NR mass spectra (Figures 5 and 6) indicate otherwise. With $H_2COH_2^{\bullet+}$, increasing the O_2 pressure increases $[H_2C^{\bullet+}]$ and $[OH_2^{\bullet+}]$, relative to $[(COH_4)^{\bullet+}]$, without increasing $[H_3C^+]$. This strongly supports a nearly 10^{-6} s lifetime for a significant portion of the **3** neutrals. Increasing the He pressure (Figure 6) also causes dissociation of the primary neutral products H_2C:, $^{\bullet}OH$, OH_2, and CH_nO, but the Figure 6D data are still also consistent with the stability of **3**. The losses of H_2 and $2H_2$ (*m*/*z* 30, 28) appear favored in the ylide spectra, possibly because they can occur in the reionized $H_2COH_2^{\bullet+}$ (and/or **3**) via symmetry-allowed[18] 1,1-H_2 losses.

Methyleneammonium Ylide. Theory[3c] finds the energies of H_2CNH_3 (**4**) to be 11 and 13 kcal/mol, respectively, below the energies of the products H_2C: + NH_3 and of the barrier for rearrangement to H_3CNH_2. This indicated stability is supported by the NR mass spectra of Figures 7 and 8. Only $H_2CNH_3^{\bullet+}$ gives an appreciable $NH_3^{\bullet+}$ (*m*/*z* 17) peak, and this triples in height with the increased O_2 pressure. Increased He pressure increases $NH_3^{\bullet+}$, but also appears to cause dissociation to NH_2^+. Multiple O_2 collisions also increase *m*/*z* 29, which could arise by a symmetry-allowed[18] 1,1-H_2 loss from **4**. The H_2 loss from $H_2CNH^{\bullet+}$ must be associated with a significant isotope effect. In the Hg/O_2 (30% T) spectrum of $H_2CND_3^{\bullet+}$ (from $DOCH_2CH_2ND_2$) the reionized precursor (*m*/*z* 34) becomes the base peak, and *m*/*z* 33 ($H^{\bullet}$ loss) the most intense fragment (99%); the abundances of the ions at *m*/*z* 32 ($H_2/D^{\bullet}$ losses), 31 (HD loss), 30 (D_2 loss), and 20 ($ND_3^{\bullet+}$) are 67, 28, 40, and 53% of the base peak abundance, respectively. Very similar isotope effects and peak shifts are observed in the CAD spectrum of $H_2CND_3^{\bullet+}$ vs. that of $H_2CNH_3^{\bullet+}$.[19]

Conclusions

The unique capability of NRMS for preparation and study of unusual neutral species has been utilized to demonstrate the surprising stability of the simple ylides H_2CYH, **1**–**4**. Unless these represent metastable states of unusually long lifetimes, this indicates that ab initio calculations overestimate ΔH_f values for such hypervalent species. A better understanding of the (H_2C)–(YH) bonding underlying this stability could be valuable in optimizing syntheses involving ylide intermediates.

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[19] Although CAD (O_2) charge stripping of $H_2CNH_3^{\bullet+}$ produces $H_2CNH_3^{2+}$ (*m*/*z* 15.5) in significant abundance (1% of the $H_2CNH^{\bullet+}$ base peak),[20] it cannot be observed in the Hg/O_2 NR mass spectrum because of the concomitant presence of intense ions at *m*/*z* 15 and 16 from the neutral dissociation of H_2CNH_3 to H_2C + NH_3; the abundance of *m*/*z* 15 and 16 under maximum sensitivity conditions (Figure 7D) are 4 and 7% of the reionized precursor abundance, respectively, obscuring any CS ions present whose intensities are substantially smaller. Similar circumstances prevent the detection of CS ions in the NR spectra of $H_2COH_2^{\bullet+}$. In the Hg/O_2 NR mass spectrum of $H_2CND_3^{\bullet+}$, [*m*/*z* 17] is 2.5% of the reionized precursor abundance (*m*/*z* 34) and flanked by [*m*/*z* 16] and [*m*/*z* 18] of 33 and 45%, respectively; $H_2CND_3^{2+}$ *m*/*z* 17 might also be NHD^+ and/or CHD_2^+.

