Picosecond and Two-Step LIF Studies of the Excited-State Proton Transfer in 3-Hydroxyxanthone and 7-Hydroxyflavone Methanol Solutions: Reinvestigation of Tautomer and Anion Formations

Hiromi Mukaihata, Takako Nakagawa, Shigeru Kohtani, and Michiya Itoh*

Contribution from the Department of Physical and Chemical Biodynamics, Graduate School, and Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan

Received May 9, 1994[⊗]

Abstract: The methanol solutions of 3-hydroxyxanthone (3-HX) and 7-hydroxyflavone (7-HF) show both strong absorption (λ_{max} 310−320 nm) and very weak bands (350−400 nm) at room temperature. The former and latter absorption bands are ascribed to normal and anion forms in equilibrium, respectively. The excitations of the normal forms (probably 1:1 and 1:2 H-bonded complexes) of both compounds exhibit a large Stokes-shifted anion and tautomer fluorescence at 430−530 nm. Picosecond fluorescence and nanosecond/picosecond two-step LIF studies demonstrate that the anion and tautomer are generated by the excited-state proton transfer (ESPT) from 1:1 and 1:2 complexes of 3-HX/CH_3OH (7-HF/CH_3OH), respectively. The rise times of tautomer and anion fluorescence were consistent with decay times of the respective normal forms. These picosecond fluorescence studies confirmed and developed the proposed mechanism of the ESPT and relaxation process in 3-HX reported previously, though two types of the tautomers of 7-HF proposed previously were partially corrected to the tautomer and anion generated by the ESPT in this paper.

Introduction

In the course of our investigations on inter- and intramolecular excited-state proton transfer (ESPT), we demonstrated that the transient absorption and two-step laser-induced fluorescence (TS-LIF)[1−7] as well as the picosecond fluorescence were very efficient in studies on the ESPT and relaxation process of a number of hydrogen-bonding systems. Wolfbeis and Furlinger[8] reported fluorescence spectra of anion, cation, and tautomer forms of 3-hydroxyxanthone (3-HX) in various basic to acidic solvent systems. Itoh and his co-workers proposed simultaneous formations of the anion and tautomer in the ESPT of the hydrogen-bonding system of 3-HX with alcohol molecules.[3] The former and latter exhibit 430−500 nm fluorescence with a decay time (τ) of 5.9 ns and 470−530 nm fluorescence with $\tau = 0.6$ ns, respectively. The transient absorption and TS-LIF demonstrated that the ground-state anion with a long lifetime (100 μs) forms at the expense of the ground-state tautomer with a 4−5 μs lifetime in the relaxation process of the ESPT of 3-HX. On the other hand, similar simultaneous formations of two types of excited species and relaxations were proposed in the ESPT of the methanol solution of 7-hydroxyflavone (7-HF) in a previous paper.[4] However, since decay times of the excited species were <0.2 ns, the excited-state dynamics and relaxations in the ESPT were obscure. This paper presents picosecond fluorescence and nanosecond/picosecond (ns/ps) TS-LIF studies of the ESPT in methanol solutions of 3-HX and 7-HF, which exhibit very similar features of ESPT and ground-state reverse proton transfer (GSRPT). The fluorescence rise times of the tautomer and anion consistent with decay times of the respective normal forms of 3-HX demonstrate that the anion and tautomer formations occur by the ESPT from 1:2 and 1:1 3-HX/CH_3OH complexes (normal forms). The ESPT takes place also in the methanol solution of 7-HF, leading to the formation of the tautomer and anion, though the formations of two types of tautomers were proposed in a previous paper.[4] These picosecond fluorescence studies confirmed and developed the proposed mechanism of the ESPT and GSRPT processes in these compounds.

Experimental Section

A mode-locked Nd:YAG laser (Coherent Antares 76-s) and a synchronously pumped dye laser (Coherent 701, kiton red and/or Pyridine II dyes) were used. The picosecond pulses were amplified by a Nd:YAG regeneratively amplified dye laser system (Continuum RGA 60 and PTA 60). The dye laser beam (kiton red and/or pyridine II) with a pulse energy of approximately 0.5 mJ at 10 Hz was used. The pulses were frequency doubled with an angle-tuned BaB_2O_4 crystal. The time-resolved fluorescence was observed through a Jobin Yvon polychromator HR250 with a 100 groves/mm grating. The time-resolved detection was performed with a photon-counting streak camera (Hamamatsu Photonics C2050/M1952/CCD temporal analyzer 3140-69) system interfaced with a Hamamatsu C3366 I/F unit. The overall instrument response function was observed to be approximately 10 ps (fwhm).[9] The rise and decay data were corrected for the temporal response function by an iterative nonlinear least-squares algorithm. The serial correlation coefficient of the residuals (R) was used to judge the quality of the fit.[10]

The transient intensities of the normal fluorescence (I_n) (the 1:1 or 1:2 H-bonded complex) and the large Stokes-shifted fluorescence (I_a,

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1994.

(1) (a) Itoh, M.; Adachi, T.; Tokumura, K. *J. Am. Chem. Soc.* **1983**, *105*, 4828. (b) Itoh, M.; Adachi, T.; Tokumura, K. *J. Am. Chem. Soc.* **1984**, *106*, 850.

