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Photophysical properties of 5-hydroxyflavone

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Abstract

To investigate the role of the excited triplet state in the deactivation process of 5-hydroxyflavone (5HF), the photophysical process of 5HF was studied by transient absorption, phosphorescence spectroscopies, and semiempirical calculations. The triplet–triplet absorption (T–T) spectra of 5HF and 5-methoxyflavone (5MF) were observed upon direct and triplet-sensitized excitation. The T–T spectrum of 5HF ($\lambda_{max} = 350$ nm, $\tau_T = 2.8\,\mu$s) was different from that of 5MF ($\lambda_{max} = 360$ nm, $\tau_T = 6.8\,\mu$s). Estimations of the triplet energies of 5HF and 5MF by quenching experiments, phosphorescence, and semiempirical (PM3/CI4) calculation revealed that 5HF underwent an intramolecular hydrogen atom transfer and formed the tautomer in the excited triplet state. The triplet energy of the normal form of 5HF was 260 kJ mol^{-1}, while that of the tautomer form (5HF′) was 197 kJ mol^{-1}. The triplet energy of 5MF, the model compound of the normal form of 5HF, was 261 kJ mol^{-1}. The PM3/CI4 calculation supported the experimental observations and suggested that the most stable conformer in the triplet state of 5HF is the tautomer form.

Keywords: 5-Hydroxyflavone; Intramolecular hydrogen bond; Hydrogen atom transfer; Proton transfer; Triplet state; Transient absorption

1. Introduction

Flavonoids are found in diverse plants, and some groups of flavonoids have been used as pigments and dyes from ancient times [1,2]. Recently, the role of flavonoids in biological systems has attracted much attention because of their anti-oxidant properties [3,4]. Naturally-occurring flavonoids generally possess OH groups or their glucocides. Especially, a number of plant-derived flavones possess an OH group at the 5 position [1,5]. For example, luteolin, galangin, kaempferol and quercetin have a 5-OH group. 5-Hydroxyflavone (5HF), which has only one hydroxyl group at the 5 position, is also found in nature [1,5]. The properties of flavones with a 5-OH group have been studied from different aspects; anti-oxidant properties against superoxide anion (O_2^-) [6], stability against photoirradiation, [2] and excited state proton transfer reactions [7–10]. Plant physiologists believe that flavonoids which possess the 5-OH group can act as photoprotectors, in which the excess light energy from the sun would be converted to heat [7]. Therefore, studying the deactivation process of flavonoids is intriguing from a biochemical point of view as well as from the photochemical aspect.

It has been well recognized by photochemists that aromatic ketones with an intramolecular O–H:O hydrogen bond virtually exhibit an intramolecular hydrogen atom transfer (or proton transfer) and form a tautomer in the excited states [9–19]. Studies of the reaction have been mainly on the excited singlet state, and numerous compounds have been reported over the past few decades [9–14]. These compounds emit large Stokes-shifted fluorescence which is attributed to the tautomer fluorescence. Therefore, the properties of the tautomer in the excited singlet state are readily observable if the tautomer is emissive. On the other hand, only a limited number of compounds, which exhibit the hydrogen atom transfer in the excited triplet state, have been reported [15–19]. For a biological system, to avoid DNA damage, it is important to have functions which efficiently quench the excited states, especially the excited triplet state which has biradicaloid properties and is usually longer lived than the excited singlet state. Singlet oxygen ($^1\Delta_g$) is often produced by the excited triplet state. Thus, studies on the excited triplet state of intramolecularly hydrogen-bonded compounds are requisite for understanding the photoprotective properties of biological systems.

Abbreviations: 5HF, 5-hydroxyflavone; 5MF, 5-methoxyflavone; T–T, triplet–triplet absorption

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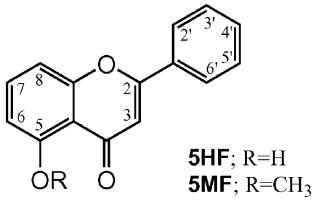
The intramolecular hydrogen atom transfer of 5HF has been previously studied by Chou and co-workers [9,10]. 5HF exhibited fluorescence around 670 nm and the emitting state was assigned to the tautomer form. However, the report was limited to the excited singlet state and the behavior of the excited triplet state was not reported. Recently, we have found that 5HF underwent the intramolecular hydrogen atom transfer in the excited triplet state and have reported the preliminary results as a communication [19].