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Two-Step Laser Excitation Fluorescence Study of the Ground- and Excited-State Proton Transfer in Alcohol Solutions of 7-Hydroxyisoflavone

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Abstract: The intermolecular excited-state proton transfer and relaxation processes to the parent molecule were investigated for the alcohol solutions of 7-hydroxyisoflavone (7-HIF) by means of nanosecond and two-step laser excitation (TSLE) fluorescence spectroscopies. The large Stokes shifted fluorescence spectra (λ_{max} 470–480 nm) were observed in methanol, ethanol, and propanol solutions of 7-HIF at room temperature to ~180 K. The fluorescence spectra consist of two component decays which were ascribed to two types of excited-state tautomers generated by the excited-state proton transfer in the intermolecularly hydrogen bonded 7-HIF with two alcohol molecules (1:2 H-bonding). The TSLE fluorescence including a variable delay technique demonstrates that the short- and long-lived ground-state tautomers are involved in the relaxation processes of the above excited-state tautomers. From the determination of lifetimes of the ground-state tautomers at various temperatures, the reaction rate and apparent activation energies of the reverse proton transfer from these two types of tautomers to the parent molecule were obtained for 7-HIF in comparison with those for 7-hydroxyflavone (7-HF), which exhibits the similar excited-state proton transfer and relaxation processes as reported in the previous paper.

In the inter- and intramolecular hydrogen bonding systems, the excited-state proton transfer to afford a so called excited-state tautomer takes place exhibiting characteristic large Stokes shifted fluorescence spectra.[1-7] Various nano- and picosecond fluorescence studies on the dynamic processes of the excited-state proton transfer and relaxation have been reported.[3-8] However, no concrete evidence of the existence of the ground-state transient, "the ground-state tautomer", was reported in the relaxation of the excited-state tautomer to the recovery of the parent molecule

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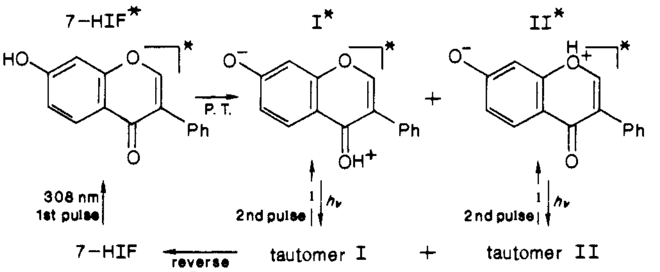
until 1983, though the intervention of an intermediate during relaxation of the tautomer generated in the excited-state proton transfer of 2-(2-hydroxy-5-methylphenyl)benzotriazole was suggested from the difference between the ground-state recovery time of the transient absorption and the fluorescence lifetime of the tautomer.[9] We have demonstrated the evidence of the intervention of the ground-state tautomer involved in the relaxation of the several inter- and intramolecular excited-state proton transfer systems by means of transient absorption and time resolved TSLE fluorescence.[10-15] The time-resolved TSLE fluorescence developed by us was proved to provide us with a novel and versatile technique to distinguish several transients with different ground- and excited-state lifetimes such as proton transfer tautomer and/or photoisomer in the isomerization reaction.

We have reported transient absorption and time-resolved TSLE fluorescence studies of the ground- and excited-state proton transfer in the methanol solution of 7-hydroxyflavone (7-HF).[14] These studies demonstrate that the excited-state proton transfer and relaxation in 7-HF takes place to afford two types of tautomers both in the ground and excited states. On the other hand, Wolfbeis and Schipfer[16] reported acidity dependence of the absorption and fluorescence spectra of 7-hydroxyisoflavone (7-HIF) and ascribed the large Stokes shifted fluorescence to "phototautomer" or "exciplex" with the solvent molecule formed in the excited state. However, the primary process of formation of the "tautomer" and the relaxation both in the excited and ground states are completely obscure. This paper presents nanosecond and TSLE fluorescence studies on the proton transfer or photoisomerization in the alcohol solutions of 7-HIF. The alcohol solutions of this compound exhibit a large Stokes shifted fluorescence which is attributable to the excited-state tautomer generated by the excited-state proton transfer in the hydrogen bonding complex with two alcohol molecules (1:2). The nanosecond and TSLE fluorescence including variable delay techniques demonstrate that the large Stokes shifted fluorescence consists of two types of tautomers followed by the relaxation to the respective ground-state tautomers. From these ground-state tautomers, the reverse proton transfer takes place to the parent molecule, whose reaction rates and activation energies of 7-HIF were obtained in comparison with those of 7-HF.



