to an oil which was dissolved in benzene, filtered again, and evaporated to give a slightly yellow oil (0.41 g, 85%), characterized by NMR and IR. The material used for kinetics runs was distilled, bp 117-120 °C (0.1 mm Hg) (lit.[27] bp 120-125 °C (0.5 mm)).

5-Bromo-2-pyridone (4a) was prepared as outlined in the literature.[28] For reasons of solubility the **sodium salt** was used for kinetic experiments. It was prepared as follows: In a minimum amount of water **4a** was dissolved with an equivalent amount of NaOH. The solution was filtered, and acetone was added to the filtrate to precipitate the sodium salt which was filtered off and washed with acetonitrile. Recrystallization from 2 parts EtOH/5 parts CH_3CN gave a product with mp 349-350 °C dec. ^1H NMR showed this to be dihydrate, as did analysis. Anal. Calcd for $C_4H_3BrNONa\cdot 2H_2O$: C, 25.89; H, 3.02; N, 6.04; Br, 34.45. Found: C, 26.21; H, 3.07; N, 6.30; Br, 34.29.

5-Bromo-1-methyl-2-pyridone (4b). To an ethanolic solution of the sodium salt of **4a** was added a slight excess of methyl iodide. The solution was refluxed for 10 min and evaporated to dryness. Recrystallization of the residue from benzene–ligroin gave slender white needles (60% yield), mp 65-67 °C (lit.[27] mp 62-63 °C), with appropriate spectra.

5-Bromo-2-methoxypyridine (6) was prepared by bromination of **2b** in acetic acid[7] and as follows: To **2b** (1.1 g, 10 mmol) and KOH (0.28 g, 5 mmol)[29] in 60 mL of water was added bromine (1.6 g, 10 mmol) in 60 mL of 1 M aqueous KBr. The solution was stirred for 3.5 h until the bromine color disappeared. The solution was made basic and extracted with 2 × 100 mL of $CHCl_3$. The extract was dried (Na_2SO_4) and reduced to an oil (1.1 g, 63%). ^1H NMR showed **6** with a trace of the starting material, **2b**.

The position of the bromine was confirmed by hydrolysis: The above oil was refluxed in 4 M sulfuric acid for 2.5 h. The cooled solution was brought to pH 4 and evaporated to dryness. The solid was extracted with benzene and evaporation of the solvent gave **4a**, identical (NMR, IR, mp) with that prepared as above.

(27) Bradlow, L.; Vanderwerf, C. A. *J. Org. Chem.* **1951**, *16*, 73.
(28) Fox, B. A.; Threlfall, T. L. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 346. Seide, O. *Chem. Ber.* **1924**, *57*, 1802.
(29) Since **2b** (and probably **6**) can be hydrolyzed in aqueous acid.

Bromination of 2-Pyridone (1a). (a) In Acetic Acid. To **1a** (1.9 g, 20 mmol) in 10 mL of acetic acid was slowly added bromine (3.2 g, 20 mmol) in 40 mL of acetic acid. When this solution was reduced to one fifth of its volume crystals of 3,5-dibromo-2-pyridone (**5a**) were deposited. Recrystallization gave **5a** (85% yield) with an IR spectrum as reported.[7]

(b) In Aqueous Base. The above amounts of **1a** and bromine were added to an aqueous solution containing 1 equiv of KOH. This resulting solution turned red and then black! After a few hours black needles were deposited which were identified from their IR spectra as **5a** (85% yield).

(c) In Water. Over a 5-min period bromine (3.2 g, 20 mmol) in 40 mL of 1 M aqueous KBr was added with stirring to **1a** (1.9 g, 20 mmol) in 20 mL of 1 M aqueous KBr. After 24 h this solution deposited crystals which were filtered off and recrystallized from acetonitrile to give 2.72 g (78%) of 3-bromo-2-pyridone (**3a**), identified by its NMR and IR spectra.[7] Methylation of this material with dimethyl sulfate (as above for **3a** → **3b**) gave **3b** as required.

