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Picosecond Photoionization Processes of N,N,N',N'-Tetramethyl-p-phenylenediamine (TMPD) in Water

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Photoionization processes of TMPD in H₂O and D₂O were studied, by measuring steady-state absorption, emission, fluorescence excitation spectra, and fluorescence lifetimes on picosecond time scale. The steady-state absorption spectra showed that there exists a cation-ion pair (Wurster's Blue) in H₂O and in D₂O in the electronic ground state. Temperature and excitation wavelength dependence were also studied and the results show that the photoionization reaction in water is an activated process and the fluorescence lifetime is independent of the vibrational excess energy in the uv excitation range of 283-310 nm.

Introduction

Upon electronic excitation, TMPD is known as one of the simplest molecules undergoing one-photon ionization in polar solvents such as water, acetonitrile, and alcohols¹⁻⁴. Recently, time-resolved nanosecond and picosecond studies have been carried out in many laboratories to elucidate dynamics of electron photoejection from TMPD in the first excited singlet state⁵⁻⁹. It seems that the photoionization process depends on the nature of solvents. For example, the fluorescence lifetimes of TMPD in alcohols are affected by solvent polarity. The lifetimes of TMPD at room temperature are 3.7, 7.3, and 7.6 ns in methanol, ethanol, and butanol, respectively¹⁰. Since the photoionization rate is roughly proportional to the inverse of the fluorescence lifetime, high solvent polarity facilitates the electron ejection by lowering the activation energy, which has been confirmed by temperature-dependent studies on fluorescence lifetime measurements¹⁰.

In acetonitrile, the fluorescence lifetime of TMPD is much shorter (1.0 ns), compared with alcohols. Mataga and coworkers extensively studied the photoionization process of TMPD and analogous molecules in acetonitrile^{5-7,11,12}. Based on their accumulated experimental data and recent experiments on the excitation wavelength dependence¹³, they concluded that the ionization occurs from the relaxed S₁ state (fluorescence state) and the rate of the electron ejection from the vibrationally unrelaxed state depends not only on the

excess energy but also on the nature of the excited vibrational modes.

The polarity of water is so strong that TMPD forms a cation-ion pair, so-called "Wurster's blue (WB)" in water even in the electronic ground state. Therefore, it is more difficult to interpret the experimental observations on photo-induced reaction process of TMPD in water. Richards and Thomas first studied the photoionization of TMPD in water-ethanol mixture with microsecond and nanosecond time resolution². They observed that the rapid fluorescence quenching of TMPD in the mixture as the concentration of water increases. From our previous measurements on fluorescence lifetimes of TMPD in water-ethanol mixture, we suggested that the decrease of the quantum yield in the high concentration of water was due to the fast electron transfer of TMPD¹⁰. However, the time resolution was limited by the instrument response so that the photoionization rate were not able to be measured accurately. It should be noted that Richards and Thomas reported that TMPD did not fluoresce in aqueous solution. However, our steady state emission and fluorescence lifetime data show that TMPD does fluoresce in H₂O and in D₂O.

In this work, we study the photoionization dynamics of TMPD in H₂O and D₂O in picosecond time scale. The lifetimes of TMPD in those solvents were measured with a 10 ps temporal resolution. The activation energy and the Arrhenius factor were measured by obtaining fluorescence lifeti-

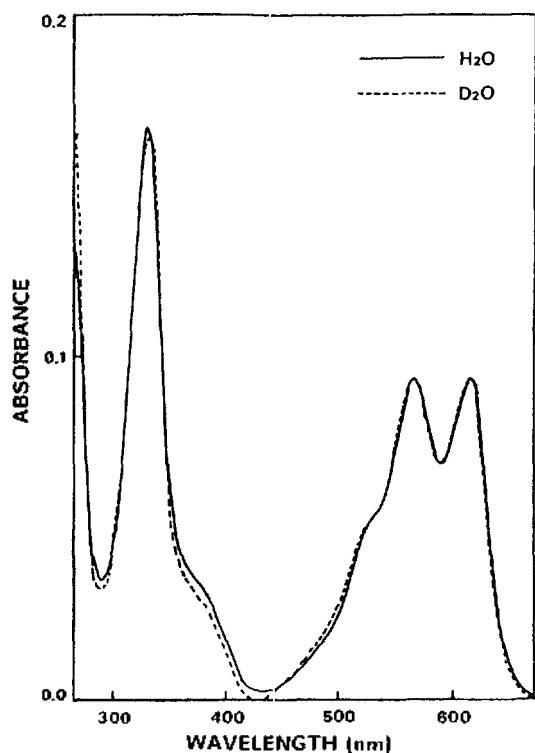


Figure 1. Absorption spectra of TMPD in H₂O and in D₂O.

mes as a function of temperature. Also, we measured the lifetimes as a function of excitation energy to see whether or not the photoionization occurs from the vibrationally unrelaxed states in water solution. The detailed reaction processes of TMPD in water are interpreted in terms of the nature of water solvents.

