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Solvent Effects on the Thermal and Photochemical Reactions of 4′-Iodo-8-methoxyflavylium and Their Consequences on the Coloring Phenomena Caused by Anthocyanins in Plants

Raquel Gomes, A. Jorge Parola, João C. Lima, and Fernando Pina*[a]

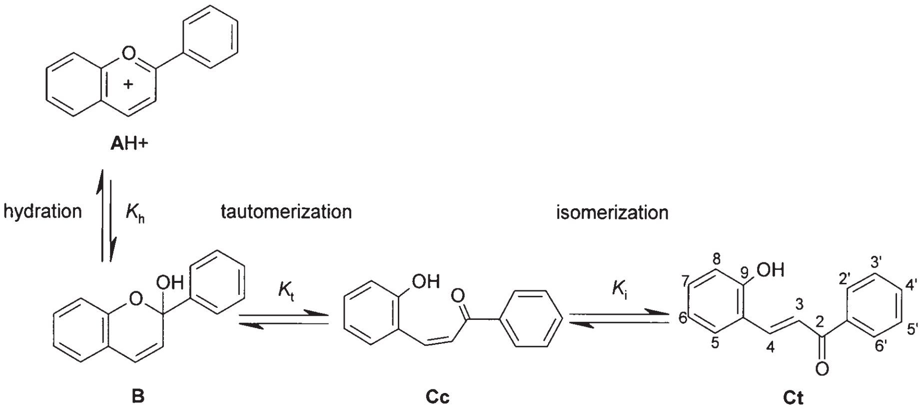
Abstract: The chemistry and photochemistry of the compound 4′-iodo-8-methoxyflavylium tetrafluoroborate was studied in solvent mixtures of water and ethanol. The *trans*-chalcone form (**Ct**) is always the most stable species at equilibrium. In particular, for the first time, **Ct** and not the flavylium cation is reported as the most stable species in mixtures containing water at pH 1.0. The rate of **Ct** formation as a function of the water content exhibits a bell-shaped dependence, showing a maximum at approximately 50 % water. These trends are explained by a slower *cis*–*trans* isomerization in ethanol relative to that in water due to the expected stabilization in polar solvents of the zwitterionic intermediate; on the other hand, the decrease in the concentration of *cis*-chalcone (**Cc**) in the pseudoequilibrium with increasing water content, gives rise to a decrease in the rate of **Ct** formation ($k_{obs}=k_{real}$[**Cc**]). The hydration reaction was found to be much more efficient when water is present in low concentrations. This result has important consequences for the interpretation of the coloring phenomena caused by anthocyanins in plants, as well as for applications of flavylium compounds in the field of optical memories.

Keywords: chalcone · flavylium salts · kinetics · photochemistry · solvent effects

Introduction

Synthetic flavylium salts are a versatile family of compounds possessing the same basic structure and the identical network of chemical reactions as anthocyanins, the ubiquitous compounds responsible for most of the red and blue colors of flowers and fruits.[1,2]

The species involved in the general network of chemical reactions undergone by a flavylium salt in moderately acidic aqueous solutions are shown in Scheme 1.[1–3] The flavylium cation itself, AH^+, is the thermodynamic stable species in water at very acidic pH values; by increasing the pH, a hydration reaction occurs leading to the hemiketal species, **B**. The rate of the hydration reaction is strongly pH dependent and typically occurs on the second or sub-second timescale. The hemiketal ring can open, leading to the *cis*-chalcone, **Cc**; this reaction also occurs on the sub-second timescale and is slightly dependent on the pH. Finally, *trans*-chal-



Scheme 1. General network of chemical reactions of a flavylium compound in acidic media.

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[a] R. Gomes, A. J. Parola, J. C. Lima, F. Pina
REQUIMTE, Departamento de Química
Faculdade de Ciências e Tecnologia
Universidade Nova de Lisboa, 2829-516 Caparica (Portugal)
Fax: (+35)121-294-8550
E-mail: fjp@dq.fct.unl.pt

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cone, **Ct**, is obtained from its *cis* isomer, on a timescale that ranges from several minutes to days.[3] If the *cis–trans* process is slow enough, a pseudoequilibrium state involving the **AH**$^+$, **B**, and **Cc** species can be defined[4] and will evolve with time to the final thermodynamic equilibrium (Figure 1).