(2) Itoh, M.; Fujiwara, Y. *J. Phys. Chem.* **1983**, *87*, 4558.

(3) Itoh, M.; Yoshida, N.; Takashima, M. *J. Am. Chem. Soc.* **1985**, *107*, 4819.

(4) Itoh, M.; Adachi, T. *J. Am. Chem. Soc.* **1984**, *106*, 4320.

(5) Itoh, M.; Fujiwara, Y. *J. Am. Chem. Soc.* **1985**, *107*, 1561.

(6) (a) Tokumura, K.; Watanabe, Y.; Itoh, M. *J. Phys. Chem.* **1986**, *90*, 2362. (b) Tokumura, K.; Watanabe, Y.; Itoh, M. *J. Am. Chem. Soc.* **1987**, *109*, 1346.

(7) (a) Itoh, M.; Fujiwara, Y.; Sumitani, M.; Yoshihara, K. *J. Am. Chem. Soc.* **1986**, *108*, 5642. (b) Itoh, M.; Fujiwara, Y.; Matsudo, M.; Higashikata, A.; Tokumura, K. *J. Phys. Chem.* **1990**, *94*, 8146 and references therein.

(8) Wolfbeis, O. S.; Furlinger, E. *J. Am. Chem. Soc.* **1982**, *104*, 4069.

(9) Mukaihata, H.; Ohkubo, T.; Fujiwara, Y.; Itoh, M. *Chem. Phys. Lett.* **1993**, *211*, 140.

0002-7863/94/1516-10612$04.50/0

Table 1. Summarized Fluorescence Decay Times of the Normal, Anion, and Tautomer Forms in ESPT of Methanol Solutions of 3-HX and 7-HF[a]

	normal form decay		anion		tautomer	
	1:1	1:2	rise	decay	rise	decay
3-HX						
room temp (300 K)	*b*	120 ps	<20 ps	5.9 ns	*c*	2.0 ns
				[6.0 ns][d]		(2.2 ns)[e]
213 K	38 ps	620 ps	59 ps	7.1 ns	680 ps	3.2 ns
7-HF						
room temp (300 K)	20 ps	55 ps	24 ps	372 ps	46 ps	127 ps
				(378 ps)[e]		(134 ps)[e]
183−193 K	60 ps	276 ps	60 ps	494 ps	273 ps	1270 ps

[a] The data were averaged from several experimental runs (errors approximately ± 15%). However, data for 7-HF were listed from those of Figures 6a and 7a. [b] Within the excitation laser pulse. [c] No significant rise time was detected at room temperature because of superimposed fluorescence due to the direct excitation of the ground-state anion without rise (see text). [d] Determined by excitation of the ground-state anion band at 360 nm. [e] Determined by the ns/ps TS-LIF.

I_t) (for the anion and tautomer) were analyzed by the following conventional equations:[10]

$$I_n = C_1 \exp(-t/\tau_1) + C_2 \exp(-t/\tau_2), \quad C_2 \gg C_1$$

$$I_a(I_t) = C_3\{\exp(-t/\tau_1) - \exp(-t/\tau_2)\}$$

where τ_2 is the decay time of the normal form fluorescence due to the 1:1 and 1:2 H-bonded complexes and τ_1 is that of the anion or tautomer.

Nanosecond/picosecond TS-LIF was measured as follows: the excimer laser (Lambda physik EMG 53MSC, 308 nm) was used for the pumping excitation of the ESPT, and the 436 nm (10 Hz, 40−50 ps fwhm) H_1 AS_2 Raman band excited by a 532 nm pulse (SHG) from a regeneratively amplified Nd:YAG laser pulse (1064 nm) was used as the probe pulse of TS-LIF. The excimer laser and the above-mentioned Nd:YAG laser were synchronously operated by a homemade circuit and a delay unit (Nucleonics 7010). The fluorescence decay of TS-LIF for 3-HX/methanol was detected by using a photomultiplier (Hamamatsu H 3284) through a grating monochromator (Ritsu MC-20N) and a digital oscilloscope (Tektronix TDS 520) and processed by computer-simulated convolution. The determination of the TS-LIF fluorescence decay of 7-HF/methanol was made by using the streak camera through an appropriate cutoff filter. The samples (3-HX and 7-HF), the deaeration of solutions, and other experimental procedures were almost the same as described in previous papers.[3,4,7] The spectral grade methanol (Nakarai Tesque, containing <0.1% H_2O) was used without further purification. Concentrations of the methanol solutions of both compounds were (2−5) × 10^{-5} M in this paper except where described otherwise.

Results and Discussion

ESPT and GSRPT in 3-HX. The deaerated methanol solution of 3-HX exhibits an absorption spectrum (λ_{max} 310 nm) with a weak shoulder band at 350−400 nm, as shown in Figure 1. Since the basic H_2O/methanol solution of 3-HX shows a remarkably red-shifted absorption spectrum peaked at 360 nm, the weak absorption at 350−390 nm in methanol may be attributable to an anion form of 3-HX generated by the interaction with a trace amount of H_2O in methanol solution.[11] The weak 350−390 nm shoulder band in the methanol solution decreased with decreasing temperature, which suggests an equilibrium between the H-bonding normal form and a trace amount of the anion of 3-HX. Figure 1a shows the fluorescence spectrum (λ_{max} 460 nm) for the excitation of the anion at 360 nm. Taking into account the excitation spectrum of the fluorescence shown in Figure 1c, the fluorescence spectra at λ_{max} 460 nm are ascribed to the anion fluorescence by the direct excitation of this ground-state anion.

