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Photoionization of N,N,N′,N′-Tetramethyl-*p*-phenylenediamine in Polar Solvents

Minyung Lee, Du-Jeon Jang, and Dongho Kim*

Spectroscopy and Color Laboratory, Korea Standards Research Institute, Taedok Science Town, Taejeon 305-606

Sun Sook Lee and Bong Hyun Boo

Department of Chemistry, Choongnam National University, Taejeon 305-746.
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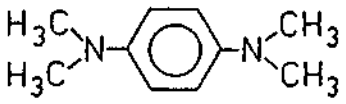
The photoinduced electron transfer reactions of N,N,N′,N′-tetramethyl-*p*-phenylenediamine (TMPD) in various polar solvents were studied by measuring time-resolved fluorescence. The temperature dependnce on the fluorescence decay rate in acetonitrile, methanol, ethanol and buthanol was carried out to obtain the activation energy and Arrehnius factor for the photoinduced electron transfer reaction. It was found that as the dielectric constant of the solvent increases, the activation energy and the reaction rate increase. This implys that the Arrehnius factor is important in controlling the photoinduced electron transfer reaction rate. In water, TMPD exists in three forms (cationic, protonated and neutral forms) due to the high dielectric constant and strong proton donating power of water. The photoinduced electron transfer reaction was found to be very fast (<50 ps) and also the long liverd component in the fluorescence decay profile attributable to the photoexcited protonated form of TMPD was observed. Probably, the reaction pathway and the reaction coordinate seem to be different depending on the solvents studied here.

Introduction

Elucidation of dynamics and mechanism of photoinduced charge or electron transfer leading to the formation of ion pair is one of the most fundamental problems in photochemical processes in polar solvents[1]. In polar solvents, an interaction between N,N,N′,N′-tetramethyl-*p*-phenylenediamine (TMPD) and solvent molecules is known to play an important role

in the formation of an ion pair[2,3].

TMPD has been known to be a typical molecule undergoing one photon ionization in polar solvents upon UV excitation. The ionization potential of TMPD is 6.6 eV in the gaseous state, but it is much lower in polar solvents due to the dipolar orientation of solvent molecules to the TMPD molecules[4].



There have been many efforts to identify the photoionization mechanism of TMPD in solution. On the basis of photocurrent measurements, Ottolenghi *et al.*[5] suggested the importance of charge transfer to the solvent state in the photoionization process. Hirata and Mataga[6,7] carried out the picosecond laser-induced transient photoconductivity measurements on the photoionization of TMPD in acetonitrile and in various alcohols. They concluded that the ion pair produced from the relaxed S_1 state of TMPD is the bound ion pair with a definite structure formed by a solute-solvent exciplex interaction. Yoshihara and coworkers[8] also performed the nanosecond and picosecond laser techniques and suggested a possible photoionization mechanism of TMPD in polar solvents in the excited state.

This work concerns the photoionization processes of electronically exccited TMPD in acetonitrile, water, water-ethanol mixtures, and various alcohols. The fluorescence lifetimes were measured by the time-correlated single photon counting (TCSPC) technique. The details of the electron transfer reaction of TMPD in polar solvents will be discussed, based on the solvent and temperature dependence of excited-state lifetimes of TMPD in solution.

Experimental

Fluorescence lifetimes of TMPD were measured by a time-correlated single photon counting system. The excitation laser source is a mode-locked Nd:YAG laser pumping a dual-jet dye laser. The cavity-dumped beam from the dye laser has 2 ps pulsewidth, average power of ca. 120 mW power at 3.8 MHz dumping rate, and the tunability of 560-607 nm when Rh6G for the gain dye and DODCI for the saturable absorber were used. To excite samples, the dye laser pulse was frequency-doubled by a KDP crystal. All the standard electronics for the TCSPC were purchased from the EG & G Ortec. The temporal instrument response function was measured by scattering from pure *n*-pentane and typically it had a 700 ps FWHM when a Hamamatsu photomultiplier tube (R928) was used.

