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# Deactivation of Excited 2-Naphthylamine Due to Hydrogen Bonding Interaction with Pyridines. Fluorescence and Picosecond Laser Photolysis Studies

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The mechanism of the strong fluorescence quenching observed when two conjugated $\pi$-electron systems are directly connected by hydrogen bonding has been studied by means of transient absorption spectral measurements with ps as well as ns laser photolysis method and fluorescence measurement. The bimolecular rate constants of quenching of 2-naphthylamine fluorescence by pyridine and 4-cyanopyridine have been determined in various solvents. The bimolecular reaction rate of fluorescence quenching by pyridine is smaller than the diffusion controlled one in many cases and depends considerably upon the dipole moment and the ability of formation of hydrogen bonding chain of solvent. However, the quenching by 4-cyanopyridine is diffusion controlled in every solvent examined here. By means of ps laser photolysis method, the state formed by charge transfer from excited 2-naphthylamine to hydrogen bonded pyridine in the quenching process has been observed for the first time. The possibility of the hydrogen atom transfer due to the mechanism of charge transfer followed by proton transfer in hexane solution is also discussed.

Many investigations have been carried out on the inter- and intramolecular hydrogen bonding interactions from various viewpoints.[1)]

Regarding the effect of hydrogen bonding interaction upon fluorescence yield, it has been observed frequently that, when two conjugate $\pi$-electronic systems are directly combined by hydrogen bonding interaction, fluorescence of proton donor or acceptor is strongly or thoroughly quenched.[1–7)] Moreover, it has been confirmed in the cases of some systems that the hydrogen bonding interaction induces strong deactivation of $S_1$ state but does not lead to the enhanced intersystem crossing.[5,7)] Especially detailed luminescence kinetic studies have been made for carbazole–pyridine systems[4,7,8)] and the lifetime of the singlet excited state of carbazole–pyridine complex was estimated to be 28 ps.[8)]

It was suggested that CT (charge transfer) interaction between proton donor and acceptor $\pi$-electron systems *via* hydrogen bond was responsible for the quenching.[2–4,6–8)] Namely, the CT state in this case was assumed very weakly fluorescent or nonfluorescent.[8)] Hydrogen atom transfer from proton donor to acceptor was also suggested as a possible mechanism of quenching.[9)]

From the investigation of naphthol–pyridine system by means of absorption-emission flash technique, it has been concluded that the fluorescence quenching in this system is partly due to hydrogen atom transfer.[10)] On the other hand, it has been proposed that the primary process in the hydrogen bonding system in the triplet state is the electron transfer followed by proton transfer between the proton donor and acceptor.[11)] However, direct proof of the electron transfer mechanism has not yet been given.

In relation to this problem, we have made ps laser photolysis studies upon naphthylamine–pyridine systems in addition to detailed investigations of solvent effects upon fluorescence quenching due to hydrogen bonding interaction.[12)]

## Experimental

*Materials.* 2-Naphthylamine (GR grade, Tokyo Kasei) was recrystallized twice from ligroine, and sublimated in a vacuum. *N,N*-Dimethyl-2-naphthylamine (GR grade, Tokyo Kasei) was recrystallized three times from ethanol–water mixture and sublimated in a vacuum. Pyridine (spectro grade, Kishida) was refluxed over calcium hydride and distilled. 4-Cyanopyridine (GR grade, Nakarai) was recrystallized twice from ether–ligroine mixture and sublimated in a vacuum. Laboratory deionized water was distilled and redistilled by nonboiling type distillation apparatus. *N*-Methylformamide (GR grade, Tokyo Kasei) and the other solvents (spectro grade) were used as received. The solvents for solutions examined by laser photolysis were refluxed over appropriate desiccant and distilled before use. All sample solutions were deaerated by freeze-pump-thaw cycles.

