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Journal of Photochemistry and Photobiology A: Chemistry 161 (2004) 111–118

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Modulation of color changing paths for flavylium salts by solvent and concentration

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Received 21 October 2002; received in revised form 2 April 2003; accepted 20 May 2003

Abstract

The modulations of the color changing paths for flavylium salt (2-phenylbenzopyrilium, abbreviated as FV) by solvent and their concentrations have been studied by observing changes in the UV-Vis absorption spectra. The feature of the spectral changes varies with the solvent and solution FV concentration. The color of the solutions in ethanol at high concentration changed from yellow to red via green. It has been proposed that the yellow, green, and red species of FV are a monomer, a monomer with charge-transfer character, and a dimer and/or aggregate of FV, respectively. The spectral changes showed different behaviors in different solvents. In ethanol solution with a low concentration, a chalcone was generated by nucleophilic addition. The PM3 calculation revealed a new reaction path where the green FV is converted to a chalcone in propylene glycol. The color changing paths for FVs were able to be modulated in different solvents and by their concentration change. The previous proposed scheme well explained the experimental results in various solvents.

Keywords: Anthocyanin; Three types of flavylium salts; Color change of flavyliums in solution; Solvent effect; Charge transfer character; Dimerization and aggregation

1. Introduction

Anthocyanin dyes have a colorful character, which gives rise to the various colors of flowers and fruits [1,2]. The molecular stacking phenomena, such as copigmentation and self-association (aggregation) via a hydrophobic interaction, produce in the variation and stabilization of natural anthocyanins [3]. In addition, they undergo color changes caused by structural transformations upon variation in the pH and stimulation with light. A synthetic flavylium salt (2-phenylbenzopyrilium, FV), which possesses the basic structure of the natural anthocyanins, undergoes similar structural transformations and color changes. Pina and co-workers [4] and Matsushima et al. [5] have independently reported that FV and 2-hydroxychalcone have a photochromic property. The photochromic studies have focused on the photochemical relations between FV and 2-hydroxychalcone [6–12]. Recently, Pina et al. reported that the photochromism of the chalcone–flavylium plays the role of logic gate [10] using light and pH switching between the various forms of FVs [11,12]. Furthermore, Matsushima et al. found a new thermochromism and solvatochromism of flavylium ions based on the aggregation [13]. In this way, for the sake of application, the photochemistry of FVs has been studied from various viewpoints.

FVs, in particular the unsubstituted FVs, have shown, however, a very unstable character. We recently reported for the first time that the FV color in an acetonitrile–water mixed solvent changed from yellow to red via green [14]. The color change, in particular from green to red, depends on the amount of water and FV concentration in the solution. We have proposed Scheme 1 for the color changes of FV in the solutions, based on the finding of the changes in the UV-Vis absorption spectra. An outline of this work is described as follows. The absorption spectrum of FV in acetonitrile showed a peak at 394 nm and the solution color was yellow. It is reasonable to identify the yellow species using the FV monomer. The green species had a charge-transfer character from ClO_4^- to FV because it had characteristics of the relation between the f-values and peak wavenumbers of solvents having an absorption band in a long-wavelength region, and low absorption intensity of the band. The color change from green to red was affected by the concentration

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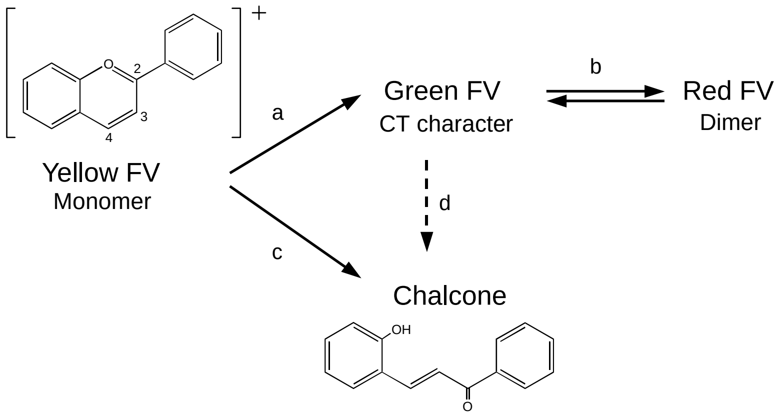
doi:10.1016/S1010-6030(03)00277-6



Scheme 1.

of FV and the water content. The red species returned to green and/or yellow species by dehydration. It has been clarified that a water molecule has a significant influence on the color change of FV from green to red. Red species would reasonably be identified with a dimer and/or an aggregate of FV.

