Contact Ion Pairs Formed from Photolyzed TMPD–CCl$_4$ and TMPD–CCl$_4$–C$_6$H$_6$ Solutions Studied by the Time-Resolved Microwave Dielectric Absorption Technique

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One-photon ionization of TMPD has been investigated by observing the time variation of microwave dielectric loss caused by irradiation of 355-nm laser pulses on a solution of TMPD in CCl$_4$ and on that containing both TMPD and CCl$_4$ in C$_6$H$_6$ solvent. In the TMPD–CCl$_4$ system the observed signal shows a rapid growth followed by a second-order decay along with much slower decays. These features can be interpreted as reflecting the formation of contact ion pairs (TMPD$^+$Cl$^-$) and their mutual association leading to ion-pair dimers and clusters. In the TMPD–CCl$_4$–C$_6$H$_6$ system a first-order growth of the dielectric absorption is observed, which corresponds to ion-pair formation by electron transfer from the excited triplet state of TMPD to CCl$_4$, and the reaction rate is diffusion-controlled. The dipole moment of the ion pair has been estimated to be 11 ± 3 D from two different methods; one based on the amplitude of the detected signal and the other on the rate constant for the ion-pair association. The dipole moment of the ion-pair dimer appears to be larger than that of the ion pair itself. The analysis of data leads to a suggestion that the quantum yield of the ion-pair formation is close to unity.

Introduction

Although various experimental techniques have been used for studies of behaviors of photochemical transients, few works have been carried out by monitoring the variation of their polarities. In a recently developed technique (the time-resolved microwave dielectric absorption (TRMDA) technique), a microwave dielectric loss is measured to detect photochemical transients when the dipole moment of the photoabsorbed species changes.[1-9] The use of a high-Q resonant cavity combined with pulsed laser irradiation allows time-resolved detection of a dipole moment variation less than 1 D. This method has been used to determine absolute values of the dipole moment of excited triplet states of aromatic ketones[1,9] and of some radicals,[3,4] and has been extended to the investigation of dielectric behavior of excited species.[8] Charge-transfer complexes possessing large dipole moments have also been detected[5-7] by using a low-Q cavity or a microwave reflection cell which has a good time resolution as short as nanoseconds.[10,11] Undoubtedly, these approaches should give us new information on the structure and behavior of photochemical transients.

N,N,N',N'-Tetramethyl-p-phenylenediamine (TMPD) is known to have a very low ionization potential and has been a useful compound in the studies of ionization phenomena in liquids.[12] It is generally accepted that the ionization of TMPD proceeds biphotonically in nonpolar solvents.[13-16] However, Meyer,[17] observing optical absorption due to the TMPD cation, has shown that one-photon halogen-sensitized ionization of TMPD can occur in several liquid halomethanes with the photon energy of 3.1 eV, and it was ascribed to the stabilization of ion-pair formation due to dissociative electron capture by halogenated compounds. By use of the microwave absorption technique, single-photon ionization has also been observed for TMPD in CCl$_4$ photolyzed by 308-nm photons.[2] The generation of TMPD$^+$ and Cl$^-$ in CCl$_4$ solvent has been confirmed by measurements using time-resolved resonance Raman spectroscopy.[18] On the other hand, the dipole moment of the ion pair has been suggested to be 8.7 $\phi^{-1/2}$ D,[2] where ϕ is the quantum yield of the ion-pair formation. However, if one uses the quantum yield $(4-8) \times 10^{-3}$[17] for one-photon ionization, which was monitored by cation formation in halomethanes, one obtains a dipole moment of more than 100 D. This value corresponds to a situation in which both ions are separated by a distance longer than 20 Å, and the pair is no longer a contact-ion pair. Then questions still arise; does the contact-ion pair truly form, and if it is formed, what is its dipole moment?

In this paper, we primarily intended to clarify these problems, using the above-mentioned TRMDA technique. We have employed a high-sensitivity microwave cavity and measured the change of the dielectric loss in the photolysis of both TMPD in CCl$_4$ solvent and TMPD–CCl$_4$ in C$_6$H$_6$ solvent. The ion pair in question is TMPD$^+$Cl$^-$, and its behavior has been investigated on the basis of the change in polarity. Determination of the dipole moments of the ion pair has been attempted, using a method different from that made previously.[2]

Experimental Section

The TRMDA technique used in this work is generally similar to that used in previous studies,[1] and the details of the principle of measurements can be found elsewhere.[1,9] A schematic diagram of the apparatus is shown in Figure 1. The X-band microwave power from a 50-mW Gunn oscillator is divided into two waveguide arms. The power in the main arm (lower) is transmitted through a circulator to a brass rectangular resonant cavity (loaded Q with a sample cell $\simeq$ 1300; resonant frequency 8.8 GHz; TE$_{011}$ mode). Any wave reflected from the cavity is sent by the circulator to the detector via an FET microwave amplifier (Micro-Device Co., 8 dB). The wave in the bias arm (upper) is adjusted to be in phase with the reflected wave. The signal is amplified with an NF BX-31 wide-band amplifier (dc–150 MHz) and fed to a Tektronix 2430 digital oscilloscope (dc–150 MHz) interfaced to

(1) Fessenden, R. W.; Carton, P. M.; Shimamori, H.; Scaiano, J. C. *J. Phys. Chem.* **1982**, *86*, 3803.
(2) Warman, J. M.; Visser, R.-J. *Chem. Phys. Lett.* **1983**, *98*, 49.
(3) Fessenden, R. W.; Hitachi, A.; Nagarajan, V. *J. Phys. Chem.* **1984**, *88*, 107.
(4) Fessenden, R. W.; Scaiano, J. C. *Chem. Phys. Lett.* **1985**, *117*, 103.
(5) Warman, J. M.; deHaas, M. P.; Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Oliver, A. M. *Chem. Phys. Lett.* **1986**, *128*, 95.
(6) Warman, J. M.; deHaas, M. P.; Oevering, H.; Paddon-Row, M. N.; Contsaris, E.; Hush, N. S.; Oliver, A. M.; Verhoeven, J. W. *Nature* **1986**, *230*, 615.
(7) Weisenborn, P. C. M.; Varma, C. A. G. O.; deHaas, M. P.; Warman, J. M. *Chem. Phys. Lett.* **1986**, *129*, 562.
(8) Fessenden, R. W.; Hitachi, A. *J. Phys. Chem.* **1987**, *91*, 3456.
(9) Shimamori, H.; Houdo, K.; Uegaito, H.; Nakatani, Y.; Uchida, K. *Nihon Kagakukaishi* **1989**, No. 8, 1397.
(10) deHaas, M. P.; Warman, J. M. *Chem. Phys.* **1982**, *73*, 35.
(11) Warman, J. M. *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*, Baxendale, J. H., Busi, F., Eds.; D. Reidel: Dordrecht, The Netherlands, 1982; p 129.
(12) For example, Christophorou, L. G.; Simos, K. *Electron-Molecule Interactions and Their Applications*; Christophorou, L. G., Eds.; Academic Press: New York, 1984; Vol. 2, Chapter 4.
(13) Johnson, G. E.; Albrecht, A. C. *J. Chem. Phys.* **1966**, *44*, 3162, 3179.
(14) Cadgan, K. D.; Albrecht, A. C. *J. Phys. Chem.* **1968**, *72*, 929.
(15) Tamir, M.; Ottolenghi, M. *Chem. Phys. Lett.* **1970**, *6*, 369.
(16) Alchalal, A.; Tamir, M.; Ottolenghi, M. *J. Phys. Chem.* **1972**, *76*, 2229.

(17) Meyer, W. C. *J. Phys. Chem.* **1970**, *74*, 2118.
(18) Isaka, H.; Suzuki, S.; Ohzeki, T.; Sakaino, Y.; Takahashi, H. *J. Photochem.* **1987**, *38*, 167.
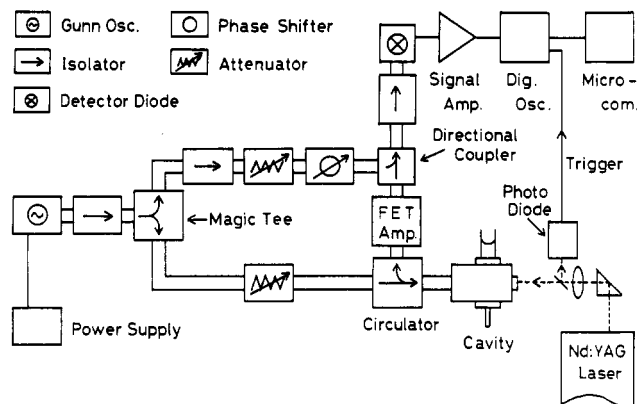
Figure 1. Block diagram of apparatus for measurements of microwave dielectric absorption signals.

a Hewlett-Packard 310 microcomputer used for data analysis. A Quanta-Ray Nd:YAG laser (355 nm, 0.2–10 mJ/pulse, 2-ns pulse width, repetition frequency 2–3 Hz) was used to irradiate the sample. A part of the laser light was taken by a photodiode to trigger the digital oscilloscope. A sample cell of fused silica was placed at the maximum in the microwave electric field. Three different cells with inner light-path lengths of 1, 2, and 3 mm were used, and the inner width was 6 mm in all cells. The response time of the detection system was about 30 ns. The observed signal was found to be dependent on the number of laser pulses as well as on the method of irradiation. With an increase in the number of laser pulses for signal averaging, the initial intensity of the signal gradually decreased and the decay rate of the signal increased (see next section). Such features became significant for more than 10 laser shots. Therefore the signal stored in the oscilloscope was normally taken by averaging waveforms over two shots, though a single shot is sufficient in most cases. Apparently there was no difference in the signals obtained for one or two pulses. TMPD–CCl$_4$–C$_6$H$_6$ systems were taken without the FET amplifier, and four or eight pulses were used in order to improve S/N ratios.

