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Single-Photon Ionization in the Flash Photolysis of *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine in Solution

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The photo-ionization of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) in solution was reported to take place by double-photon process through the triplet state.[1,2] Recently, it was reported that the formation of TMPD cation passing through no triplet state also takes place,[3,4] and that no evidence of double-photon process was obtained in other experiments using the method of laser photolysis.[5]

As a result of our investigation of the effect of light intensity on the photocurrent induced by the ionic species and caused by the flash photolysis of TMPD in acetonitrile at a room temperature, we obtained evidence of ionization by the single-photon rather than the double-photon process.

Experimental details were given previously.[6] Light intensity was regulated by setting the brass wire-gauzes of various transmittances. The photocurrent was measured at the initial maximum peak.

Figure 1 (A) shows the photocurrent *vs.* relative light intensity logarithmically. The linear relation in the formation of ionic species is obvious. The lower curve (b) was obtained when only the light with wavelengths greater than 3100 Å was irradiated with a cut-off filter.

The initial concentration of the generated ionic species should be proportional to the initial value (i_0) of the photocurrent as measured at the maximum peak, and should depend only on the total light intensity (L), since the decay of the photocurrent ($>10^{-2}$ sec) was extremely slow compared with the duration of a flash ($<10^{-5}$ sec). The recombination of the ionic species and the other decay processes may be practically neglected during the flash firing. Therefore, the relation $i_0 \propto L^n$ will hold directly, where $n=1$ and 2 according to the ionization for the single- and the double-photon process, respectively. The experimental results indicate that $n=1$.

When the whole body of the sample including the electrodes was uniformly irradiated by removing the slit, the linear curves in Fig. 1 (B) were again obtained notwithstanding the fact that the exchange of charges between the electrodes and excited TMPD, or the additional generation of the ionic species near the electrodes, can easily take place.

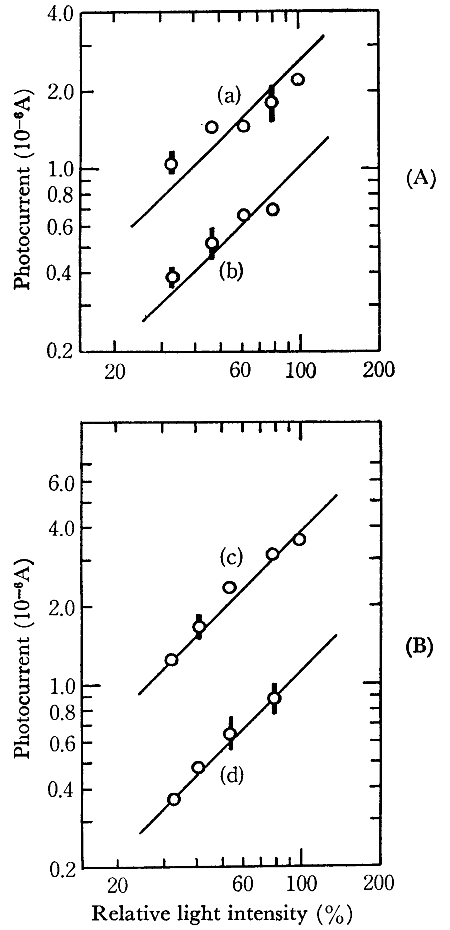

Fig. 1. Effect of light intensity on the photocurrent of TMPD in acetonitrile.
Solid lines correspond to the slope 1.0.
Cut-off filter (λ>3100 Å) was used in (b) and (d).
(A) Slit was used. Flash input: 275 J.
(a) 3.7×10^{-3}M, (b) 3.8×10^{-3}M.
(B) No slit was used. Flash input: 210 J, 2.7×10^{-4}M.

A sort of semi-ionized state (I) having the CT character can be considered for the ionization.

$$\mathrm{TMPD} \xrightarrow{h\nu} \mathrm{TMPD}^* \longrightarrow \underset{\mathrm{I}}{[\mathrm{TMPD}^{\delta+}\cdots(\mathrm{CH_3CN})_m{}^{\delta-}]^*} \quad (m\geqq1)$$

It seems that TMPD cation and the counter-anionic species[7] are liberated so spontaneously from state I that no more photon is needed. Examples of the fragmen-

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[2] H. S. Pilloff and A. C. Albrecht, *J. Chem. Phys.*, **49**, 4891 (1968).

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

[4] M. Tamir and M. Ottolenghi, *Chem. Phys. Lett.*, **6**, 369 (1970).

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

[6] T. Imura, N. Yamamoto, and H. Tsubomura, This Bulletin, **43**, 1670 (1970).

[7] Though the initial anionic species was not confirmed, it may be a solvated electron. *cf.* A. Singh, H. D. Gesser, and A. R. Scott, *Chem. Phys. Lett.*, **2**, 271 (1968).

tation into cation and anion from the excited CT state are found.[6,8] As acetonitrile easily accepts electrons from Na metal (ionization potential of Na atom=5.138 eV), the same kind of reaction can be expected by the transfer of electron from TMPD in the excited state (ionization potential of TMPD(gas phase)$\fallingdotseq$6 eV[9]) to acetonitrile through CT interaction.

Photoconductive measurements were also tried in ethanol solution, where the ionization through a double-photon process was demonstrated by the effect of light intensity on the optical density of generated TMPD cation,[1] but the photocurrent could hardly be detected.[5,6]

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[9] H. Tsubomura, "Chemistry of the Excited State," Tokyo Kagaku Dozin, Tokyo (1967), p. 160.