

Short Communication

Effective fluorescence quenching and triplet sensitization of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine by acetone

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It was found that no fluorescent-state-derived monophotonic ionization of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) takes place in acetone, in contrast with the situation in other polar solvents such as acetonitrile and various alcohols. Neither semi-ionized species nor TMPD cation was detectable by transient absorption spectroscopy in the N₂-laser pulse excitation of TMPD in acetone, in spite of effective TMPD fluorescence quenching by acetone (solvent). It was demonstrated that the strong charge transfer to solvent (CTTS) interaction or electron capturing ability of acetone is not effective for the formation of the semi-ionized species but is for TMPD fluorescence quenching.

1. Introduction

The photo-ionization of TMPD in condensed media has been extensively studied by various methods, because of its relatively low ionization potential and symmetrical structure as well as its stable cationic form (Wurster's blue). The monophotonic ionization of TMPD in acetonitrile (AN) at room temperature was first proposed by Imura *et al.* [1] on the basis of the linear relationship between photocurrent and flash light intensity ($\lambda \geq 310$ nm). Very recently, it was reexamined by the picosecond and nanosecond laser pulse excitation of TMPD in AN, and the ionization has been demonstrated to take place via the semi-ionized species (CTTS state or bound ion pair) formed from the fluorescent state of TMPD [2, 3]. For TMPD in various alcohols, Hirata and Mataga [4] proposed that the monophotonic ionization takes place through a fluorescent-state-derived ion-pair intermediate consisting of a TMPD cation (TMPD⁺) and a solvated electron. Furthermore, Warman and Visser [5] confirmed that the single-photon ionization takes place through the ion pair (TMPD⁺Cl⁻) formed from the S₁ state, even for TMPD in the non-polar solvent carbon tetrachloride, by a

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time-resolved microwave conductivity measurement. For the acetone solution in the present study, however, no transient absorptions due to ionized species were detected with the N_2 -laser pulse excitation of TMPD despite complete fluorescence quenching, and only a weak transient absorption exhibiting growth was observed. The present communication describes this unusual transient absorption and the effective fluorescence quenching (by acetone) which does not result in the formation of the intermediate leading to $TMPD^+$.

2. Experimental details

TMPD was obtained by the neutralization of its dihydrochloride (Nakarai Chemicals) with ammonia water, and was then sublimed twice *in vacuo*. Spectral grade acetone and ethanol were used as received from Nakarai Chemicals. Spectral grade AN (Nakarai Chemicals) was purified by distillation.

Transient absorption spectra were measured using a laser photolysis apparatus consisting of an actinic N_2 -laser (Molelectron UV 12), monitoring xenon flash (USSI 3CP-3) and HTV R-666 photomultiplier. The electric signals from the tube were sent to the Tektronix 7904 oscilloscope with the plug-in units 7A 13 (differential comparator) and 7B 80. Fluorescence lifetimes were determined by a computer-simulated convolution for the signals collected by a time-correlated single-photon counting system (Ortec) with a multichannel analyser (Norland) and with a D_2 nanosecond light pulser (PRA model 510).

3. Results and discussion

The N_2 -laser pulse excitation of TMPD in polar solvents such as AN and various alcohols resulted in a blue-colouration due to the formation of $TMPD^+$ via the semi-ionized species formed from its fluorescent state. Upon N_2 -laser pulse excitation of various concentrations of TMPD in acetone at room temperature, however, only weak transient absorption exhibiting a growth and decay (about 100 μs) was detected in contrast with the transient absorptions for TMPD in AN and various alcohols. Typical oscillogram traces and the spectrum of the growing-in transient absorption are shown in Fig. 1. The spectrum is very similar to the reported $T_n \leftarrow T_1$ absorption spectrum [6, 7] in non-polar solvents. The rise time τ_r of the growing-in transient absorption was evaluated from the slope of the logarithmic plot of $\{D_\infty - D(t)\}$ against time. Here, D_∞ denotes the optical density at its plateau. The rise time decreases with increasing TMPD concentration C . The plot of the inverse of τ_r versus C yields a good straight line, as shown in Fig. 2, and the second-order rate constant was determined to be $2.3 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ which is very close to the diffusion-controlled rate constant ($2.2 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) at 298 K. However, appreciable amounts of TMPD triplet may be produced by N_2 -laser pulse excitation ($\lambda = 337.1 \text{ nm}$) of the weak absorption due to the acetone solvent, because of the high $S_1 \rightarrow T_1$ inter-system crossing probability (0.90) [8]. Thus, it is reasonable to conclude