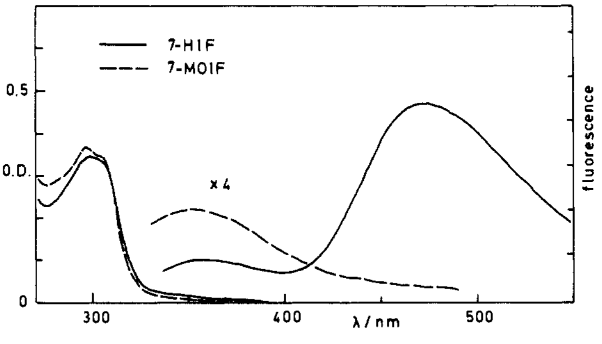


Figure 1. Absorption and fluorescence (uncorrected) spectra of methanol solutions of 7-hydroxyisoflavone and 7-methoxyisoflavone at room temperature. Both concentrations are 3.5×10^{-5} M.

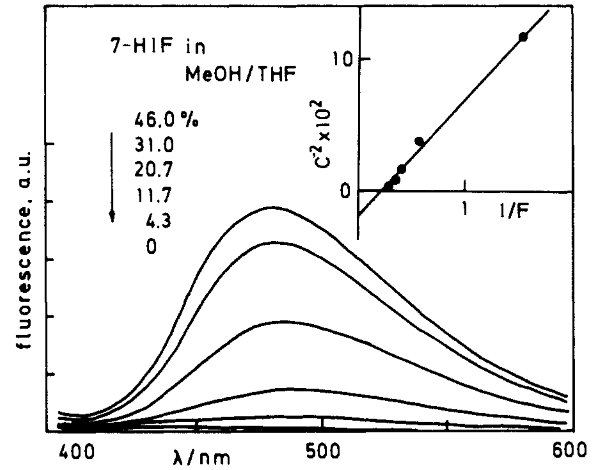


Figure 2. Fluorescence spectra of 7-HIF (3×10^{-5} M) in CH_3OH/THF mixed solvent system at room temperature. Concentration of CH_3OH is volume %. An inset shows plots of C^{-2} vs. F^{-1} according to the following equation for the 1:2 H-bonding equilibrium: $C^{-2} = F^{-1} + K$, where C and F are methanol concentration (M = mol/L) and fluorescence intensity (arb), respectively, and K is the equilibrium constant.

Experimental Section

Materials. 7-Hydroxyisoflavone was synthesized according to the literature[16] and purified chromatography and repeated recrystallizations from spectrograde ethanol, mp 221 °C. Structure and purity were confirmed by elementary analysis and mass, NMR, and UV spectra. 7-Methoxyisoflavone was prepared by methylation in an ethyl ether solution of diazomethane. Spectrograde alcohols were used without further purification. Tetrahydrofuran (Nakarai, spectrograde) was used after refluxing with $LiAlH_4$ and distillation. Samples were deaerated by the conventional repeated freeze-pump-thaw cycles, if necessary.

Spectroscopies. Electronic absorption and fluorescence spectra were measured by Hitachi U-3200 absorption and MPF-4 or 850 fluorescence spectrophotometers, respectively. Fluorescence lifetimes were determined by a single photoncounting system (Ortec) with a nanosecond light pulser (PRA). The transient absorption and TSLE fluorescence measurements were performed by the same methods as described in the previous papers.[13-15] Since a small fluorescence signal due to the stable ground-state 7-hydroxyisoflavone conjugate acid[16] present in methanol was detected only by the second laser excitation, the TSLE fluorescence spectra were constructed by subtraction of this signal of conjugate acid from the TSLE fluorescence intensity observed. The former was less than 20% of the latter at small delay time. In the low-temperature measurements, temperature was controlled by flowing cold nitrogen gas around the sample in a dewar.

