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Bull. Chem. Soc. Jpn., 72, 2429—2435 (1999)

Laser Flash Photolysis Studies of the Photo-Ring-Opening Reaction of Flav-3-en-2-ol

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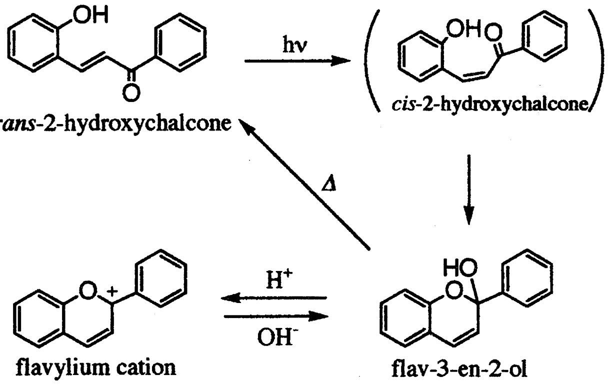
(Received June 22, 1999)

Electronic structure and photodynamics of flav-3-en-2-ol have been studied by steady-state and time-resolved absorption measurements, and by semi-empirical MO calculations. The photo-ring-opening reaction to produce 2-hydroxychalcone has been determined to be a monophotonic process with the quantum yield of 0.29. The precursor to 2-hydroxychalcone has been assigned to the ground-state enol-form by nanosecond laser flash photolysis study at room temperature and steady-state photolysis study at 77 K. The efficiency of the tautomerization from the ground-state enol-form to keto-form of 2-hydroxychalcone has been estimated to be unity. The enol-form is transformed into 2-hydroxychalcone with the rate constant of 3.2×10^4 s^{-1} in neat acetonitrile, and this process is accelerated by protic molecules. The PM3 calculation of flav-3-en-2-ol showed that the dissociative potential surface in the first excited singlet-state is responsible for the ring-opening reaction.

A number of studies on flash photolyses of plant pigments were carried out to clarify the mechanisms of photosynthesis,[1—5] biosynthesis,[6] and protection against UV-induced damage in plants.[7] Chalcone derivatives are one type of flavonoids, and the plant dyes such as flavones and anthocyans are known to be biosynthesized from chalcone derivatives by photochemical reactions.[8—10] Much attention has been paid for the photochemical properties of chalcones. It is also known that the reversible reaction between chalcone and anthocyan is photochromic, and many studies were devoted to clarifying the mechanism.[8—19]Scheme 1 shows one of the simplest photochromic systems between the 2-hydroxychalcones and flavylium cations.[6,15—19] The coloration process consists of two steps : The first one is photo-ring-closure from *trans*-2-hydroxychalcone to flav-3-en-2-ol and the second is acid-base reaction from flav-3-en-2-ol to flavylium cation. In the decoloration process, attention has been paid for thermal processes because flavylium cation (colored form) is photochemically stable.[6,13] Flavylium cation and flav-3-en-2-ol are in rapid acid-base equilibrium; the rate-determining step of this thermal process is the reaction from flav-3-en-2-ol to *trans*-2-hydroxychalcone.[6,13] The reaction rate is slow in acetonitrile at room temperature (a few weeks) compared with that of the coloration process (less than 1 second).



Scheme 1.

In this work, we studied the photochemical processes of flav-3-en-2-ol to clarify the photo-ring-opening reaction to give *trans*-2-hydroxychalcone. Results of nanosecond laser flash photolysis have shown that this photochemical reaction is completed within 200 μs and that the photo-ring-opening reaction proceeds from the ground-state enol-form to the keto-form of 2-hydroxychalcone with a rate constant of 3.2×10^4 s^{-1} in acetonitrile. We have also clarified that the enol-form was not transformed into the parent molecule, but produces *trans*-2-hydroxychalcone with an efficiency of 100%. This tautomerization to 2-hydroxychalcone is different from a normal photochemically induced keto-enol tautomerization, where the parent molecule (keto-form) is reproduced from the enol-form generated upon excitation.[20—30] Such a ground-state tautomerization was studied by the laser photolysis and/or two-step laser excitation fluorescence measurements.[20—30] Their tautomerization rate constants are 10^4—10^5 s^{-1} in aprotic solvents at room temperature.[21—25,27,28,30] Acceleration of the tautomerization by protic solvents has been observed.[27,29] In our system, similar decay rate constants and acceleration of tautomerization have been observed.

Experimental

Chemicals ; 2-hydroxychalcone was synthesized by condensation of acetophenone with 2-hydroxybenzaldehyde.[31] It was purified by repeated recrystallizations from aqueous ethanol. Acetonitrile (MeCN : more than 99.5%, Wako Pure Chemical Industries, Ltd.) was used after drying with $MgSO_4$ anhydrous. All other chemicals used were the best available commercial grade.

