BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2480—2485 (1967)

The Photo-ionization of Molecules in Solutions. V. The Mechanism of the Photo-ionization of an Aromatic Diamine in the Polar Media

Yoshihiro NAKATO, Naoto YAMAMOTO and Hiroshi TSUBOMURA

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka

(Received March 23, 1967)

The photo-ionization of *N, N, N′, N′*-tetramethyl-*p*-phenylenediamine (TMPD) in nonpolar solvents was found to occur by the two-step process, with the triplet state as the intermediate. It will be reported here that the photo-ionization of TMPD in polar solvents occurs by the same two-step process, both at 77°K and at room temperature. The flash method was used for the experiments at room temperature. On the other hand, the photo-ionization of TMPD occurs by the single-photon process in ethanol solutions at room temperature when a naphthalene molecule encounters TMPD in the singlet-excited state. The ionization mechanism will be discussed on the basis of these results.

For the past few years, it has been growingly recognized that the photo-ionization of organic compounds in solid matrices generally occurs by the two-step mechanism (biphotonic process), with the triplet state as the intermediate. Joussot-Dubien and Lesclaux may have been the first to propose this two-step photo-ionization in the case of triphenylene in the boric acid glass.¹⁾ Such a mechanism was also suggested by Charlesby and Partridge to account for the photo-ionization of carbonyl compounds in polyethylenes.²⁾ In rigid hydrocarbon glasses at 77°K, the same mechanism was also proposed by Gibbons, Porter, and Savadatti for the photo-ionization of several aromatic hydrocarbons,³⁾ and by Cadogan and Albrecht for *N, N, N′, N′*-tetramethyl-*p*-phenylenediamine (TMPD).⁴⁾

In polar solvents, however, the photo-ionization might proceed by a different mechanism, because of the strong stabilization of ions by the solvent. Rather little work has been done on photo-ionization in polar media. Hélène and his collaborators suggested the same mechanism for frozen aqueous solutions of nucleic acid derivatives.⁵⁾ Grossweiner and his collaborators made flash photolytic experiments on a large number of benzene derivatives in aqueous solutions.⁶⁾ They observed an absorption band with a peak at 700 mμ; they assigned this band to the solvated electrons. They also reported that the intensity of this band was proportional to the flash-light intensity. From these results they concluded that, in solvents with high dielectric constants, such as ethanol or water, at room temperature, the photo-ionization occurred by a single-step excitation process, and that the biphotonic process could not be applied in this case.

We previously studied the photo-ionization of TMPD by the flash illumination of ethanol solutions of TMPD at room temperature and reported that TMPD$^+$ was formed in deaerated solutions, but not in aerated solutions.⁷⁾ This seems to suggest that the photo-ionization in ethanol occurs biphotonically *via* the triplet state of TMPD.

We also previously observed that the fluorescence of TMPD was quenched when naphthalene was added to the TMPD solution, and that in nonpolar solvents a new fluorescence band appeared at the longer wavelength region.⁸⁾ This system does not seem to form any charge transfer complex in the ground state, as may be seen from the absorption spectra.⁹⁾ A similar phenomenon had already been found by Leonhardt and Weller¹⁰⁾ in the case of perylene and *N, N*-dimethylaniline. They classified the new band as a CT fluorescence band. By the flash-photolytic experiments in polar solvents

---

1) J. Joussot-Du, Dubien and R. Lesclaux, *Compt. Rend.*, **258**, 4260 (1964).

2) A. Charlesby and R. H. Partridge, *Proc. Roy. Soc.*, **A283**, 329 (1965).

3) W. A. Gibbons, G. Porter and M. I. Savadatti, *Nature*, **206**, 1355 (1965).

4) K. D. Cadogan and A. C. Albrecht, *J. Chem. Phys.*, **43**, 2550 (1965).

5) C. Hélène, R. Santus and P. Douzou, *Photochem. and Photobiol.*, **5**, 127 (1966).

6) G. Dobson and L. I. Grossweiner, *Trans. Faraday Soc.*, **61**, 708 (1965); L. I. Grossweiner and H. I. Joschek, "Advances in Chemistry Series," No. 50, American Chemical Society, New York (1965), p. 279; H. I. Joschek and L. I. Grossweiner, *J. Am. Chem. Soc.*, **88**, 3261 (1966).

