BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 451—455 (1967)

The Photo-Ionization of Molecules in Solutions. IV. Electron Capture and Charge Transfer Fluorescence Phenomena Occurring between *N*, *N*, *N*′, *N*′-Tetramethyl-*p*-phenylenediamine and Electron Acceptors in Organic Solvents

Naoto YAMAMOTO, Yoshihiro NAKATO and Hiroshi TSUBOMURA

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

(Received July 1, 1966)

A mixture of *N, N, N′, N′*-tetramethyl-*p*-phenylenediamine (TMPD) and pyrene in some rigid matrices was illuminated at a low temperature in the near ultraviolet region. It was found that TMPD$^+$, pyrene anion, and solvated electrons are formed in the medium. The ratio of the formation of pyrene anion and TMPD$^+$ has been studied at various concentrations of pyrene. The behavior of the photo-ejected electron, particularly its extent of migration has then been discussed on the basis of the experimental results. The thermoluminescence spectrum of the UV-irradiated matrix containing TMPD and pyrene was measured after it had been illuminated in the infrared region. The luminescence may tentatively be assigned to the charge transfer fluorescence. The emission spectra were investigated for a mixture containing TMPD and α-methylnaphthalene in several solvents by exciting the TMPD. It was found that a new emission band appeared at 480 mμ. It was assigned to the charge transfer fluorescence.

The photolysis of *N, N, N′, N′*-tetramethyl-*p*-phenylenediamine (TMPD) either in rigid matrices at a low temperature or in solutions at room temperature has been studied extensively by several investigators, especially by Albrecht.[1-3]

---

[1] E. Dolan and A. C. Albrecht, *J. Chem. Phys.*, **37**, 1149 (1962); E. Dolan, *ibid.*, **37**, 2508 (1962); K. D. Cadogan and A. C. Albrecht, *ibid.*, **43**, 2550 (1965); G. E. Johnson, W. M. McClain and A. C. Albrecht, *ibid.*, **43**, 2911 (1965); W. M. McClain and A. C. Albrecht, *ibid.*, **43**, 465 (1965).

[2] R. F. Clarridge and J. E. Willard, *J. Am. Chem. Soc.*, **87**, 4992 (1965).

[3] H. Tsubomura, N. Yamamoto, K. Kimura, T. Sato, H. Yamada, M. Kato, G. Yamaguchi and Y. Nakato, This Bulletin, **38**, 2021 (1965); H. Tsubomura, N. Yamamoto and Y. Nakato, *ibid.*, **39**, 1092 (1966); N. Yamamoto, Y. Nakato and H. Tsubomura, *ibid.*, **39**, 2603 (1966).

The results obtained earlier have been summarized in Part III of this series.[3] More recently, Albrecht *et al.* have reported some interesting results concerning the photo-ionization of TMPD in a matrix at 77°K. They found, by using polarized photoselection techniques, that most of the electrons photo-ejected from TMPD have a limited range of migration in the rigid matrix.[4] They also found, from the ESR measurement of the TMPD matrix containing carbon dioxide, that a narrow ESR signal which has been previously assigned to the solvated electron is to be identified as the carbon dioxide anion.[5] Hamill *et al.* conclude that γ-irradiated 3-methylpentane at 77°K shows the absorption bands of solvated electrons. With TMPD, other amines, or hydrocarbons added to the matrix, cations and anions are formed. These systems show emission spectra stimulated by the infrared light, which are identified as the phosphorescence of the solute molecules.[6]

It was found by Leonhardt and Weller that new fluorescence bands appear when perylene is excited in nonpolar solvents containing various amines or anilines, although there is no complex formation in the ground state.[7] They attributed these bands to the emission from the transient charge transfer state formed between perylene as an electron acceptor and amine or aniline as electron donors to the ground state (CT fluorescence). Also, Mataga *et al.* found the CT fluorescence for mixtures containing an electron donor (amines) and an electron acceptor (aromatic hydrocarbons) and measured the lifetime of the CT fluorescence.[8]

In this paper, we will report our further findings concerning the photo-ionization of TMPD in solutions or in matrices. The problem studied is the behavior of electron acceptors present in the medium (pyrene and naphthalene derivatives). As the findings reported later in this paper will reveal, there are two different aspects of this behavior of electron acceptors; the capture of photo-ionized electrons, and the transient CT complex formation between TMPD and the acceptor.