As reported in the previous investigation on the ESPT in the methanol solution of 7-hydroxyquinoline (7-HQ),[1] the ESPT leading to the tautomer formation occurs only from the two methanol H-bonding state (1:2), though this compound is nonfluorescent in THF (shown in Figure 1 of ref 1). In the excitation of the absorption band (300 nm) of the methanol solution of 3-HX, the large Stokes-shifted (420−520 nm) and UV (λ_{max} 380−390 nm) fluorescence spectra were observed.

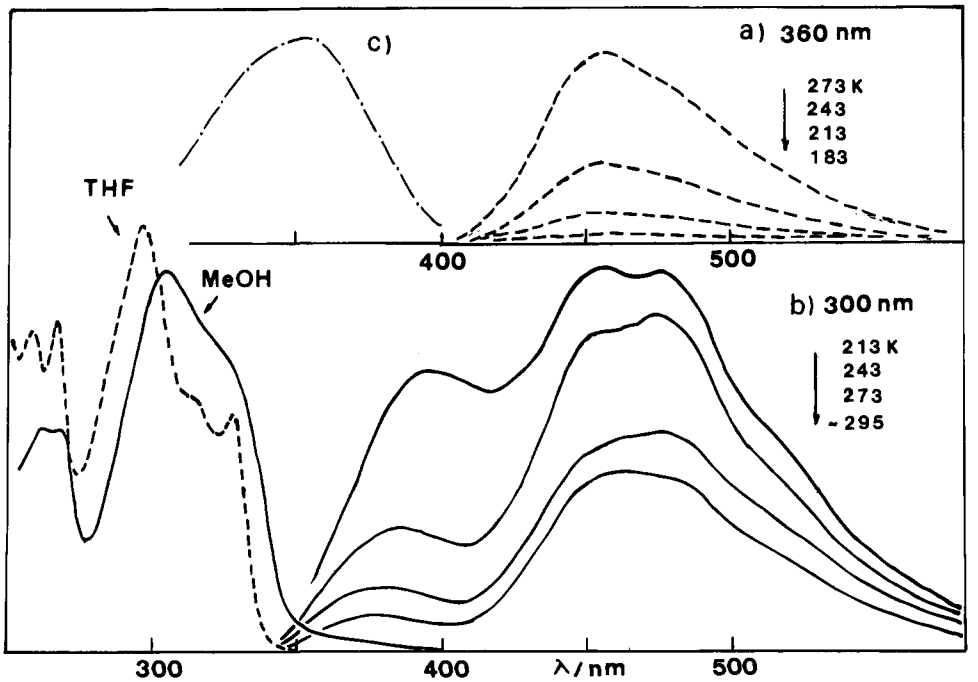

Figure 1. Absorption and fluorescence spectra of 3-HX (3 × 10^{-5} M) in a methanol solution[11] (the THF solution is actually nonfluorescent). Fluorescence intensities are arbitrary units. (a) Fluorescence spectra of the methanol solution were excited at 350 nm at several temperatures, and (b) the temperature dependence of the same solution was determined in the excitation at 300 nm. (c) The fluorescence (detected at 480 nm) excitation spectrum of the methanol solution was determined at room temperature.

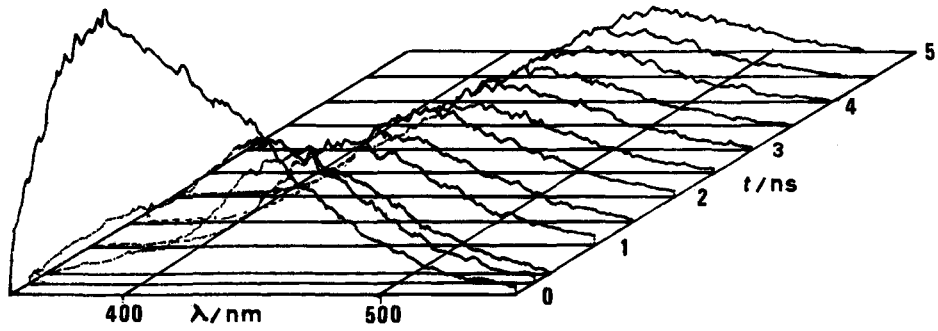

Figure 2. Picosecond time-resolved fluorescence spectra of the methanol solution of 3-HX at room temperature.

