

PICOSECOND LASER PHOTOLYSIS STUDIES UPON PHOTOCHEMICAL ISOMERIZATION AND PROTOLYTIC REACTION OF A STILBAZOLIUM BETAINE

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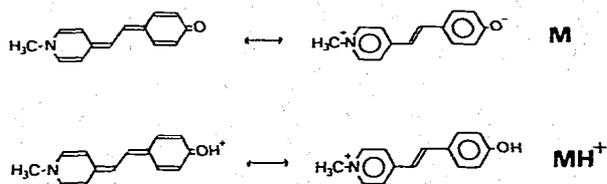
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The dynamical behavior of a stilbazolium betaine (M) and its protonated form (MH⁺) in their excited singlet states (S₁) was studied using picosecond laser flash photolysis. From the time-resolved transient spectra direct evidence was obtained for the deprotonation of trans-MH⁺ in the S₁ state, competing with isomerization.

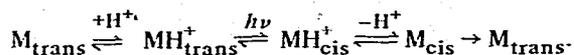
1. Introduction

The photoinduced trans/cis isomerization is one of the most important fundamental processes in photochemical and photobiological reactions, and many investigations have been carried out in order to elucidate its mechanism. Recently, direct observation of the isomerization process in the singlet excited state has become possible owing to the development of picosecond laser spectroscopy. Up to now, however, the systems studied with this method are rather limited. The picosecond studies have been concentrated on stilbenes [1] and rhodopsins [2]. A picosecond laser photolysis study of the singlet excited state of thioindigo has also been reported recently [3,4].

On the other hand, a detailed study of the photoisomerization has been made in the merocyanine dye of stilbazolium betaine (M) type by making the measurements of the reaction yields with the stationary method [5]. According to this study, M_{trans} is more stable than M_{cis} and does not show photoisomerization. However, the O-protonated form (MH⁺) readily



undergoes trans/cis photoisomerization. Owing to this peculiar behavior in aqueous solution, M shows the following reaction cycle:



This reaction cycle is interesting as a chemical model related to the molecular mechanism of some important photobiological phenomena such as the light-driven proton pump of *Halobacterium halobium* or the process of vision [5].

Because of its interesting properties of intramolecular charge transfer as well as protonation coupled with photoisomerization, we have examined this system by means of picosecond laser photolysis in order to observe directly the relevant processes and to elucidate the details of the reaction mechanism.

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2. Experimental

The merocyanine dye, 4'-hydroxy-1-methylstilbazolium betaine (MH^+), was the same sample as used before [4]. Deionized and distilled water was distilled again with a non-boiling type distillation apparatus made of quartz. 98% H_2SO_4 and pH 6 as well as pH 10 buffer solutions (Puffer-Titrisol Merk) were used to control the pH of the sample solutions.

Absorption and fluorescence spectra were measured by using respectively a JASCO UVIDEK-1 type spectrophotometer and an Aminco-Bowman spectrofluorometer.

Picosecond time-resolved transient absorption spectra and fluorescence decay curves were measured by means of a microcomputer-controlled picosecond laser photolysis system with a repetitive mode-locked Nd^{3+} :YAG laser as the excitation source, details of which were reported elsewhere [6,7].

In order to minimize the permanent trans/cis conversion in the observed volume, the solution in the sample cell was stirred after every shot. The sample solutions were deoxygenated by irrigating them with a purified nitrogen gas stream. Measurements were carried out at room temperature ($26 \pm 1^\circ C$).

3. Results and discussion

The absorption spectra of M and MH^+ are shown in fig. 1a. At $pH \geq 10$, the concentration of the protonated species is negligible and the solution of M is photochemically stable. At $pH \leq 6$, only the MH^+ species is present in the ground state. MH^+ shows trans/cis photoisomerization and irradiation of MH^+_{trans} leads to a trans/cis mixture. The broken curve in fig. 1a shows the spectra of the cis form calculated by Steiner et al. [5]. The fluorescence spectra are also shown in fig. 1b. The absorption spectrum of the merocyanine in 5% H_2SO_4 solution was the same as that obtained at pH 6.

