# Laser Photoionization and Light-Initiated Redox Reactions of Tetramethylbenzidine in Organic Solvents and Aqueous Micellar Solution

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**Abstract:** The 347.1-nm ruby laser photolysis of *N,N,N′,N′*-tetramethylbenzidine (TMB) was studied in organic solvents, i.e., cyclohexane and methanol, and micellar solution. The main photoreaction in the organic solvents is triplet formation. The energy of the triplet was determined as 2.7 ± 0.05 eV. The triplet spectrum has an absorption maximum at 475 nm and the extinction coefficient at this wavelength is $(4.1 \pm 0.3) \times 10^4\ M^{-1}\ cm^{-1}$ in methanol. It is almost identical with the spectrum of $TMB^+$ cation radicals. In methanol small amounts of ions, $TMB^+$, and solvated electrons are produced monophotonically by the laser pulse, the relative efficiency of ion vs. triplet formation being $r = 0.17$. The $r$ value observed in micellar solution of sodium lauryl sulfate (NaLS) is 36 times greater, indicating pronounced enhancement of the photoionization process by the anionic micelles. Hydrated electrons and $TMB^+$ cation radicals are also produced by sunlight irradiation of TMB solution in NaLS micelles and possible utilization of the micellar effects are discussed. TMB triplets were found to have strongly reducing properties and in methanolic solution transfer an electron to acceptors such as duroquinone (DQ) and $Eu^{3+}$. The rate constants for the transfer processes are $2.3 \times 10^{10}$ and $6.4 \times 10^9\ M^{-1}\ s^{-1}$ for duroquinone and $Eu^{3+}$, respectively. These light-initiated redox processes are reversible, the back transfer from $DQ^-$ and $Eu^{2+}$ to $TMB^+$ occurring at specific rates of $2 \times 10^9$ and $1.4 \times 10^7\ M^{-1}\ s^{-1}$, respectively. Similar redox processes are observed in NaLS micellar solution, the intramicellar forward and backward electron transfer to $Eu^{3+}$ and from $Eu^{2+}$ occurring with specific rates of $2.3 \times 10^7$ and $8.5 \times 10^2\ s^{-1}$, respectively.

## Introduction

In two previous papers we reported studies of the photoionization of phenothiazine and reactions of its triplet state with various electron acceptors in methanol and micellar solution.[2] It was found that incorporation of the dye into an anionic surfactant micelle drastically increased the probability of photoejection as compared to the homogeneous alcoholic solution. This effect was explained in terms of tunneling of photoelectrons from the micellar into the aqueous phase.[2b] In the present paper this line of research is extended to the photoreactions of aromatic amines. Tetramethylbenzidine (TMB) was chosen as a suitable molecular probe. Its low gas-phase ionization potential of 6.1 to 6.8 eV[3] makes feasible, in polar media, monophotonic photoionization by 347.1-nm light. Also TMB fulfills the requirement of being very hydrophobic, and hence in aqueous micellar solution will be associated exclusively with the micellar phase. The present paper will be concerned with comparing relative efficiencies of the two main primary channels of TMB photolysis, i.e., photoionization and triplet formation, in solvents of different polarity (cyclohexane, methanol) and micellar solution. It will be shown presently that anionic micelles greatly promote ion formation while cationic ones inhibit it. In addition, subsequent reactions of TMB triplet states and TMB cation radicals will be investigated. The strongly reducing nature of aromatic amine triplet states will be established via analysis of redox reactions involving various electron acceptors. As will be illustrated both TMB photoionization and triplet states reactions may provide possible avenues for photochemical utilization of solar energy.

## Experimental Section

**Materials.** Sodium lauryl sulfate (Merck, "for tenside investigations") and dodecyltrimethylammonium chloride (Eastman) were purified by recrystallization from alcohol-ether mixtures.; *N,N,N′,N′*-Tetramethylbenzidine (Aldrich) was used as supplied. Purification of this material by repeated recrystallization from ethanol was found to have no observable effect on the results.

**Sample Preparation.** Tetramethylbenzidine (TMB) was solubilized in micelles by injecting an aliquot of a stock solution in benzene into the aqueous micellar solution. Subsequently the benzene was removed by flushing argon through the sample for several hours. The concentration of solubilized TMB was determined by spectrophotometric measurements. If necessary, the samples were deoxygenated by bubbling with highly purified argon.

**Apparatus.** Laser photolysis experiments were carried out using a Q-switched Korad K1QP ruby laser. The 347.1-nm pulse had a duration of 15 ns and maximum energy of 100 mJ as measured by a bolometer. Transient species were detected by fast kinetic spectroscopy and fast dc conductance techniques. A detailed description of this setup has been published elsewhere.[4] Suitable cutoff filters were placed in the analyzing light beam to prevent photolysis. Solutions were flowed through a 1-cm$^2$ quartz cell to obviate interference from product accumulation. Absorption spectra were recorded with a Unicam SP.70DC spectrophotometer.

