Magnetic field modulation of the delayed fluorescence yield in the photoionization reaction of N,N,N′,N′-tetramethyl-*p*-phenylenediamine in water

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ABSTRACT. External magnetic field effects on the recombination fluorescence (MARY effect) in the photoionization reaction of N,N,N′,N′-Tetramethyl-*p*-phenylenediamine (TMPPD) in water and DMSO/water mixture are studied. Relatively large magnetic field effects (MFE), ~ 2–4%, on the fluorescence yield are observed in the extremely polar water solvent under magnetic fields as small as 3 mT. Such MFE is hardly expected in water due to instability and very fast escape of the solvated electron from the solvent cage. Enhancement in the signal-to-noise ratio and superior time resolution characterizing the technique of field modulation allowed the detection of a very short lived radical ion pair (about 1 ns). The observed MARY spectra illustrate that the singlet radical ion pair is more reactive than the triplet one.

1. INTRODUCTION

Photoionization process and delayed fluorescence in liquid solutions of N,N,N′,N′-tetramethyl-*p*-phenylenediamine (TMPPD) are reported as early as 1969 [1]. But since the relatively early work of Hirata and Mataga [2], photophysics and photochemistry of TMPPD is rather contraversial. TMPPD has a rather low oxidation potential of 0.16 V, and can thus be ionized by low-energy photons. According to Mataga [2], TMPPD ionizes from its fluorescent state ($\tau_f = 1.2$ ns) and produces a contact ion pair, the transient absorption of which, cannot be distinguished from that of the dissociated $TMPD^{\cdot+}$ radical cation. It was suggested that two types of intermediate radical ion pairs (RIP) are involved depending on the number of photons absorbed in photoionization process. These are, a bound RIP formed by moderately fast kinetics through monophotonic ionization, and geminate RIP formed *via* extremely fast kinetics through biphotonic ionization. From the decay analysis of the $TMPPD^{\cdot+}$, it was however discerned that only the geminate RIP formed through the biphotonic ionization undergoes fast in cage recombination.

Transient absorption and photocurrent measurements indicated however that the photoionization of TMPPD in alcohols occurs through a long-lived RIP consisting of $TMPPD^{\cdot+}$ cation and solvated electron [3, 4]. Tanimoto *et al.,* studied the external magnetic field effect (MFE) on the photoconductivity resulting from the diffused ions during photoionization of TMPPD in 2-propanol [5]. The singlet excited state is conceived to be the precursor of the RIP, whereas the quenching channel the triplet one. No MFEs were observed in aerated and deaerated methanol or ethanol for reasons related to short lifetime of the intermediate RIP in these alcohols.

Murai and coworkers extensively studied this system by CIDEP [6], and RYDMR [7] techniques. Interestingly, two different RYDMR methods detected two different RIPs. Namely, a weakly interacting short-lived RIP is detected through the delayed fluorescence, whereas monitoring the photoconductivity revealed the presence of a strongly interacting RIP formed from monophotonic ionization [7].

Accumulation of the above experimental results is not yet enough to stop debating about the TMPPD system, but rather it seems to convey a peculiar message: even though the photoionization of TMPPD is expected to be very simple reaction, the mechanism is packed with complexities. For instance, both singlet and triplet precursors are reactive. Moreover, reactions from both singlet and triplet RIPs are also possible. This leaves the whole system with many aspects to be explored. Techniques employed in the previous studies are very informative, yet interference from various channels renders the problem with indecisive or even incomplete conclusions in some cases.

One may suggest that the mechanistic aspects of TMPPD photoionization can be inferred through fragmentary approach, that is, to eliminate all observational channels but one. Accordingly, MARY spectroscopy provides a good candidate to explore some aspects of the present system. This is because only recombination from the singlet RIP is monitored through acquiring the magnetic field modulation of the delayed fluorescence intensity. In an earlier work [8], this group reported such effect in benzene/DMSO binary solvent mixture. In contrast to the previous reports [5, 7], the MFE on the delayed fluorescence [8] can only be explained if the singlet RIP is more reactive than the triplet one. In the present study we report on the MFE on the delayed fluorescence from TMPPD in water and water/DMSO mixture using modulation technique [9–10]. This technique enables the characterization of the RIP observed and allows the registration of its lifetime.