Time-resolved transient absorption spectra of MH^+_{trans} in buffer solution of pH 6 are shown in fig. 2a. Fig. 3a shows semilogarithmic plots of transient absorbance at 430 and 700 nm. The absorbance at 430 nm shows a two-component decay. The decay time of the fast component estimated by subtracting the slow component from the observed decay curve

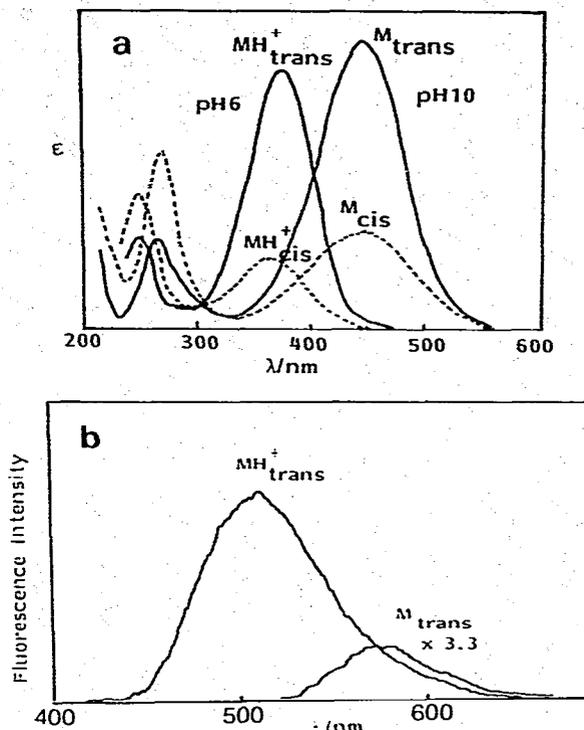


Fig. 1. (a) Ground-state absorption spectra of M and MH^+ in aqueous solution. (b) Fluorescence spectra of M (pH 10) and MH^+ (pH 6) in aqueous solution.

was very short: this corresponds to the very short fluorescence lifetime observed for the same solution by means of a streak camera (see fig. 3b). These results indicate that the transient absorption at 430 nm which shows rapid decay is due to the $S_n \leftarrow S_1$ transition of MH^+_{trans} .

The absorbance in fig. 2a shows negative values around 500 nm. This wavelength region coincides with that of the fluorescence band of MH^+_{trans} , which indicates that the monitoring light pulse of the picosecond continuum is a little amplified by the induced emission from the S_1 state of MH^+_{trans} in the wavelength region of fluorescence. On the other hand, the strong absorption band around 700 nm is typical of the hydrated electron (e^-_{sol}) [8], which seems to be produced by a biphotonic process.

In the time-resolved spectra in fig. 2a an absorption peak is observed at 440 nm after rapid decay of the fast component at 430 nm. It might be possible