To advance the proposed scheme reported in a previous paper, it is important to investigate the effects of solvents and solution concentration on the FV color changes. For practical application, it is necessary to obtain information about selection of the best matrix in order to control the FV color changes. In this paper, we report the modulation of the color-changing path for FVs by changing the solvent and their concentrations. The relations between the color changes and the molecular species in solution have been investigated based on the UV-Vis absorption spectral changes. It is found that the color changes of the FVs in various solvents and solution concentrations show quite different phenomena. The different behavior will be consistently explained on the basis of Scheme 1. Furthermore, the green FV will also be a precursor of a chalcone based on the changes in the absorption spectra of FV in propylene glycol, and the results from the PM3 calculation support the proposed scheme.

2. Experimental

Propylene glycol, and 2-butanone (ethyl methyl ketone; Wako Chemicals, S grade), dioxane (Dojin Chemicals, luminasol grade) were used without further purification. Ethanol (Wako Chemicals, S grade) was stored over molecular sieves 3 A and then passed through a silica gel column to minimize the water content. The FV synthesis method was reported in a previous paper [14].

The UV-Vis absorption spectra were observed using a Shimadzu UV-2500 PC recording spectrophotometer or a Hitachi U-3210 recording spectrophotometer. The cell with an 1 cm or 1 mm path length was used depending on the solution concentration. Changes in the absorption spectra were recorded as a function of time. Furthermore, influence of the molecular structure on the chemical reaction will be examined using the PM3 method (MOPAC 93 Fujitsu Labs, Ltd.).

3. Results and discussion

3.1. Color changes of FV in ethanol solution

In a previous paper, it was shown that the color changes of FV in the acetonitrile–water mixed solvents depend on the FV concentration and water amount [14]. It was concluded that the color change from green to red is due to dimerization. There was a characteristic relation between the f'-values and peak wavenumbers of the absorption band in the long-wavelength region; as the f'-value increased, the peak wavenumbers shift to red, and the band had a very low absorption intensity [14]. Therefore, the green species had a charge-transfer character from ClO_4^- to the FV skeleton. We have observed the absorption spectra of yellow FV in ethanol solution as a function of time. Fig. 1 shows the absorption spectra of yellow FV in ethanol solution (solution concentration of: (a) 5×10^{-3}, (b) 1×10^{-3}, and (c) 5×10^{-4} mol dm^{-3}) as a function of time. For the 5×10^{-3} mol dm^{-3} system (Fig. 1(a)), the spectrum showed only a peak at 394 nm and the solution color was yellow. The absorption spectrum agrees with a previous report [15]. There was no absorption band longer than 450 nm just after the preparation. Several minutes after the preparation, a broad and structureless band appeared at 600 nm, while the intensity of the peak at 400 nm decreased. The solution color changed from yellow to green. With time, a peak at 525 nm appeared with a decrease in the absorption band at 400 nm, and the solution changed from green to red. The color change in FV in the high-concentration system is comparable with that in the acetonitrile:water = 100:10, 2×10^{-2} mol dm^{-3}. The conversion yield of the yellow FV is defined by $1 - \mathrm{Abs}_{(t=\infty)}/\mathrm{Abs}_{(t=0)}$, where $\mathrm{Abs}_{(t=\infty)}$ is the absorbance at the end of the spectral measurements and $\mathrm{Abs}_{(t=0)}$ is the absorbance just after the preparation of the solutions. In

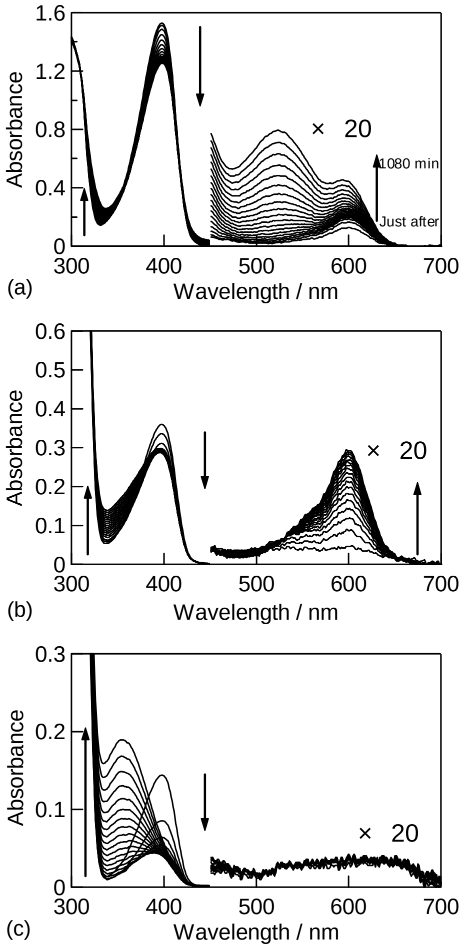


Fig. 1. Changes in the absorption spectra of yellow FV in ethanol as a function of time from just after preparation to 1080 min, solution concentrations: (a) 5.0×10^{-3}, (b) 1.0×10^{-3}, and (c) 5.0×10^{-4} mol dm^{-3}.

