The Photoionization Mechanism of *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine in Acetonitrile

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The photoionization mechanism of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) in an acetonitrile solution was investigated by means of the fluorescence lifetime measurement, picosecond and nanosecond laser photolyses, and photocurrent measurement. The temperature dependence of the fluorescence lifetime was interpreted in terms of the thermally activated monophotonic ionization or the ion-pair-formation mechanism from the $S_{1,0}$ excited level. Picosecond laser photolysis clearly showed that a direct ionization from higher S_1 levels took place before relaxation into the $S_{1,0}$ level. The relative yields of triplet, ion-pair, and cation formation were estimated from analyses of the transient spectra and the photocurrent.

Considerable efforts have been devoted to the study of the photoionization mechanism of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) in nonpolar and polar solvents. Tsubomura and his co-workers[1,2] have found a biphotonic ionization process in a nonpolar solvent by means of microsecond flash photolysis, and have suggested a monophotonic process in an acetonitrile solution on the basis of photocurrent measurements.[3] Ottolenghi[4–6] and his group performed an extended spectral study indicating the importance of the singlet-intermediate state. Richards and Thomas[7] have used microsecond and nanosecond flash photolysis techniques for studying the photoionization in cyclohexane, ethanol, and water; they established the characters of the triplet and ion-pair states and discussed a possible mechanism of photoionization in water. Ottolenghi[8] suggested a charge transfer to the solvent (CTTS) state as an intermediate in the photoionization of several organic molecules. The importance of the CTTS state has been shown in the decay and photoionization of sodium 8-anilino-1-naphthalenesulfonate.[9,10] In spite of many investigations so far performed, however, no fast method of analyzing the monophotonic ionization process in a polar solvent has yet appeared.

In this paper we present a combined investigation of the photoionization mechanism of TMPD in an acetonitrile solution by using the results of picosecond and nanosecond laser photolyses and photocurrent and fluorescence-lifetime measurements.

Experimental

Materials. The TMPD was obtained from the Aldrich Chem. Co., and was purified by vacuum sublimation in a furnace with a temperature gradient. The acetonitrile was refluxed over P_2O_5 and distilled. The hexane was a spectrograde product of Merck. The 1,3-pentadiene, a mixture of cis and trans isomers from Wako Pure Chem., was purified, while a zone-refined naphthalene from Tokyo Kasei was used without further purification.

Fluorescence-lifetime Measurements. The fluorescence-lifetime measurements were performed by two methods. One was a photon-counting technique employing a discriminator and a TAC (Canberra 1443A) combined with a MCA system. The light source was a free-running lamp in air at 1 atm; the 337-nm light was selected after passing it through a Nikon G250 monochromator. The half-band width of the pulse duration was 2.5 ns. Picosecond laser (a mode-locked Nd-YAG laser) excitation, followed by recording the fluorescence decay with a streak camera (HTV C-1000), was also used for the lifetime measurements in the range of a few nanoseconds. The temperature dependence of the fluorescence lifetimes was measured by circulating cooled nitrogen gas around the sample cell, while the temperature was kept constant with an accuracy of ±0.5 °C. The results obtained with the photon-countig method are tabulated in Table 1.

Nanosecond Laser-flash Photolysis. The transient absorption in the nanosecond and microsecond time domain was measured by means of nanosecond laser-flash-photolysis apparatus. The nitrogen laser was a home-made TEA type with a peak power of 500 kW and a time duration of 2 ns. All the solutions used for the fluorescence-lifetime and laser-photolysis experiments were degassed at least five times by means of a freeze-pump-and-thaw method. The temporal changes in the absorbance were recorded with an oscilloscope (Tektronix 485) at twenty points of significant absorbance; these data were then used to obtain the time-resolved transient absorption spectra.

