CHEMISTRY LETTERS, pp. 2131-2134, 1994.

Time-resolved Infrared Spectroscopic Diagnosis of a Bimolecular Chemical Reaction in Room Temperature Solution. The CCl_3 Radical Produced from Photoexcited trans-Stilbene and Carbon Tetrachloride

Koichi IWATA, Shuichi KATAOKA, and Hiro-o HAMAGUCHI
Molecular Spectroscopy Laboratory, The Kanagawa Academy of Science and Technology,
KSP East 301, 3-2-1 Sakato, Kawasaki 213

The newly found photochemical reaction between trans-stilbene and carbon tetrachloride was examined with time-resolved infrared spectroscopy. On the photoexcitation of trans-stilbene in a carbon tetrachloride solution at room temperature, an intense infrared band was observed at 896 cm^{-1}. This band is identified as a band from the trichloromethyl (CCl_3) radical. It has been clarified that photoexcited trans-stilbene abstracts hydrogen from carbon tetrachloride to generate the CCl_3 radical.

We reported recently that the first excited singlet state of trans-stilbene (S_1 tSB) has a lifetime of 3 ps in carbon tetrachloride, which is shorter than the previously known lifetimes in other solvents by a factor of ten or more.1) The reason of this lifetime shortening proved to be a new bimolecular reaction which takes place between the photoexcited tSB and carbon tetrachloride. In the present study, we measured the time-resolved infrared spectra of photolyzed tSB in carbon tetrachloride at room temperature and detected the trichloromethyl (CCl_3) radical which is one of the direct products of the reaction between tSB and carbon tetrachloride. We now have strong evidence which supports an idea that the effective quenching of S_1 tSB is caused by a radical reaction with the solvent carbon tetrachloride.

It has long been known that the fluorescence of many aromatic compounds is quenched in carbon tetrachloride solutions.2,3) Some of these reactions have been considered to be radical reactions between the excited state solute molecules and carbon tetrachloride. On the quenching of the excited state anthracene,4) pyrene and perylene,5) or free-base tetraphenyl porphin,6) hexachloroethane was detected among the reaction products. The formation of hexachloroethane is explained well by the dimerization of two CCl_3 radicals. Similarly, HCl and $CHCl_3$ were found on the quenching of naphthalene fluorescence by carbon tetrachloride in methanol.[7)] In the carbon tetrachloride solutions of naphthalene, anthracene, diphenylanthracene, phenanthrene, and perylene, the concentration of a radical scavenger (diphenylpicrylhydrazyl radical) was found to decrease on the photoirradiation.[8,9)] This indicates the participation of radical species in these reactions. To the best of our knowledge, however, there has been no direct observation of key radical species which would characterize these photochemical reactions unequivocally.

The sample solution (11×10^{-3} mol dm^{-3} tSB in carbon tetrachloride) was excited with the fourth harmonic of a cw Q-switched Nd:YLF laser (Spectra Physics TFR, 264 nm, 190 Hz, 20 mW). The photolyzed reaction intermediates were detected with a time-resolved infrared spectrometer consisting of a dispersive infrared monochromator and an MCT detector whose output was ac-coupled to a low-noise amplifying system.[10, 11)] The output of the amplifier was processed with a digital oscilloscope. The sample solution was circulated through a BaF_2 flow cell which is transparent for both the infrared and 264 nm light. To preclude the effect of oxygen, the sample solution was kept under an Ar atmosphere.

The lifetime as short as 3 ps makes it impossible to detect S_1 tSB itself in carbon tetrachloride with our time-resolved infrared spectrometer. However, if the intermediates of the reaction between tSB and carbon tetrachloride have lifetimes of sub-microseconds or longer, we can observe those species. The time-resolved infrared spectra of a carbon tetrachloride solution of tSB are shown in Fig. 1. In the figure, a positive peak at 896 cm^{-1} represents the increase of absorbance caused by the generation of a new transient species, that is, a reaction intermediate. A negative peak at 960 cm^{-1} means the decrease of absorbance corresponding to the depletion of the reactant molecules. This band is assigned to a CH out-of-plane vibration of the ground state tSB. It is clear that the number of stilbene molecules is certainly decreased after the photoexcitation, along with the generation of a reaction intermediate.