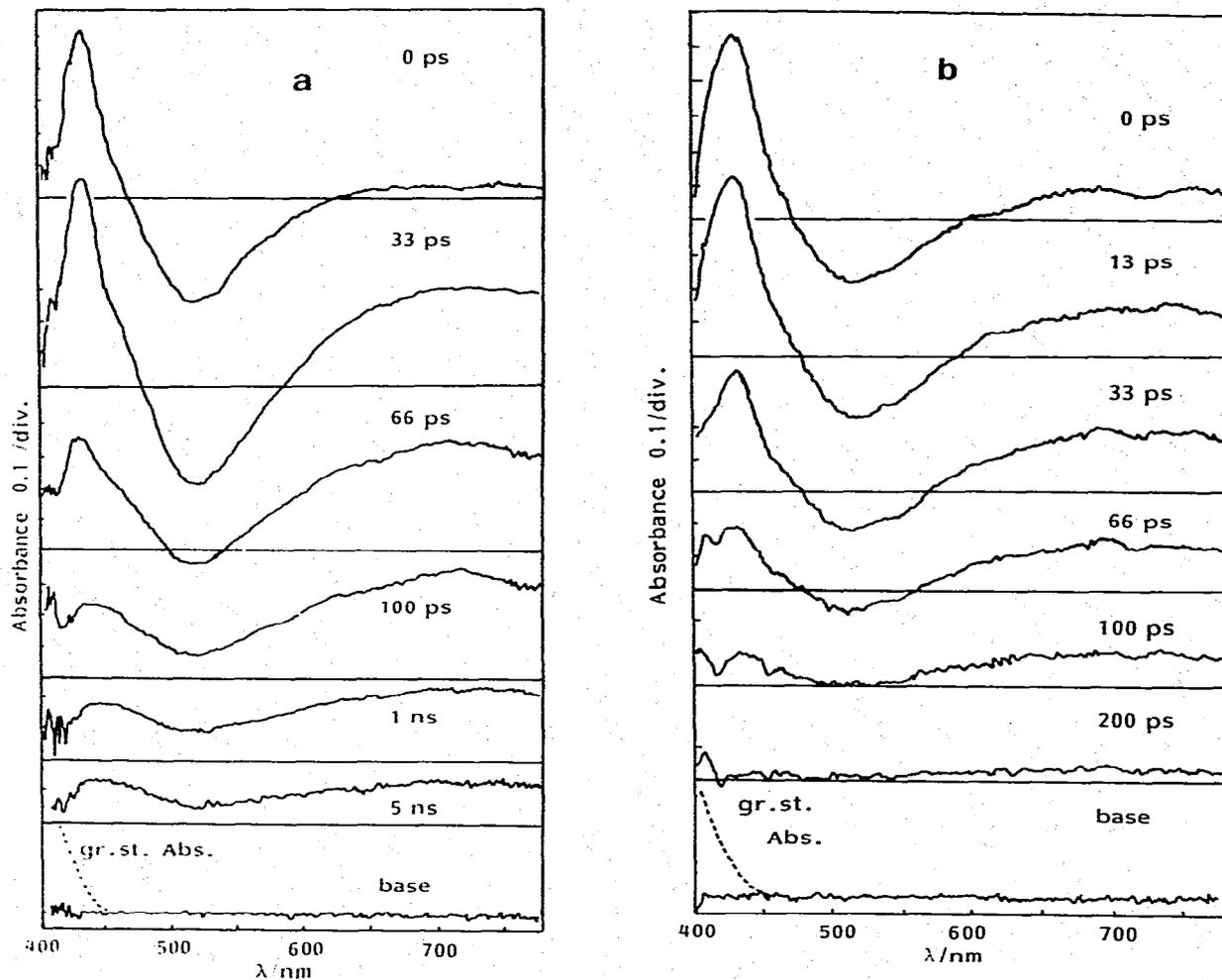


Fig. 2. (a) Time-resolved transient absorption spectra of MH^+ in aqueous solution (pH 6). Concentration of MH^+ : 7×10^{-5} M. (b) Time-resolved transient absorption spectra of MH^+ in 5% H_2SO_4 aqueous solution. Concentration of MH^+ : 4×10^{-5} M.

that the absorption around 440 nm is due to a radical species such as MH^{2+} produced by electron photoejection from MH^+ . To check this possibility we have examined how the transient absorbance, detected with a delay time of 100 ps, at 440 nm and 700 nm depends on the excitation pulse intensity. We found that the species absorbing 440 nm radiation is produced by a monophotonic process whereas a biphotonic process is responsible for the formation of the species absorbing 700 nm radiation. Thus one may

conclude that the absorption band at 440 nm is not due to the radical species MH^{2+} .

On the other hand, the peak wavelength of this absorption band coincides with that of the ground-state absorption band of M_{trans} . This result strongly indicates the occurrence of protolytic dissociation of the excited MH_{trans}^+ in competition with isomerization. In fact such a process is to be expected, since MH^+ has a pK^* of ≈ 1.9 in the S_1 state [9,10], indicating that the molecule is a much stronger acid in the ex-