Results and Discussion

Absorption and Fluorescence Spectra. The electronic absorption spectra of the methanol solutions of 7-HIF and 7-methoxyisoflavone (7-MOIF) exhibit absorption bands at 290-310 nm. Figure 1 shows fluorescence spectra of these compounds upon excitation of these absorption bands. The methanol solution of 7-HIF shows a weak fluorescence at 350-400 nm and strong large Stokes shifted fluorescence at 450-500 nm as shown in Figure 1, while the tetrahydrofuran solution shows very weak fluorescence at 350-400 nm. Figure 2 shows fluorescence spectra of this compound in the methanol/THF mixed solvent system. If the concentration of methanol increases, the large Stokes shifted fluorescence appears at 450-500 nm, which remarkably increases in intensity with increasing concentration of methanol (C) as shown in Figure 2. The linear plots of C^{-2} vs. F^{-1} shown in an inset of Figure 2 suggest that the large Stokes shifted fluorescence is attributable to the 1:2 H-bonding complex formation with two

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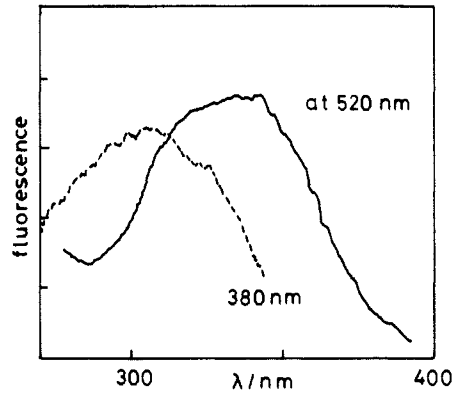

Figure 3. Uncorrected fluorescence excitation spectra monitored at 520 and 380 nm of a methanol solution of 7-HIF (5×10^{-6} M).

methanol molecules as follows: 7-HIF + $2(CH_3OH) \rightleftarrows$ 7-HIF-$(CH_3OH)_2$,[12,14,17-19] where F is the intensity of the large Stoke shifted fluorescence. The equilibrium constant was obtained to be 1.5×10^{-2} M^{-2} from the linear plots. By the analogy to the fluorescence behavior of 7-HF reported previously,[14] the large Stokes shifted fluorescence spectrum (450–500 nm) in 7-HIF may be assigned to a phototautomer generated by the intermolecular excited-state proton transfer in the 1:2 H-bonding complex. The excitation spectrum of the 450–500-nm fluorescence may be corresponding to an absorption band of this 1:2 H-bonding complex, though only a very weak absorption band was observed at 320–360 nm in the methanol solution as shown in Figure 1.

If the large Stokes shifted fluorescence is ascribed to the excited-state tautomer generated by the excited-state proton transfer in the 1:2 H-bonding complex, the normal form fluorescence of the 1:2 complex might be observed in the shorter wavelength region. However, a complete different excitation spectrum of the 350–400-nm fluorescence from that of the 450–500-nm one was observed, as shown in Figure 3. Therefore, the 350–400-nm fluorescence is not ascribed to the normal form of 1:2 H-bonding complex but probably to the 1:1 H-bonded 7-HIF with a methanol molecule. The 450–500 nm fluorescence is gradually quenched below ~200 K, which implies that this intermolecular excited-state proton transfer requires some amount of activation energy.

The fluorescence decay profiles of the 450–500-nm fluorescence of this compound in methanol and in ethanol exhibit double exponential without rise throughout room temperature to ~150 K. The short and long decay components are almost independent of detected wavelength and also independent of concentration of solution. Similar two decay components of the excited-state tautomers were observed in the methanol solution of 7-HF reported in the previous paper.[14] In one of these tautomers, 7-HF may pick up a proton at a carbonyl oxygen from the solvent and release one at the 7-hydroxyl group. A proton in another tautomer seems to transfer from the solvent to the ether oxygen of the pyrone ring and to be released from the 7-hydroxyl group to the solvent. Therefore, the short and long decays of the 450–500-nm fluorescence in 7-HIF may be tentatively ascribed to the similar two types of tautomers. These assignments will be confirmed by the TSLE fluorescence spectroscopy. Both short and long fluorescence decay times increase with decreasing temperature as summarized in Table I. These temperature dependences of lifetimes may be attributable to the temperature dependence of the nonradiative process of the tautomer fluorescence.