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2. MATERIALS AND METHODS

TMPPD was purchased from EGA-Chemie (98%) and thoroughly purified by vacuum sublimation to give white crystals that were stored under nitrogen. The perchlorate salt $TMPD^{\cdot+}ClO_4$ was prepared according to reported method [11]. Dimethylsulfoxide (Aldrich, HPLC, 99.99%) was predried over molecular sieve and then rectificated from calciumhydride under reduced pressure in a nitrogen atmosphere. The pH of the water solutions were controlled by phosphate buffer. Deoxygenating the samples was achieved by purging the solutions with purified argon for about 15 minutes.

MFE on fluorescence yield was monitored by a field-modulation setup similar to that built by McLauchlan and Steiner [9]. Light from a highly stabilized 150 watt high pressure xenon arc lamp is collimated and passed through an appropriate collection of solution filters, UV band pass filters, diaphragms, and a Lumatec Series 300 liquid light guide ($300\,\text{nm} < \lambda_{\text{trans}} < 650\,\text{nm}$) to control excitation wavelength. Using diaphragms, the excitation light intensity was kept as low as possible to avoid photodissociation processes. The light is then focused on the sample suited in a 2 mm quartz-glass cuvette located in the cavity of a Bruker research magnet B-E 10 with a B-MN 60/20 SI-6 type power supply together with a field sweep unit. A series-connected pair of additional home-made coils were placed onto the pole shoes of the magnet in order to establish a modulated magnetic field as well as a constant magnetic field offset. Modulation frequencies up to 500 Hz and various modulation amplitudes up to ±3.0 mT could be generated with these additional pair of coils. Fluorescence light was collected from the perpendicular lower direction by liquid light guide and conducted to selected interference filters before falling on the photomultiplier tube. Its DC output is applied to a Princeton Applied Research Model 128A lock-in amplifier which is fed with a reference signal from the function generator that applies currents to the modulation coils *via* an amplifier. The magnetic field was recorded and controlled by a gaussmeter type F. W. Bell Model 9200. The detected signal is plotted against the strength of the static magnetic field directly with an XY recorder.

3. RESULTS AND DISCUSSION

Radical partners of a RIP in polar solvents are expected to diffuse apart very rapidly and the effective lifetime of the correlated radical pair is not therefore enough for spin interactions to ensue. As a result, no appreciable magnetic field effects are expected under these conditions. In some cases however the RIP's lifetime is long enough for effective spin mixings but the detection methods are too slow to register or/and insensitive to very small variations accompanying these spin mixings. Introduction of the modulation technique to the methods of detection of MFEs introduced much better signal-to-noise ratio and higher time resolution to the detection of radical pairs in solution [9, 10, 12]. MARY (MAgnetic field modulation of the Reaction Yield) spectra, or more precisely the MFEs on the recombination fluorescence yield, exhibit relatively narrow lines. The shape and position of these lines are determined by the same parameters as the EPR spectrum of the pair. However, in contrast to EPR spectroscopy, the lines are formed due to spin evolution driven by the hyperfine interactions (hfi) in the partners of the pair, which exceed the maximum attainable microwave field by 1–2 orders of magnitude [13]. Consequently, the technique allows registration of radical ions with lifetimes as short as 1 ns without need for pulsed methods.

We utilized these advantages of the modulation technique and studied the photoionization of TMPPD in highly polar water solution. Indeed, an appreciable MARY signal was observed during the photolysis of water solution of TMPPD (Figure 1). TMPPD is sparingly soluble in water, therefore, a weight of pure TMPPD (intended for concentration of 6.0×10^{-4} M) was ultrasonicated for 3 minutes and the MARY experiments were carried out immediately. Absorption spectrum of such solution (not shown) showed the formation of the $TMPD^{\cdot+}$ cation (450 nm–650 nm, [2]) with parallel decrease in the absorption of the parent TMPPD. No other major absorption bands were observed within 24 hours of sample preparation. Our experiments were always performed on freshly prepared solutions.