Steady-state photolysis was carried out by using outputs from a 500W Xe short-arc lamp (Ushio UI-502Q) passed through a monochromator (266 and 355 nm ; Japan Spectroscopic Co., Ltd. CT-10). The intensity (I_0) of the irradiation light (266 nm) was determined to be 1.5×10^{-9} einstein per second by using tris(oxalato)-ferrate(III) as a chemical actinometer.[32] The quantum yield of photo-ring-opening reaction was determined by monitoring the absorbance of 2-hydroxychalcone at 341 nm. Absorption spectra were recorded on a Hitachi U3300 spectrophotometer. ^{1}H NMR spectrum was determined on a JEOL α-50 spectrometer at 500 MHz. Chemical shifts are reported as δ units (ppm) relative to tetramethylsilane, and residual solvent peaks were used as standards. Transient absorption spectra were measured at room temperature by a Unisoku TSP601H nanosecond laser photolysis system with photolysis light of 266 nm (fourth harmonic) from a Nd^{3+} : YAG laser with 20-ns pulse width (Quanta-Ray GCR-130, Spectra Physics), and was monitored with a Xe lamp perpendicular to the photolysis light. Sample solutions were flowed through a cell of 10 mm light-path-length with a flow-rate faster than 20 mL min^{-1} to ensure that the sample for an excitation light pulse was always fresh. Sample concentrations used for steady-state and time-resolved photolyses were 1—2×10^{-4} M (1 M = 1 mol dm^{-3}). Semiempirical molecular orbital calculations were performed by the PM3 method (MOPAC 97) for structure optimization. Electronic spectra were calculated by the CNDO/S-CI method (MOS-F ver 4.1, Fujitsu Labs Ltd.) for the optimized molecular structures.

Results and Discussion

Dewar and Sutherland reported that the photolysis of 2-hydroxychalcone in alcohol produces 2-alkoxyflav-3-ene in yield of 97%. It was produced from flav-3-en-2-ol by the replacement of a hydroxy group with an alkoxy group of the solvent.[11] To prepare flav-3-en-2-ol, the photolysis of 2-hydroxychalcone was carried out with 355-nm light in MeCN ; the resulting spectral change is shown in Fig. 1. There is an isosbestic point at 236 nm; the spectral change was completed within 100 min. The photoproduct was identified by the NMR spectrum, which consisted of a singlet at δ = 5.02 ppm (1H), a doublet at δ = 5.88 (J = 9.7 Hz, 1H), a doublet at δ = 6.73 (J = 9.7 Hz, 1H), a doublet at δ = 6.97 (J = 7.9 Hz, 1H), a triplet at δ = 7.00 (J = 7.5 Hz, 1H), a multiplet at δ = 7.25—7.29 (2H), a multiplet at δ = 7.36—7.44 (3H) and a doublet at δ = 7.61 (J = 7.0 Hz, 2H). These signals can be assigned as follows. Two doublets at δ = 5.88 and 6.73 are assigned to two olefinic protons which are in *cis*-configuration and are well correlated with those reported by Dewar and Sutherland (δ = 5.75: J = 9 Hz, δ = 6.69: J = 9 Hz).[11] The singlet at δ = 5.02 is assigned to a proton of the hydroxy group bonded to benzyl carbon. This chemical shift corresponds to that of the benzyl alcohol (around 5 ppm).[33] All remaining signals are assigned to the aromatic protons. From these results, the photoproduct is identified with flav-3-en-2-ol. The purity of this product was estimated to be more than 98% in MeCN. These results are consistent with the reaction scheme given by Dewar and Sutherland.[11]

Electronic structure of flav-3-en-2-ol was studied by measuring the UV absorption spectrum in MeCN. This UV absorption spectrum shows maxima at 257 nm, ca. 266 nm, and ca. 300 nm, as shown in Fig. 2. Molar absorption coefficients were determined to be 8990 and 3150 M^{-1} cm^{-1} at 257 and 300 nm, respectively. The optimized molecular structure of the ground-state was calculated by the PM3 method. The electronic spectrum was calculated for the optimized structure by the CNDO/S-CI method by taking into account singly-excited electronic configurations. The calculated spectrum is shown in Fig. 2 by sticks (with circle) in comparison with the observed spectrum (full line). The observed spectrum is well explained by the calculated one : the broad band around 300 nm (4.13 eV) and the moderately intense band at 257 nm (4.82 eV) are assigned to the first and second excited singlet-states, calculated to be at 283 nm (4.38 eV) and 262 nm (4.73 eV), respectively. Molecular orbitals concerned with these electronic transitions are all π-orbitals, as shown in Fig. 3. The main configurations of the first excited singlet-state are LUMO+2←HOMO (40%), LUMO←HOMO-1 (32%) and LUMO←HOMO (17%) transitions. The characters of HOMO and HOMO-1 are both bonding with respect to the C(3)–C(4) bond while that of LUMO is anti-bonding. LUMO+2 has no electron distribution on C(3) and C(4) atoms. Therefore the C(3)–C(4) bond is considered to be weakened in the first excited singlet-state, and twisting about the C(3)–C(4) bond can be expected to occur upon excitation, as in the case of stilbene.[34] The results of CNDO/S-CI calculation and the assignment of the elec-