The TMPD was purchased from the Aldrich Chem. Co., The deionized water was triply distilled. High purity solvents were used and all the TMPD solutions (1×10^{-4} mol/*l*) were deaerated by using several freeze-pump-thaw cycles before static and lifetime measurements.

Results and Discussion

Photoionization of TMPD in Polar Solvents. Figure 1 presents the absorption spectra of TMPD in acetonitrile, methanol, ethanol and buthanol, respectively. As reported previously[6,7], the absorption band only in the UV region and the single emission peak at ca. 400 nm were observed. Figure 2 presents the fluorescence decay profiles in these solvents. As the dielectric constant increases, the fluorescence decay time becomes shorter. The increase in solvent polarity helps the charge separation in the ground and/or the photoexcited states and consequently renders the photoinduced electron transfer reaction process faster. The fluorescence lifetimes in these solvents are given in Table 1. To have more information on the photoinduced electron transfer reaction in each solvent, the temperature dependence experiment on the fluorescence decay rate was carried out in the temperature range of 7-77℃. The electron transfer rate was plotted in Figure 3 in acetonitrile and in alcohol solutions (methanol, ethanol, and butanol) as a function of temperature. The results of Arrhenius plot was tabulated in Table 1. Temperature dependence studies were previously performed by Yoshihara

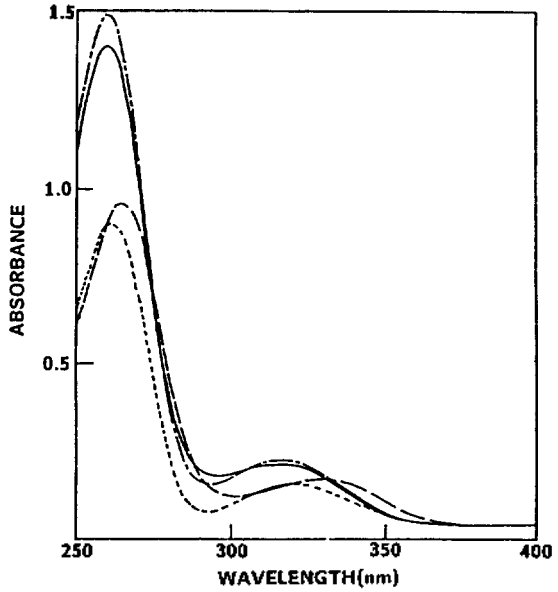


Figure 1. The series of absorption spectra of TMPD in methanol (——), ethanol (– – –), buthanol (------) and acetonitrile (— —), respectively.

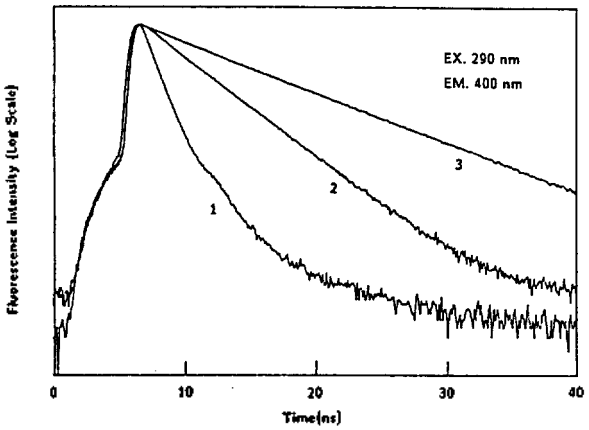


Figure 2. The fluorescence decay profile of TMPD in acetonitrile (1), methanol (2) and ethanol (3), showing single exponential decay.