Their fluorescence spectra exhibit temperature dependence as shown in Figure 1b. Comparison of the fluorescence spectra in Figure 1a,b suggests that the large Stokes-shifted fluorescence consists of the anion (λ_{max} 460 nm) and tautomer (480−500 nm) fluorescence,[3] while the short wavelength fluorescence at 380 nm may be attributable to the normal form (methanol H-bonded 3-HX). It seems that the excited-state anion and tautomer in methanol are generated by the ESPT from 1:1 and 1:2 methanol H-bonded complexes of 3-HX, respectively, and the 380 nm normal form fluorescence is composed of these two complexes. However, there is no experimental evidence for these arguments at the present stage. Picosecond time-resolved fluorescence spectra of the deaerated methanol solution of 3-HX were determined for the excitations at 300 nm, as shown in Figure 2. In the 300 nm excitation at room temperature, a very short single-exponential decay (τ = 120 ps) was observed at the 380 nm region, while a double-exponential decay (2.0 and 5.9 ns)[12] without significant fluorescence rise was observed in the 460 nm fluorescence, as shown in Figure 3a. However, at considerably low temperature (213 K), double-exponential decay times (38 and 620 ps) were obtained in the 380 nm normal form fluorescence (Figure 3c). Further, in the >500 nm fluorescence, two component rise (59 and 680 ps) and double-exponential decay times (3.2 and 7.1 ns) were obtained at 213 K, as shown in Figure 3b, and the component of the 680 ps rise time and that of the 3.2 ns decay time considerably increased with the longer wavelength region. The 680 ps rise time of the long wavelength fluorescence with 3.2 ns decay time was well consistent with the 620 ps decay times of the normal form fluorescence at 380 nm within experimental error. Taking account of the observation of tautomer fluorescence rise (680 ps) consistent with the UV fluorescence decay (620 ps) at 218 K, the tautomer fluorescence rise corresponding to the UV fluorescence decay time (120 ps) should be observed even at room temperature. However, no significant tautomer fluorescence was detected at room temperature as mentioned above. It seems to be because the tautomer fluorescence rise is overlaid with fluorescence of a trace amount of the ground-state anion directly excited by a 300 nm picosecond pulse at room temperature. As seen in Figure 1a, since the ground-state anion fluorescence decreased at low temperature, the tautomer fluorescence rise was observed at 218 K, as mentioned above.

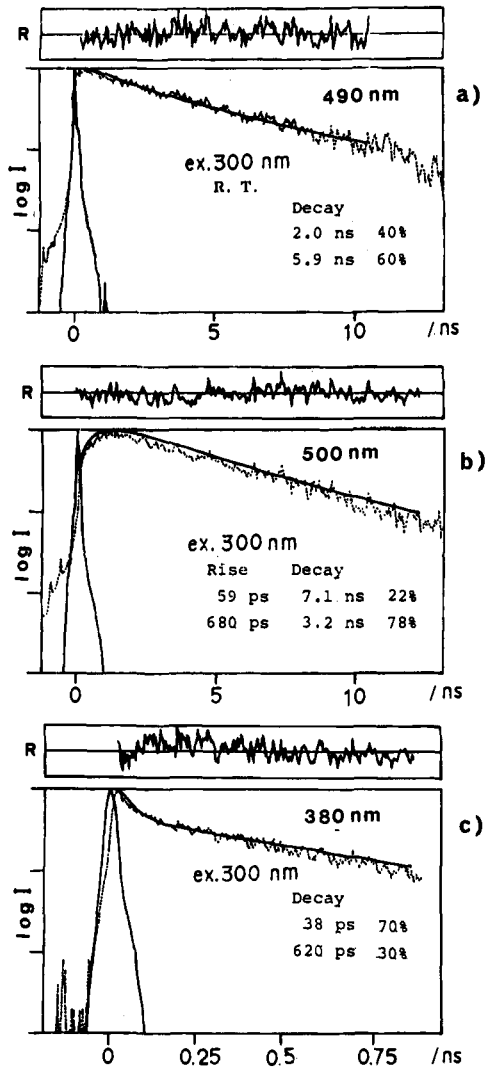

Figure 3. Fluorescence rise and decay curves of the 3-HX/methanol solution excited at 300 nm pulse at room temperature, detected at (a) 490, (b) 500, and 380 nm.

On the other hand, the 360 nm excitation of the absorption band due to the ground-state anion exhibits a completely single-exponential decay (τ = 6.0 ns) without rise at room temperature and decay time increased to 7.0 ns at 213 K. These decay times were well consistent with those obtained in the large Stokes-shifted fluorescence (τ = 7.1 ns at 213 K) by the 300 nm excitation, as mentioned above. Therefore, it was demonstrated that the excited-state anion may be generated within several picoseconds at room temperature from the excited state of the normal form (probably the 1:1 methanol complex), though the rise time of the anion fluorescence was obtained to be 38−40

(10) O'Connor, D. V.; Phillips, D. *Time-correlated Single Photon Counting*; Academic Press: New York, 1985.

(11) The weak shoulder band at 350−400 nm in methanol (<0.1% H_2O) increased several percent in intensity when water as impurity was added in methanol solution to 1.0% (H_2O v/v %).

(12) In a previous paper (ref 3), the fluorescence decay times of the tautomer and anion were obtained to be 0.54 and 5.87 ns from the double-exponential decay curve by the nanosecond excimer laser excitation (10 ns fwhm). However, these data are much less accuracy than the present results. (In Table 1 of ref 3, the anion and tautomer should be read as the tautomer and anion, respectively.)

