Picosecond LIF Studies on the Base-Catalyzed Proton-Transfer Reactions of Some Aminopyridines in Aqueous Solutions

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Fluorescence quenching phenomena for systems of 2-aminopyridine (2-AP), 2,6-diaminopyridine (2,6-DAP), and 3,4-diaminopyridine (3,4-DAP) with sodium hydroxide in aqueous solutions were investigated by means of picosecond laser-induced fluorescence time-profile measurements. A comparison with the steady state fluorescence spectra of these systems showed that the former two amino compounds are successively catalyzed with sodium hydroxide in the excited state to form hydrogen-bonded exciplexes and anions, while 3,4-DAP showed normal fluorescence. The relations among the reaction rate constants for three aminopyridines are discussed.

Hydrogen bonding and proton transfer in the excited state of heterocyclic compounds are elementary processes which play important rolls in organic and biochemical reactions. Recently, the dynamics concerning such reactions were elucidated by measurements of the fluorescence time profiles in the picosecond region.[1—3] On the other hand, fluorescence quenching by sodium hydroxide has been reported by Boaz et al.[4] for 1- and 2-naphthylamines and by Testa et al.[5] for 2- and 3-aminopyridines. The observed quenching rate constant of 3-aminopyridine in the first excited state was 6.6×10^9 M^{-1} s^{-1} (1 M=1 mol dm^{-3}).

Previously, we measured the fluorescence spectra of 2-aminopyridine (2-AP) and 2,6-diaminopyridine (2,6-DAP) in alkaline solutions,[6,7] where we observed, in common, two distinct peaks, one with a small Stokes shift and the other with a much larger shift. Judging from the appearance of the latter peak in highly alkaline solutions, we assigned this fluorescence with a large Stokes shift to have originated from the anion, which is formed by a fast intermolecular proton-transfer reaction from 2-AP (or 2,6-DAP) to sodium hydroxide.

In the present study we measured the fluorescence quantum yield with cw light excitation parallel to a measurement of the fluorescence time profile (rise and decay) with picosecond pulse laser excitation. The observed systems were 2-AP, 2,6-DAP, and 3,4-DAP in aqueous solution with sodium hydroxide ranging from 10^{-3} to 3.5 mol dm^{-3} at room temperature. 3,4-DAP was tested in order to check the effect of amino groups in number and of substituted positions. The results of the experiments offered a quantitative interpretation of base-catalyzed proton-transfer reactions in the excited states of aminopyridines.

Experimental

Materials. 2-AP and 2,6-DAP were treated in the same way as previously reported.[6,7] 3,4-DAP (Aldrich Chemical Co.) was purified by recrystallizing twice from ligroine to give a sample of with a melting point of 219—220°C. Sodium hydroxide of extra-pure grade (Kanto Chemical Co.) was used as supplied. Distilled water was used to prepare the solutions.

UV Absorption and Fluorescence Measurements. The apparatuses used for UV absorption and fluorescence measurements were the same as those described previously.[6,7] The concentration of the aminopyridines was kept as 10^{-4} mol dm^{-3}. The spectra were measured at room temperature over the range of 10^{-3} to 3.5 mol dm^{-3} of sodium hydroxide concentration (hereafter denoted as [NaOH]). The fluorescence quantum yields were determined by using quinine sulfate as a standard (the fluorescence quantum yield=0.55 in 5×10^{-2} mol dm^{-3} of H_2SO_4 at room temperature).[8]

Fluorescence Time-Profile Measurements. A synchronously pumped cavity-dumped dye laser (Spectra Physics 375B-374), operated with a mode-locked Nd-YAG laser (Spectra Physics 3460), was used as a picosecond excitation light source. The laser was operated with a pulse width (FWHM) of 6 ps (estimated with an autocorrelator; Inrad 5-14) and a repetition rate of up to 800 kHz. The excitation wavelength was covered by the second harmonic emissions (SHG crystal; β-BBO) of Rhodamine 6G and DCM lasers. Fluorescence emission was detected by a multichannel plate photomultiplier (Hamamatsu Photonics R2809U-01). A single-photon counting system (EG & G ORTEC) connected to a 0.25 meter monochromator (NIKON G250) was used for time-profile measurements. Signals from the photomultiplier were amplified with a 1.3 GHz preamplifier (Heulette Paccard HP-8447F) and shaped with a constant-fraction differential discriminator (ORTEC 583). The properly line-delayed (ORTEC 425A) output pulse was used as a stop pulse for a biased time-to-pulse height converter (ORTEC 457). The dye laser pulse was monitored with a high-speed PIN-photodiode (Hamamatsu Photonics S1722-02), discriminated with a 100 MHz discriminator (ORTEC 436) and used as a start pulse. A multichannel analyzer (ORTEC 7800) was coupled with a microcomputer system (NEC PC9801VX) for saving data. Through a modification of the detecting systems, the apparent pulse width of the exciting laser was found to be about 60 ps; the rise and decay shapes of the sample emissions were analyzed by a convolution-simulation method using the observed time profile of scattered laser light as a reference.