Experimental

The details of the laser system and TCSPC electronics were given elsewhere¹⁴. Briefly, the excitation source is the frequency doubled pulses (1 ps) from the cavity-dumped Rh6 G/DODCI dye laser. The TCSPC electronics consists of EG&G TAC and Tennelec Quad discriminators and other components. A microchannel plate tube (Hamamatsu model R2809 U-07) was used to detect emission and the overall instrument response function is 70 ps with the PMT. The non-linear least square fitting for the measured decay curves was carried out and data gave acceptable weighted residuals ($\chi^2 = 1.0-1.2$). For the excitation of TMPD, the UV pulse was generated from the Rh6G/DODCI dye laser, using a 5×5×5 mm β -BBO crystal. The tuning range is from 283 nm to 310 nm.

The TMPD was purchased from Aldrich Chem. Co and D₂O from Merck. H₂O was distilled three times before use.

Results and Discussion

Figure 1 shows the absorption spectra of TMPD in H₂O and in D₂O at room temperature. The absorption spectra in other solvents such as acetonitrile, methanol, cyclohexane have been reported^{1-4,15}. In those solvents, the absorption spectra have peaks at 270 nm and at 320 nm with molar

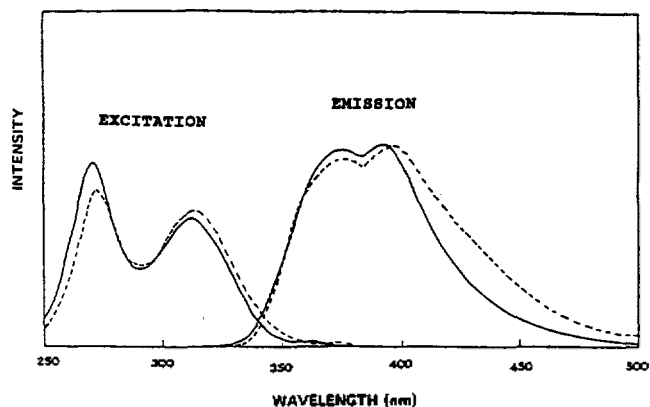


Figure 2. Fluorescence excitation and emission spectra of TMPD in H₂O (—) and D₂O (---). The monitored emission wavelength for excitation spectra and the excitation wavelength for emission spectra are 400 nm and 300 nm respectively.

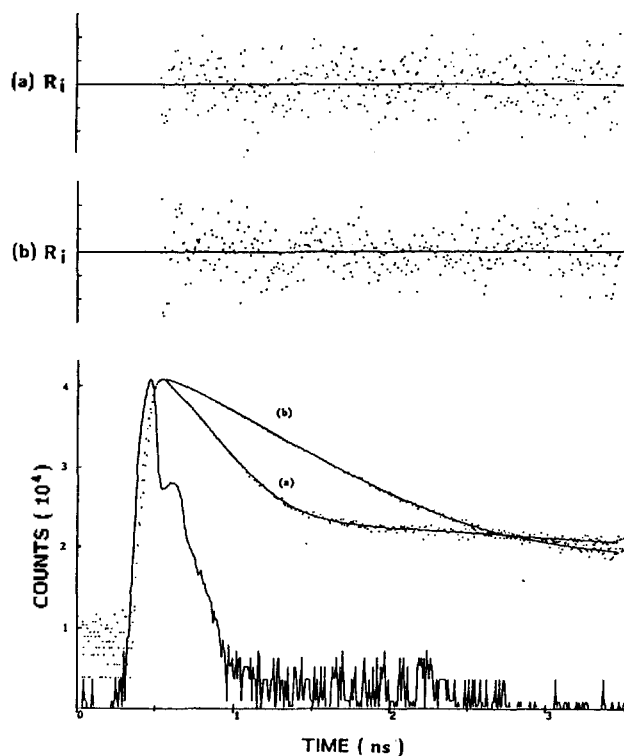


Figure 3. Picosecond lifetime profiles of TMPD in H₂O (a) and D₂O (b). The calculated curves (solid lines) obtained by a non-linear least square fitting and the weighted residuals were also shown.