TMPD (Aldrich Chemical Co.) was purified by recrystallization from ethanol or by vacuum sublimation. Carbon tetrachloride and benzene (Wako Chemicals, Spectrograde) were dehydrated by contact with molecular sieve 3A. Diphenylcyclopropenone (Aldrich) was recrystallized. (Dimethylamino)benzonitrile (Wako) was sublimed. Before irradiation all the samples were deaerated by bubbling with Ar gas for more than 20 min.

The intensity of the laser pulse was monitored by using a power meter at the outside of the laser-beam inlet of the cavity. However, the intensity so measured should be regarded as approximate or relative because, even if the monitored intensity is the same, the actual intensity at a sample cell may be altered by lens focusing as well as by the quartz cell used. Moreover, because of the limited diameter of the inlet aperture and the relatively narrow width of the sample cell, all the photons monitored at the outside of the cavity do not irradiate the sample. Therefore, when the same photoabsorption is required for different samples all the irradiation conditions (the cell and the optics) are kept unaltered. The absolute number of photons absorbed by a sample with a known absorbance for a known laser intensity has been determined as follows. On the basis of the fact that diphenylcyclopropenone (DPCP) decomposes upon UV-photolysis into diphenylacetylene and carbon monoxide with unit quantum yield,[1] a sample cell of 1-mm thickness containing a solution of 10.97 mM DPCP in benzene (absorbance = 1.46, sample volume = 1.9 mL) was irradiated by 300 shots of 355-nm laser light with an intensity of 9.5 mJ/pulse at 1 Hz with stirring of the sample cell every 30 shots, and the difference in the absorbance at about 346 nm (the wavelength giving a maximum absorbance with no contribution from the products of photolysis) before and after photolyses was measured. Two sets of measurements were made in this way, and the absolute number of photons absorbed by the sample was determined to be $(4.9 \pm 0.1) \times 10^{15}$ per pulse. A similar mea-

surement was also made for a sample cell with a 3-mm thickness under the conditions of 10.1 mM DPCP, sample volume = 1.7 mL, and 1000 laser pulses with an intensity of 1.9 mJ/pulse at 3 Hz. In this case, the number of photons absorbed by the sample was $(1.0 \pm 0.1) \times 10^{15}$ per pulse. On the basis of these values, the absolute number of photons absorbed by samples for laser intensities of 10.0 and 8.0 mJ/pulse for 1-mm cells and 3.7 mJ/pulse for 3-mm cells, which will be discussed in a later section, are calculated, assuming that the number of photons is proportional to the monitored laser intensity. The photoirradiated cross sections were 21 ± 4 mm^2, which were determined by measuring the color-changed area of a thermosensitive paper irradiated by several hundred shots of laser pulses. Then we can also calculate the concentrations of the transients formed by single-shot irradiation with a known laser intensity. The reliability of the above actinometry was double-checked by the standard method using 0.006 M ferrioxalate aqueous solutions. It was found that photon numbers per pulse measured for both DPCP (benzene solvent) and ferrioxalate solutions agreed each other within 25% fluctuations for three sets of measurements using the same cell and irradiation conditions for both solutions.

In the determination of the dipole moment of an ion pair, a measurement of reflected microwave power as a function of concentration of solute compound (in the ground state) was necessary, to know the dielectric relaxation parameters (see below). The procedures are the same as those previously described.[1,9]

Results and Discussion

The amplitude of the observed signal in our measurements can be expressed by[1]

$$V = \tfrac{1}{2}V_0 A\beta^{-1}Q_0\eta[S]\,\Delta(\mu^2)g(\tau) \qquad (1)$$

where V_0 is the amplitude of the microwave incident to the cavity, $A = (\epsilon_s + 2)^2(4000\pi)/(27kTN)$ (ϵ_s, dielectric constant of the solvent; k, Boltzmann's constant; T, temperature; N, Avogadro's number), β is the coupling factor of the cavity, Q_0 is the unloaded Q of the cavity, η is the filling factor of the cell in the cavity, [S] is the molar concentration of the transient, $\Delta(\mu^2) = \mu^2 - \mu_g^2$ (μ, dipole moment of the transient; μ_g, dipole moment of the solute in the ground state), and $g(\tau) = \omega\tau/(1+(\omega\tau)^2)$ (ω, microwave angular frequency; τ, dielectric relaxation time for the transient). If the photoabsorbed species is originally nonpolar or has a very small dipole moment (<1 D), $\Delta(\mu^2)$ can be replaced or approximated by μ^2, and the amplitude of the signal observed becomes proportional to the square of the dipole moment of the photoabsorbed species.

TMPD in CCl$_4$. Figure 2a shows a typical dielectric absorption signal observed upon photolysis of a solution of TMPD in CCl$_4$. The signal shown was obtained by averaging two laser shots, and no change was observed for irradiation with only a single shot, except for noise levels. The concentration of TMPD was chosen so that the absorbance (OD) was unity. The signal initially increases very rapidly and then decreases, not down to the base line but to a certain level above the base line. As the laser intensity increases, the decay becomes faster. In our method, a signal observed in the upper direction corresponds to an increase in dielectric loss due to an increase in dipole moment of the photoabsorbed species. Therefore, the signal shown in Figure 2a indicates that certain high-polarity species are initially formed and then decay into another species with less dielectric absorption. Such a decay of the signal was not reported in previous work by Warman and Visser[2] who photolyzed TMPD in CCl$_4$ at 308 nm and detected the ion pair by measuring a change in the microwave power reflected from a sample cell consisting of a part of the waveguide. We have found that when the laser intensity is relatively low (<0.5 mJ/pulse) the decay of the signal almost disappears, and the resulting signal is similar to that observed previously by Warman and Visser. The apparent flat level of the signal decreases gradually with a lifetime of several tens of microseconds, as seen in Figure 2b. This decay also reaches another flat level that lasts for milliseconds. After several measurements the solution turned light blue (possibly Wurster's blue), and some
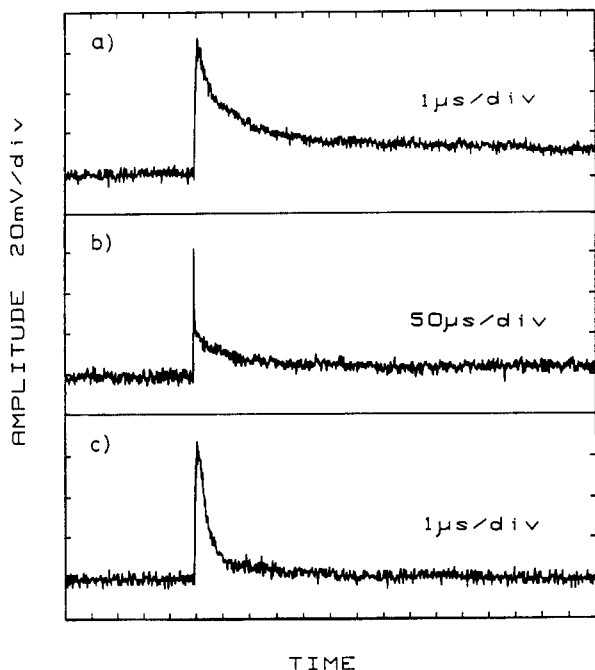
Figure 2. Time dependence of apparatus output for solutions of TMPD in carbon tetrachloride. The signals shown are taken by averaging two laser pulses. (a) 4.76 mM TMPD in CCl_4: the sample cell is of 1-mm optical path length (OD = 1.0), laser intensity = 4.0 mJ/pulse. (b) 1.58 mM TMPD in CCl_4: the sample cell is of 3-mm optical path length (OD = 1.0), laser intensity = 3.1 mJ/pulse. (c) Sample condition the same as in (a), but without a sufficient interval after the previous measurement comprising irradiation by more than 16 pulses. See text for details.

Figure 3. Dependence on laser intensity of maximum height of the dielectric absorption signal observed for solutions of TMPD in carbon tetrachloride. The intensity was monitored just in front of the microwave cavity.

precipitations were observed. Moreover, an addition of a small amount of $AgNO_3$ solution to a sample, which was irradiated by more than 100 laser shots, gave a milky turbidity. It was found that the signal decreased down to the original base line when the measurement was made without stirring the sample cell immediately after the previous measurement in which at least 16 laser pulses, for example, were irradiated on a sample with OD = 1.0. This can be seen in Figure 2c. On the other hand, no such feature was observed in a successive measurement after irradiation of very few laser pulses (4 shots, for example) or with a sufficient interval after the previous measurement with rather many laser pulses. Furthermore, even after irradiation of many laser pulses almost the same signal as that shown in Figure 2a was observed when the sample was thoroughly stirred before the second measurement.

