7.10–6.61 (m 3 H, H-3′,4′,6′), 2.62 (t, 2 H, H-2 or H-4, J = 7 Hz), 2.41 (t, 2 H, H-4, or H-2, J = 7 Hz), 2.23 (s, 3 H, CH_3), 1.88 (pentet, 2 H, H-3, $J_{2,3} = J_{3,4}$ = 7 Hz); MS, m/z 196 (M^+).

3,4-Dihydro-8-fluoro-5-methyl-1(2*H*)-naphthalenone (6). Treatment of 4.9 g (0.025 mol) of carboxylic acid **5** with polyphosphoric acid at 90–94 °C for 8 min, followed by aqueous workup, gave a pale yellow solid. Sublimation of this material at 50 °C and 0.005 torr gave 3.7 g (83%) of ketone **6** as colorless prisms, mp 54–57 °C. Recrystallization of the sublimate from hexane gave colorless needles of **6** with mp 56.3–57.2 °C: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.22 (dd, 1 H, H-6, $J_{6,7}$ = 8 Hz, $J_{6,8}$ = 5 Hz), 6.80 (dd, 1 H, H-7, $J_{6,7}$ = 8 Hz, $J_{7,8}$ = 11 Hz), 2.82 (t, 2 H, H-2 or H-4, J = 6 Hz), 2.62 (t, 2 H, H-4 or H-2, J = 6 Hz), 2.24 (br s, 3 H, CH_3), 2.10 (pentet, 2 H, H-3, $J_{2,3} = J_{3,4}$ = 6 Hz); ^{19}F NMR (188.3 MHz, 0.30 M in $CDCl_3$) 2.34 ppm upfield from TTC[7] (dd of q, $J_{7,8}$ = 11.4 Hz, $J_{6,8}$ = 5.3 Hz, $J_{CH_3,8}$ = 1.1 Hz). Anal. ($C_{11}H_{11}FO$) C, H.

3,4-Dihydro-8-fluoro-5-methyl-1(2*H*)-naphthalenone Oximes (1a and 1b). Treatment of 0.50 g (2.8 mmol) of ketone **6** with 0.42 g (6.0 mmol) of hydroxylamine hydrochloride, 5 mL of pyridine, and 10 mL of 95% ethanol gave, after one recrystallization from 95% ethanol, 0.50 g (93%) of oxime **1b**, mp 193–196 °C. A second recrystallization from 95% ethanol gave long, colorless needles of **1b** with mp 197.5–199.0 °C: ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 10.4 (br s, 1 H, OH), 7.09 and 6.90 (AB part of ABX, 2 H, H-6 and H-7, respetively, $J_{6,7}$ = 8.3 Hz, $J_{6,8}$ = 5.3 Hz, $J_{7,8}$ = 12.0 Hz), 2.89 (t, 2 H, H-2, $J_{2,3}$ = 6.7 Hz), 2.68 (t, 2 H, H-4, $J_{3,4}$ = 6.1 Hz), 2.25 (br s, 3 H, CH_3), 1.86 (pentet, 2 H, H-3, apparent J = 6.4 Hz); ^{19}F NMR (188.3 MHz, 0.27 M in $CDCl_3$) see Figure 3 and Table I. Anal. ($C_{11}H_{12}FNO$) C, H.

Similar treatment of 0.64 g (3.6 mmol) of ketone **6** with 0.30 g (4.3 mmol) of (^{15}N)hydroxylamine hydrochloride (Cambridge Isotope Laboratories, Inc., 95% ^{15}N), 7 mL of pyridine, and 14 mL of 95% ethanol gave, after recrystallization of the crude product from 95% ethanol, 0.63 g (90%) of oxime **1a**, mp 196.8–198.4 °C: ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 10.4 (br s, 1 H, OH), 7.09 and 6.90 (AB part of ABX, 2 H, H-6 and H-7, respectively, $J_{6,7}$ = 8.3 Hz, $J_{6,8}$ = 5.3 Hz, $J_{7,8}$ = 12.0 Hz), 2.89 (t of d, 2 H, H-2, $J_{2,3}$ = 6.7 Hz, $J_{2,N}$ = 1.8 Hz), 2.68 (t, 2 H, H-4, $J_{3,4}$ = 6.1 Hz), 2.25 (br s, 3 H, CH_3), 1.86 (pentet, 2 H, H-3, apparent J = 6.4 Hz); ^{19}F NMR (188.3 MHz, 0.27 M in $CDCl_3$) see Figure 3 and Table I; MS, m/z 194 (M^+).

***o*-Fluorobenzaldehyde Oximes (2a and 2b).** A mixture of 0.30 g (2.4 mmol) of *o*-fluorobenzaldehyde, 0.23 g (3.3 mmol) of hydroxylamine hydrochloride, 1 mL of water, 1 mL of 10% aqueous sodium hydroxide, and about 10 drops of 95% ethanol (to bring the aldehyde into solution) was heated in a boiling water bath for 15 min. Then the solution was cooled thoroughly in ice, and 0.2 g (59%) of oxime **2b** was collected by filtration. Recrystallization from hexane gave 0.13 g of **2b** as white needles, mp 61.8–62.3 °C (lit.[18] mp 63 °C): ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 9.2 (br s, 1 H, OH), 8.38 (s, 1 H, CH=N), 7.77 (t of d, 1 H, H-6, apparent J = 7.4 and 1.8 Hz), 7.37 (t of dd, 1 H, H-4, apparent J = 7.8, 5.3, and 1.8 Hz), 7.16 (br t, 1 H, H-5, apparent J = 7.5 Hz), 7.09 (ddd, 1 H, H-3, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 8.2 Hz, $J_{3,5}$ = 1.2 Hz); ^{19}F NMR (188.3 MHz, 0.63 M in $CDCl_3$) 4.44 ppm upfield from TTC[7] (ddd, $J_{2,3}$ = 10.4 Hz, $J_{2,4}$ = 5.3 Hz, $J_{2,6}$ = 7.2 Hz).