Fluctuations of the laser power result in timing jitter. In this work, the laser system was stabilized so as to ensure long-time accumulations with minimum time walk. Fur-

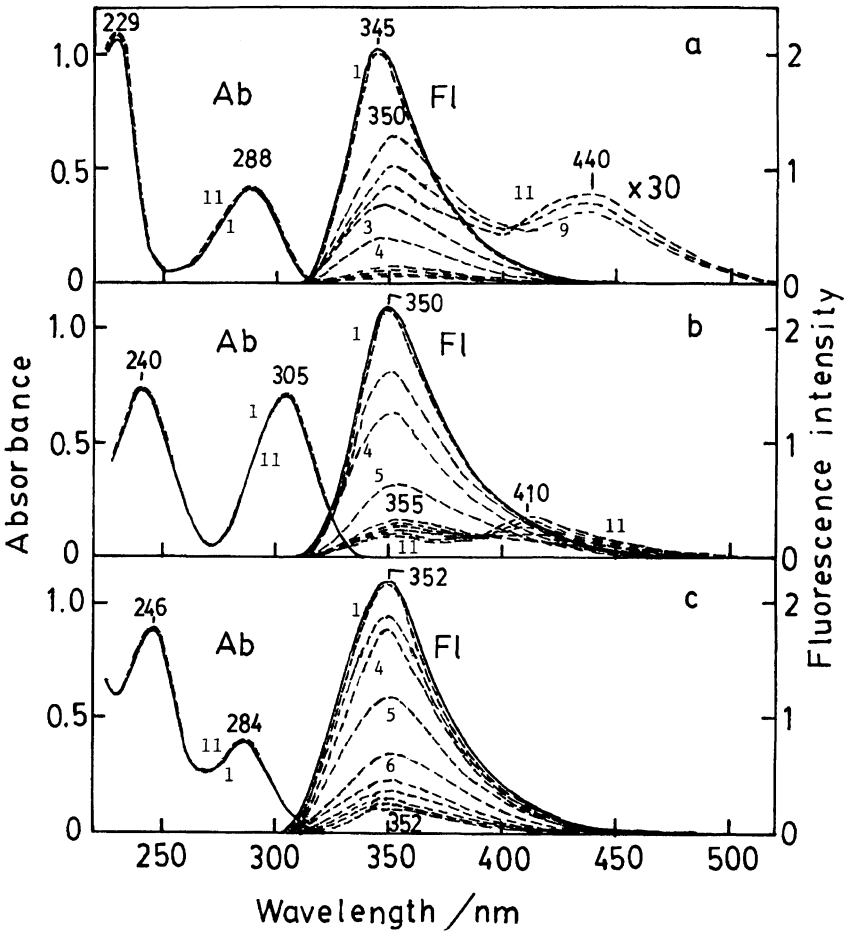


Fig. 1. UV absorption (Ab) and fluorescence (Fl) spectra of 2-AP/NaOH (a), 2,6-DAP/NaOH (b), and 3,4-DAP/NaOH (c) in various concentrations of sodium hydroxide in aqueous solution at room temperature. Concentration of aminopyridine: 1.0×10^{-4} mol dm^{-3}; concentration of NaOH (mol dm^{-3}): (1) 1×10^{-3}, (2) 1×10^{-2}, (3) 5×10^{-2}, (4) 1×10^{-1}, (5) 5×10^{-1}, (6) 1.0, (7) 1.5, (8) 2.0, (9) 2.5, (10) 3.0, (11) 3.5.

thermore, the time profiles of the laser pulse just before and after a sample measurement were compared in order to obtain the upper limit of the time walk. Details concerning the single-photon counting system for picosecond regions have been reported by Yamazaki et al.[9]