## Results and Discussion

**Laser Photolysis of TMB in Cyclohexane Solution: TMB Triplet Spectrum and Triplet Energy.** The 347.1-nm laser photolysis of TMB in cyclohexane produces a transitory species whose absorption spectrum is presented in Figure 1. The spectrum is characterized by a broad band with a maximum around 475 nm, a half-width of roughly 3600 cm$^{-1}$, and long tails extending into the uv and red wavelength region. In deaerated solution, the transient absorption decays after the laser pulse with a first lifetime of 10–20 μs, depending on the laser intensity. Addition of oxygen drastically reduces the lifetime of the transient. This behavior suggests that the absorption is due to TMB triplet states produced by the laser light. (The lifetime of TMB singlet excited states is only a few nanoseconds.)

The correctness of this assignment is further substantiated by results from triplet energy transfer studies. For example, in solutions containing both naphthalene and TMB the latter is exclusively excited by the laser light. The TMB triplet state subsequently transfers excitation energy to naphthalene.

$$TMB^T + N \underset{}{\overset{k_1}{\rightleftharpoons}} N^T + TMB \quad (1)$$

This process manifests itself in an enhanced decay of the TMB triplet absorption at 470 nm and a concomitant formation of naphthalene triplets ($N^T$) which have maximum absorption at 415 nm. Oscilloscope traces showing the kinetics of the energy transfer reaction are presented as inserts in

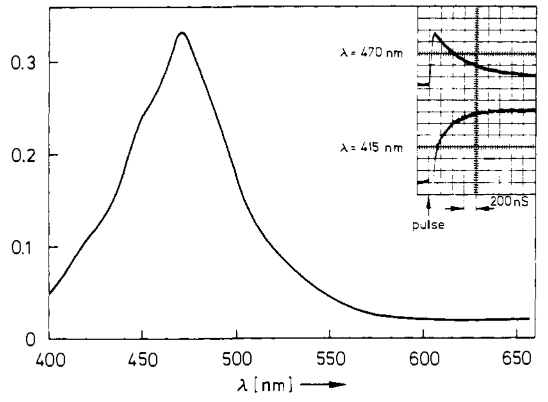


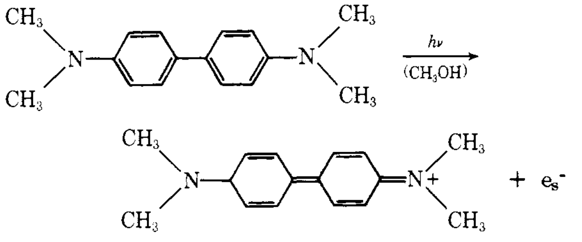
**Figure 1.** Absorption spectrum of *N,N,N',N'*-tetramethylbenzidine triplet in cyclohexane. Insert: Oscilloscope traces which show the quenching of TMB triplets by naphthalene (λ 470 nm) producing naphthalene triplets (λ 415 nm).

Figure 1. The rate constant for reaction 1 was determined as $k_1 = 2 \times 10^9$ $M^{-1}$ $s^{-1}$, which approaches the limit for a diffusion-controlled reaction. At lower naphthalene and higher TMB concentration, an equilibrium between $N^T$ and $TMB^T$ states was observed. In such a situation the triplet energy of TMB can be determined. An analogous procedure has been used previously to derive the nonvertical triplet energies of several polycyclic aromatic hydrocarbons and has been described in detail in this context.[5] From the equilibrium constant and the known triplet energy of naphthalene, one derives for the energy of TMB triplets a value

$$E_T(\text{TMB}) = 2.7 \pm 0.05 \text{ eV}$$

In oxygenated solution of TMB in cyclohexane, the quenching reaction is completed within the laser pulse. Nevertheless, a longer lived species with spectral features similar to $TMB^T$ could be detected under such conditions. The absorption was very weak and increased with the square of the laser light intensity. As will become apparent from the subsequent sections of the paper, this absorption is due to TMB cation radicals formed in cyclohexane via a biphotonic photoionization process.

**Alcoholic Solutions: Photoionization and Redox Reactions of TMB Triplets.** The transient spectrum obtained from the laser photolysis of TMB solutions in methanol is shown in Figure 2. It has a similar shape like the spectrum observed in cyclohexane, indicating that mainly TMB triplets are produced by the light flash. However, one notices also a small absorption in the red with a maximum between 600 and 650 nm. This band is removed by typical electron scavengers such as acetone, and therefore is attributed to the solvated electron ($e_s^-$). The concentration of $e_s^-$ present immediately after the laser pulse was calculated from the contribution of $e_s^-$ absorption to the total optical density changes at 600 nm and its extinction coefficient at this wavelength:[6] $[e_s^-] = OD_{600}(e_s^-)/\epsilon_{600}(e_s^-)$. $[e_s^-]$ was found to vary linearly with the laser intensity, indicating that solvated electrons are formed via the monophotonic photoionization process:



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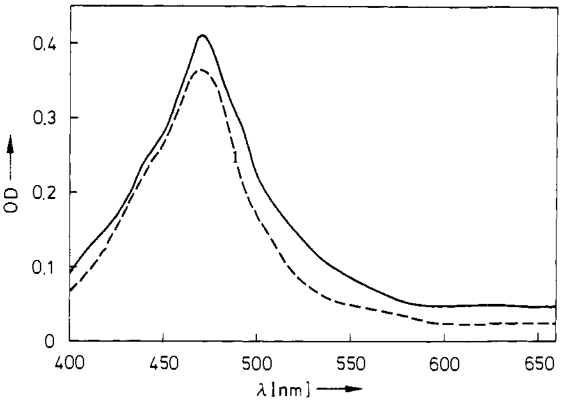

**Figure 2.** Spectra of transients obtained in the laser photolysis of $5 \times 10^{-5}$ M TMB in deaerated methanol: (–) no additives, (- - -) contained $10^{-3}$ M acetone.

Photoionization of TMB in polar organic solvents has been reported previously[7] and the spectrum of $TMB^+$ semiquinone-type cation radicals is well established.[7,8] It is characterized by two electronic transitions at 1100 and 470 nm which are expected from theoretical calculations of the $TMB^+$ energy levels.[9] Our present concern is to establish the relative efficiencies of the two competing channels of TMB photolysis, i.e., photoionization vs. triplet formation. The individual contributions of $TMB^+$ and $TMB^T$ to the overall optical density at a given wavelength, $OD_\lambda(TMB^+)$ and $OD_\lambda(TMB^T)$, were assessed by carrying out laser photolysis experiments with TMB solutions containing small amounts of oxygen. Oxygen quenches $TMB^T$ very efficiently ($k = 2.8 \times 10^{10}$ $M^{-1}$ $s^{-1}$), but it does not react with $TMB^+$. Hence, under such conditions the latter has a much longer lifetime than the former, which allows one to distinguish between them by evaluating the kinetics of the transient absorbance decay. The $TMB^+$ spectrum obtained from such an analysis has a maximum at 475 nm with two side peaks at λ 460 and 440 nm, and agrees well with literature data. The contribution $OD_\lambda(PTH^+)$ to the transient absorption immediately after the laser pulse is small, remaining always below 20%. From $OD_{475}(TMB^+)$ and the concentration of $TMB^+$, $[TMB^+] = [e_s^-]$, the extinction coefficient of cation radicals at 475 nm is determined as $(4.1 \pm 0.3) \times 10^4$ $M^{-1}$ $cm^{-1}$, which is almost identical with the value $\epsilon_{474}(TMB^+) = 4 \times 10^4$ $M^{-1}$ $cm^{-1}$ measured in acetonitrile solution.[8a]

A quantitative comparison of $TMB^T$ and $TMB^+$ yields requires a knowledge of the extinction coefficients for both species. Earlier investigations with phenothiazine[1] have shown that triplet states of compounds with low ionization potentials may be strong reductants and hence may be converted into cation radicals via redox reactions using suitable electron acceptors. These results prompted us to inquire into similar reactions of TMB triplet states for which a general formulation is:

$$TMB^T + A \rightarrow TMB^+ + A^- \qquad (3)$$

Figure 3 shows transitory spectra and oscilloscope traces from the laser photolysis of TMB solutions containing duroquinone (DQ) as electron acceptor. The spectrum after the laser pulse essentially displays the features of the $TMB^T$ absorption. However, the triplet lifetime which is about 10 μs in pure methanolic solution is shortened drastically upon addition of DQ. In $1 \times 10^{-4}$ M DQ solution the triplet decay is completed after 1.4 μs and the spectrum measured at this time is represented by the dashed line in Figure 3. This curve is readily interpretable in terms of a composition of $TMB^+$ and $DQ^-$ anion radical spectra, $TMB^+$ contributing peaks at 475 and 460 nm while the hump at 430 nm and the absorption maximum at 440 nm originate mainly from $DQ^-$.[10] Apparently

$TMB^T$ behaves similarly to phenothiazine triplets[2b] and reduces duroquinone. The oscilloscope traces inserted in Figure 3 illustrate the kinetics of this transfer process. As the absorption band of $TMB^+$ falls off much more sharply towards the red as compared to that of $TMB^T$, a suitable wavelength to observe the disappearance of the triplet states is 510 nm. The kinetics of this decay match those of the $DQ^-$ growth at 440 nm. It is not possible to monitor optically the formation of the second product of reaction 3, $TMB^+$, as its extinction coefficient within the investigated spectral range (400-650 nm) was found to be always slightly smaller or comparable with that of $TMB^T$. However, charge transfer from the triplets to duroquinone produces ionic species which makes it possible to monitor the course of reaction 3 by a conductivity technique. The lowest oscillogram in Figure 3 shows a conductance vs. time curve obtained under the same conditions as the optical results, An immediate increase of the conduction of the solution is observed, occurring simultaneously with the laser pulse, which is attributed to direct photoionization of TMB (eq 2). Subsequently, during the reaction of $TMB^T$ with duroquinone, a further and much more pronounced augmentation of the conductance is noted. The kinetics of this growth match those of the triplet absorption decay indicating that the $TMB^T$ quenching process is described correctly and quantitatively by eq 3. A series of optical and conductivity experiments with different duroquinone concentration gave for the rate constant of the electron transfer reaction the values

$$k_3(\mathrm{A} = \mathrm{DQ}) = 2.3 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