As mentioned above, it has been considered that the quenching process in carbon tetrachloride involves radical reactions. The CCl_3 radical has been assumed as a key intermediate. It was reported that the CCl_3 radical can be isolated in low temperature matrices and that it gives an intense infrared band at 898 cm^{-1} in an Ar matrix[12)] and at 902 cm^{-1} in a N_2 matrix.[13)] Because the position of the infrared band of the present reaction intermediate, 896 cm^{-1}, agrees with those of the matrix isolated CCl_3 radical, we identify the reaction intermediate that gives the transient infrared band as the CCl_3 radical.

It should be noted that we can obtain specific information on the structure of the Cl added stilbene by using time-resolved infrared spectroscopy. We observe the decrease of the CH out-of-plane vibration of the central C=C double bond after the photoexcitation but do not detect such changes for other infrared bands from the phenyl ring vibrations. It is most probable that the Cl atom is added to one of the carbon atoms forming the central C=C double bond and that the two phenyl rings are kept intact at least during the primary step of the reaction.

To examine the temporal behavior of each transient infrared band, we set the monochromator at its peak wavenumber and recorded the time dependence of the signal intensity. The results are shown in Fig. 2. Within the time-resolution of the apparatus, the number of parent tSB molecules shows a sharp decrease upon the photoexcitation without delay (Fig. 2(a)). The signal keeps a constant value thereafter. (The gradual recovery of

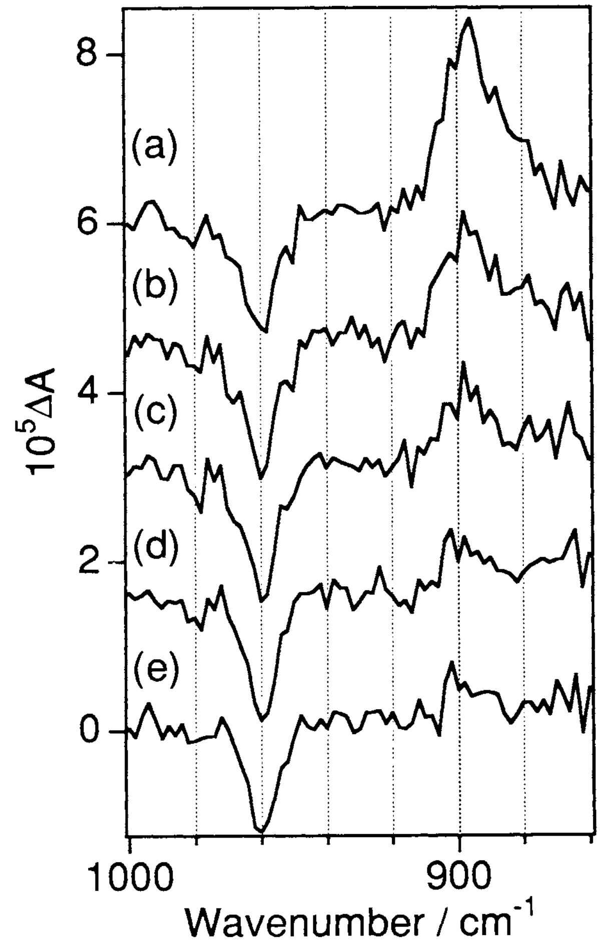

Fig. 1. Time-resolved infrared spectra of trans-stilbene in carbon tetrachloride. The positive peak represents the increase of absorbance due to the newly generated reaction intermediate, while the negative peak means the decrease of absorbance as the result of the depletion of the parent molecule. Each spectrum is the average of the spectra for (a) 0 - 50 μs, (b) 50 - 100 μs, (c) 100 - 150 μs, (d) 150 - 200 μs, and (e) 200- 250 μs.