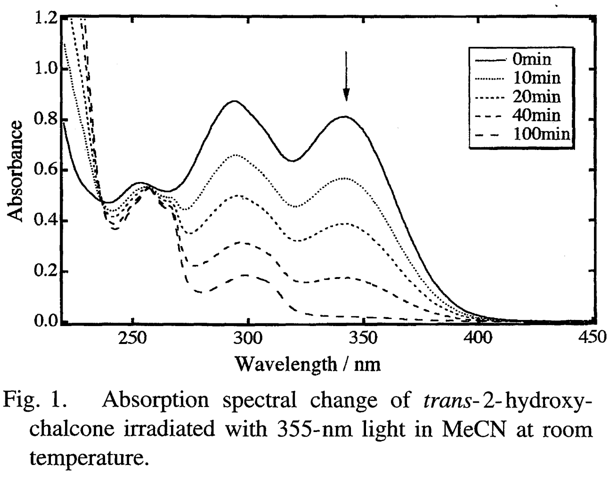


Fig. 1. Absorption spectral change of *trans*-2-hydroxychalcone irradiated with 355-nm light in MeCN at room temperature.

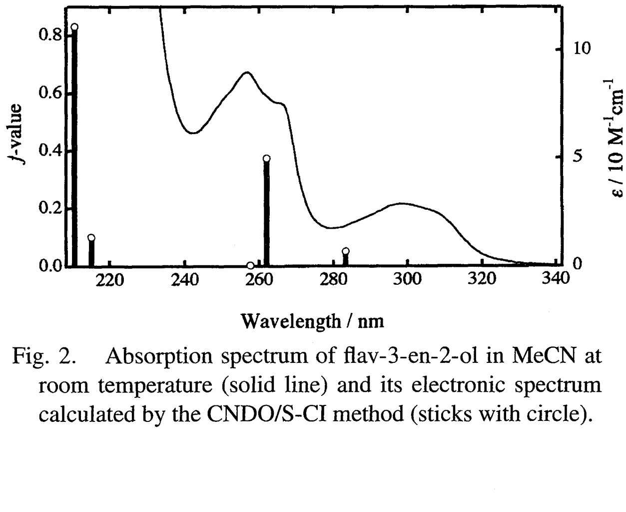


Fig. 2. Absorption spectrum of flav-3-en-2-ol in MeCN at room temperature (solid line) and its electronic spectrum calculated by the CNDO/S-CI method (sticks with circle).

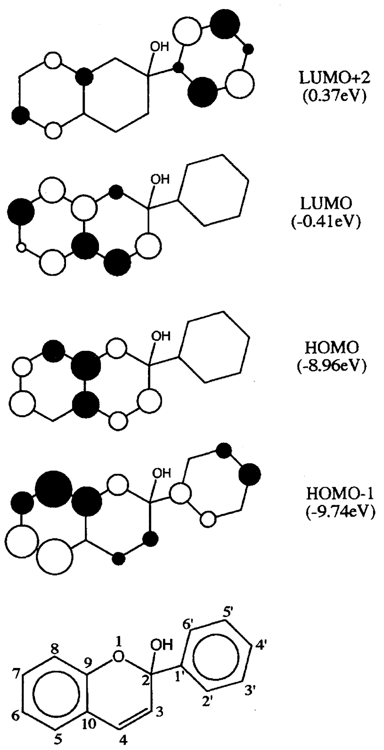


Fig. 3. Molecular orbitals of flav-3-en-2-ol calculated by the PM3 method.

tronic bands are summarized in Table 1. We tried to measure the emission spectrum of flav-3-en-2-ol at room temperature and 77 K. But no emission was observed, and therefore emission quantum yield was estimated to be less than 10^{-4}. This non-emissive property should be related to the character of the excited singlet-state, for which the twisting about the C(3)–C(4) bond is expected.

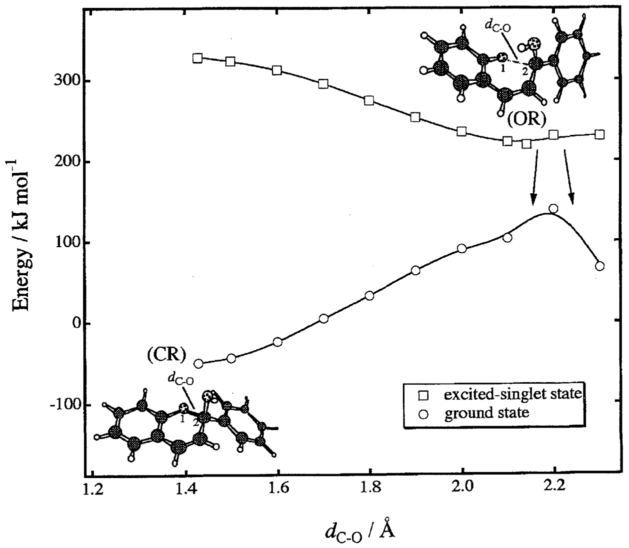


Fig. 4. Plots of the heat of formation of flav-3-en-2-ol against the interatomic distance (d_{C-O}) in the ground and excited-singlet states calculated by the PM3 method ; the CR and OR are most stable structures of flav-3-en-2-ol in the ground and excited-singlet state, respectively.