Bromination of 1-Methyl-2-pyridone (1b) in Acid Solution. 1b (0.73 g, 6.7 mmol) was dissolved in 10 mL of an aqueous solution which was 0.1 M in $HClO_4$ and 1 M in KBr. To this solution was added with stirring bromine (1.07 g, 6.7 mmol) in 10 mL of the same medium. After the solution was left to stand for 3 h 0.6 g (67%) of the 3,5-dibromo product **5b** crystallized out. Its IR spectrum was identical with that reported.[7]

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Registry No. 1a, 142-08-5; **1a**·Na, 930-70-1; **1b**, 694-85-9; **1b**·HBr, 1121-27-3; **2b**, 1628-89-3; **3a**, 13466-43-8; **3b**, 81971-38-2; **4a**, 13466-38-1; **4a**·Na, 13472-92-9; **4b**, 81971-39-3; **5a**, 13472-81-6; **5b**, 14529-54-5; **6**, 13472-85-0.

Supplementary Material Available: Rate constants for reaction of bromine with **1a** (Table S1), **1b** (Table S2), **2b** (Table S3), and **3a**, **3b**, **4a**, and **4b** (Table S4) (5 pages). Ordering information is given on any current masthead page.

Time-Resolved and Steady-State Fluorescence Studies of the Excited-State Proton Transfer in 3-Hydroxyflavone and 3-Hydroxychromone

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Abstract: The 2-methyltetrahydrofuran (MTHF) solution of 3-hydroxyflavone (3-HF) exhibits dual fluorescence at room temperature due to the normal form (N*) of 3-HF and the tautomer (T*) generated from N* by the excited-state proton transfer. The fluorescence rise time of the T* fluorescence was in good consistency with the N* fluorescence decay time. The activation energy and the Arrhenius factor were determined to be ca. 2.9 kcal mol^{-1} and 3.3×10^{12} s^{-1}, respectively, from the temperature dependence of the intensity ratio and lifetimes of dual fluorescence. Furthermore, the temperature dependence of the fluorescence lifetime of T* yields an activation barrier of 4.1 kcal mol^{-1} for the nonradiative decay process of T*. The MTHF solution of 3-hydroxychromone (3-HC) exhibits neither N* nor T* fluorescence. The 3-methylpentane (MP) solution of 3-HC exhibits only T* fluorescence at room temperature to ~180 K. The fluorescence rise time of T* in 3-HC was too fast to be determined by nanosecond pulse excitation, though the rise time in 3-HF was observed to be ~1-0.5 ns at 160-195 K. The difference of the fluorescence behavior between 3-HF and 3-HC was discussed in terms of the effect of the phenyl group of the γ-pyrone ring on the excited-state proton transfer and the stabilization of the tautomer form (T*).

A large number of studies have been reported on the intramolecular proton-transfer reaction. In recent years, kinetic studies with picosecond spectroscopy have revealed the following facts.[2-7] (a) Intramolecular excited-state proton transfer occurs very rapidly, usually faster than 10 ps. (b) In most cases, the pro-

(1) (a) Kanazawa University. (b) Tokyo Institute of Technology.

(2) Shizuka, H.; Matsui, S.; Hirata, Y.; Tanaka, I. *J. Phys. Chem.* **1976**, *80*, 2070; **1977**, *81*, 2243 and references therein.

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ton-transfer reaction has no potential barrier; even at 4 K, the reaction occurs within 10 ps. (c) There exists temperature-dependent deactivation process(es) in the proton-transfer species.

3-Hydroxyflavone (3-HF) shows dual fluorescence with maxima at ca. 530 and 400 nm.[8] Sengupta and Kasha have assigned the former to the fluorescence from the tautomer generated by the intramolecular excited-state proton transfer across a barrier in the double-minimum hydrogen-bonding potential.[9,10] In this excited-state proton transfer, the barrier height for the tautomerization was suggested to be dependent on the viscosity of the solvent media, the origin of which was ascribed to the torsional motion of the phenyl group about its junction axis to the γ-pyrone ring system.

This paper describes comprehensive time-resolved and steady-state fluorescence studies on the excited-state proton transfer in 3-hydroxyflavone (3-HF) and 3-hydroxychromone (3-HC). The fluorescence rise time of the tautomer (T*) in the 2-methyltetrahydrofuran (MTHF) solution of 3-HF was shown to be in good consistency with the fluorescence decay time of the normal form (N*) of 3-HF. The activation energy of the excited-state proton transfer was estimated from the temperature dependence of fluorescence lifetimes of N* and T* and the fluorescence intensity ratio of N* and T*. The intramolecular excited-state proton transfer of 3-HF is revealed to be a fairly peculiar case because this reaction is rather slow and has a potential barrier.