7) H. Tsubomura, N. Yamamoto, K. Kimura, T. Sato, H. Yamada, M. Kato, G. Yamaguchi and Y. Nakato, This Bulletin, **38**, 2021 (1965); N. Yamamoto, Y. Nakato and H. Tsubomura, *ibid.*, **39**, 2603 (1966). (III of this series)

8) N. Yamamoto, Y. Nakato and H. Tsubomura, *ibid.*, **40**, 451 (1967). (IV of this series)

9) This statement is only for dilute solutions. In cases where one or both two components are very much concentrated, a CT interaction is probably expected to occur.

10) H. Leonhardt and A. Weller, *Ber. Bunsenges. physik. Chem.*, **67**, 791 (1963).

they found a transient absorption spectrum of perylene monoanion.[11] From these results they concluded that perylene in the excited singlet state forms a charge transfer complex with dimethylaniline, and changes into a solvated perylene anion in polar solvents. This conclusion suggests that the single-step ionization process is possible if an appropriate electron acceptor is present nearby.

Experimental

TMPD, ethanol, ether, and isopentane were purified in the same way as has been reported previously.[7] Commercial-grade naphthalene was purified twice by sublimation.

The absorption spectra of rigid glasses at 77°K were measured with a Cary Spectrophotometer Model 15. Those in liquid solutions at room temperature were measured by the flash method. The duration of the flash was 5 μsec at most. The apparatuses for these measurements have been described in detail elsewhere.[7,8]

All the sample solutions were prepared by dissolving TMPD into solvents after they had been deoxygenated, because TMPD in polar solvents is gradually oxidized by atmospheric oxygen.

Results

In order to confirm experimentally whether the photo-ionization occurs by the biphotonic process, we have examined the relation between the exciting light intensity (I) and the concentration of TMPD$^+$ produced (x). If the single-photon mechanism is assumed, the relation will be clealy be $x \propto I$ in the case where $x \ll c_0$, c_0 being the initial concentration of TMPD, On the other hand, if the two-step mechanism is assumed, the $x \propto I^2$ relation may be expected if the following conditions hold; (1) the recombination of the TMPD$^+$ and the electron produced is neglected, (2) x is much smaller than c_0, and (3) c_0 is as small as possible. The condition (2) is necessary because the TMPD$^+$ formed has a considerably strong absorption band between 300 mμ and 340 mμ and so will act as an inner filter. In the case of the stationary excitation light, the relation is independent of the lifetime of the intermediate. The results obtained will be described below.

In Rigid Matrices at 77°K. Figure 1 shows the results on the yield of TMPD$^+$ produced by the excitation of TMPD in the EPA matrices at 77°K; (a) is for the case where the matrix contains only TMPD, and (b) for the case where both TMPD and pyrene are present. Here, EPA is a mixed solvent consisting of 8 parts (in volume) ether, 3 parts isopentane, and 5 parts ethanol. By using the Cary Spectrophotometer Model 15, it is possible to measure an optical density as small as 0.001 fairly accurately. A 250 W high-pressure mercury lamp was used as the excitation light source. The light intensity was controlled by changing the distance between the light source and the sample cell. A glass cell was used which is transparent only for the light with wavelengths longer than 310 mμ; hence, the TMPD is excited mainly to the lowest singlet excited state. Care was taken that the concentration of TMPD$^+$ formed did not exceed 5×10^{-6} mol/l. c_0 was 5.8×10^{-4} mol/l. It has been ascertained experimentally that TMPD$^+$ is stable for a long time in an EPA rigid matrix at 77°K, and that its illumination at wavelengths longer than 390 mμ does not change the quantity of TMPD$^+$ formed. Therefore, the recombination terms can be neglected.