The initial increase in the dielectric absorption signal cannot be due to the excited state of TMPD. TMPD in the ground state is known to have a small dipole moment of 1.20 ± 0.13 D,[19,20] but in order to explain the observed high-intensity signal after photoirradiation, the excited state formed must have a dipole moment larger than 10 D (see a later section for this), which is quite unrealistic. Consequently, we ascribe the initial part of the signal to the formation and decay of a contact ion pair $TMPD^+Cl^-$. Since the initial amplitude of the signal was found to be proportional to the laser intensity (see Figure 3), the formation of the ion pair is a one-photon process as represented by (2) and (3),

$$TMPD + h\nu \rightarrow TMPD^* \qquad (2)$$

$$TMPD^* + CCl_4 \rightarrow TMPD^+Cl^- + CCl_3 \qquad (3)$$

where $TMPD^*$ represents an excited state of TMPD. The additional decays at longer times can be ascribed to the formation of ion-pair dimers
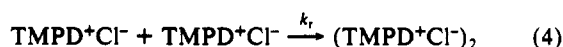
$$TMPD^+Cl^- + TMPD^+Cl^- \xrightarrow{k_f} (TMPD^+Cl^-)_2 \qquad (4)$$
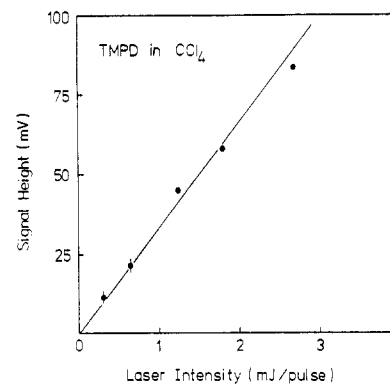
and the coagulation processes of these dimers to form larger clusters

$$(TMPD^+Cl^-)_2 + (TMPD^+Cl^-)_2 \rightarrow (TMPD^+Cl^-)_4 ... \qquad (5)$$

According to such assignments, the signal shown in Figure 2c can be explained as follows. At the end of the first measurement ion-pair clusters with relatively large size remain in a narrow region of the cell, namely in the vicinity of the irradiated portion. The next measurement without a sufficient interval produces new ion pairs, but they readily attach to a large cluster present already in their vicinity. This should cause a sudden decrease in the dipole moment. When the sample cell is stirred the clusters present near the irradiated portion are dispersed over the entire solution in the cell, thus further irradiation of a laser pulse can be regarded as that onto a fresh sample. These arguments are based on the assumption that a large cluster gives very little *dielectric absorption* (not the dipole moment). This is not unreasonable, because a large cluster must give a very long dielectric relaxation time, and then a signal amplitude represented by eq 1 becomes very low through a very small value of $g(\tau)$ ($\simeq (\omega\tau)^{-1}$).

Since the initial growth rate for the signal was found to be comparable to that expected from the response time of the detection system, the formation of the ion pairs seems to be very fast. Measurements for air-saturated samples gave no appreciable change in the maximum amplitude of signal. As the concentration of oxygen molecules in an air-saturated solution is about 13 mM, the lifetime for the diffusion-controlled quenching by oxygen may be about 10 ns. This means that the electron transfer from $TMPD^*$ to CCl_4 proceeds within a time much shorter than 10 ns. The lifetime of the lowest triplet state of TMPD is longer than microseconds,[21,22] whereas that for the lowest excited singlet state is about 5 ns.[22-24] Then there may be a possibility that $TMPD^*$ in reaction 3 is an excited singlet state or a Rydberg state that has been regarded as an intermediate state for the one-photon ionization in polar solvents.[24-27] A time-resolved resonance Raman study for TMPD–CCl_4 systems reported the appearance of Raman bands attributed to $TMPD^+$ but no triplet TMPD bands detectable at 200 ns after UV irradiation.[18] Nevertheless, if the excited triplet state undergoes reaction 3 very rapidly (shorter than 10 ns), there will be no effect of oxygen anyway.

The postulate of ion-pair dimer formation needs further confirmation. If the decay of the signal at earlier times corresponds

(19) Everard, K. B.; Kumar, L.; Sutton, L. E. *J. Chem. Soc.* **1951**, 2807 and a reference therein.

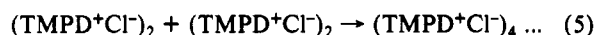(20) McClellan, A. L. *Tables of Experimental Dipole Moments*, Rahara Enterprises: El Cerrito, CA, 1974; Vol. II.

(21) Takeda, S. S.; Houser, N. E.; Jarnagin, R. C. *J. Chem. Phys.* **1971**, *54*, 3195.

(22) Peterson, S. H.; Yaffe, M.; Scultz, J. A.; Jarnagin, R. C. *J. Chem. Phys.* **1975**, *63*, 2625.

(23) Richard, J. T.; Thomas, J. K. *Trans. Faraday Soc.* **1970**, *66*, 621.

(24) Nakamura, S.; Kanamaru, N.; Nohara, S.; Nakamura, H.; Saito, Y.; Tanaka, J.; Sumitani, M.; Nakashima, N.; Yoshihara, K. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 145.

(25) Nakato, Y.; Ozaki, M.; Tsubomura, H. *J. Phys. Chem.* **1972**, *76*, 2105; *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1299.

(26) Imura, T.; Yamamoto, N.; Tsubomura, H.; Kawabe, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3185.

(27) Hirata, Y.; Mataga, N. *J. Phys. Chem.* **1983**, *87*, 1680, 3190.

to dimer generation, the decay should be of second order, and the rate must be dependent on the laser intensity (the initial ion-pair concentration). It should be noted, however, that the initial part of the decays, as shown in Figure 2a, was found not to be pure second order but somewhat higher order than that. This is understandable because the data were taken for samples with OD = 1 for which inhomogeneous production of the ion pairs along the light path causes a superposition of second-order reactions with different rates. Actually this effect was pronounced for samples with higher optical densities. In order to avoid this problem, further measurements should be made, using solutions of TMPD with much lower concentrations giving absorbances as low as about 0.1. On the other hand, the presence of nonzero amplitude at longer times in the signal shown in Figure 2a indicates that the ion-pair dimer, if it is produced, has a definite dipole moment. Since the observed signal reflects all the dielectric losses caused by polar species present, it is very likely that the signal at any time in the decaying period is a superposition of that due to ion pairs and that from ion-pair dimers. Let us analyze the observed signal more quantitatively. Denoting the ion pair and the ion-pair dimer by the subscripts 1 and 2, respectively, the dependence of their concentrations $[S]_1$ and $[S]_2$ on time t can be expressed, respectively, by

$$[S]_1 = \frac{[S]_0}{1 + 2k_r[S]_0 t} \tag{6}$$

$$[S]_2 = \frac{[S]_0}{2}\left(1 - \frac{1}{1 + 2k_r[S]_0 t}\right) \tag{7}$$

where $[S]_0$ ($\equiv [TMPD^+Cl^-]_0$) is the initial concentration of $TMPD^+Cl^-$ and k_r is the rate constant of reaction 4. Substituting each concentration in eq 1 and taking the sum of both amplitudes, we can obtain an expression for the time variation of the total amplitude as

$$V_s(t) = B[S]_0 g(\tau_1)\left(\mu_2^2/2\gamma + \frac{\mu_1^2 - \mu_2^2/2\gamma}{1 + 2k_r[S]_0 t}\right) \tag{8}$$

where $B = {}^1/_2 V_0 A \beta^{-1} Q_0 \eta$ and $\gamma = g(\tau_1)/g(\tau_2)$. Equation 8 can be simplified to

$$V_s(t) = \Delta V(t) + V_s(\infty) \tag{9}$$

where

$$\Delta V(t) = B[S]_0 g(\tau_1)\frac{\mu_1^2 - \mu_2^2/2\gamma}{1 + 2k_r[S]_0 t} \tag{10}$$

$$V_s(\infty) = B[S]_0 g(\tau_1)\mu_2^2/2\gamma \tag{11}$$

$V_s(\infty)$ corresponds to the amplitude of the first flat level of the signal, and $\Delta V(t)$ is the difference between the total signal height and $V_s(\infty)$. Since eq 10 is rewritten as

$$\Delta V(0)/\Delta V(t) = 1 + 2k_r[S]_0 t \tag{12}$$

one can expect a linear relationship between $\Delta V(0)/\Delta V(t)$ and time t.

Now we can use eq 12 for confirmation of the dimer formation process. We have made two sets of measurements. In each series the decays were observed as a function of laser intensity under the same irradiation conditions, though we have not determined the absolute number of photons absorbed by each solution. One series of measurements was made for solutions with 0.222 mM TMPD in a 1-mm path length cell (OD = 0.048) with variation of the laser intensity from 2.4 to 11 mJ/pulse. Another series was for 0.235 mM TMPD in a 2-mm cell (OD = 0.10) with the laser intensity from 1.1 to 7.2 mJ/pulse. In the latter, the laser beam was adjusted to be rather out of focus to obtain a low initial concentration of the transients. The observed signals for the former set are shown in Figure 4. To make plots according to eq 12, it is necessary to determine the flat level corresponding to $V_s(\infty)$. We took it as $0.35V_s(0)$, since profiles of signals at longer times
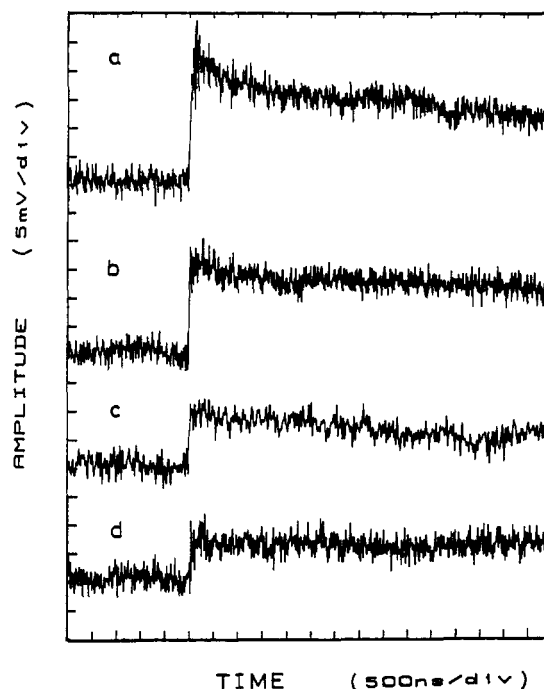