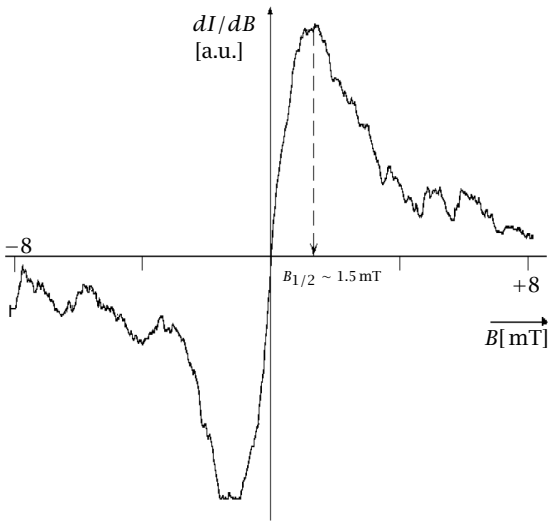


Figure 1. *Field-modulated MARY spectrum acquired during the photonization of TMPPD in water.*

To obtain the spectrum of Figure 1, the static magnetic field was swept from −8 mT to +8 mT while a small sinusoidal modulation magnetic field (modulation frequency 153 Hz, modulation amplitude ±2 mT) was applied. Modulation amplitude higher than 2 mT was avoided because it caused line broadening and shift in the extrema of the MARY spectra.

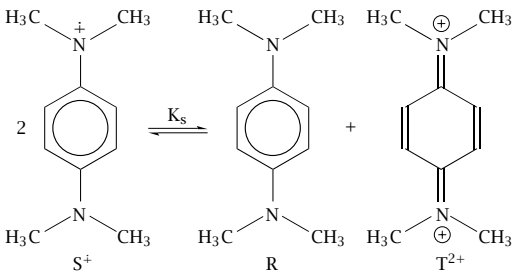
All MARY spectra exhibit an inversion symmetry around the zero field. It consists of only a single broad peak that can be explained, at the first sight, in terms of an S-T mixing dominated by the hfi. However,

more inspection of the spectrum would reveal non-correspondence between the expected and observed $B_{1/2}$ values. This is a sign that the hyperfine mechanism is not the only operating one, we will return to this point later.

As mentioned above, both TMPPD and $TMPD^{\cdot+}$ cation are present in the solution. To exclude the possibility that the cation is taking part in any process leading to the MARY effect, we performed the following experiments:

(a) Obtaining the MARY spectrum of the buffer solution of $TMPD^{\cdot+}$ ClO_4^-(at pH ~ 8.4): The following protolytic reactions are taking place as a function of pH:

1. Disproportionation [14]



where K_s is expressed by

$$K_s = \frac{[S^{\cdot+}]^2}{[R][T^{2+}]},$$

2. Two-step protonation [15]

$$R + H \overset{K_1}{\rightleftharpoons} RH^+ \qquad pK_1 = 6.5 \qquad (1)$$

$$RH^+ + H^+ \overset{K_2}{\rightleftharpoons} RH^{2+} \qquad pK_2 = 2.3 \qquad (2)$$

Now, dissolving $TMPD^{\cdot+}ClO_4^-$ salt ($S^{\cdot+}$) in water imply that the solution contains $S^{\cdot+}$, R and T^{2+}. At pH ~ 5.5, a complete protonation of R to RH^+ takes place and no magnetic field effect should be anticipated in the light of our proposed mechanism. On the other hand, at pH ~ 8.5 the free base (R) prevails and magnetic field effect is expected.

Strong MARY effect was indeed observed in phosphate buffer solution of $TMPD^{\cdot+}ClO_4^-$ salt at pH ~ 8.4, the results are shown in Figure 2(a). The modulation amplitude applied to acquire the spectrum of Figure 2(a) is reduced to ±0.5 mT in order to discern the low-field feature of the MARY effect. Qualitatively similar result was obtained in the case of buffer TMPPD solution. Accordingly, one can conclude that the free base (R) is the species responsible for the occurrence of the MARY effect.

