Excited-state Electronic Interaction of *m*-Aminoacetophenone with Aliphatic Alcohols

Yoshifumi TANIMOTO,* Kenji INOUE, Yoshihiko FURUKAWA, Yoko SEGAWA, and Michiya ITOH

Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920

(Received November 1, 1978)

The electronic interaction of both ground-state and excited-state *m*-aminoacetophenone (MAAP) with several aliphatic alcohols in nonpolar viscous solvent was investigated by steady-state and nanosecond fluorescence spectroscopies. Concentration dependence of several alcohols in liquid paraffin-hexane (LPH) mixed solvent upon fluorescence and absorption spectra suggests a complex formation of MAAP with aliphatic alcohols in the ground state. In the typical LPH solution of MAAP containing high concentration of alcohol, the complex fluorescence exhibits two-component decay and a longer wavelength fluorescence than the complex fluorescence exhibits a rise and decay. The results demonstrate that the complex in the excited state further associates with alcohol to make an exciplex including an alcohol molecule.

The fluorescence properties of many aromatic molecules strongly depend on the solvent system; fluorescence maximum, fluorescence quantum yield, and lifetime remarkably change from nonpolar to polar solvent. In most cases, these changes have been explained in terms of "the solvent effect," which usually involves dispersion force of solvent, and dipole-dipole and dipole-induced dipole interactions between solute and solvent.[1] However, the possibility of a new type of the electronic interaction was reported by Lumry and his coworkers;[2] they suggested the importance of the excited-state solute-solvent complex (exciplex) formation in the polar solvent. Actually, they investigated the fluorescence of indole and indole derivatives in the mixed systems of nonpolar-polar solvents (mainly in pentane–alcohol systems), and showed that an excited-state solute-solvent complex is responsible to a large red shift and loss of vibrational structure in the fluorescence spectra of indole and indole derivatives in the polar solvents. However, since the possibility of the ground state solute-solvent complex was not strictly excluded and since they did not show any dynamical experimental evidence, their explanation does not seem to be generally accepted. On the other hand, Ware and his coworkers[3] investigated the problem of the origin and nature of the temperature-dependent spectral shift characteristic of aminophthalimides in alcoholic solvents by the aid of nanosecond time-resolved emission techniques. They showed that at least two relaxation times characterize the phenomenon. One relaxation time was observed to be subnanosecond in character and may be associated with the exciplex that presumably is present in the system. The other relaxation time was presumably associated with the nonspecific dipolar reorientation. Recently, the interaction of 2-anilinonaphthalene with ethyl alcohol and glycerol in the excited state was studied by DeToma and Brand.[4] They showed a direct kinetic evidence that 2-anilinonaphthalene undergoes a specific reversible association with ethyl alcohol and glycerol in the excited state.

In the previous paper,[5,6] we have clarified that *m*-aminoacetophenone (MAAP) makes a complex with *t*-pentyl alcohol in the ground state and that the complex further associates with alcohol in the excited state (*i.e.*, the complex in the excited state makes an exciplex with alcohol). However, *t*-pentyl alcohol may be not so popular as ethyl alcohol in spectroscopic studies, and the results look some special case. Therefore, we have extended the study to other alkanols. This paper describes the excited-state complex formation (exciplex formation) of MAAP with several alcohols, and the results clearly suggest the general importance in studying the fluorescence properties of polar aromatic molecules in the alcoholic solvents.

Experimental and Kinetic Analysis

MAAP (Nakarai EP Grade) was recrystallized twice from ethyl alcohol, followed by vacuum sublimation. *t*-Butyl alcohol, butyl alcohol (both Nakarai EP Grade) were dried with molecular sieve and thereafter distilled. Isopropyl alcohol (Merck Uvasol) and ethyl alcohol (Nakarai Spectro Grade) were used as supplied. Liquid paraffin and hexane (both Nakarai Spectro Grade) were also used as supplied. The mixture of them (9: 1 volume ratio) was used as a viscous nonpolar solvent. Solutions for lifetime measurements were degassed with the freeze-thaw technique.