Picosecond Laser-flash Photolysis. The transient absorption in the picosecond time region was measured by

TABLE 1. FLUORESCENCE LIFETIMES IN VARIOUS SOLVENTS AT DIFFERENT TEMPERATURES, AND ACTIVATION ENERGY FOR THE DECAY RATE OF THE TMPD $S_{1,0}$ STATE

Temperature / K Solvent	Lifetime/ns										Activation energy / kJ mol^{-1}
	313	298	274	260	246	232	217	202	186	168	
Acetonitrile	0.8	1.3	3.5	6.9	9.5	12.4					33.9
Methanol	3.0	4.0	7.2	10.1	11.6	12.1	13.1	13.2	13.0		30.1
Ethanol	6.9	7.8	9.0	9.6	9.8	10.2	11.0	11.5	12.1	12.3	5.0
Hexane	4.9	4.9	4.9								—

means of a laser excitation of a third harmonics of a mode-locked Nd:YAG laser (355 nm) with a 20-ps pulse width. The laser light from the YAG oscillator was amplified and used for excitation and for recording transient absorption by means of multichannel photo-diode system with a pulsed-continuum light source (D_2O+2-propanol) or a fast-photomultiplier tube system (HTV R1294U), with a Xe arc lamp as a monitoring light. The Xe lamp was fired by a strong laser pulse focussed onto the arc electrode.[11]

Photocurrent Measurements. The photocurrents induced in irradiated solutions were measured in order to determine the decay of the transient carrier. The induced current in the solution was measured with Pt-electrodes separated by 0.3 mm after excitation from a YAG laser. The transient current was amplified through a preampifier (model 115, PAR) and recorded by means of an oscilloscope (Hewlett·Packard, 1744A). Between the electrodes, a constant voltage of 20 V was applied during the photocurrent measurements. All solutions were bubbled with nitrogen gas at least for 30 min or longer, because otherwise the dissolved oxygen would quench the photocurrent.

Results and Discussions

Fluorescence Lifetime. As is shown in Table 1, a temperature dependence of fluorescence lifetimes was found in ethanol, methanol, and acetonitrile; however, it was not observed in hexane. This observation might be correlated with the temperature independence of the intersystem crossing and the absence of monophotonic ionization in hexane. Richards and Thomas[7] reported that the triplet yield of TMPD in cyclohexane was 0.96± 0.10 and that the fluorescence yield was 0.09. Since hexane is as inert as cyclohexane, all excited species may decay either into the triplet state through intersystem crossing at the rate k_{ISC} or to the ground state at the fluorescence rate k_f in hexane. Then the fluorescence lifetime in hexane, τ_h, is given as:

$$\tau_h = 1/(k_{ISC} + k_f) = 4.9\ \text{ns},$$

where $k_{ISC}=\phi_T/\tau_h=1.96\times10^8\ s^{-1}$, $k_f=\phi_f/\tau_h=0.18\times10^8\ s^{-1}$, and other radiationless processes are ignored. In a polar solvent such as acetonitrile, the monophotonic ionization process with the rate k_{ion} is involved, as will be discussed later, and the fluorescence lifetime, τ_f, will be shrunk as is described by:

$$\tau_f = 1/(k_{ion} + k_{ISC} + k_f) = 1.0\ \text{ns}.$$

k_{ion} is estimated as $8\times10^8\ s^{-1}$ at 300 K if k_{ISC} and k_f are assumed to be independent of the solvent and the temperature (Here the value of τ_f is obtained with a streak camera after picosecond excitation.). If we assume that the temperature dependence of the fluorescence lifetime is to be ascribed to the activation of the ionization process, then k_{ion} will be represented as $k_{ion}=k_0\exp(-\Delta E/RT)$, where other processes are considered to be temperature-independent. These assumptions are supported by the variation in the activation energies for acetonitrile, methanol, and ethanol (Table 1).

From the slope of $\ln(1/\tau_f-1/\tau_0)$ shown in Fig. 1, the activation energies for the temperature-dependent ionization process are determined to be as is shown in Table 1. Here, τ_0 is the fluorescence lifetime obtained at a lower temperature, where the thermal process can be neglected. In an acetonitrile solution, the thermally activated decay process is most evident; below it will be connected with thermally activated monophotonic ionization process found by means of picosecond laser photolysis.