Table 1
The ratios of the absorbance after 18 h to that of yellow FV (398 nm) just after preparation

Concentration (mol dm^{-3})	Relative intensity ratio to the absorbance at 398 nm			
	600 nm	525 nm	350 nm	333 nm
5×10^{-4}	0.012 ± 0.002	0.008 ± 0.001	1.29	1.13
1×10^{-3}	0.042	0.008	0.45	0.43
2×10^{-3}	0.024	0.009	0.32	0.27
5×10^{-3}	0.014	0.025	0.22	0.18

the 5×10^{-3} mol dm^{-3} solution, the conversion yield was 0.18. For the 1×10^{-3} mol dm^{-3} system (Fig. 1(b)), the appearance of the band at 600 nm was similar to the high-concentration system, but the band at 525 nm was obviously not observed. The appearance of the absorption band at 525 nm is related to the solution concentrations. These results indicate that the color change in the FV solution from green (600 nm) to red species (525 nm) requires a high FV concentration. These spectral features agree with the results obtained for the acetonitrile–water mixed solvent system as previously reported [14]. Therefore, the color changes in FV from green to red in ethanol can also be ascribed in the dimerization and/or aggregation of the FV molecules. In this case, the conversion yield was 0.20. For the 5×10^{-4} mol dm^{-3} system (Fig. 1(c)), the absorption spectrum after 18 h from the preparation clearly differs from the FV's absorption spectra, but it is similar to the absorption spectrum of 2-hydroxychalcone described in a previous paper [6]. The conversion yield was 0.72. This value was greater than those described for the previous two systems. It is indicated that the conversion to 2-hydroxychalcone at the low concentration efficiently occurs compared with the change from the yellow FV to green one. An isosbestic point was not observed in the absorption spectra in ethanol. This indicates that the opening reaction is dominated by nucleophilic addition in the dilute ethanol solution, because 2-hydroxychalcone was easily formed by the nucleophilic addition of water to the skeleton base of FV via a hemiacetal in aprotic solvents. This result agrees with the results reported by Horiuchi et al. [6]. The first step is the nucleophilic addition of ethanol to FV (formation of hemiacetal) and the second step is an opening reaction of the hemiacetal (formation of 2-hydroxychalcone). The lack of an isosbestic point is due to no absorption band for the hemiacetal around the observed wavelength region and another coexisting species. The spectral change shorter than 380 nm obtained for the 5×10^{-4} mol dm^{-3} system was greater than those obtained for the other systems.

To quantitatively evaluate the color change of FVs in ethanol, we estimated the relative absorption intensity ratios of green FV (600 nm), red FV (525 nm) and chalcone (350 and 333 nm) to yellow FV (398 nm) just after preparation. The relative intensity is defined as the ratio of the absorbance after 18 h to that of yellow FV (398 nm) just after preparation. The relative ratio is summarized in Table 1. For the 600 nm (green species), the relative ratio decreases with the increasing solution concentration. For the 525 nm (red species), the relative ratio increases with the increasing solution concentration. It is indicated that the color change from green to red mainly occurs with increasing the solution concentration. These results are consistent with the acetonitrile–water mixture systems reported in a previous study about the concentration dependence [14]. On the other hand, concerning the short-wavelength region (absorption of chalcone at 350 nm), the relative ratio decreases with the increasing solution concentration. This means that the color change from yellow to chalcone occurs with the decreasing solution concentration. Scheme 1 explains the above results. When the solution concentration of FV is low, the change from green to chalcone is predominant over that from green to red. On the other hand, when the solution concentration of FV is high, the major reaction is the change from green to red. It is noted that there is no N_2 gas bubbling effect on the color change in the ethanol solutions. These observations indicate that a chemical and/or photophysical process

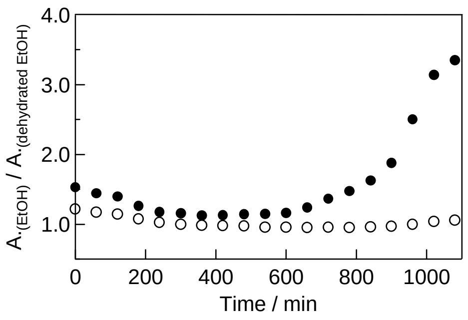


Fig. 2. Changes in the absorbance ratios of the dehydrated and non-dehydrated ethanols as a function of time from just after preparation to 1080 min. Opened circle indicates the absorbance ratio at 600 nm and the closed circle, the absorbance ratio at 525 nm.