A comparison of the fluorescence behavior of 3-HC, which has no phenyl group, with that of 3-HF is informative to clarify the effect of torsional motion of the phenyl group. The MP solution of 3-HC was observed to show only the T* fluorescence between room temperature and 150 K. The rise of the T* fluorescence observed was too fast to permit the time constant to be determined. The excited-state proton transfer is concluded to be faster in 3-HC than in 3-HF. The results are discussed in terms of the role of the phenyl group in the excited-state proton-transfer reaction.

Experimental Section

3-Hydroxyflavone (Tokyo Kasei Co.) was purified by recrystallization several times from ethanol. 3-Hydroxychromone was synthesized from 4-chromanone (Aldrich Chemical Co.) and purified by sublimation, mp 177 °C. Anal. Calcd for $C_9H_6O_3$: C, 66.67; H, 3.73. Found: C, 66.60; H, 3.63. The purity of these compounds was confirmed by IR, UV, and TLC analysis.[11] The solvents (MP and MTHF) used were purified by the method described previously.[12] The solutions of samples in a rectangular quartz cell (1 cm) with graded seals were degassed by freeze–pump–thaw cycles.

Absorption and fluorescence spectra were determined with a Hitachi 323 spectrophotometer and MPF-4 spectrofluorometer, respectively. The nanosecond fluorescence system is as follows: A nitrogen laser pumped dye laser (Molectron UV-12 and DL-14) and a frequency doubler (Lambda Physik KDP crystal unit) were used for the exciting light pulse (293 nm, light width 0.1 nm and pulse width fwhm 3–3.5 ns). Fluorescence was detected through appropriate cutoff filters and/or a 20-cm monochromator (Ritsu 20N) by a 1P28 photomultiplier, which was operated with subnanosecond response time (rise time ~350 ps), developed by Beck.[13] The signals were determined by a Tektronix oscilloscope Model 7904 (7A19 and 7B85 plug-in). Fluorescence decay curves were analyzed by a computer-simulated deconvolution.[12] Temperature control in the measurements of fluorescence spectra and lifetimes was carried out by the method described previously.[12]

Picosecond fluorescence spectroscopy was performed with a mode-locked ruby laser system described previously.[14] The second harmonic of the ruby laser (347 nm) was used as the exciting light pulse, and the fluorescence was time resolved by a transient disperser (streak camera, HTV C979), a SIT camera (HTV C1000-18), a transient analyzer (HTV C1098), and a personal computer. The temperature of the sample was controlled by an Oxford DN704 cryostat.

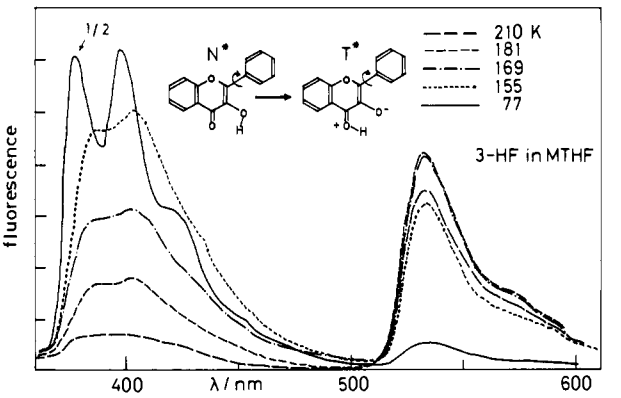

Figure 1. Fluorescence spectra (uncorrected) of MTHF solutions of 3-HF (concentration, 5×10^{-6} M) at several temperatures; excitation wavelength, 350 nm).

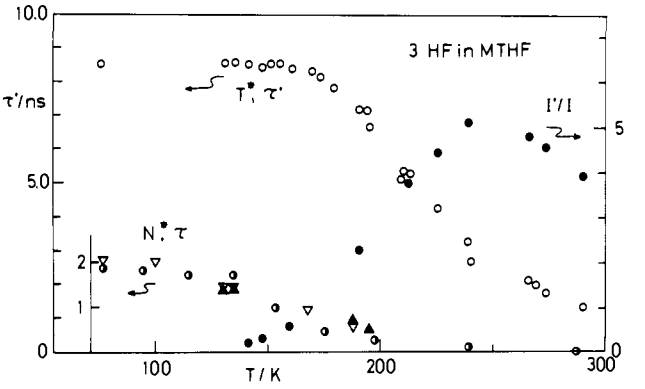

Figure 2. Temperature dependence of the fluorescence intensity ratio (●) of N* (I at 402 nm) to T* (I' at 532 nm) of 3-HF in MTHF (spectra are uncorrected). Temperature dependence of fluorescence lifetime (○) and rise time (▲) of T* (530 nm) and lifetime (▽) of N* (420 nm) determined by nanosecond spectroscopy and of rise time (◑) of T* determined by picosecond spectroscopy.

