June, 1982] © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **55**, *1795—1797 (1982)* 1795

# Nanosecond Laser Flash Photolysis of 1-Anilinonaphthalene

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The photoionization mechanism of 1-anilinonaphthalene (1-AN) was investigated by a nanosecond laser flash photolysis and the result was compared with that of 8-anilino-1-naphthalenesulfonate (ANS). The photoionization of 1-AN in polar solvent is shown to occur through a biphotonic process *via* a triplet state; the mechanism is different from those of ANS, in which an intermediate of a charge transfer to solvent (CTTS) state was observed. Thus the major deactivation process of the lowest excited singlet state is an intersystem crossing in 1-AN, while it is a transition to the CTTS state in ANS which might be stabilized by the sulfonato group.

The fluorescence spectra, quantum yields, and lifetimes of naphthylamine derivatives, especially 8-anilino-1-naphthalenesulfonate (ANS) and 6-(*p*-toluidino)-2-naphthalenesulfonate (TNS) are extremely sensitive to their environment.[1–6] For example, ANS shows a dramatic decrease in fluorescence lifetime by increasing the solvent polarity (ethanol (12.5 ns) and water (0.2 ns)).[6] These properties have been used as probes for structural studies of biological molecules for many years.[1,3,7] Fleming *et al.*[8] proposed that the major deactivation process of the excited singlet state of ANS and 1-anilinonaphthalene (1-AN) in polar solvents may be a monophotonic ionization from their excited singlet state with a result of nanosecond laser flash photolysis. We reported that the photoionization of ANS is a biphotonic process *via* a charge transfer to solvent (CTTS) state.[9] It has been recognized that 1-AN, which has no sulfonato group, shows the red shift of fluorescence spectrum accompanying with the increase of the solvent polarity;[10] the behavior is analogous to ANS and TNS. However, 1-AN does not show a drastic decrease of fluorescence lifetime by increasing the solvent polarity.[11] It is conceivable that the sulfonato group of anilinonaphthalenesulfonate plays an important role in the deactivation process of the lowest excited singlet state in polar solvents. We studied the mechanism of photoionization of 1-AN, which has no sulfonato group, by comparing it with that of ANS.

## Experimental

1-AN obtained from Nakarai Chemical Ltd. was used after twice recrystallizations from ethanol. *trans*-Stilbene and potassium iodide were used as received from Nakarai Chemical Ltd. Spectroscopic grade water, methanol, ethanol, and cyclohexane were used as solvents. The degassed samples were sealed after repeated freeze-pump-thaw degassing cycles. Fluorescence spectra were measured on a Hitachi MPF-2A spectrofluorometer located at Chemical Instrument Center of Nagoya University. Details of the laser flash photolysis and the fluorescence lifetime measurement were described previously.[6,9] The exciting source for the laser flash photolysis was a XeF excimer laser (Lambda Physik EMG-500) with an emission line at 351 nm and a pulse width of 12 ns.

## Results and Discussion

Fleming *et al.*[8] found a transient absorption spectrum of 1-AN in methanol–water (1 : 1) mixed solvent which is similar to that of ANS in an aqueous solution. They proposed that the major deactivation process of 1-AN in polar solvent is a photoionization because of a similarity of transient spectrum. We also measured the transient absorption spectrum of 1-AN in a degassed methanol–water (1 : 1) mixed solvent. The spectrum which we obtained is somewhat different from that reported by Fleming *et al.* in the longer wavelength region than 580 nm as shown in Fig. 1 (curve A). Both the 420 and 800 nm bands are similar to the absorption of ANS radical which has peaks at 450 and 800 nm, respectively. These bands are assigned to the absorption of 1-AN cation radical. Furthermore we observed a transient absorption of 1-AN having a decay time identical with the fluorescence lifetime in the wavelength region above 700 nm, and these absorptions are assigned to the $S_n \leftarrow S_1$ absorption of 1-AN (Fig. 1 (curve B)).