Our main interest is to investigate the deactivation process of the hydrogen-bonded compounds, especially the intramolecular hydrogen atom transfer reaction in the excited triplet state. In this work, the photophysical properties of 5HF were investigated by means of transient absorption, phosphorescence spectroscopies and semiempirical molecular orbital calculations (PM3/CI4). As a model compound for the normal form of 5HF, the photophysical properties of 5-methoxyflavone (5MF) were also studied.



5HF; R=H
5MF; R=CH_3

2. Experimental details

2.1. Materials

Benzene, methylcyclohexane, ethanol and methanol were spectroscopic grade (Dojin Chem. Co. or Kanto Chem. Co.) and were used as received. Isopentane and diethyl ether were distilled prior to use. Biacetyl was distilled at reduced pressure. Michler's ketone (4,4′-bis(dimethylamino)-benzophenone) and benzophenone were recrystallized from ethanol. Pyrene was purified by activated carbon and silica gel column chromatography. 5-Hydroxyflavone was purchased from Sigma and recrystallized three times from ethanol. 5-Methoxyflavone was purchased from Avocado and recrystallized three times from the benzene–hexane mixed solvent.

2.2. Measurements

UV-Vis absorption spectra were measured by JASCO Ubest-55 spectrophotometer. Phosphorescence spectra were measured by Hitachi F-4000 spectrofluorophotometer equipped with a phosphorescence unit. Sample solutions for phosphorescence measurements were deaerated by bubbling nitrogen gas.

Transient absorption spectra were measured with 308 nm pulses (XeCl, 10 ns fwhm) from an excimer laser (Lambda Physik LPX-100), 425, 430 nm pulses (Stilben 3, 10 ns fwhm), or 390 nm pulses (QUI, 10 ns fwhm) from an excimer laser-pumped dye laser (Lambda Physik FL-3002). The laser power was ∼20 and ∼5 mJ per pulse for 308 nm and dye laser pulses, respectively. A pulsed xenon arc (Wacom, KXL-151, 150 W) was used as a monitoring light source. The detailed set-up was described previously [20–22]. Some of the sample solutions were deaerated by bubbling argon. All transient absorption measurements were carried out in benzene solution. Concentration of sample solutions was adjusted so that the absorbance was 0.8–1.0 at excitation wavelength.

The quantum yield of intersystem crossing of 5HF was determined by laser flash photolysis comparing the absorbance (ΔO.D.) of the triplet states of the sample and a standard compound generated by direct and sensitized excitation. Naphthalene ($\Phi_{ISC} = 0.75$ [23]) was used as a standard.

2.3. Calculation

The semiempirical calculations were performed using CAChe MOPAC ver. 94.10 on Macintosh G3 with parameters in reference [24]. The optimized geometries, energy parameters, and the MO coefficients were calculated by the semiempirical PM3 method. Molecular geometries were totally optimized.

3. Results and discussion

3.1. Absorption and fluorescence spectroscopies

There was an appreciable difference in the UV-Vis absorption spectra of 5HF and 5MF. The UV spectra of 5HF and 5MF in benzene are shown in Fig. 1. The absorption maximum (λ_{max}) of 5HF is 337 nm ($\varepsilon = 6300\,M^{-1}\,cm^{-1}$), while that of 5MF is 318 nm ($\varepsilon = 11{,}400\,M^{-1}\,cm^{-1}$). The bathochromic shift of the absorption band of 5HF compared to that of 5MF may be due to the extended π conjugation by the intramolecular hydrogen bonding.