Results and Discussion

The Excited-State Proton Transfer of 3-HF. The MTHF solution of 3-HF exhibits dual fluorescence in the 380–430 nm (violet) and 510–560 nm (green) regions, of which excitation spectra are well consistent with the absorption spectrum of this compound. The violet fluorescence in the former region is a good mirror image of the absorption spectrum. The fluorescence at 380–430 nm is, therefore, attributable to that of the normal form 3-HF (N*). Since the green fluorescence exhibits no concentration dependence, the fluorescence can be ascribed not to the bimolecular process such as excimer but to the intramolecular process such as the intramolecular proton transfer or a kind of conformational transition in the excited state. Sengupta and Kasha have proposed that the intramolecular proton transfer between the 3-hydroxyl group and the carbonyl group of γ-pyrone ring occurs in the excited state of 3-HF, and the green fluorescence is assigned to the fluoresence of tautomer (T*) generated from the normal form (N*).[8] The fluorescence spectra of 3-HF in MTHF showed remarkable temperature dependence, as shown in Figure 1. The violet fluorescence from N* increased with decreasing temperature,

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(14) Shizuka, H.; Tsutsumi, K.; Takeuchi, H.; Tanaka, I. *Chem. Phys.* **1981**, *59*, 183.

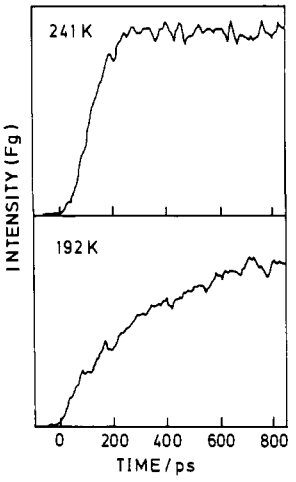
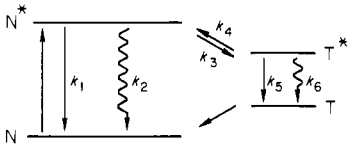


Figure 3. Typical fluorescence rise curves of 3-HF in MTHF (1×10^{-5} M) at 241 and 192 K measured by picosecond spectroscopy. Each curve is an integration of 3–5 shots.

while the T* fluorescence decreased. The fluorescence intensity ratios of N* to T* vs. temperature are plotted in Figure 2.

Each fluorescence lifetime varied with temperature, as shown in Figure 2. Reducing temperature, the lifetimes increased up to the limiting values, 1.8 ns for the green fluorescence and 8.6 ns for the violet fluorescence (Figure 2). By means of picosecond spectroscopy, the rise time of the green fluorescence was found to be rather slow and temperature dependent (Figure 3). The rise time was identical with the lifetime of the violet fluorescence in the temperature range 173–241 K. Below 150 K, the rise time becomes apparently faster than the lifetime. At lower temperature, where the green fluorescence is very weak, the longer wavelength tail of the strong violet fluorescence should have a considerable influence on the measurement of the rise of the green fluorescence (T*). The apparent fast rise time of the green fluorescence may be due to the experimental errors caused by this reason.

The coincidence of both fluorescence excitation spectra and the coincidence of the lifetime of the violet fluorescence and the rise time of the green fluorescence are the rational evidence for the fact that the tautomer is formed in the excited state. Then the mechanism can be proposed as



where N and T are the normal molecule and the tautomer formed by the intramolecular proton transfer, respectively, k_1 and k_5 are radiative rate constants, k_2 and k_6 are nonradiative deactivation rate constants, and k_3 and k_4 are the rate constants of the intramolecular proton-transfer processes. We can get eq 1 and 2 for pulse excitation:[15]

$$[N^*] = \frac{[N^*]_0}{\lambda_2 - \lambda_1}\left[(\lambda_2 - X)e^{-\lambda_1 t} + (X - \lambda_1)e^{-\lambda_2 t}\right] \quad (1)$$