extinction coefficients 20000 and 3000 l mol⁻¹ cm⁻¹ respectively. The absorption spectra of WB were also reported in 3-methylpentane at 77 K¹⁵. It shows peaks at 632, 575, 325 nm with extinction coefficients 19300, 16100, and 23400 l mol⁻¹ cm⁻¹ respectively. Therefore, the absorption band below 280 nm is due to the absorption of TMPD and the double peaks in the visible are attributable to the absorption of WB. The absorption peak around 325 nm is mostly originated from the absorption from WB with minor contribution

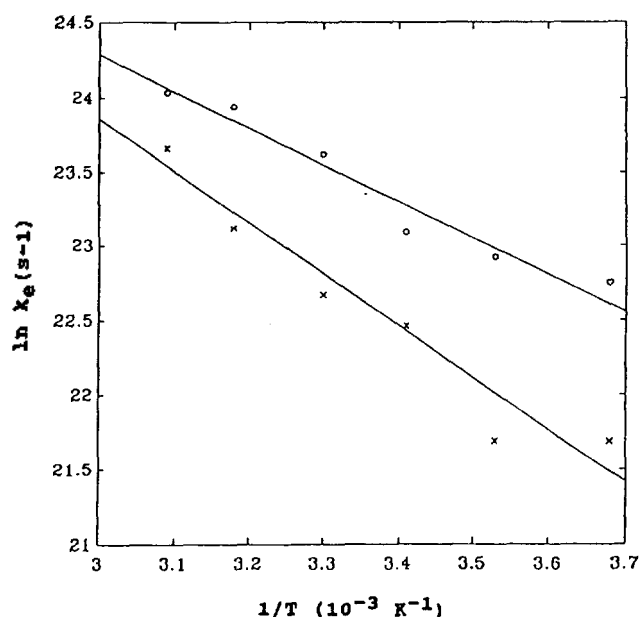


Figure 4. The Arrhenius plot of the electron transfer rate of TMPD in H₂O (○) and D₂O (×).

from TMPD. The existence of WB in water in the electronic ground state is evident from the absorption spectra of TMPD shown in Figure 1.

To further clarify these assignments, we measured the fluorescence spectra and fluorescence excitation spectra of TMPD in water, which are plotted in Figure 2. The excitation wavelength was 300 nm. The emission spectra in H₂O and in D₂O are structured with two peaks. The first peak appears at 375 nm in both H₂O and D₂O solvents, while the second one appears differently at 393 nm in H₂O and at 397 nm in D₂O. The fluorescence excitation spectra were recorded from 250 nm to 380 nm with probe wavelength of 375 nm and 393 nm and it did not show any appreciable difference. This indicates that the two peaks in the emission spectra are originated from the same species. The fluorescence from WB was not observed in the range of 460 nm. It has been known that the cations normally do not fluoresce.

Figure 3 shows the fluorescence lifetime of TMPD in H₂O and in D₂O at -1°C with the excitation wavelength of 300 nm. The collection wavelength is 400 nm. The instrument function having the time width of 70 ps is also shown. The TMPD decay data fit double exponential. The decay times of short components are 160 ps and 370 ps in H₂O and D₂O respectively and the long component is ca. 5 ns for both solvents. The amplitude of the long component is less than 1% of the short components. The decay times are independent of collection wavelengths (350-450 nm). It is expected that the emission comes from the same species, because the fluorescence excitation spectrum is independent of the emission wavelength. The short components are due to fast electron transfer from TMPD to water solvents in the excited state. The origin of the long components is unclear at the moment and, in this paper, we will only concern the dynamics of the fast process.

Sometime ago, Yoshihara and coworkers⁹ carried out a pump-probe experiment with 33 ps pulses to resolve the

Table 1. Excitation Wavelength Dependence of TMPD Lifetime in H₂O and in D₂O

Excitation Wavelength (nm)	Lifetime (ps)	
	H ₂ O	D ₂ O
283	55 ± 8	150 ± 10
289	60 ± 1	162 ± 9
293	53 ± 1	147 ± 10
298	62 ± 5	158 ± 5
304	63 ± 7	158 ± 5
310	57 ± 9	148 ± 7

photoionization mechanism of TMPD in acetonitrile. They observed two independent ionization channels for the photoexcited TMPD. One is direct and the other is thermal ionization process. The quantum yield of the thermal process is about twice larger than that of the direct ionization process. Our fluorescence lifetime measurements, however, do not show any faster component.