Results and Discussion

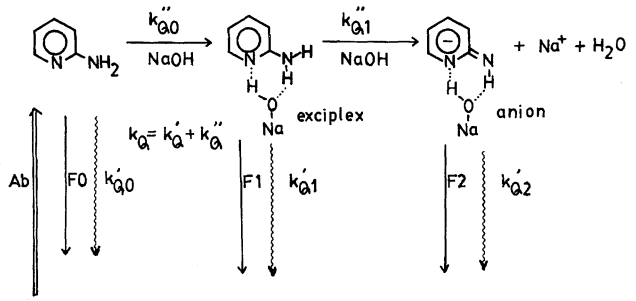
UV Absorption and Fluorescence Spectra. In previous papers,[5—7] 2-AP and 2,6-DAP in pure water were observed to exhibit absorption of the neutral-form molecule overlapped with that of the pyridinium form molecule; that the pyridinium band vanishes upon the addition of a small amount of NaOH.

Figures 1a, 1b, and 1c include the observed absorption and fluorescence spectra of 2-AP, 2,6-DAP, and 3,4-DAP, respectively, in water with various concentrations of NaOH. Numbers on eleven lines of absorption and fluorescence spectra correspond to the concentrations of NaOH (10^{-3} mol dm^{-3} for line 1 and up to 3.5 mol dm^{-3} for line 11). Here, we can see that the pyridinium species of these aminopyridines are almost absent in the ground state as well as in the excited state in the case of a solution with [NaOH] of 10^{-3} mol dm^{-3} (line 1). We adopted this condition (aminopyridines in water with 10^{-3} mol dm^{-3} of [NaOH]) as the standard for a neutral form fluorescence measurement in order to minimize the contribution of the pyridinium forms.

Numbers 1 and 11 on the absorption band (288 nm for 2-AP, 305 nm for 2,6-DAP, and 284 nm for 3,4-DAP) indicate that there were no changes in either the intensities or the band positions of the UV absorption spectra upon further additions of NaOH. This result infers that the ground and first excited states of these systems remain unchanged over the concentration range of the NaOH tested.

The fluorescence spectra of these molecules changed drastically upon the addition of NaOH. Figure 1c shows that 3,4-DAP gives a very weak fluorescence band at 352 nm. Although this band is quenched rapidly as the concentration of NaOH increases, the band shape and position remain unchanged. We designate this normal fluorescence as F0.

Figures 1a and 1b show, on the contrary, that there appear two fluorescence bands in the cases of 2-AP and



Scheme 1.

2,6-DAP. The relatively strong band at 345 nm for 2-AP and at 350 nm for 2,6-DAP (hereafter called as F1) continually loses its intensity while another new weak band, F2 (440 nm for 2-AP and 410 nm for 2,6-DAP), grows up as [NaOH] increases up to 3.5 mol dm^{-3}. Lines 9 to 11 of 2-AP are exaggerated for clarity to show the isofluorescing point at 405 nm. The isofluorescing point for 2,6-DAP at around 390 nm is not very clear.

As was described previously, band F1 is ascribed to the fluorescence of a hydrogen-bonded exciplex between the neutral form of aminopyridines and NaOH. Band F2 was assigned to emission from the moiety of 2-pyridylamide ions formed by proton extraction (Scheme 1).

In this Scheme, k_Q is the quenching rate constant, and should be the sum of the internal conversion rate (k'_Q) and the exciplex, or anion, formation rate (k''_Q) in the case of 2-AP.

Quenching Dynamics Observed by ps LIF. The fluorescence time profiles (rise and decay) of aminopyridines were measured by picosecond pulse laser excitation. The sample conditions were the same as those in the cw excitation experiment mentioned above.

Figure 2 shows the fluorescence time profile of 3,4-DAP (F0). This time profile has a very fast rise, which indicates that the fluorescence comes directly from an excited state which is populated immediately by the laser pulse. The decay is a single-exponential over the entire range of [NaOH] (10^{-3} to 3.5 mol dm^{-3}). Figure 3 is the time profile of 2,6-DAP under standard conditions (10^{-3} mol dm^{-3} [NaOH]), excited at 300 nm and observed in the F1 region. Here, the shape of the exciting laser pulse is indicated by the hatched region. When we assume an instant rise the time profile convoluted with the laser pulse shape should be the dashed line. The difference between this line and the observed data (dotted line) clearly indicates that this emission is not the direct fluorescence. Fitting to the observed data requires a considerably slow rise (260 ps) and long decay (2 ns), as shown by the solid line.