$$[T^*] = \frac{k_3[N^*]_0}{\lambda_2 - \lambda_1}\left[e^{-\lambda_1 t} - e^{-\lambda_2 t}\right] \quad (2)$$

and eq 3 for steady excitation,[16]

$$\phi_T/\phi_N = \frac{k_3 k_5}{k_1 Y} \quad (3)$$

where $X = k_1 + k_2 + k_3$, $Y = k_4 + k_5 + k_6$, $X_1, X_2 = {}^1/_2\,[X +$

(15) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York, 1970.
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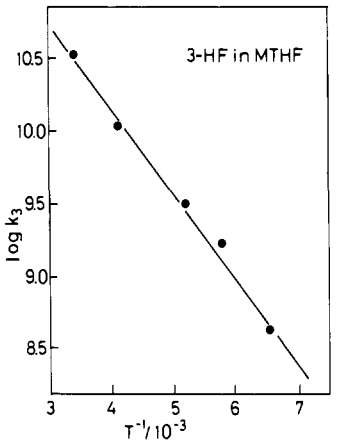

Figure 4. Plots of log k_3 vs. $1/T$ of 3-HF in MTHF, 1.0×10^{-5} M.

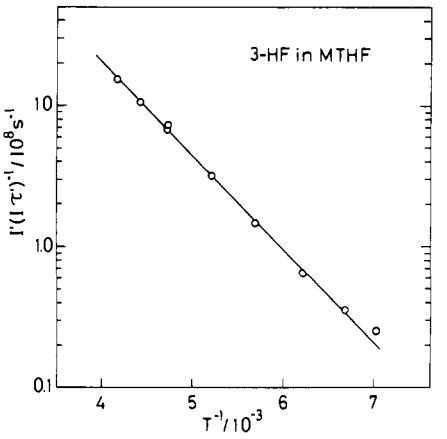

Figure 5. Plots of $I'(I\tau')^{-1}$ vs. $1/T$ of 3-HF in MTHF (5×10^{-6} M). I and I' are monitored at 402 and 532 nm, respectively, here ϕ_T/ϕ_N in eq 3 was replaced by the fluorescence intensity ratio, I'/I, assuming that the shapes of fluorescence and absorption spectra are almost independent of temperature.

$Y \mp [(X - Y)^2 + 4k_3k_4]^{1/2}$, and $\phi_{N,T}$ is the quantum yield of the violet and the green fluorescence. The violet fluorescence was observed to decay single exponentially. It infers $(\lambda_2 - X)$ of eq 1 is negligibly small compared with $(X - \lambda_1)$. In this case, we can regard λ_1 and λ_2, which were determined at several temperatures, as Y and X, respectively. Then the value of k_3 can be evaluated by eq 4 and 5:

$$k_3 = \lambda_2 - k_N \quad (4)$$

$$k_3 = \frac{k_1\phi_T}{k_5\phi_N}\lambda_1 \quad (5)$$

where k_N represents $k_1 + k_2$ and corresponds to the decay rate constant of the violet fluorescence at lower temperature, 5.5×10^8 s^{-1}. Arrhenius plots of eq 4 and 5 are shown in Figures 4 and 5, respectively. From Figure 4, we can determine the activation energy to be 2.8 kcal/mol and the Arrhenius factor to be 3.3×10^{12} s^{-1}. The plot in Figure 5 also gives a straight line with a slope equal to 3.0 kcal/mol.

The lifetime of the green fluorescence also increased with decreasing temperature and became constant (τ_0') at temperatures lower than 150 K. The decay rate of T*, therefore, is thought to consist of the temperature-independent term $(1/\tau_0')$ and dependent term $(1/\tau' - 1/\tau_0')$. The activation energy of the latter is obtained to be 4.1 kcal/mol from the Arrhenius plot of $1/\tau' - 1/\tau_0'$ shown in Figure 6.

Excited-State Proton Transfer of 3-HF and 3-HC in MP Solutions. Since 2-phenyl group in γ-pyrone ring of 3-HF has been pointed out to take an important role in the excited-state proton transfer, 3-HC, which lacks the phenyl group in 3-HF, is investigated in comparison with 3-HF.