Chou and co-workers [9,10] reported that 5-hydroxyflavone exhibits large Stokes-shifted fluorescence around

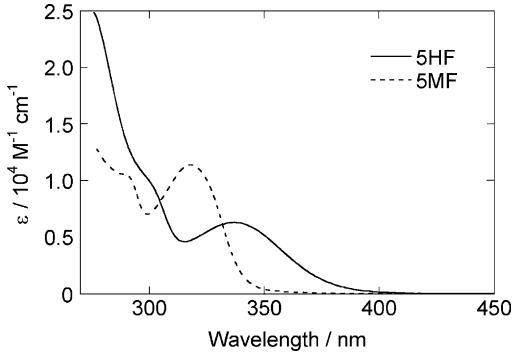


Fig. 1. Absorption spectra of 5HF and 5MF in benzene.

670 nm and they assigned the emitting state to the tautomer form. However, the emission is very weak ($\Phi_{f'} \sim 5.0 \times 10^{-6}$) [9] and could not be detected by our conventional spectrofluorometer. The large Stokes-shift of the tautomer emission and its low fluorescence efficiency indicate the very short lifetime of the S_1 state of 5HF. Recently, Chou et al. [9] has determined the fluorescence lifetime of the tautomer to be 1.2 ps by the upconversion method. The hydrogen atom transfer rate was beyond the response time (ca. 160 fs) of their instruments. Such very low fluorescent property of 5HF is due to the fast intramolecular hydrogen atom transfer in the excited singlet state, fast internal conversion by a 'proximity effect' [7,25] and/or fast intersystem crossing by the small energy gap between S_1 and T_1 of the tautomer as discussed in the later section.

3.2. Phosphorescence spectroscopy

In an alcoholic solvent (EPA; diethylether:isopentane: ethanol = 5:5:2 (v/v)), 5HF exhibited phosphorescence which peaked at 465 nm. The spectrum is shown in Fig. 2. The emitting state was previously assigned to the intermolecularly hydrogen-bonded 5HF with alcohol [10]. Our observations are consistent with the assignment. The phosphorescence intensity was quenched in aprotic solvents such as MP (methylcyclohexane:isopentane = 1:1 (v/v)), and phosphorescence lifetime (τ_p) was also quenched (τ_p = 200 ms and <15 ms in EPA and MP, respectively). These results indicate that the intermolecular hydrogen bond between 5HF and solvent molecule(s) inhibit the non-radiative decay process such as the intramolecular hydrogen atom transfer.

The phosphorescence spectrum of 5MF was similar to those of 5HF observed in alcoholic solvents (Fig. 2). The peak attributed to the 0–0 band was observed at 459 nm in a mixed solution of ethanol and methanol (1:1 (v/v)). From the peak of the spectra, the triplet energy of 5MF was determined to be 261 kJ mol^{-1}. This value is in fair agreement with the literature value of the triplet energy of flavone (259 kJ mol^{-1}) [23].

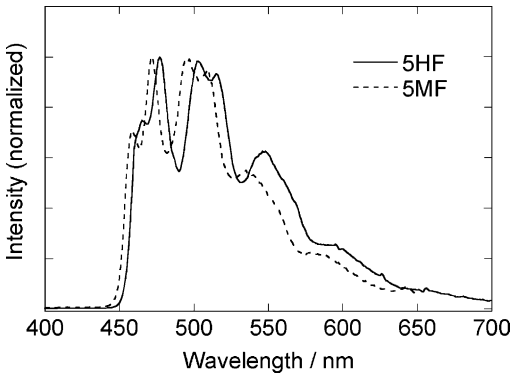


Fig. 2. Phosphorescence spectra of 5HF in EPA and 5MF in EtOH/MeOH = 1/1 at 77 K.

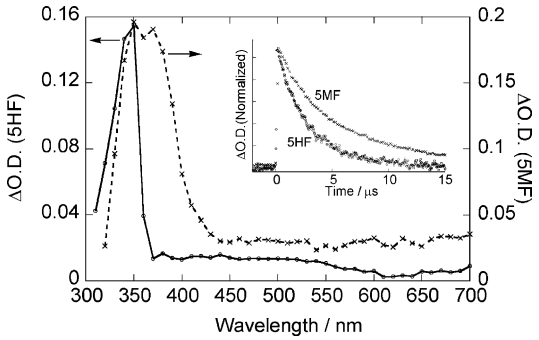


Fig. 3. Transient absorption spectra of 5HF observed at 468 ns and 5MF at 625 ns after the 308 nm laser pulse in benzene. Inset shows the transient absorption decay signals of 5HF and 5MF monitored at 350 and 360 nm, respectively.