Figure 4 includes the observed and calculated time profiles of another case (2,6-DAP, [NaOH] = 1.0 mol dm^{-3} (line 6 of Fig. 1b), excitation 300 nm, observed at 330 nm and 440 nm). The F1 band at 330 nm again shows a finite rise. This result shows that

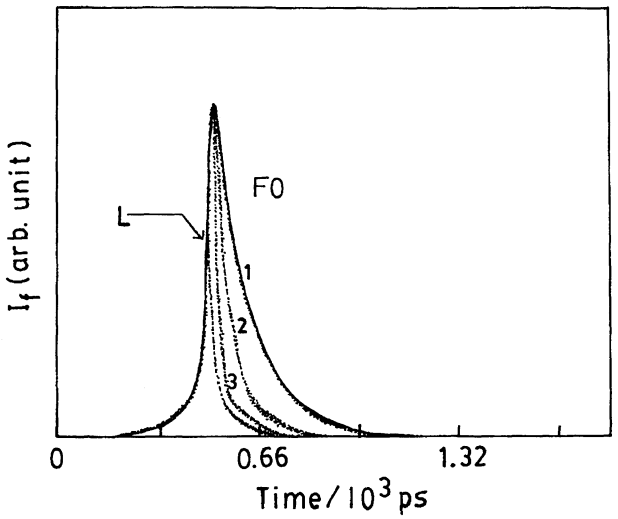


Fig. 2. Time profiles of the excitation laser (L) and F0 fluorescence measured with the single-photon counting system for 3,4-DAP/NaOH in different concentrations of NaOH at room temperature. Concentration of 3,4-DAP is 1×10^{-4} mol dm^{-3} and concentrations of NaOH, (1) 1×10^{-3}, (2) 1×10^{-1}, (3) 2.0 mol dm^{-3}. The wavelengths of the excitation and observation were 290 and 360 nm. The decays were simulated with the laser shape, the values of which were (1) 169, (2) 132, and (3) 26 ps, respectively.

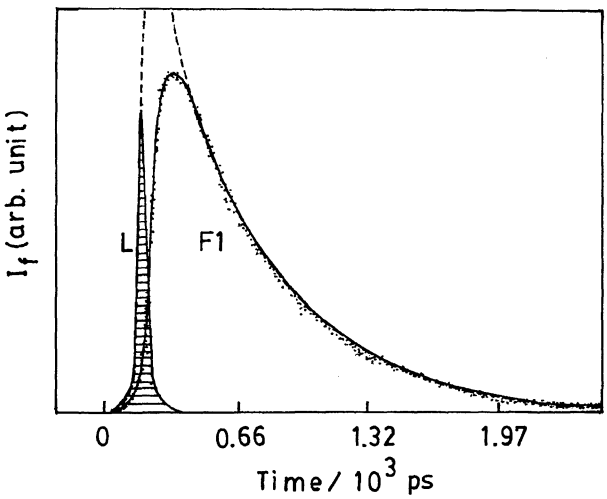


Fig. 3. Time profiles of the excitation laser (L) and F1 fluorescence measured with the single photon counting system for 2,6-DAP at the standard conditions (10^{-3} mol dm^{-3} [NaOH]). Wavelengths of excitation and observation were 300 and 330 nm, respectively. The fitting to the observed data was simulated with slow rise 260 ps and long decay 2 ns.

the F1 band is not of the first excited state (monomer), but of the exciplex, and thus supports the former assignment on the bases of observed small Stokes shift and the CNDO calculations.[6] The time profile of the F2 band observed at 440 nm was found to have both a rise and decay slower than those for F1. The real shape of F2

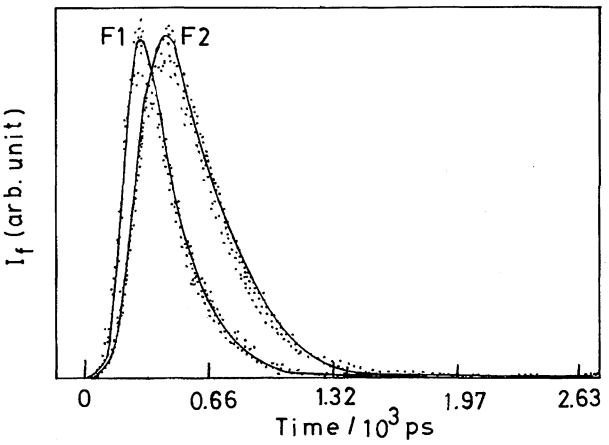


Fig. 4. The observed and calculated time profiles of 2,6-DAP/NaOH (2,6-DAP = 1×10^{-4} mol dm^{-3}, [NaOH] = 1.0 mol dm^{-3}). Wavelength of excitation was 300 nm, those of observation at 330 nm (F1) and 440 nm (F2). F1 ; the rise and decay were 66 and 477 ps, respectively. F2 ; the decay was simulated with the shape of F1 and the decay value was 181 ps.