Light-initiated redox processes involving TMB triplets as reductants were observed also with ionic acceptors. For example, $TMB^T$ readily reduces europium ions the rate constant $k_3(\mathrm{A} = \mathrm{Eu}^{3+})$ being $6.4 \times 10^9$ $\mathrm{M}^{-1}$ $\mathrm{s}^{-1}$. In order that electron transfer can occur at such a rapid rate, the redox potential of TMB triplets must be more negative than that for $Eu^{3+}$ ions: $E_0(\mathrm{Eu}^{3+}/\mathrm{Eu}^{2+}) = -0.43$ V. This result emphasizes the strongly reducing nature of the TMB triplet state.

The possibility of converting TMB triplet states into radical cations by use of a suitable acceptor system such as $Eu^{3+}/Eu^{2+}$, which has no contribution to the transient absorption at λ 475 nm, opens a way to determine the extinction coefficient of $TMB^T$ at this wavelength. During the course of this transfer reaction one fails to observe any significant changes of the optical density at 475 nm, indicating that the extinction coefficients for $TMB^+$ and $TMB^T$ are approximately equal. The precise value obtained for $\epsilon_{475}$ ($TMB^T$) is: $(4.0 \pm 0.3) \times 10^4$ $\mathrm{M}^{-1}$ $\mathrm{cm}^{-1}$.

With the knowledge of this extinction coefficient it is now possible to evaluate from the total optical density change at 475 nm the concentrations of $TMB^+$ and $TMB^T$ produced simultaneously by the laser pulse. The parameter $r = [\mathrm{TMB}^+]/[\mathrm{TMB}^T]$ expresses the efficiency of the photoionization channel relative to that for triplet formation. From the optical analysis a $r$ value of 0.17 is obtained, implying that absorption of 347.1 nm light by TMB produces roughly six times as many triplets as cation radicals. A somewhat larger number ($r \simeq 0.25$) is derived from evaluation of the conductivity trace in Figure 3. Here the desired parameter $r$ is given by the ratio of the initial conductance change $\kappa_0$ and the conductance change $\kappa_P - \kappa_0$ produced by the electron transfer reaction, $\kappa_P$ representing the heights of the signal in the plateau region. $R$ parameters derived from such conductivity analysis are considered to be less reliable than optical results due to reltively large errors made in determining $\kappa_0$ and $\kappa_P$. For example, evaluation of the conductance trace in Figure 3 yields too large $\kappa_0$ values because the electron transfer is so rapid that it already occurs partially during the laser pulse (this effect is also apparent from the end of pulse spectrum in Figure 3 in which small humps from $DQ^-$ and $TMB^+$ appear on top of the triplet spectrum). Conversely, at lower duroquinone concentration where better separation of photoionization and charge transfer processes is achieved, too low values for $\kappa_P$ are obtained. This is due to back transfer of electrons from $DQ^-$ to $TMB^+$, which at lower DQ concentration overlaps with the forward reaction (eq 3). From these considerations the conductivity method is expected to give too large $r$ values, which is consistent with the experimental data.

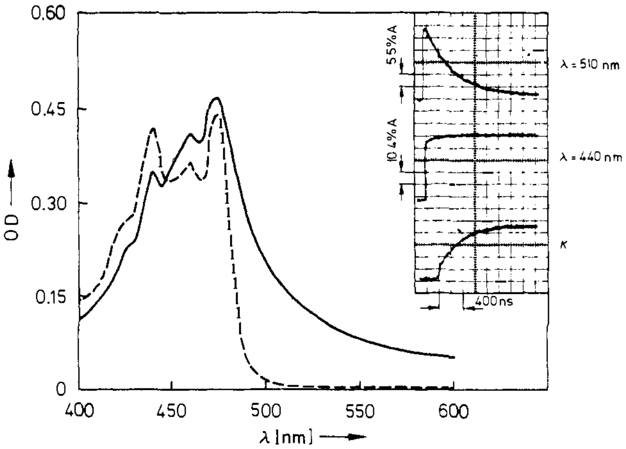

Figure 3. Spectra of transients obtained in the laser photolysis of $5 \times 10^{-5}$ M TMB and $10^{-4}$ M duroquinone in deaerated methanol: (–) end of pulse, (- - -) 1.4 μs after pulse. Insert: oscilloscope traces showing quenching of TMB triplet by duroquinone (λ 510 nm), growth of duroquinone anion radical (λ 440 nm), and the production of ionic species in the quenching process (κ).