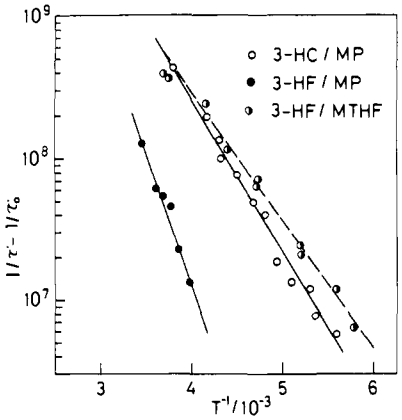

Figure 6. Plots of $(1/\tau' - 1/\tau_0')$ vs. $1/T$ of 3-HF in MTHF (◑) and in MP (●) and 3-HC in MP (○): 5×10^{-6} M 3-HF in MTHF; 1.1×10^{-6} M 3-HF in MP; 1.0×10^{-6} 3-HC in MP.

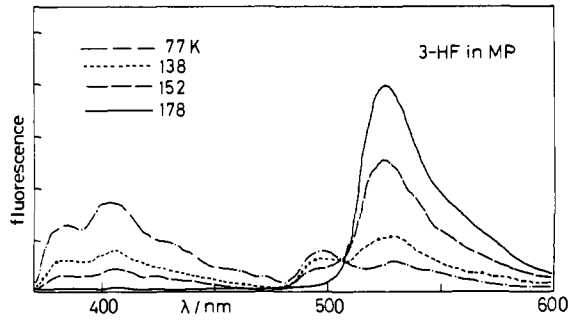

Figure 7. Fluorescence spectra (uncorrected) of 3-HF in MP (1.1×10^{-6} M) at several temperatures; excitation wavelength, 300 nm.

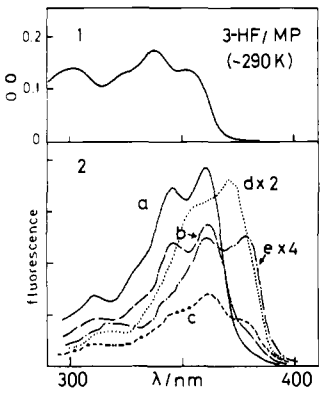

Figure 8. Absorption spectrum (1) of an MP solution of 3-HF (1.2×10^{-5} M) and fluorescence excitation spectra (2) (uncorrected) of 3-HF in MP (1.1×10^{-6} M) monitored: (a) at 530 nm at 178 K; (b) at 530 nm at 152 K; (c) at 530 nm at 138 K; (d) at 430 nm at 77 K; (e) at 495 nm at 77 K.

It is desirable to study the fluorescence of 3-HF and 3-HC in the same solvent. However, we could observe neither N* nor T* fluorescence of 3-HC in MTHF. Therefore, 3-methylpentane (MP) was used as solvent for comparison of fluorescence behavior. The MP solution of 3-HF exhibits almost no violet fluorescence at room temperature to 200 K, while the solution shows the green fluorescence with the excitation spectrum corresponding to the absorption spectrum. Upon decreasing the temperature of the MP solution below 180 K, the green fluorescence decreases and violet fluorescence appears, as shown in Figure 7. The excitation spectrum of the violet fluorescence was different from that of the green fluorescence. Therefore, it seems that the weak N* fluorescence is hidden by the violet fluorescence with a different excitation spectrum below 180 K (Figure 8), though the T* fluorescence was observed. This complicated fluorescence behavior of 3-HF in MP below 180 K would come from the low solubility

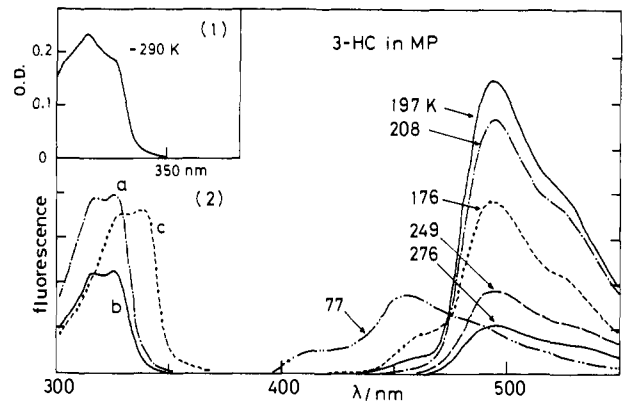

Figure 9. Fluorescence spectra (uncorrected) of 3-HC in MP (7×10^{-6} M) at several temperatures; excitation wavelength, 300 nm. Absorption spectrum (1) of 3-HC in MP (1.6×10^{-5}) and fluorescence excitation spectra (2) (uncorrected) of 3-HC in MP at 197 K (7×10^{-6} M) monitored (a) at 500 nm; (b) at 530 nm; (c) at 460 nm.