was uniformly analyzed by convoluting with the pulse shape of the F1 band (not of the laser) with the postulated decaytime constants of 181 ps. A fitting curve for the F2 band is also shown in Fig. 4. The success in convoluting the F2 time profile with that of F1 indicates that the F2 band with a large Stokes shift originates from a secondary product via the exciplex.

The risetime of F1 is expected to be the same as the decay of the first excited state emission (F0), if it could be observed. Three decayrate constants (k_0, k_1, and k_2 (=1/decaytime)) of the F0, F1, and F2 bands were thus deducted for 2-AP, 2,6-DAP, and 3,4-DAP for various alkaline concentrations. Figure 5 is a plot of these decayrates as a function of [NaOH] in the log–log scale. The results clearly show that k_0 of three molecules gradually becomes larger with the increasing [NaOH] values. The values of k_1 for 2-AP and 2,6-DAP also increase, while those of k_2 decrease, depending on the increase in the concentration of NaOH.

We analyzed the results based on the assumption of the reaction scheme shown as Scheme 1 in the preceding section. Here, we can take the emission lifetime as being a measure of base-catalyzed three-step successive reactions, where the decayrate constants for F0, F1, and F2 are expressed as follows:

$$k_i = k_{fi} + k_{Qi} \times [\mathrm{NaOH}], \qquad i = 0, 1, \text{ and } 2. \quad (1)$$

Here, the first term on the right-hand side of Eq. 1 (k_{fi}) represents the fluorescing rate of the sample under standard conditions; the second term, which is linearly dependent on [NaOH], is the reaction rate. If the attack of NaOH accelerates the reaction, the slope of the

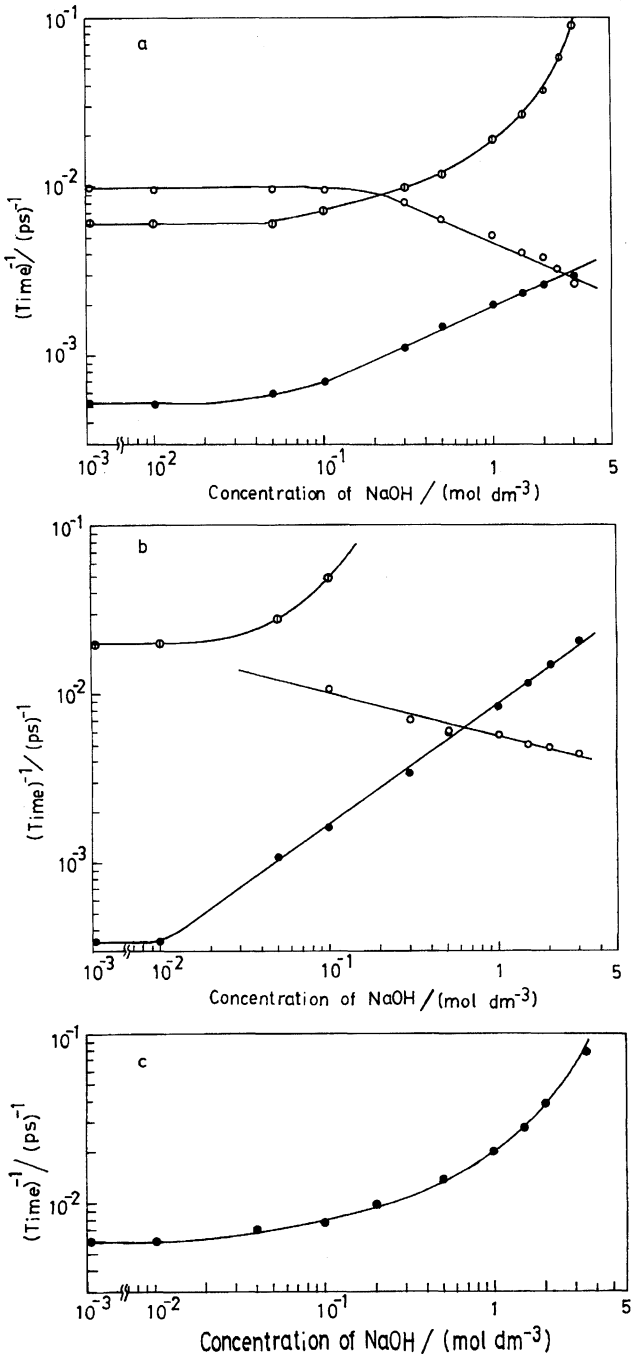


Fig. 5. Plots of decayrate constants k_0(●), k_1(Φ), and k_2(○) of F0, F1, and F2 bands vs. the concentrations of NaOH for 2-AP (a), 2,6-DAP (b), and 3,4-DAP (c), respectively.