To obtain more information on the molecular structure, PM3 calculations were performed for the ground- and first excited singlet-states as a function of the interatomic distance between O(1) and C(2), d_{C-O}, for which some lengthening is expected as a result of the twisting about the C(3)–C(4) bond upon excitation. Figure 4 shows heat of formation calculated for the optimized geometry at the fixed value of d_{C-O} from 1.43 to 2.30 Å for both the ground- and first excited-states. The full optimized structure of the ground-state is the same as the structure obtained at d_{C-O} = 1.43 Å, which is denoted as CR in Fig. 4. The heat of formation calculated for the structure of the Franck–Condon state (d_{C-O} = 1.43 Å) was calculated to be 356 kJ mol^{-1}, which is slightly larger than that of the structure optimized at d_{C-O} = 1.43 Å. The stable structure of the first excited singlet-state at d_{C-O} = 2.14 Å is the same as the full optimized structure calculated for the first excited singlet-state (denoted as OR). A dissociative potential surface due to the twisting about the C(3)–C(4) bond was obtained for the excited singlet-state. The dihedral angle (θ) of C(2)–C(3)–C(4)–C(10) in the ground-state is 0° (d_{C-O} = 1.4 Å), while the θ in the excited singlet-state increased with increasing d_{C-O} up to 1.7 Å as follows : θ = 9.4° (d_{C-O} = 1.4 Å), 12.9° (1.5 Å), 15.8° (1.6 Å) and 16.8° (1.7 Å). In the region of 1.7—2.1 Å, θ decreased with increasing d_{C-O}.

Figure 5a shows the absorption spectral change of flav-3-en-2-ol irradiated with 266-nm light in MeCN. The absorption band in the region of 270—400 nm increased with increasing irradiation time, and no spectral change was observed over the irradiation time of 90 min. The difference spectrum between the spectra at the irradiation time of 90 and 0 min has two maxima at 341 and 292 nm, as shown by the full line in Fig. 5b. The difference spectrum between the absorption spectra of flav-3-en-2-ol and 2-hydroxychalcone is also shown in Fig. 5b by a dashed line. Both difference spec-

Table 1. Calculated Electronic Transitions for Flav-3-en-2-ol

	Calcd				Obsd	
Electronic transition	Energy / eV (nm)	Oscillator strength	Main configurations	CI coef.	Energy / eV (nm)	ε / M^{-1} cm^{-1}
I	4.38 (283)	0.05	HOMO → LUMO+2 HOMO−1 → LUMO HOMO → LUMO	−0.63 (40%) −0.57 (32%) −0.41 (17%)	4.13 (300)	3150
II	4.73 (262)	0.37	HOMO → LUMO HOMO → LUMO+2	−0.88 (78%) 0.38 (15%)	4.82 (257)	8990

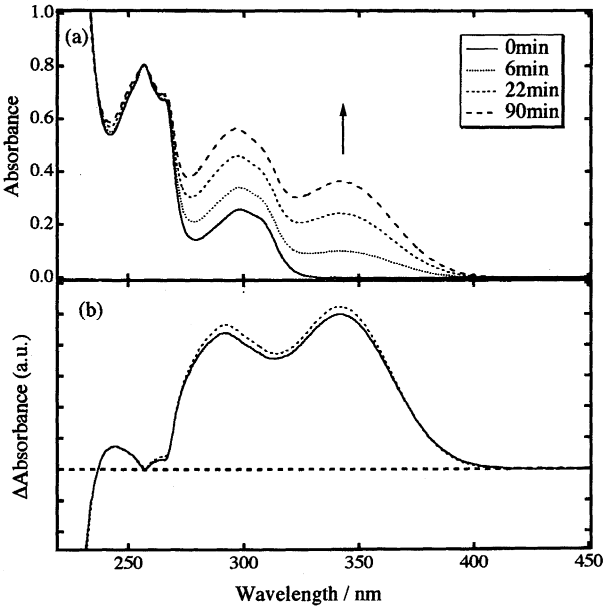


Fig. 5. Absorption spectral change of flav-3-en-2-ol irradiated with 266-nm light in MeCN at room temperature (a), and difference spectra between the absorption spectra of flav-3-en-2-ol at irradiation time of 90 and 0 min (solid line) in comparison with that between the absorption spectra of *trans*-2-hydroxychalcone and flav-3-en-2-ol (dashed line) (b).

tra are essentially the same, indicating that the ring-opening of flav-3-en-2-ol takes place to give 2-hydroxychalcone upon irradiation. The yield of 2-hydroxychalcone was estimated to be 30% at the irradiation time of 90 min by use of molar absorption coefficients of 0 and 1370 $M^{-1}\,cm^{-1}$ at 341 nm for flav-3-en-2-ol and 2-hydroxychalcone, respectively.