Experimental

The method of purifying TMPD was described in an earlier paper.[3] Pyrene was recrystallized from an ether solution and was sublimed in vacuum. α-Methylnaphthalene was purified by distilling it under reduced pressure.

The solvents used were MP (1 part methylcyclohexane and 1 part isopentane), EPA (8 parts ether, 3 parts isopentane, and 5 parts ethanol), and liquid paraffin. Ethanol was purified by drying it over a magnesium ribbon and by then distilling it in a 120-cm column. Ether, isopentane, and methylcyclohexane were dried with sodium for a day and then purified by distillation. EP-grade liquid paraffin was used without further purification.

The degassed solutions were prepared by using the technique described in the earlier paper.[3]

The measurements of the absorption spectra were made using a Cary spectrophotometer, model 15. For the measurements of the emission spectra, the samples were illuminated by monochromatic light ($\lambda=340$ mμ), obtained from a 500-W xenon lamp, through a Shimadzu monochromator GF-16. The emission spectra were then recorded on the Cary spectrophotometer. The characteristics of the instrument used for the flash photolysis have been described previously.[3]

Results and Discussion

A. Behavior of the Photo-ejected Electron from TMPD at 77°K. A mixture of TMPD and pyrene in a rigid matrix at 77°K was illuminated in the ultraviolet region by focusing the light from a 250 W high-pressure mercury lamp (Ushio HMB-250D) through a Toshiba UV-D2 filter transparent from 230 to 390 mμ. The absorption spectra of the UV-irradiated samples in the MP and in the EPA matrix are shown by Curves a and b in Fig. 1. The absorption from 520 to 650 mμ is identified as being due to TMPD$^+$. The peak of the absorption at 492 mμ is identical with that of the pyrene anion formed by the reduction of pyrene with sodium.[9]

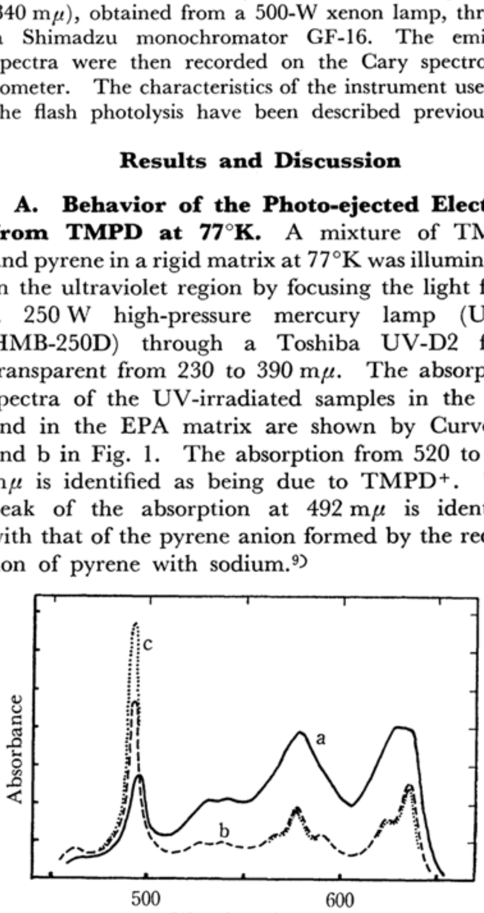

Fig. 1. Absorption spectra of the UV-irradiated sample of the mixture of (a) 2.0×10^{-4} mol/l TMPD and 1.0×10^{-3} mol/l pyrene in EPA matrix and (b) 1.3×10^{-3} mol/l TMPD and 2.1×10^{-3} mol/l pyrene in MP matrix at 77°K. Curve c shows the absorption spectrum taken after the UV-irradiated sample in a MP matrix was illuminated with the infrared light.