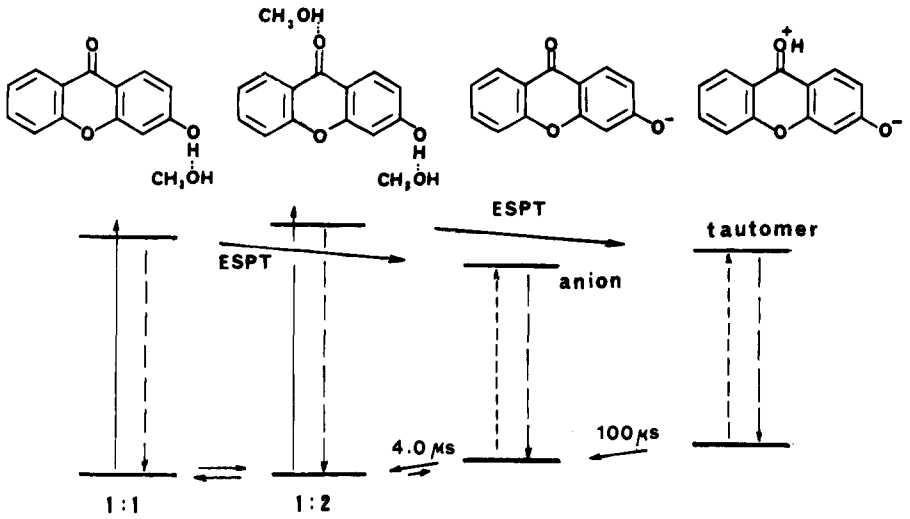

Figure 4. Proposed reaction scheme of the ESPT and relaxation in the 3-HX/methanol system.

ps at low temperature (213 K). The decay time of the tautomer was suggested to be 0.2 ns by the nanosecond fluorescence in the previous paper.[3,12] However, the present reinvestigation by picosecond fluorescence studies indicates that the anion and tautomer decay times are 5.9−6.0 and 2.0 ns at room temperature, respectively.

As reported in the previous paper,[3] the transient absorption spectra due to the ground-state anion and tautomer generated by the ESPT and relaxation of the methanol H-bonded 3-HX were observed in the 340−380 nm region. The anion form absorption band grew at the expense of the tautomer transient absorption band. The rise of the anion absorption band (4.3 μs at 340 nm) was well consistent with the decay time of tautomer absorption (4.4 μs at 370 nm), and the anion band decayed approximately 100 μs. These reaction dynamics in the ground-state were also reproduced and confirmed in this paper. Since the ground-state anion of 3-HX exists in the methanol solution (<0.1% H_2O) in an equilibrium as mentioned above, the rise (4.3 μs) and decay (≈100 μs) times of the ground-state anion by ESPT and relaxation imply that the ground-state relaxation process takes place in the equilibrium state at room temperature. These reaction schemes are shown in Figure 4.

In order to confirm the correlation between the ground and excited states of the tautomer, the fluorescence decay time of the tautomer was determined by ns/ps TS-LIF at room temperature. Since the transient absorption band of the ground-state tautomer spreads to about 480 nm (Figure 5 in ref 3), the ground-state tautomer was directly excited by the picosecond 436 nm pulse (AS_2 of H_2, 40−50 ps fwhm) after a 2 μs delay from the pumping excimer laser (308 nm) excitation of the methanol solution of 3-HX. The fluorescence decay time of the tautomer was obtained to be 2.2 ns at room temperature. Taking into account the less accuracy of the ns/ps TS-LIF decay time, the obtained 2.2 ns decay time was well consistent with that observed (2.0 ns at room temperature) in the picosecond measurements of the ESPT mentioned above.

In a previous paper, the simultaneous formations of the excited-state anion and tautomer were proposed by the ESPT in a methanol solution of 3-HX.[3] However the excited-state primary process of their formations was not presented, though the details of the ground-state relaxation dynamics of these species were presented by transient absorption and TS-LIF studies. If the excited-state anion and tautomer are generated from the same excited species, such as 1:1 or 1:2 H-bonded 3-HX, only one component of decay time of the 370−390 nm fluoresence and one component of rise time of the 450−500 nm fluorescence should be observed. However, the experimental results demonstrated that two decay times of the short wavelength fluorescence (~380 nm) corresponding to the rise times of the long wavelength anion and tautomer fluorescence were observed, as mentioned above. Therefore, the anion and tautomer are generated from the different excited species, probably 1:1 and 1:2 H-bonded 3-HX, respectively, as illustrated in Figure 4. The assignment of the number of methanol molecules involved in the anion and tautomer formations cannot be characterized in the solution spectroscopy, though the recent supersonic jet spectroscopies reported the cluster size dependent ESPT in H-bonded systems such as phenol,[13,14] naphthol,[15−17] and 7-azaindole[18] and also the intramolecular ESPT.[19−21] However since a detailed solute−solvent interaction is still not known in the bulk solvent environment, the actual structures of 1:1 and 1:2 H-bonded complexes leading to the ESPT are not obvious at the present stage.