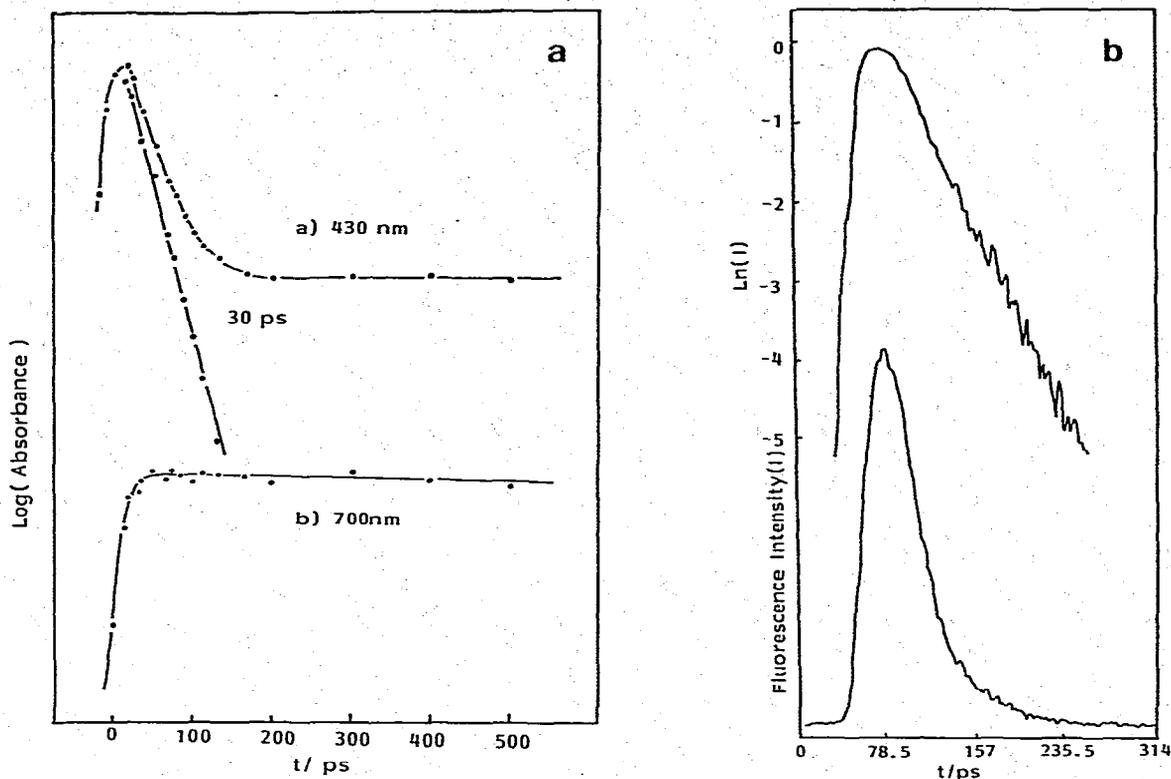


Fig. 3. (a) Semilogarithmic plot of transient absorbance of MH^+ in aqueous solution (pH 6). (b) Fluorescence decay curve of MH^+ in aqueous solution (pH 6).

cited state than in the ground state ($pK_G = 8.54$ at $25^\circ C$ [9]).

If $*MH_{trans}^+$ undergoes deprotonation, fluorescence from $*M_{trans}$ should be observable even if no M_{trans} exists at pH 6 in the ground state. However, the yield of M_{trans} is apparently not very large, and since its fluorescence yield is quite small (cf. fig. 1b), the detection of the $*M_{trans}$ fluorescence will be difficult in the presence of the strong MH^+ fluorescence.

We made a comparative study of the behavior of $*MH_{trans}^+$ in solutions buffered at pH 6 and solutions with 5% H_2SO_4 . We found that in such a strongly acidic solution the fluorescence yield was higher by $\approx 20\%$ and the same applied to the quantum yield ϕ_{tc} of $trans \rightarrow cis$ photoisomerization. On the other hand a slight shift in the photostationary state towards

a greater cis fraction \ddagger , when irradiated at 365 nm, indicated that ϕ_{ct} did not change to a comparable extent. These findings altogether provide convincing evidence that deprotonation of $*MH_{trans}^+$ is suppressed in the strongly acidic solution.