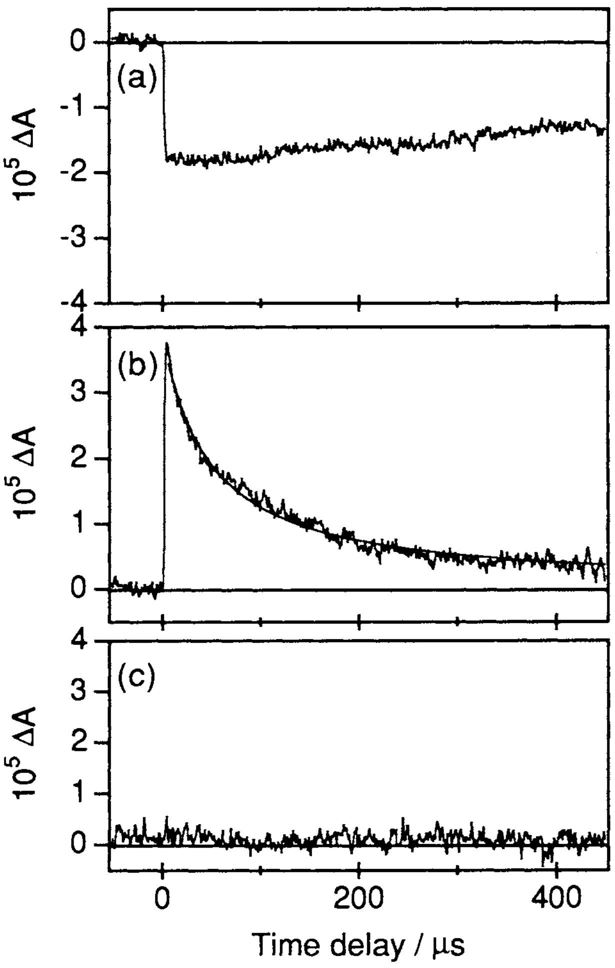

Fig. 2. Temporal profiles of (a) the depletion of the ground state trans-stilbene band at 960 cm^{-1} and (b) the new absorption band at 896 cm^{-1} from the CCl_3 radical. The best fit to the second order decay kinetics is also shown in (b). No change is observed at 896 cm^{-1} when only carbon tetrachloride is photoexcited (c).

the signal is the result of the recovery of the number of tSB molecules caused by the circulation of the sample solution.) This means that once tSB reacts with carbon tetrachloride after the excitation, in 3 ps, it is not recovered for at least several hundred microseconds. The CCl_3 radical is also produced at $t = 0$, again without any delay (Fig. 2(b)). The fact that there is no delay observed for the rise of the CCl_3 radical concentration agrees with the reaction scheme that the photoexcited tSB extracts Cl atom from carbon tetrachloride, which results in the destruction of the tSB central C=C double bond and the simultaneous formation of the CCl_3 radical from carbon tetrachloride. The signal intensity in Fig. 2 (b) is well explained by a second order decay kinetics, $A(t) = A(0)/(1+A(0)\ k_2\ t)$. This means that there are further radical-radical recombination reactions proceeding in a hundred microsecond time scale. In Fig. 2 (c) is shown the result when carbon tetrachloride was photoexcited without tSB. No infrared signal for the CCl_3 radical is obtained at 896 cm^{-1}. This confirms that, with our choice of the pumping wavelength, the radical is not produced by the direct photolysis of carbon tetrachloride, but that it is formed as the consequence of a bimolecular reaction between tSB and carbon tetrachloride.

We believe that this is the first direct observation of the CCl_3 radical as a reaction intermediate in a room temperature solution. We are currently studying the initial state of the reaction with picosecond time-resolved Raman spectroscopy. This reaction can serve as an extremely useful prototype of bimolecular chemical reaction which is suitable for detailed mechanistic studies with various time-resolved spectroscopies.

References

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

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

3) J.B.Birks, “Photophysics of Aromatic Molecules,” John Wiley & Sons, London (1970).

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

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

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

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

8) G.K. Oster, *Acta Physica Polonica*, **26**, 435 (1964).

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

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

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

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

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

(Received August 17, 1994)