Absorption and fluorescence spectra were measured on Hitachi 323 and MPF-4 spectrophotometers at room temperature unless denoted. Fluorescence lifetimes were measured with a similar method described in a previous paper.[5] Observed lifetimes were analyzed by a nonlinear least-squares method including the exciting pulse shape.[7]

For the fluorescence quantum yield measurements,[8] the spectral response of the observed system was corrected by using the fluorescence of quinine sulfate in 0.5 M sulfuric acid as a standard. Fluorescence spectra of both ethyl alcohol solutions of MAAP and quinine sulfate standard solution were measured successively, and after correcting absorbances and refractive indices, the quantum yield of ethyl alcohol solution of MAAP was determined. Here, the quantum yield of quinine sulfate solution was assumed to be 0.55, and solutions were excited by the 360 nm light. The yields of other solutions were then determined by using the ethyl alcohol solutions of MAAP as a second standard and by correcting similarly.

The experimental results are shown to be consistent with the kinetic scheme given below.[9]

$$\mathrm{MAAP} + \mathrm{A} \overset{K}{\rightleftharpoons} \mathrm{C} \qquad (1)$$

$$\mathrm{C} \xrightarrow{h\nu} \mathrm{C}^* + \mathrm{A} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{E}^* \qquad (2)$$

$$\mathrm{E}^* \xrightarrow{k_1} \mathrm{C} + h\nu' \qquad \mathrm{E}^* \xrightarrow{k_2} \mathrm{C} \qquad \mathrm{E}^* \xrightarrow{k_5} \mathrm{C} + \mathrm{A} + h\nu'' \qquad \mathrm{E}^* \xrightarrow{k_6} \mathrm{C} + \mathrm{A}$$

where A, C, C*, and E* are alcohol, the complex, the complex in the excited state, and excited-state complex (exciplex) generated from C* and A, respectively; K is equilibrium constant of the complex formation in the ground state, and k's are rate constants of respective processes.

Under photostationary state, the process 2 gives the following equations;

$$[C]/F_C = c'\{k_3(k_5+k_6)[A]/(k_4+k_5+k_6)+k_1+k_2\} \quad (3)$$

$$F_E/F_C = c''k_3k_5[A]/\{k_1(k_4+k_5+k_6)\} \quad (4)$$

$$\phi = \{(k_4+k_5+k_6)k_1+k_3k_5[A]\}/\{(k_1+k_2+k_3[A]) \times (k_4+k_5+k_6)-k_3k_4[A]\} \quad (5)$$

In Eqs. 3, 4, and 5, F_C and F_E are the fluorescence intensities of C* and E*, respectively; [A] and [C] are the concentrations of the alcohol and the complex, respectively, ϕ is the fluorescence quantum yield of total emission, and c' and c'' are proportional constants.

For the pulse excitation, following equations are also obtained.

$$[C^*] = c_1 \exp(-\lambda_1 t) + c_2 \exp(-\lambda_2 t) \quad (6)$$

$$[E^*] = c_3\{\exp(-\lambda_1 t)-\exp(-\lambda_2 t)\} \quad (7)$$

where

$$\lambda_{1,2} = 1/2[k_1+k_2+k_3[A]+k_4+k_5+k_6 \mp \{(k_4+k_5+k_6 -k_1-k_2-k_3[A])^2+4k_3k_4[A]\}^{1/2}]$$