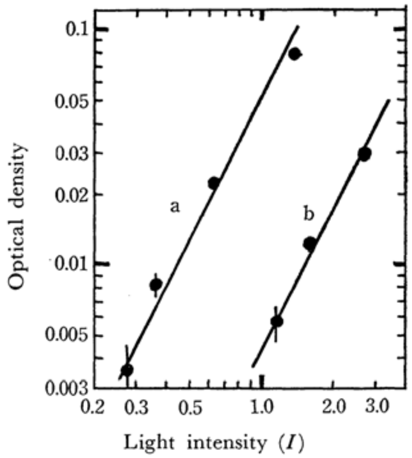


Fig. 1. Relation between the optical density of TMPD$^+$ (at λ=630 mμ) and the exciting light intensity (I) in the rigid EPA matrices at 77K°. a) For the case where only 5.8×10^{-4} mol/l TMPD is contained. b) For the case where 1.3×10^{-3} mol/l TMPD and 1.0×10^{-2} mol/l pyrene are contained. The experimental errors estimated are shown by the lengths of vertical and horizontal lines at the points of experimental values.

From Fig. 1, it may be seen that the logarithm of the optical density for the TMPD$^+$ is in a linear relation with the logarithm of the excitation light intensity. The slope of the line is found to be 2; therefore, the relation $x \propto I^2$ holds. The photoionization in the EPA matrices at 77°K may, therefore, be concluded to occur by the two-step mechanism, both when only TMPD is present and when TMPD and pyrene are both present.

For the purpose of determining the wavelengths region effective for the photo-ionization, crossbeam experiments were carried out. EPA solutions of TMPD at 77°K were photoionized, on the one hand, by a 100 W mercury lamp, and, on the other hand, by the same lamp plus a 250 W xenon lamp with a VY-42 Toshiba filter (transparent for $\lambda > 420$ mμ). In both cases, no difference in the

---

[11] H. Leonhardt and A. Weller, *Z. physik. Chem. N. F.*, **29**, 277 (1961); "Luminescence of Organic and Inorganic Materials," ed. by H. P. Kallman, John Wiley and Sons Inc., New York (1962), p. 74.

optical densities for the TMPD$^+$ could be found. This result shows that the light in the region of the T-T′ absorption spectra of TMPD (500—650 mμ) found by our earlier work⁷⁾ is not effective for the second step of the photo-ionization process in the EPA matrices, and that the effective wavelength is shorter than 420 mμ.

In Liquid Solutions at Room Temperature. The TMPD$^+$ cation has a long lifetime when it is formed by the flash photolysis of TMPD in ethanol solutions at room temperature. Figure 2 shows an example of the decay curve of TMPD$^+$ monitored at 615 mμ. A tungsten lamp was used as the spectral light source, and the light in the wavelength region shorter than 390 mμ was cut with a Toshiba UV-39 filter (transparent for $\lambda > 390$ mμ) so that the TMPD should not be photoionized. As the lifetime of TMPD$^+$ is very long, the decay curve is almost straight. It has also been ascertained by the photographic method that no rapid decay of TMPD$^+$ takes place from the first few microseconds until a few milliseconds after the flash. It was reported previously that the lifetime of the solvated electrons in ethanol solutions is 3 μsec as measured by pulse radiolysis experiments.¹²⁾ These results seem to indicate that all the solvated electrons produced react with the solvent molecules or some impurities possibly contained in the solution as soon as they are formed and probably turn into stable forms. This interpretation may explain why TMPD$^+$ has a long lifetime.¹³⁾

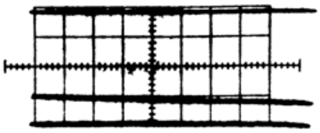


Fig. 2. A decay curve of TMPD$^+$ (at $\lambda = 615$ mμ) formed by flash illumination of ethanol solutions of TMPD (5.0×10^{-5} mol/l) at room temperature. The upper and lower lines indicate 100% and 0% transmittance, respectively. The time scale is 5 msec per main division.

In Fig. 3, the optical density of TMPD$^+$ at 615 mμ, obtained by extrapolating the decay curve to zero msec, is plotted against the square of the exciting light intensity. The light intensity was changed by changing the charging voltage of the storage condenser of the photolysis flash lamp. The flash-light intensity has been found to be proportional to the square of the voltage.⁷⁾ The light was cut in the region of wavelengths shorter than 310 mμ by using a glass tube as a filter. The charging voltage was made as low as possible, so as to keep the concentrations of TMPD$^+$ formed less than 1.0×10^{-6} mol/l. c_0 was 5.0×10^{-5} mol/l.