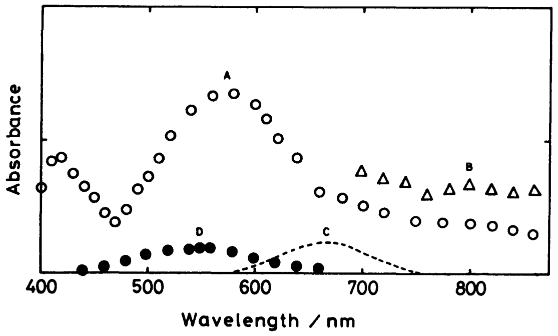


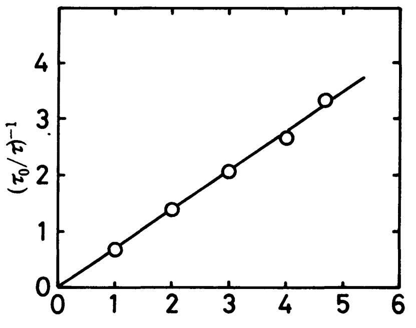
Fig. 1. Transient absorption spectra of 1-AN.
A: 70 ns after the laser pulse in a degassed methanol–water (1 : 1) mixed solvent, B: the $S_n \leftarrow S_1$ absorption, C: the absorption spectrum of solvated electron, D: the $T_n \leftarrow T_1$ absorption in cyclohexane.

The strongest absorption band with the maximum at 580 nm is not assigned to that of solvated electron because the peaks of solvated electron in water and methanol appear at 720 and 640 nm,[12,13] respectively. Moreover, we measured the transient spectrum in solution containing an electron scavenger ($N_2O$), which will diminish the absorption of solvated electron. The differential transient spectrum between the solution in a degassed and $N_2O$ saturated methanol–water (1 : 1) mixed solvent gives the absorption spectrum of solvated electron with a maximum at about 670 nm as shown in Fig. 1 (curve C). Since the peak of solvated electron is found at normal wavelength region, the absorption band at 580 nm is regarded as the $T_n \leftarrow T_1$ absorption. Furthermore the following reasons are available to support the $T_n \leftarrow T_1$ assignment.

(1) The absorption maximum lies in the position of the $T_n \leftarrow T_1$ absorption observed in cyclohexane (Fig. 1 (curve D)). The latter spectrum agreed with that reported by Fleming *et al.*[8]

(2) The dependence of the absorbance at 580 nm on the light intensity shows a linear relationship. It shows that the absorption at 580 nm is produced by a monophotonic process.

(3) The transient absorption at 580 nm is extensively quenched by adding a triplet quencher such as oxygen and *trans*-stilbene into solution. The quenching by *trans*-stilbene was investigated with varying concentration in methanol–water (4 : 1) mixed solvent. Figure 2 shows the Stern-Volmer relationship of the decay time of the absorption at 580 nm. The quenching rate obtained from the slope of this plot is $4.5 \times 10^9$ (mol$^{-1}$ s$^{-1}$). The relation shows that the quenching is a diffusion-controlled process.



[*trans*-Stilbene] × 10$^3$/mol dm$^{-3}$

Fig. 2. Stern-Volmer plot of the decay time of the $T_n \leftarrow T_1$ absorption at 580 nm against the concentration of *trans*-stilbene in a methanol–water (4 : 1) mixed solvent.

In order to find whether the photoionization process occurs through the monophotonic or biphotonic one, we measured the dependence of the yield on the light intensity. The photoionization yield was monitored by the absorbance of 1-AN cation radical at 420 nm and the absorbance was plotted against the square of the light intensity in Fig. 3. The plot shows a linear relation, indicating that the photoionization is a biphotonic process.