An identical procedure, except for the use of (^{15}N)hydroxylamine hydrochloride (Cambridge Isotope Laboratories, Inc., 95% ^{15}N), was employed to prepare 0.14 g of oxime **2a**, mp 62.0–63.2 °C: ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 9.2 (br s, 1 H, OH), 8.38 (d, 1 H, CH=N, J_{HN} = 2.3 Hz), 7.77 (t of d, 1 H, H-6, apparent J = 7.4 and 1.8 Hz), 7.37 (t of dd, 1 H, H-4, apparent J = 7.8, 5.3, and 1.8 Hz), 7.16 (br t, 1 H, H-5, apparent J = 7.5 Hz), 7.09 (ddd, 1 H, H-3, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 8.2 Hz, $J_{3,5}$ = 1.2 Hz); ^{19}F NMR (188.3 MHz, 0.63 M in $CDCl_3$) 4.44 ppm upfield from TTC[7] (dddd, $J_{2,3}$ = 10.4 Hz, $J_{2,4}$ = 5.3 Hz, $J_{2,6}$ = 7.2 Hz, $J_{2,N}$ = 3.2 Hz); MS, m/z 140 (M^+).

Acknowledgment. We are grateful to Dr. George R. Furst for assistance with the ^{19}F NMR measurements, and to IBM Instruments, Inc. for the loan of a ^{19}F preamplifier. We than Debbie E. Fishbein, who, for another purpose, first worked out the synthesis of ester **4**.

Registry No. 1a, 97072-88-3; **1b**, 97072-89-4; **2a**, 97072-90-7; **2b**, 24652-66-2; **3**, 1422-53-3; **4**, 97072-91-8; **5**, 97072-92-9; **6**, 97072-93-0; (^{15}N)-hydroxylamine hydrochloride, 40711-48-6; *o*-fluorobenzaldehyde, 446-52-6; 3-(5-fluoro-2-methylbenzoyl)propionic acid, 97072-94-1; 4-nitrotoluene, 99-99-0; 2-bromo-4-nitrotoluene, 7745-93-9; 3-bromo-4-methylaniline, 7745-91-7; carbomethoxypropionyl chloride, 1490-25-1; hydroxylamine hydrochloride, 5470-11-1.

(18) Shoesmith, B.; Sosson, C. E.; Slater, R. H. *J. Chem. Soc.* **1926**, 2760–2761.

Transient Absorption and Two-Step Laser-Excitation Fluorescence Studies on the Proton Transfer in the Ground and Excited States of 3-Hydroxyxanthone in Alcohols

Michiya Itoh,* Noriyasu Yoshida, and Masanobu Takashima

Contribution from the Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan. *Received February 14, 1985*

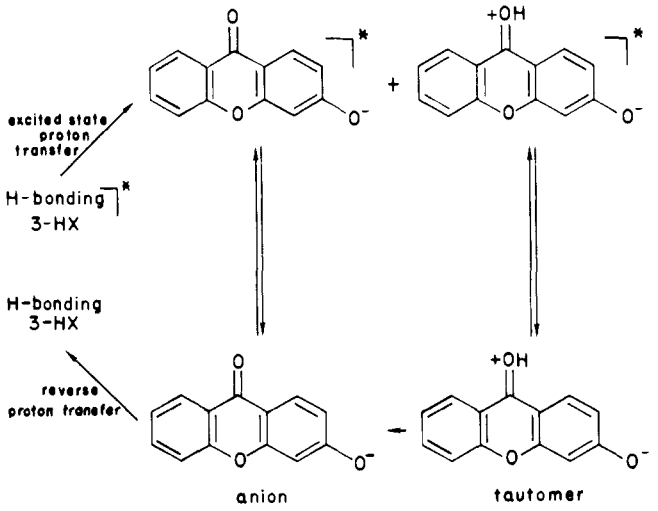
Abstract: The alcoholic solutions of 3-hydroxyxanthone (3-HX) exhibit considerably large Stokes-shifted fluorescence in the 430–530-nm region at room temperature. In the deaerated methanol solution, the 450-nm fluorescence decays almost single exponentially with a lifetime of 5.9 ns, while the longer wavelength fluorescence (470–530 nm) shows double exponential (τ = 0.5 and 5.8 ns). The long and short decay fluorescences were ascribed to anion and tautomer simultaneously generated by the excited-state proton transfer in 3-HX, respectively. The transient absorption of the deaerated methanol solution of 3-HX shows a strong absorption band with a rise at 355 nm and broad bands at 370–460 nm. These absorption bands were ascribed to the ground-state anion and tautomer formed in the relaxation of their excited states. The two-step laser-excitation (TSLE) fluorescence by the second laser excitation of the transient absorption was measured at room temperature. The second laser excitations at 440 and 457 nm exhibit the short lived fluorescence spectra (τ = ~0.6 ns) at 470–530 nm, which is ascribed to the tautomer fluorescence. The second laser excitations of 406 and/or 420 nm at several delay times afford the TSLE time-resolved fluorescence spectra. The TSLE fluorescence at 470–530 nm decreases rapidly in intensity with increasing delay time, while the intensity in the 460-nm region gradually increases at long delay times. The former and latter were ascribed to the tautomer and anion of 3-HX, respectively. The rise and decay of the ground-state anion and tautomer obtained by TSLE variable delay are consistent with those obtained by transient absorption spectra. This fact suggests that the ground-state anion may be generated at the expense of the ground-state tautomer in addition to the formation from its excited state, and this anion relaxes to the parent molecule by the reverse proton transfer in the ground state.