Table 1. The Arrehenius Pre-factor, Fluorescence Lifetime and Activation Energy for the Photoionization Reaction

Solvent	Dielectric constant	A (ns^{-1})	Lifetime (ns)[a]	E_a (kcal/mol)
CH_3CN	38.8	676500	1.0	8.0
MeOH	32.6	17700	3.7	6.7
EtOH	24.3	79	7.3	4.2
t-BuOH	17.1	3	7.6	2.4

[a]Probe wavelength is 400 nm and temperature is 24℃.

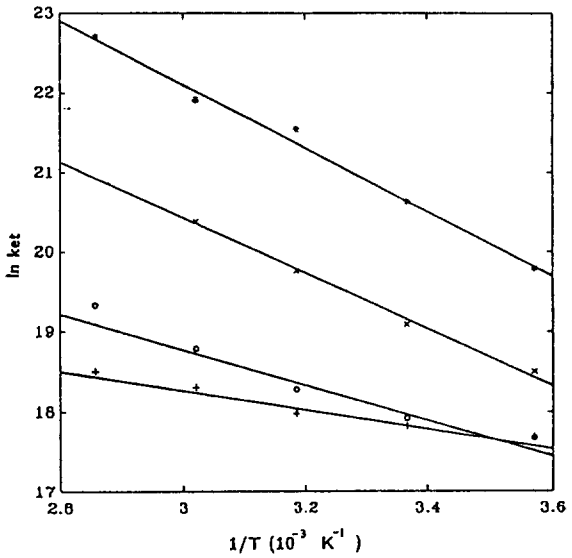


Figure 3. The Arrhenius plot of the electron transfer rate of TMPD in acetonitrile (*), methanol (×), ethanol (○), and butanol (+), respectively.

and coworkers in the range of 40℃ to −105℃[8]. In acetonitrile, the activation energy of 8.1 kcal/mol of our data is close to the value reported previously[6]. However, in ethanol, the differences are noticeable. For example, Yoshihara and coworkers[8] measured E_a of 12 kcal/mol in ethanol. Our measurements show almost three times smaller value (4.2 kcal/mol), even though the reason for this discrepancy is unclear. We also measured the activation energy of 2.4 kcal/mol for the TMPD photoionization process in butanol. It appears that E_a monotonously decreases as the solvent dielectric constant decreases. The change of the Arrhenius factor, however, is rather dramatic from solvent to sovlent. The A-factor for k_{et} in acetonitrile (ε=38.8 at 20℃) is ca. 10^6 larger than that in butanol (ε=15.8 at 25℃).

Although there have been numerous investigations about the solvent effect on the electron transfer reaction of photoexcited TMPD molecule, studies in water solution are rare in the literature, probably due to the possible complexity in the gorund and/or the photoexcited state caused by the facile charge separation imposed by the high dielectric constant of water. The absorption spectrum of TMPD in water is presented in Figure 4. Unlike other polar solvents, the TMPD molecule in water denotes a blue color and a strong absorption band in the visible region is observed. More interestingly, the absorption spectrum in the visible region is the

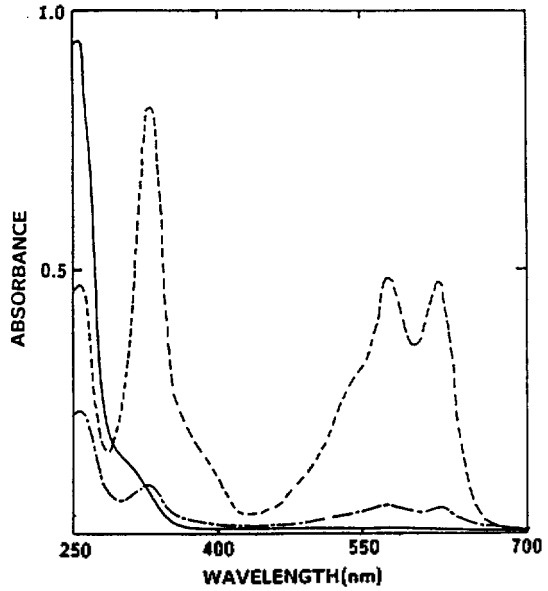


Figure 4. The absorption spectra of TMPD in pH 2 (——), pH 7 (-----) and pH 12 (———), buffer solutions, respectively.