$$c_1 = [(\lambda_2-X)/(\lambda_2-\lambda_1)][C^*]_0$$

$$c_2 = [(X-\lambda_1)/(\lambda_2-\lambda_1)][C^*]_0$$

$$c_3 = k_3[A][C^*]_0/(\lambda_2-\lambda_1)$$

$$X = k_1 + k_2 + k_3[A]$$

and

$$\lambda_1 + \lambda_2 = k_1 + k_2 + k_3[A] + k_4 + k_5 + k_6 \quad (8)$$

Results and Discussion

Absorption and Fluorescence Spectra of MAAP. Figure 1 shows the absorption and fluorescence spectra of MAAP in several solvents. In hexane, absorption maximum appears at 325 nm and no fluorescence band is practically observed. In 2-methyltetrahydrofuran (MTHF), the absorption maximum of MAAP shifts to the longer wavelength (λ_{max} 340 nm), while a strong fluorescence band appears at ≈420 nm. The absorption maxima of this compound in tetrahydrofuran, MTHF, and several alcohols appear in similar wavelength region each other, while the fluorescence in alcohols remarkably shifts to 490—510 nm. The Stokes shifts in alcoholic solvents are about 9000—10000 cm^{-1}, though about 5600 cm^{-1} in MTHF. The unusually large Stokes shift seems to suggest some specific interaction between MAAP and alcohols. Since general feature of the absorption and fluorescence spectra was common in all systems reported here (*i.e.*, MAAP–*t*-butyl alcohol, MAAP–butyl alcohol, MAAP–isopropyl alcohol, and MAAP–ethyl alcohol), the results on the MAAP–*t*-butyl alcohol in liquid paraffin–hexane mixed system (abbreviated to LPH hereafter) were mainly described in this paper. Figure 2 shows the concentration dependence of *t*-butyl alcohol (TBA) in the LPH solution of MAAP upon fluorescence spectra. Although MAAP is practically non-fluorescent in LPH, the fluorescence with a short lifetime appears at ≈430 nm by adding a small amount of TBA, and the band increases in intensity with increasing the concentration of TBA (<0.2 M) (1 M=1 mol dm^{-3}). Furthermore, including a small red shift, a new band with a long lifetime appears at ≈490 nm, and increases in intensity with further increasing the concentration of the alcohol (>0.2 M).

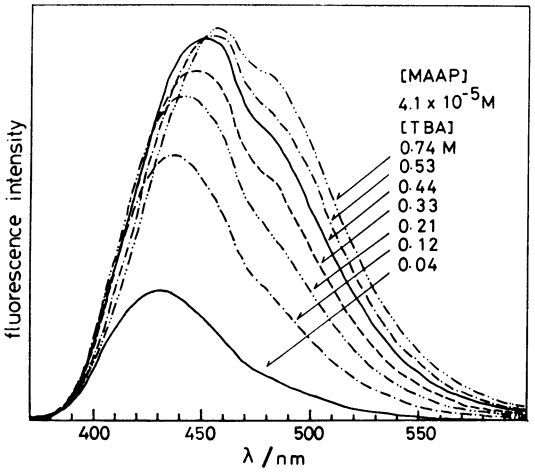

Fig. 2. Fluorescence spectra of MAAP in LPH containing several concentrations of TBA. The excitation wavelength is 360 nm.

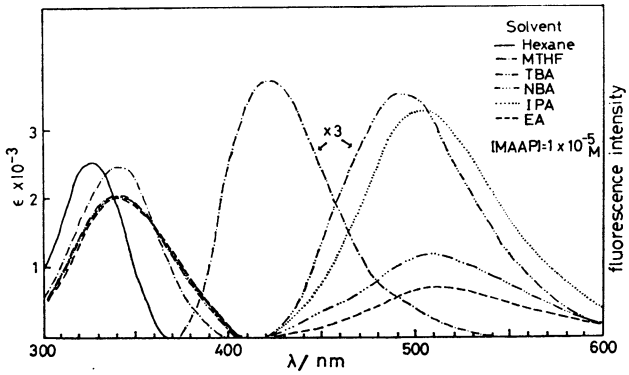

Fig. 1. Absorption and fluorescence spectra of MAAP in various solvents; MTHF, 2-methyltetrahydrofuran; TBA, *t*-butyl alcohol; BA, butyl alcohol: EA, ethyl alcohol. The excitation wavelength is 360 nm.

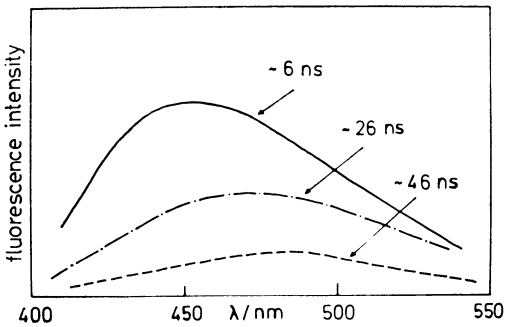

Fig. 3. Time-resolved fluorescence spectra of MAAP (1.4 $\times 10^{-5}$ M) in LPH containing TBA (1×10^{-1} M). Times indicated are after a peak of an exciting laser pulse.

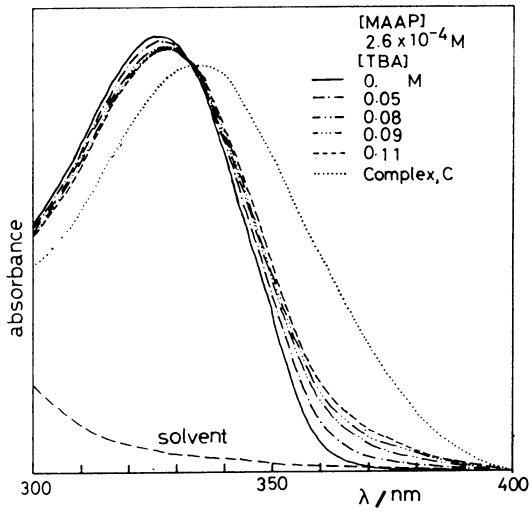

Fig. 4. Absorption spectra of MAAP in LPH, containing several concentrations of TBA. Absorption spectrum of the complex, C, was depicted from K and concentrations of MAAP and TBA.