second term plotted on the log–log scale should be +1,

$$\mathrm{d}\ (\log K_Q)/\mathrm{d}(\log[\mathrm{NaOH}]) = 1. \quad (2)$$

Figures 6, 7, and 8 are log–log plots of the second term of Eq. 1 for k_0, k_1, and k_2, respectively, which were deduced as the difference of the observed decayrates for several values of [NaOH] (k_i) and that of the standard conditions (k_{fi}). The values of k_{fi} are given in the fig-

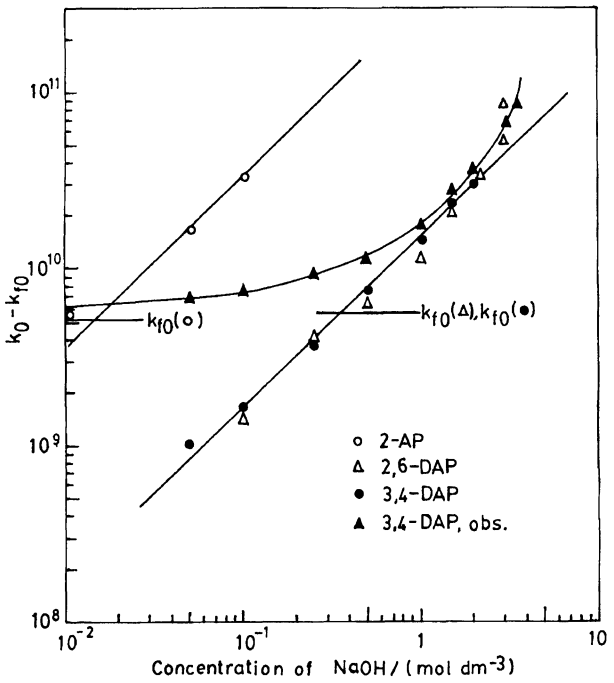


Fig. 6. Log–log plots of k_0-k_{f0} vs. the concentration of NaOH for 2-AP(○), 2,6-DAP (△), and 3,4-DAP (●, observed k_0, ▲).

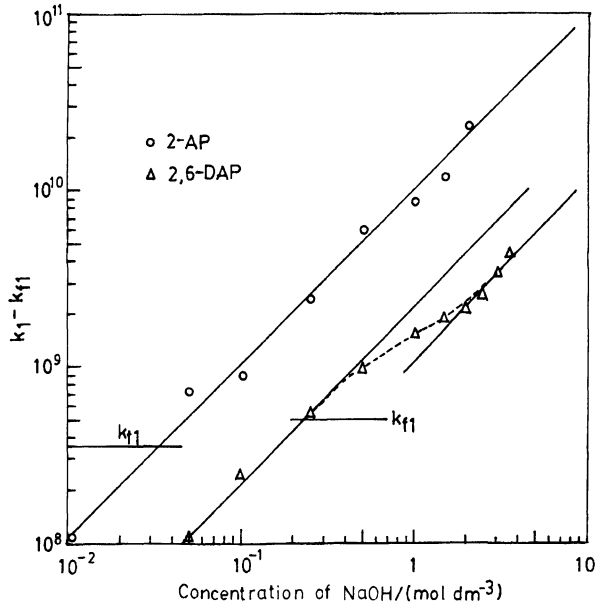


Fig. 7. Log–log plots of k_1-k_{f1} vs. the concentration of NaOH for 2-AP (○) and 2,6-DAP (△).

ures with short horizontal lines. The values of the tangent of the slopes for k_0 and k_1 are seen to be +1, as expected, while those for k_2 are negative and smaller than 1. The k_{Qi} values were read from the crossing points of the slopes with the vertical line at [NaOH]=1 mol dm^{-3}. The final values of the rate constants are summarized in Table 1. Figure 9 shows the plots of the initial intensities (preexponential factors) of F1 and F2 emissions, deduced from the observed fluorescence

