl_3$ radicals is smaller than the rate for the stilbene-Cl adduct–$\cdot CCl_3$ reaction. It is most likely that the $\cdot CCl_3$ radical is quenched by the reaction with the stilbene-Cl adduct.

When the sample solution is exposed to the air, the decay kinetics of the 896 cm^{-1} band is heavily affected. The $\cdot CCl_3$ radical decays much faster in the presence of oxygen.

Our excitation wavelength (266 nm) was located far from the absorption maximum of carbon tetrachloride. However, we examined if the observed $\cdot CCl_3$ radical is formed as a result of the direct photoexcitation of carbon tetrachloride. The recorded time-dependent absorption profile of pure carbon tetrachloride at 896 cm^{-1} is shown in Fig. 7c. This time profile was measured under exactly the same conditions as the *trans*-stilbene solution (Fig. 7b). No formation of the $\cdot CCl_3$ radical was observed from pure carbon tetrachloride. It is confirmed that the $\cdot CCl_3$ radical is a product of the photoreaction between *trans*-stilbene and carbon tetrachloride.

Cl Atom Transfer Process. As mentioned in the introduction, the involvement of the $\cdot CCl_3$ radical has been presumed in many photochemical reactions between aromatic compounds and carbon tetrachloride. In some cases, it was suggested that the primary process of the reaction is electron transfer from the aromatic molecule to carbon tetrachloride.[12,15,33] After electron transfer, the cation radical of the parent aromatic molecule and the carbon tetrachloride anion are formed. Then, in the second step of the reaction, the Cl anion moves to the parent aromatic cation to form the Cl-adduct of the aromatic molecule and the $\cdot CCl_3$ radical. This two-step mechanism, however, does not hold for the photochemical reaction between *trans*-stilbene and carbon tetrachloride. If the electron transfer occurs as the first step of the reaction, the absorption band of the *trans*-stilbene cation radical[35] should appear in Fig. 2 at around 480 nm as the population of the S_1 state of *trans*-stilbene is decreased. In Fig. 2, however, no absorption band of the *trans*-stilbene cation radical is detected. It is concluded that, within the time-resolution of our experimental apparatus, the Cl atom is directly transferred from carbon tetrachloride to S_1 *trans*-stilbene.

In the time-resolved infrared spectra (Fig. 6), the 960 cm^{-1} band (CH out-of-plane bend) is depleted upon photoexcitation. The 960 cm^{-1} vibrational mode is localized to the central portion of the molecule. The observed disappearance of the 960 cm^{-1} band indicates that the structural change induced in stilbene by the Cl atom transfer heavily affects the central C=C double bond part. The conversion of the central C=C double bond to a C–C single bond is consistent with the results from the steady-state photoirradiation experiment (Fig. 1). Upon photoirradiation, the strong absorption at 300 nm, which is most likely the $\pi^*\pi$ transition of the central conjugated C=C bond, disappears. Therefore, it is strongly suggested that the Cl atom is added to one of the central carbon atoms of S_1 *trans*-stilbene.

The reaction rate between S_1 *trans*-stilbene and carbon tetrachloride as well as its temperature dependence is well explained if we assume that this reaction is diffusion-controlled.[30] Therefore, we can assume that the reaction barrier for the transfer of the Cl atom should be considerably small.

Overall Reaction Scheme. We conclude that S_1 *trans*-stilbene reacts with carbon tetrachloride in the following reaction scheme: In the carbon tetrachloride solution, the S_1 state of *trans*-stilbene is quenched in 3.1±0.2 ps after photoexcitation. One of the Cl atoms of carbon tetrachloride is transferred to stilbene to form a stilbene-Cl adduct. The $\cdot CCl_3$ radical is formed as another reaction product. It is most likely that the Cl atom is attached to one of the two central carbon atoms of stilbene. Then, the stilbene-Cl adduct and the $\cdot CCl_3$ radical are likely to react further following second-order kinetics.

Although the whole scheme of this new photochemical reaction is mostly clear, the quantum yield for the reaction is not yet known. It is possible that some portion of the S_1 state of *trans*-stilbene is simply deexcited to the ground state after interacting with carbon tetrachloride. The quantum yield of the reaction should be determined in the near future.

By using the newly found photochemical reaction between *trans*-stilbene and carbon tetrachloride, we can now initiate an ultrafast bimolecular chemical reaction with a light pulse. Recently, we reported that the kinetics of the reaction between *trans*-stilbene and carbon tetrachloride is well reproduced by the Smoluchowski model of diffusion-controlled reactions.[30] We believe that this reaction can serve well as a prototype bimolecular reaction in studying the microscopic mechanism of chemical reactions in solution.