It should be noted that the flash light in this experiment is not a stationary light. It is shown, however, from a simple kinetic consideration that the same $x \propto I^2$ relation is obtained in the case of the two-step mechanism under our present experimental conditions.¹⁴⁾ The sample solution was prepared in a sealed glass system, and the solution in a cell was renewed whenever it was exposed by one flash light.

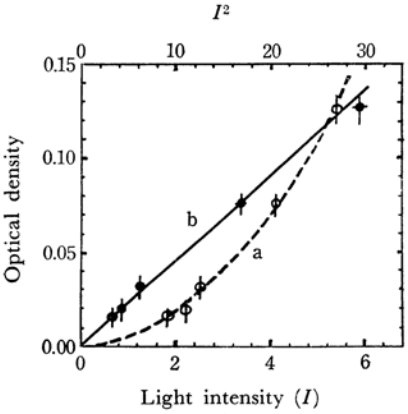


Fig. 3. Relation between the optical density of TMPD$^+$ (at $\lambda = 615$ mμ) and the flash light intensity (I) in ethanol solutions of TMPD at room temperature.

a) The optical density is plotted for I.

b) The optical density is plotted for I^2.

The experimental errors estimated are shown in the same way as in Fig. 1.

From Fig. 3, it may be seen that the optical density of TMPD$^+$ is proportional to the square of the light intensity, within the range of experimental errors. Therefore, it can be concluded that, even in ethanol solutions at room temperature, the photo-ionization occurs by the biphotonic process. The fact that TMPD$^+$ is not produced in the presence of oxygen seems to give evidence that the intermediate is the triplet of TMPD; recall that oxygen shortens the lifetime of the triplet state remarkably.

In the Presence of Some Electron Acceptors at Room Temperature. We have made flash photolytic experiments on TMPD in ethanol solutions containing naphthalene at room temperature. The transient absorption spectrum is shown

---

12) I. A. Taub, D. A. Harter, M. C. Sauer and L. M. Dorfman, *J. Chem. Phys.*, **41**, 979 (1964).

13) Photolysis of TMPD with the mercury lamp in the 77°K ethanol matrix showed an electron spin resonance spectrum which mainly consists of a pattern most probably attributable to the $CH_3\dot{C}HOH$ radical. (Unpublished results in our laboratory.)

14) To get the above relation, the following conditions in addition to the conditions (1), (2) and (3), as noted before, are required: (4) the concentration of TMPD in the triplet state is negligible compared with that in the ground state, (5) the production of TMPD$^+$ by light absorption from the triplet state is not so large as to change the concentration of the triplet state TMPD. Under these conditions, the relation is independent of the lifetime of the triplet state and of the rise and fall of the light intensity.

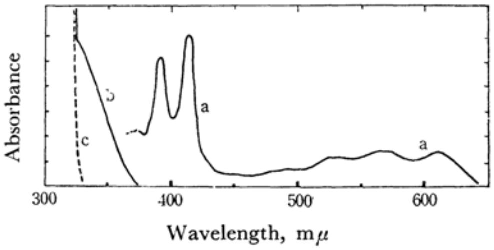


Fig. 4. a) Transient absorption spectrum formed by the flash illumination of TMPD (1.1×10^{-3} mol/l) and naphthalene (1.1×10^{-2} mol/l) in an ethanol solution at room temperature. Both photolysis and spectral flash lamps are fired at the same time. A 0.1 M naphthalene solution is used as a filter. b) Absorption spectrum of the above sample. c) Absorption spectrum of the filter solution.

in Fig. 4, with both photolysis and spectral flash lamps being fired at the same time. The transient spectra clearly show strong T-T′ absorption bands of naphthalene and weak absorption bands of TMPD$^+$. Before the flash, no absorption band was found in this wavelength region. In this experiment, a 0.1 mol/l ethanol solution of naphthalene was used as a filter.[15] The shape and position of the absorption bands of TMPD$^+$ as shown in Fig. 4 are identical with those without naphthalene, but the absorbance is considerably suppressed. The lifetime of TMPD$^+$ is very long, and little change in the color of the solution can be found in an hour. The T-T′ absorption band of naphthalene appearing in Fig. 4 is also identical with that found for the ethanol solutions of naphthalene. The spectrum of the naphthalene monoanion could not be detected. This may be explained by taking account of its weak and broad absorption spectrum.[16] The long lifetime of TMPD$^+$ may also be ascribed to the fast reaction of the naphthalene anions with solvent molecules,[12,17] resulting in some stable species.