Two-step laser-excitation fluorescence or two-step laser-induced fluorescence spectra have been reported for the investigations of unstable molecules[1-3] and/or transient states.[4] We have reported in several papers of the transient absorption and TSLE fluores-

0002-7863/85/1507-4819$01.50/0

cence studies on the proton transfer and isomerization not only in the excited state but also in the ground state of the several hydrogen bonding systems.[3,5,6] The selective wavelength excitation of transient absorption by the second laser with selective delay time from the first one affords the TSLE time-resolved fluorescence spectra, which enable us to distinguish several transients with different ground-state lifetimes. Recently, Itoh and Adachi[6] have demonstrated the formation of two different types of phototautomers in the excited-state proton transfer in the methanol solution of 7-hydroxyflavone by the TSLE time-resolved fluorescence spectra and its kinetics. Further, Itoh and Fujiwara[7] have reported the kinetics and dynamics of intramolecular photoisomerization and the ground-state relaxation processes in 2-(2-hydroxyphenyl)benzothiazole and 2-(2-hydroxyphenyl)benzoxazole.

Schipfer et al. reported a series of pH-dependent fluorescence spectra (steady state) of several phenols in protic solvents. Wolfbeis and Fürlinger[9] have suggested fluorescence spectra of anion, cation, and tautomer forms of 3-hydroxyxanthone (3-HX) in various basic to acidic solvent systems. However, the primary processes of formation of these species and the relaxation processes both in the ground and excited states are completely obscure. This paper presents transient absorption and TSLE fluorescence spectroscopies as well as an ordinary nanosecond fluorescence of 3-HX in several alcoholic solvents. The paper demonstrates simultaneous formations of anion and tautomer in the excited state of the hydrogen bonding system of 3-HX with alcohol molecules. The former and latter exhibit fluorescence spectra at 430–500 nm (lifetime τ = 5.9 ns) and at 470–530 nm (τ = 0.6 ns), respectively, which are superimposed in almost the same wavelength region. Transient absorption and TSLE fluorescence including variable delay plots demonstrate the rise of formation of the ground-state anion (rise time 4–5 μs) at the expense of the ground-state tautomer (decay time ~4.1 μs) in addition to the anion formation from its excited state. These rise and decay are completely consistent with the data obtained by the transient absorption spectroscopy. The ground-state anion may relax to the parent molecule by the reverse proton transfer in the solvent molecule. The proposed reaction scheme in both the ground and excited states is as follows:



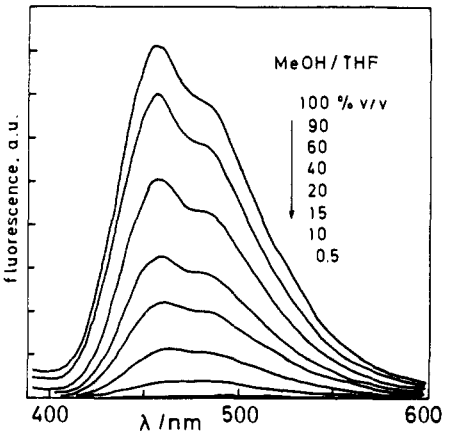


Figure 1. Fluorescence spectra of 3-HX (2.3×10^{-5} M) in the CH_3OH/THF mixed solvent system at room temperature; excitation wavelength 340 nm.

Experimental Section

Materials and Procedures. 3-Hydroxyxanthone was prepared from resorcinol and ethylsalicylate (both Nakarai Chem.) by the method described in the literature[10] and purified by chromatography (silica gel/petroether–benzene) and recrystallization from benzene, mp 241 °C. Structure and purity were confirmed by elementary analysis and mass, NMR, and UV spectra. Spectrograde alcohols and THF (Nakarai Chem.) were used without further purification. Samples were deaerated by the conventional method reported previously.

Transient Absorption and Two-Step Laser-Excitation Fluorescence Spectroscopies. Transient absorption spectra were determined by using an excimer laser (Lambda Physik, EMG-50E, 308 nm) and a monitoring steady Xe lamp with a synchronously operated shutter. For the TSLE fluorescence, the excimer laser was used as the first excitation light pulse, and the second N_2 laser pumped dye laser (Molectron UV-12 and DL-14) was synchronously operated with the excimer laser by a pulse generator and a variable delay circuit. The detection and signal analysis were performed by almost a similar method to those reported previously,[5-7] except with a transient scope (Iwatsu TS 8123) and a microcomputer. The TSLE time-resolved fluorescence spectra were constructed point-by-point by changing the delay time between the first and second laser pulses. Since a small fluorescence signal due to the stable ground-state anion present in methanol was detected only by dye laser excitation, the TSLE fluorescence was constructed by subtraction of this anion signal from the TSLE fluorescence intensity obtained by the first and second excitations. The former was less than 20% of the latter at rather small delay time.

Results and Discussion

Steady-State and Nanosecond Fluorescence. Wolfbeis and Fürlinger suggested three species (anion, cation, and tautomer) of 3-HX in pH-dependent absorption and fluorescence spectroscopies.[9] The anion fluorescence (λ_{max} 461 nm) was observed in the pH 14–2 range, while the cation fluorescence (λ_{max} 453 nm) was detected only in solutions of strong acidity such as 95% sulfuric acid. Further, they observed unusually long wavelength fluorescence spectra (λ_{max} 481–515 nm) of this compound in cyclohexane saturated with methanol, which was ascribed to the excited-state tautomer.