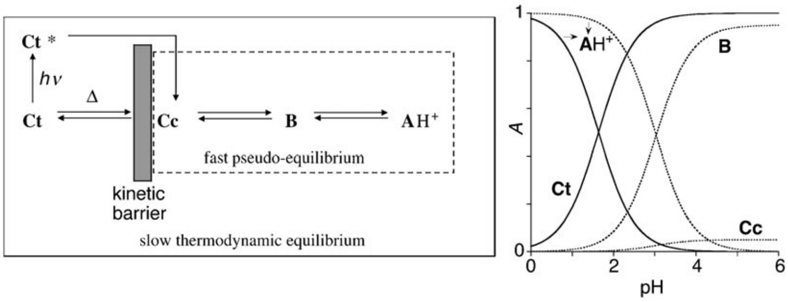


Figure 1. Left: Pseudoequilibrium involving **AH**$^+$, **B**, and **Cc** (dashed box) and final thermodynamic equilibrium containing **AH**$^+$, **B**, **Cc**, and **Ct** (solid box). Right: Mole-fraction distribution of the several species as a function of pH: upon pH jumps from a very acidic solution the system may be described as a pseudoequilibrium involving **AH**$^+$, **B**, and **Cc** (dashed curve) that evolves slowly to the final thermodynamic equilibrium (solid curves) also containing **Ct**; frequently, **B** and **Cc** are not detectable at the final equilibrium such as in the case of benzopyrylium (unsubstituted flavylium) exemplified here.[5]

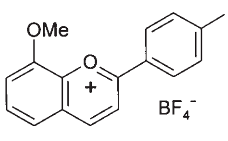
At the final thermodynamic equilibrium (Figure 1, solid curves), the isomerization reaction leads to **Ct**, at the expense of **AH**$^+$, **B**, and **Cc**. One of the interesting features of these compounds is that **AH**$^+$ and **B** can be reversibly interconverted by pH changes, whereas **Cc** and **Ct** can be interconverted by photoexcitation. The kinetic stability of the species in the pseudoequilibrium (**AH**$^+$, **B**, and **Cc**) at moderately acidic pH values ($pH > 3$) depends on the height of the kinetic barrier separating the *cis-* and *trans*-chalcone isomers and has great importance in the application of these compounds as optical memories.

The mole-fraction distribution (Figure 1, right) at the pseudo- as well as at the thermodynamic equilibrium can change significantly depending on the nature and position of the substituents in the 2-phenyl-1-benzopyrylium skeleton. Furthermore, the rates of the different kinetic processes involved are also dependent on the substitution pattern.[6] However, irrespective of all the differences brought by the nature and position of the substituents, a general pattern is maintained for this family of compounds: the flavylium is the most stable species in acidic or very acidic media, and at higher pH values, the hemiketal and the chalcones are the dominant species.

In spite of the fact that anthocyanins and synthetic flavylium salts have a common basic structure, and that both families follow the transformations shown in Scheme 1—as discovered by Dubois and Brouillard[7] for anthocyanins, and reported three years later by Gedge and McClelland[3] for synthetic flavylium salts—the synergies that can be obtained from these coincidences have not been sufficiently emphasized. In fact, synthetic flavylium salts are good and versatile model compounds for anthocyanins; for example, the fine details of the kinetics of Scheme 1 were only realized for anthocyanins upon the work of Gedge and McClelland.[3] It is also curious that synthetic flavylium salts were synthesized by Wagner and Bullow[8] before the elucidation of the anthocyanin chemical structure by Willstätter et al.[9]

Among the reactions described in Scheme 1, the hydration reaction is particularly relevant. The hydration reaction (and the coupled fast tautomerization) is important for the establishment of color in the vacuoles of plant cells, because it is the key step for color loss of these dyes at moderately acidic pH values.[10] The pH inside the vacuoles of plant cells, where anthocyanins are located in vivo, ranges roughly between 3 and 6.[11] At these pH values, anthocyanin solutions in vitro are essentially colorless and so nature must have developed strategies for stabilizing the color of anthocyanins inside the vacuoles.[12] These strategies involve the association of flavylium cations with other polyphenols (copigmentation) and complexation with metal ions, giving rise to beautifully organized supramolecular structures.[13–17] It is usually believed that copigmentation is driven by hydrophobic-stacking interactions and that the hydration is reduced mainly by exclusion of water from the vicinity of the reactive center.[16]

Despite several studies devoted to the determination of the equilibrium and kinetic constants of flavylium salts and anthocyanins in aqueous solution[2–4,16] and micelles,[18–21] there has been little reported about the effect of lower polarity media on the equilibrium and kinetic behavior of these compounds.[22–26] In this work, we describe the interesting behavior of 4′-iodo-8-methoxyflavylium tetrafluoroborate (**1**) in solvent mixtures of water and ethanol.