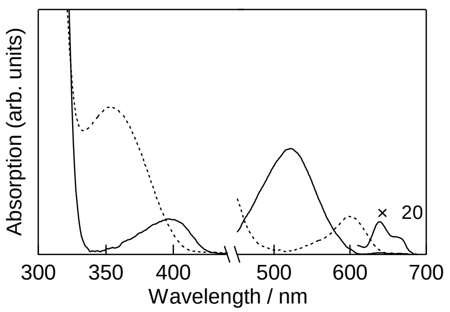


Fig. 3. Resolved absorption spectra for the changes in the absorption spectra of FV in ethanol as a function of time. Short-wavelength region (300–450 nm): solid line, the yellow species; broken line, the 2-hydroxychalcone; long-wavelength region (450–700 nm): broken line, the green species; solid line, the red species.

is responsible for the color changes, but the changes are not affected by the oxygen molecule.

As mentioned in a previous study for the color change of FV from green to red in the acetonitrile–water mixtures, water molecule plays an important role [14]. In order to eliminate the water effect on the color change in ethanol, we observed the change in the absorption spectra of FV both in dehydrated and non-dehydrated ethanol as a function of time. The ratios of the absorbance in the non-dehydrated ethanol to that in the dehydrated ethanol at 600 or 525 nm of the $2 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ FV are shown in Fig. 2 as a function of time. The absorbance ratio at 600 nm, which is shown by the open circle in Fig. 2, is almost unity for all the spectral measurements. This indicates that the color change from yellow to green is not affected by the water. The effect of water on the absorbance change agrees with the acetonitrile–water mixtures. On the other hand, for the absorbance ratio at 525 nm shown by the closed circle in Fig. 2, the ratio is found to reach 3 at 1080 min. The results mean that there is a large influence of the water content in the solutions on the color change from green to red. This behavior is also seen in the acetonitrile–water mixtures. For the $5 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ system, however, the color of the FV solution is converted from yellow to red via green. In addition to the concentration effect, the hydroxyl group of ethanol and/or a trace of the water in ethanol are responsible for the change from green to red. The water effect on the color change is significant only for the change from green to red. In the present investigation, the color change from green to red is observed only in the $5 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ ethanol and the $5 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ propylene glycol (see Section 3.2). The trace of water contained in the solvents is scarcely related to the color change in the other systems.

To clarify the relation between the absorption change and the molecular species of FV in ethanol solution, we attempted to resolve the absorption spectra of the FVs into its components (yellow, green, red FVs, and chalcone) using a simple trial and error procedure. The resolved spectra are shown in Fig. 3. There are two components in the short-wavelength region (below 450 nm). One (solid line in Fig. 3 left-hand) has a peak at 400 nm corresponding to the absorption spectrum of yellow FV; another (dotted line in Fig. 3 left-hand) has a peak around 350 nm corresponding to the absorption spectrum of the 2-hydroxychalcone [5,6]. In the long-wavelength region (above 450 nm), two other components were obtained. One (dotted line in Fig. 3 right-hand) has a peak at 600 nm corresponding to the absorption of the green species; another (solid line in Fig. 3 right-hand) has a strong absorption peak at 525 nm and a weak absorption peak at 640 nm corresponding to the red species. The red species could be explained by an exciton splitting caused by the dimer and/or an aggregation of the green species. The green species is a precursor of the red species from the results of the absorption spectra of FV (see Scheme 1). The absorption peak at the short-wavelength (higher energy) corresponds to an allowed transition and the absorption peak at the long-wavelength (lower energy) corresponds to a forbidden transition. This characteristic of the spectrum of the red species corresponds to the H-dimer (H-aggregation), which is a face-to-face aggregation of the green FV [16].