It is of interest to re-examine the quantum yield data obtained by Steiner et al. [5] in the light of these results. It was suggested that the photoisomerization of MH_{trans}^+ to MH_{cis}^+ and vice versa proceeds via a common intermediate X. Thus the photochemical quantum yields may be decomposed as follows:

\ddagger It should be noted here that in 5% H_2SO_4 solution the thermal back isomerization $MH_{cis}^+ \rightarrow MH_{trans}^+$ occurs – obviously acid catalyzed – at an appreciable rate (half conversion time being $\approx 2-3$ h at $25^\circ C$).

$$\phi_{tc} = \phi_{tX}\phi_{Xc} \quad (1)$$

$$\phi_{ct} = \phi_{cX}\phi_{Xt} \quad (2)$$

with the underlying assumption

$$\phi_{Xc} + \phi_{Xt} = 1. \quad (3)$$

On the other hand, ϕ_{cX} is generally assumed to equal 1, so that

$$\phi_{Xt} = \phi_{ct} \quad (4)$$

and, combining (1), (3) and (4):

$$\phi_{tX} = \phi_{tc}/(1 - \phi_{ct}). \quad (5)$$

With $\phi_{tc} = 0.33$ and $\phi_{ct} = 0.57$ we obtain $\phi_{tX} = 0.77$. In other words, 23% of $^*MH_{trans}^+$ disappear through other channels than isomerization. This figure compares well with the increase of ϕ_f and ϕ_{tc} upon acidification of the solution, meaning that deprotonation of $^*MH_{trans}^+$ in weakly acid solution is the main side channel of deactivation besides isomerization.

Assuming that dissociation of $^*MH_{trans}^+$ contributes 20% of the decay rate constant, which was obtained as $1.67 \times 10^{10} \text{ s}^{-1}$ in weakly acid solutions [5], the rate constant of deprotonation would be $\approx 3 \times 10^9 \text{ s}^{-1}$, which compares well with observed values for molecules with strongly acidic excited states [11].

The results obtained with the 5% H_2SO_4 solution of MH_{trans}^+ in the picosecond laser experiments are shown in fig. 2b, where the transient absorption spectra at early delay times from the excitation pulse are nearly the same as in fig. 2a. However, the absorption band at 440 nm observed at a delay time of ≈ 100 ps in the case of the solution with *pH* 6 cannot be recognized for this strongly acidic solution. Furthermore, at ≈ 200 ps, not only the 430 nm band but also the absorption due to e_{solv}^- can be hardly observed.

The rapid disappearance of e_{solv}^- absorption in strongly acidic solution may be ascribed to the reaction of e_{solv}^- with high concentration hydronium ions. The decay of the transient absorption due to e_{solv}^- in 5% H_2SO_4 solution was exponential, and the decay time was obtained to be ≈ 70 ps.

It should be noted here that, in strongly acidic solution, after the rapid decay of the $S_n \leftarrow S_1$ absorption band of MH_{trans}^+ and that of e_{solv}^- , no absorption band due to long-lived excited species can be recognized in the visible region. No such absorption

band can be recognized also in weakly acidic solution except for the absorption bands due to the transiently produced M_{trans} and e_{solv}^- . These results support the mechanism of direct trans/cis photoisomerization from the S_1 state assumed in the previous report in analogy to the case of stilbene or stilbazoles [5].

We have examined also the excited state of M_{trans} by means of picosecond laser photolysis method. Although we observed a fluorescence decay curve similar to that of MH_{trans}^+ by means of a streak camera, no appreciable transient absorption band except for that of e_{solv}^- was detected in the measurable wavelength region (500–800 nm).