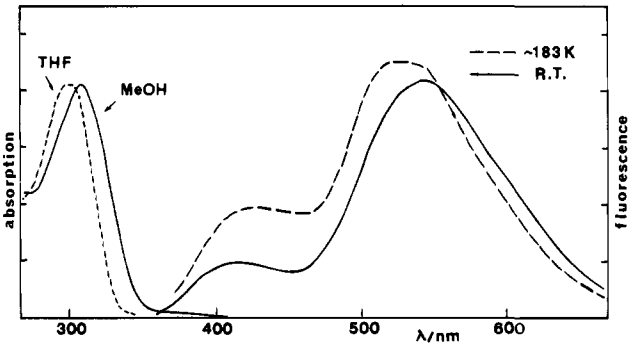

Figure 5. Absorption and fluorescence spectra (intensities, arbitrary units) of the methanol solution of 7-HF (5×10^{-5} M).

(13) Solgadi, D.; Jouvet, C.; Tramer, A. *J. Phys. Chem.* **1988**, *92*, 3313.
(14) Jouvet, C.; Lardeux-Dedonder, C.; Richard-Viard, M.; Solgadi, D.; Tramer, A. *J. Phys. Chem.* **1990**, *94*, 5041.
(15) Knoechenmuss, R.; Leutwyler, S. *J. Chem. Phys.* **1989**, *91*, 1268 and references therein.
(16) Cheshnovsky, O.; Leutwyler, S. *J. Chem. Phys.* **1988**, *88*, 4127.
(17) Kim, S. K.; Shijan, L.; Bernstein, E. R. *J. Chem. Phys.* **1991**, *95*, 3119.
(18) Fuke, K.; Yoshiuchi, H.; Kaya, K. *J. Phys. Chem.* **1984**, *88*, 5840.
(19) (a) Ito, A.; Fujiwara, Y.; Itoh, M. *J. Chem. Phys.* **1992**, *96*, 7474 and references therein. (b) Takasu, R.; Fujiwara, Y.; Itoh, M. *Chem. Phys. Lett.* **1994**, *217*, 478.
(20) Ernsting, N. P.; Dick, B. *Chem. Phys.* **1989**, *136*, 181.
(21) (a) Ernsting, N. P. *J. Phys. Chem.* **1985**, *89*, 4932. (b) Ernsting, N. P.; Arthen-Engeland, Th.; Rodriguez, M. A.; Thiel, W. *J. Chem. Phys.* **1992**, *97*, 3914.

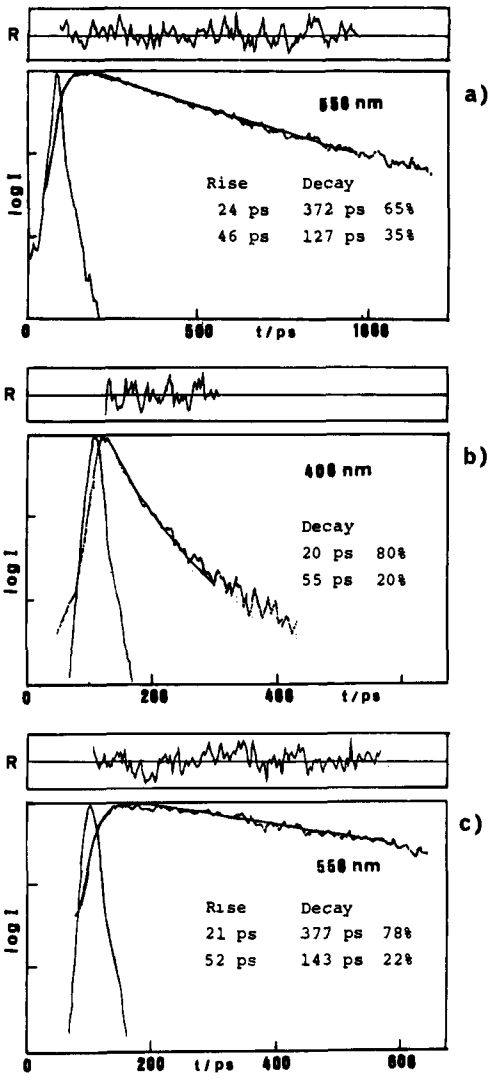

Figure 6. Picosecond time-resolved fluorescence decay curves (excited at 300 nm pulse) of the methanol solution of 7-HF at room temperature. The detection wavelengths were (a) 550, (b) 408, and (c) 545−550 nm. Decay times of the anion and tautomer of a may be more reliable than those of c, but rise times of the expanded time scale c may be more reliable than those of a. However, data in Table 1 were listed from a.