3.3. Transient absorption spectroscopy

The transient absorption spectra of 5HF and 5MF upon direct irradiation at 308 nm in benzene are shown in Fig. 3. A sharp peak at 350 nm and a very broad band from 380 to 600 nm were observed in 5HF. These two bands decayed with the same lifetime (2.8 μs) and were quenched by oxygen at the rate constant of $k_q = 2.7 \times 10^9$ M^{-1} s^{-1} in benzene. The same transient absorption spectrum was observed on the triplet-sensitized excitation of 5HF using benzophenone or Michler's ketone. Thus, the observed transient is assigned to the excited triplet state. The T–T absorption was not observed in the previous study of Chou et al. [9] Probably this was because 5HF shows very small T–T absorption in the wavelength region where they monitored (400–800 nm).

A broader band peaked around 360 nm and a very broad band throughout 430–800 nm were observed in 5MF (Fig. 3). The transient had a lifetime of 6.8 μs, which was longer than that of 5HF, and was quenched by the addition of oxygen; again, it is assigned to the excited triplet state.

The peak of the T–T absorption of 5HF is sharp and blue-shifted comparing with that of 5MF (Fig. 3). The difference in the T–T absorption spectra and the lifetime of 5HF and 5MF indicates that the conformation of each triplet might be different. In 5HF, there are two candidates for the observed triplet: the normal form and the tautomer form. Thus, regarding the triplet state of 5MF as a model of the normal form of 5HF triplet, the observed triplet of 5HF cannot be assigned to the normal form. If 5HF undergoes the hydrogen atom transfer in the excited triplet state, there should be a considerable difference between the triplet energy which is required to sensitize 5HF to the excited triplet state and that of the relaxed triplet (tautomer form) observed by the transient absorption spectroscopy.

3.4. Quenching experiments

To make clear the assignment of the observed triplet state of 5HF, its triplet energy was estimated by quenching experiments. First, the triplet excitation energy (the triplet

energy of the normal form) of 5HF was estimated as follows. On benzophenone (287 kJ mol^{-1}) [23] or Michler's ketone (275 kJ mol^{-1}) [23] sensitization, 5HF gave T–T absorption spectra which are similar to that observed on direct excitation as mentioned above. The rate constants of the energy transfer from these triplet sensitizers to 5HF were diffusion-controlled [$(7.5\pm1.0)\times10^9$ M^{-1} s^{-1}], revealed by observing the triplet lifetimes of the sensitizers. Thus, these triplet energy transfer processes are exothermic. In contrast, 5HF was not sensitized by the biacetyl triplet (236 kJ mol^{-1}) [23] indicating that the process is highly endothermic. Therefore, from these observations, the triplet energy of the normal form of 5HF must be higher than 236 kJ mol^{-1} (E_T of biacetyl) and lower than 275 kJ mol^{-1} (E_T of Michler's ketone).

A similar quenching experiment was also carried out using 5MF, a model compound for the normal form of 5HF, with Michler's ketone as a triplet sensitizer. The quenching process was diffusion-controlled and it indicates that the triplet energy of 5MF is lower than that of Michler's ketone. It is consistent with the value of the triplet energy of 5MF determined by the phosphorescence spectra (261 kJ mol^{-1}). From these quenching experiments together with the phosphorescence spectra (vide supra) of 5HF and 5MF, the triplet energy of the normal form of 5HF was estimated to be 260 kJ mol^{-1}.