Figure 1 exhibits unusually large Stokes-shifted fluorescence spectra of 3-HX in several concentrations of methanol in tetrahydrofuran (THF). The fluorescence spectra increase in intensity with increasing methanol concentration, though this compound is nonfluorescent in THF. The fluorescence excitation spectra are almost completely identical with the longest absorption band in methanol (λ_{sh} 325–338 nm).[11] Taking account of the large Stokes shift of fluorescence and the spectral assignment by Wolfbeis and Fürlinger,[9] the broad fluorescence spectra at 430–530 nm may be attributable to the anion generated in the excited state of a hydrogen bonding system of 3-HX in methanol. The

(1) Kelley, D. F.; Milton, S. V.; Huppert, D.; Rentzepis, P. M. *J. Phys. Chem.* **1983**, *87*, 1842. Hilinski, E. F.; Huppert, D.; Kelly, D. F.; Milton, S. V.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 1951.
(2) Sitzmann, E. V.; Wang, E. V.; Eisenthal, K. B. *J. Phys. Chem.* **1983**, *87*, 2283.
(3) Itoh, M.; Adachi, T.; Tokumura, K. *J. Am. Chem. Soc.* **1983**, *105*, 4828; **1984**, *106*, 850.
(4) Tobita, S.; Tanaka, I. *Chem. Phys. Lett.* **1983**, *96*, 517.
(5) Itoh, M.; Fujiwara, Y. *J. Phys. Chem.* **1983**, *87*, 4558.
(6) Itoh, M.; Adachi, T. *J. Am. Chem. Soc.* **1984**, *106*, 4320.
(7) Itoh, M.; Fujiwara, Y. *J. Am. Chem. Soc.* **1985**, *107*, 1561.
(8) Schipfer, R.; Wolfbeis, O. S.; Knierzinger, A. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1443 and references therein.
(9) Wolfbeis, O. S.; Fürlinger, E. *J. Am. Chem. Soc.* **1982**, *104*, 4069.
(10) Ravji, J. P.; Tyivedi, K. N. *Indian J. Chem.* **1083**, *22B*, 444.
(11) Two peaks at 315 and 329 nm in THF are shifted to these wavelengths (shoulders) in methanol.

Table I. Fluorescence Lifetimes (ns) and Composition (in Parentheses, %) of the Excited-State Anion and Tautomer in the Deaerated Solutions at Room Temperature (15 °C) Determined by a Single Photon Counting System[3,6]

solvent	anion	tautomer
methanol	0.54 (68.4)[a]	5.87 (31.6)[a]
ethanol	0.57 (60.3)	5.60 (39.7)
propanol	0.51 (54.0)	5.14 (56.0)
butanol	0.65 (40.1)	4.98 (59.9)

[a] Determined from the decay components of the double exponential decay curve collected through Toshiba L-42 filter. [b] Errors of fluorescence lifetimes are approximately less than 10%.

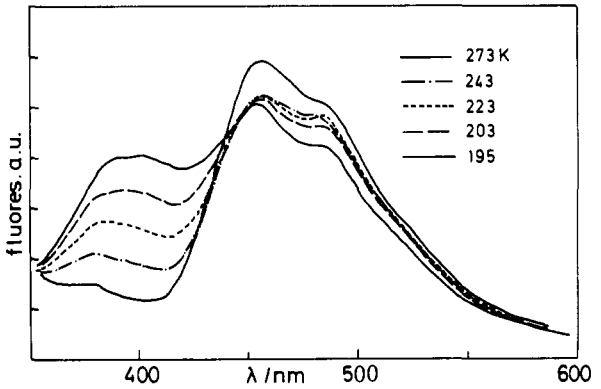


Figure 2. Temperature dependence of fluorescence spectra of 3-HX (2.8×10^{-5} M); excitation wavelength 340 nm.

fluorescence decay curve of the deaerated methanol solution of 3-HX at ~450 nm was observed to be a single exponential with a lifetime of 5.9 ns, while the decay at longer wavelength (~470 nm) was expressed by a double exponential with lifetimes of 5.8 and 0.6 ns at room temperature. Therefore, two fluorescence spectra with short and long lifetimes may be involved in the ~470–530-nm region. These long and short lifetime fluorescence spectra are tentatively ascribed to the anion and tautomer superimposed, respectively. These assignments will be confirmed by the two-step laser-excitation fluorescence spectroscopy. Almost similar fluorescence spectra and lifetimes were observed in several other alcohols (ethanol, propanol, and butanol). Therefore, it was suggested that the anion and tautomer are generated in the excited state of 3-HX in several neutral alcohols. Composition of anion and tautomer seems to be dependent on the solvent polarity and hydrogen-bonding character. The composition of anion and tautomer was determined from the relative component of long and short fluorescence lifetimes in double exponential decay curves obtained in several alcohols, whose data are summarized in Table I. As seen in Table I, the anion formation decreases with decreasing dielectric constant and refractive index of alcohols, while the tautomer formation increases.

The methanol solution of 3-HX shows remarkable temperature dependence of fluorescence spectra (>195K), and a short wavelength fluorescence (Figure 2) appears and increases with decreasing temperature. This 380–400-nm fluorescence seems to be attributable to a normal form fluorescence of the hydrogen-bonding system of 3-HX with methanol. However, since the 430–530-nm fluorescence consists of two fluorescence spectra owing to anion and tautomer, it is rather difficult to obtain kinetic data of the excited-state proton transfer such as an activation energy for the anion and tautomer formations from temperature dependence of fluorescence spectra and lifetimes at the present stage.

Transient Absorption Spectroscopy. Transient absorption spectra of the deaerated methanol solution of 3-HX were determined at room temperature, and these spectra are shown in Figure 3. A very long lived absorption band observed at 330–360 nm may be attributable to the anion form of this compound, since a strong absorption band was observed in the basic methanol solution at 355 nm, which was ascribed to the anion form by Wolfbeis and Fürlinger.[9] In addition to this transient absorption,

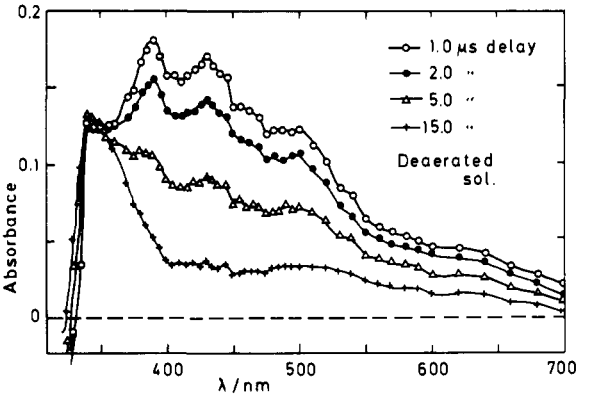


Figure 3. Transient absorption spectra of the deaerated methanol solution of 3-HX (6.0×10^{-5} M) at room temperature.