The fluorescence lifetimes of TMPD in water were measured in the temperature range of -1°C to 50°C. Since the radiative lifetime of TMPD is very long (ca. 13 ns), the electron transfer rate of TMPD in water is approximately proportional to the inverse of the measured fluorescence lifetime. The Arrhenius plot is shown in Figure 4 for the photoionization process of TMPD in the excited state, in which the k_e is the electron transfer rate. The activation energies obtained in the plot are 4.9 kcal/mol and 7.0 kcal/mol for H₂O and D₂O, respectively. These values are a little higher than those in pure ethanol (4.2 kcal/mol). Since the TMPD lifetime in water is ca. 70 times shorter than that in ethanol, the Arrhenius factor in water should be much larger, compared with that in ethanol. The plot of Figure 4 gives the Arrhenius factor of $5.8 \times 10^{13} \text{ s}^{-1}$ in H₂O and $7.9 \times 10^{14} \text{ s}^{-1}$ in D₂O respectively.

It is unclear why the activation energy and the Arrhenius factor are so different between H₂O and D₂O. The dielectric constants of H₂O and D₂O are similar (78.54 for H₂O and 78.25 for D₂O). Therefore, the differences in photoionization dynamics in two solvents may arise from the influence of solvents on potential surface and/or the vibronic contribution of solvents.

Fluorescence lifetimes of TMPD were also measured in CH₃OH and in CH₃OD solvents. The lifetimes were identical ($3.8 \pm 0.2 \text{ ns}$) within experimental errors. This result indicates that the differences in lifetimes in H₂O and D₂O are not originated from the deuterated effect.

In order to elucidate the vibronic coupling of solvents to the photoionization pathways, the fluorescence lifetimes of TMPD in water were measured as a function of excitation wavelength. The excitation wavelengths were used from 283 nm to 310 nm. The data show that the lifetimes are independent of the excitation wavelength within experimental error. It does not seem that the photoionization dynamics are affected by the vibrational excess energy in the experimental excitation wavelength range. Recently, Mataga and coworkers¹³ have measured the fluorescence quantum yields of TMPD in acetonitrile as a function of excitation wavelength. They reported that the quantum yield markedly depends on the

vibrational excess energy. This is unusual because in liquid the vibrational relaxation occurs with the comparative time scale of collision process so that the excess energy is distributed *via* intermolecular vibrational relaxation, so excitation energy dependence may not be observed. They conclude that the ionization may compete with the intramolecular vibrational redistribution (IVR) and that the rate may depend on the optically excited vibrational mode. In their experiment, wide excitation wavelengths (270-350 nm) were used and the dependence was remarkable in the absorption edge. It will be interesting to check the dependence of fluorescence lifetimes in water in the absorption edge.

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Cobalt Catalyzed Carbonylation of Benzal Chloride Derivatives to Alkyl Phenylacetates(II)

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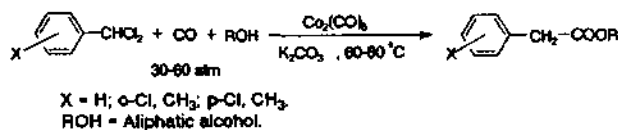
Treatment of benzal chloride, alcohol, K_2CO_3 , and a catalytic amount of $Co_2(CO)_8$ at $80^\circ C$ for 24 hours under 30 atm of CO gave the corresponding alkyl phenylacetate in good yield.

Introduction

The technology of transition metal complexes catalyzed carbonylation reaction is being currently used for the production of large volume chemicals.¹ Many applications were reported on the carbonylation of benzyl halide with carbon monoxide using cobalt,² iron,³ ruthenium,⁴ rhodium,⁵ and palladium.⁶ However, there are few reports on the carbonylation of benzal halides as the geminal dihalide compound to give alkyl phenylacetates⁷ and phenylacetic acid.⁸ Recently, we reported that carbonylation of benzal bromide by $Co_2(CO)_8$ gave phenylacetic acid under phase transfer catalysis.⁸ Now we wish to report in some details on the carbonylation of benzal chloride under homogeneous catalyst. A preliminary report of this work was published in this journal.⁹

Results and Discussions

Reaction of benzal chloride with ethanol in the presence of K_2CO_3 and $Co_2(CO)_8$ as a catalyst at $80^\circ C$ for 24 hours under 30 atm of carbon monoxide gave ethyl phenylacetate in good yield.



From investigation of base effect,⁹ potassium carbonate was superior for the carbonylation to other bases such as calcium hydroxide, triethylamine, potassium hydroxide, and pyridine. Carbon monoxide pressure played a decisive role in the carbonylation of benzal chloride. At the higher carbon monoxide pressure than 30 atm, ethyl phenylacetate was generated in excellent yield. The product yields dropped significantly with