Figure 4. Time dependence of apparatus output for solutions of TMPD in CCl₄ irradiated with different laser intensities. The concentration of TMPD is 0.222 mM for a sample cell of 1-mm optical path length (OD = 0.049). Laser intensity (mJ/pulse) at the inlet of the cavity; (a) 11; (b) 8.6; (c) 5.5; (d) 2.4.
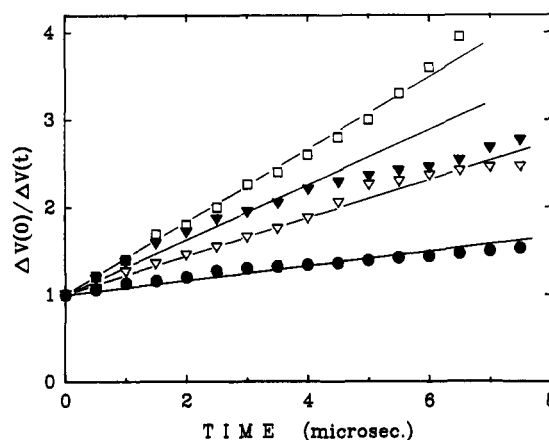

Figure 5. Plots of $\Delta V(0)/\Delta V(t)$ as a function of time for decay curves shown in Figure 4. The symbols □, ▼, ▽, and ● correspond, respectively, to the curves a, b, c, and d in Figure 4. $\Delta V(t)$ corresponds to the signal amplitude at time t measured relative to the flat level at longer times (= $(0.35)V(0)$).

for more than 20 data points give $V_s(\infty) = (0.35 \pm 0.05)V_s(0)$. Shown in Figure 5 are plots based on eq 12 for decay curves listed in Figure 4. Similar plots made for data of another set (solutions with OD = 0.10) are shown in Figure 6. In both sets the linearity appears to be good for all the plots. The slope of each line corresponds to $2k_r[TMPD^+Cl^-]_0$ and is proportional to the laser intensity. This is well represented by straight lines, shown in Figure 7. Note that in Figure 7 two straight lines give different slopes because of different focusing conditions of the laser beam. These results may be a proof of the ion-pair formation process, as proposed above.

Next, we have attempted to determine the value of k_r by knowing $[TMPD^+Cl^-]_0\phi$, where ϕ is the quantum yield of the ion-pair formation. For this purpose we have made four sets of measurements with different $[TMPD^+Cl^-]_0$'s, which were attained by using solutions with different OD and in different irradiation cells and by varying the laser intensity. The absolute number of photons absorbed by each solution can be determined by the number of decomposed DPCP molecules for the same laser in-
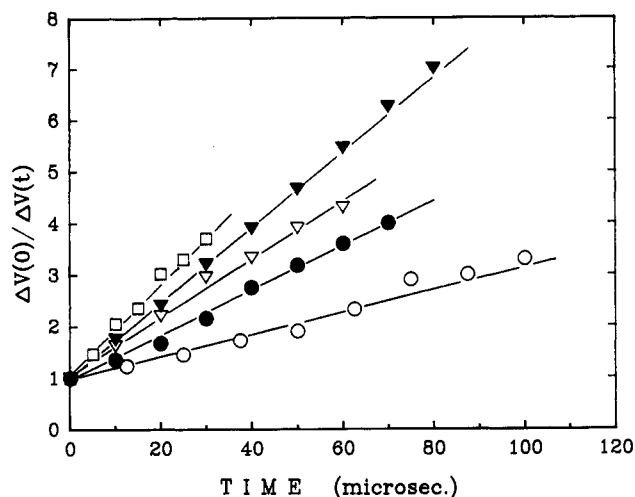
Figure 6. Plots of $\Delta V(0)/\Delta V(t)$ as a function of time for decay curves obtained for solutions of TMPD in CCl_4 irradiated with different laser intensities. The concentration of TMPD is 0.235 mM in a sample cell of 2-mm optical path length (OD = 0.10). Laser intensity (mJ/pulse): (□) 7.2; (▼) 6.4, (▽) 5.0, (●) 3.0, and (○) 1.1. The laser beam was adjusted to be out of focus in comparison with the case for measurements shown in Figure 4.
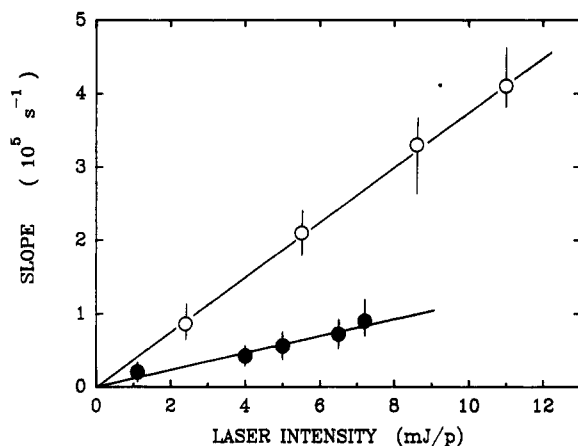

Figure 7. Plots of the slopes of straight lines in Figures 5 and 6 as a function of laser intensity.

TABLE I: Parameters Relevant to Determination of Rate Constant of the Ion-Pair Association Reaction and Values of Rate Constant (k_r), Critical Reaction Radius (r_c), and Derived Dipole Moment (μ) of the Ion Pair

$10^5[S]_0$,[a] M	(10^{-5})slope,[b] s^{-1}	$10^{-9}k_r$, M^{-1} s^{-1}	r_c, Å	μ, D
$4.5\phi^c$	8.9	$9.9\phi^{-1}$	$12.8\phi^{-1}$	$12.6\phi^{-3/2}$
$3.8\phi^d$	7.8	$8.3\phi^{-1}$	$10.8\phi^{-1}$	$9.74\phi^{-3/2}$
$1.9\phi^e$	3.5	$9.2\phi^{-1}$	$11.8\phi^{-1}$	$11.1\phi^{-3/2}$
$0.92\phi^f$	1.7	$9.3\phi^{-1}$	$11.9\phi^{-1}$	$11.2\phi^{-3/2}$

[a] Initial concentration of the ion pair, determined by the method described in the text. ϕ is the quantum yield for the ion-pair formation. [b] Slope of the straight line of the plot, based on eq 12. [c] Conditions: 0.242 mM TMPD, 1-mm cell, OD = 0.053, laser intensity 10 mJ/pulse. [d] Conditions: 0.242 mM TMPD, 1-mm cell, OD = 0.053, laser intensity 8.0 mJ/pulse. [e] Conditions: 0.304 mM TMPD, 3-mm cell, OD = 0.20, laser intensity 3.7 mJ/pulse. [f] Conditions: 0.153 mM TMPD, 3-mm cell, OD = 0.10, laser intensity 3.7 mJ/pulse.

tensity as that used in each measurement for a TMPD–CCl_4 system. The details of the procedure are described in the Experimental Section. Observed decay curves and plots based on eq 12 are shown in Figure 8 and 9, respectively. Determined values of the initial concentration of ion pairs, the slope of straight line in Figure 9, and the obtained rate constant k_r are listed in Table I. We can see that the values for k_r determined for four different [TMPD⁺Cl⁻]$_0$'s agree well with each other, and hence the proposal
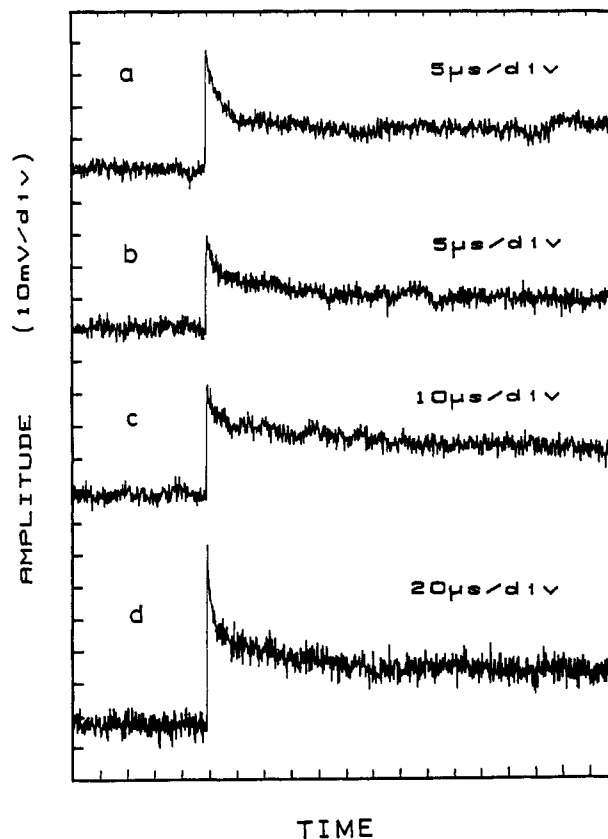

Figure 8. Time dependence of apparatus output for solutions of TMPD in CCl_4 observed under different conditions for OD, the optical path length of the cell, and the laser intensity: (a) 0.243 mM TMPD with 1-mm cell (OD = 0.053), 10 mJ/pulse; (b) 0.243 mM TMPD with 1-mm cell (OD = 0.053), 8.0 mJ/pulse; (c) 0.304 mM TMPD with 3-mm cell (OD = 0.20), 3.7 mJ/pulse; (d) 0.153 mM TMPD with 3-mm cell (OD = 0.10), 3.7 mJ/pulse.