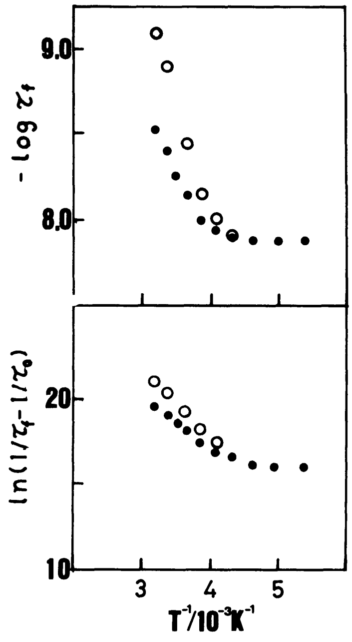

Fig. 1. Temperature dependence of fluorescence lifetime (τ_f) and $\ln(\tau_f^{-1}-\tau_0^{-1})$. ○: Acetonotrile and ●: methanol solutions.

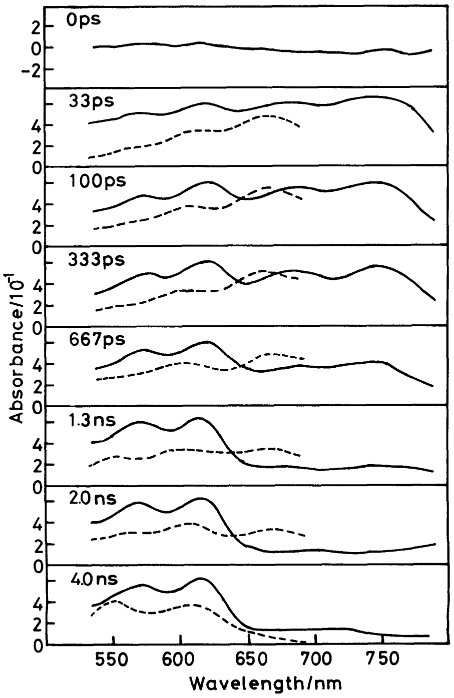

Fig. 2. Transient spectra of photolyzed TMPD measured with MCPD system in acetonitrile (——) and hexane (------) solutions.

Picosecond Laser-flash Photolysis. *Hexane Solution*: The transient absorption spectra after picosecond-laser excitation are illustrated in Fig. 2. In a hexane solution, the $S_n \leftarrow S_1$ absorption bands were observed immediately after excitation to have peaks at 670, 610, and 560 nm (the 700-nm region was not recorded); all these bands decayed with a time constant of 5 ns. The fluorescence lifetime (Table 1) in hexane was 4.9 ns; therefore, these bands were assigned to the $S_n \leftarrow S_1$ absorption. In the transient spectra in the 610—520 nm region, new bands grew with a time constant of $\simeq$5 ns, and the spectral shape was coincident with the previously reported $T_n \leftarrow T_1$ absorption.[1]

In a hexane solution, the biphotonic ionization may occur via the siglet- or triplet-excited states under a high-intensity light, but the present laser has not enough power and has the very short duration of 20 ps; therefore, the biphotonic process can be neglected.

When the temporal changes in the transient spectra are superposed, an isosbestic point of the $S_n \leftarrow S_1$ and $T_n \leftarrow T_1$ absorptions is found at 620 nm. The molar-extinction coefficient of the $T_n \leftarrow T_1$ at 570 nm was determined by Richards and Thomas[7] to be 11900. The molar absorption coefficient of the $S_n \leftarrow S_1$ absorption at 670 nm could be determined as 18000 by using the data at a time delay of 100 ps and the above-mentioned value for the $T_n \leftarrow T_1$ absorption. Thus, the picosecond laser photolysis in hexane showed the band shapes of the $S_n \leftarrow S_1$ and $T_n \leftarrow T_1$ absorptions and their molar-absorption coefficients.