We reported in an earlier paper that, in solutions of the same constitution, the fluorescence of TMPD was quenched and that, in non-polar solvents, a new fluorescence appeared in the longer-wavelength region.[8] In the sample used for the above flash-photolysis experiment, the fluorescence of TMPD is quenched almost completely. This means that almost all the excited TMPD molecules interact with naphthalene, which is in the ground state.

In order to ascertain the mechanism by which the TMPD$^+$ in the above flash photolysis experiments was produced, we made photo-ionization experiments by using either a 250 W mercury lamp or the flash apparatus (with 5 μF condenser charged to 10^4 V). The intensity of the former is of the order of 10^{-6} smaller than the latter. However, the total light energy emitted by it in one second is about the same as that of a single flash discharge. Therefore, if TMPD$^+$ is to be formed by the biphotonic process, it may be expected that there will be an extremely great difference in the yields of TMPD$^+$. If, on the other hand, TMPD$^+$ is produced by a single-photon process, the yields will be about the same. With ethanol solutions of TMPD (1.0×10^{-3} mol/l) and naphthalene (1.0×10^{-2} mol/l), the experimental results confirmed that the latter is the case; namely, the same order of TMPD$^+$ was produced by the two methods. This result, enormously different from those obtained from the photolysis of solutions containing only TMPD (see above), confirms that, in the presence of naphthalene, the photo-ionization occurs by the single-photon process and confirms the mechanism proposed by Weller and Leonhardt.[10,11]

Discussion

It has been confirmed from our present results that the photo-ionization of TMPD occurs in the two-step process in EPA rigid matrices and even in ethanol solutions at room temperature. The intermediate state in the case of ethanol solutions at room temperature is thought to be the triplet state of TMPD, because the production of TMPD$^+$ is suppressed in aerated solutions. The photo-ionization of TMPD in the EPA rigid matrices must proceed in the way described above, although we have no direct experimental evidence for this case.[18] It has also been ascertained that the light effective for the photo-ionization of TMPD is at least in the region of wavelengths shorter than 420 mμ in EPA rigid matrices. Taking the energy of the triplet state to be 2.9 eV higher than the ground state, this implies that at least 5.9 eV is required for the photo-ionization of TMPD. No ionization potential for TMPD as determined by a direct experimental method is available. However, it can be estimated to be around 7.0 eV.[19] Thus,

---

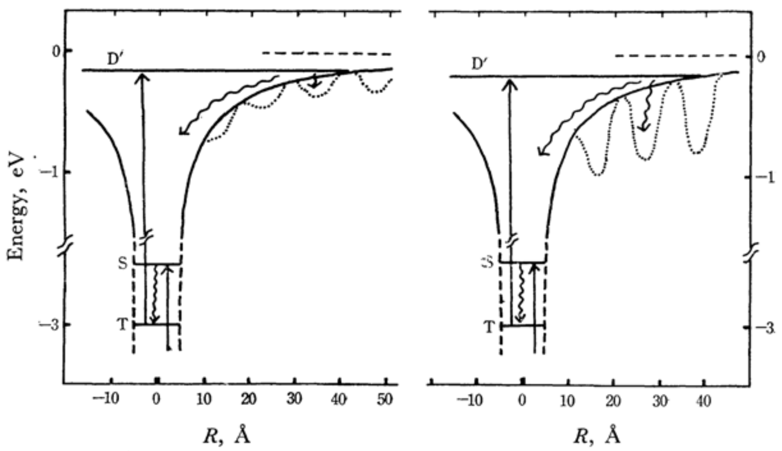
[15] Using the same filter, the flash photolysis of naphthalene in ethanol (0.01 mol/l) showed no transient spectrum.

[16] P. Balk, S. de Bruijtink and G. J. Hoijtink, *Rec. trav. Chim.*, **76**, 907 (1957).

[17] S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **41**, 2190 (1964).