Time-resolved fluorescence spectra in Fig. 3 exhibit these two kinds of fluorescence bands. Since it can be expected that MAAP and TBA make a hydrogen-bonding complex in the ground state, the shorter wavelength band, which is predominant in the low concentration of TBA, is most probably due to the hydrogen-bonding complex. Figure 4 shows the effect of TBA concentration upon the absorption spectra of MAAP in LPH. A new band appears at ≈360 nm and gradually increases in intensity with increasing the concentration of TBA (an isosbestic point at 334 nm). Therefore, assuming the complex formation in the ground state, the spectra were analyzed in terms of an ordinary 1 : 1 complex formation, shown in Eq. 1.[6] Figure 5 shows the Scott plots of absorption intensity of the new band (I_C) *vs.* [TBA]. The plots exhibit linear relationship, as is clear from Fig. 5, affording an equilibrium constant of 4.6 M^{-1}. Fluorescence intensity of the shorter wavelength band (F_C) was also analyzed in the same manner by assuming that the intensity is proportional to the absorption intensity of the new band. Figure 6 shows the plots of [TBA]/F_C *vs.* [TBA], which afford the equilibrium constant of 3.4 M^{-1}. Both results agree each other within experimental errors.

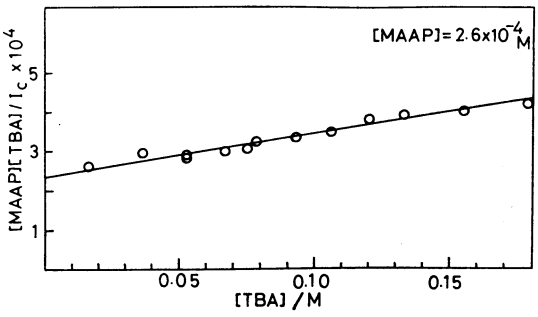

Fig. 5. Plots of [MAAP][TBA]/I_C *vs.* [TBA]. Absorption intensities (I_C) were monitored at 370 nm.

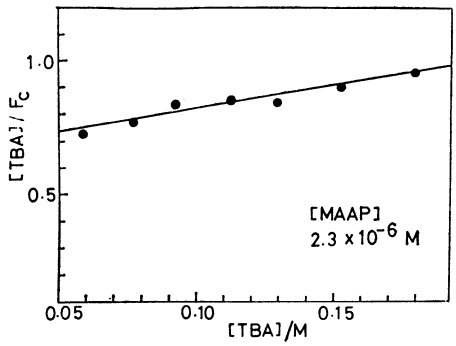

Fig. 6. Plots of [TBA]/F_C *vs.* [TBA]. Fluorescence intensities (F_C) were monitored at 430 nm. In the range of TBA concentration (0.05—0.2 M), spectral shift of the fluorescence was small.

Now, let us examine the longer wavelength fluorescence which appears at rather concentrated solution of TBA. The excitation spectrum monitored at 530 nm (*i.e.*, at the longer wavelength band) is identical with that at 430 nm (*i.e.*, at the shorter wavelength band). Fluorescence intensity of the longer wavelength band increases with increasing the concentration of TBA, as mentioned above. Figures 7 and 8 show the plots of

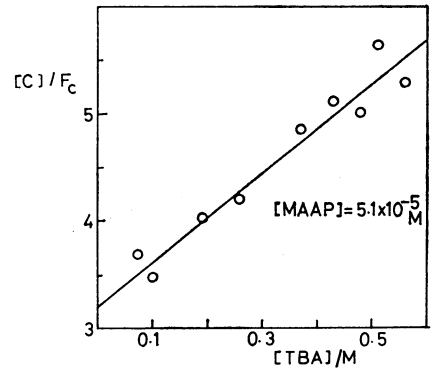

Fig. 7. Plots of [C]/F_C *vs.* [TBA]. Fluorescence intensities (F_C) were monitored at 430 nm. Concentrations of C in the plots were evaluated from K, [MAAP] and [TBA].