The aforementioned thermal back transfer of electrons from reduced acceptors to $TMB^+$ deserves further attention. Obviously the photoionitiated reactions in the presence of such acceptors can be formulated as

$$\mathrm{TMB} + \mathrm{A} \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} \mathrm{TMB}^+ + \mathrm{A}^- \qquad (4)$$

The kinetics of the back reaction was examined for $A^- = DQ^-$ and $Eu^{2+}$ by monitoring the decay of $TMB^+$ absorption and also, in the case of duroquinone, the decrease of the solution conductance. The following rate constants were obtained from second-order plots of the transient signal vs. time.

$$k_\Delta(\mathrm{A}^- = \mathrm{DQ}^-) = 2 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$
$$k_\Delta(\mathrm{A}^- = \mathrm{Eu}^{2+}) = 3.5 \times 10^7 \text{ and } 1.4 \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

where the two $k_\Delta$ values for $Eu^{2+}$ originate from solutions containing $3 \times 10^{-3}$ and $10^{-3}$ M $Eu(NO_3)_3$. The rate parameter observed for duroquinone anion radicals indicates that back transfer takes place at almost diffusion-controlled rate, while it is much slower for $Eu^{2+}$. The difference is attributed to Coulombic interactions leading to repulsion of the reactants when $Eu^{2+}$ is the transferring agent. This is also reflected in a pronounced salt effect leading to the observed increase of $k_\Delta$ with $Eu(NO_3)_3$ concentration.

Equation 4 designates the reversible and photochromic character of the TMB photooxidation in the presence of electron acceptors. The occurrence of the thermal back reaction is expected from thermodynamic considerations. Ample electrochemical data are available concerning the one-electron oxidation of TMB,[11] and the reversible half-wave potential in methanol/benzene mixtures was determined as $E_{1/2} = 0.360$ V (vs. SCE).[12] This corresponds to an $E_0$ value of approximately 0.6 V as compared to $E_0 = -0.41$ and $-0.24$ for europium and duroquinone[13] in aqueous solution, respectively. Thus the back reaction in eq 4 is expected to be exergonic by

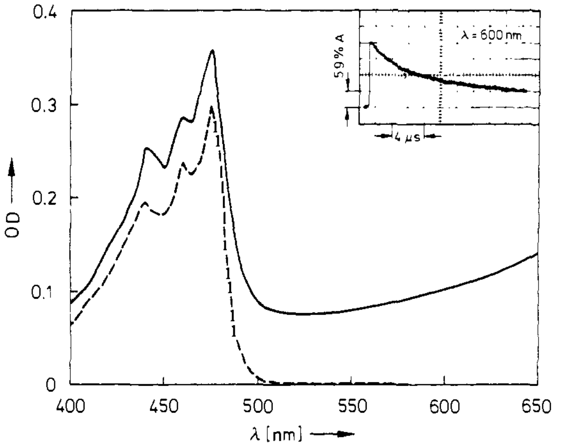

Figure 4. Spectra of transients obtained in the laser photolysis of $5 \times 10^{-5}$ M TMB in aqueous 0.1 M sodium lauryl sulfate: (–) end of pulse, (- - -) 10 ms after pulse. Insert: oscilloscope trace showing kinetic behavior of solvated electrons.

some 0.7–1 eV and can, in principle, take place at a diffusion-controlled rate.

**Anionic Micellar Solution: Laser Photolysis and Sunlight Experiments.** Transitory spectra obtained from the 347.1-nm laser photolysis of $5 \times 10^{-5}$ M TMB in 0.1 M NaLS micellar solution are presented in Figure 4. Considering first the end of the pulse spectrum one notices significant differences between this and the transitory spectra observed in methanolic or cyclohexane solution. A strong band appears in the long-wavelength region, which was absent in the latter solvents, and the peak between 400 and 500 nm shows more fine structure than the absorption curves in Figures 1 and 2. As the transient absorption in the red is removed by adding selected electron scavengers to the solution, it is attributed to the hydrated electron ($e_{aq}^-$). The three peaks at shorter wavelengths, on the other hand, are readily identified with the $TMB^+$ spectrum. Apparently $TMB^+$ and hydrated electrons are the main species present after the laser pulse. This contrasts to the results obtained in methanolic or cyclohexane solution where TMB triplets were formed predominantly by the 347.1-nm light flash. These results suggest that the photoionization of TMB is promoted by anionic micelles as was observed previously for phenothiazine.[2a] The yield of hydrated electrons was found to vary linearly with the light intensity, indicating a monophotonic character of the photoionization process

$$(TMB)_M \xrightarrow{h\nu} (TMB^+)_M + e_{aq}^- \qquad (5)$$

where the subscript M denotes association with the micelle.