On the other hand, the energy of the relaxed triplet state observed by laser photolysis was estimated by the quenching experiments as follows. Several compounds were used as triplet quenchers to estimate the energy transfer process from the observed 'relaxed' 5HF triplet to the quencher. Biacetyl (E_T = 236 kJ mol^{-1}) did not quench the 5HF triplet, indicating that the energy transfer from the 5HF triplet to biacetyl is highly endothermic: the triplet energy of 5HF transient is much less than that of biacetyl. Pyrene (E_T = 203 kJ mol^{-1}) [23] quenched the 5HF triplet by the rate constant of $k_q = 5.8\times10^8$ M^{-1} s^{-1}; the energy transfer process is slightly endothermic by 5.7 kJ mol^{-1} estimated from Eq. (1), where k_{dif} is the diffusion-controlled rate constant, k_q is the observed quenching rate constant, and ΔE_a is the energy difference between the triplet energy donor and the acceptor [26]. Therefore, the triplet energy of the transient observed by the transient absorption was estimated to be 197 kJ mol^{-1}.

$$k_q = k_{dif}\frac{\exp(-\Delta E_a/RT)}{1+\exp(-\Delta E_a/RT)} \quad (1)$$

The same quenching experiment was performed using 5MF. The triplet state of 5MF, sensitized by Michler's ketone, was quenched by pyrene by the rate constant of $k_q = 7.0\times10^9$ M^{-1} s^{-1}. This strongly indicates that the quenching process is diffusion-controlled. Thus, the triplet energy of the observed triplet of 5MF is much higher than that of pyrene as can be expected from the phosphorescence data. It should be emphasized that the triplet energy of the observed triplet of 5HF is comparative to that of pyrene, while that of 5MF is much higher. From these observations, in 5HF, there is a relaxed triplet state with the triplet energy of 197 kJ mol^{-1}, while that of the normal form of 5HF was estimated to be 260 kJ mol^{-1}. Therefore, we may propose the relaxed triplet of 5HF to be the tautomer. In order to support the assignment, semiempirical MO (PM3/CI4) calculations were carried out.

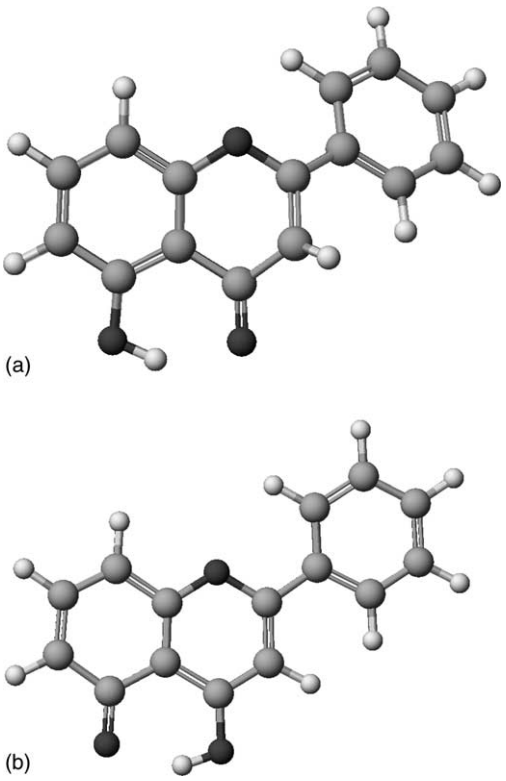


Fig. 4. Optimized structures of normal (a) and tautomer form (b) of 5HF in the excited triplet state obtained by PM3/CI4 calculations.

3.5. Calculations

The optimized structures of the normal form of 5HF and the tautomer form (5HF′) in the excited triplet state are shown in Fig. 4. In the normal form, the benzopyranone ring is distorted. The C=C bond between the 2 and 3 positions is twisted: the torsion angle of the C(phenyl)–C(2)–C(3)–C(4) bond was −123°. On the other hand, in the tautomer form, the benzopyranone ring was fairly planar and was coplanar to the benzene ring. The calculated heats of formation (ΔH_f) of 5HF and 5HF′ in the ground, the excited singlet, and the excited triplet states are shown in Fig. 5. In the ground state, the normal form is more stable than the tautomer by 52.3 kJ mol^{-1}. This value indicates that the most stable species is the normal form and the tautomerization hardly takes place in the electronic ground state. The reported value of the calculated energy difference between the normal and tautomer forms of related compounds are; 78–98, 74, 47, and 55 kJ mol^{-1} in salicylic acid, [27] methyl salicylate, [11]