---

4) W. M. McClain and A. C. Albrecht, *J. Chem. Phys.*, **44**, 1594 (1966).

5) P. M. Johnson and A. C. Albrecht, *ibid.*, **44**, 1845 (1966).

6) D. W. Skelly and W. H. Hamill, *ibid.*, **43**, 3497 (1965).

7) H. Leonhardt and A. Weller, *Z. Physik. Chem. (Frankfurt)*, **29**, 277 (1961); H. Leonhardt and A. Weller, *Z. Elektrochem., Ber. Bunsenges. Physik. Chem.*, **67**, 791 (1963).

8) N. Mataga, K. Ezumi and T. Okada, *Mol. Phys.*, **10**, 201 (1966); N. Mataga, T. Okada and K. Ezumi, *ibid.*, **10**, 203 (1966).

9) J. D. W. van Voorst and G. J. Hoijtink, *J. Chem. Phys.*, **42**, 3995 (1965).

In these experiments, the solute molecules are thought to be separated from each other by a large average distance, since there is no sign of complexing between them (*vide infra*). Therefore, it is concluded that TMPD is first excited to its lowest singlet excited state; then, *via* a two-photon mechanism, it ejects an electron into the matrix, since the two-photon mechanism is necessary for the molecule to get sufficient energy for the photo-ionization. As the absorption spectrum of pyrene overlaps with that of TMPD, it is possible that pyrene is also excited. However, as no change was observed when a matrix containing only pyrene was illuminated, it may reasonably be concluded that the excitation of pyrene does not influence the formation of ionic species in the present experiment. The present results indicate, therefore, that part of the photo-ejected electrons are captured by the pyrene forming the pyrene anion. The spectrum persists for a long time at 77°K. When these molecules in the MP matrix were irradiated by the mercury lamp without using the filter, no photo-ionization was observed, indicating that the light in the visible and infrared regions remarkably stimulates the recombination of the photo-ionized species.

We have also made experiments varying the concentration of pyrene at 77°K. The concentrations of the pyrene anion, pyr^-, and $TMPD^+$ formed by the photolysis were determined spectroscopically by using the molecular extinction coefficients. For pyr^-, we used the value of the absorption peak at 492 mμ obtained by the reduction of pyrene with sodium.[10] For $TMPD^+$, the value at 630 mμ was obtained from an ethanol-water solution of chemically-formed Wurster's blue perchlorate.[11] The $\omega=[pyr^-]/[TMPD^+]$ ratio was plotted against the concentration of pyrene, [pyr], in the matrix, as is shown in Fig. 2.

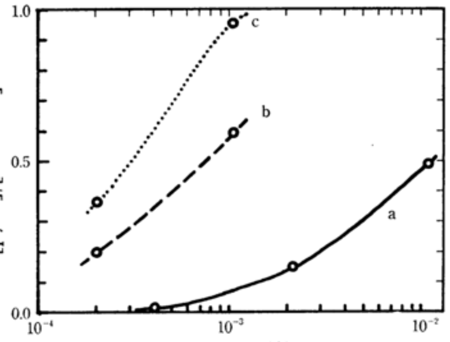

Fig. 2. Formation of ions by ultraviolet excitation of TMPD; (a) in EPA matrix, (b) in MP matrix and (c) the same, illuminated with infrared light.

Curves a and b in Fig. 2 show that, at very low concentrations of pyrene, the ω values are low, indicating that the ejected electrons are trapped mainly by the solvents. As the concentration of pyrene increases, the ω values increase. These results may be explained by assuming that the electron can move only a limited distance from TMPD after photo-ejection. From the absorption spectra of the solution of TMPD and pyrene at room temperature and at 77°K, we have found no new bands arising from interactions between these compounds; hence, no complex of any type seems to exist. Therefore, it may reasonably be concluded that the solute molecules are distributed randomly in the matrix. Also, as the concentration of TMPD is much smaller than that of pyrene, the average distance between these molecules may be taken to be determined only by the concentration of pyrene. On the basis of these assumptions, we can estimate the range of migration of the ejected electrons made from TMPD as below.