3.2. Color changes in propylene glycol

It is instructive to consider the solvent viscosity effects on the intermolecular interactions such as dimerization. In order to investigate the effect on the solvent viscosity for the color change of yellow FV in the solutions, we have observed the absorption spectra of yellow FV in propylene glycol solution as a function of time. Propylene glycol is a high-viscosity solvent ($\eta = 56.0\,\mathrm{mPa\,s}$ at 20 °C [17]) compared with the other solvents used in the present investigation (i.e. viscosity of ethanol at 20 °C: $\eta = 1.19\,\mathrm{mPa\,s}$ [18]). Fig. 4 shows the absorption spectra of yellow FV in propylene glycol as a function of time, and the solution concentrations are: (a) 5×10^{-3} and (b) $1 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$. For the high solution concentration (Fig. 4(a)), the color change behavior of FV was the same as that observed in the ethanol systems, except for a short-wavelength region (below 370 nm). With time, a new peak at around 600 nm

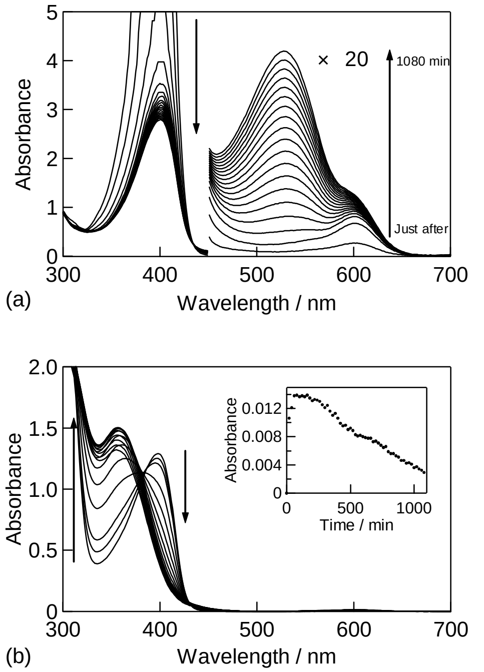


Fig. 4. Changes in the absorption spectra of yellow FV in propylene glycol as a function of time from just after preparation to 1080 min, solution concentrations: (a) 5.0×10^{-3} and (b) 1.0×10^{-3} mol dm^{-3}. Inset: time evolution of the absorbance at 600 nm.

(indicating existence of green FV) appeared, followed by a peak appearance at 525 nm (indicating existence of red FV) with decreasing absorbance at 400 nm. The conversion yield was 0.46. The color change from yellow to red via green in this system was similar to the acetonitrile–water mixed systems [14]. A remarkable absorbance change was not observed below 370 nm. It is noted that the chalcone was not formed in this system. However, for the low solution concentration (Fig. 4(b)), the color change behavior of FV was different from that of the high-concentration system. For the low-concentration system, just after the preparation of the solution, there was no absorption peak at longer than 450 nm and the solution color was yellow. With time, a new peak at around 600 nm appeared followed by an increase in the peak at 360 nm and a decrease in the peak at around 600 nm. The appearance of the 360 nm band indicates that a chalcone was produced at the low concentration. The time evolution of the absorbance at 600 nm is shown in the inset of Fig. 4(b). It seems that this change at 600 nm obeys a consecutive reaction in propylene glycol. The conversion yield was 0.59. The solution color of FV was yellow again after 18 h. This result indicates that a chalcone is also produced via the green species. A comparison between the two systems indicates that the color change behavior is sensitive to the concentration. The contrasting color change seen in propylene glycol is ascribed to the difference in viscosity. As comparison of the color change in propylene glycol with that in ethanol is summarized in Table 1, the relative ratios of the 600, 525 and 350 nm absorbances to the yellow FV's peak has also been estimated. The ratios are estimated to be 0.0006 ± 0.0005, 0.00079 ± 0.0003 and 3.12 at 600, 525 and 350 nm for the 1×10^{-3} mol dm^{-3} system, respectively, and 0.020, 0.074 and 0.034 ± 0.003 for the 5×10^{-3} mol dm^{-3} system, respectively. Except for the relative intensity of 600 nm for the 5×10^{-3} mol dm^{-3} system, the relative ratios of the propylene glycol systems differ from those in the ethanol systems at the same concentration. Though nearly the same value obtained at 600 nm for the 5×10^{-3} mol dm^{-3} system, the time evolution of the peak at 600 nm in the propylene glycol system is distinct from that in the ethanol system. It is assumed that the color change from yellow to green obeys the first-order kinetics during the initial stage of the color change. The rate constants of the absorbance change at 600 nm for the 5×10^{-3} mol dm^{-3} system are 0.040 min^{-1} in propylene glycol and 0.059 min^{-1} in ethanol. This means that the solvent viscosity has a significant effect on the color change of the FVs. In the higher concentration, therefore, the aggregation and/or an encounter with another FV is the dominant path. On the other hand, in the lower concentration, FV molecules scarcely encounter other FVs and the predominant reaction is the conversion of the green species to a chalcone. This reaction path is illustrated by the dashed arrow in Scheme 1. It is of interest to point out that the dimerization and/or the aggregation of FV would be related to the color variation in the flowers and fruits, in which copigmentation, association, and stacking of the natural anthocyanin dyes are responsible for their color changes.