From the fact that M_{trans} does not show photoisomerization and that the fluorescence radiative transition probability obtained from the fluorescence quantum yield and lifetime is considerably smaller than the value calculated from the absorption band, the following two alternative mechanisms have been proposed [5] for the behavior of excited M_{trans} : (a) the singlet state S_1 reached upon excitation relaxes very rapidly to a lower singlet state S_1' with a smaller fluorescence transition probability; and (b) vibrational relaxation in S_1 state competes with an internal conversion to a singlet state S_1'' (situated above the zero-point vibrational state of S_1) which is very efficiently deactivated non-radiatively. The present result of picosecond laser photolysis seems to indicate that the $S_n \leftarrow S_1$ band of the fluorescent state cannot be detected due to the very small concentration of S_1 state, i.e. mechanism (b). However, it might also be

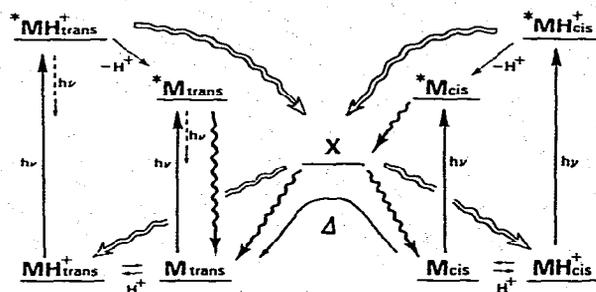


Fig. 4. A schematic diagram for the photochemical processes of M and MH^+ . At *pH* 6, the distribution of the decay of various species over their respective decay channels is as follows. $^*MH_{trans}^+ \rightarrow MH_{trans}^+ + hv$: 1.5%, $^*MH_{trans}^+ \xrightarrow{-H^+} ^*M_{trans}$: 20%, $^*MH_{trans}^+ \rightarrow X$: 77%, $^*MH_{cis}^+ \rightarrow X$: 100%, $X \rightarrow MH_{trans}^+$: 57%, $X \rightarrow MH_{cis}^+$: 43%.

possible that the $S_n \leftarrow S_1$ band is hidden in the region of the strong ground-state absorption band of M_{trans} .

Summarizing the above results together with the previous ones, the photochemical processes of the present system may be represented schematically as indicated in fig. 4.

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References

- [1] B.I. Greene, R.M. Hochstrasser and R.B. Weisman, *Chem. Phys. Letters* 62 (1979) 427; M. Sumitani, N. Nakashima and K. Yoshihara, *Chem. Phys. Letters* 68 (1979) 255.
- [2] R. Callender, in: *Biological events probed by ultrafast laser spectroscopy*, ed. R.R. Alfano (Academic Press, New York, 1982) p. 239; K.E. Peters and N. Leontis, in: *Biological events probed by ultrafast laser spectroscopy*, ed. R.R. Alfano (Academic Press, New York, 1982) p. 259; T.G. Ebrey, in: *Biological events probed by ultrafast laser spectroscopy*, ed. R.R. Alfano (Academic Press, New York, 1982) p. 271.
- [3] S.A. Krysanov and M.V. Alfimov, *Chem. Phys. Letters* 76 (1980) 221; 82 (1981) 51.
- [4] N. Mataga, Y. Maeda and T. Okada, to be published.
- [5] Y. Steiner, M.H. Abdel-Kader, P. Fischer and H.E.A. Kramer, *J. Am. Chem. Soc.* 100 (1978) 3190.
- [6] H. Masuhara, N. Ikeda, H. Miyasaka and N. Mataga, *J. Spectry. Soc. Japan* 31 (1982) 19.
- [7] H. Miyasaka, H. Masuhara and N. Mataga, *Laser Chem.*, submitted for publication.
- [8] J.W. Boag and E.J. Hart, *Nature* 197 (1963) 45; M. Imamura, A. Kira and S. Arai, in: *Kagakusosetsu*, No. 24, Chem. Soc. Japan (Japan Scientific Societies Press, 1979) p. 181.
- [9] J.E. Kuder and D. Wychik, *Chem. Phys. Letters* 24 (1974) 69.
- [10] M.H. Abdel-Kader, Thesis, Stuttgart University (1978) p. 114.
- [11] M. Hauser, H.-P. Haar and U.K.A. Klein, *Ber. Bunsenges. Physik. Chem.* 81 (1977) 27; F. Hafner, J. Wörner, U. Steiner and M. Hauser, *Chem. Phys. Letters* 73 (1980) 139; H. Shizuka, K. Tsutsumi, H. Takeuchi and I. Tanaka, *Chem. Phys. Letters* 62 (1979) 408.