(b) Dependence of the observed MARY spectrum on the excitation wavelength: MARY effect disappears completely by cutting the UV-irradiation bellow 550 nm, which excludes the excitation of the free base

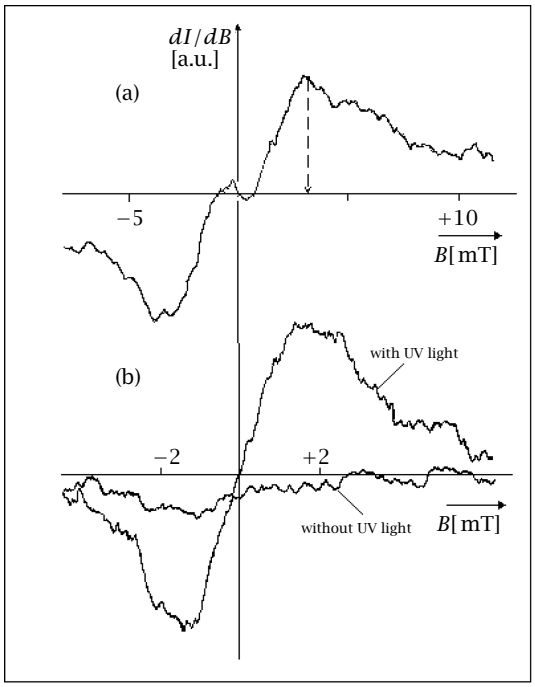


Figure 2. *Field-modulated Mary spectra recorded during the photolysis of the perchlorate salt ($TMPPD^{\cdot}+ClO_4^-$) in (a) phosphate buffer (pH~8.4), concentration = 6.0×10^{-4} M, and (b) phosphate buffer (pH~8.2), concentration = 6.0×10^{-4} M. The small modulation amplitude applied to acquire spectrum (a) enabled the observation of the low-field feature. Cutting the UV light < 550 nm almost killed the magnetic field effect.*

and not the cation Figure 2(b). In Figure 2(b), MARY spectra recorded during the photolysis of a buffer solution (pH ~ 8.2) of the $TMPD^{\cdot+}ClO_4^-$ perchlorate salt with concentration of 6.0×10^{-4} M with and without UV-irradiation. Consequently, interference from the cation $TMPD^{\cdot+}$ can be securely excluded.

In order to avoid the solubility problem and to express the concentration of TMPPD more precisely, we performed MARY measurement on a DMSO/water binary solvent mixture. It was found that the composition of water required to optimize the MARY effect is around 5% of the mixture. Figure 3 shows the MARY spectrum of 6.0×10^{-4} M solution of TMPPD in DMSO/water (95:5 v/v). The spectrum is essentially similar to that obtained in buffer solutions (pH ~ 8.4) of the perchlorate salt when large modulation amplitude of about ±1.5 mT was applied. This confirm that the origin of the MARY effect is essentially the same in both cases, *vide infra.*

The observed modulation of the recombination fluorescence by external magnetic field can be explained in terms of the mechan ism depicted in Figure 4. Photoionization of TMPPD occurs from the singlet state to yield the singlet RIP $\{TMPD^{\cdot+}e_{solv^-}\}$. Initially, the three triplet sublevels are unpopulated, but hyperfine interaction induces fast intersystem crossing (ISC) tothe triplet state of the RIP and the singlet and triplet states of the RIP

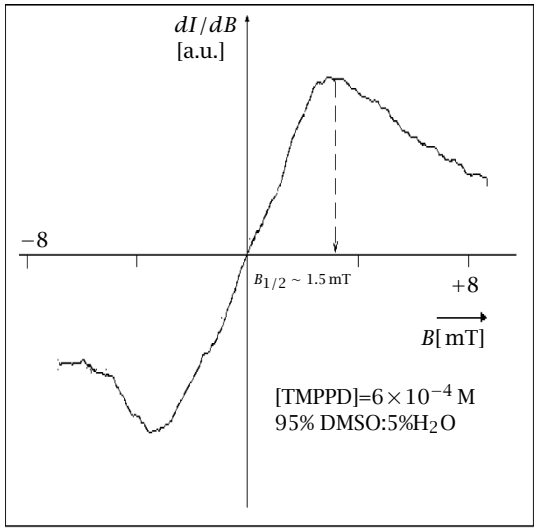


Figure 3. *Field-modulated MARY spectra recorded during the photolysis of* 6.0×10^{-4} *M solution of TMPPD in DMSO/water (95:5 v/v).*