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Experimental Section

Synthesis: All reagents and solvents used were of analytical grade. NMR spectra were recorded on a Bruker AMX400 spectrometer, MS spectra were run on a Micromass GCT mass spectrometer, and elemental analyses were obtained by using a Thermofinnigan Flash EA 1112 analyzer. Compound **1** was prepared by condensation of 4-iodoacetophenone (0.984 g, 4 mmol) and *o*-vanillin (0.609 g, 4 mmol), on the basis of a method described by Katritzky et al.[27] The reagents were dissolved in acetic acid (5 mL) and tetrafluoroboric acid (1 mL). Acetic anhydride (ca. 5 mL) was then added, while keeping the temperature below 60 °C. The solution became yellow, then red, and was stirred overnight. The yellow solid that precipitated was filtered and washed with diethyl ether. A yield of 38.9% was obtained; 4′-iodo-8-methoxyflavylium tetrafluoroborate can be recrystallized from glacial acetic acid. ^{1}H NMR (400 MHz, D_2O/DCl, pD ≈ 1.0, 300 K, $\mathbf{AH}^+$ species): $\delta = 3.97$ (s, 3H; OCH_3), 7.53–7.73 (m, 3H; H5, H6, H7), 7.98–7.92 (m, 4H; H2′, H6′, H3′, H5′), 8.50 (d, $^3J = 8.9$ Hz, 1H; H3), 9.27 ppm (d, $J = 9.0$ Hz, 1H; H4); MS-FD: *m*/*z* (%): 364 $[M+H]^+$ (100); elemental analysis calcd for $C_{16}H_{12}BF_4IO_2$: C 42.71, H 2.64; found: C 42.54, H 2.57.

The corresponding basic form of *trans*-chalcone ($\mathbf{Ct}^-$) was prepared according to the method described by Robinson et al.[28] Potassium hydroxide (0.75 g, 13.4 mmol) dissolved in the minimal amount of water was added to a solution of *o*-vanillin (0.304 g, 2 mmol) and 4-iodoacetophenone (0.492 g, 2 mmol) in ethanol (2.5 mL). The mixture became yellow and then orange. The red precipitate that formed was filtered and washed with cold ethanol. A crude yield of 8.0% was obtained. The product was neutralized with HCl to obtain the neutral *trans*-chalcone isomer, then extracted with dichloromethane, dried over magnesium sulfate, and purified by means of flash chromatography (dichloromethane/hexane 60:40). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): $\delta = 3.93$ (s, 3H; OCH_3), 6.86–6.95 (m, 2H; H6, H5, or H7), 7.17 (dd, $^3J = 7.0$ Hz, $^4J = 2.3$ Hz, 1H; H5 or H7), 7.68 (d, $^3J = 15.7$ Hz, 1H; H3), 7.73 (d, $^3J = 8.4$ Hz, 2H; H3′, H5′), 7.85 (d, $^3J = 8.4$ Hz, 2H; H2′, H6′), 8.01 ppm (d, $^3J = 15.7$ Hz, 1H; H4).

General methods: UV/Vis absorption spectra were recorded on Shimadzu UV2501-PC or Varian-Cary 100 Bio spectrophotometers. Irradiation was carried out by using a medium-pressure mercury arc lamp (Helius), and the excitation bands were isolated by using interference filters (Oriel). The incident light intensity (2.15×10^{-7} einstein min^{-1}) was measured by using ferrioxalate actinometry.[29]