*Apparatus and Measurements.* Absorption and fluorescence spectra were measured using respectively a JASCO UVIDEC-1 type spectrophotometer and an Aminco-Bowman spectrophotofluorometer. Fluorescence lifetimes were determined by using a pulsed nitrogen laser with 1 kW peak power as an exciting light source, combined with a monochromator, 1P28 photomultiplier, a sampling oscilloscope and a XY recorder. The time resolution of this system was about 2.5 ns. Nanosecond laser photolysis apparatus was the same as described elsewhere.[13)]

Picosecond laser photolysis measurements were made as follows. Single picosecond pulse of the second harmonic from a mode-locked ruby laser was used for excitation. Pulse width was *ca.* 30 ps. Picosecond continuum for monitoring the transient absorption spectra was generated by focussing the single fundamental pulse into heated polyphosphoric acid solution, BK-7 glass or fused quartz plate. The generated picosecond continuum was split into two beams one of which was passed through the excited sample solution. Both beams were detected by multichannel detectors of photodiode arrays (abbreviated as MCPD) through polychromators, respectively. Both MCPD's were connected with a microcomputer system for data processing and transient absorption spectra at various delay times were stored in disk and displayed on a recorder or oscilloscope.

The transient absorption spectrum can be obtained by measuring intensities of monitoring light pulse in the presence

($I(\lambda)$) as well as in the absence ($I^0(\lambda)$) of exciting pulse, and by evaluating the absorbance $A(\lambda)$ at the wavelength $\lambda$ according to the following equation. $\lambda$ covers wavelength range of 200 nm in one measurement.

$$A(\lambda) = \log\{I_1(\lambda)/I_2(\lambda)\} - \log\{I_1^0(\lambda)/I_2^0(\lambda)\},$$

where the subscripts 1 and 2 mean the light intensities detected by MCPD1 and MCPD2, respectively, and MCPD2 receives the monitoring light passed through the sample solution. More details of the picosecond apparatus will be described elsewhere.[14)]

## Results and Discussion

(*A*) *Hydrogen Bonding Equilibrium in the Ground State.* The change of absorption spectra of 2-naphthylamine (NA) caused by hydrogen bonding interaction with pyridine (P) is not so large and the equilibrium constant $K_g$ of the hydrogen bond formation in the ground state is rather small. For example, $K_g$ of NA–P in hexane is 0.6 $M^{-1}$ (1 M=1 mol $dm^{-3}$) at 20 °C, while it was reported that $K_g=0.2\ M^{-1}$ in benzene at 13 °C[3)] and $K_g=12\ M^{-1}$ in cyclohexane at 15 °C.[4)] In the case of NA-4-cyanopyridine (CNP) system in hexane solution, the absorption spectra of NA were little affected by the addition of CNP in the range of concentration (up to $4\times10^{-2}$ M) used in the measurements. We have confirmed that the ability of CNP to make hydrogen bond with NA is considerably smaller than that of pyridine. Moreover, the hydrogen bonding interaction between NA and pyridine or NA and CNP in polar solvents becomes much weaker than in nonpolar solvents probably owing to solvation of NA as well as pyridines. Therefore, hydrogen bonding interaction in the ground state of these systems in polar solvents can be neglected.

(*B*) *Fluorescence Quenching Reaction and Its Solvent Dependence.* As is well-known, the hydrogen bonding ability of aromatic hydroxy and amine compounds is considerably larger in the lowest excited singlet state than in the ground state, which results the red shift of electronic spectra due to the hydrogen bonding interaction. Actually, in the case of naphthylamines and carbazole, the change of the fluorescence spectra caused by the hydrogen bonding interaction with proton acceptors in nonpolar solvents was confirmed to arise at much smaller concentrations of acceptor than those of absorption spectra.[3,4,8)]

The progressive changes of fluorescence spectra of NA caused by adding pyridine in hexane solution are indicated in Fig. 1. In relation to the hydrogen bonding quenching of fluorescence, we have examined the *N*,*N*-dimethyl-2-naphthylamine (DMNA)–P system, and have confirmed that the fluorescence of DMNA is not quenched by pyridine in hexane. This result shows evidently that the hydrogen bonding interaction is essential for the quenching of NA–P system. In pure pyridine solution of NA, a very weak fluorescence band which is a little red-shifted compared with that of NA in hexane was observed. Analogous results were obtained also in the case of carbazole–pyridine system.[8)] The very weak fluorescence band seems to be ascribed to the hydrogen bonded complex. In the case of the strong quenching by CNP, no red-shifted fluorescence band was observed. Moreover, CNP quenches not only the fluorescence of NA but also the fluorescence of DMNA in hexane, which indicates that the quenching by CNP is due to the molecular interaction other than hydrogen bonding, probably the direct charge transfer interaction.