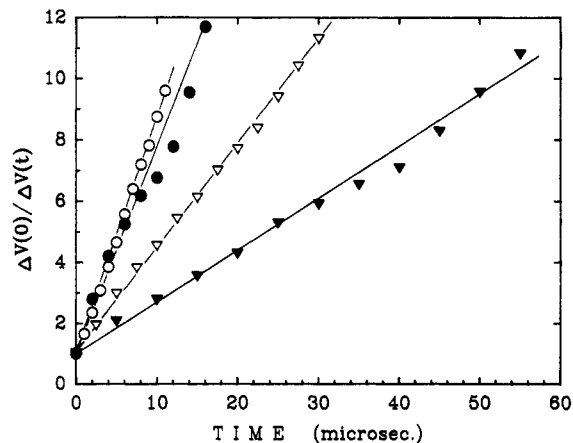**Figure 9.** Plots of $\Delta V(0)/\Delta V(t)$ as a function of time for decay curves shown in Figure 8. The symbols ○, ●, ▽, and ▼ correspond, respectively, to the curves a, b, d, and c in Figure 8.

of dimerization of ion pairs seems again to be reasonable. It should be noted that the rate constant still contains a factor associated with the quantum yield for the ion-pair formation in a form of ϕ^{-1}. Since $\phi > 1$ is unlikely, the value of $k_r = (9.1 \times 10^9)\phi^{-1}$ M^{-1} s^{-1} is definitely larger than that for a typical rate constant for the diffusion-controlled reaction in CCl_4 (= 7.3×10^9 M^{-1} s^{-1}). This subject will be discussed later.

From eqs 8 and 10 we can obtain a ratio

$$V_s(\infty)/V_s(0) = (\mu_2^2/2\gamma)/\Delta(\mu_1^2) \tag{13}$$

Using the ratio = 0.35 as described above, we obtain a relation

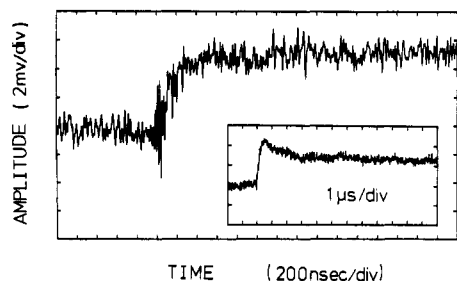$$\mu_2 = [0.35(2\gamma)\Delta(\mu_1^2)]^{1/2} \tag{14}$$

Figure 10. Time dependence of apparatus output for solutions of TMPD and carbon tetrachloride in benzene. The concentrations are 3.75 mM for TMPD and 0.38 mM for CCl_4; the sample cell is of 3-mm optical path length (OD = 1.4); the laser intensity = 1.5 mJ/pulse. The inset shows a signal obtained with the following conditions: TMPD 7.70 mM, CCl_4 0.19 mM, laser intensity = 4.5 mJ/pulse.
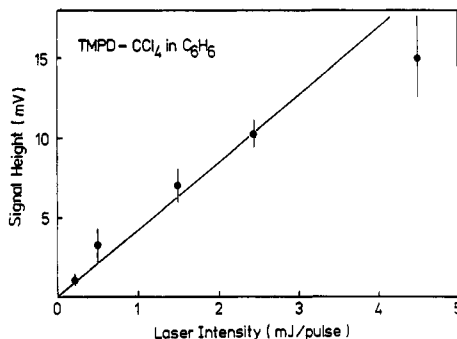

Figure 12. Dependence on concentration of CCl_4 of first-order growth rate of the dielectric absorption signal observed in solutions of TMPD and CCl_4 in benzene. The dashed line corresponds to the diffusion-controlled rate.

Figure 11. Dependence on laser intensity of maximum height of the dielectric absorption signal observed for solutions of TMPD and CCl_4 in benzene. The signals were measured without the FET amplifier. The intensity was monitored just in front of the microwave cavity. Note that at a high laser intensity the appearance of decay in the amplitude causes the maximum signal height to be somewhat lower than that expected from the signal obtained at lower laser intensity.

The actual values of the dipole moments are estimated and discussed in a later section.

TMPD–CCl₄ in C₆H₆. Measurements for mixtures with small amounts of TMPD and CCl_4 dissolved in benzene have been made to examine whether or not the ion pair can be formed in this system. Shown in Figure 10 is a typical example of the signal observed. The signal shows a relatively slow growth reaching a constant level, but in a measurement with higher laser intensity or with a sample of high absorbance the signal again decays at longer time scales, just like the case shown in Figure 2 (see the inset in Figure 10 for this result). Since the signal height is proportional to the laser intensity (see Figure 11), the signal is produced by a one-photon process. For mixtures with a constant concentration of TMPD the growth rate was found to be of first order and proportional to the concentration of CCl_4, as seen in Figure 12. The rate is found to be diffusion-controlled. (See the broken line in Figure 12 corresponding to the diffusion-controlled reaction.) We ascribe the signal to the formation of the ion pair from the reaction of excited TMPD with CCl_4, expressed as follows:

$$TMPD_t^* + CCl_4 \rightarrow TMPD^+Cl^- + CCl_3 \qquad (15)$$

where $TMPD_t^*$ should represent an excited triplet state of TMPD, because the lifetime of the excited singlet state is much shorter (about 5 ns[21-23]) than the observing time scale. This assignment was confirmed by a result that the signal was totally quenched in air-saturated solutions. It is also obvious that no polar species is formed by reaction of $TMPD_t^*$ with oxygen.

It is interesting to compare the magnitude of the maximum amplitude of the signal for TMPD–CCl₄–C₆H₆ (three-component system) shown in Figure 10 and that for TMPD–CCl₄ (two-component system), because those amplitudes should reflect the efficiencies of ion-pair formation from the respective excited states of TMPD. A direct comparison between both signals is not appropriate because the same detection sensitivity cannot be
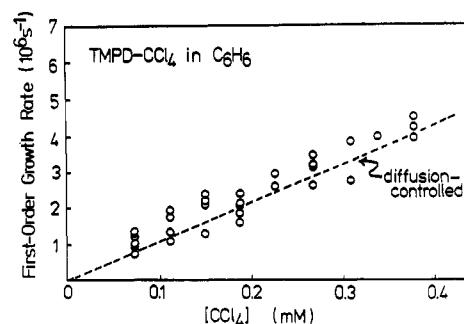
obtained for samples with different solvents. However, the relative magnitude can be known by comparing each amplitude with that observed in a sample containing a third (reference) compound both in CCl₄–C₆H₆ and in CCl₄. As was already described in the experimental section and also used in the measurements described below, diphenylcyclopropenone (DPCP) is a good reference compound, since it decomposes upon UV photolysis into diphenylacetylene and carbon monoxide with unit quantum yield, and this behavior is common in both C₆H₆ and CCl₄ solvents. We have compared the signal amplitudes obtained from measurements made under the same conditions for laser intensity, absorbance, and sample cell used, and it has been found that the ratio of the signal amplitude for the TMPD–CCl₄–C₆H₆ system to that for the DPCP–C₆H₆ system is 3.8 ± 0.3 from three sets of measurements, while the ratio of the amplitude for the TMPD–CCl₄ system to that for the DPCP–CCl₄ system ranges from 3.4 to 4.1 (see Table II). Clearly the concentration of the ion pair formed in the three-component system is almost the same as that in the two-component system. This result leads to either of the following two suggestions: (i) the excited states involved in two- and three-component systems may be the same, namely the triplet state or (ii) if the excited state in the bicomponent system is an excited singlet state, the efficiency of intersystem crossing for formation of triplet TMPD is almost unity. We note that Richard and Thomas[23] reported a value of 0.96 ± 0.10 for the quantum yield of triplet production in the photolysis of TMPD in c-C₆H₁₂.

Although somewhat scattered values, 6.6 eV,[28] 6.2 eV,[29] and 5.9 eV,[30] have been reported for the ionization potential (I_g) of TMPD in the gas phase, much lower energies are evident for the ionization threshold (I_l) for TMPD in liquids. Actually in various hydrocarbon liquids the values range from 4.4 to 5.2 eV.[29,31,32] A lower value of I_l compared with I_g has been ascribed to the effect of the polarization energy of a cation (P_+) and that of an electron (P_e). As demonstrated in the present results for the three-component system, the ionization can occur through triplet TMPD*, whose energy is only 2.9 ± 0.1 eV above the ground state.[33,34] This energy is much lower than I_l described above. In the present case, however, the final species is an ion pair that does not involve a free electron but a negative ion, and both the energy released by dissociative electron attachment to CCl₄ (P_{da}) and the polarization energy of the negative ion (P_-) must be taken into account. Thus in this case the threshold energy for ion-pair production (I_{ip}) is given by

$$I_{ip} = I_g + P_+ + P_e - P_{da} + P_- + P_i \qquad (16)$$

(28) Briegleb, G.; Czekalla, J. *Z. Elektrochem.* **1956**, *63*, 6.
(29) Holroyd, R. A.; Russel, R. L. *J. Phys. Chem.* **1974**, *78*, 2128.
(30) Faidas, H.; Christophorou, L. G.; Datskos, P. G.; McCorkle, D. L. *J. Chem. Phys.* **1989**, *90*, 6619.
(31) Bullo, J.; Gauthier, M. *Can. J. Chem.* **1977**, *55*, 1821.
(32) Hoffman, G. J.; Albrecht, A. C. *J. Phys. Chem.* **1990**, *94*, 4455.
(33) Kalantar, A.; Albrecht, A. C. *Ber. Bunsen-Ges. Phys. Chem.* **1964**, *68*, 361.
(34) Yamamoto, N.; Nakato, Y.; Tsubomura, H. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2603.

where P_i is the energy required for formation of the ion pair from a separated cation and negative ion. The polarization energy of an ion is usually described by Born's formula:[12]

$$P = -e^2/2r_i(1 - 1/\epsilon_s) \qquad (17)$$

where e is the charge of the electron, r_i is the radius of the ion, and ϵ_s is the dielectric constant of the solvent ($\epsilon_s = 2.3$ for benzene). Assuming the radii for TMPD$^+$ and Cl$^-$ are 5 and 1.8 Å, respectively,[35] we obtain, from eq 17, $P_+ = -0.8$ eV and $P_- = -2.3$ eV. The value of P_e can be approximated by V_0,[29] which is the energy of the quasifree electron at the bottom of the conduction band ($V_0 = -0.4$ eV in benzene[36]), and P_{da} is taken to be 0.58 eV.[37] With these values along with $I_g < 6.6$ eV, eq 16 reduces to

$$I_{ip} < 2.8 + P_{ip} \quad (eV) \qquad (18)$$

Although it is difficult to find the exact value of P_{ip}, a negative value is quite reasonable. After all, the threshold for ion-pair formation is lower than the triplet energy and ion-pair formation from triplet TMPD becomes energetically possible in CCl$_4$. The consideration made above leads to a general conclusion that in an electron-attaching liquid the ionization of a solute compound becomes possible at an energy much lower than the usual threshold energy at which free electrons are generated. By production of a free molecular ion pair, the required energy can be reduced by more than 2 eV, and this amount can be further increased by forming a contact ion pair.