Acetonitile Solution: In an acetonitrile solution, the spectra immediately after the excitation show peaks at 750, 680, 620, and 570 nm. The longer-wavelength peaks at 750 and 680 nm decayed with a lifetime of 1 ns, which indicated that these bands were due to the $S_n \leftarrow S_1$ absorption since the lifetime of the fluorescence was determined as 1 ns. The peaks at 620 and 570 nm should be assigned to the absorption bands of the photoionized product, either the cation or the ion-pair or the CTTS state, because these band positions coincide with those reported for cations.[1] No distinction between the spectra of the ion-pair and the CTTS states with a cation is discernible, but we consider that the ion-pair state is the only singlet intermediate before the ionization because the CTTS state may have a similar electronic structure. Moreover, we can not say simply at this moment that the product is a cation, because there are several decay processes for this transient absorption. In the spectrum at 33 ps after the excitation, these peaks were already found, implying that a direct ionization or ion-pair formation took place before relaxation to the $S_{1,0}$ state. In the spectrum of the 4-ns time lag, some contribution of the triplet state might overlap. As is well known,[1] the cation spectra and the $T_n \leftarrow T_1$ absorption bands are very close to each other, and so the separation of the transient spectra into these components is rather difficult without the aid of other means. The results of nanosecond flash photolysis and the photocurrent measurements were used for this analysis. In the picosecond photolysis spectra, the cation-like species were found immediately after the excitation; in addition to this, another process to produce this species was indicated because the cation-like band increased in intensity with a time constant of 1.2 ns. This temporal change in the spectra was also confirmed by the measurement of the transient absorbance with a fast photomultiplier tube, as is shown in Fig. 3. The analysis of the growth of the absorbance at 610 and 540 nm showed the rise time of 1.1 ns, which is in perfect agreement with the fluorescence lifetime in acetonitrile. After subtracting the contributions of the $S_n \leftarrow S_1$ and $T_n \leftarrow T_1$ transitions and the direct ionization from the transient spectra, the second process was found to have a yield twice that of the first direct ionization process. Thus, the cation-like band grows accompanied by the decay of the $S_{1,0}$ state. As has been discussed in the fluorescence-lifetime section, this decay process is thermally activated. Thus, the monophotonic ionization occurred by means of the 355-nm excitation, either from the higher S_1 level or from the bottom of the S_1 state ($S_{1,0}$), with the aid of thermal activation.

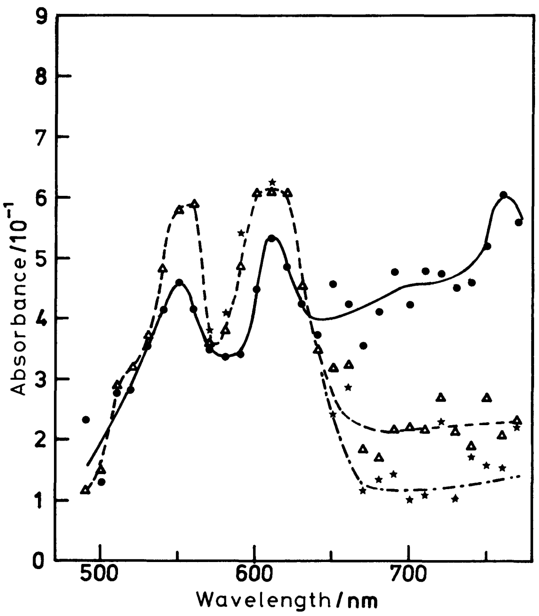

Fig. 3. Transient spectra measured by a fast photomultipler system at zero (●), 3 ns (△), and 10 ns (*) time delay.

Another important experiment to find the overall reaction scheme is that of the power dependence of the transient absorption. The intensity of the transient absorption at 620 nm was measured by varying the laser power in the range of 0.3—2 mJ; the absorbance was shown to be linear with the excitation energy as is shown in Fig. 4. This measurement was made with a photomultiplier tube with a rise time of 2 ns (RU928); therefore, the results showed that the overall ionization process is monotonic rather than the biphotonic process which was considered to occur in ethanol.[1]

In the photolysis spectra above the 700-nm region, there remained a broad, residual transient absorption with a lifetime longer than the $S_n \leftarrow S_1$ transition; its lifetime was estimated as about 50 ns. In the literature, the spectra of CH_3CN^- is reported to have a maximum at 1.45 μm;[12] therefore, we may observe the tail of the absorption band of CH_3CN^- in the 700-nm range. The short lifetime as compared with the literature value ($\simeq$900 ns) might be due to the presence of an efficient scavenger or a fast reaction with the cation produced.