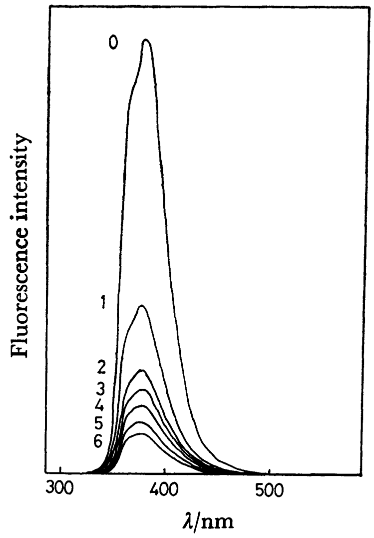

Fig. 1. Quenching of NA fluorescence caused by added P in hexane solution.
[NA]=$3.6\times10^{-4}$ M, [P]/M: 0. 0, 1. 0.004, 2. 0.008, 3. 0.012, 4. 0.016, 5. 0.020, 6. 0.030.

In general, for the fluorescence behaviors of hydrogen bonding as well as the other molecular complex forming systems, the following mechanism may be assumed.

$$\begin{tikzcd}
\mathrm{DH}^* + \mathrm{A} \arrow[r, shift left, "k_q"] \arrow[d, shift left, "(k_f+k_i)"] & (\mathrm{DH}\cdot\mathrm{A})^* \arrow[l, shift left, "k_{-q}"] \arrow[d, shift left, "(k'_f+k'_i)"] \\
\mathrm{DH} + \mathrm{A} \arrow[u, shift left, "I_{abs}\cdot\delta"] \arrow[r, shift left] & (\mathrm{DH}\cdot\mathrm{A}) \arrow[l, shift left, "K_g"] \arrow[u, shift left, "I_{abs}\cdot\delta'"]
\end{tikzcd} \tag{1}$$

In the above scheme, $I_{abs}$ is the total light quanta absorbed by the solution. $\delta$ and $\delta'$ are the fractions absorbed by free DH and complex, respectively. $k_q$ and $k_{-q}$ are rate constants of complex formation and decomposition reactions, respectively. $k_f$ and $k_i$ are rate constants of radiative and radiationless transitions of the excited free DH, respectively, and $k'_f$ and $k'_i$ are those of the excited complex.

When the equilibrium constant $K_g$ of the complex formation in the ground state is very small and, moreover, $k'_i \gg k'_f$, $k_{-q'}$, simple Stern-Volmer equation may be valid approximately to reproduce the observed fluorescence yield.

$$I_f^0/I_f = 1 + k_q\tau_0[\mathrm{A}], \tag{2}$$

where $\tau_0=1/(k_f+k_i)$. Equation 2 holds approximately for NA–P and NA–CNP systems in various solvents, from which the quenching rate constants have been obtained.

As typical examples, the Stern-Volmer plots for NA–P and NA–CNP systems in hexane as well as aqueous solutions are shown in Fig. 2. Values of the quenching rate constant in various solvents are indicated in

TABLE 1. SOLVENT DEPENDENCE OF THE FLUORESCENCE QUENCHING RATE CONSTANTS (~25°C)