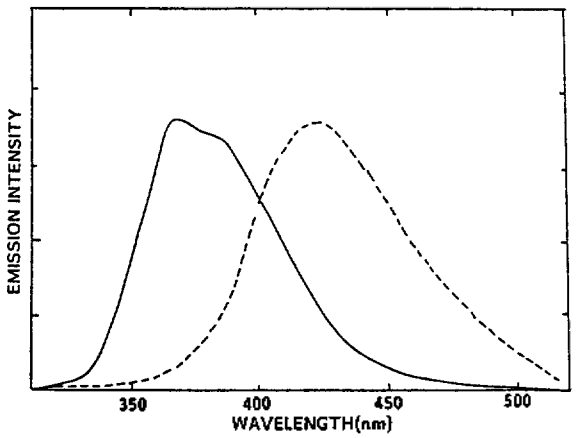


Figure 5. The emission spectra of TMPD in pH 7 (——) and pH 12 (-----) buffer solutions, respectively. The emission spectrum in pH 2 buffer solution is similar to that in pH 7 buffer solution. the excitation wavelength is 320 nm.

same as that of TMPD cation radical ($TMPD^{+\cdot}$) reported previously[2,3]. This indicates that the $TMPD^{+\cdot}$ is formed in the ground state, favored by the large dielectric constant of water and the low ionization potential of TMPD molecules in water. In addition, there are two strong absorption bands in the ultraviolet region, one has the absorption maximum at 260 nm and the other one at 320 nm. It is believed that the 260 nm absorption band is originated from the neutral form of TMPD and the 320 nm and the visible absorption bands from $TMPD^+$, since the absorption band at 260 nm increases in the high pH water solution compared with those in neutral and low pH solutions and the 320 nm absorption band has the same pH dependence as the visible absorption band (Figure 4). Also some contributions to the absorption band in the ultraviolet region from the protonated TMPD molecule is expected. The steady state fluorescence spectra of TMPD were recorded in pH 7, and 12 solutions, respecti-

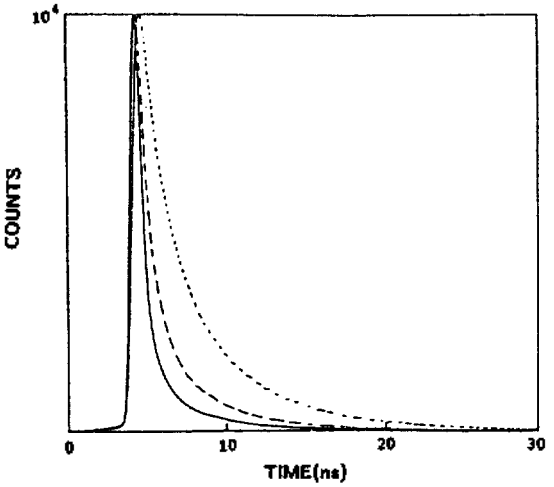


Figure 6. The wavelength dependent emission decay profiles off TMPD in water. The excitation wavelength is 290 nm and the collection wavelengths are 370 nm (------), 400 nm (— —) and 430 nm (——), respectively.

vely (Figure 5). pH 2 data are similar to pH 7. The fluorescence spectra in pH 7 solutions are probably originated from the protonated TMPD and the neutral TMPD, since TMPD cation is non-emissive. On the while, the emission spectra having the maximum peak at 430 nm of TMPD in pH 12 solution is mainly from the neutral form of TMPD. And the time-resolved fluorescence measurement also gives an information on the emitting species involved in aqueous solution.