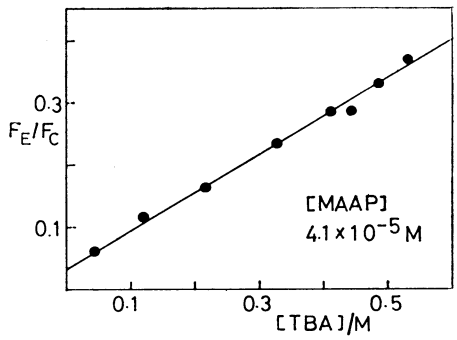

Fig. 8. Plots of F_E/F_C *vs.* [TBA]. Fluorescence intensities, (F_C and F_E) were monitored at 430 nm and at 530 nm, respectively.

[C]/F_C *vs.* [TBA], and F_E/F_C *vs.* [TBA], respectively. They show the linear relationships expected from Eqs. 3 and 4, respectively, though fluorescence intensities, F_C and F_E, may include the spectral shift owing to the change of solvent polarity. With these findings and time evolution of the fluorescence intensities which will be mentioned later, the longer wavelength fluorescence is tentatively ascribed to the exciplex (E*) formed between the complex in the excited state (C*) and TBA.

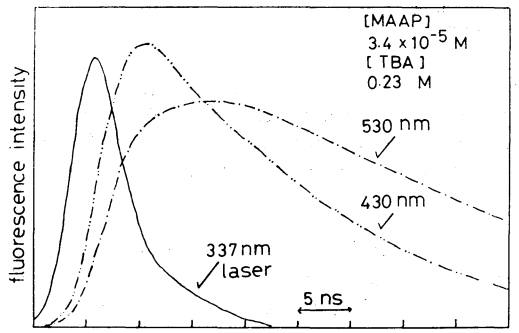

Fig. 9. Time evolution of the fluorescence intensities of MAAP in LPH.

The Time Evolution of Fluorescence and the Estimation of Kinetic Parameters. From Eq. 1, one can expect a simple two-component decay for [C*] and a growth and decay for [E*]. Figure 9 shows the typical time evolutions of the fluorescence of [C*] and [E*], in the MAAP–TBA–LPH system. The shorter wavelength band (C*) exhibits typical two-component decay, and the longer one (E*) shows a growth and decay as expected. The λ_1 and λ_2 obtained from both fluorescence bands coincide with each other within experimental errors. Therefore, these findings provide an evidence that the longer wavelength fluorescence (F_E) is ascribed to the exciplex, E*, generated from C* and TBA.

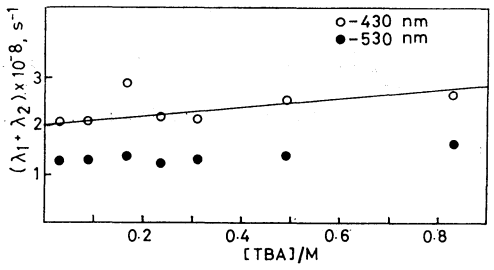

Fig. 10. Plots of $\lambda_1+\lambda_2$ *vs.* [TBA]. Fluorescence intensities were monitored both at 430 nm and at 530 nm. The fluorescence intensities at 530 nm was analyzed as a superposition of the fluorescence of both C* and E*, since both spectra partly overlapped each other in this region. Concentration of MAAP is 3.4×10^{-5} M.

Equation 8 gives k_3 from the plots of $\lambda_1+\lambda_2$ *vs.* [TBA]. As [TBA]$\longrightarrow$0,

$$\lambda_1 \longrightarrow k_1 + k_2$$

$$\lambda_2 \longrightarrow k_4 + k_5 + k_6$$

Thus k_3, k_1+k_2, and $k_4+k_5+k_6$ can be obtained (see Fig. 10). The results were shown in Table 1. Then combining Eq. 4 and the above values obtained, k_4 and k_5+k_6 can be calculated separately (see Fig. 7). If one may calculate the fluorescence quantum yields of more than two TBA concentrations of the solution, one may solve Eq. 5 to estimate k_1 and k_5. From this analysis, the radiative and nonradiative rate constants of respective states, C* and E*, were estimated to be of nearly the same order of magnitude. Furthermore, if only the exciplex formation is an activation process, the energy barrier may be obtained from the plots of F_E/F_C *vs.* $1/T$ (T: temperature, K), assuming that only k_3 in Eq. 4 is temperature dependent.[10] Figure 11 shows this relationship and the activation energy was obtained to be 7 kcal mol^{-1}.