It is illustrative to examine the kinetic behavior of the three transients, $TMB^+$, $e_{aq}^-$, and $TMB^T$ produced by the laser pulse in more detail. The oscillogram inserted in Figure 4 shows the time dependency of the absorption at 600 nm, where the hydrated electron contributes more than 90% to the total optical density change. The photoejection of electrons from micelles into the water and their subsequent hydration is a very rapid process[14,15] which is reflected by the immediate increase of optical density at 600 nm occurring simultaneously with the laser pulse. Subsequently the absorption signal decays via second-order kinetics with a first half-life time of 6 μs. As has been pointed out previously,[2,14,15] recombination of $e_{aq}^-$ with the parent cation inside the micelle, i.e., the reverse of photoreaction 5, is prevented by the negative micellar surface potential. The most likely reaction of $e_{aq}^-$ in the absence of other scavengers is, therefore, conversion into hydrogen via:

$$e_{aq}^- + e_{aq}^- \xrightarrow{H_2O} H_2 + 2OH^- \qquad (6)$$

for which a rate constant of $6 \times 10^9$ $M^{-1}$ $s^{-1}$ has been reported.[5] From this value and $e_{aq}^-$ concentrations of $10^{-5}$–$2 \times 10^{-5}$ M produced by the laser pulse, half-life times of 6–12 μs are predicted in agreement with the experimental observation.

In NaLS micellar solution the lifetime of TMB triplet states is much longer than in methanol. The decay of the absorption at 510 nm occurs here with a first half-life time of 500–800 μs depending on the laser dose. A rationale for the increase in triplet lifetime is provided by micellar inhibition of triplet-triplet annihilation and slow exit of $TMB^T$ from the micelles. The kinetic background for these phenomena has been provided elsewhere.[16] The slow decay of $TMB^T$ is also indicative of the strong association of TMB with NaLS micelles. As the triplet decay curve is smooth without any initial fast component, the TMB must be almost quantitatively incorporated in the micellar aggregates.

Finally, $TMB^+$ cation radicals in NaLS micellar solution display exceptionally high stability, which allows one to distinguish them readily from the other transients. The dashed curve in Figure 4 shows the transitory spectrum of a TMB/NaLS solution which is observed 10 ms after the light flash. At this time $e_{aq}^-$ and $TMB^T$ have disappeared, and hence $TMB^+$ alone contributes to the absorption. It should be noted that the absorbance in the 470 nm region decreases only slightly during this 10-ms time period. This demonstrates that contributions from $TMB^T$ and $e_{aq}^-$ to the initial optical density $OD_{475}$ must be small. The cation radical spectrum persists for many hours, the half-life time of $TMB^+$ being at least 2 days in the micellar system.

For a comparison of the efficiencies of triplet and cation radical formation it is necessary to determine the extinction coefficients for both species in NaLS micellar solution. The extinction coefficient of $TMB^+$ is readily obtained by dividing $OD_{475}$ ($TMB^+$) through the concentration of cation radicals, which can be equated with the hydrated electron concentration. A value of $3.9 \times 10^4$ $M^{-1}$ $cm^{-1}$ is obtained which agrees within experimental error with $\epsilon_{475}$ ($TMB^+$) measured for the methanolic solution.

The extinction coefficient for TMB triplets in micellar solution can be derived from laser photolysis experiments in the presence of $Eu^{3+}$ ions. From the results in the preceding chapter it is expected that these ions accept electrons from $TMB^T$, thereby converting it into cation radicals according to eq 3. In anionic micellar solution a multiply charged cation such as $Eu^{3+}$ will be strongly associated with the surface, while TMB is probably located in the outer core region of the aggregates. Hence the redox reaction involves electron transport from the lipoidic part of the micelle across the electrolytic double layer to the site of the acceptor in the interface. Figure 5 shows laser photolysis data obtained from a deaerated solution of TMB in 0.1 M NaLS in the presence of $3 \times 10^{-3}$ M $Eu(NO_3)_3$. The end of pulse spectrum corresponds to that in Figure 4, except for the absence of the hydrated electron absorption band. This is due to scavenging of $e_{aq}^-$ by both $Eu^{3+}$ and $NO_3^-$, which occurs already during the light flash. The presence of triplets after the laser pulse is reflected by the tail of the 475-nm peak extending into the red wavelength region. This part of the absorption is extremely short-lived, the half-life time of the decay being only 30 ns. This indicates that electron transfer from $TMB^T$ to $Eu^{3+}$ occurs very rapidly. Similar high rates have been observed for phenothiazine triplet[2a] redox reactions and the unique kinetic features of such intramicellar electron transfer processes have been discussed in this context. It has been suggested[2b] that the transport of electrons from triplet states to acceptors in micelles proceeds via a tunneling mechanism and therefore does not require diffusional encounter between the reactants. Similar evidence has been obtained by Carapelluci and Mauzerall[17] from a study of por-