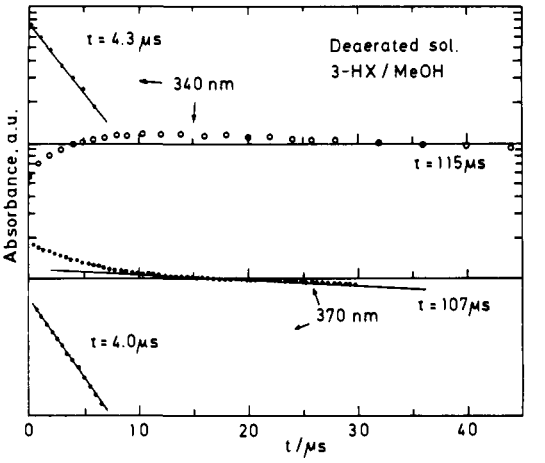


Figure 4. Time-dependent profiles of transient absorption bands monitored at 340 and 370 nm in deaerated methanol solution of 3-HX shown in Figure 3. The 340-nm absorption (○) shows a rise and decay of absorption. Linear plots at the top of the figure indicate a rise of the 340-nm absorption obtained from the rise and decay curve. Further, the 370-nm absorption (●) shows a double exponential decay, from which linear plots exhibiting a short decay time (4.0 μs) were obtained.

Table II. Decay (or Rise) Times (μs) of Transient Absorption Bands in the Deaerated Methanol Solution of 3-HX at Room Temperature (15 °C)

	monitored at		
	340 nm	370 nm	420 nm[a]
tautomer	rise 4.3	4.0	4.4
anion	115	107	

[a] Data monitored at 420 nm have less accuracy because of a very small amount of a long lived component involved in the decay curve. Errors are approximately ±10%.

the spectra show rather strong bands in the 370–460-nm region.[12] The decay profile of the band monitored at 370 nm is shown in Figure 4. The decay curves indicate that these absorptions consist of two absorption bands with short and very long decay times of 4.4 and ~100 μs. Since the singlet excited states of anion and tautomer were observed to be 5.9 and 0.6 ns, as mentioned above, the decay times of the transient absorption bands may be ascribed to those of the ground-state species. Taking account of the observation of fluorescence spectra owing to the tautomer at 470–530 nm as mentioned in the last section, it seems that the longer wavelength transient absorption band is attributable to the ground-state tautomer, which is confirmed by the TSLE fluorescence, as will be mentioned in the next section. Data are summarized in Table II.

(12) Garner, A.; Wilinson, F. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1010.

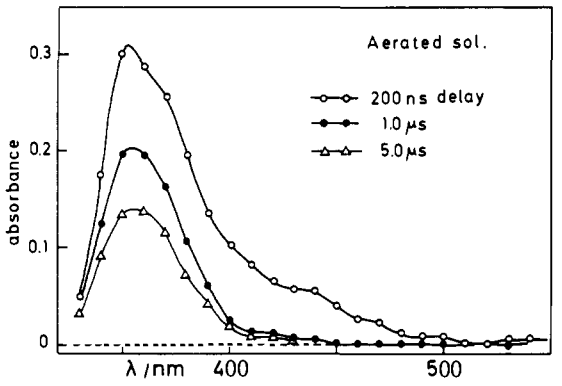


Figure 5. Transient absorption spectra of the aerated methanol solution of 3-HX (7.0×10^{-5} M) at room temperature.

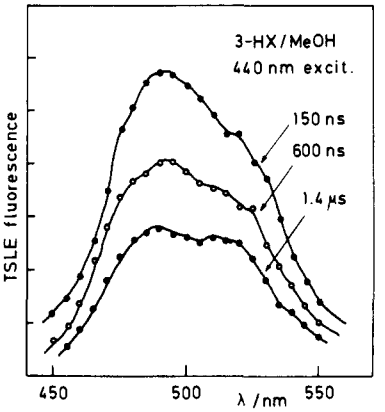


Figure 6. The TSLE fluorescence spectra of the deaerated methanol solution of 3-HX (7.0×10^{-5} M) in the 440-nm second laser excitation. Delay times from the first pulse are 150 and 600 ns and 1.4 μs.

Figure 4 also shows a time-dependent profile of the transient absorption band at 340 nm, which exhibits a rise and long decay of absorption. The rise and decay times were obtained to be 4.3 and 115 μs, respectively. It is noteworthy that these rise and decay times are in fair agreement with short and long decay times of the 360–460-nm absorption band, as mentioned above. Therefore, if the absorption bands at 350–420 and 380–470 nm are ascribed to the anion and tautomer, respectively, it is suggested that the ground-state anion may be generated at the expense of tautomer by releasing a proton from the tautomer to the solvent molecule. The rise time of anion and the decay of tautomer may reflect the reaction rate of this process in the ground state. These arguments are confirmed by the TSLE time-resolved fluorescence spectra and variable delay plots, as will be mentioned in the next section. Further, a long-lived absorption band was observed at 480–600 nm. Taking account of an observation of the T_n–T_1 absorption band of xanthone at 600–650 nm,[12] this band may be attributable to the T_n–T_1 absorption of 3-HX because of complete quenching in the aerated solution.