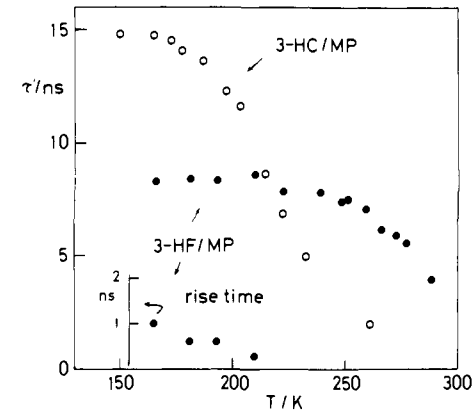

Figure 10. Fluorescence lifetimes of T* (●) of an MP solution of 3-HF and its rise times (● at the bottom of the figure) measured by nanosecond spectroscopy and T* lifetime (○,τ') of 3-HC in MP (1.0×10^{-6} M) at several temperatures.

of 3-HF in MP, which seems to result in the dimer and/or oligomer formations.

The fluorescence spectra of 3-HC in MP are shown in Figure 9. The fluorescence intensity that peaked at 490 nm increased with decreasing temperature above 200 K, but the band that peaked at 455 nm appeared to compensate for the former fluorescence below this temperature. No fluorescence was observed on a mirror image of the absorption spectrum; 3-HC in MP shows practically no N* fluorescence. The absorption and fluorescence excitation spectra of 3-HC are shown in Figure 9. The excitation spectrum of the 495–530-nm fluorescence is in good consistency with the absorption spectrum. Upon consideration of this fact and the large Stoke's shift, the fluorescence that peaked at 495 nm is concluded to be emitted from T* generated by the excited-state proton transfer. The excitation spectrum of the fluorescence band at 455 nm was different from that of the longer wavelength one. The fluorescence that appeared below 180 K might also result from the dimer and/or oligomer formation of the parent molecule. In this paper, therefore, the study of 3-HF and 3-HC in MP was limited to the excited-state proton transfer in the very dilute solutions of MP from room temperature to ca. 150 K.

The fluorescence rise and decay curves of T* in the MP solution of 3-HF and 3-HC were measured at 150–250 K. The rise and decay times of T* in 3-HF were observed at 160–250 K by nanosecond pulse excitations, though the rise times obtained (1–0.5 ns at 160–195 K) have a rather poor precision, the data of which are plotted in Figure 10. However, no N* fluorescence decay consistent with the rise time of the T* fluorescence was observed because of the weak N* fluorescence and the complication of the temperature dependence mentioned above. In the MP solution

of 3-HC, the rise time of the T* fluorescence was so rapid that the time constant could not be determined by nanosecond pulse excitation. Taking into account the time resolution of the apparatus, we estimated the rise time to be less than 300 ps. However, we could not use our picosecond equipment because of the short wavelength of the absorption spectrum of 3-HC. The rapid buildup of T* fluorescence implies that the excited-state proton transfer takes place much faster in 3-HC than in 3-HF. The lifetime of the T* fluorescence increased remarkably with decreasing temperature below 250 K and approached a constant value of ca. 15 ns (Figure 10). Similar temperature dependence of the fluorescence lifetime of T* in 3-HF was observed. However, an increase of the lifetime occurs at higher temperature than in 3-HC. From the Arrhenius plots shown in Figure 6, activation barriers of the temperature-dependent decay process of the T* fluorescence were estimated to be 4.5 kcal/mol for 3-HC and 8.6 kcal/mol for 3-HF.

Mechanism of the Excited-State Proton Transfer. Numerous investigations have been reported on the intramolecular excited-state proton transfer. Smith and Kaufmann[4] reported that the rate of intramolecular proton transfer in methyl salicylate was faster than 10^{11} s^{-1} even at 4 K. Barbara et al.[5,6] revealed that the excited-state tautomeric proton transfer occurred within 5 ps at temperatures above 4 K in salicylideneaniline and 2-(2-hydroxyphenyl)benzothiazole. Woolfe and Thistlethwaite[7] reported that the excitation of the "closed-ring" conformer of salicylamide led to extremely fast intramolecular proton transfer to give a fluorescent zwitterion, but gave no fluorescence from the uncharged excited state (a normal form). Shizuka et al.[2,3] proposed the intramolecular rapid proton transfer in 6-(2-hydroxy-5-methylphenyl)-*s*-triazines in MP solution without potential barrier, where no fluorescence was observed from the excited normal form.