Nanosecond Laser-flash Photolysis. The transient

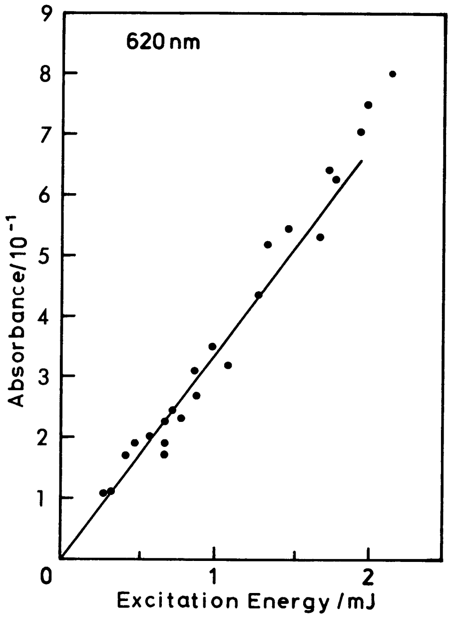

Fig. 4. Laser power dependence of transient absorption measured at 620 nm.

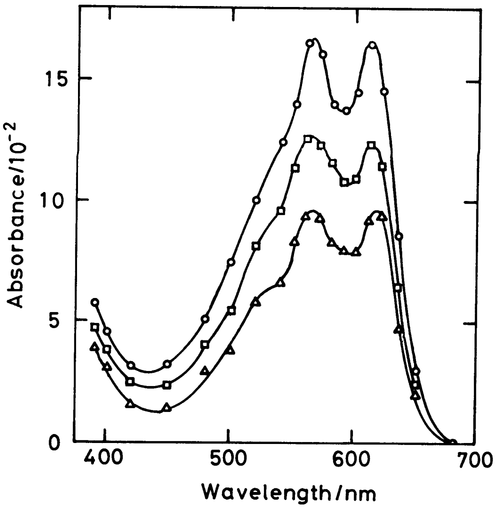

Fig. 5. Transient spectra obtained by nanosecond laser photolysis at 0.1 μs (—O—O—), 1.0 μs (—□—□—) and 4.0 μs (—△—△—) time delay.

absorption spectra as determined by nanosecond laser-flash photolysis, are shown in Fig. 5. The time-resolved absorption spectra after time delays of 100 ns, 1 μs, and 4 μs are illustrated. The decay of the absorbance at each wavelength was analyzed by a linear combination of several first-order decay curves, and at least three or four components were confirmed. The extrapolation to $t=0$ after the excitation gave three different absorption curves, as is shown in Fig. 6, where the height of the absorption represents the relative quantities of the photoproducts. The spectrum of the longest-lifetime component ($\tau>1$ s) is exactly the same as that of the cation; the medium-lifetime ones ($\tau\simeq 2$ μs and $\simeq 50$ μs) also resemble the cation spectrum.

The shortest-lifetime component ($\tau\simeq 500$ ns) has a slightly different spectral shape; it is very close to the $T_n \leftarrow T_1$ absorption reported in the literature.[1)]

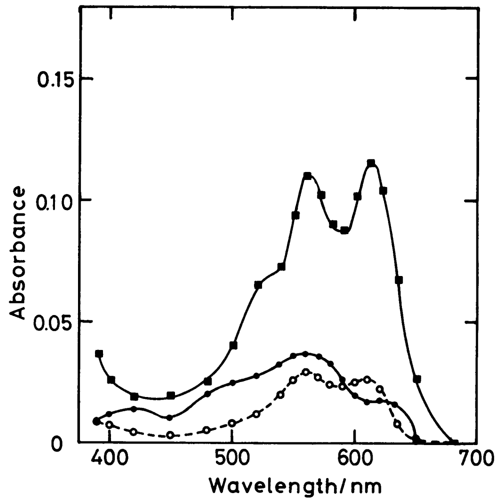

Fig. 6. Absorption spectra of the stable cation (—O—O—), the long lived component ($\tau=2$ and 50 μs (—■—■—), and the short lived component ($\tau=0.5$ μs) (—●—●—).