In the aerated methanol solution, the transient absorption band due to the tautomer was remarkably quenched, while the T_n–T_1 absorption was completely quenched, as seen in Figure 5. The shorter decay time at 420–460 nm decreased to ~300 ns, and no rise of the anion band at 350 nm was observed. The decreasing transient absorption intensity and shortening of the decay time of the ground-state tautomer seem to be attributable to the oxygenation reaction of tautomer in the aerated solution, though no reaction product was detected.

Two-Step Laser-Excitation Time-Resolved Fluorescence. The TSLE fluorescence spectra by the second laser excitations of 440 and 420 nm of the deaerated methanol solution of 3-HX are shown in Figures 6 and 7. These fluorescence spectra in the 440-nm excitation are almost identical with each other irrespective of delay times. The intensities of these TSLE fluorescence spectra are plotted vs. delay times of the second laser from the first one, as

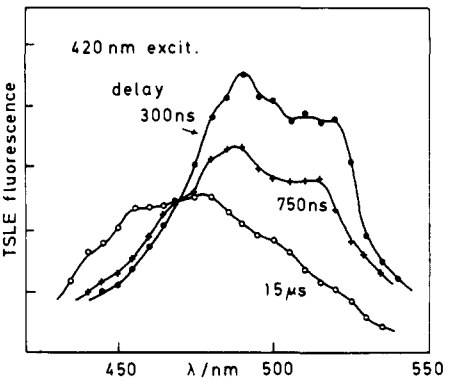


Figure 7. The TSLE fluorescence spectra of the deaerated methanol solution of 3-HX in the 420-nm second laser excitation.

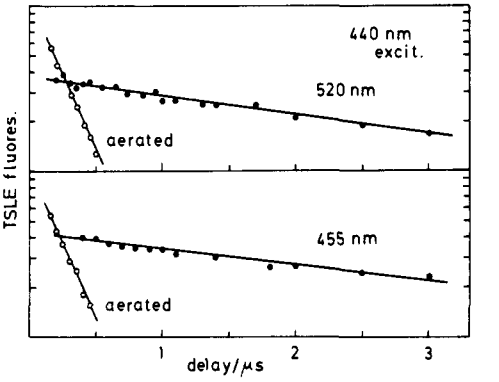


Figure 8. Variable delay plots of TSLE fluorescence intensity monitored at 520 (upper) and 455 nm (lower) of the aerated (○) and deaerated (●) methanol solutions of 3-HX.

shown in Figure 8. The slope of this linear plot observed throughout 460–530 nm indicates the decay time of 4.1 μs of the ground-state species. The decay time of 4.1 μs coincides perfectly with that of the transient absorption band at 450 nm. Further the fluorescence lifetime of this TSLE fluorescence by the 440-nm second laser excitation (delay time ~300 ns) was observed to be approximately 0.6 ns. The obtained lifetime of the TSLE fluorescence is consistent with that of an ordinary pulse excitation, though the former has much less accuracy. Almost the same TSLE fluorescence spectra and lifetime were observed in the second laser excitation of 456 nm. These results demonstrate that the ground-state transient (τ = 4.1 μs) exhibiting the TSLE fluorescence at 460–530 nm may be attributable to the ground-state tautomer of 3-HX, as shown in the reaction scheme of the introductory section.

In the second laser excitation at 420 nm, the TSLE fluorescence spectra at several delay times (~300 ns to several microseconds) are shown in Figure 7. The fluorescence in the 470–530-nm region decreases rapidly in intensity with increasing delay time, while the intensity in the 460-nm region gradually increases at long delay times. These spectra indicate that the long-lived transient exhibiting 460-nm fluorescence is generated at the expense of the short-lived transient showing long wavelength fluorescence (460–530 nm). The plots of TSLE fluorescence intensity monitored at 460 and 520 nm vs. delay times are shown in Figure 9. The plots of 460 nm show a rise and decay of TSLE fluorescence intensity, while the plots at 520 nm show double exponential decays, whose data are summarized in Table III. The long lifetimes obtained at 460 and 520 nm may be ascribed to the lifetime of the anion. The rise at 450 nm and the short decay at 520 nm, which are almost identical with each other, demonstrate the anion formation at the expense of tautomer, as mentioned above. However, no significant rise of transient absorption due to anion was observed at 350–450 nm, possibly because the short lived band is much greater in intensity than the long lived one of this region, and on the contrary the quantum yield of the TSLE

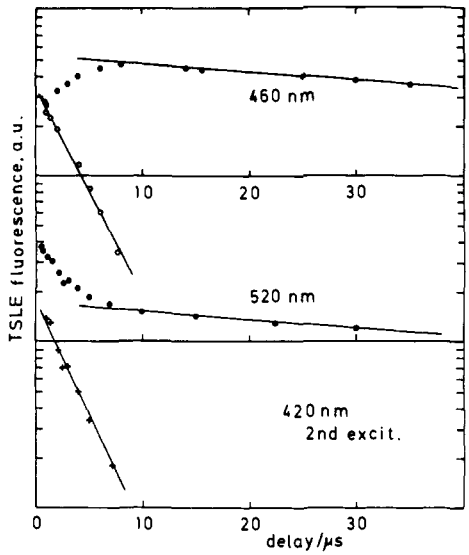


Figure 9. Variable delay plots of TSLE fluorescence intensity of the deaerated methanol solution of 3-HX; monitoring wavelengths 460 and 520 nm; the second laser, 420 nm. Two linear plots in the short time region are rise and decay of TSLE fluorescence intensity.