| Solvent | $\mu$/Debye[c)] | $\varepsilon/\varepsilon_0$ | $\tau_0$/ns | $k_q^P/M^{-1}s^{-1}$ [d)] | $k_q^C/M^{-1}s^{-1}$ [e)] | $k_d/M^{-1}s^{-1}$ [f)] | $k_q^P/k_d$ |
|---|---|---|---|---|---|---|---|
| Benzene | 0 | 2.27 | 12 | $8.7\times10^9$ | $1.5\times10^{10}$ | $1.1\times10^{10}$ | 0.8 |
| Hexane | 0.085 | 1.9 | 14 | $2.4\times10^{10}$ | $2.9\times10^{10}$ | $2.2\times10^{10}$ | 1.1 |
| Toluene | 0.31 | 2.38 | 15 | $8.2\times10^9$ | $1.3\times10^{10}$ | $1.2\times10^{10}$ | 0.7 |
| Ethanol | 1.66(20 °C) | 24.55 | 17 | $1.8\times10^9$ | $1.1\times10^{10}$ | $6.1\times10^9$ | 0.3 |
| Water | 1.84 | 78.4 | 21 | $4.0\times10^9$ | $9.3\times10^9$ | $7.4\times10^9$ | 0.5 |
| Acetone | 2.69(20 °C) | 20.7 | 10 | $6.0\times10^8$ | $2.1\times10^{10}$ | $2.1\times10^{10}$ | 0.03 |
| Methanol | 2.87(20 °C) | 32.7 | 16 | $3.2\times10^9$ | $1.9\times10^{10}$ | $1.2\times10^{10}$ | 0.3 |
| Acetonitrile | 3.44(20 °C) | 37.5 | 19 | $3.5\times10^8$ | $1.9\times10^{10}$ | $1.7\times10^{10}$ | 0.02 |
| NMF[a)] | 3.86 | 182.4 | 11 | $2.4\times10^8$ | $7.3\times10^9$ | $4.0\times10^9$ | 0.06 |
| DMF[b)] | 3.86 | 36.7 | 18 | $8.2\times10^7$ | $1.0\times10^{10}$ | $8.2\times10^9$ | 0.01 |

a) *N*-Methylformamide. b) *N,N*-Dimethylformamide. c) 1 Debye=$3.33564\times10^{-30}$ Cm. d) $k_q$ value of NA–P system. e) $k_q$ value of NA–CNA system. f) $k_d=8RT/3000\eta$.

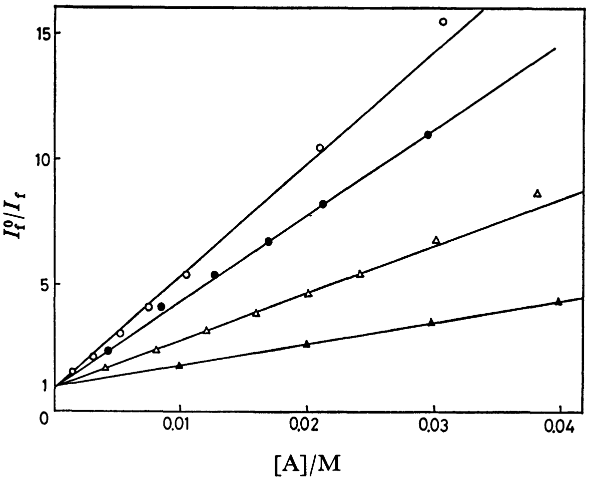

Fig. 2. $I_f^0/I_f$ *vs.* [A] relation for NA–P and NA–CNP systems in hexane and water.
●: NA–P in hexane, ▲: NA–P in water, ○: NA–CNP in hexane, △: NA–CNP in water.

Table 1 together with those of solvent dielectric constant and dipole moment as well as $\tau_0$ values of NA measured in various solvents. Moreover, $k_q$ values are compared with the values of the diffusion controlled rate constant estimated by, $k_d=8RT/3000\,\eta$.

As can be seen from Table 1, the quenching by CNP is almost diffusion controlled in every solvent used here. Although the quenching by pyridine is also approximately diffusion controlled in nonpolar solvents, it shows remarkable solvent dependence in polar solvents. The dipole moment of the solvent molecule seems to be an appropriate parameter representing the solvent effect upon the interaction between pyridine and excited NA, except in the case of protic solvents. This result indicates that the solvation by polar solvent molecules hinders more or less the hydrogen bonding interaction. The quenching efficiency ($k_q^P/k_d$) changes about one order of magnitude around the value of the solvent dipole moment equal to that of pyridine (2.37 D).

The ability of solvent to form hydrogen bonding chains seems to affect also the quenching efficiency. For example, the quenching efficiency ($k_q^P/k_d$) in methanol (0.3) is much larger than that in acetone (0.03) which has dipole moment very close to that of methanol. Similar result can be seen in the case of NMF as compared to DMF solvents. Thus, the quenching efficiency in protic solvent is larger than in aprotic solvent which has dipole moment close to that of the protic solvent. This result suggests that the hydrogen bonding chains in solvents assist in some way the quenching of NA–P system.