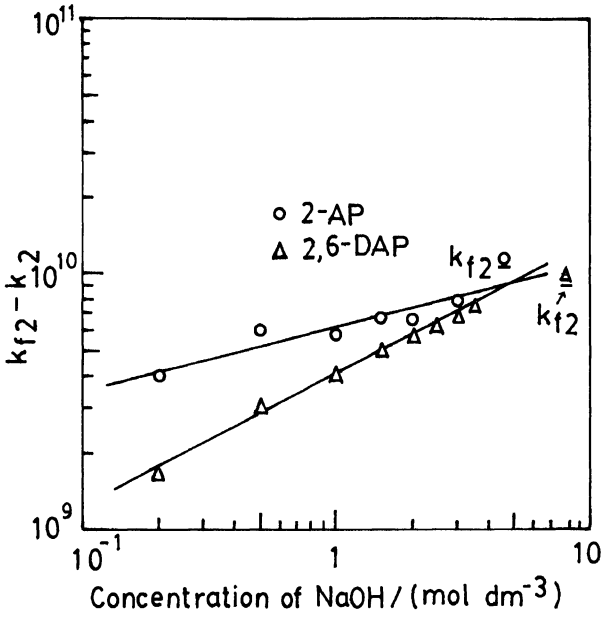


Fig. 8. Log–log plots of $k_{f2}-k_2$ vs. the concentration of NaOH for 2-AP (○) and 2,6-DAP (△).

quantum yields and the decay rates for various [NaOH] for 2-AP and 2,6-DAP.

Discussion Concerning the Nature of the Reaction for Aminopyridines. An inspection of Table 1 shows that the first step of excitation is similar for three aminopyridines ($k_{f0}=5$—6×10^9 s^{-1}). The following reactions are characteristic for three aminopyridines. We observed several points concerning each of them.

(1) 3,4-DAP. 3,4-DAP has no amino groups adjacent to the N atom in the pyridine ring, and the excited molecules seem to be quenched directly back to the ground state ($k_{Q0}=1.4\times10^{10}$ M^{-1} s^{-1}). Since the quenching pattern of 3,4-DAP is the same as that for 2,6-DAP, there may be an intermediate state, exciplex or anion, as suggested by Testa et al.,[5] however, we could not observe any emission bands attributable to such intermediates. So thus believe that although quenching due to collisions of NaOH is deactivative, it is not reactive in the case of 3,4-DAP.

(2) 2-AP. In the case of 2-AP, the quenching of the first excited state is about one order faster than that of the other two samples (3.6×10^{11} M^{-1} s^{-1}). This value is about the same as that of recombination $H^+ + OH^-$ in water.[10] In this case, the quenching rate of F0 is the sum of the deactivation rate and the exciplex formation rate. Because the initial intensities are in the same order for a wide range of [NaOH], as shown in Fig. 9, the exciplex formation rate is estimated to be much larger than the deactivation rate.

Although the quenching of F1 for 2-AP is also fast (1.0×10^{10} M^{-1} s^{-1}), the reaction is typically linear for all of the NaOH concentration regions investigated. Substitution of an amino group at the ortho position

Table 1. Observed Fluorescence Rate Constants (k_f) and Quenching Rate Constants (k_Q) for Three Reaction States of 2-AP, 2,6-DAP, and 3,4-DAP in H_2O with NaOH (Picosecond LIF)[a)]

System	F0		F1		F2	
	k_{f0}/s^{-1}	$k_{Q0}/M^{-1}\,s^{-1}$	k_{f1}/s^{-1}	$k_{Q1}/M^{-1}\,s^{-1}$	k_{f2}/s^{-1}	$k_{Q2}/M^{-1}\,s^{-1}$
2-AP/NaOH	5.2×10^9	3.6×10^{11}	3.5×10^8	1.0×10^{10}	1.0×10^{10}	-6×10^9
2,6-DAP/NaOH	6.1×10^9	1.5×10^{10}	5.0×10^8	2.2×10^9 (<[NaOH] : 0.1 M) 1.1×10^9 (>[NaOH] : 1 M)	1.0×10^{10}	-4.5×10^9
3,4-DAP/NaOH	5.9×10^9	1.4×10^{10}				

a) 1 M=1 mol dm^{-3}.