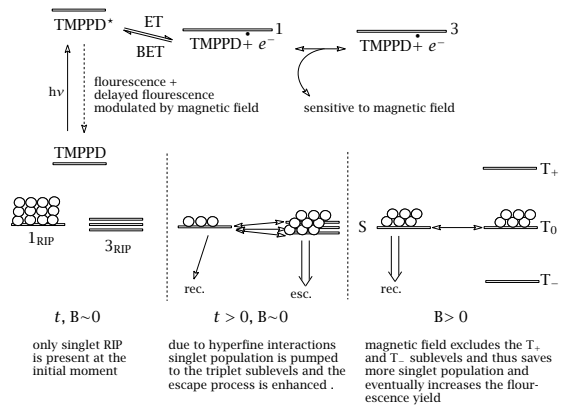


Figure 4. *Suggested mechanism to account for our experimental results.*

are mixed. Some of the RIP recombine back to the excited singlet TMPPD, which induces a delayed fluorescence. The triplet RIP can recombine to a lower triplet state (which is not detectable in our experiments) or escape from the solvent cage to give free radical ions. Because the rate of ISC within a radical pair is dependent on the strength of an applied magnetic field, then it is expected that the application of an external magnetic field would change the recombination probability of the pair. That is to say, when the hfi energy is comparable with the Zeeman one in the external magnetic field, the singlet state S mixes with all three triplet sublevels (T_+, T_0, T_-) of the RIP. As the strength of the external magnetic field increases, the mixing efficiency decreases because the triplet T_+ and T_- states are depleted due to Zeeman interactions [16,17]. This in turn is expected to cause a parallel increase in the probability of recombination and thus in the fluorescence yield.

It is important to notice that the above mechanism relies on a RIP in which the singlet state is more reactive than the triplet one. This is contrasting the mechanism proposed in previous papers [5,7] in which recombination is suggested to be more efficient from the triplet RIP. We believe however that all the previous results can be explained by conceiving our proposed mechanism.

There exist considerable difference between the observed peak maximum at ~ 1.5 mT and that calculated $B_{1/2}$ value from the formula [18]

$$B_{1/2} = \frac{1}{2}\cdot\frac{A_1^2 + A_2^2}{A_1 + A_2},$$

where,

$$A_i = \sum_k [A_k^2 I_k (I_k + 1)].$$

Here A_k is the hyperfine coupling constant of the k'th nucleus on the radical *i*, and I_k is its spin quantum number. For the cation $TMPD^{\cdot+}$ the hyperfine coupling constants are: $A(2N)$ =0.705 mT, A(methyl groups, 12H)= 0.677 mT, and A(aromatic, 4H) = 0.199 mT. The effective hyperfine of the RIP is thus 6.4 mT, and $B_{1/2}$ reads 3.2 mT because the counter anion in our case is the solvated electron and does not exhibit any hyperfine interaction. Whereas the observed $B_{1/2}$ values in basic buffer solutions and in DMSO/water mixture are very close to the calculated value, those measured in water solutions are smaller than 3.2 mT. Moreover, the signals do not return to zero at higher magnetic fields which imply that the unmodulated MARY spectra do not show saturation behavior. These observations point out that the Δg- and/or the relaxation mechanisms are operating in parallel with the hyperfine mechanism in the present case [16,17]. Line broadening due to chemical exchange between the neutral TMPPD and the cation $TMPD^{\cdot+}$ is also possible. Further experiments are needed to explore the dependence of the MARY line width on the concentration of TMPPD and the ratio of the cation present in the solution which is currently under investigation.

4. CONCLUSION

External magnetic field effects on the recombination fluorescence in the photoionization reaction of N,N,N′,N′-Tetramethyl-*p*-phenylenediamine in water and DMSO/water mixture are studied. Only one reaction channel was observed, namely, the photoionization from the excited singlet state of TMPPD followed by the recombination of the resultant radical ion pair. Relatively large magnetic field effects, ~ 2–4%, on the fluorescence yield are observed in the extremely polar water solvent under magnetic fields as small as 3 mT. Such MFE is hardly expected in water due to instability of the solvated electron and its expected very fast escape from the solvent cage. Lifetime(s) of the intermediate radical ion pair(s) are estimated from the MARY spectra recorded. Enhancement in the signal-to-noise ratio and superior time resolution characterizing the technique of field modulation allowed the detection of a very short lived radical ion pair (about 1 ns). The observed MARY spectra inevitably illustrate that the sin-

glet radical ion pair is more reactive than the triplet one, which contrasts previously suggested mechanism.

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