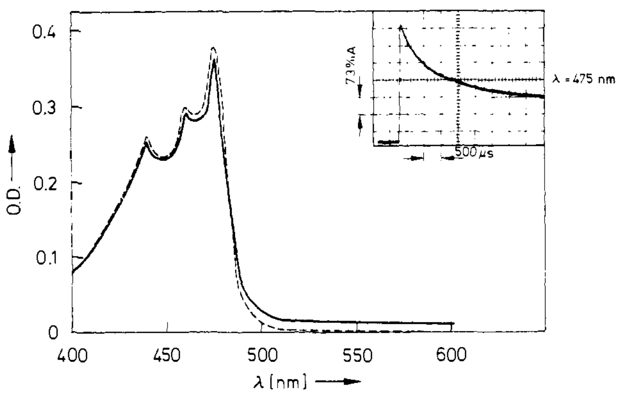

**Figure 5.** Spectra of transients obtained in the laser photolysis of 5 × $10^{-5}$ M TMB in deaerated aqueous 0.1 M sodium lauryl sulfate containing 3 × $10^{-3}$ M Eu$(NO_3)_3$: (-) end of pulse, (- - -) 1 μs after pulse.

phyrin excited-state redox reactions. The electron transfer distance derived from these experiments (~22 Å) is some 11 Å greater than the sum of the radii of the reactants. A comparison of the end of pulse spectrum in Figure 5 with that obtained 1 μs after the light flash (dashed curve) reveals that conversion of $TMB^T$ into $TMB^+$ is not accompanied by any significant change in the absorbance at 475 nm. Apparently both species have a similar extinction coefficient at this wavelength. From such an analysis one obtains $\epsilon_{475}$ ($TMB^T$) = (4 ± 0.2) × $10^4$ $M^{-1}$ $cm^{-1}$.

With the knowledge of the extinction coefficients for $TMB^+$ and $TMB^T$, it is possible to evaluate the concentrations of these species produced by the 347.1-nm light flash. In particular, the relative cross-section of ion vs. triplet formation expressed by the parameter $r = [TMB^+]/[TMB^T]$ for TMB photolysis in NaLS micellar solutions can now be determined. As was described before, the contributions, $OD_{475}$ ($TMB^+$) and $OD_{475}$ ($TMB^T$), to the total optical density change can be assessed by kinetic analysis of the 475 nm absorbance decay. Thus a single oscilloscope trace obtained from a laser pulse yields the desired parameter $r$. Using this method we obtain for $r$ a value of 6, indicating that six times as many $TMB^+$ cation radicals as triplets are produced by the light flash.

The observation of thermal back transfer of electrons from $Eu^{2+}$ to $TMB^+$ in methanolic solution suggests that a similar process might also occur in the micellar system. Indeed, the inserted oscillogram in Figure 5 shows that the $TMB^+$ absorption at 475 nm in the presence of $Eu^{2+}$ is no longer stable but rather decays within a time range of several milliseconds. This process is attributed to reduction of $TMB^+$ by $Eu^{2+}$, which is formed by $e_{aq}^-$ and $TMB^T$ reaction with $Eu^{3+}$. As $Eu^{2+}$ ions are located on the surface of NaLS micelle, the back transfer can be considered as a summation of intramicellar events occurring between donor ($Eu^{2+}$) and acceptor ($TMB^+$) pairs on isolated host micelles. Such a reaction should obey first-order kinetics, as is observed experimentally. The kinetic analysis gives a rate constant of 8.5 × $10^2$ $s^{-1}$, corresponding to a mean lifetime of a $Eu^{2+}$-$TMB^+$ pair on a micelle of 1.18 ms. The fact that the $TMB^+$ absorption in Figure 5 does not decay completely to the zero line indicates that only part of the $TMB^+$ is engaged in the back reaction. This is a consequence of the side reaction of $e_{aq}^-$ with $NO_3^-$ ions leading to a situation where less $Eu^{2+}$ is available than needed to reduce $TMB^+$ quantitatively. The intramicellar reduction of $TMB^+$ by $Eu^{2+}$ is an illustrative example of how, in micellar solution, restoration of the dye from its photooxidized form may be achieved. Such cyclic processes are important to study if the dye is to be used as a catalyst for light-induced water decomposition or initiation of redox processes.

One point of particular interest and potential practical importance is whether photoionization processes in micellar systems can be applied for photochemical utilization of solar light energy. In a first exploration of such possibilities we have checked the effect of sunlight on a solution of TMB in NaLS which was of identical composition with the one used in the laser experiments. After thorough deaeration the solution contained in a Pyrex flask was placed in the sunlight. A few minutes of irradiation were sufficient to produce an intense greenish-yellow color which corresponds to an absorption spectrum shown in Figure 6. This spectrum is identical with the $TMB^+$ spectrum. In particular, the absorption around 475 nm matches exactly with the transitory optical density in Figure 4 observed 10 ms after the laser pulse. These observations indicate that photoionization of TMB is readily achieved by sunlight, which has a much lower intensity than the laser flash. The monophotonic mechanism of hydrated electron production is thus confirmed. Useful ways of exploiting the strong reducing power of hydrated electrons are conceivable. For example, $e_{aq}^-$ is readily convertible into hydrogen or may be employed to reduce carbon dioxide. However, a second redox system for restoration of the dye from its oxidized form has to be found to make feasible practical application of the photoionization process. In addition, it would be desirable to explore photoionizable dyes with absorptions extending further in the visible than those of phenothiazine or TMB in order to assure better utilization of the light present in the solar spectrum.