Table 1. KINETICAL PARAMETERS OF THE MAAP–ALCOHOL SYSTEMS IN LPH AT ROOM TEMPERATURE

Alcohol	TBA	BA	IPA	EA
ε[a]	12.5	17.5	19.9	24.5
ϕ[b]	0.56	0.08	0.19	0.05
K, M^{-1} [c]	4.6	5.7	5.6	12.2
$k_3\times10^{-9}$, M^{-1} s^{-1}	0.09	0.31	0.19	0.68
$(k_1+k_2)\times10^{-8}$, s^{-1}	0.58	0.49	0.52	0.69
$(k_4+k_5+k_6)\times10^{-9}$, s^{-1}	0.17	0.15	0.14	0.35

a) Dielectric constant of alcohol. b) Total fluorescence quantum yield (see text). c) Equilibrium constant of the complex formation at room temperature.
TBA, *t*-butyl alcohol; BA, butyl alcohol; IPA, isopropyl alcohol; EA, ethyl alcohol.

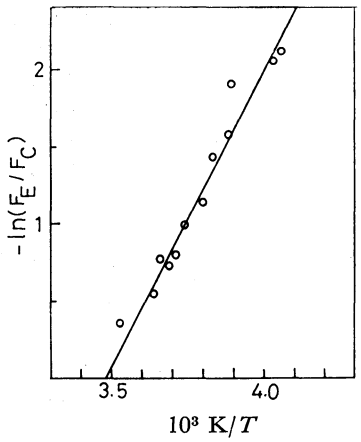

Fig. 11. Plots of $-\ln(F_E/F_C)$ *vs.* $1/T$. Fluorescence intensities, F_C and F_E, were monitored at 430 nm and at 530 nm, respectively. Concentrations of MAAP and TBA are 3.4×10^{-5} M and 0.82 M, respectively.

Fluorescence behavior of the MAAP–butyl alcohol, MAAP–isopropyl alcohol, and MAAP–ethyl alcohol in LPH is essentially parallel to that of MAAP–TBA mentioned above, and observed data in these systems were analyzed in the same procedure as mentioned above. Unfortunately, the activation energy of these systems could not be obtained, because of lack of the solubility of the alcohols at low temperature. The results obtained were listed in Table 1. From the Table,

equilibrium constants of the complex formation seem to increase with increasing strength of the dielectric constant of the alcohols. The rate constants of the exciplex formation, k_3, also seem to increase with the dielectric constant of the alcohols.

Generally, unusually large spectral change observed in the high concentration of TBA (>0.2 M) (see Fig. 2) might be explained in terms of following mechanisms; 1) the internal rotation of MAAP leading to the intramolecular CT interaction in MAAP, 2) the general solvent effect, 3) the reorientation of alcohols around MAAP, and 4) the exciplex formation with the solvent molecules. As for the mechanism 1, the process may be expected to occur very fast in the order of some picoseconds, which is inconsistent with our observation. The mechanism 2 means that the long-range intermolecular interaction between solute and solvent molecules such as dispersion force, dipole-dipole interaction, *etc.*[1] In this mechanism, the effect of alcohol upon the fluorescence band shape may be considered to be small, and wavelength-independent decay in a certain fluorescence spectrum may be expected. However, these are in contradiction to the observation reported here, since Figs. 2, 3, and also 9 show the drastic change of fluorescence band with increasing the TBA concentration, and the time-resolved fluorescence spectra including two different fluorescent species. Then, the mechanism 3 may be ruled out as follows. If MAAP molecule may be surrounded by TBA molecules by adding small amount of TBA in the LPH solution, it is unlikely that there are the two different fluorescent states stable in the excited state of MAAP surrounded by unspecified alcohol molecules. The rate for the reorientation of surrounding molecules may be of the order of picosecond. However, if the alcohol molecule may diffuse to make an interaction with MAAP in LPH, the rate may be of the order of some nanosecond. The diffusion rate constant in LPH is approximately estimated to be of the order of 10^8 M^{-1} s^{-1} from the viscosity of LPH (≈100 cp). With this mechanism, observations shown in Figs. 2, 3, and 9 may be qualitatively explained. Figure 8 shows a linear relationship of F_E/F_C *vs.* [TBA], and may strongly suggest the stochiometric complex formation in the excited state. The mechanism 4 may suggest the specific intermolecular interaction between the complex and another alcohol molecule (*i.e.*, stochiometric excited-state complex formation). As already shown, all the observations have been quantitatively explained with this mechanism. The mechanism 4 seems to be most reasonable in the interpretation of the results observed in this paper.