If n molecules of pyrene are randomly distributed around a TMPD molecule in a certain volume, V, the probability that no pyrene molecule will be found within a sphere with a radius of r is equal to $(1-4\pi r^3/3V)^n$. The probability that a pyrene molecule will be found in a spherical shell between r and $r+dr$ is given by $n\cdot 4\pi r^2 dr/V$. Therefore, the probability, $\rho(r)dr$, that the nearest-neighbor pyrene molecule will be found in the spherical shell may be expressed by:

$$\rho(r)dr=(1-4\pi r^3/3V)^n\cdot 4\pi n r^2 dr/V \qquad (1)$$

We can get $\bar{r}$, which is the radius for the maximum value of $\rho(r)$, from the equation $d\rho(r)/dr=0$:

$$\bar{r}=(V/2\pi n)^{1/3} \qquad (2)$$

If V/n is expressed by the molar concentration of pyrene, we have:

$$\bar{r}=6.42\,[pyr]^{-1/3}\,\text{Å} \qquad (3)$$

The $\bar{r}$ value may be approximately taken to represent the most probable distance between TMPD and the nearest-neighbor pyrene molecule. Now, if one tentatively inserts into (3) the concentration of pyrene corresponding to $\omega=0.5$ in Fig. 2, one can get an approximate order of magnitude for the extent of the migration of the ejected electron. The values obtained are 72 Å for the MP matrix and 30 Å for the EPA matrix. These values are in fairly good agreement with the corresponding values obtained by others using different methods. Namely, McClain and Albrecht concluded that the ejected electrons move within a cube with the volume of $(250\ \text{Å})^3$ in 3-methylpentane,[4] while Ronayne, Guarino and Hamill gave a value of $(50\ \text{Å})^3$ for the 2-methyltetrahydrofurane matrix.[12]

---

[10] P. Balk, S. de Bruijtink and C. J. Hoijtink, *Rec. Trav. Chim. Pays-Bas*, **76**, 813 (1957).

[11] L. Michaelis, M. P. Schubert and S. G. Granick, *J. Am. Chem. Soc.*, **61**, 1981 (1939).

[12] M. Ronayne, J. P. Guarino and W. H. Hamill, *ibid.*, **84**, 4230 (1962).

These values, converted to our $\bar{r}$ value, lead to 135 and 27 Å respectively.

The present value for the EPA matrix is considderably smaller than that for the MP matrix. This suggests that the extent of the migration of photo-ejected electrons for the polar matrix is reduced by the large electron-capture cross section of the solvents.

Under illumination in the infrared region (0.7—5 μ) using a mercury lamp through a filter (Toshiba VR-69), the photolyzed mixture in the MP matrix emits light. At the same time, it was found, from the change in the absorption spectrum, that [TMPD$^+$] slightly decreases, while [pyr$^-$] greatly increases (Fig. 1, Curve c and Fig. 2, Curve c). This shows that the electrons trapped in the MP matrix are excited by the infrared light and migrate in the matrix untill some of them are caught either by pyrene or by TMPD$^+$. Although we did not measure the emission, it is probably due to the fluorescence and the phosphorescence of TMPD. The depth of the trap in the MP matrix can be estimated from the bleaching with infrared illumination to be less than about 1.24 eV.

After the UV-irradiated sample was illuminated by infrared light, the sample cell was taken out of the Dewar vessel. As the matrix warmed up, a thermoluminescence was observed. The photographic measurement of its spectrum showed that there is only one band, with a maximum at 476 mμ, shown by Curve b in Fig. 3. The emission band thus obtained agrees so well with the phosphorescence band of TMPD that it seems quite natural to assign the thermoluminescence to the phosphorescence of TMPD. If so, the following mechanism may be assumed:

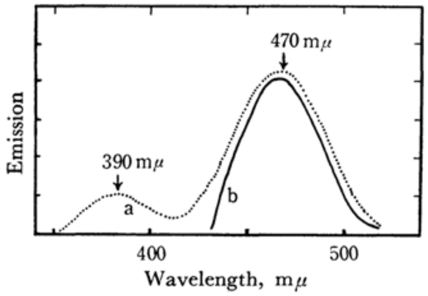

Fig. 3. Thermoluminescence spectrum of the UV-irradiated MP matrix containing TMPD and pyrene taken photographically after it was illuminated in the infrared light (curve b). Curve a shows the thermoluminescence spectrum of the UV-irradiated MP matrix containing TMPD.3)

$$\text{pyr}^- + \text{TMPD}^+ \rightarrow [\text{pyr}^-\cdots\text{TMPD}^+]\ \text{(transient charge transfer state)} \qquad \text{(I)}$$

$$[\text{pyr}^-\cdots\text{TMPD}^+] \rightarrow \text{pyr} + \text{TMPD (triplet state)} \qquad \text{(II)}$$

$$\text{TMPD (triplet state)} \rightarrow \text{TMPD(ground state)} + h\nu\text{(phosphorescence)} \qquad \text{(III)}$$

However, the emission is observed at a fairly high temperature, where the matrix becomes a fluid. Under such conditions, no phosphorescence from organic molecules is usually observed. It might, therefore, be suggested that the emission is due to the charge transfer fluorescence, due, that is, to the transition from [pyr$^-\cdots$TMPD$^+$] to the ground state. In this connection, it is worth noting that Chandross, Longworth and Visco found, from the electrolysis of a solution of aromatic hydrocarbon, a luminescence band which they attributed to the excimer fluorescence.13)

For the photolized EPA matrix, the illumination in the infrared region and down to 690 mμ does not change [TMPD$^+$] or [pyr$^-$], nor does it cause the stimulated emission. Illumination in the range of the absorption spectrum of the pyrene anion ($\lambda < 500$ mμ) largely bleaches the color of the pyrene anion. This indicates that the threshold energy of the photo-ionization of pyrene anion is 2.5 eV in the EPA matrix. The color of the sample fades instantaneously when the matrix is warmed, although a small amount of the cation remains for some time. However, no thermoluminescence is observed upon this warming. It may, therefore, be concluded that when the matrix is warmed, the recombination of the electron with TMPD$^+$ will lead to the ground state of TMPD either directly or *via* the triplet state. These results indicate that the electron is trapped much more tightly in EPA than in MP.14)

B. Emission Spectra of the Mixture of TMPD and Naphthalene Derivatives. A fluorescence which may be assigned to the π^*-π transition of TMPD is observed when TMPD is excited in the range of the π-π^* band ($\lambda = 340$ mμ) at room temperature. It was found that the emission is not quenched by oxygen dissolved in MP or liquid paraffin solutions.

The emission spectrum of the mixture of TMPD and α-methylnaphthalene in MP solutions, with various concentrations of the latter, has been measured by exciting it in the range of the π-π^* band of TMPD. As the concentration of α-methylnaphthalene is increased, the fluorescence of TMPD gets weaker, and a new emission band begins to appear at 480 mμ, as is shown in Fig.

---

13) E. A. Chandros and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964); E. A. Chandros, J. W. Longworth and R. E. Visco, *ibid.*, **87**, 3259 (1965); Also see E. A. Chandross and F. I. Sonntag, *ibid.*, **88**, 1089 (1966).

14) Unpublished results from our laboratory. The detail will be published in the future.

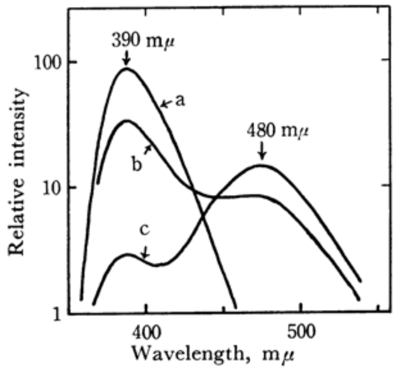

Fig. 4. Emission spectra of the mixture of TMPD and α-methylnaphthalene with various concentrations in MP at room temperature.
(a) 4.6×10^{-4} mol/l TMPD only
(b) 4.6×10^{-4} mol/l TMPD + 5×10^{-3} mol/l α-methylnaphthalene
(c) 4.6×10^{-4} mol/l TMPD + 6×10^{-2} mol/l α-methylnaphthalene