Therefore, this shortest component in the nanosecond flash photolysis is ascribed to the triplet state. Quite recently, Tokumura *et al.*[13)] reported the decay of the T_1 state in acetonitrile to have a lifetime of 660 ns, thereby confirming our finding that the shortest-lifetime component of $\tau\simeq 500$ ns is ^{3}TMPD. The relative yields of these three components have been estimated by an extrapolation to $t=0$; the yields and lifetimes are summarized in Table 2.

Table 2. Lifetimes and yields of laser-photolysis products in microsecond time range

Species	Lifetime	τ	Yield/%
^{3}TMPD	Shortest	0.5 μs	0.22±0.07
Cation and ion-pair or CTTS state	Medium	14 μs (2 and 50)	0.60±0.06
Stable cation	Longest	>1 s	0.18±0.07

In this table the medium-lifetime components are represented as having a common decay time of 14 μs, but the detailed analysis showed that these are at least two components with 2 and 50 μs. It is apparent, therefore, that there are several decay processes of the cation and ion-pair state. However, the lifetimes of these intermediates are independent of the laser power; accordingly, these decays might be first-order processes. It is conceivable that a geminate recombination of the ion pair is a major decay process.

Photocurrent. In order to determine the mechanism of transient phenomena in detail, the photocurrent produced after the YAG laser excitation was measured with a time resolution of $\simeq 10$ ns. The current was found to be linear with the intensity of the exciting light, which is in good agreement with the results of an earlier study.[3)] The transient current was analyzed with a linear combination of several components with different lifetimes; it may be described as:

$$I_p(t) = \sum_j A_j e^{-t/\tau_j},$$

where A_j is a preexponential factor for the j-th decay component of the lifetime τ_j and where numerical values are as follow:

τ_j	0.08	0.7	1.6	40	240	(μs)	>1 ms
A_j	0.24	0.26	0.18	0.08	0.07		0.18

These lifetimes are independent of the power of the laser light. The shortest lifetime coincides with those of CH_3CN^- in transient spectra. The origin of the second component is not clear, but it may be due to the free cation produced immediately after the excitation. The third and fourth components have decay times similar to that found by nanosecond laser photolysis; therefore, they may be related to the ion-pair state. Although no report has yet been presented on the current originating from the ion-pair without a rise time, the present coincidence of the decay of the transient-cation spectra with that of the current might indicate that the ion-pair gives a current under an electric field near the electrode surface. The independence of the decay times of the power intensity may indicate that most of the ejected electrons are still bound close to the cation, forming an ion-pair or a CTTS state, and that they exhibit a photocurrent under the applied field by dissociation. The presence of several decay times may mean the existence of inhomogeneous electron-trapped states, in which electrons are loosely bound to the cation but give a transient current under the applied electric field. Although all these measurements were carried out with nitrogen-bubbled samples, the effect of oxygen on the photocurrent was also examined. The shortest- and the medium-lifetime transient currents were significantly quenched, the former being reduced to one-tenth, and the latter, to about one-fifth. Therefore, both the CH_3CN^- and the ion-pair were shown to be quenched by oxygen.

Conclusion

The photoionization mechanism of TMPD in an acetonitrile solution was investigated by means of picosecond and nanosecond laser photolyses and photocurrent and fluorescence-lifetime measurements. Although the monophotonic ionization from the higher S_2 state has been studied by several groups,[14,15] little attention has been given to that from the higher S_1 level except for the work by Siomos *et al.*[16] They showed the photocurrent in a heptane solution excited by a two-photon process, but the photoionization from the $S_{1,0}$ level was not indicated. In this study, however, both the monophotonic direct ionization from the higher S_1 level and the thermally activated process from the $S_{1,0}$ is confirmed by picosecond laser photolysis. However, not all the cation-like species in the transient spectra may be due to the free cation, since the final yield after the photolysis is $\simeq 0.18$. In the initial stage of photolysis, the yield of the cation-like species is $\simeq 0.77$ as a whole; the direct ionization is estimated as $\simeq 0.25$, and the second thermal process is $\simeq 0.52$, as is shown in Fig. 7. The yield of the triplet state was estimated by nanosecond laser photolysis to be $\simeq 0.21$. The fluorescence yield was evaluated as 0.02 by comparing the fluorescence lifetimes in acetonitrile and cyclohexane and the quantum yield in cyclohexane.