Table III. Lifetimes of the Ground-State Transients (Anion and Tautomer) in the Deaerated Methanol Solution of 3-HX Determined by TSLE Fluorescence at Room Temperature (Data in Parentheses Are in the Aerated Solution)

	monitored wavelength	
second excitation	460 nm	520 nm
420 nm	4.2[a] μs rise (–) 90 μs (110)	4.4 μs (250 ns) 100 μs (–)[b]
440 nm	4.2 μs (240 ns)[c]	4.1 μs (240 ns)[c]

[a] Determined from a rise of TSLE fluorescence intensity in the variable delay plots. [b] No fluorescence owing to the long-lived ground-state anion was detected in the aerated solution at this wavelength. [c] No anion fluorescence was detected in this second laser excitation.

fluorescence of the anion may be much greater than that of the tautomer.

The difference of the TSLE fluorescence spectra in the second laser excitation between 440 and 420 nm suggests that transient absorption bands of the anion and tautomer are superimposed on each other at 420 nm, while almost no absorption band due to anion is involved at 440 nm. Figure 10 shows the TSLE time-resolved fluorescence spectra of the deaerated methanol solution by the second laser excitation of 386 nm. The spectra by this second excitation demonstrate a remarkable rise in intensity at longer delay time and small contribution of the tautomer fluorescence. The similar variable delay plots of TSLE fluorescence intensity afford the rise and decay times of the ground-state anion, which are almost identical with the respective data obtained by the other wavelength excitations (406 nm) within experimental error.

In the aerated methanol solution of 3-HX, TSLE fluorescence spectra by the 440 and 420-nm second excitations are shown in Figure 11. The fluorescence spectra in the 440-nm excitation are almost independent of delay time. The fluorescence intensity decays much faster than the deaerated solution shown in Figure 3, though both spectra in the short delay times are almost identical with each other. The variable delay plots of the fluorescence intensities shown in Figure 8 indicate the much shorter decay time of the ground-state tautomer in the aerated solution than in the deaerated one. Further similar TSLE fluorescence spectra of the 420-nm second excitation are also shown in Figure 11. It is noteworthy that fluorescence of the 420-nm excitation shows a somewhat blue shift at 200-ns delay time compared with the 440-nm excitation fluorescence, and a shorter wavelength fluorescence appears at the long delay time. The decay behavior of the ground-state transients exhibiting these fluorescence spectra

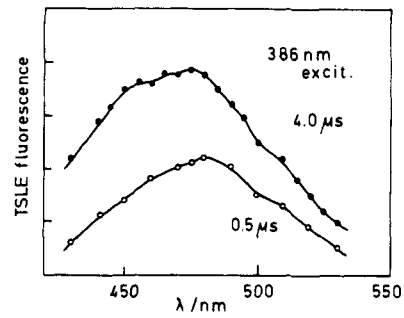


Figure 10. Time-resolved TSLE fluorescence spectra of the deaerated methanol solution of 3-HX (6.0×10^{-5} M) by the 386-nm second laser excitation. The spectra show a rise of fluorescence spectra at the delay times 0.5 and 4.0 μs.

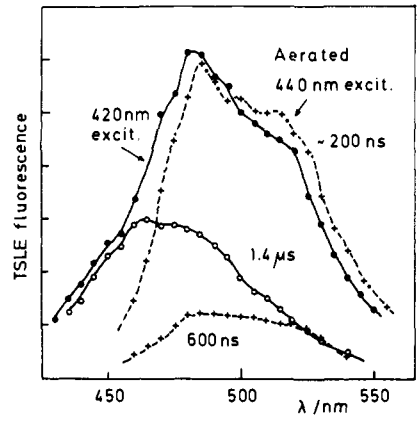


Figure 11. Time-resolved TSLE fluorescence spectra of the aerated methanol solution of 3-HX (6.5×10^{-5} M) by the 420- and 440-nm second laser excitations; times indicated, delay time from the first laser pulse.

(430–530 nm) was demonstrated by similar variable delay plots. The fluorescence monitored at 520 nm decays almost single exponentially, and that of 460 nm shows double exponential decay without rise. These short and long decay times were obtained to be 240 ns and ~100 μs from these plots. The short decay time is in agreement with that of the transient absorption band at 450 nm as mentioned in the last section, which was ascribed to the ground-state tautomer in the aerated solution. Further, it is noteworthy that the variable delay plots of 460-nm fluorescence do not exhibit any rise of fluorescence intensity in the aerated solution. This fact is consistent with the absence of a significant rise in the transient absorption band at 340 nm, as mentioned in the last section. These results coincide with the short lifetime of the ground-state tautomer in the aerated solution. However, the lifetime of the long-lived transient ascribed to the anion was determined to be ~100 μs, which seems to be independent of aeration. The fact implies no influence of oxygen upon the reverse proton transfer from anion to the parent molecule in the ground state.

Mechanism of the Anion and Tautomer Formations in the Excited State and Their Relaxation Processes. In the previous papers, Itoh et al.[3,5] and Itoh and Adachi[6] have reported the excited-state proton transfer in the methanol solutions of 7-hydroxyquinoline and -flavone which have two functional groups for hydrogen bonding with alcohols. It has been demonstrated that two methanol molecules were required for the excited-state proton transfer to form their respective phototautomers. In this paper, both anion and tautomer formations of 3-HX have been demonstrated in methanol and other alcohols. If the structure of the tautomer is expressed by a zwitterion form as shown in the reaction scheme mentioned above, two methanol molecules may be involved for the tautomer formation. However, a stoichiometric investigation for the formation of these species between 3-HX and methanol cannot be performed because of superimposed fluorescence spectra of the anion and the tautomer.

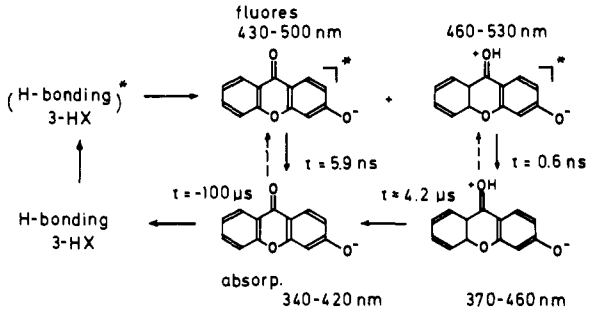


Figure 12. Comprehensive reaction scheme and data of the excited-state proton transfer in the methanol solution of 3-HX (deaerated) and of the relaxation processes both in the ground and excited states.