Determination of Dipole Moment. Warman and Visser[2] using the microwave absorption technique described earlier have estimated the dipole moment of the ion pair based on the measured magnitude of the microwave conductivity signal along with the known sensitivity factor for their detection cavity and knowledge of the rotational relaxation time of *p*-(dimethylamino)benzonitrile (DMABN) as a model compound. The present technique also allows determination of the dipole moment of photochemical transients as demonstrated in the application to various aromatic ketones.[1,9] The intensity of the observed signal, V_s, can be related to the dipole moment μ (hereafter the subscript 1 will be removed) of the ion pair by eq 1. The values of μ can be determined by comparing the signal with that for a reference compound. The ratio of the signal intensity (the initial amplitude) for the ion pair to that of the reference compound is

$$V_s/V_r = \beta_1^{-1}[S]_0\mu^2 g(\tau_1)/\beta_r^{-1}[S]_r\Delta(\mu_r^2)g(\tau_r) \qquad (19)$$

where the subscript r corresponds to the reference compound and $\Delta(\mu_1)^2$ has been approximated by μ^2 (the square of the dipole moment of the ion pair itself) because the square of the dipole moment for ground-state TMPD is very small compared to μ^2 (see below). Since the values of the β's can be determined by a procedure already described,[1,9] the only problem is to find the values of $g(\tau_1)$ and $g(\tau_r)$. With $\omega = 6 \times 10^{10}$ s^{-1} and a typical rotational relaxation time of 100 ps for a molecule the size of TMPD, the expression of $g(\tau)$ can be approximated by $(\omega\tau)^{-1}$. Thus $g(\tau)$ is proportional to τ^{-1}. In a case where the electronically excited state is concerned, the value of $g(\tau)$ in the excited state is regarded as the same as in the ground state because the size of the molecule changes very little upon excitation, and the rotational relaxation time is approximately proportional to the molecular volume (rigid-sphere model).[38] In the present case, however, we need to know $g(\tau)$ of the ion pair for which we have no information on the exact geometrical structure. It is safe, though, to employ a molecule of similar size as a model compound. For this purpose we chose *p*-(dimethylamino)benzonitrile, which has a molecular structure similar to that of TMPD; its dipole moment in the ground state is well known (6.6 D).[20] We can also

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(35) The molecular size of TMPD can be estimated from known lengths of the constituent bonds in the molecule. The radius of Cl$^-$ can be found in a standard handbook.

(36) Schiller, R.; Vass, Sz.; Mandics, J. *Int. J. Radiat. Phys. Chem.* **1973**, *5*, 491.

(37) This value is calculated by EA - BE, where EA is the electron affinity of the Cl atom and BE is the bond-dissociation energy of CCl$_3$-Cl.

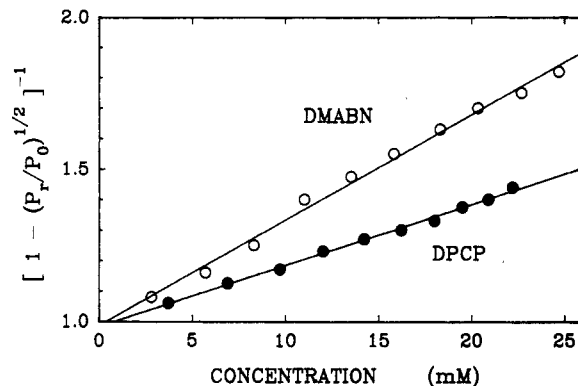(38) Debye, P. *Polar Molecules*; Dover: New York, 1928.

Figure 13. Plot of appropriate function of reflected microwave power against concentration of *p*-(dimethylamino)benzonitrile (DMABN) and diphenylcyclopropenone (DPCP) in carbon tetrachloride.
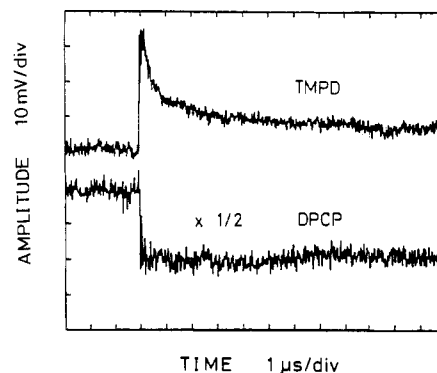

Figure 14. Comparison between time dependence of apparatus output for TMPD–CCl$_4$ solution and that for DPCP–CCl$_4$ solution. The concentrations are 4.34 mM for TMPD and 7.70 mM for DPCP; the sample cell is of 1-mm optical path length (OD = 1.0); the laser intensity = 1.45 mJ/pulse.

compare our result with that by Warman and Visser.[2] The relative magnitudes of the $g(\tau)$'s for the model compound and the reference compound (DPCP in the present case) can be found from measurement of the microwave power, P_r, reflected from the cavity against the concentration, [S], of these solutes. This is called the "static measurement"[1] and is based on the following relation

$$[1 - (P_r/P_0)^{1/2}]^{-1} = (1 + \beta^{-1})/2 + \beta^{-1}C[S] \qquad (20)$$

where P_0 is the microwave power incident on the cavity and $C = {}^1/_2 AQ_0\eta g(\tau)\mu^2$. Plots based on eq 20 for DMABN and DPCP as the model (denoted by the subscript m) and reference compounds, respectively, in CCl$_4$ are shown in Figure 13. The slope of each straight line gives the value of C. Since the ratio C_m/C_r is equal to $[g(\tau_m)/g(\tau_r)](\mu_m^2/\mu_r^2)$, eq 19 reduces to

$$V_s/V_r = (\beta_s^{-1}[S]_0 C_m\alpha\mu^2/\mu_m^2)/(\beta_r^{-1}[S]_r C_r\Delta(\mu_r^2)/\mu_r^2) \qquad (21)$$

where $\alpha = g(\tau_1)/g(\tau_m)$. If we make measurements under the same irradiation conditions of laser intensity, absorbance of the solution, and sample cell for a pair of samples of TMPD and DPCP, the ratio $[S]_0/[S]_r$ can be replaced by the ratio of the quantum yields, ϕ/ϕ_r. Since $\phi_r = 1$ and $\Delta(\mu_r^2)/\mu_r^2 = -1$ for DPCP,[1] we finally obtain

$$V_s/V_r = -\beta_s^{-1}\phi C_m\alpha\mu^2/\beta_r^{-1}C_r\mu_m^2 \qquad (22)$$

We have made four sets of measurements using two different cells. An example of the comparison of both signals is shown in Figure 14. The values of C's, β^{-1}'s, and measured amplitudes, V's, are shown in Table II. Using the value $\mu_m = 6.6$ D, we can calculate the values for μ's from eq 22. These values are listed at the last column of Table II. Four values of μ are in good agreement with each other, and we take the averaged value $\mu = (8.5 \pm 0.4)(\phi\alpha)^{-1/2}$ D as a reliable one. Warman and Visser[2] obtained $\mu = (8.7 \pm 0.9)\phi^{-1/2}$ D, assuming that the relaxation time for the ion pair is about 1.4 times that for DMABN. This corresponds to $\alpha =$

TABLE II: Values of Parameter C Obtained from "Static Measurements" Using Different Sample Cells (A and B) for the Model Compound (DMABN) and the Reference Compound (DPCP), Amplitudes of Signals for the Ion Pair (V_s) and the Reference Compound (V_r), and Dipole Moment (μ) of the Ion Pair, Determined from Eq 24

	C_m, M^{-1}	C_r, M^{-1}	$\beta_1^{-1\,a}$	$\beta_2^{-1\,a}$	V_s, mV	V_r,^{b} mV	μ, D
A	34.6	20.8	1	0.76	30.1	−8.82	$8.18(\phi\alpha)^{-1/2}$
					39.3	−9.57	$8.97(\phi\alpha)^{-1/2}$
B	34.3	19.6	1	0.77	30.9	−8.94	$8.14(\phi\alpha)^{-1/2}$
					38.9	−10.0	$8.85(\phi\alpha)^{-1/2}$

$^a\beta^{-1} = (1 + 2C[S])^{-1}$ corresponds to the actual coupling factor for a solution with concentration [S] of polar solute. For a nonpolar or near nonpolar solute, $\beta^{-1} = 1$. See ref 1 for details. ^{b}The direction of the signal for DPCP is downward, so the amplitude is a negative value.
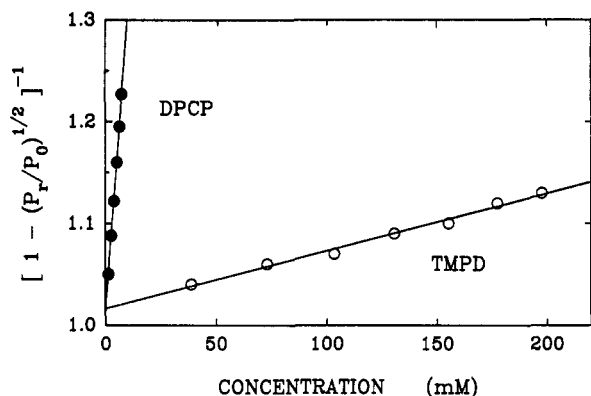

Figure 15. Plot of appropriate function of reflected microwave power against concentration of TMPD and diphenylcyclopropenone (DPCP) in carbon tetrachloride.