Compound **1** is only slightly soluble in water. As a routine procedure, 3–5 mg of the compound were weighed and rapidly dissolved in the ethanol/water media to obtain a final concentration in the order of 10^{-4} M. The water/ethanol media was previously prepared by adding 10 mL of a 1 M HCl solution to the required volume of water (0 to 80 mL) and ethanol was then added to give a final volume of 100 mL; the solutions prepared in this way had a water content ranging from 10 to 90% (v/v). For the 5% fraction of water, the water/ethanol medium was prepared by adding ethanol to 5 mL of a 2 M HCl solution to give a final volume of 100 mL. The experiments were performed at 40 °C. This temperature was used to keep the compound soluble and also to decrease the time consumed by each experiment. In order to prepare the 10^{-4} M solutions of the compound in a medium as close to water as possible, approximately 5 mg of the compound were dissolved in approximately 2 mL of ethanol and 0.1 M HCl was added to give a final volume of 100 mL. This solution is not stable and a precipitate was formed after approximately one hour. This period of time is, however, long enough to allow the measurement of the respective rate constants.

Semiempirical calculations: Ground and first singlet excited heats of formation and dipole moments were obtained from single-point calculations (AM1-RHF-CI, 99 single excited configurations) on geometries previously optimized (AM1-UHF) by using the Hyperchem software package.[30]

Results and Discussion

Equilibrium constants: Comparison of thermodynamic data obtained from using solvents other than water requires some care, essentially because the meaning of the equilibrium constants can vary. For instance, an acid–base reaction in water is usually expressed as an ionization constant that implicitly incorporates the concentration of water. However, in water/organic solvent mixtures, if the organic solvent is unable to accept protons (or if the proton concentrations are kept well below the basicity constant of the solvent), an acid–base equilibrium should be described by an equilibrium constant that explicitly shows the concentration of water in its mathematical expression.

The network of chemical equilibria reported in Scheme 1 can be accounted for by using Equations (1)–(3):

$$\mathbf{AH}^+ + 2\,\mathrm{H_2O} \rightleftharpoons \mathbf{B} + \mathrm{H_3O^+} \qquad K_\mathrm{h}^\mathrm{S} \tag{1}$$

$$\mathbf{B} \rightleftharpoons \mathbf{Cc} \qquad K_\mathrm{t} \tag{2}$$

$$\mathbf{Cc} \rightleftharpoons \mathbf{Ct} \qquad K_\mathrm{i} \tag{3}$$

Equations (1) to (3) can be substituted by a single acid–base equilibrium,[4] as shown by Equation (4), in which $[\mathbf{CB}] = [\mathbf{B}] + [\mathbf{Cc}] + [\mathbf{Ct}]$, and Equation (5):

$$\mathbf{AH}^+ + 2\,\mathrm{H_2O} \rightleftharpoons \mathbf{CB} + \mathrm{H_3O^+} \qquad K'^\mathrm{S}_\mathrm{a} \tag{4}$$

$$K'^\mathrm{S}_\mathrm{a} = K_\mathrm{h}^\mathrm{S} + K_\mathrm{h}^\mathrm{S} K_\mathrm{t} + K_\mathrm{h}^\mathrm{S} K_\mathrm{t} K_\mathrm{i} \tag{5}$$

In the cases where an activation barrier exists for the interconversion of *cis*- to *trans*-chalcone, a pseudoequilibrium can also be defined as shown in Equations (6) and (7):[4]

$$\mathbf{AH}^+ + 2\,\mathrm{H_2O} \rightleftharpoons (\mathbf{Cc} + \mathbf{B}) + \mathrm{H_3O^+} \qquad K^{\wedge\mathrm{S}}_\mathrm{a} \tag{6}$$

in which

$$K^{\wedge\mathrm{S}}_\mathrm{a} = K_\mathrm{h}^\mathrm{S} + K_\mathrm{h}^\mathrm{S} K_\mathrm{t} \tag{7}$$

In this set of equations [Eqs. (1), (4)–(7)], all the terms refer to the concentration of the species in the water/organic solvent mixture, and the superscript S refers to the fact that water is expressed as a reagent in a medium other that water and its concentration is not incorporated into the constant. A slight modification to the usual treatment[6,7] was introduced in order to deal with the pH-dependent hydration of the flavylium cation in water/organic solvent mixtures, because the hydration in the mixture must involve two water molecules instead of one. This is due to the fact that one molecule of water is necessary for the hydration step at position 2, while the other is needed to accept the proton and yield the neutral hemiketal form. In pure water this is not relevant, because the solvent can accept the released proton, but it becomes important when water is mixed with other solvents. On this basis, the equilibrium constants of Equations (1), (4), and (6) are given by Equations (8), (9), and (10), respectively.