Two-Step Laser Excitation Fluorescence Spectroscopy. The transient absorption spectra of the methanol solution (deaerated) of 7-HIF were measured. Considerably strong absorption bands were observed at 330 nm ($\log I_0/I$ = ~0.38) and 430–580 nm (~0.15), whose decays exhibit double exponential.[20] Since these transient absorption bands were remarkably quenched in intensity and decay time in the aerated solution (approximately 1/10 of the deaerated ones), the spectra were ascribed to the triplet–triplet ($T_n \leftarrow T_1$) absorption. However, a very weak absorption band with a long lifetime was observed at 350–430 nm, as shown in Figure 4, though an accurate determination of decay time is almost impossible because of very weak absorption intensity. Taking account of the observation of transient absorption bands due to the ground-state tautomers in the several systems of the excited-state proton transfer in the previous papers,[10-15] the observed weak absorption band seems to be attributable to the ground-state tautomer of 7-HIF. In order to confirm this assignment, the TSLE fluorescence of the aerated methanol solution of this compound was measured at room temperature by the second laser excitation (386 nm) of the transient absorption band, as shown in Figure 4. However, no TSLE fluorescence was observed in the deaerated solution. It is because the long-lived $T_n \leftarrow T_1$ absorption formed by the first laser excitation may absorb the second laser light pulse.[21] The TSLE fluorescence spectra obtained are almost independent of delay time of the second laser and almost identical with the steady-state fluorescence spectra due to the tautomers.

Table I. Fluorescence Lifetimes and Components of the Excited-State Tautomers in Alcohol Solutions of 7-HIF Which Were Analyzed by $I(t) = A \exp(-t/\tau_1) + (1 - A) \exp(-t/\tau_2)$[a]

temp (K)	τ_1 (ns)	(A)	τ_2 (ns)
	Solvent: CH_3OH		
294	0.47	(0.48)	2.33
250	0.98	(0.61)	3.11
228	1.21	(0.66)	4.54
203	1.26	(0.70)	5.48
183	1.27	(0.86)	6.38
	Solvent: C_2H_5OH		
294	0.47	(0.66)	3.42
213	1.03	(0.58)	5.62
203	1.08	(0.54)	5.65
183	1.25	(0.69)	5.91

[a] The data analysis for the equation was performed by a computer-simulated deconvolution method. The criterion for "best fit" was the minimum sum (Q) for the square of the difference between observed (D_i) and calculated (D_i') data: an actual allowance was $Q < 0.0002$; $Q = \sum_i^n (D_i - D_i')^{2/n}$, where n is the number of data. Errors are approximately less than 5%.

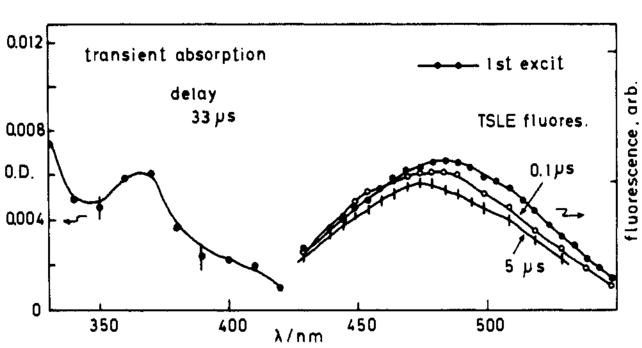

Figure 4. Transient absorption spectrum of a methanol solution of 7-HIF (1×10^{-4} M) depicted at 33 μs delay time. The first laser induced fluorescence (●) and TSLE fluorescence spectra: delay times are 0.1 μs (○) and 5 μs (+) of the second laser from the first one at room temperature.

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(19) The 350–400-nm fluorescence intensity (f) increases with increasing small concentration (C) of methanol in mixed system. Linear plots of f/C vs. f were observed, which suggest the 1:1 complex formation of 7-HIF with methanol ($C < 10^{-1}$ M).

(20) Two decay times of approximately 0.7 and 3 μs observed at room temperature seem to be attributable to two triplet states of 7-HIF in the absence and presence of hydrogen bonding with methanol molecule. Details will be published elsewhere.