0.70 in the present case, which gives $\mu = (10.2 \pm 0.5)\phi^{-1/2}$ D. This is slightly larger than that obtained by Warman and Visser. We have also attempted the determination of the dipole moment of the ion pair, using the same method as described above but employing the ground-state TMPD molecule as the model compound. Since TMPD has a small dipole moment of 1.20 ± 0.13 D, a little dielectric absorption is expected when it is dissolved in CCl$_4$ solvent. Plots based on eq 20 for the results of static measurements made for both TMPD and DPCP using an identical sample cell are shown in Figure 15. As expected very different values for the C's are obtained; 0.60 and 11.6 M^{-1} for TMPD and DPCP, respectively. As the sample cell used in this measurement is different from those used for DMABN, the value of C for DPCP is rather small compared with values listed in Table II, but in applying eq 22 the required value is the ratio C_m/C_r, which is independent of the type of the cell used. Thus, using $C_m/C_r = 0.052$, $\mu_m = 1.20 \pm 0.13$, and the signal amplitudes V_s and V_r listed in Table II, we can calculate the value of the dipole moment to be $(9.0 \pm 1.3)(\phi\alpha)^{-1/2}$ D.

The above treatment involves the use of two unknown parameters ϕ and α. There is, however, another useful way of estimating the value of μ, which does not involve any parameters associated with the rotational relaxation time such as α. We utilize the value of the rate constant for ion-pair association reaction 4. According to the theory of the stationary diffusion-controlled reactions in solutions,[39] the rate constant can be expressed by eq 23, where

$$k_D = 4\pi D_i r_c/\xi \tag{23}$$

$D_i/2$ is the diffusion constant of the ion pair, r_c is the distance at which the potential energy $V(r)$ of the interaction between two particles is equal to kT, and

$$\xi = r_c \int_R^\infty \exp[V(r)/kT]r^{-2}\, dr \tag{24}$$

where R is the actual reaction radius. The potential energy for two identical ion pairs with moderate dipole moments is mostly of a dipole–dipole electrostatic interaction, represented by

$$V(r) = -2\mu^4/(3\epsilon_s kTr^6) \tag{25}$$

For this potential energy we obtain, from eq 24

$$\xi = \int_0^{r_c/R} \exp(-x^6)\, dx = 0.928 \tag{26}$$

for $r_c/R \geq 1.3$. Even for $r_c/R = 1$ the value of ξ becomes slightly lower (0.888). Thus, as long as $r_c > 1.3R$, which holds in usual cases, the rate constant becomes independent of the reaction radius R. Substituting experimental values of k_r listed in Table I for the value of k_D in eq 23 and using $\xi = 0.928$ ($r_c/R \geq 1.3$ is assumed) and $D_i/2 = 4.8 \times 10^{-6}$ cm^2 s^{-1} calculated from the viscosity of CCl$_4$ ($= 0.91 \times 10^{-2}$ g cm^{-1} s^{-1}) at 298 K, we obtain the values of r_c's and, therefore, the values of μ_i's. These are also listed in Table I. It must be pointed out that the value of r_c derived here appears to be slightly longer than the molecular size of TMPD$^+$ or an ion pair (see later sections). This is consistent with the short-range interaction potential of two ion pairs. The assumption of $r_c/R \geq 1.3$ seems reasonable and may not introduce a serious error in our estimation of r_c.

The obtained value $\mu = (11.2 \pm 1.4)\phi^{-3/2}$ D may be compared to that determined above from the signal amplitudes. Note that both approaches give similar values, but each expression contains an additional factor of ϕ with different powers. Since the values from both approaches must coincide with each other, we may put $10.2\,\phi^{-1/2} = 11.2\,\phi^{-3/2}$ to obtain $\phi = 1.1$. Since it is unlikely that $\phi > 1.0$, we suggest that the quantum yield for the ion-pair formation is very close to unity. If we take $\phi = 1$, the original expression for the value of the dipole moment determined from the signal amplitude reduces to $(8.5 \pm 0.4)\alpha^{-1/2}$ and $(9.0 \pm 1.3)\alpha^{-1/2}$ for DMABN and TMPD as the model compounds, respectively. Wherever around TMPD$^+$ the Cl$^-$ ion is attached, the molecular size of the ion pair may not differ much from that of DMABN nor TMPD. As to the DMABN case, regarding the uncertainty of the ratio of molecular size of the ion pair to that of DMABN as being between 1.0 and 1.2, the ratio of the molecular volume may be between 1.0 and 1.7. This leads to a relation, 8.1 D $< \mu <$ 11.6 D. For the TMPD case the size ratio may be slightly smaller than for the DMABN case because of the difference between the dimethylamino and cyano groups. If we take the ratio of the molecular size to be between 1.0 and 1.1 in this case, we obtain 7.7 D $< \mu <$ 11.8 D. Taking into account the value 11.2 ± 1.4 D obtained from the rate constant, k_r, we can conclude that the value of the dipole moment of the ion pair is 11^{+2}_{-3} D.

As to the structure of TMPD cation, it has been suggested that the semiquinone-type conformation is the most probable,[40] and therefore, the positive charge is symmetrically distributed in the radical cation and the electrons are delocalized over the benzene ring and the N–ring bonds. This implies that the most probable geometrical structure for the ion-pair is such that Cl$^-$ is placed on the center of the benzene ring. The value of the dipole moment, 11 D, corresponds to a configuration where a positive and a negative charge are separated by a distance of about 2.3 Å.

With the value $\mu = 11$ D we can also estimate the value of the dipole moment of the ion-pair dimer, using eq 14; namely

$$\mu_2 = [(0.35)(2\gamma)]^{1/2}(11)\ \text{D} \tag{27}$$

The value of γ depends on the structure (or the molecular size) of the ion-pair dimer, and according to the rigid-sphere model, we have the relation

$$\gamma = g(\tau_1)/g(\tau_2) \simeq \tau_2/\tau_1 \simeq a_2^3/a_1^3 \tag{28}$$

where the a's are molecular radii associated with the dielectric relaxation. Obviously $a_2/a_1 > 1$, and the ratio is at most 2^3 where

(39) Hummel, A. *Radiation Chemistry, Principles and Applications*, Farhataziz, Rodgers, M. A. J., Eds.; VCH Publishers: New York, 1987; Chapter 4.

(40) Poizat, O.; Bourkba, A.; Buntinx, G.; Deffontaine, A.; Bridoux, M. *J. Chem. Phys.* **1987**, *87*, 6379.

the two ion pairs align linearly and the molecular length is doubled, though this is unlikely. If the geometrical structure of the ion pair is as described above, a probable configuration for the ion-pair dimer is such that two ion pairs align parallel and one Cl⁻ is sandwiched by two benzene rings. The molecular size of the TMPD⁺ in a solid state is reported to be roughly 10.9 Å × 3.8 Å, and the effective hydrodynamic diameter is slightly less than the maximum dimension of the solid.[41] If we assume the length of TMPD⁺ to be about 10 Å and also take the distance between the benzene ring and Cl⁻ to be 2.3 Å (estimated above), the radius for molecular rotation, due to the high-frequency electric field, with respect to the axis perpendicular to the long molecular axis passing through two nitrogen atoms may increase slightly, roughly from 5 Å for the ion pair to about 6 Å for the dimer. This results in $a_2/a_1 = 1.2$ or $\gamma = 1.7$, and therefore $\mu_2 = 12$ D. If the rotation occurs with respect to an axis parallel to the N–N axis, the ratio a_2/a_1 will be larger than the above. The actual rotation may be an intermediate case or an averaged one between the two extremes. On the other hand, one can imagine a structure in which one Cl⁻ ion is sandwiched by two benzene rings but the two N–N axes align perpendicularly. This conformation can be more stable than the former structure because of the reduction of the steric factor due to dimethylamino groups. In this case, regardless of the axis of rotation, the ratio a_2/a_1 is larger than unity, probably close to the value 1.2 that we estimated above. In any event, the dipole moment of the dimer appears to be larger than that of ion pair itself.

In the analysis of second-order-decay signals, we have assumed that the efficiency of dimer formation in the collision of two ion pairs is unity. If this is not so, we must multiply the right side of eq 7 by a certain efficiency factor. However, it can be easily shown that such a factor causes no change in the expression of eq 12. The only change is associated with the evaluation of $V_s(\infty)$ (eq 11), which is related, as discussed above, to the magnitude of the dipole moment of the dimer. It is clear that the presence of the efficiency factor further increases the dipole moment of the dimer as compared with values estimated on the basis of 100% efficiency of dimer formation.

In the evaluation of the signal amplitudes we have neglected the effect of the CCl₃ that is produced in the process of ion-pair formation and may have a dipole moment. The CCl₃ radical has a pyramidal structure,[42] but its dipole moment has not been reported. It is reasonable to regard CCl₃ as having an intermediate structure between those analogous to CH₃ and CHCl₃. It is known that the CH₃ radical has a planar structure[42] with no dipole moment and the dipole moment of CHCl₃ is 1.1 D.[20] Thus the dipole moment of CCl₃ may be about 1 D or less. If the dipole moment of the ion pair is around 10 D and that of CCl₃ is, for example, 1.0 D, their contributions to the observed signal amplitude are estimated to be 100 and 1 in relative magnitudes, because the signal amplitude is proportional to a change in the square of the dipole moment. As a result the effect of CCl₃ on the signal can be neglected. This is also the reason why the dipole moment of TMPD in the ground state ($\simeq 1.2$ D) can be neglected in our calculation.