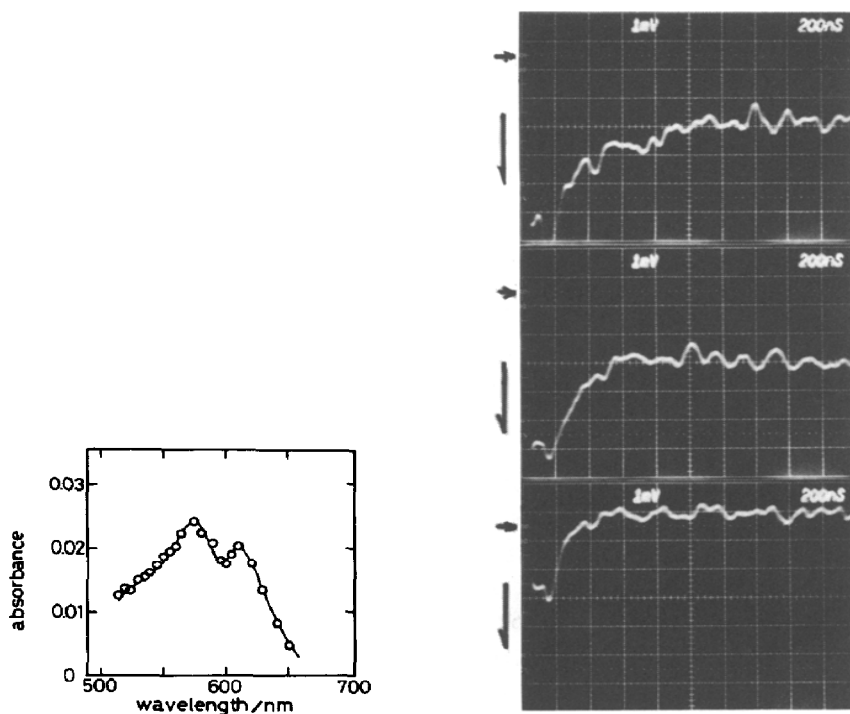


Fig. 1. The transient absorption spectrum obtained at 400 ns delay from the N_2 -laser pulse excitation of a deaerated acetone solution of TMPD ($6.0 \times 10^{-4} \text{ mol dm}^{-3}$). Also shown are oscillogram traces for various concentrations of TMPD in acetone (top, $2.0 \times 10^{-4} \text{ mol dm}^{-3}$; middle, $3.5 \times 10^{-4} \text{ mol dm}^{-3}$; bottom, $6.0 \times 10^{-4} \text{ mol dm}^{-3}$). The observed wavelength is 580 nm. The vertical and horizontal scales are $1 \text{ mV (division)}^{-1}$ and $200 \text{ ns (division)}^{-1}$ respectively. The base lines ($I = 0$) of the traces are shifted away by the application of an offset voltage (43 mV) and those without an offset voltage are indicated by a short arrow.