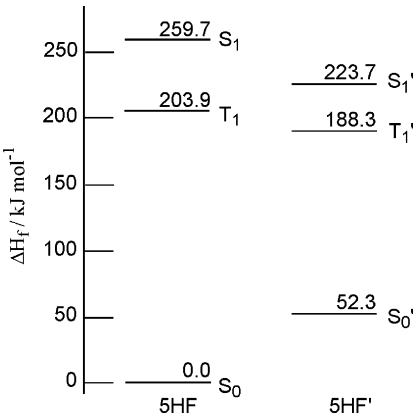


Fig. 5. Heats of formation (ΔH_f) of 5HF and 5HF′ in the ground, the excited triplet and the excited singlet states calculated by PM3/CI4.

o-hydroxyacetophenone, [11] and 2′-hydroxychalcone [28], respectively. In the excited states, on the other hand, the tautomer form (5HF′) is more stable than the normal (5HF) form by 15.6 kJ mol^{-1} and by 36 kJ mol^{-1} in the excited triplet and singlet states, respectively. In 2′-hydroxychalcone, the tautomer (T_1') is more stable than the normal form (T_1) by 17.5 kJ mol^{-1} [28]. These calculations are in fair agreement with the experimental observations, and therefore, it can be concluded that the hydrogen atom transfer can take place in the excited triplet state of 5HF.

3.6. Potential energy surface of 5-hydroxyflavone

On the basis of the experimental and theoretical results, the potential energy diagram of the intramolecular hydrogen atom transfer of 5HF in the excited singlet and the triplet states is depicted in Fig. 6. The shapes of the potential curves were estimated from those of analogues which have been studied experimentally and theoretically [11–18,29–31]. On direct excitation, the S_1 state of the normal form 5HF is initially formed. There are two possible deactivation pathways from the S_1 state of 5HF except for the direct deactivation to the ground state; intersystem crossing to the triplet state of the normal form (T_1), or intramolecular hydrogen atom transfer to yield the tautomer form (S_1'). The latter process is most likely to take place because it has been reported that the process is generally very fast. In methyl salicylate, the hydrogen atom transfer takes place within 60 fs in the excited singlet state [32]. Although an aromatic ketone generally exhibits very fast intersystem crossing ($k_{ISC} \sim 5 \times 10^8$–$10^{11}$ s^{-1}), [33] it is still slower than the hydrogen atom transfer. In addition, the observation of fluorescence around 670 nm [10] strongly indicates that the hydrogen atom transfer occurs along the S_1 surface. Recently, Chou et al. [9] observed fluorescence from the normal form ($\lambda_{fl} \sim$ 420 nm) with a lifetime of shorter than 160 fs, indicating that the hydrogen atom transfer is dominant on the S_1 surface. The difference in the calculated ΔH_f value between the normal and the tautomer (36 kJ mol^{-1}) in S_1 also suggests the process is dominant. Thus, the S_1'–T_1' intersystem crossing takes place after the hydrogen atom transfer. The quantum yield for intersystem crossing of 5HF (the quantum yield of the formation of the T_1' state, $\Phi_{ISC'}$) was estimated to be 0.02. One might expect that the internal conversion process from the S_1' state is very fast due to the 'proximity effect' [7,25]; however, the S_1'–T_1' intersystem crossing is also accelerated due to the small energy gap between S_1' and T_1'.

