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Bull. Chem. Soc. Jpn., **54**, *1559—1560 (1981)*

Monophotonic Ionization Mechanism of *N,N,N′,N′*-Tetramethyl-1,6-pyrenediamine in Acetonitrile Solution

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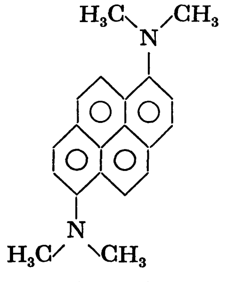
(Received July 7, 1980)

Synopsis. Monophotonic ionization of *N,N,N′,N′*-tetramethyl-1,6-pyrenediamine (TMPDA) in acetonitrile was studied by means of ns laser photolysis and transient photocurrent measurement. The time dependences of the absorption of TMPDA cation radical and of the photocurrent were different. Photoionization thus occurs through an ion-pair state.

Photoionization of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) in organic solvent has been extensively studied in order to clarify the primary process of the photoionization.[1] These studies showed that biphotonic ionization occurs through excited singlet and triplet states as the intermediates in non- or less-polar solvents. On the other hand, monophotonic ionization was observed in polar solvents such as acetonitrile.[2] However, the mechanism of the monophotonic ionization in such a solvent as acetonitrile has not yet been clarified. The difficulty encountered in the photolysis of TMPD in organic solvent is that the triplet-triplet (T-T) absorption of TMPD and the absorption of TMPD cation radical are observed in the same wavelength region, which makes kinetic treatment difficult.[1] We noticed that *N,N,N′,N′*-tetramethyl-1,6-pyrenediamine (TMPDA) has a low ionization potential compared to TMPD,[3] and that the absorptions of the T-T transition and of the TMPDA cation radical are well separated. In order to clarify the mechanism of the monophotonic ionization, we studied the photoionization of TMPDA in acetonitrile by ns laser photolysis and transient photocurrent measurements.



TMPDA

Experimental

TMPDA was synthesized according to the reported procedure.[4] Acetonitrile was distilled four times in the presence of phosphorus pentoxide, followed by distillation in the presence of potassium carbonate. It was finally distilled without any additives. In the case of ns photolysis, we used a nitrogen laser (peak power of 400 kW and pulse width of 5 ns) as an excitation light source, and a Xe-flash lamp (3CP-3, EG & G Co., Ltd) as a monitor light. In the transient photocurrent measurements, we also used the nitrogen laser as an excitation light source. The sample cell has two stainless steel electrodes (1.45 cm × 0.95 cm) with a spacing of 0.8 cm: 110 V was applied between them. Special care was taken not to irradiate the electrodes. A load resistance of 1 kΩ was used: this results in the time constant of 0.4 μs. The sample solution was always degassed several times by a freeze-pump-thaw method.

Results and Discussion

Figure 1 (a) shows the change of the electronic absorption spectra of the acetonitrile solution of TMPDA after N_2 laser excitation ([TMPDA] = 3.5×10^{-4} mol/l). We can assign the absorption bands at 510 and 560 nm as the T-T absorption and that at 595 nm as the TMPDA cation radical.[5] The absorption band longer than 600 nm is probably due to the solvated electron.[6] Figure 1 (b) shows the change of the absorption of $TMPDA^+$ at 590 nm with time in the ns time range. Although we could not measure

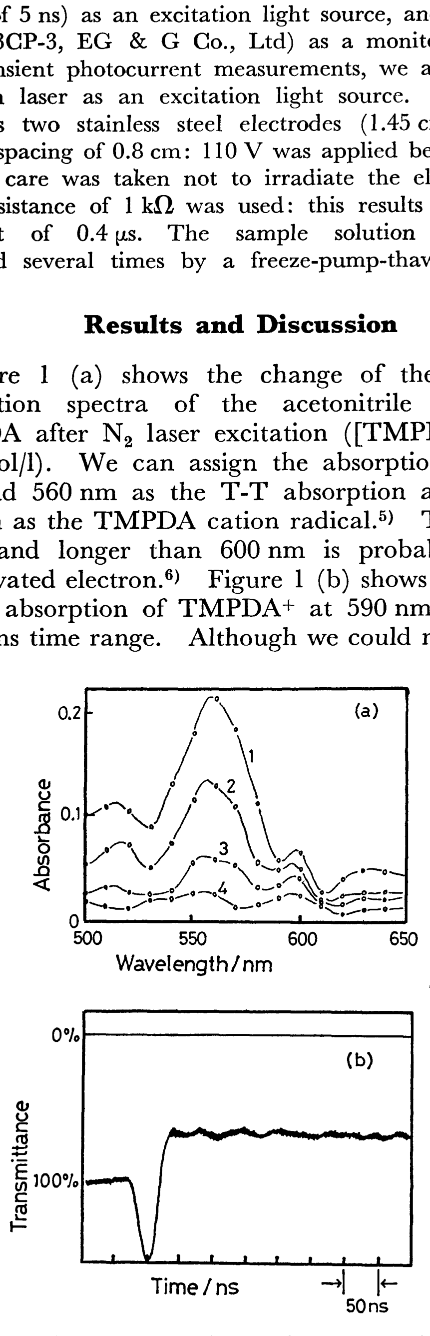


Fig. 1. (a) Time dependence of the absorption spectra of TMPDA in acetonitrile after N_2 laser excitation. 1, 0.4 μs; 2, 3 μs; 3, 10 μs; 4, 18 μs. (b) The change of the absorption of $TMPDA^+$ at 590 nm with time.