In relation to this effect of hydrogen bonding solvent upon the NA–P hydrogen bonding quenching of fluorescence, we have confirmed that the fluorescence of DMNA is not quenched by P not only in nonpolar solvent but also in polar aprotic solvent, but even in the case of DMNA–P system, fluorescence is quenched remarkably in aqueous ($k_q=3.2\times10^9$ M$^{-1}$ s$^{-1}$) and ethanol solutions, to almost the same extent as in the case of NA–P system. Thus, the important role of hydrogen bonding interaction among solvent molecules which assists the interaction between solute fluorescer and quencher leading to the fluorescence quenching has been confirmed, although its mechanism is not very clear at the present stage of investigation.

Contrary to the case of the quenching by pyridine, fluorescence of DMNA is quenched strongly by CNP not only in polar protic solvent ($k_q=7.4\times10^9$ M$^{-1}$ s$^{-1}$ in water), but also in polar aprotic solvent ($k_q=1.8\times10^{10}$ M$^{-1}$ s$^{-1}$ in acetonitrile) just as in the nonpolar solvent ($k_q=3.2\times10^{10}$ M$^{-1}$ s$^{-1}$ in hexane). These values of the bimolecular rate constant are rather similar to those of NA–CNP system in various solvents which are approximately diffusion controlled. As it is discussed already, this result shows that the quenching is due to the direct complex formation in the excited state rather than hydrogen bonding interaction.

(*C*) *Measurements of Transient Absorption Spectra by Means of Picosecond and Nanosecond Laser Spectroscopy.* If the charge transfer interaction between the hydrogen bonded pair in the excited state is responsible for the fluorescence quenching in the case of NA–P system, one may expect to observe the transient CT state by means of laser spectroscopy.

Results of ps laser photolysis measurements upon NA and NA–P systems in hexane solution are shown in Fig. 3. In Fig. 3, the spectra of NA cation radical[15)] produced by $\gamma$-irradiation in *s*-butyl chloride solution at 77 K are indicated for the purpose of comparison. The spectra of NA in hexane at the delay time of 200

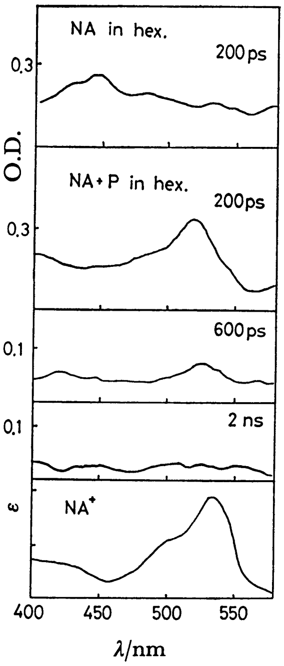

Fig. 3. Transient absorption spectra of NA and NA–P systems in hexane solution obtained by ps laser photolysis method.
[NA]=3.45×10⁻⁴ M, [P]=0.37 M.

ps may be due to the $S_n \leftarrow S_1$ transition. With addition of sufficient P, completely different spectra appeared. The spectra at 200 ps are similar to the spectra of NA cation radical. The delay time of 200 ps is necessary in order to convert completely the excited NA into the hydrogen bonded complexes at [P]=0.37 M. We have examined also the ps transient spectra of NA in pure pyridine solvent and observed again the band similar to that of NA cation radical.

The observed transient spectra are most probably due to the state formed by CT from excited NA to hydrogen bonded pyridine, ($D^{+\delta}$–H···$A^{-\delta}$). Thus, we have directly demonstrated for the first time that the CT state is responsible for the deactivation of excited singlet hydrogen bonded species. The absorbance of the CT state decays during a few hundreds ps and at 2 ns we cannot recognize any characteristic band due to the CT state. We have examined also the very weak fluorescence of the hydrogen bonded complex by means of ps streak camera and obtained the decay time of a few hundred ps.[17]

The possibility of intermolecular electron transfer in the excited state may be examined by evaluating the standard free energy change $\Delta G^\circ$ for the process, $D^*\cdots A \rightarrow D^+\cdots A^-$, in the encounter complex according to Eq. 3.