Quantum Yield of Ion-Pair Formation. Although our data and analysis indicate that the quantum yield for ion-pair formation is close to unity, this is in serious disagreement with much lower values ($<10^{-2}$) reported by Meyer[17] for TMPD in CHCl₃, CH₂Cl₂, CH₂Br₂, and CHBr₃ solvents, though a value in CCl₄ is not reported. Similar low values have been reported for molded polymer films containing TMPD and halomethanes.[43] These data have been obtained by recording continuous photoabsorption of Wurster's blue (TMPD⁺) at about 570 nm during irradiation by 280–390-nm UV light. As described in the Introduction a very small quantum yield gives rise to a gigantic dipole moment of the

ion pair if one uses a previously reported expression[2] for the dipole moment. However, this point has been confirmed by the present work, since the obtained expression for the dipole moment is not much different from the previous one (see Table II). Hence, there exists a serious problem in interpreting our results.

One may claim that the signal that we observed, especially that on a microsecond time scale, does not correspond to the contact ion pairs. If so, what is responsible for it? One might explain that the initial growth represents the formation of free ion pairs, namely TMPD⁺ and an electron (or a negative ion), and the second-order decay of the signal corresponds to their recombination forming a contact ion pair. For free ions, a large microwave conductivity can be produced if they have large mobilities in liquids.[11] Although the mobility of electrons in nonpolar solvents is known to be several orders of magnitude larger than that of molecular ions, the possibility of free electrons as negative charge carriers in the present case can be excluded not only because the production of free electrons is energetically unlikely but because the surrounding solvent CCl₄ molecules capture electrons very rapidly even if free electrons are formed. Let us then consider the possibility of recombination between TMPD⁺ and Cl⁻ for the observed second-order decays. Again expression 23 can be used for the rate constant k_D for a diffusion-controlled ion-recombination reaction, but in this case D_i is the sum of the diffusion constants of the positive and the negative ions ($D^+ + D^-$). Equation 23 may be combined with $D = \mu_i kT/e$ (μ_i, the mobility), to obtain

$$k_D = 4\pi r_c(\mu_i^+ + \mu_i^-)kT/e \qquad (29)$$

For a pair of oppositely charged ions, the potential energy is Coulombic, and the critical distance r_c is the so-called "Onsager length". For CCl₄ solvent ($\epsilon_s = 2.23$), $r_c = 250$ Å and $r_c/R \gg 1$. Then one obtains $\xi = 1$. With these values and a value of 6 × 10⁻⁴ cm² V⁻¹ s⁻¹ as a reasonable estimate for the mobility sum of TMPD⁺ and Cl⁻ in CCl₄,[44] eq 29 gives $k_D = 3 \times 10^{11}$ M⁻¹ s⁻¹. This rate constant is more than an order of magnitude larger than k_r obtained from the actual signals if one assumes $\phi = 1$ (see Table I). In order for the measured rate constant to be in agreement with the above-estimated value, the quantum efficiency of the ion production needs to be 0.12. On the basis of their observed signal, Warman and Visser[2] suggested a value of 0.15 for the quantum efficiency of the ionization if the signal were interpreted as being due to the free ions. Note that these values are still very large compared with (4–8) × 10⁻³ reported by Meyer.[17] The model of production of freely diffusing ions is confronted with another problem regarding the present results for three-component systems. The observed diffusion-controlled rate for the ion-pair production suggests that the oppositely charged ions produced when a TMPD* molecule collides with a CCl₄ molecule exist at a very close distance to each other, and no free homogeneous diffusion can occur. The initial products then should be regarded as contact ions. Consequently, the model of formation of free TMPD⁺ and Cl⁻ ions followed by their recombination may not be appropriate to explain the observed second-order-decay signals. We cannot find any other initial species that gives a large conductivity signal or has a dipole moment of about 10 D.

There might be a possibility that the decaying part of the signal is due to the geminate recombination of the ion pair with the CCl₃ radical to yield neutral TMPD and CCl₄ because that reaction would also show a second-order decay. However, should all the ion pairs decay by this process, the signals would have reached the base line, which was not observed in our measurements. On the other hand, if a part of the ion pairs could suffer from such decays, we would expect the experimentally observed decays not being of a pure second order but of a superposition of two different types, since the geminate recombination between species existing close each other should be faster than the homogeneous recombination. We could not see definite evidence of such decays within experimental errors, as is clear from Figures 4–9. We can consider a rare case that two types of decays have, for some reason, very

(41) Lombardi, J. R.; Raymonda, J. W.; Albrecht, A. C. *J. Chem. Phys.* **1964,** *40,* 1148.
(42) Herzberg, G. *The Spectra and Structures of Simple Free Radicals, An Introduction to Molecular Spectroscopy*; Cornell University Press: New York, 1971.
(43) Meyer, W. C. *J. Phys. Chem.* **1970,** *74,* 2122.

(44) van den Ende, C. A. M.; Luthjens, L. H.; Warman, J. M.; Hummel, A. *Radiat. Phys. Chem.* **1982,** *19,* 455.

similar recombination rate constants. Then all the analyses made above may be unaffected, except that the flat level observed in the signal at a longer time scale corresponds to ion-pair dimers with concentrations smaller than that expected from the initial concentration of the ion pairs. This might lead to a suggestion that the dipole moment of the dimer is much larger than that estimated above.

It may be possible that the low quantum yield obtained by Meyer does not reflect that for the ion pair formed immediately (say, microseconds) after the photoirradiation. Continuous irradiation by UV photons may cause a similar situation to that represented in Figure 2c; that is, most of the ion pairs then formed turn immediately into a part of a large cluster. This interpretation assumes that as the aggregation of ion pairs proceeds the absorption at 570 nm characteristic of TMPD$^+$ decreases considerably for some reason and also that a Sargent SR recorder used in the absorption measurement by Meyer has a limited time resolution, though we are not sure about the latter. It must be noted that a TMPD–CCl₄ sample at several tens of seconds after irradiation by several hundred laser pulses gave a Wurster's-blue like color, but only a weak broad absorption spectrum was observed, which spans from 450 to 900 nm with a slight maximum at around 530 nm, and no structure characteristic of TMPD$^+$ was seen at 570 nm. To our knowledge there have been no direct determinations of the quantum yield for formation of the ion-pair itself at such shorter times as microseconds.

It is possible that the efficiency of the ion-pair formation in CCl₄ solvent is very large compared with that in other halomethanes. We have measured the microwave dielectric absorption signals for mixtures of TMPD and several halogenated compounds in benzene and n-hexane solvents[45] and found that the initial signal intensity decreases in the order $CCl_4 \geq C_2H_5I > C_2H_5Br > C_2H_5Cl$, and especially the signal for C_2H_5Cl is immeasurably small, possibly more than two orders of magnitude lower than that for CCl₄. A similar trend has been observed for halobenzenes.[45] Since the intensity is approximately proportional to the concentration of the ion pair TMPD$^+$X$^-$ (X, a halogen atom), the efficiency of the ion-pair formation may vary as in the above order. We have also found that the trend in the efficiency correlates very well with the rates of capture of thermal electrons by these halogenated compounds, measured in the gas phase.[45] It seems that the relative position of the potential energy surfaces between a neutral compound and its negative ion determines the rate and the efficiency of the electron transfer from TMPD to halogenated compounds. CCl₄ is probably the most effective in capturing low-energy electrons. The thermal electron attachment rate

constants for CHCl₃ (2×10^{-9} cm³ molecule^{-1} s^{-1} [46]), CH₂Cl₂ (6.5×10^{-13} cm³ molecule^{-1} s^{-1} [46]), and CH₂Br₂ (3.2×10^{-8} cm³ molecule^{-1} s^{-1} [47]) are much lower than for CCl₄ (4×10^{-7} cm³ molecule^{-1} s^{-1} [46]), though a value for CHBr₃ is not known. Therefore, lower efficiencies of ion-pair formation for these compounds can be expected.

It is obvious from the above discussion that further studies, preferably spectroscopic measurements with a good time-resolution, with a specific focus on the quantum yield for formation of the ion pair itself are needed for clearing up this problem.

Conclusions

Using the microwave dielectric absorption technique, we have observed the formation of the ion pair TMPD$^+$Cl$^-$ and its association processes leading to coagulates. TMPD can be ionized by single 355-nm photons in CCl₄, though no free electrons are produced. The electron-attaching ability of CCl₄ is the main factor for ion-pair formation. This is clearly demonstrated by results for the three-component system where the ion pair is formed via excited triplet TMPD, whose energy is only 2.9 eV above the ground state. The dipole moment of the ion pair has been determined on the basis of the initial amplitudes of the dielectric absorption signals. The fact that a good agreement is found between the determination of the dipole moment from the signal amplitude and that from the ion-pair association rate suggests that the quantum yield for the ion-pair formation is close to unity. The dipole moment of the ion-pair dimer seems to be larger than that of the ion pair. Finally, we must point out that our approach is to investigate photochemical transients solely on the basis of the polarity change, and therefore the data always accompany some ambiguity in the identity of the species involved. The problem on the quantum yield of ion-pair formation demonstrates this clearly. However, it is also obvious that observation of polarity changes gives us new information on the nature of transients that cannot be easily explored by conventional means.

(45) Shimamori, H.; Hanamuro, K.; Uegaito, H. To be published.

(46) Christophorou, L. G.; McCorkle, D. L.; Christodoulides, A. A. *Electron–Molecule Interactions and Their Applications*; Christophorou, L. G., Ed.; Academic Press: New York, 1984; Vol. 1, Chapter 6.

(47) Lee, T. G. *J. Phys. Chem.* **1963**, *67*, 360.