Hydrogen Atom Transfer of 5-Hydroxyflavone in the Excited Triplet State

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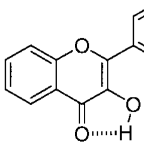
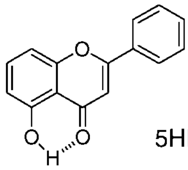
Behavior of 5-hydroxyflavone (5HF) in the excited triplet state was studied for the first time by transient absorption and phosphorescence spectroscopies. 5HF underwent the intramolecular hydrogen atom transfer in the excited triplet state at room temperature.


3HF


5HF

The photochemical properties of hydrogen bonded systems are interest to many chemists. The intramolecular hydrogen atom transfer reaction in the excited singlet state has been the subjects of numerous ultrafast and steady-state spectroscopic studies with the goal of elucidating the dynamic and energetic properties of the electronic excited states of various compounds.[1] However, only a few compounds, which exhibit the intramolecular hydrogen atom transfer in the excited triplet state, have been reported.[2,3] Recently, we have reported the hydrogen atom transfer of methyl salicylate (MS) in the triplet state at room temperature in benzene by estimating the energy of the triplet state observed by transient absorption.[3]

The intramolecular hydrogen atom transfer of hydroxyflavones has been attractive from the view point of not only photochemical properties[4a,5] but also biological applications.[4b] The hydrogen atom transfer of 3-hydroxyflavone (3HF) has been extensively studied for decades[2e,4] mainly on the behavior of the excited singlet state. On the other hand, the photochemical behavior of 5-hydroxyflavone (5HF) has not been clarified.[5] Chou et al. reported that 5HF exhibits the large Stokes-shifted emission around 670 nm (Φ_f ~10^{-6}) attributed to the tautomer form.[5a] However, to our knowledge, the intramolecular hydrogen atom transfer of 5HF in the excited triplet state has not been reported. In this study, the photochemical behavior of the excited triplet state of 5HF has been investigated by means of laser flash photolysis and phosphorescence spectroscopies. We wish to report here that 5HF undergoes the intramolecular hydrogen atom transfer in the excited triplet state. The potential energy surface of the reaction is also discussed.

A transient absorption was observed on excitation of 5HF in benzene with 308 nm laser pulse as shown in Figure 1(a). A sharp band peaked at 350 nm and a very broad band from 380–600 nm were observed. The two bands decayed with the lifetime of 2.8 μs under argon atmosphere and was quenched by addition of O_2; the quenching rate constant by oxygen in benzene was determined to be 2.7×10^9 M^{-1} s^{-1}. Thus, the observed transient was assigned to a triplet state. There are two candidates for the observed triplet: the normal form and the tautomer form. In order to make clear the conformation of the observed triplet, its triplet energy was estimated. Quenching experiments were applied for the estimation of the triplet energies.

The triplet excitation energy (the triplet energy of the normal form) of 5HF was determined as follows. On benzophenone or Michler's ketone sensitization 5HF gave a transient absorption spectra. The transient absorption spectra observed on Michler's ketone sensitization is shown in Figure 1(b). The initial absorption at delay time of 390 ns is mainly due to the T–T absorption of Michler's ketone. The spectra changed with the delay time and at 1.0 μs after the laser pulse the spectra became similar to that observed on direct excitation (Figure 1(a)). The rate constants of the energy transfer processes from benzophenone (287 kJ mol^{-1})[6] triplet and Michler's ketone triplet (275 kJ mol^{-1})[6] to 5HF were determined to be diffusion controlled value [$(7.5 \pm 1.0) \times 10^9$ M^{-1} s^{-1}].[7] Thus, these processes are exothermic. In contrast, 5HF was not sensitized by biacetyl triplet (236 kJ mol^{-1})[6] indicating that the process is highly endothermic. Therefore, the triplet energy of the normal form of 5HF must be higher than 236 kJ mol^{-1} (biacetyl) and lower than 275 kJ mol^{-1} (Michler's ketone). This value is supported by the triplet energy of flavone (259 kJ mol^{-1}).[6] In order to deduce the more clear value of the triplet energy, the phosphorescence spectra was measured at 77 K. In alcoholic solvent (EPA; ether:isopentane:ethanol = 5:5:2 in volume ratio), 5HF exhibited phosphorescence at 465 nm. The emitting species was attributed to the intermolecularly hydrogen bonded 5HF[5a] with ethanol because the phosphorescence intensity was quenched in aprotic solvents such as MP (methylcyclohexane:isopentane = 1:1 in volume ratio), and phosphorescence lifetime (tp) was much shorter in MP (tp < 1.5 ms) than in EPA (tp = 200 ms). There

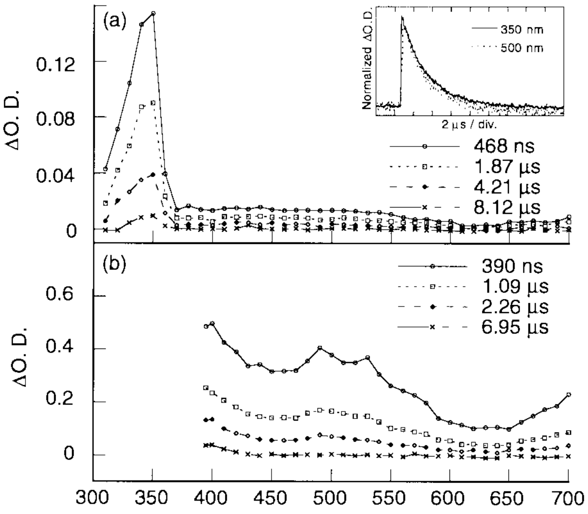


Figure 1. Transient absorption spectra of 5HF observed on direct excitation at 308 nm (a) and on Michler's ketone sensitization (b) in benzene. Time indicates the delay time after laser pulse. Inset; decay profiles observed at 350 and 500 nm.

should be little change in triplet energy by the substitution of hydroxy group in the 5 position or the intermolecular hydrogen bonding with solvent. Therefore, the triplet energy of the normal form with intramolecular hydrogen bond was estimated to be 260 kJ mol^{-1}.