It is noteworthy that 3-HF in MTHF exhibits a significantly different result from the usual intramolecular fast proton transfer mentioned above: the rather slow rate of the proton transfer with an activation energy. The basicity of the carbonyl oxygen depends on the torsional motion of the phenyl group on the pyrone ring and may take an important role in the proton transfer in 3-HF, the barrier height of which is thought to be temperature dependent. The angle between γ-pyrone and the phenyl planes has not been determined experimentally yet, even in the ground state. The estimated values by MO calculations are reported to be 40°[17] and 21°.[18] In the excited state of the normal form, N*, the phenyl group rotates about its junction axis to the pyrone ring to increase the basicity of the carbonyl oxygen. Then the intramolecular proton transfer occurs in the excited state. The rather slow proton transfer in 3-HF compared with that in 3-HC is thought to result from this torsional motion of the phenyl group associated with the proton transfer, as Sengupta and Kasha have pointed out, though the effect of solvent orientational relaxation cannot be neglected in a polar solvent such as MTHF.

The Arrhenius factor was found to be 3.3×10^{12} s^{-1}. If it is inherent in the pure proton-transfer rate, the value obtained is an instance of the rate constant of the intramolecular proton-transfer reaction in the excited state. The values of the intramolecular proton-transfer rate have been reported to be faster than 10^{11} s^{-1} in most cases.[2-7,19] The value obtained is consistent with the above estimation but fairly slow when compared to the OH vibrational frequency (10^{14} s^{-1}). The intramolecular distance between the hydroxyl hydrogen and the carbonyl oxygen in 3-HF is larger than that of the general intramolecular proton transfer via a five-membered ring. Further, Jose et al.[20] concluded from an IR absorption experiment that the intramolecular hydrogen bonding is weak in carbon tetrachloride. The absorption spectra of 3-HF were measured in a mixed solvent of MTHF and MP and showed a typical concentration dependence with isosbestic points.[21] This fact indicates that the intermolecular H bonding of 3-HF with MTHF overcomes the intramolecular H bonding in 3-HF. The proton transfer rate constant in 3-HF may be smaller than the ordinary case. The long interatomic distance and the intermolecular H bonding with MTHF may make the proton-transfer rate smaller than the usual case.

Smith and Kaufmann[4] found a nonradiative decay path from the tautomer of methyl salicylate with an activation energy of 3.7 kcal mol^{-1}. They did not carry out the identification of this channel. Barbara et al.[6] showed two temperature-dependent radiationless decay processes in 2-(2-hydroxyphenyl)benzothiazole at $T > 200$ K. The values of the activation energy are 4.0 and 11.4 kcal mol^{-1} in isopentane. They proposed that these processes involved torsional motion about the C_1–C_7 bond in the excited state. Our results that T* has a nonradiative decay with an activation energy of 4.1 kcal mol^{-1} for 3-HF in MTHF (8.6 kcal mol^{-1} in MP) and 4.8 kcal mol^{-1} for 3-HC in MP are consistent with these results. In the case of 3-HF, a double minimum potential might be proposed in contrast in the very rapid proton transfer mentioned above.[2-7] In such a case, we cannot neglect the possibility of the existence of the reverse proton-transfer process as a temperature-dependent nonradiative process. If the reverse proton-transfer rate constant, k_4, is smaller than k_3, the temperature dependence of k_4 and k_6 gives the same effect on the fluorescence lifetime and quantum yield, and hence the observed temperature-dependent process is not determined to be either k_4 or k_6. However, k_6 is supposed to be the dominant temperature-dependent process, at least above 200 K. Since no phosphorescence was observed in the visible region, the nonradiative decay channel seems to be internal conversion assisted by torsional motion, which is the mechanism that Barbara et al. have proposed and one of the mechanisms Smith and Kaufmann have mentioned.

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(21) With increasing MTHF content in the MP–MTHF mixed solution, the absorption maxima (340 and 355 nm) show red shifts with isosbestic points at 344, 355 and 358 nm. The Scot plot of the absorption intensity of 3-HF suggests the weak complex formation (H bonding) between 3-HF and MTHF.