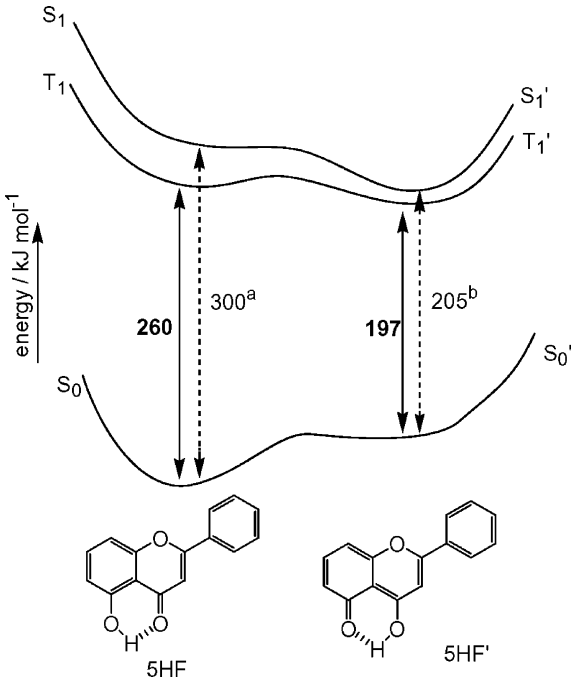


Fig. 6. Potential energy diagram of intramolecular hydrogen atom transfer of 5HF. (a) Calculated from absorption spectra. (b) Calculated from fluorescence spectra in reference [9,10].

On triplet sensitization, the T_1 state of the normal form of 5HF is initially formed. However, the triplet observed by the transient absorption was assigned to the T_1 state of the tautomer form (T_1') as described above. Thus, the lifetime of the T_1 state of the normal form should be shorter than or comparable to the time scale for the triplet–triplet energy transfer process so that the T_1 state of the normal form could not be detected by the transient absorption. Therefore, it can be concluded that the intramolecular hydrogen atom transfer of 5HF takes place along the T_1 surface adiabatically and the reaction is completed within the nanosecond time scale. Attempts to estimate the shape of the potential energy surface of the hydrogen atom transfer using PM3 calculation were unsuccessful in either the ground or the excited states. It gave too high energies near the transition states. Hartree-Fock or DFT calculations might be required to depict the potential energy surface of 5HF in the excited states as well as in the ground state.

The phosphorescence behavior of 5HF is noteworthy. In a protic solvent, the phosphorescence of 5HF was observed. It was assigned to the conformer whose hydroxyl moiety is

intermolecularly hydrogen-bonded to solvent molecule(s). In an aprotic nonpolar solvent, the phosphorescence was quenched. When the 5HF molecule forms an intermolecular hydrogen bond with a solvent molecule, the intramolecular hydrogen atom transfer (S_1–S_1') is suppressed and the S_1–T_1 intersystem crossing becomes more efficient. The hydrogen atom transfer along the triplet state (T_1–T_1') is also suppressed, and therefore, the T_1–S_0 emission was observed. We could not observe the phosphorescence from the triplet tautomer (T_1'), because the radiationless transition from T_1' to S_0' is very fast due to the small energy gap between the two electronic states.

Recently, Arai and co-workers [28,34,35] have reported the hydrogen atom transfer in the triplet manifold of O–H:O and O–H:N hydrogen-bonded compounds. Those hydrogen atom transfer reactions are coupled with another photoreaction such as photoisomerization of C=C or C=N bonds. According to those reports, photochemical reactions can be affected by an intramolecular hydrogen bond because the hydrogen atom transfer reaction efficiently 'quenches' the reactive state by forming the tautomer in the excited triplet state as well as in the excited singlet state. An excited tautomer (which can be considered as a 'relaxed' excited state) has a lower excitation energy than that of the normal form, and therefore, the tautomer hardly reacts intramolecularly (e.g. isomerization) or intermolecularly (e.g. energy transfer). Thus, by choosing the suitable structure, a reaction can be controlled by a hydrogen bond. Actually, isomerization around the C=C bond in 2′-hydroxychalcone is controlled in a one-way (*cis–trans*) direction by an intramolecular hydrogen bond [28,31,34].

4. Conclusion

The deactivation process of photoexcited 5-hydroxyflavone was investigated by spectroscopic and theoretical methods. The intramolecular hydrogen atom transfer reaction takes place in the excited triplet state. The observed tautomer of 5HF had a lifetime of 2.8 μs and the triplet energy was 197 kJ mol^{-1}. The intermolecular hydrogen atom transfer in the excited triplet state as well as in the excited singlet state might play an important role in the quenching process of photoexcited molecules in biological systems.

Acknowledgements

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