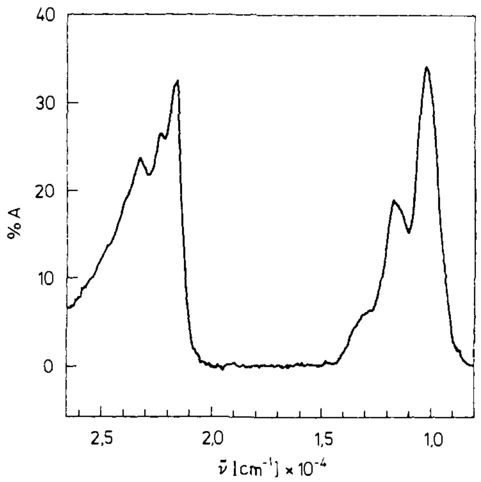

**Figure 6.** Spectrum of $TMB^+$ cation radical after formation by a ≈5 min exposure to sunlight of a deaerated 5 × $10^{-5}$ M TMB, 0.1 M sodium lauryl sulfate aqueous micellar solution.

**Laser Photolysis in Cationic Micellar Solution: Photoionization vs. Triplet Formation.** The transitory spectrum obtained from the laser photolysis of TMB in aqueous micellar solution of dodecyltrimethylammonium chloride (DTAC) is shown in Figure 7. This spectrum has much more similarity with the absorption curves obtained in the organic solvents than with that observed for NaLS micelles. In fact, an analysis of optical density contributions from the three transients, $e_{aq}^-$, $TMB^+$, and $TMB^T$, analogous to the procedure described above, yields for the $r$ parameter a value of 0.3 which is comparable to the methanol results. Apparently, the favored pathway of the photoreaction in the case of cationic micelles is triplet formation and not photoionization. This finding is particularly interesting in the light of previous theoretical predictions[2b] based on a tunneling model for monophotonic photoionization of phenothiazine in micellar solution. From these considerations the charge of the micelle should play a crucial role for the efficiency of the photoionization process. High yields are predicted for compounds with gas phase ionization potentials around 6.5 eV if they are incorporated into anionic micelles,

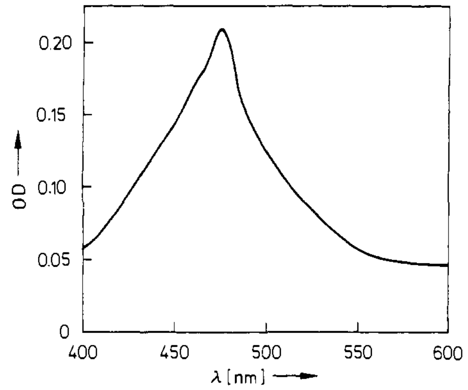

**Figure 7.** Spectrum of transients obtained in the laser photolysis of a deaerated $5 \times 10^{-5}$ M TMB, $4 \times 10^{-2}$ M dodecyltrimethylammonium chloride aqueous micellar solution.

as the negative potential inside the aggregates assists the photoionization process. Alternatively, in cationic micelles the potential is a few hundred millivolts positive against bulk water, which should drastically decrease the probability of electron photoejection from the micellar aggregate.

It is interesting to juxtapose these results to studies where hydrated electrons were formed via biphotonic photoionization of aromatic molecules in micellar solution. For example, the yield of $e_{aq}^-$ produced by 347.1-nm laser photolysis is the same in NaLS and DTAC solution.[14] In this case, the excess energy of the photoejected electrons is approximately 1 eV, which exceeds the electrostatic contribution of the micelle to the energetics of the photoionization process.

## Concluding Remarks

One major goal of the present study of TMB photolysis in organic and micellar solution was to establish a correlation between the photochemical yields of triplet and cation radical formation. In cyclohexane, where monophotonic photoionization of TMB by 347.1-nm light cannot occur for energetic reasons, the major photoreaction apart from singlet formation is the production of triplets. In methanol and micellar solution high triplet yields are associated with small cation radical yields and vice versa, a finding which parallels results obtained with phenothiazine.[2a] This indicates a common precursor, i.e., excited TMB singlet state, for both photoprocesses, which either autoionizes or relaxes into the triplet state. Ionization is greatly favored in anionic micellar solution for various reasons which have been stated elsewhere.[2] The absolute yield of hydrated electrons, although difficult to gather from laser experiments, is about 0.5 in NaLS micellar solution, which makes feasible practical usage of the photoionization process.

A second feature of this investigation was to inquire into light-initiated redox reactions where the excited state acts as an electron donor. Contrary to the reverse reaction, where excited states are an oxidant, little research has been done until now on such processes. The present data show that TMB triplets are strong reductants, a property which could be exploited by using TMB in a photogalvanic cell. Such possible applications are presently under investigation.

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