[18] An intermediate state different from the triplet state was proposed by Johnson and Albrecht, from the experiments of photoconductivity in rigid hydrocarbon matrices. They emphasized that the critical charge-carrier production apparently proceeds by a mechanism radically different from that for TMPD$^+$ production. G. E. Johnson and A. C. Albrecht, *J. Chem. Phys.*, **44**, 3179 (1966); **44**, 3162 (1966).

[19] The adiabatic ionization potential of *N*, *N*-dimethylaniline is proposed to be 7.14 ± 0.03 eV from the photo-ionization in gas phase (A. Terenin and F. Vilessov, "Advances in Photochemistry," Vol. 2, ed. by Noyes, Hammond and Pitts, Interscience Publishers, New York (1964), p. 419). That of TMPD is expected to be somewhat lower because of the para dimethylamino substituent.



a) in non-polar media b) in polar media

Fig. 5. A schematic illustration of the two-step photo-ionization of TMPD in solutions. The dotted lines (······) show the electron traps formed by the solvent molecules after TMPD is excited up to the D′ state. The scales for the enengy and distance are only qualitative.

the difference between Ip's in the gas phase and in solutions is rather small (∼1 eV). This result might look curious, in view of the large solvation energy of ions in polar solvents (∼2—3 eV), but it may be understood by the application of the Franck-Condon principle. Namely, the photo-ionization process is so rapid that the orientation of the polar solvent molecules does not follow it, and only the electronic polarization, which is about the same for polar and for non-polar media, will lower the energy of the excited states (see also Fig. 5).

The process of the photo-ionization of TMPD in polar solvents *via* the CT states $\{\mathrm{TMPD} \xrightarrow{h\nu}$ excited singlet, or triplet state $\dashrightarrow (\mathrm{TMPD}^+\cdots \mathrm{Solvent}^-) \dashrightarrow \mathrm{TMPD}^+ + \mathrm{Solvent}^-\}$ has been proved not to occur.

There is, however, a great difference between the yield of TMPD$^+$ in polar media and that in non-polar media. This is another fact which should be clarified. It seems to the present authors that the present process of the photo-ionization of molecules in solutions by the two-step mechanism may be described by the following scheme;

$$
\begin{array}{lll}
 & & \overset{(2)}{\dashrightarrow} \mathrm{D}^+_{\mathrm{solv.}} + \mathrm{e}^-_{\mathrm{solv.}} \\
{}^3\mathrm{D} \xrightarrow[(1)]{h\nu} \mathrm{D}' & & \\
 & & \underset{(3)}{\dashrightarrow} \mathrm{D}^* \text{ (lower excited states)}
\end{array}
$$

Here ^{3}D indicates TMPD in the lowest triplet state, and D′ indicates a 'pseudo-ionized state', where the electron excited from the solute molecule is still moving around it in an orbital spreading out over the solvent molecules. In this state, the solvent molecules still retain their orientations for the triplet state of the solute molecule. The spatial extent of the wave function of the D′ state is, therefore, thought to be nearly the same in both polar and non-polar media. Process (2) indicates the trapping of this electron by the solvent molecules, and process (3), the degradation to the lower excited states. It may, then, be deduced that many of the molecules excited up to D′ will be degraded by process (3) and that the remainder will form ions by process (2), although only the latter part can be detected experimentally.

The photo-ionization process described above may be schematically illustrated as in Fig. 5. While the molecules stay at the D′ state, potential wells will be formed by the solvent orientation, as Fig. 5 illustrates. In polar solvents, the wells formed will be deep, while in non-polar solvents they will be shallow. It can be supposed that the rate of this process (2) is quite large in polar solvents. Consequently, a larger part of the electrons will be trapped in the former than in the latter. By introducing this concept of a pseudo-ionized state, D′, the large yields of the TMPD$^+$ in polar solvents may be nicely explained.

We reported in our earlier papers that the photo-ejected electrons are trapped at a greater average distance from the cation in non-polar matrices than in polar matrices.[8,20] This may also be explained by the above mechanism. As has been discussed above, the wave function of the D′ state may be supposed to have almost the same spatial extent in both cases. When pyrene molecules exist around TMPD molecules, the process of the trapping of the electron by the pyrene molecule seems to be independent of the polarity of the matrices, while the rate of process (2) in the polar

---

20) H. Tsubomura, N. Yamamoto and Y. Nakato, This Bulletin, **39**, 1092 (1966). (II of this seris)

matrices will be considerably larger than that in the non-polar matrices. Therefore, the [Pyr$^-$]/[TMPD$^+$] ratio in the non-polar matrices may be understood to become larger than that in polar matrices.