Three species are conceivable as the intermediate of the biphotonic ionization; (1) the CTTS state, (2) the lowest excited singlet state, and (3) the triplet state. The CTTS state seems to be not involved because no evidence is obtained about the transient spectrum with a short lifetime. In order to find which of the singlet or the triplet excited state is the intermediate, we measured the change of the photoionization yield by adding different kind of quenchers.

The fluorescence of 1-AN was quenched by potassium iodide and we obtained the value of the quenching rate $k_q$ from the Stern-Volmer plot ($k_q = 2.6 \times 10^8$ mol$^{-1}$ s$^{-1}$). We also observed that both absorbances of the $T_n \leftarrow T_1$ absorption and 1-AN cation radical are intensified with a linear relation by increasing the concentration of potassium iodide. This shows that potassium iodide enhances the intersystem crossing from the excited singlet state to the triplet state and the yield of the biphotonic ionization is increased. Therefore the photoionization process *via* the lowest triplet state is more probable.

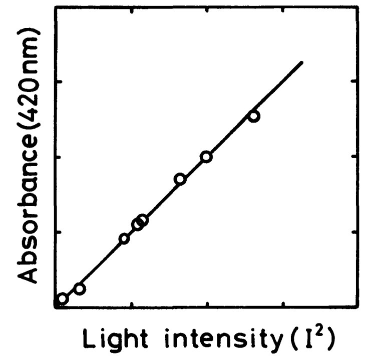


Fig. 3. Dependence of the absorbance at 420 nm on the square of the exciting light intensity in a degassed methanol–water (1 : 1) mixed solvent.

Then, the change of the yield with the triplet quencher is investigated. The absorbance of 1-AN cation radical at 420 nm and the $T_n \leftarrow T_1$ absorption at 580 nm are decreased accompanying with the increase of the concentration of *trans*-stilbene. *trans*-Stilbene is a triplet quencher, therefore the photoionization is considered to take place through the triplet state. Following this result, the photoionization of 1-AN is given by the following scheme.

$$\begin{tikzcd}
\text{1-AN}^* \arrow[r, "k_{\text{isc}}"] \arrow[d, shift left, "\text{F}"] & \text{1-AN}^{\text{T}} \arrow[r, "h\nu"] \arrow[dl, "k'_{\text{isc}}"] & \text{1-AN}^{+} + e^{-}_{\text{sol}} \\
\text{1-AN} \arrow[u, shift left, "h\nu"] & &
\end{tikzcd}$$

To distinguish the reaction mechanism of ANS and 1-AN in the excited singlet state, the fluorescence properties are measured and compared. Table 1 shows the fluorescence maxima and the fluorescence lifetimes of ANS and 1-AN in several solvent. The fluorescence maximum of 1-AN is shifted to the longer wavelength by increasing the solvent polarity as well as ANS. DeToma and Brand[14] reported the shift of the fluorescence maximum of 2-anilinonaphthalene in cyclo-

TABLE 1. UNCORRECTED FLUORESCENCE MAXIMA AND LIFETIMES IN SEVERAL SOLVENT AT 25°C

| Solvent | ANS | | 1-AN | | | |
|---|---|---|---|---|---|---|
| | $\lambda_{\max}$ nm | $\tau_f$ ns | $\lambda_{\max}$ nm | $\tau_f$ ns | $\tau_f$[a] ns | $\tau_f$[b] ns |
| Water | 514 | 0.20 | 461 | 2.6 | | 5.0 |
| Methanol–Water (1 : 1) | | | 450 | 5.4 | | |
| Methanol | 473 | 8.5 | 419 | 7.4 | 5.3 | |
| Ethanol | 466 | 12.5 | 412 | 7.6 | 5.6 | 5.75 |
| Cyclohexane | | | 374 | 5.8 | 4.1 | 4.1 |

a) For non-degassed samples. b) Ref. 11.