McClelland and Gedge [19] and Devine and McClelland [20] reported that 2-hydoroxychalcone was easily formed by the nucleophilic addition of water to the skeleton base of FV via the hemiacetal in aprotic and dilute solutions. They showed that water addition at the position C2 of a flavylium cation reversibly caused the production of the hemiacetal in an acetonitrile–water mixture [19]. This product reversibly opens a central ring and yields a chalcone catalyzed by water, as is typical of the hemiacetal decomposition reactions. A similar addition reaction, which occurred in the acetonitrile–water or ethanol systems of the substituted FVs, was proposed to take place for FV [20]. Thus, it is interesting to refer to the relation between FV and 2-hydroxychalcone shown in Scheme 1. To estimate the nucleophilic substitution to FV and to elucidate the structural relation between FV and 2-hydroxychalcone, the PM3 calculations for a flavylium cation (charge $= +1$) depicted in Scheme 1 and a charge transfer type molecule (charge $= 0$) have been done. The calculated results show that the LUMO coefficients for C4 and C2 are -0.5082 and 0.5607 for the flavylium cation, respectively, and 0.3985 and -0.1519 for the charge transfer molecule, respectively.

The results indicate that the nucleophilic addition will occur at both the positions for the flavylium cation, while it will occur preferentially at the C4 position for the charge transfer molecule. McClelland and Gedge [19], Devine and McClelland [20] and Matsushima et al. [21] reported that the nucleophilic addition to flavylium skeletons occurs at the C4 position in protic solvents. They also showed that the substituent at the C4 position rapidly migrates to the C2 position to form a more stable hemiacetal [20]. This rearrangement corresponds to the formation of 2-hydroxychalcone in the present case. The calculated results well agree with the experimental results by McClelland and Gedge [19], Devine and McClelland [20] and Matsushima et al. [21]. However, the MO calculations about the charge transfer molecule were not performed in these reports. According to the calculation, a green FV has the charge transfer character and will also be a precursor of a chalcone. The green species has not been observed in the flavylium–chalcone interconversion system [5]. This reason may be attributed to the low absorption intensity at 600 nm, since the reported experiments were performed in very dilute solutions ($<10^{-4}$ mol dm^{-3}). In conclusion, the existence of a reaction path from a green FV to a chalcone is confirmed by the color change behavior in the propylene glycol and the PM3 calculation.

3.3. Color changes in other solvents

For further examination of the solvent effect on the color change behavior of the FVs, we have investigated the changes in absorption spectra for various solvents. Fig. 5 shows the changes in the absorption spectra of yellow FV in: (a) dioxane and (b) 2-butanone, as a function of time. These behaviors of the spectral changes differ from the protic solvents. For dioxane (Fig. 5(a)), the observed absorption spectrum just after the preparation had only one peak at around 400 nm. With time, the absorbance at 400 nm decreased, and the solution color changed from yellow to colorless. The color change to green or red was not observed. The conversion yield was 0.88. In dioxane, the color change of FV differed from that in the other polar solvents. The results indicate FV is unstable because of the polarity of dioxane. On the other hand, in case of 2-butanone (Fig. 5(b)), the spectrum just after the preparation was the same as that observed in the other solutions and the solution color was yellow. With time, the absorbance at 400 nm decreased with an increase at 338 nm and a slight increase at 500 and 580 nm. The solution color changed from yellow to almost colorless. The changes in the absorption spectra have been observed from just after the preparation to 20 min. The change in 2-butanone was faster than that in the other solutions. The conversion yield was 0.19. The absorption band in the long-wavelength region (around 580 nm) has a charge-transfer characteristic reported in the previous paper and shows weak absorbance [14]. A peak around 500 nm is not assigned to the red FV. Though the peak at 500 nm is not obvious, the two peaks at 580 and 500 nm in 2-butanone similarly increased. This behavior differs from that in the other solvents (inset in Fig. 5(b)). The changes in the absorption spectra and an isosbestic point at 374 nm agree with a previous report in the presence of acid except for the long-wavelength region [5].