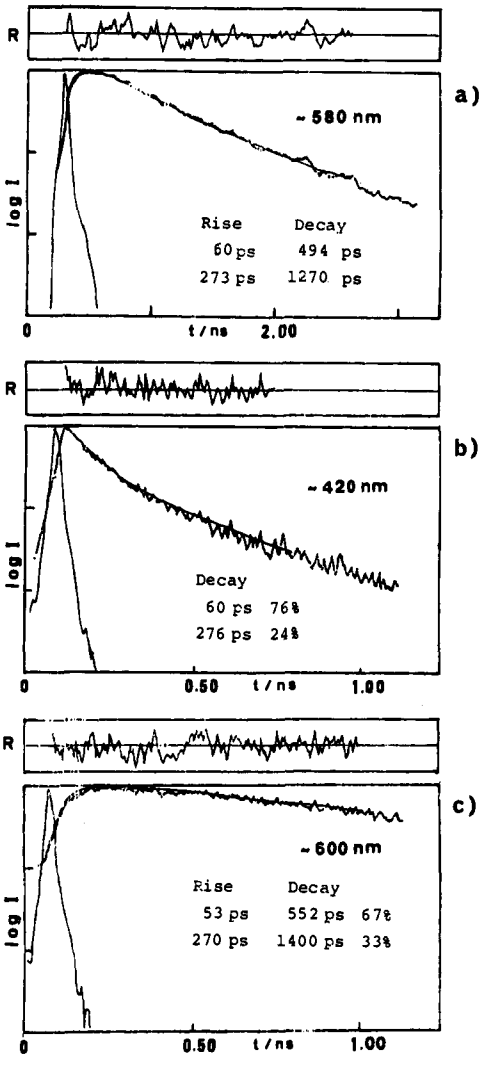

Figure 7. Picosecond time-resolved fluorescence decay curves (excited at 300 nm pulse) of the methanol solution of 7-HF at 183−193 K. The detection wavelengths were (a) 575−585, (b) 415−425, and (c) 595−605 nm. The reliability of the data is the same as described in Figure 6. However, data in Table 1 are from a.

ESPT and GSRPT in 7-HF. The deaerated methanol solution of 7-HF shows a very weak absorption at 350−500 nm in addition to a strong UV absorption at λ_{max} 310 nm.[4] Since a basic solution of 7-HF shows an anion form absorption band in the 360 nm region as suggested by Schipfer *et al.*,[22] the very weak shoulder band at 350−400 nm is ascribed to an anion formed in the interaction with a trace amount of water in methanol (<0.1% H_2O). The 360 nm band excitation shows anion form fluorescence (λ_{max} 515−520 nm). On the other hand, the fluorescence spectrum in the excitation of 310 nm band exhibits a large Stokes-shifted fluorescence at λ_{max} 530−540 nm together with the 400−440 nm fluorescence, while actually no significant fluorescence was observed in the THF solution.[4] These absorption and fluorescence spectra are shown in Figure 5. As will be mentioned later, the large Stokes-shifted fluorescence in the excitation of the 310 nm band consists of the tautomer and anion form fluorescences, though two types of the tautomers were proposed in the ESPT of this compound in methanol solution.[4] These steady-state spectral features are very similar to those of 3-HX.

The picosecond time-resolved fluorescence spectrum of the methanol solution of the 7-HF excited at 353 nm, which corresponds to the anion absorption band, shows the λ_{max} 515−520 nm fluorescence with a single-exponential decay (τ = 360 ps) without rise at room temperature. In the 300 nm pulse (fwhm, 10−15 ps) excitation of this solution, the 520−600 nm fluorescence exhibits a double-exponential decay (τ = 127 ps and 372 ps) with a double-component fluorescence rise (46 ps an 24 ps) at room temperature, while the 408 nm fluorescence shows a double-exponential decay with very short decay times of 20 and 55 ps. These fluorescence decay curves are shown in Figure 6a,b. Figure 6c shows the expanding time scale of the rise and decay curves observed at 550 nm, whose data are consistent with those of Figure 6a,b within the experimental error. Taking into account the fluorescence decay time (360 ps) of the anion obtained by the direct excitation (354 nm), the decay times of 372 and 127 ps obtained by the 300 nm excitation may be attributable to the anion and tautomer at room temperature, respectively. With decreasing temperature of the solution, the double-exponential decay times of the 500−600 nm fluorescence gradually increased and their decay times were obtained to be 494 and 1270 ps at 183−193 K. These large

(22) Schipfer, R.; Wolfbeis, O. S.; Knierzinger, A. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1442.

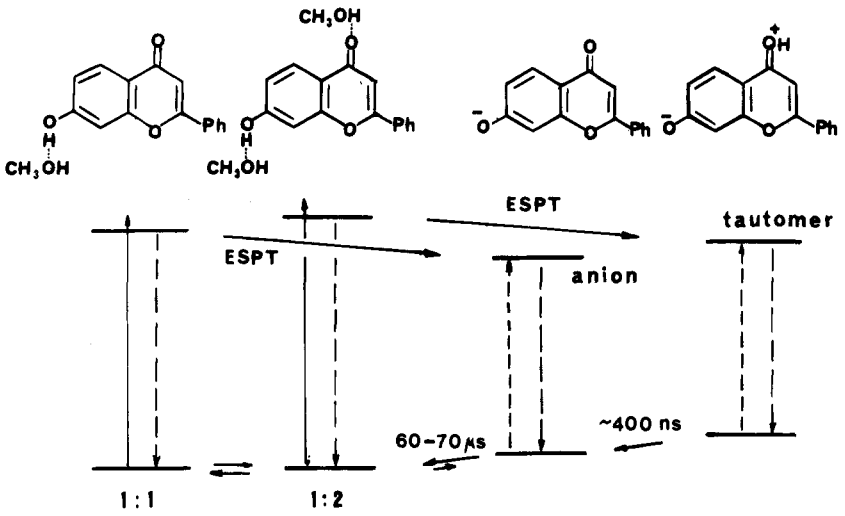

Figure 8. Proposed reaction scheme of ESPT and relaxation in the methanol solution of 7-HF.