In the tautomer formation in the excited state, there may be two possible mechanisms: the simultaneous formation of tautomer from a hydrogen-bonding 3-HX with two methanol molecules and a step-wise formation by proton transfer from methanol to anion (probably to carbonyl oxygen). However, the latter mechanism, the step-wise formation, may be negligible or at least insignificant because the TSLE fluorescence spectrum of tautomer is not significant in the second laser excitation of the transient absorption band of the anion, as mentioned above. Therefore, it seems that the anion and tautomer are generated individually from their respective excited states of one and two methanol H-bonding complexes of 3-HX. This excited-state behavior is in contrast to the fact that the ground-state tautomer relaxes stepwise to the parent molecule through the formation of anion by releasing a proton from carbonyl oxygen. The proposed mechanism and data are shown in Figure 12.

The excited-state anion and tautomer dissipate their excitation energy with lifetimes of 5.9 and 0.6 ns to the respective ground states. The transient absorption and TSLE time-resolved fluorescence spectra demonstrated a notable evidence of the anion formation from tautomer in the ground state—the fact that the ground-state anion is generated not only from the energy dissipation of this excited state but also from the ground-state tautomer ($\tau = \sim 4.1$ μs). The rise of TSLE fluorescence intensity reflects the latter slow process (T → A). Further, the very long lifetime of the ground-state anion (~ 100 μs) implies a very slow reaction rate of the reverse proton transfer to the parent molecule. On the other hand, a weak fluorescence signal due to the stable ground-state anion was detected only by dye laser excitation as mentioned in the Experimental Section. Therefore, a small amount of the stable anion present in the solvent which is generated by a simple ground-state dissociation may be involved in the reaction scheme.[13,14] However, the reaction kinetics and dynamics obtained by the transient absorption and TSLE fluorescence cannot be disturbed by this stable anion. In the aerated solution, neither rise of TSLE fluorescence intensity in the variable delay plots was observed nor rise of the transient absorption at 340–360 nm owng to the anion was detected. The fact is consistent with the short lifetime (τ = 300–400 ns) of the ground-state tautomer, which seems to imply the oxygenation reaction in aerated condition as mentioned in the last section.

Acknowledgment. This work was supported by a Grand-in-Aid for Scientific Research (No. 58470125) from the Ministry of Education, Science and Culture of Japan.

Registry No. 3-Hydroxyxanthone, 3722-51-8.

(13) A similar stable anion formation of methyl salicylate and related compounds in alcohols was encountered in the case of TSLE fluorescence study on the excited-state proton transfer: Nishiya, A.; Yamauchi, S.; Hirota, N.; Fujiwara, Y.; Itoh, M., to be published.
(14) Kloepffer, W.; Naundorf, G. *J. Lumin.* **1974**, *8*, 457.

Free Cyclohexyl Cations from the Decay of Tritiated Cyclohexane

Marina Attinà,[†] Fulvio Cacace,*[†] Romano Cipollini,[†] and Maurizio Speranza*[‡]

Contribution from the University of Rome, 00100 Rome, Italy, and Istituto di Chimica Nucleare del CNR, Monterotondo Scalo (Rome), Italy. *Received February 4, 1985*

Abstract: The question concerning the existence, the stability, and the isomerization rate of free, unstabilized cyclohexyl cation has been addressed by using the decay technique. Labeled cyclohexyl ions, unsolvated and free of counterions, have been generated in gaseous and liquid systems by the decay of a constituent atom of multitritiated cyclohexane. The daughter ions possess up to ca. 30 kcal mol^{-1} excess internal energy, being formed in a geometry reminescent of the neutral parent rather than in the most stable structure of the cyclohexyl cation. The analysis of the tritiated products from the reaction of the decay ions with suitable nucleophiles in different environments has provided compelling evidence for the existence of free cyclohexyl ion as a legitimate ionic intermediate having a lifetime of at least 10^{-8}–10^{-7} s. The cation corresponds to a local minimum on the $C_6H_{11}^+$ energy surface, whose depth, deduced from the rate of isomerization to the more stable 1-methylcyclopentyl structure, is estimated below 10 kcal mol^{-1}. The results confirm earlier conclusions from a radiolytic study and provide, in addition, useful information on the relative reaction rate of free cyclohexyl and 1-methylcyclopentyl cations toward several nucleophiles.

Introduction

While the occurrence of *solvated* c-$C_6H_{11}^+$ as a charged intermediate in solution is well documented,[1] its existence as a *free* cation, either in the gas phase or in condensed media of low nucleophilicity, is uncertain at the present time. Indeed, until very recently the general consensus, based on the persistent failure to detect unstabilized cyclohexyl cation **1** by mass spectrometric or NMR techniques, was that **1** does not exist at all in the free state, owing to its prompt rearrangement to the 1-methylcyclopentyl isomer **2**.[2]

[†] University of Rome.
[‡] Istituto di Chimica Nucleare del CNR.

(1) (a) Olah, G. A.; Schleyer, P. v. R., Eds. "Carbonium Ions"; Wiley-Interscience: New York, 1970; Vol. 2, Chapters 14 and 15. (b) For a theoretical approach to the energetics of the hydride shifts within c-$C_6H_{11}^+$, and to the relative stability of its chair and boat conformations, see: Dannenberg, J. J.; Abrams, C.; Decoret, C.; Rayez, J. C. *J. Org. Chem.* **1983**, *48*, 3315.

0002-7863/85/1507-4824$01.50/0