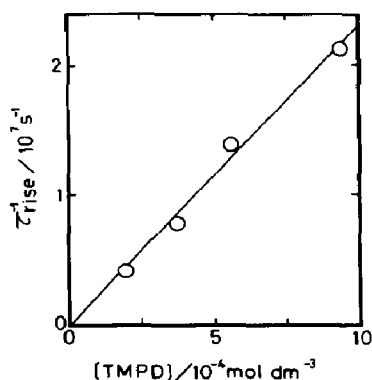


Fig. 2. Plot of the inverse of the rise time vs. the concentration of TMPD in degassed acetone at room temperature.

that the very weak growing-in transient absorption reflects the TMPD triplet ($\tau \sim 100 \mu\text{s}$) generation through the diffusion-controlled sensitization by acetone triplet. It is well known that the spectra of the TMPD lowest triplet (T_1) and TMPD^+ are extremely similar to each other in the visible region

[9, 10]. In various polar solvents, hitherto, the absorption spectrum of T_1 has been detected together with those of TMPD^+ and its precursors. It should be noted that a reliable $T_n \leftarrow T_1$ absorption spectrum was obtained in the N_2 -laser pulse excitation of TMPD in acetone.

Here, it is necessary to consider why no transient absorption due to the ionization of TMPD was detected in the N_2 -laser pulse excitation of TMPD in acetone. As described in Section 1, it was confirmed that the fluorescent state (relaxed S_1 state) is the reactive state for the monophotonic ionization of TMPD in AN and alcohols [2, 3]. We determined the fluorescence lifetimes of TMPD to be 1.9 ns (in AN) and 5.3 ns (in ethanol). For the acetone solution of TMPD , however, no TMPD fluorescence was detected. Then, the fluorescence lifetime (τ_F) of TMPD in ethanol was determined in the presence of various concentrations of acetone. The plot of the inverse of τ_F versus acetone concentration is shown in Fig. 3. From the slope of the linear plot in the figure, the fluorescence quenching rate by acetone was determined to be $7.0 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ which is much larger than that by AN ($3.0 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$). Thus, it is reasonable to assume that complete fluorescence quenching is attained for TMPD in neat acetone, and this complete fluorescence quenching is consistent with the apparent absence of absorption due to the lowest triplet state (T_1) formed via $S_1 \rightarrow T_1$ intersystem crossing of TMPD . To account for the absence of the transient absorption due to ionized TMPD , furthermore, it is strongly suggested that the fluorescence quenching does not result in the formation of the intermediate leading to TMPD^+ , in contrast to the monophotonic ionization in AN and alcohols. In other words, there exists no simple correlation between TMPD^+ formation and the absence of TMPD fluorescence. Bolton and Freeman [11] studied the reaction of solvated electrons with various scavengers in methanol, and reported a much larger scavenging rate constant for acetone ($4.3 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) compared with that for AN ($8.6 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$). The trend in the scavenging rate is parallel to that in the quenching of TMPD fluorescence described above, and it is highly probable that a CTTS interaction is mainly responsible for the TMPD fluorescence quenching by solvent molecules such as acetone and AN. On the other hand, the

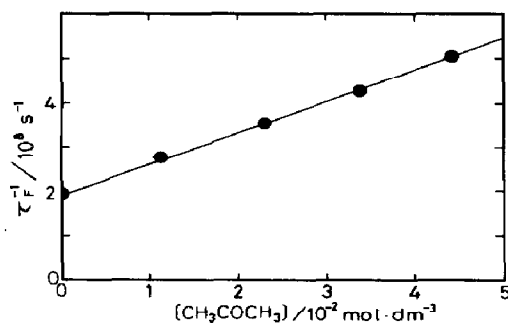


Fig. 3. Plot of the inverse of the TMPD fluorescence lifetime vs. the concentration of acetone in degassed ethanol at room temperature. The concentration of TMPD is $2.1 \times 10^{-4} \text{ mol dm}^{-3}$.

probability of formation of the semi-ionized intermediate (CTTS state or ion-pair species) may be governed by the factors that determine the stability of the intermediate. It was demonstrated that the strong CTTS interaction or electron-attaching ability of acetone is not effective for the formation of the semi-ionized species but is for TMPD fluorescence quenching.

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