Stokes-shifted fluorescence spectra exhibit a two-component rise of fluorescence. Figure 7 shows two-component rise and double-exponential decay curves of the large Stokes-shifted fluorescence together with the normal form fluorescence decay curve of the 7-HF/methanol solution at 183 K. Taking account of two rise and two decay time components, the short rise time of 60 ps corresponds to the 494 ps decay component, while the longer rise time of 273 ps corresponds to the 1270 ps decay time component at 183 K. These short and long decay times of the large Stokes-shifted fluorescence may be attributable to the tautomer and anion forms generated by the ESPT. Further, the normal form fluorescence detected at 420 nm exhibits a double-exponential decay with decay times of 60 and 276 ps at 183 K (Figure 6b), though the two decay times 20 and 55 ps were observed at room temperature (Figure 6b). These double-exponential decay times of the normal form are well consistent with rise times of the tautomer and anion fluorescences. Therefore, the facts suggest that the ESPT leading to the anion and tautomer takes place from the respective excited states, probably 1:1 and 1:2 H-bonded 7-HF. These ground- and excited-state reaction schemes are shown in Figure 8.

The transient absorption spectra (350−450 nm) of the ground-state species with short and long decay times (τ = 400 ns and 60−70 μs) in the methanol solution of 7-HF were reported previously.[4] Further, the nanosecond time-resolved TS-LIF demonstrated that the λ_{max} 530 nm (τ = <0.2 ns at 216 K) was corresponding to the short-lived ground-state species, while the 518 nm fluorescence (τ = 0.7 ns at 216 K) was correlated to the very long lived ground state. In the methanol solution of 3-HX, as mentioned in the last section, the variable delay plots of TS-LIF demonstrated that the ground-state anion was generated at the expense of the ground-state tautomer.[4]. In the 7-HF/methanol system, if the ground-state anion is generated from the ground-state tautomer with its decay time of 400 ns, the rise of the variable delay plot of the anion TS-LIF intensity should be observed. However, since TS-LIF spectra of the tautomer (λ_{max} 530 nm) and anion (518 nm) are considerably close to each other, no significant rise in the variable delay plots of TS-LIF intensities of the ground-state anion can be obtained. Nevertheless, it is likely that the ground-state anion is formed at the expense of the ground-state tautomer with the decay time of 400 ns. These excited-state and ground-state features in the 7-HF/methanol are completely similar to those of 3-HX/methanol, as mentioned above.

Furthermore, in order to confirm the fluorescence decay times of the tautomer and anion, the time-resolved ns/ps TS-LIF decay

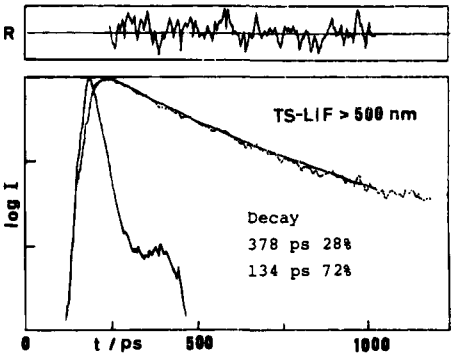

Figure 9. Ns/ps TS-LIF decay curve of the methanol solution of 7-HF at room temperature.

curves were determined at the delay times of 500 ns and 6 μs of the second picosecond laser pulse. A typical decay curve measured at 500 ns delay time is shown in Figure 9. The double-exponential decay curve of TS-LIF without fluorescence rise was observed at a 500 ns delay time from the first laser excitation. The decay times of 134 ps (72%) and 378 ps (28%) were obtained at room temperature. The greater decay component (72%) due to the tautomer (134 ps) contrasts well with the small component (22−35%) of the ordinary picosecond pulse excitation (Figure 6a,c). Further, at the long delay time of 6 μs, the tautomer fluorescence decay component decreased compared with that of the anion. It is because the ground-state tautomer mostly disappeared at the long delay time. These TS-LIF decay times are well consistent with those obtained by the ordinary picosecond time-resolved fluorescence, mentioned above. Of course, since the TS-LIF means the direct excitation of their respective ground states, these decay curves do not exhibit a fluorescence rise. Therefore, the former (134 ps) and latter (374 ps) decay times were firmly ascribed to the tautomer and anion fluorescences, respectively.

Concluding Remarks

The intermolecular ESPT and relaxation processes in methanol solutions of the 3-HX and 7-HRF were reinvestigated by picosecond fluorescence and ns/ps TS-LIF spectroscopies. In both methanol solutions of these compounds, two-component fluorescence rise and decay times were observed in the large Stokes-shifted fluorescence attributable to the anion and tautomer. These fluorescence rise times are well consistent with the respective decay times of the normal form fluorescences of

1:1 and 1:2 methanol H-bonded states. The facts demonstrate that the tautomers of 3-HX and 7-HF may be generated from the excited states of the 1:2 methanol H-bonded compounds, while the anions are probably from the excited states of 1:1 methanol complex. The picosecond dynamics suggest that the double proton transfer probably takes place concertedly in the tautomer formations of both compounds. However, the assignment of the number of methanol molecules and structures of H-bonded complexes involved in the anion and tautomer formations cannot be characterized in the solution spectroscopy.

Acknowledgment. This work was partially supported by a Grand-in-Aid for Scientific Research (No. 05453018) from the Ministry of Education, Science, and Culture of Japan.