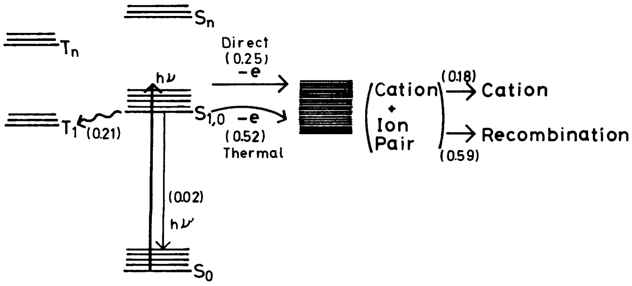

Fig. 7. Monophotonic ionization scheme of TMPD in acetonitrile solution.

In order to estimate the relative yields of the decay processes, quenching experiments with 1,3-pentadiene (1.0×10^{-3} M), naphthalene (1.2×10^{-3} M), and an air-saturated solution were performed. About one-third of the transient absorptions were quenched, indicating that most of the triplet absorption and some of the cation-like absorptions disappeared upon the use of the quenchers. The triplet yield of TMPD was found to be $\simeq 0.20$ by means of the $T_n \leftarrow T_1$ absorption of naphthalene. This value was consistent with the value estimated by the nanosecond laser photolysis. Summarizing the whole photoionization scheme, the overall processes are illustrated in Fig. 7. The relative yields for each process might have uncertainties of ± 0.05.

In the initial statge of photolysis, two independent pathways leading to the ionization or the ion-pair formation were indicated, but 80% of the cation-like absorption decayed through the recombination process. The photo-ejected electrons in an acetonitrile solution may exist in several different environmental conditions, which means that some of them are bound to acetonitrile molecules; some are closely connected with $TMPD^+$, forming an ion-pair; some are free, and some decay rapidly by reacting with scavengers. The monophotonic ionization process from the S_1 state of TMPD in a polar solvent is thus found to be the main process, and the present analysis may throw light on the unsolved problems regarding the photoionization mechanism of TMPD in polar media.

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References

1) N. Yamamoto, Y. Nakato, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **39**, 2603 (1966).

2) Y. Nakato, N. Yamamoto, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **40**, 2480 (1967).

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

4) R. Potashnik, M. Ottolenghi, and R. Bensasson, *J. Phys. Chem.*, **73**, 1912 (1969).

5) A. Alchalal, M. Tamir, and M. Ottolenghi, *J. Phys. Chem.*, **76**, 2229 (1972).

6) A. Alchalal and M. Ottolenghi, *Chem. Phys. Lett.*, **17**,

117 (1972).

7) J. T. Richards and J. K. Thomas, *Trans. Faraday Soc.*, **66**, 621 (1970).

8) M. Ottolenghi, *Chem. Phys. Lett.*, **12**, 339 (1971).

9) H. Nakamura, J. Tanaka, N. Nakashima, and K. Yoshihara, *Chem. Phys. Lett.*, **77**, 419 (1981).

10) H. Nakamura and J. Tanaka, *Chem. Phys. Lett.*, **78**, 57 (1981).

11) M. Sumitani and K. Yoshihara, *Bull. Chem. Soc. Jpn.*, **55**, 85 (1982).

12) I. P. Bell, M. A. Rodgers, and H.D. Burrows, *J. Chem. Soc., Faraday Trans. 1*, **73**, 315 (1977).

13) K. Tokumura, K. Endo, and M. Itoh, Presented at the National Meeting of Chem. Soc. Jpn., Spring, 1983.

14) J. Bullot, P. Cordier, and M. Gauthier, *J. Phys. Chem.*, **84**, 3516 (1980).

15) H. T. Choi, D.S. Sethi, and C.L. Braun, *J. Chem. Phys.*, **77**, 6027 (1982).

16) K. Siomos, G. Kourouklis, and L.G. Christophorou, *Chem. Phys. Lett.*, **80**, 504 (1981).