$$\Delta G^\circ = E(D/D^+) - E(A^-/A) - (e^2/\varepsilon R) - \Delta E + \Delta G_s$$
$$\Delta G_s = (e^2/2)\left(\frac{1}{R^+} + \frac{1}{R^-}\right)\left(\frac{1}{\varepsilon} - \frac{1}{37.5}\right), \quad (3)$$

where $E(D/D^+)$ and $E(A^-/A)$ are respectively the oxidation potential (*vs.* SCE) of electron donor and the reduction potential of the electron acceptor in acetonitrile. $R$ is the center to center distance between $D^+$ and $A^-$ assumed to be 7 Å. $\Delta E$ is the electronic excitation energy of D and $\Delta G_S$ is the correction term for solvation energy of cation and anion with radius $R^+$ and $R^-$, respectively, in a solvent with dielectric constant $\varepsilon$. Values of $E(D/D^+)$ and $E(A^-/A)$ were taken from literatures[9,16,18] and $\Delta G^\circ$ values were estimated for the present systems as shown in Table 2.

TABLE 2. $\Delta G^\circ$ FOR NA–P AND NA–CNP SYSTEMS

| | $\Delta G^\circ$/kcal mol$^{-1}$ | | | |
|---|---|---|---|---|
| | Hexane | Acetonitrile | Water | Pyridine |
| NA–P | 14.4 | −8.1 | −11.4 | −4.4 |
| NA–CNP | −13.3 | −35.7 | −39.0 | — |

For example, $\Delta G^\circ$ value of NA–P system in hexane is estimated to be 14.4 kcal/mol, which means that the electron transfer in the encounter complex is not possible. Even if we take a little smaller encounter distance $R$=5 Å, $\Delta G^\circ$ is estimated to be 4.4 kcal/mol, which means that the reaction is much slower than the diffusion-controlled one. Since the fluorescence quenching reaction was observed to be diffusion-controlled in the case of NA–P system and the quenching is caused by hydrogen bonding interaction as it is discussed in (*B*), the above result shows that the hydrogen bonding interaction assists the $\pi$-electronic CT state formation. It is expected that the hydrogen bonding decreases the ionization potential of NA and increases the electron affinity of pyridine.

Contrary to the case of NA–P system, the fluorescence quenching by CNP is almost diffusion-controlled not only in nonpolar solvents but also in polar solvents in both cases of NA and DMNA, which indicates the direct CT interaction without hydrogen bonding as it is discussed already in (*B*). Actually, we have observed by means of ps laser photolysis an absorption band which is very similar to that of DMNA cation in the case of DMNA–CNP system in benzene. This absorption band may be ascribed most probably to non-fluorescent heteroexcimer formed by excited DMNA and CNP. In the case of NA–CNP system in hexane as well as in benzene, however, the characteristic absorption band due to the CT state was not observed in the ps transient spectra. Very rapid deactivation process associated with the CT interaction seems to be predominant in this case.

We have examined the transient absorption spectra of NA–P system in hexane also by means of ns laser photolysis method. The results of measurements are indicated in Fig. 4. The spectra of NA in hexane at the delay time of 100 ns seems to be due to $T_n \leftarrow T_1$ transition. Similar absorption spectra were observed at the delay time of 100 ns also in the case of NA–P system in hexane. However, it might be possible to assign the band around 450 nm of the NA–P system to the absorption spectra of 2-naphthylaminyl radical which are similar to the $T_n \leftarrow T_1$ spectra of NA.[19,20]

If the observed spectra of NA–P system are due to the 2-naphthylaminyl radical, it may be produced by the mechanism of CT followed by proton transfer competing

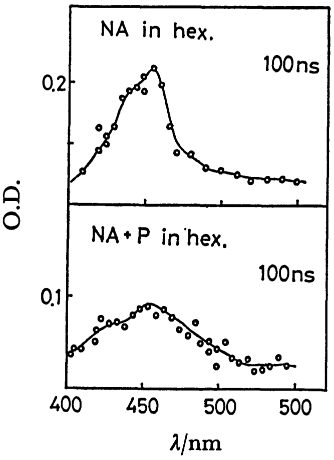

Fig. 4. Transient absorption spectra of NA and NA–P systems in hexane solution obtained by ns laser photolysis method at 100 ns. Concentrations of NA and P are respectively the same as in Fig. 3.