$$K_\mathrm{h}^\mathrm{S} = \frac{[\mathbf{B}][\mathrm{H_3O^+}]}{[\mathbf{AH}^+][\mathrm{H_2O}]^2} \tag{8}$$

$$K'^\mathrm{S}_\mathrm{a} = \frac{[\mathbf{CB}][\mathrm{H_3O^+}]}{[\mathbf{AH}^+][\mathrm{H_2O}]^2} \tag{9}$$

$$K^{\wedge\mathrm{S}}_\mathrm{a} = \frac{[\mathbf{Cc} + \mathbf{B}][\mathrm{H_3O}]}{[\mathbf{AH}^+][\mathrm{H_2O}]^2} \tag{10}$$

Thermal equilibrium and rates: The spectral modifications that occur immediately after dissolution of **1** are exemplified in Figure 2 for an ethanol/water 40:60 solvent mixture as well as for absolute ethanol.

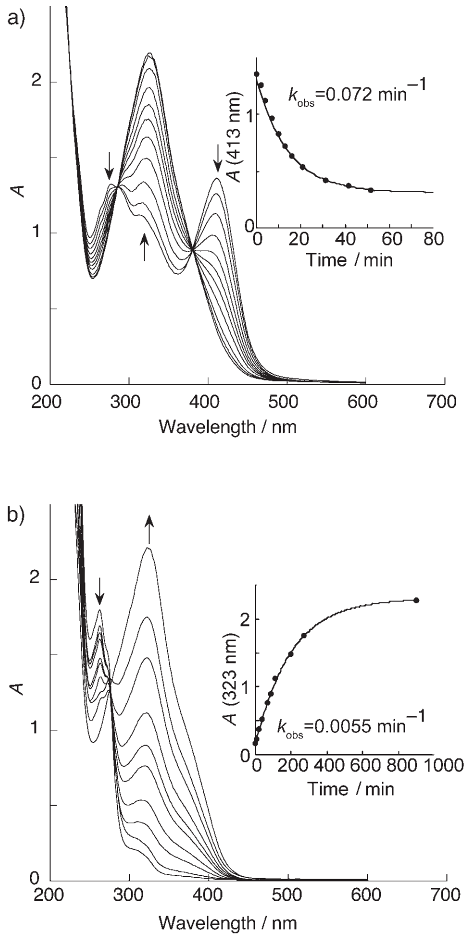

Figure 2. Spectral modifications observed immediately after dissolution of **1** at 40 °C in a) a solvent mixture of ethanol/water (40:60) and b) absolute ethanol.

For solvent mixtures with more than 10 % water, the absorption spectrum obtained immediately after the dissolution of compound **1** (Figure 2a) presents an absorption band centered at approximately $\lambda = 410$ nm, characteristic of the flavylium cation. The flavylium cation is in pseudoequilibrium with **B** and **Cc** until the final equilibrium is attained. Inspection of this figure indicates that the same final product, with an absorption maximum at $\lambda = 323$ nm, is formed in the two cases. This product, whose formation follows first-order kinetics (insets in Figure 2) independent of the water content, should be *trans*-chalcone.

In order to prove this hypothesis, compound **1** was dissolved in a basic aqueous solution, leading in a few minutes to the formation of a stable orange-brown solution, whose spectrum is identified as **Ct**$^-$ in Figure 3. Acidification of this solution led to a spectrum identical to the final spectra reported in Figure 2. The *trans*-chalcone of 4′-iodo-8-methoxyflavylium, synthesized according to a method described by Robinson et al.,[28] and characterized by the large coupling constant between the protons in the 3- and 4-positions ($^3J_{3,4} = 15.7$ Hz),[31,32] exhibits again the same absorption spectrum. This allowed us to assign **Ct** as the only species present in the final equilibrium of 4′-iodo-8-methoxyflavylium, at 40 °C and pH ≈ 1, independent of the water content of the solution. The absorption spectra of the species described through this work are shown in Figure 3. Elaboration of the data of Figure 2 and of similar experiments using other solvent proportions allowed us to obtain values for $K_a^{\wedge S}$ (Table 1).