Most of the experimental part of this work has been performed at Kanagawa Academy of Science and Technology.

References

1) R. M. Hochstrasser, *Pure Appl. Chem.*, **52**, 2683 (1980).

2) G. R. Fleming, "Chemical Applications of Ultrafast Spectroscopy," Oxford University Press, New York (1986).

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

4) G. Rothenberger, D. K. Negus, and R. M. Hochstrasser, *J. Chem. Phys.*, **79**, 5360 (1983).

5) S. K. Kim, S. H. Courtney, and G. R. Fleming, *Chem. Phys. Lett.*, **159**, 543 (1989).

6) K. Iwata, B. Toleutaev, and H. Hamaguchi, *Chem. Lett.*, **1993**, 1603.

7) K. Iwata and T. L. Gustafson, unpublished results.

8) E. J. Bowen and K. K. Rohatgi, *Discuss. Faraday Soc.*, **14**, 146 (1953).

9) J. B. Birks, *Chem. Phys. Lett.*, **38**, 437 (1976).

10) K. Iwata, S. Kataoka, and H. Hamaguchi, *Chem. Lett.*, **1994**, 2131.

11) G. K. Oster, *Acta Phys. Polo.*, **26**, 435 (1964).

12) W. M. Wiczk and T. Latowski, *Z. Naturforsch., A*, **46a**, 259 (1991).

13) M. P. Fogarty and I. M. Warner, *Appl. Spectrosc.*, **34**, 438 (1980).

14) W. M. Wiczk and T. Latowski, *Pol. J. Chem.*, **64**, 373 (1990).

15) G. S. S. Saini, N. K. Chaudhury, and A. L. Verma, *Photochem. Photobiol.*, **55**, 815 (1992).

16) G. Schlicht and D. Schulte-Frohlinde, *Photochem. Photobiol.*, **16**, 183 (1972).

17) K. Iwata, S. Yamaguchi, and H. Hamaguchi, *Rev. Sci. Instrum.*, **64**, 2140 (1993).

18) K. Iwata and H. Hamaguchi, *Appl. Spectrosc.*, **44**, 1431 (1990).

19) T. Yuzawa, C. Kato, M. W. George, and H. Hamaguchi, *Appl. Spectrosc.*, **48**, 684 (1994).

20) T. Tahara and H. Hamaguchi, *Appl. Spectrosc.*, **47**, 391 (1993).

21) S. Yamaguchi and H. Hamaguchi, *Chem. Phys. Lett.*, **227**, 225 (1994).

22) S. Yamaguchi and H. Hamaguchi, *Appl. Spectrosc.*, **49**, 1513 (1995).

23) S. Abrash, S. Repinec, and R. M. Hochstrasser, *J. Chem. Phys.*, **93**, 1041 (1990).

24) H. Hamaguchi, C. Kato, and M. Tasumi, *Chem. Phys. Lett.*, **100**, 3 (1983).

25) T. L. Gustafson, D. M. Roberts, and D. A. Chernoff, *J. Chem. Phys.*, **79**, 1559 (1983).

26) K. Iwata and H. Hamaguchi, *Chem. Phys. Lett.*, **196**, 462 (1992).

27) W. L. Weaver, L. A. Huston, K. Iwata, and T. L. Gustafson, *J. Phys. Chem.*, **96**, 8956 (1992).

28) R. E. Hester, P. Matousek, J. N. Moore, A. W. Parker, W. T. Toner, and M. Towrie, *Chem. Phys. Lett.*, **208**, 471 (1993).

29) J. Qian, S. L. Schultz, G. R. Bradburn, and J. M. Jean, *J. Phys. Chem.*, **97**, 10638 (1993).

30) K. Iwata and H. Hamaguchi, *Chem. Phys. Lett.*, **261**, 208 (1996).

31) L. Andrews, *J. Chem. Phys.*, **48**, 972 (1968).

32) E. E. Rogers, S. Abramowitz, M. E. Jacox, and D. E. Milligan, *J. Chem. Phys.*, **52**, 2198 (1970).

33) Y. Ito, K. Kunimoto, M. Tone, and T. Matsuura, *J. Photochem. Photobiol. A: Chem.*, **57**, 293 (1991).

34) K. Iwata and H. Hamaguchi, *J. Mol. Struct.*, in press.

35) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2375 (1966).