We have ascertained that, even in rigid EPA glasses containing pyrene ($\sim 10^{-2}$ mol/l) as well as TMPD, the same biphotonic mechanism takes place. It is highly probable that these two compounds undergo a certain kind of CT interaction with each other in a concentrated solution. In this case, however, the mean distance between TMPD and pyrene is estimated to be 20 to 30 Å. Owing to this large distance, the possibility of producing TMPD$^+$ and the pyrene anion *via* a charge-transfer state between them (one-photon process) may be ruled out. This, in turn, proves that pyrene and TMPD molecules are distributed randomly in the matrix, forming no complex or aggregate between TMPD and pyrene in the ground states.

It has been pointed out in the preceding section that there is no possibility of direct ionization from the excited singlet or triplet state, although the energy of the TMPD$^+_{\mathrm{solv}}$ and e$^-_{\mathrm{solv}}$ states must be lower than the excited singlet or triplet state because of the large solvation energies.[21] This result indicates that a large activation energy is necessary for the photo-ionization of TMPD in liquid ethanol solutions.

On the other hand, we have confirmed that the photo-ionization of TMPD can occur by the singlephoton process in ethanol solutions at room temperature when an electron acceptor, such as naphthalene, encounters TMPD in the excited singlet state. In this case, the most probable process is the formation of a charge-transfer complex between TMPD and naphthalene, as evidenced by the appearance of a new fluorescence in non-polar media.[8] Such a complex will induce the reorientation of the solvent molecules, which in turn will make the bond between donor and acceptor more and more ionic, gradually causing the solvated ions to be formed. An ethanol molecule does not interact with the excited state of TMPD in such a way as naphthalene does. This consideration is supported by the fact that, in ethanol solutions, no new absorption or new emission spectrum appears.[7]

For the ethanol solutions of TMPD and naphthalene, not only TMPD$^+$ but the triplet state of naphthalene appears, as Fig. 4 shows. As has been mentioned above, the fluorescence of TMPD is almost completely quenched by the presence of naphthalene. If the singlet state of TMPD is not affected by naphthalene, the fluorescence of the former will not be quenched. Also, the excitation energy transfer from TMPD (singlet) to naphthalene (singlet) can not occur in this case, because the singlet excited state of TMPD is energetically lower than that of naphthalene. It may, therefore, be concluded that almost all the excited singlet state of TMPD changes into the charge-transfer state formed with naphthalene. Consequently, most of the triplet state of naphthalene is not formed from the triplet state of TMPD, but mainly form the CT state.

$$\mathrm{TMPD^*(S)} + \mathrm{Naph} \rightsquigarrow$$
$$\text{in ethanol}$$
$$\text{CT state}\text{—}\begin{cases} \rightsquigarrow \mathrm{TMPD^+} + \mathrm{Naph^-} \\ \rightsquigarrow \mathrm{Naph\ (T)} \end{cases}$$

Here Naph indicates naphthalene. Such a process has been discussed by Leonhardt and Weller[11] and by many others. It should be noted that the T-T′ absorption spectrum of naphthalene obtained here is quite identical with that obtained for an ethanol solution containing naphthalene alone. This means that there is no interaction between TMPD in the ground state and naphthalene in the triplet state. Although a molecular complex with a charge-transfer character in the excited triplet state was found by Iwata, Tanaka, and Nagakura from their phosphorescence measurements,[22] such a complex does not seem to be present in this case.

---

21) The solvation energy of an electron in ethanol will be estimated to be about 2—3 eV from the absorption spectrum of the solvated electron and that of TMPD$^+$ will be nearly the same. The sum of these may amount to about 4—6 eV. This estimation will also be justified by the fact that the thermoluminescence, which can be measured in non-polar media, can not be observed in polar media.[7]

22) S. Iwata, J. Tanaka and S. Nagakura, *J. Chem. Phys.*, to be published.