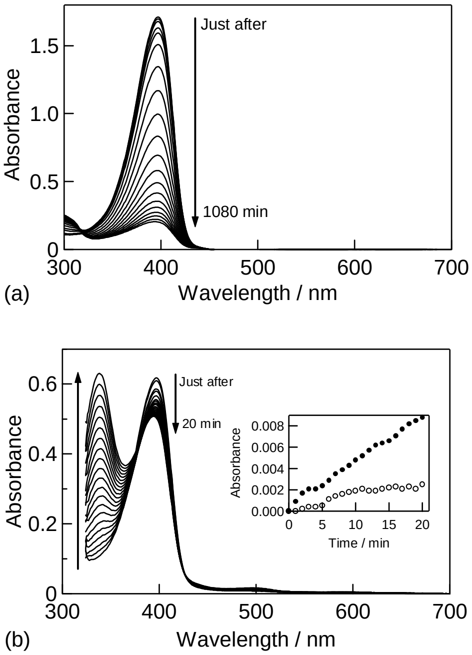


Fig. 5. Changes in the absorption spectra of yellow FV: (a) in dioxane as a function of time from just after preparation to 1080 min and (b) in 2-butanone as a function of time from just after preparation to 20 min. Inset: time evolution of the absorbance at (●) 500 and (○) 580 nm.

3.4. Classification of the color changes and molecular species in solutions based on the proposed scheme

In our study, the concentration and solvent dependences of the color changes of FV in solutions were investigated by observing the UV-Vis absorption spectra. In order to clarify the relation between the FV's color and the molecular structure in solutions, we have classified the reaction paths into a few categories based on Scheme 1. The relation among the solvent, concentration, and the reaction paths for the color changes in the FVs is summarized in Table 2.

The characteristic color changes of FVs in acetonitrile and acetonitrile–water [14] are summarized as follows. In pure acetonitrile, no spectral change in the absorption spectra occurred. This means that FV is stable in the pure acetonitrile solvent. However, when the acetonitrile–water mixture was used as the solvent and the concentration of FV was high enough, the color of the FV solution changed from yellow to red via green. The changes in the absorption spectra depend on the water contents in the solutions and concentration. Under the water-rich solvents and the high-concentration, the change rapidly occurred and generated the red FV, while under the water-poor solvents and the low-concentration solutions, the reaction slowly occurred or not occurred.

In the present study, we measured the changes in the absorption spectra in ethanol, propylene glycol, dioxane and 2-butanone as a function of time. For the solution concentration, the spectral changes in ethanol agreed with the results obtained for the acetonitrile–water mixtures. In addition to

Table 2
Relation among the solvent, concentration, and the reaction paths for the color changes in the FVs

Solvent	Concentration ($mol\,dm^{-3}$)	Reaction path[a]
Acetonitrile	Arbitrary	No reaction
Acetonitrile:H_2O (100:10)[b]	2.0×10^{-2}	a, b
	5.0×10^{-3}	a
Acetonitrile:H_2O (100:1)[b]	2.0×10^{-2}	a, b
	5.0×10^{-3}	a
Ethanol	5.0×10^{-3}	a, b, c
	1.0×10^{-3}	a, c
	5.0×10^{-4}	c
Propylene glycol	5.0×10^{-3}	a, b
	1.0×10^{-3}	a, c, d
Dioxane	1.0×10^{-4}	Degradation products
2-Butanone	1.0×10^{-3}	a, c

[a] The codes indicate the reaction paths indexed in Scheme 1. (a) From yellow FV to green FV; (b) from green FV to red FV; (c) from yellow FV to a chalcone; (d) from green FV to a chalcone.

[b] Details of the experimental results are shown in [14].

the color change in the acetonitrile–water mixtures, a chalcone was generated in the ethanol solution by the nucleophilic addition of ethanol. For propylene glycol, the spectral changes showed a different behavior depending on the solution concentration. In additions the spectral change in propylene glycol and the PM3 calculation revealed a new reaction path, which is the conversion from the green FV to a chalcone. It is difficult to explain the changes in dioxane using the proposed scheme, because the observed spectral changes did not correspond to the other systems and unknown products were generated in the solution. In 2-butanone, most of the yellow FV is converted into a chalcone, and some of species are converted into green FV. In order to quantitatively clarify the solvent effects on the color change, we have considered the relation between the color change in FV and the solvent parameter such as $E_T(30)$ and f'-value. However, an unclear correlation was observed between the solvent parameters and the color change of FV. Since the green FV and the red FV were unstable in the solution, the equilibrium constants between these species were not clear and we were not able to exactly determine these molar absorption coefficients of the color species. It is known that the flavylium–chalcone interconversion is affected by the pH of the solution. Nevertheless, in this study, we did not consider the pH effects on the color change because of focusing of the solvent and concentration effects on the color change of FVs at this stage.