Irradiation light power dependence of the formation of 2-hydroxychalcone was studied in MeCN. The log–log plot of the absorbance change at 341 nm against the relative intensity of irradiation light was analyzed by a linear function with a slope of 1.0, indicating that the formation process of 2-hydroxychalcone is mono-photonic. The formation quantum yield (ϕ_{reaction}) was determined by measuring numbers of absorbed photons and generated 2-hydroxychalcone molecules. The number of absorbed photons was determined to be 1.5×10^{-9} einstein s^{-1} by using tris(oxalato)ferrate(III) as a chemical actinometer.[32] The number of generated 2-hydroxychalcone molecules was determined to be 4.4×10^{-10} mol s^{-1} by monitoring the initial absorbance change at 341 nm. From these results, the ϕ_{reaction} was estimated to be 0.29.

Figure 6 shows the transient absorption spectra of flav-3-en-2-ol in Ar-saturated MeCN observed upon excitation with 266-nm light pulse. The transient absorption spectrum observed at 2 μs after the laser flash shows three maxima: at 290, 350, and around 530 nm. The absorption in the region of 280—360 nm increased while that of 360—680 nm decreased, with an isosbestic point at ca. 360 nm. The spectrum at 200 μs has two maxima at 290 and 340 nm, and is essentially the same as the difference spectrum between the absorption spectra of flav-3-en-2-ol and 2-hydroxychalcone

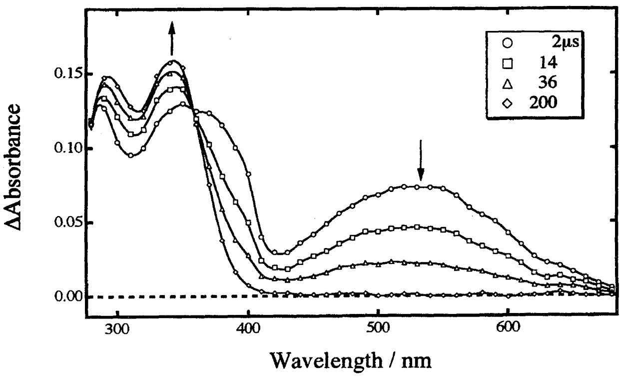


Fig. 6. Transient absorption spectra of flav-3-en-2-ol observed upon excitation with 266-nm light pulse in Ar-saturated MeCN at room temperature.

shown in Fig. 5b (dashed line). The photochemical reaction from flav-3-en-2-ol to 2-hydroxychalcone was completed within 200 μs.

The decay time profile monitored at the broad band in the visible region (530 nm) is shown in Fig. 7a by dots. This was analyzed by a single exponential function with the decay rate constant of $3.2\times10^{4}\ s^{-1}$; the lifetime is 31 μs. Rise time profile monitored at 340 nm is shown by dots in Fig. 7b. This time profile consists of decay of the transient species and rise of 2-hydroxychalcone; however, it was well analyzed by the following equation with the rate constant of $k = 3.2\times10^{4}$ s^{-1}, the same as the decay rate constant at 530 nm.

$$\Delta\text{Absorbance} = C - A\ \exp(-kt).$$

This indicates that the decay rate constant of the transient

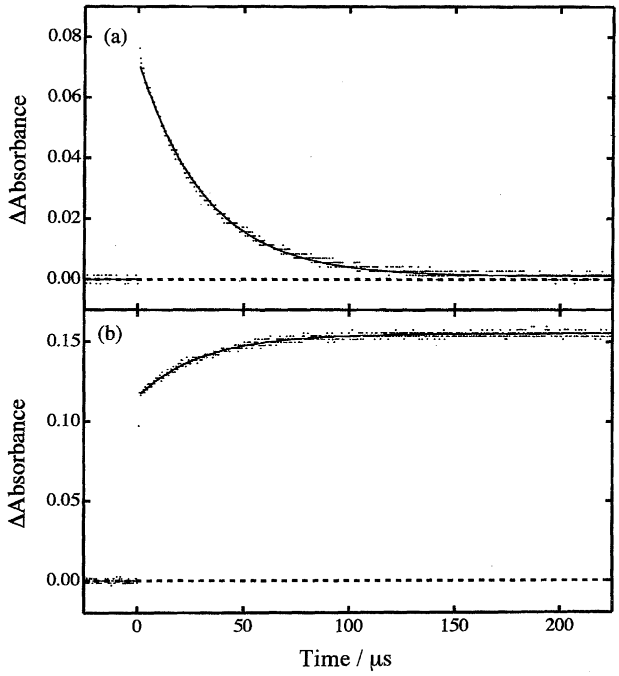


Fig. 7. Time profiles of transient absorption monitored at 530 nm (a) and 340 nm (b) of flav-3-en-2-ol observed upon excitation with 266-nm light pulse in Ar-saturated MeCN at room temperature.