Preliminary results on the fluorescence of *m*-dimethylaminoacetophenone[11,12] (DMAAP) show essentially the similar fluorescence property to that of MAAP. Although the weak fluorescence band appears at ≈405 nm in LPH, a new fluorescence band appears at ≈430 nm by adding a small amount of TBA, and increases in intensity with increasing the TBA concentration (<0.15 M). Furthermore, with further increasing the TBA concentration, another new fluorescence band appears at ≈490 nm (>0.15 M). The LPH solution of DMAAP containing high concentration of TBA exhibits the two-component decay of the shorter wavelength (at 440 nm), and the rise and decay of the longer wavelength fluorescence (at 530 nm). The similar kinetic analysis suggests that DMAAP makes the 1:1 complex with TBA in the ground state (K=4—10 M^{-1}), and the complex in the excited state (C*) further associate with the alcohol molecule ($k_3=0.08\times10^9$ M^{-1} s^{-1}, $k_1+k_2=0.4\times10^8$ s^{-1}, and $k_4+k_5+k_6=0.1\times10^9$ s^{-1}). Here, if the complex formation in the ground state might be tentatively attributable to a kind of the hydrogen-bonding with alcohol, the interaction between carbonyl of MAAP and hydroxylic hydrogen of alcohol seems to be most reasonable to the complex formation in the ground state. Furthermore, it is likely that the exciplex may be stabilized by the weak electronic interaction such as charge-transfer between C* and alcohol molecule, as already discussed in indole fluorescence by Lumry and his coworkers.[2] However, this is not obvious at this stage.

The authors wish to thank Dr. Kiyokazu Fuke for his help in the analysis of fluorescence lifetimes by a nonlinear least-squares fit, and for valuable discussions.

References

1) N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Dekker, New York (1970), p. 371.

2) M. S. Walker, T. W. Bednar, and R. Lumry, *J. Chem. Phys.*, **45**, 3455 (1966); M. S. Walker, T. W. Bednar, and R. Lumry, *J. Chem. Phys.*, **47**, 1020 (1967); M. S. Walker, T. W. Bednar, and R. Lumry, "Molecular Luminescence," ed by E. C. Lim, Benjamin, New York (1969), p. 135; M. S. Walker, T. W. Bednar, R. Lumry, and F. Humphries, *Photochem. Photobiol.*, **14**, 147 (1971).

3) W. R. Ware, S. K. Lee, C. J. Brant, and P. P. Chow, *J. Chem. Phys.*, **54**, 4729 (1971).

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

5) Y. Tanimoto and M. Itoh, *Chem. Phys. Lett.*, **57**, 179 (1978).

6) In Ref. 5, the 1:2 complex formation of the ground-state MAAP with *t*-pentyl alcohol was presented. The discrepancy between the previous and present results may be explained by the following two possibilities. The difference might be attributable to the nature of *t*-pentyl alcohol somewhat different from others, since the dielectric constant of *t*-pentyl alcohol (ε: 5.8) is much smaller than that of alcohols used in the present work. Otherwise, the spectral changes observed in the previous system may exhibit the 1:2 complex formation in appearence, since the equilibrium constant of the 1:1 complex of MAAP with *t*-pentyl alcohol may be very small.

7) P. R. Berington, "Data Reduction and Error Analysis for the Physical Sciences," McGraw-Hill, New York (1969).

8) J. N. Demas and G. A. Crosby, *J. Phys. Chem.* **75**, 991 (1971).

9) W. R. Ware, D. Watt, and J. C. Holmes, *J. Am. Chem. Soc.*, **96**, 7853 (1974).

10) M. Itoh, T. Mimura, H. Usui, and T. Okamoto, *J. Am. Chem. Soc.*, **95**, 4388 (1973), and references therein.

11) H. Rupe, A. Braun, and K. von Zembrzuski, *Ber.*, **34**, 3522 (1901).

12) R. Nakagaki, S. Nagakura, T. Kobayashi, and S. Iwata, *Bull. Chem. Soc. Jpn.*, **51**, 2867 (1978).