Our interest focuses on the color change behavior of FV in various solvents. It may be important to mention the potential for application of the colorful FV. From the viewpoint of the stability of FVs, the best solvent is pure acetonitrile. As described in Section 1, the unsubstituted FV except in pure acetonitrile is unstable. The stability of FVs in various matrices is a significant factor for their application. When FVs are considered as a functional material, it is necessary to use stable FVs such as substituted FVs. Nevertheless, FV species with the colorful character will be a fascinating molecule with great potential for producing many applications, such as photochromism and photosynthesis. Actually the color changing paths for FVs are able to modulate the color character by solvents and their concentration.

4. Conclusion

FV in solution has a variety of color change behaviors. The color change behavior of FV depends on the solvent and concentration. FV in protic solvents shows the color changes from yellow to red via green. It can be explained that the yellow, green, and red species of FV are a monomer, a monomer with the charge-transfer character, and a dimer and/or an aggregate of FV, respectively. In addition to the proposed scheme, the existence of the reaction path from green FV to a chalcone is confirmed by the color change behavior in propylene glycol and the PM3 calculation. The color changing paths for the FVs are able to be modulated in different solvents and by their concentration changes, and the experimental results in the various solutions are explained by the proposed scheme. The studies of the solvent effects on the color change in FVs will provide information about the stability of FV dyes.

Acknowledgements

The authors thanks Prof. S. Tero-Kubota, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, for his fruitful discussion and measurements for the elementary microanalysis. A. Katsuki acknowledges the partial financial support by the Ministry of Education, Culture, Sports, Science, and Technology, Grant-in-Aid for Encouragement of Young Scientists (No. 14740396).

References

[1] R. Brouillard, in: J.B. Harborne (Ed.), The Flavonoids, Advances in Research, Chapman and Hall, London, 1988.
[2] G.A. Iacobucci, J.G. Sweeny, Tetrahedron 39 (1983) 3005.
[3] Y. Yoshida, T. Kondo, Y. Okazaki, K. Kato, Nature 373 (1995) 291 (For example).
[4] P. Figueiredo, J.C. Lima, H. Santos, M.C. Wigand, R. Brouillrad, A.L. Macanita, F. Pina, J. Am. Chem. Soc. 116 (1994) 1249.
[5] R. Matsushima, K. Miyakawa, M. Nishihata, Chem. Lett. (1998) 1915;
R. Matsushima, M. Suzuki, Bull. Chem. Soc. Jpn. 65 (1992) 39.
[6] H. Horiuchi, A. Yokawa, T. Okutsu, H. Hiratsuka, Bull. Chem. Soc. Jpn. 72 (1999) 2429.
[7] H. Horiuchi, H. Shirase, T. Okutsu, R. Matsushima, H. Hiratsuka, Chem. Lett. (2000) 96.
[8] K. Tokumura, N. Taniguchi, T. Kimura, R. Matsushima, Chem. Lett. (2001) 126.
[9] R. Matsushima, A. Ogiue, S. Fujimoto, Chem. Lett. (2000) 590.

[10] F. Pina, M.J. Melo, M. Maestri, P. Passaniti, V. Balazani, J. Am. Chem. Soc. 122 (2000) 4496.

[11] M. Maestri, F. Pina, A. Roque, P. Passaniti, J. Photochem. Photobiol. A 137 (2000) 21.

[12] F. Pina, L. Benedito, M.J. Melo, A.J. Parola, A. Bernardo, J. Chem. Soc., Faraday Trans. 92 (1996) 1693.

[13] R. Matsushima, H. Okuda, M. Aida, A. Ogiue, Bull. Chem. Soc. Jpn. 74 (2001) 2295.

[14] F. Ito, N. Tanaka, A. Katsuki, T. Fujii, J. Photochem. Photobiol. A 150 (2002) 153.

[15] G. Haucke, P. Czerney, C. Igney, Ber. Bunsenges. Phys. Chem. 93 (1989) 805.

[16] M. Kasha, H.R. Rawls, M. Ashraf El-Bayoumi, Pure Appl. Chem. 11 (1965) 371.

[17] J.A. Riddick, W.B. Bunger, Organic Solvents, Wiley, New York, 1970.

[18] K. Kisohen (Ed.), The Chemical Society of Japan, Fourth ed., Maruzen, Japan, 1993.

[19] R.A. McClelland, S. Gedge, J. Am. Chem. Soc. 102 (1980) 5838.

[20] D.B. Devine, R.A. McClelland, J. Org. Chem. 50 (1985) 5656.

[21] R. Matsushima, H. Mizuno, H. Itoh, J. Photochem. Photobiol. A 89 (1995) 251.