species is equal to the rise rate constant of 2-hydroxychalcone. From these results, the transient species is attributable to the precursor to 2-hydroxychalcone. The lifetime (31 μs) is too long to assign the transient species to the excited singlet-state of the parent molecule. As one possible candidate for the transient, the triplet-state of the parent molecule and the ground-state enol-form of 2-hydroxychalcone are suggested.

The effect of oxygen on the decay rate constant of the transient species was studied to examine whether the triplet-state is responsible for the transient absorption or not. The decay time profiles of the transient species were determined at 530 nm in Ar- and O_2-saturated MeCN. Both decay profiles were analyzed by a single exponential function with essentially the same decay rate constant, indicating that oxygen gave no effect on the decay and therefore the transient species can not be assigned to the triplet state.

As the next candidate, the ground-state enol-form of 2-hydroxychalcone is considered. The decay rate constants of the ground-state enol-forms of 2-hydroxybenzaldehyde, 3-hydroxyflavone, 2-(2-hydroxyphenyl)benzoxazole, etc. were reported to be 10^4—10^5 s^{-1} in aprotic solvents.[21—25,27,28,30] The decay rate constant of the transient species (3.2×10^4 s^{-1}) is comparable to these values. It is known that enol–keto tautomerization is accelerated by protic molecules.[27,29] The decay rate constants of the transient species were studied in MeCN in the presence of an additive such as methanol, ethanol, water, diethylether and tetrahydrofuran. Figure 8 shows plots of the observed decay rate constants of the transient species (k_{obs}) against the concentration of the additives to MeCN. These plots could not be analyzed by a linear function, but did fit a quadratic function ($k_{obs} = k+k'[A]+k''[A]^2$). Here [A] is the concentration of the additives (protic molecules), k is the decay rate constant of the enol-form in neat MeCN, and k' and k'' are quenching rate constants of bimolecular[27] and termolecular[29] processes, respectively. This fact indicates that there are conformations with close energies which interact with one or two protic molecule(s) to induce the efficient tautomerization. The quenching rate constants obtained are summarized in Table 2. Although the rate was not accelerated by aprotic molecules (diethylether and tetrahydrofuran), it was accelerated by protic molecules (methanol, ethanol, and water). These results support the assignment that the transient species is the ground-state enol-form of 2-hydroxychalcone. In neat ethanol, 2-hydroxychalcone was produced within the laser-pulse and the transient absorption spectrum of the enol-form could not be observed, being in consistent with the great decay rate constant of the enol-form in ethanol.

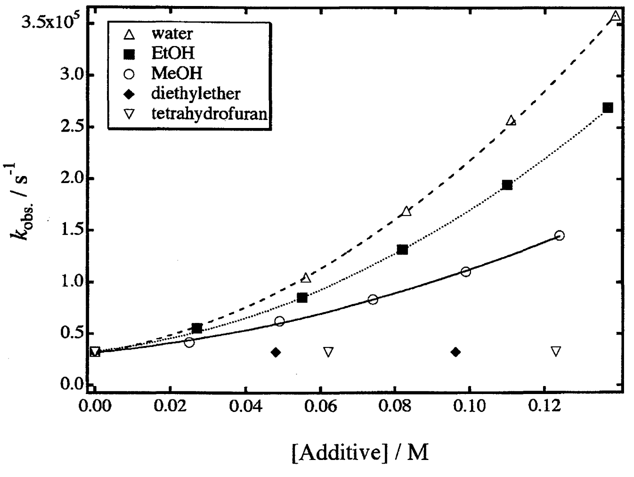


Fig. 8. Plots of the decay rate constants of the transient species observed upon excitation of flav-3-en-2-ol with 266-nm light pulse against the concentration of additives.

It was reported that there is an energy barrier of ca. 16 kJ mol^{-1} in the process of ground-state enol-keto tautomerization of 2-hydroxybenzaldehyde.[28] Thus, it is expected that there will also be an energy barrier in the process of enol–keto tautomerization in the ground-state 2-hydroxychalcone and the tautomerization will not proceed at 77 K. Based on the results of PM3 calculation that the photo-ring-opening process of flav-3-en-2-ol is adiabatic, photolysis of flav-3-en-2-ol at 77 K is considered to yield the ground-state enol-form of 2-hydroxychalcone. To confirm this, steady-state photolysis was carried out at 77 K in butyronitrile. Figure 9a shows the absorption spectral change of flav-3-en-2-ol irradiated with 266-nm light. New absorption bands appeared at 290, 345, and 520 nm upon photolysis. The difference spectrum between the absorption spectra before and after irradiation is shown by the dotted line in Fig. 9b. This spectrum has three peaks around 290, 340, and 520 nm. The transient absorption spectrum of the ground-state enol-form of 2-hydroxychalcone is also shown by open circles in Fig. 9b. The difference spectrum corresponds to the transient absorption spectrum of the enol-form and therefore the photoproduct at 77 K is attributable to the enol-form. From this result, it is understood that the photo-ring-opening reaction of flav-3-en-2-ol occurs even at 77 K, and this fact supports the result that the ring-opening process of flav-3-en-2-ol is adiabatic.