The fluorescence lifetime of TMPD measured in water solution with 290 nm excitation wavelength by varying the collection wavelength (370, 400 and 430 nm (Figure 6)). The decay profile curve fits a double exponential form with <50 ps and ca. 5 ns components. The amplitude of the long lived (5 ns component) component increases in the short wavelength region. Therefore the long lived compoments is contributed by the excited state fluorescence of the protonated form of TMPD as confirmed by the steady state emission spectra of TMPD in various pH solutions. On the while, the short lived (<50 ps) component is attributable to the photoionization time, since it is expected that the photoionization process becomes faster in highly dielectricc media like water as confirmed by the fluorescence decay measurements done in acetonitrile and alcohol solutions. However, the continuous exposure to UV pulses from our laser (average power 5 mW) onto TMPD in water gradually change the blue color into colorless. Although this color change is a reversible process, the average power of UV pulses was kept low (less than 2 mW) and the fresh sample was employed for each decay time measurement to avoid any possible contribution to the fluorescence decay profile from the photoproduct. To have more information on the photoinduced electron transfer reaction process in water, the temperature dependence of the fluorescence decay time was studied. The instrument response function of our TCSPC system is too long (700 ps) to see the change in the fluorescence decay time of the short lived component (<50 ps). The decay time of the long lived component does not change in the temperature range of 7-77℃ we have studied. This supports that the long lived component in the fluorescence decay profile is originated from

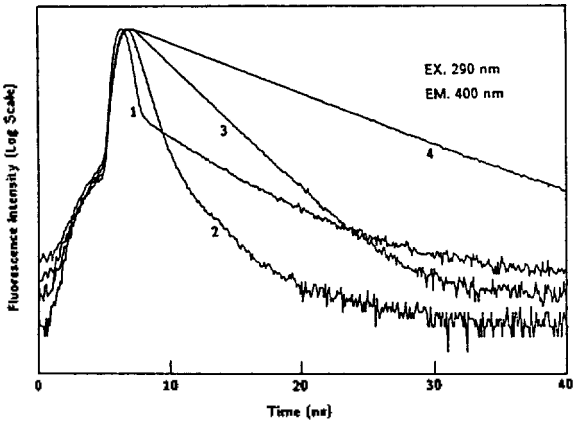


Figure 7. The fluorescence decay profile of TMPD in water-ethanol mixtures, showing multiple exponential decays. The numbers 1, 2, 3, and 4 indicate the ethanol volume percent of 0, 33, 67, and 100%, respectively.

the fluorescence decay of the photoexcited protonated form of TMPD, since it is believed that the decay process of this molecule is less temperature dependent than the photoexcited electron transfer reaction of the neutral TMPD molecule.

Figure 7 shows the fluorescence decay profile of TMPD in water and ethanol mixture. The 5 ns component persists up to the 50% of ethanol (not shown). In overall, as the volume fraction of ethanol increases, the electron transfer rate decreases. The long lived component becomes undertectable when the ethanol volume concentration exceeds 50%. In other words, the protonated species is not stable in these concentrations because of the dilution of the water concentration in the solvent mixtures.

Photoionization Process. The photoionization process is one of various non-radiative processes which deplete the population of the photoexcited molecules. The electron transfer rate from TMPD to solvent(s) can be calculated from the following relation:

$$k_{et}=1/\tau_F-(k_r+k_{nr})$$

where k_r is the radiative decay rate and k_{nr} accommodates the nonradiative decay rate except for the electron transfer rate. One way of determining the value of k_r+k_{nr} is to do the low temperature experiments. If the photoionization is the only activated rate process among the non-radiative decay channels, then the lifetimes will show a plateau at very low temperatures, as they are plotted as a function of temperature. The inverse of the low temperature lifetime can be assigned to k_r+k_{nr}. The value of 13 ns was taken from the low temprature data by Yoshihara and coworkers[8].

The rapid fluorescence quenching of TMPD in water-ethanol mixture by increasing water concentration was previously observed by Richards and Thomas[9] in the micro and nanosecond time scale. Our data verified that the decrease of the quantum yield in the high water concentration was due to the fast photoexcited electron transfer of TMPD.