On the other hand, the triplet state observed by transient absorption, on direct and triplet sensitized excitation, was not quenched by biacetyl, indicating that the energy transfer from 5HF triplet to biacetyl is highly endothermic: triplet energy of the transient is much less than that of biacetyl (236 kJ mol^{-1}). Pyrene (203 kJ mol^{-1})[6] quenched the triplet by the rate constant of $k_q = 5.8 \times 10^8$ M^{-1} s^{-1}; the process was slightly endothermic by 5.7 kJ mol^{-1} estimated from eq 1,[8] where k_{dif} is the diffusion controlled rate constant,[7] k_q is the observed quenching rate constant, and ΔE_a is the energy difference between the triplet energy donor and the acceptor. Therefore, the triplet energy of the transient observed by direct excitation and triplet sensitization was estimated to be 197 kJ mol^{-1}.

$$k_q = k_{dif} \exp(-\Delta E_a / RT) / [1 + \exp(-\Delta E_a / RT)] \qquad (1)$$

If the observed transient were assigned to the triplet state of the starting conformer (the normal form), the two quenching experiments should give similar triplet energies. However, the triplet energy of the normal form was estimated to be 257 kJ mol^{-1}, while that of the triplet transient was 197 kJ mol^{-1}. Therefore, we may propose that 5HF gives the tautomer form in the excited triplet manifold.

On direct and triplet sensitized excitation, similar transient absorption spectra were observed (Figures 1(a) and 1(b)). These results indicate that excited triplet state of the tautomer was formed from either S_1 or T_1 of the normal form of 5HF. On direct excitation of 5HF, S_1 state of the normal form of 5HF is initially formed. The intramolecular hydrogen atom transfer should efficiently occurs on the S_1 surface, because fluorescence with maximum at 670 nm assigned to S_1 state of the tautomer form has been reported on direct excitation with 355 nm Nd:YAG laser.[5a] The intersystem crossing from S_1 to T_1 takes place after the hydrogen atom transfer. On the other hand, T_1 state of the normal form is initially formed on triplet sensitized excitation. However, the observed triplet state was assigned to the T_1 state of the tautomer form by the quenching experiments. In this case, the lifetimes of the T_1 state of the normal form should be shorter than or comparative to the time scale for the energy transfer process so that T_1 state of the normal form could not be detected by the transient absorption spectroscopy. Therefore, the intramolecular hydrogen atom transfer of 5HF takes place on T_1 surface adiabatically and the reaction is completed within the nanosecond time scale. The reaction scheme is shown in Figure 2.

We have studied the effect of O: H–O hydrogen bonding on the photoisomerization of C=C double bond. For example, 2'-hydroxychalcone (2HC), which has an intramolecular hydrogen bonding, underwent one-way cis-trans isomerization induced by the intramolecular hydrogen atom transfer.[9] It is notable that the reaction proceeds in the triplet state. 5HF possesses the same type of O–H:O hydrogen bond and analogous framework to 2HC, but the isomerization around the C=C double bond is inhibited. Thus, exploring the possibility of intramolecular hydrogen atom transfer in the triplet state of 5HF is intriguing as a model compound of 2HC. The result that 5HF exhibits the intramolecular hydrogen atom transfer in the excited triplet manifold is compatible with the results of MS[3] and 2HC.[9] In those compounds, the only observable triplet is the tautomer form and the keto–enol equilibrium in the triplet state lies so far to the tautomer form. It is in contrast with O–H:N[2a,b] and N–H:O[2c] hydrogen bonded compounds which exhibit the equilibrium between keto and enol forms in the excited triplet state.

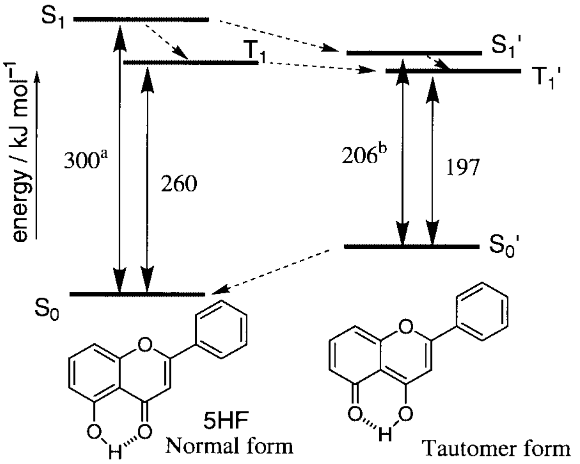


Figure 2. Potential energy diagram of intramolecular hydrogen atom transfer of 5-hydroxyflavone. a) Calculated from absorption spectra. b) Calculated from fluorescence spectra in ref 5a.

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7 In our experimental condition, benzophenone triplet was quenched by naphthalene with the rate constant of 6.3×10^9 M^{-1} s^{-1}, and therefore, the diffusion controlled rate constant (k_{dif}) was estimated as 6.3×10^9 M^{-1} s^{-1}.

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