The solution of flav-3-en-2-ol irradiated at 77 K was warmed up to room temperature ; the absorption spectrum is shown by the solid line in Fig. 10a. The absorption bands at 341 and 296 nm increased on warming up, with disappearance of absorption spectrum due to the ground-state enol-form of 2-hydroxychalcone. The absorption spectrum of flav-3-en-2-ol at room temperature is also shown in Fig. 10a by the dotted line. The difference spectrum between these absorption spectra is shown in Fig. 10b by a solid line. There are two peaks at 341 and 296 nm, and the spectrum is es-

Table 2. Quenching Rate Constants of the Ground-State Enol-Form of 2-Hydroxychalcone

	Quenching rate constants	
Additives	k' / M^{-1} s^{-1}	k'' / M^{-2} s^{-1}
Methanol	3.8×10^5	4.3×10^6
Ethanol	4.4×10^5	9.3×10^6
Water	6.3×10^5	12.5×10^6

Error : ±15%.

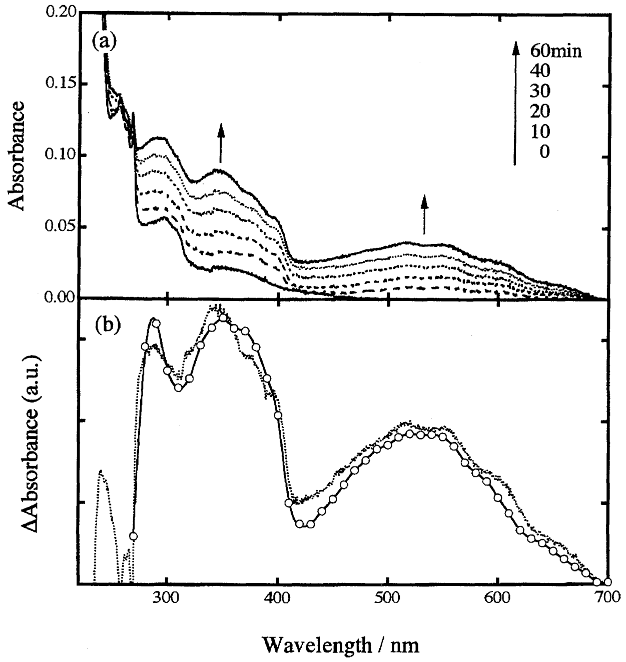


Fig. 9. Absorption spectral change of flav-3-en-2-ol in butyronitrile at 77 K upon excitation with 266-nm light (a), and difference spectrum between the absorption spectra before and after irradiation (dotted line) in comparison with the absorption spectrum of the transient species (open circles) (b).

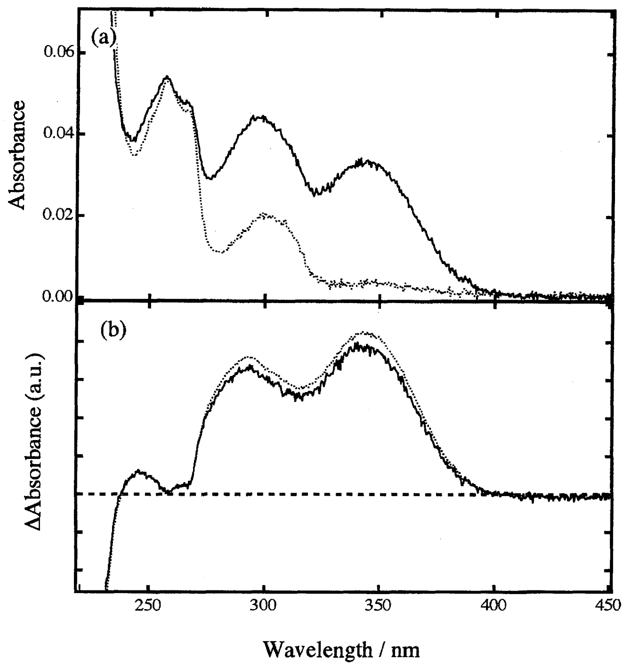
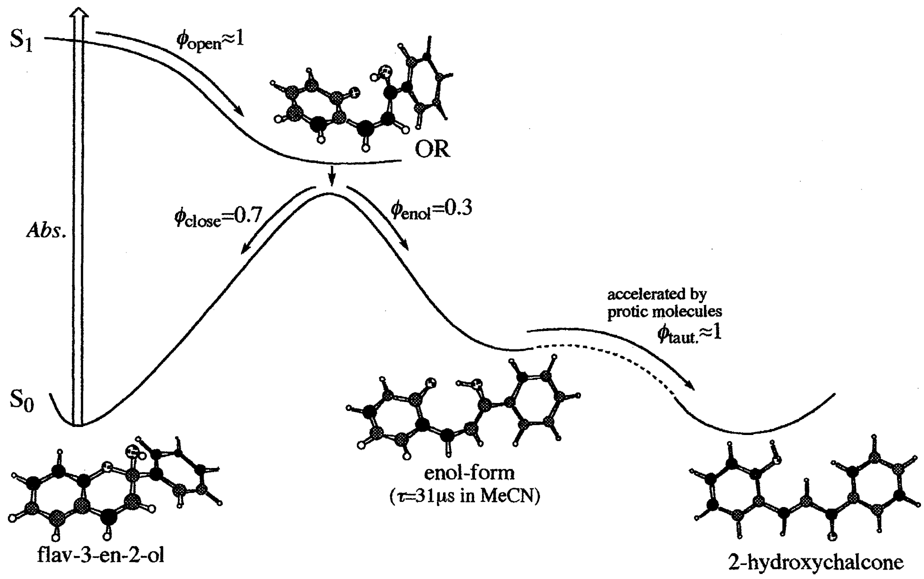