hexane–ethanol ($<0.2$ mol dm$^{-3}$) mixed solvent and we also observed the red shift of the fluorescence spectrum of 1-AN in mixed solvent of the same composition. It appears that the red shift is due to the solvent relaxation through the dipole-dipole interaction between the excited molecule and the polar solvent molecules during the lifetime of the excited singlet state, because the dipole moment of the first excited singlet state is greater than that of the ground state.[2,15]

We reported that the major deactivation process of ANS in polar solvent is the transition from the excited singlet state to the CTTS state and the $T_n \leftarrow T_1$ absorption is not detected.[9] The fluorescence lifetime of ANS is dramatically decreased by increasing the solvent polarity because the CTTS state is formed and the transition to it is enhanced in polar solvents. On the other hand the major deactivation process of the excited singlet state of 1-AN is shown to be the intersystem crossing to the triplet state, and it is less dependent on the polarity of the solvent. Hence the fluorescence lifetime of 1-AN is not shrunk significantly in polar solvent.

The biphotonic ionization occurs through the CTTS state in ANS, while it takes place *via* the triplet state in 1-AN. The difference of the photoionization mechanism between ANS and 1-AN is distinct. The presence of the sulfonato group in ANS may be connected with the formation of the CTTS state. Sadkowski and Fleming[11] suggested that the $SO_3^-$ group of ANS forms a solvent trap through the hydrogen bond with the solvent molecules and the photoionization process from the excited ANS molecule could be interpreted by an electron transfer to the solvent trap. However we proposed the electron is transfered to the CTTS state rather than to bulk solvents before the photoionization and the $SO_3^-$ group may stabilize the CTTS state by forming a zwitter-ion like structure. The zwitter-ion like structure is supported from the similarity of the transient absorption spectra between ANS radical and 1-AN cation radical. A similar phenomenon was reported in pyrene and pyrenesulfonic acid by Grätzel *et al.*[16]

## References

1) L. Stryer, *J. Mol. Biol.*, **13**, 482 (1965).

2) D. C. Turner and L. Brand, *Biochemistry*, **7**, 3381 (1968).

3) J. Yguerabide, *Meth. Enzymol.*, **26**, 498 (1972).

4) E. M. Kosower, H. Dudiuk, K. Tanizawa, M. Ottolenghi, and N. Orbach, *J. Am. Chem. Soc.*, **97**, 2167 (1975).

5) G. W. Robinson, R. J. Robbins, G. R. Fleming, J. M. Morris, A. E. W. Knight, and R. J. S. Morrison, *J. Am. Chem. Soc.*, **100**, 7145 (1978).

6) H. Nakamura and J. Tanaka, *Chem. Phys. Lett.*, **78**, 57 (1981).

7) L. Brand and J. R. Gohlke, *Ann. Rev. Biochem.*, **41**, 843 (1972).

8) G. R. Fleming, G. Porter, R. J. Robbins, and J. A. Synowiec, *Chem. Phys. Lett.*, **52**, 228 (1977).

9) H. Nakamura, J. Tanaka, N. Nakashima, and K. Yoshihara, *Chem. Phys. Lett.*, **77**, 419 (1981).

10) A. Kawski and C. Strzalkowska, *Z. Naturforsch., Teil A*, **27**, 916 (1972).

11) P. J. Sadkowski and G. R. Fleming, *Chem. Phys.*, **54**, 79 (1980).

12) L. M. Dorfman, F. Y. Jou, and R. Wageman, *Ber. Bunsenges. Phys. Chem.*, **75**, 681 (1971).

13) R. R. Hentz and G. Kenney-Wallace, *J. Phys. Chem.*, **76**, 2931 (1972).

14) R. P. DeToma and L. Brand, *Chem. Phys. Lett.*, **47**, 231 (1977).

15) A. Kawski, B. Bortoszewicz, and C. Stralkowska, *Z. Chem.*, **12**, 275 (1972).

16) M. Grätzel, K. Kalyanasundaram, and J. K. Thomas, *J. Am. Chem. Soc.*, **96**, 7869 (1974).