(21) If the excited-state proton transfer in the triplet state followed by the intersystem crossing to afford the singlet tautomer takes place efficiently; the TSLE fluorescence might be detected by the second laser excitation of the $T_n \leftarrow T_1$ absorption band. However, no TSLE fluorescence was observed at the present stage.

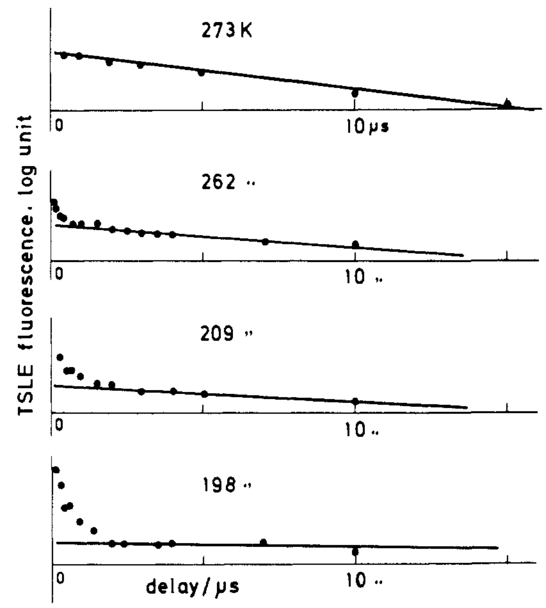

Figure 5. Variable delay plots of TSLE fluorescence intensity at 500 nm of a methanol solution of 7-HIF (1×10^{-4} M) at several temperatures. The TSLE fluorescence intensities (ordinates) are log scale.

Figure 4 also shows the fluorescence spectrum determined by the first laser excitation (308 nm) in the completely same condition as that of the TSLE fluorescence. The first laser induced fluorescence spectrum exhibits approximately a 10-nm red shift from the TSLE fluorescence. This finding seems to be in accordance with the fact that the tautomer fluorescence consists of two components of fluorescence as mentioned in the last section.

Figure 5 shows plots of the TSLE fluorescence intensity vs. variable delay times of the second laser. The variable delay plots exhibit a single exponential decrease of the TSLE fluorescence intensity at room temperature. However, it is noteworthy that a very short-lived component appears in the variable delay plots at low temperature below 230 K. The variable delay plots at several temperatures are shown in Figure 5. These facts demonstrate that two ground-state tautomers are involved in the relaxation processes of the excited-state proton transfer. If it is the case, a short-lived transient absorption band might be observed in the 386-nm region in addition to the long-lived one as mentioned above. However, such a transient absorption band was not detected because of overlapping by the strong and short-lived $T_n \leftarrow T_1$ absorption in the aerated solutions. Furthermore, no significant difference of the TSLE fluorescence spectra at different delay times was observed even at low temperature. These experimental facts indicate that two excited-state tautomers exhibit very similar fluorescence spectra of each other, which is consistent with no significant wavelength dependence of the short- and long-lived components of the tautomer fluorescence, as mentioned in the last section. Nevertheless, taking account of the ~10-nm red shift of the first laser induced fluorescence from the TSLE fluorescence, it is likely that the short-lived ground-state tautomer exhibits a little red-shifted fluorescence from that of the long-lived one.

If no significant chemical reaction takes place in the ground-state tautomer, the decay rate constants of their ground-state tautomers seem to reflect reaction rates of the ground-state reverse proton transfer to the parent molecule probably in the H-bonding state. Since no photochemical reaction of the methanol solution of 7-HIF was detected during measurements of transient absorption and TSLE fluorescence spectra, the short and long decay times of the ground-state tautomers were determined at several temperatures, as plotted in Figure 6. The decay constants obtained are considered to be reaction rates of the reverse proton transfer from two tautomers. Therefore, the activation energies of the reverse proton transfer were estimated from the linear temperature dependence of the decay constants vs. $1/T$, as shown in Figure 6. Figure 6 also shows similar temperature dependence of decay rate constants for the tautomers of 7-HF which were obtained in the same condition as 7-HIF.