Fig. 10. Absorption spectrum of flav-3-en-2-ol irradiated with 266-nm light at 77 K followed by warming up from 77 K to room temperature (solid line) in comparison with that of flav-3-en-2-ol at room temperature (dotted line) in butyronitrile (a). Difference spectrum between them (solid line) and that between the absorption spectra of 2-hydroxychalcone and flav-3-en-2-ol (dotted line) (b).



Scheme 2.

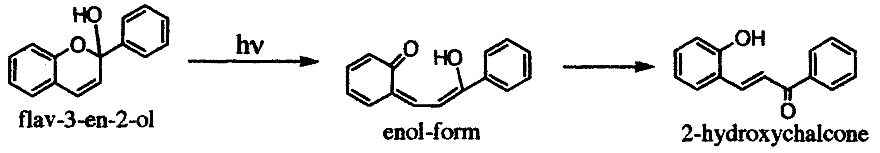


Chart 1.

sentially the same as the difference spectrum between 2-hydroxychalcone and flav-3-en-2-ol, shown by a dotted line. This indicates that 2-hydroxychalcone is produced from the ground-state enol-form by raising the temperature.

Based on these results, the photochemical processes shown in Scheme 2 are proposed. Franck–Condon excited singlet-state is formed upon excitation and it proceeds along the dissociative potential surface to give the OR form. By relaxation it gives rise to both the ground-state enol-form and the parent molecule. The enol-form gives 2-hydroxychalcone with the rate constant of 3.2×10^4 s^{-1} in neat MeCN, and this tautomerization is accelerated by protic molecules. Although the tautomerization in neat ethanol was too fast to determine a rate constant, ϕ_{reaction} was determined to be essentially the same as that in neat MeCN. This indicates that the efficiency of the tautomerization from the ground-state enol-form to the keto-form of 2-hydroxychalcone ($\phi_{\text{taut.}}$) is unity in MeCN. Therefore by using the data of Figs. 5b and 6, the molar absorption coefficients of the enol-form were estimated as to be 12800, 10300, and 5800 $M^{-1}\,cm^{-1}$ at 290, 350 and 530 nm, respectively. Since the potential surface in the excited singlet-state of flav-3-en-2-ol is calculated to be dissociative and no emission was observed even at 77 K, the efficiency (ϕ_{open}) of the process from the Franck–Condon state to the OR form is reasonably assumed to be unity. In this case, the formation quantum yield of the enol-form (ϕ_{enol}) and flav-3-en-2-ol (ϕ_{close}) from the OR form were estimated to be 0.3 and 0.7, respectively, by using the following equations.

$$\phi_{\text{reaction}} = \phi_{\text{open}} \times \phi_{\text{enol}} \times \phi_{\text{taut.}}.$$

$$\phi_{\text{close}} = \phi_{\text{open}} - \phi_{\text{enol}}.$$

Concluding Remarks

A photo-ring-opening reaction of flav-3-en-2-ol to produce 2-hydroxychalcone was found for the first time. This reaction proceeds via the ground-state enol-form as follows (Chart 1). This photochemical reaction is completed within 200 μs and is much faster than the thermal one. The reaction is monophotonic and the reaction quantum yield was estimated to be 0.29. In the photostationary state, the yield of *trans*-2-hydroxychalcone from flav-3-en-2-ol is 30%.

This work was partially supported by a Grant-in-Aid from the Ministry of Education, Science and Culture, and also by The Circle for the Promotion of Science and Engineering.

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