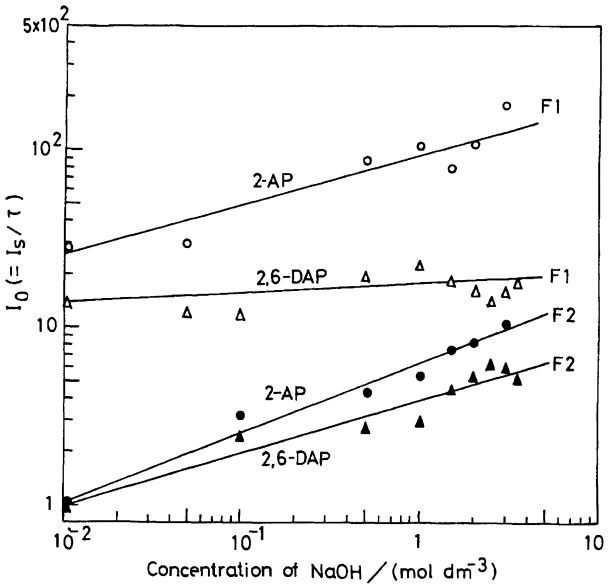
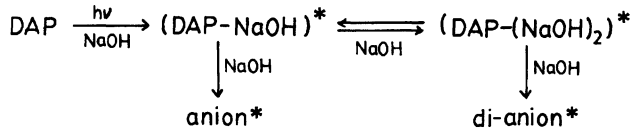


Fig. 9. Polts of the initial intensities (preexponential factors ; $I_0=I_S/\tau$; I_S (total band intensity)) of F1 and F2 fluorescences vs. the concentration of NaOH for 2-AP and 2,6-DAP.

makes the formation of exciplex with NaOH very easy, and in accord, the substraction of a proton from the amino group is accelerated.

(3) 2,6-DAP. 2,6-DAP with two amino groups at ortho positions is more complicated than 2-AP. The behavior of F0 seems to be the same as that of 2-AP. The reaction of the hydrogen-bonded exciplex to an anion appears, however, to involve two steps, as revealed by the two slopes of the tangent (+1), connected in a reversed S shape in Fig. 7. As shown in Scheme 2, we can postulate the formation of a di-anion, because: 1) the plotted S-shaped line is just the same as the titration curve for acid-base conversions; 2) the ratio of the quenching rates for these two slopes is 2.0; 3) the errors of the decay measurement (less than 10 percent) are much smaller than the deviation of the data from one single line; and 4) the ambiguity of the isofluorescing point for F1–F2 overlapping is seen only for this molecule. Two values of k_Q are listed in Table 1, along with the valid NaOH concentration regions.

Apart from these considerations, the N atom in the pyridine ring of 2,6-DAP seems to be less reactive than that of 2-AP.



Scheme 2.

(4) Stabilization of Anions. As for the F2 band, a precise measurement of the time profile is rather difficult in dilute NaOH regions because of the overlap of the stronger F1 band. In more basic regions, the k_Q term does not follow the quenching relation (Eq. 2), but decreases with increasing [NaOH], as can be seen in Fig. 8. This tendency implies stabilization of the anion under highly basic conditions. Satisfactory explanations for this stabilization are presently absent. Figure 9 shows the initial intensities of the F2 band for 2-AP and 2,6-DAP against [NaOH]. The increase in the initial intensity with increasing [NaOH] is a measure of the k''_{Q1} term increasing relative to the k'_{Q1} term in Scheme 1. The F2 band earns its intensity in highly basic solutions partly due to the increasing k''_{Q1} term, and partly due to the longer decay mentioned above.

(5) Kinetic Relations. The k_Q values given in Table 1 demonstrate that diffusion-controlled collisional quenching phenomena occur even in the time range shorter than 10 ps, much faster than the molecular reorientation time.[11] The competition between the original emission rate (k_{fi}) and the base-catalyzed reaction speed ($k_{Qi} \times$[NaOH]) determines the patterns of the reaction. If the rate equation is governed by the statistical formula, first or intermediate state emission should have double-exponential decay originating from the back reaction rate.[12] In the present study, the emissions from three reaction states were safely convoluted with each other without any supposition of particular rate-determining steps, such as back reactions or potential hindrance. This result supports the findings by Konijnenberg et al.[1] concerning the barrierless double-proton transfer in pyrrolo[2,3-*b*]pyridine. We can expect that in the present case one way and a successive reaction scheme is probable, partly because the excitation, as well as the reaction, is so fast, and partly because the energy difference between the exciplex (F1) and anion (F2) states is sufficiently large (about 5000 cm^{-1} measured at maxima of emission bands) as a result of proton transfer.

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