The photoionization scheme of TMPD in the excited state has been proposed by Yoshihara and coworkers[8] in acetonitrile solution and by Hirata and Mataga[6,7] in alcoholic solution. The major concern was the pathway of forming the ion pair. In acetonitrile, Yoshihara *et al.*[8] suggested that there

are two processes for the pathway. One is the direct ionization occurring from the unrelaxed S_1 state, and the other is thermally activated process. In alcohol solution, Hirata and Mataga[6,7] did not observe the direct photoionization pathway occurring from the unrelaxed S_1 state. Instead, they proposed that there exists a short lived gateway state (the semi-ionized state) which may be formed by charge transfer from TMPD S_1 state to the solvent cluster. In addition, since they did not observe the cation band in the early stage of picosecond transient absorption spectra, they proposed that the triplet, ion pair and ground state may be formed through the gateway state[10]. However, the existence of the so-called "semi-ionized state" seems to depend on solvents. Isaka *et al.*[11] carried out a time-resolved resonance Raman studies on TMPD ionization in acetone and they did not observe the intermediate state proposed by Hirata and Mataga[10].

Our data of solvent and temperature dependence also reveal the difference. The dielectric constants of acetonitrile and methanol are similar, but the Arrhenius factor in acetonitrile is 40 times larger than that in methanol. As the dielectric constant increases, the activation energies and the fluorescence decay rates also increase. This implies that the Arrhenius factor also plays an important role in controlling the reaction rate. Hence the so-called gateway or the intermediate solvent rearrangement state in favor of the charge separation process is possible[10]. However, since the wide range values in Arrehnius factor in the same series of reaction were obtained, the electron transfer reaction coordinate and/or pathway in acetonitrile and in alcohol could be different each other. The suggested mechanism for the photoinduced charge separation process of TMPD in polar solvents may be classified into two cases[12]:

$$\text{TMPD} + \text{S} \xrightarrow{h\nu} \text{TMPD}^* + \text{S} \rightarrow \text{TMPD}^* - \text{S} \rightarrow (\text{TMPD}^+ \text{--} \text{S}^-) \rightarrow$$

dissociation or recombination

S = ethanol, buthanol

$$(\text{TMPD}^{+\delta}\text{S}^{-\delta}) \xrightarrow{h\nu} (\text{TMPD}^{+\delta}\text{S}^{-\delta})^* \rightarrow (\text{TMPD}^+ \text{--} \text{S}^-) \rightarrow$$

dissociation or recombination

S = water, acetonitrile

As shown above, the electron transfer reaction in highly dielectric media like water and acetonitrile seems to follow the Scheme 1 owing to the strong solvent-solute interaction in the ground state, whereas the reaction in moderately dielectric solvents seems to follow the Scheme 2. In methanol, the photoinduced reaction pathway is unclear since the Arrehnius plot shows a relatively large Arrehnius factor compared with other alcoholic solvents. Probably it has both channels, since this reaction has a high activation energy and the methanol has a high dielectric constant.

Conclusion

Our data showed that there are three distinct species in water in the electronic ground state; neutral TMPD, TMPD cation, and the protonated form. The time resolved emission decay profile consists of two components. The <50 ps component is the photoexcited electron transfer time from TMPD to water solvent and the ca. 5 ns component is attributable to the fluorescence lifetime of the photoexcited protonated form of TMPD. As the dielectric constant of the solvents studied here increases, the activation energy and the reaction rate increases. This observation implies that the solvent rearrangement to favor the charge separation in the ground and/or the photoexcited states is important in controling the photoinduced electron transfer rate. Depending on the solvent, the reaction pathway and/or the reaction coordinate in the charge separation process seems to be different, which is supported by the wide range of the Arrehnius factor in the photoinduced electron transfer reaction in the series of solvents studied in this work.

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