TABLE 1. TEMPERATURE DEPENDENCE OF THE RATIO, I_c/I_s, OF THE MP SOLUTIONS OF TMPD IN THE PRESENCE OF α-METHYLNAPHTHALENE WITH VARIOUS CONCENTRATIONS

Concn. of α-methyl-naphthalene mol/l	Temperature		
	20°C	−70°C	77°K
0	0	0	0
5×10^{-3}	0.50	0.20	0.07
6×10^{-2}	2.24	0.66	—
3×10^{-1}	—	1.2	—

4. The intensity of the new band is strongly dependent on the concentration of α-methylnaphthalene, while the shape of the band is simple, broad peak. As the exciting light is very weak, it is not conceivable that the emission is due to a species formed by a two-photon mechanism, such as the triplet-triplet anihilation. No new absorption band was observed upon mixing TMPD and the naphthalene derivative; hence, the formation of any complex between the solute molecules seems impossible, at least under the present experimental conditions. The most plausible conclusion as to this new emission is, therefore, that it is due to the formation of a transient charge transfer complex between excited TMPD and α-methylnaphthalene; the new emission band may be identified as the CT fluorescence analogous to the emission found by Weller *et al.* from excited perylene and amines in non-polar solutions.⁷⁾

The intensity of the CT fluorescence decreased as the temperature was lowered. The ratios of the intensity of the new fluorescence (I_c) to that of the fluorescence of TMPD (I_s), with various concentrations of α-methylnaphthalene, at 20°C, −70°C and 77°K are tabulated in Table 1. The temperature dependence of the intensity of the CT fluorescence seems to be due to the different diffusion rate of the solutes in the solution, because the formation of the CT complex depends on the diffusion-controled encounter of the solute molecules within the lifetime of the excited state of TMPD. For liquid paraffin solutions, the intensity of the CT fluorescence is smaller than that in the MP solutions under the same conditions. This also indicates that a solvent with a high viscosity lowers the diffusion rate of the solutes. In the case of a mixture in a EPA solution, the CT fluorescence does not appear.

Weller *et al.* pointed out that, in the case of the mixture in polar solvents, the CT complex in the excited state is very short-lived, dissociating into the cation of the donor and the anion of the acceptor; the CT fluorescence, therefore, is not observed. This is in accord with our finding that no new emission was observed in EPA solutions.

We have above used the terminology of "the transient CT complex" and the "CT fluorescence". However, the transient state may not be purely $D^{+}\cdots A^{-}$ but may contain, abundantly, the $D^{*}\cdots A$ or $D\cdots A^{*}$ structure.

A very similar "CT fluorescence" was also found when naphthalene was used instead of α-methylnaphthalene. By the flash photolysis of liquid paraffin solutions of TMPD at room temperature with naphthalene, α-methylnaphthalene or α-chloronaphthalene added, we have found the characteristic absorption bands due to the T–T′ transition (from the lowest triplet state to the higher triplet state) of the naphthalene derivatives. In this case, however, the T–T′ band of TMPD reported earlier³⁾ was not observed. There is no way to decide now whethere the energy of the excited TMPD transfers to the naphthalene *via* the former's triplet state or *via* the transient CT state. We are attempting to carry out some experiments to clarify these points.¹⁵⁾

All these findings indicate that, as a result of the presence of a suitable electron acceptor at a sufficient concentration, TMPD excited to the (π–π^{*}) level can transfer into a CT state. In this case, a sort of photo-ionization (electron transfer) occurs from TMPD to the acceptor by a one photon-process. If there is no encounter of the electron-acceptor and the excited TMPD, however, a two-step excitation process is necesary for the TMPD to be photo-ionized. Our finding concerning the CT fluorescence is the first one obtained by exciting a donor molecule.

---

15) The detail will be reported in the nexst paper of this series.