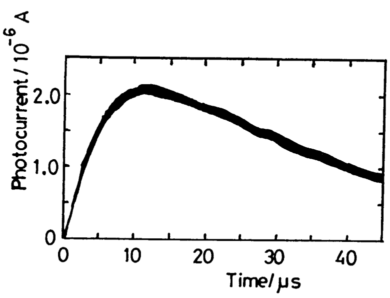
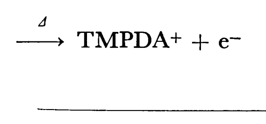


Fig. 2. Transient photocurrent of TMPDA in acetonitrile after N_2 laser excitation at 20 °C.

the absorption spectra of $TMPDA^+$ during the initial 50 ns after the laser pulse excitation because of the interference of the fluorescence of TMPDA, we assume that a TMPDA cation radical be produced immediately after the laser excitation. Figure 2 shows the transient photocurrent of the acetonitrile solution of TMPDA excited by the nitrogen laser at 20 °C ($[TMPDA]=1.4\times10^{-4}$ mol/l). The curve showed gradual increase of the photocurrent during the initial 10 μs, and then the gradual decay of the current.[7] The plot of the peak photocurrent against the laser light intensity showed a linear relation, thus verifying the one-photon ionization of the present system.[8] In order to see whether photoionization occurs through the triplet state or not, we did the photocurrent measurement using a POPOP dye laser[10] ($\lambda_{max}=418$ nm) as an excitation light source and anthracene as a triplet quencher of TMPDA.[11] The photocurrent measurement of the mixture of the acetonitrile solution of TMPDA and anthracene ($[TMPDA]=1.04\times10^{-4}$ mol/l, $[anthracene]=1.04\times10^{-3}$ mol/l) showed no obvious reduction of the photocurrent. On the other hand, the flash photolysis in the same system showed complete quenching of the T-T absorption. Thus, photoionization does not occur through the lowest triplet state of TMPDA.

If the electron were ejected directly by the laser pulse excitation in the one-photon ionization, the time-dependence of the absorption of $TMPDA^+$ and photocurrent should coincide. Figures 1 and 2 clearly show that this is not the case in the present system. The observed difference between the absorption and current may be ascribed to a cationic transient, which gives no current but shows an absorption similar to that of $TMPDA^+$. This transient seems to be an ion-pair of $TMPDA^+$ and an electron ($TMPDA^+e^-$). The ion-pair is produced by the laser pulse excitation



$$\mathrm{TMPDA} \xrightarrow{h\nu} \mathrm{TMPDA^*} \xrightarrow{\text{fast}} \underset{\text{ion-pair}}{\mathrm{TMPDA^+e^-}} \xrightarrow{\Delta} \mathrm{TMPDA^+} + e^-$$

(probably through the singlet excited state) and dissociates thermally into free ions or recombines to give neutral TMPDA. One may ask whether an ion-pair can exist as long as 10 μs. It is noteworthy that the absorption of the solvated electron is observed for about 10 μs after the laser pulse excitation (Fig. 1 (a)). One possibility is that the TMPDA cation radical and a solvated electron form an ion-pair.

We are grateful to Dr. Masaaki Yokoyama, Faculty of Engineering, Osaka University, for constructing the nitrogen laser.

References

1) For example, J. T. Richards and J. K. Thomson, *Trans. Faraday Soc.*, **66**, 621 (1970); Y. Nakato, N. Yamamoto, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **40**, 2480 (1967).

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

3) The half-wave oxidation potentials of TMPDA and TMPD are 0.49 and 0.1 V (*vs.* SCE), respectively (see Ref. 4).

4) H. Vollman, H. Becker, M. Correll, and H. Streek, *Ann.*, **531**, 1 (1937); A. Zweig, A. H. Maurer, and B. G. Roberts, *J. Org. Chem.*, **32**, 1322 (1967); TMPDA was purified by column chromatography (silica gel) using benzene as an eluent, and purified finally by two vacuum sublimations.

5) The 510 and 560 nm bands are assigned as the T-T absorption because of the following reasons. These bands decay exponentially with a life time of 11 μs, and they disappear completely by the addition of the triplet quencher, anthracene. The 595 nm band is assigned as the TMPDA cation radical because of the following reason. The same absorption spectrum is obtained by the one-electron oxidation of TMPDA with ferric nitrate, and by thermal ionic dissociation reaction of TMPDA with chloranil in acetonitrile.

6) A. Singh, H. D. Gesser, and A. R. Scott, *Chem. Phys. Lett.*, **2**, 271 (1968).

7) Similar curves are also obtained at 11, 30, and 40 °C.

8) When we compare the dependence of the photocurrent with the excitation laser intensity, we must consider the saturation effect. This effect is significant when the value EH exceeds 1 (see Ref. 9). Here E and H denote the absorption cross section of the molecule and photon number per unit area. In the present experimental condition, the maximum value of EH is 0.05. Thus, we need not worry about the saturation effect.

9) U. Lachish, A. Schafferman, and G. Stein, *J. Chem. Phys.*, **64**, 4205 (1976).

10) A dioxane solution of 1,4-bis(5-phenyl-2-oxazolyl)-benzene was excited by N_2 laser light to obtain the POPOP dye laser light.

11) The lowest singlet (S_1) and triplet (T_1) states o TMPDA and anthracene are as follows. TMPDA: S_1 2.91 eV, T_1 1.97 eV (estimated from the phosphorescence spectrum); anthracene: S_1 3.31 eV, T_1 1.85 eV.