with the deactivation to the ground state. This interpretation seems to be supported by the fact that the intersystem crossing rate constant is little influenced by hydrogen bonding interaction.[5,7,21] Namely, the $S_1 \rightsquigarrow T_1$ intersystem crossing seems to be negligible owing to the other overwhelming non-radiative processes from $S_1$ state of the NA–P hydrogen bonded complex. Thus, the formation of 2-naphthylaminyl radical from the CT state seems to be probable. Nevertheless the rise of its absorption band was not recognized clearly by means of ps laser photolysis at the delay time of 2 ns. This result may be due to the smaller extinction coefficient of 2-naphthylaminyl radical than that of NA cation and the lower power of exciting ps pulse compared with ns pulse.

We have examined also the transient spectra of NA–P and NA–CNP systems in polar solvents such as acetonitrile and water by means of ps as well as ns laser photolysis, and have observed clearly the spectra due to NA cation in both 100 ps and 10 ns —100 ns time regions. This result shows clearly that dissociated ion radicals are produced in these polar solvents. However, contrary to the case of nonpolar solvent, cation radicals can be produced not only by electron transfer from excited NA to pyridines followed by ionic dissociation but also by laser induced electron ejection to polar solvent. Therefore, more quantitative studies are necessary for the elucidation of the details of reaction mechanism. In Fig. 5, transient absorption spectra in water observed by means of ps and ns laser photolysis methods are indicated in the case of NA–P system.

*Peculiar Nature of the Quenching by Pyridine.* There is a definite relation between the bimolecular quenching rate constant $k_q$ and the free energy change $\Delta G^\circ$ of Eq. 3 in acetonitrile solution for some typical electron donor acceptor systems including heteroexcimers.[9] According to this relation between $k_q$ and $\Delta G^\circ$, the $\Delta G^\circ$ value estimated for NA–P system in acetonitrile (−8.1 kcal/mol, Table 2) corresponds to almost diffusion-controlled value of $k_q$ ($\approx 10^{10}$ $M^{-1}$ $s^{-1}$), contrary to the observed value of $10^8$ $M^{-1}$ $s^{-1}$. Moreover, since the ionization potential of DMNA may be smaller than that of NA, the $\Delta G^\circ$ value of DMNA–P system in acetonitrile seems to be more negative predicting diffusion-controlled $k_q$ value. Actually, however, fluorescence of DNMA is not affected by added pyridine in acetonitrile solution. These results clearly show that the ordinary $k_q$-$\Delta G^\circ$ relation of electron transfer quenching does not hold for the NA–P and DMNA–P systems. Thus, even if the reaction is sufficiently exothermic, the electron transfer reaction does not occur in the case of DMNA–P system in acetonitrile and the hydrogen bonding interaction is necessary in the case of NA–P system in acetonitrile. Although the reason for this result is not very clear at the present stage of investigation, one should note this specific nature of photochemical electron transfer.

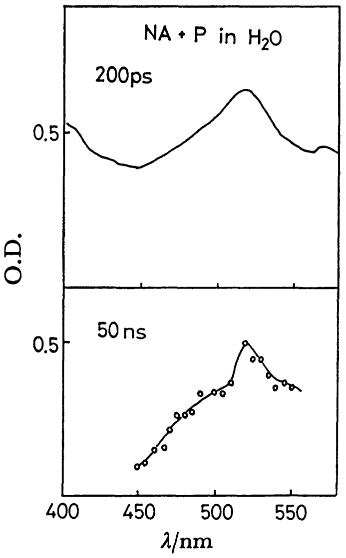

Fig. 5. Transient absorption spectra of NA–P system in water obtained by ps and ns laser photolysis method. [NA]=$3 \times 10^{-4}$ M, [P]=0.25 M.

The hydrogen bonding interactions between chromophores as well as between chromophores and environmental water seem to play important roles in biological systems. The present results may be of some importance also from such a point of view. More detailed fluorescence quenching and ionic photodissociation studies upon various hydrogen bonding systems are now going on in this laboratory.

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