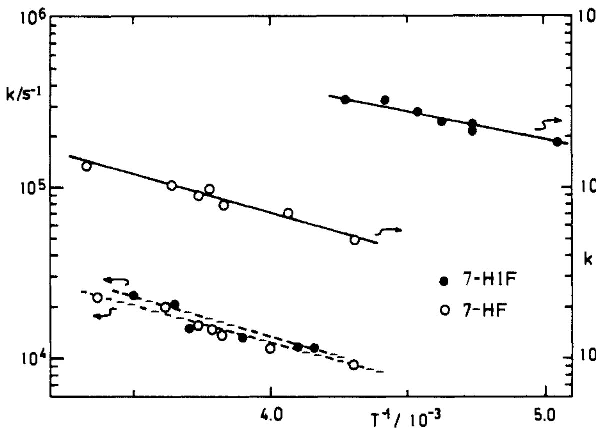

Figure 6. The temperature dependence of the fast and slow rate constants of the reverse proton transfer in the ground state of 7-HIF and 7-HF in the methanol solutions; both concentrations are approximately 1×10^{-4} M.

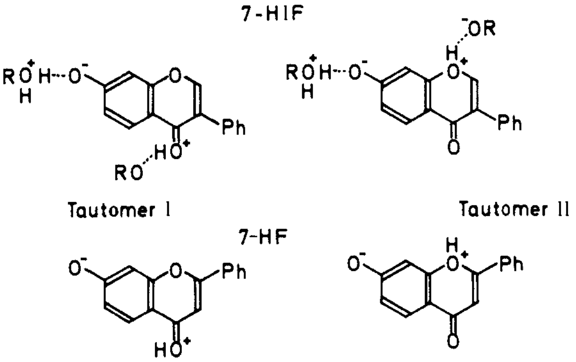

Figure 7. Tentatively proposed structures of two types of tautomers generated by the excited-state proton transfer and relaxation in 7-HIF and 7-HF.

According to the models for the short- and long-lived tautomers in 7-HF proposed in the previous paper, two protons may be involved in the excited-state proton transfer in a 1:2 H-bonding complex with two methanol molecules (Figure 7). These two protons seem to transfer simultaneously with rate constants of approximately 10^9–10^{10} s^{-1} M^{-1} or more,[22] though the rate constant has never been obtained in these intermolecular excited-state proton-transfer systems because of no rise time observed.[14,15] In the ground-state reverse proton transfer, it is not obvious at the present stage if a two proton transfer takes place in "concerted" or in "step-wise" in the microsecond time domain. The concerted or step-wise two proton transfer in the ground state is responsible for the kinetic data obtained here. The activation energy of the reverse proton transfer in 7-HIF/MeOH is smaller in the tautomer II (1.4 kcal mol^{-1}) than in the tautomer I (2.1 kcal mol^{-1}). However, no difference between tautomers I and II in 7-HF/MeOH was observed, though a preexponential factor is considerably greater in tautomer II than I. Recently, Shizuka et al. have reported the kinetic data of the ground- and excited-state proton transfer in 6-(2-hydroxy-5-methylphenyl)-*s*-triazines in poly(methylmethacrylate),[23] and they have indicated that the strength of hydrogen bonding in the parent molecule is favorable in the excited-state proton transfer but not to the ground-state reverse proton one. Since the hydrogen bonding concerned with ether oxygen of the pyrone ring, one of two 1:2 H-bonding complexes, seems less stable than that concerned with carbonyl oxygen, the barrier for the reverse proton transfer should be smaller in the tautomer II than I. However, 2-phenyl as an electron-donating group may enhance the H-bonding of ether oxygen with methanol

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hydrogen.[24] Therefore, it seems that the activation energy of the reverse proton transfer in the tautomer II of 7-HF is greater as compared with that in 7-HIF, and as a result, it becomes comparable to that of tautomer I. The ground- and excited-state proton transfer was reported in the methanol solution of 7-hydroxyquinoline in the previous paper. The activation energy of this reverse proton transfer was obtained to be 4.2 kcal mol^{-1}, which is approximately two times greater than those of 7-HIF and 7-HF (2.1 kcal mol^{-1}). The fact indicates that the ground-state tautomer is more stable than those of 7-HIF and 7-HF. The transient resonance Raman study of the actual structures of two tautomers in 7-HF is now in progress by Moore and Phillips in the Royal Institute of London.

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Mixed-Valence 1′,6′-Dihalobiferrocenium Cations: Counterions Micromodulating Intramolecular Electron Transfer

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Abstract: The effects on the rate of electron transfer of replacing I_3^- by Br_2I^- in the mixed-valence compounds 1′,6′-diiodobiferrocenium triiodide (**3**), 1′,6′-dibromobiferrocenium triiodide (**4**), and 1′,6′-dichlorobiferrocenium triiodide (**2**) are examined. Replacing I_3^- by Br_2I^- in the first two complexes leads to an appreciable decrease in the rate of electron transfer, whereas in the case of the third complex an increase in the rate is seen. The triiodide complex **3** shows a single "average-valence" ^{57}Fe Mössbauer doublet at 4.2 K; that is, the electron-transfer rate is in excess of $\sim 10^7$ s^{-1} at 4.2 K. Two doublets are seen at 4.2 K for 1′,6′-diiodobiferrocenium dibromoiodate (**9**). It is necessary to heat **9** to $\sim$80 K so that the rate exceeds $\sim 10^7$ s^{-1}. Two Mössbauer doublets are also seen at 4.2 K for 1′,6′-dibromobiferrocenium dibromoiodate (**10**), whereas **4** shows one doublet. The mixed-valence complex **10** needs to be heated to $\sim$180 K to have the rate be in excess of $\sim 10^7$ s^{-1}. Complex **2** is Mössbauer-localized up to $\sim$340 K; however replacing the I_3^- by Br_2I^- to give **8** changes this such that **8** begins to show some Mössbauer-delocalized species at $\sim$100 K, and at 300 K there are approximately equal amounts of Mössbauer-localized and -delocalized species present. This increase in rate by replacing I_3^- by Br_2I^- is what was seen before for biferrocenium triiodide (**1**). A qualitative model is presented to explain these anion effects on the *intra*molecular electron-transfer rate of mixed-valence biferrocenes. It is shown that the difference in response of I_3^- replacement by Br_2I^- reflects the different packing arrangements in the solid state. The occurrence of a phase transition is strongly indicated. In **1** there are stacks of mixed-valence cations, and cation–cation interactions are important. The greater electron-transfer rate in biferrocenium dibromoiodate than in biferrocenium triiodide could be a reflection of three possibilities: 1, charge oscillation between two asymmetric forms of the trihalide anion is easier in Br_2I^- than in I_3^-; 2, the Br_2I^- ion begins to move between two lattice positions at lower temperatures than the I_3^- anion; and 3, the replacement of I_3^- by Br_2I^- reduces the intrastack cation–cation interactions which lead to valence trapping. The packing arrangement in **3**, **4**, **9**, and **10** is comprised of alternating stacks of cations and anions. Unlike the situation for **1**, IR and EPR results for these complexes show that the mixed-valence cation is appreciably influenced by changing the anion. The origin of this is the appreciable in-stack interaction between the terminal atom of the trihalide anion and the iodine atom on the cyclopentadienyl ring. Thus, changing I_3^- in **3** to give the Br_2I^- salt **9** leads to an increase in the in-stack cation–anion interaction, and a higher temperature is needed for **9** to achieve an electron-transfer rate in excess of $\sim 10^7$ s^{-1}.

In the last year or two there has been considerable progress made in understanding what factors control the rate of intramolecular electron transfer in the *solid state* for mixed-valence biferrocenes[2-7] and oxo-centered trinuclear iron acetates.[7-12] The exact positioning of a counterion, a ligand, or even a solvate molecule relative to the mixed-valence complex in the solid state can have a dramatic impact on the rate of intramolecular electron transfer. When there is an onset of dynamics associated with the counterion,[4,7] ligand,[7,8] or solvate molecule,[9,11,12] this probably will influence the rate of intramolecular electron transfer. In fact, because there are interactions between molecules in the solid state, frequently changes in the rate of intramolecular electron transfer are coupled to phase transitions.[7,9,10,11]

Mixed-valence compound **2** crystallizes with half a mole of I_2. The X-ray structure[5] of this compound shows that not only is the I_3^- anion asymmetric but the I_3^- counterion sits closer to one half of the cation, the iron(III) metallocene moiety. As a result, mixed-valence compound **2** is localized on the Mössbauer time scale even at 340 K.[5,13] The ground-state double-well potential-energy surface for the mixed-valence cation in **2** is asymmetric

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