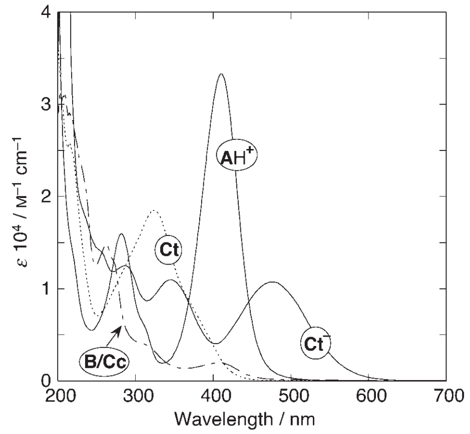

Figure 3. Absorption spectra of the several species arising from the dissolution of **1**: **AH**$^+$ in 0.1 M HCl, **B/Cc** in ethanol/water 80:20 (v/v), **Ct**$^-$ in aqueous solution at pH 11, and **Ct** in aqueous solution at pH 1.0.

Table 1. Molar fraction of the species at the pseudoequilibrium and values of $K_a^{\wedge S}$ at 40 °C in several water/ethanol solvent mixtures.

Water % (v/v)	x_{AH^+} (pseudoequilibrium)	x_{B+Cc} (pseudoequilibrium)	$K_a^{\wedge S}$ [M^{-1}]
0	0	1	–
5	0	1	–
10	0.066	0.934	0.046
20	0.07	0.93	0.011
35	0.11	0.89	2.4×10^{-3}
50	0.24	0.76	4.1×10^{-4}
60	0.52	0.48	8.3×10^{-5}
80	1	0	–
90	1	0	–

It is an interesting feature of the system that the lower the percentage of water in the solvent, the larger the amount of **B** and **Cc** in the pseudoequilibrium at the expense of **AH**$^+$. In absolute ethanol, the pseudoequilibrium shows no trace of the flavylium cation. This observation conflicts with the common belief, in anthocyanin and in flavylium salts chemistry, that a decrease in water concentration would lead to a stabilization of the flavylium cation as a result of a decrease in the extent of the hydration reaction.[16] Taking into account that disappearance of **AH**$^+$ should result from the attack of water at position 2 of the flavylium cation, the contradiction is evident, because we found that less water leads to a more efficient disappearance of AH^+. However, this contradiction is easily accounted for by the fact that the flavylium cation is a charged species, and thus strongly destabilized in media with low dielectric constants, thus facilitating the hydration step to yield the neutral hemiketal species, even when water is present in only small amounts. Another interpretation would be that the presence of aggregates in water would protect the flavylium cation from hydration, and an increasing concentration of ethanol would destroy the aggregates thus enhancing hydration. This last interpretation was carefully checked and discarded (see the Supporting Information).

The rate constants for *trans*-chalcone formation, measured as a function of the water percentage in the solvent mixture, are shown in Figure 4. Inspection of this figure shows a bell-shaped curve: the rate constant increases with decreasing water content up to ≈50% water and then decreases thereafter until pure ethanol is reached. The increase of the rate constant with decreasing water content would be expected on the basis of the previous arguments if the hydration reaction were the rate-limiting step for *trans*-chalcone formation. However, in the majority of flavylium compounds studied to date,[6,7] it is the *cis–trans* isomerization that controls the overall kinetics, with the pH-dependent hydration reaction usually being faster than the isomerization. Moreover, the experimental data reported above shows that the pseudoequilibrium involving species AH^+, **B**, and **Cc** is reached immediately upon dissolution, leading (at the pseudoequilibrium) to decreasing concentrations of AH^+ with decreasing water content. In spite of the fact that the *cis–trans* isomerization is undoubtedly the slowest process, it is still the extent of hydration (and the flavylium cation stability) that is indirectly controlling the overall rate. In other words, the flavylium cation equilibrates with **B** and **Cc** (pseudoequilibrium) rapidly, and its mole fraction at the pseudoequilibrium decreases with increasing ethanol content of the mixture (Table 1). Taking into account that the isomerization reaction is proportional to the concentration of **Cc** at the pseudoequilibrium (rate $\propto k_i[\mathbf{Cc}]$), decreasing the water content leads to a lower flavylium cation concentration (as observed experimentally) and as a consequence to an increase in **Cc** concentration. Consequently, whatever the rate-controlling step, it remains clearly shown that less water leads to more efficient hydration.

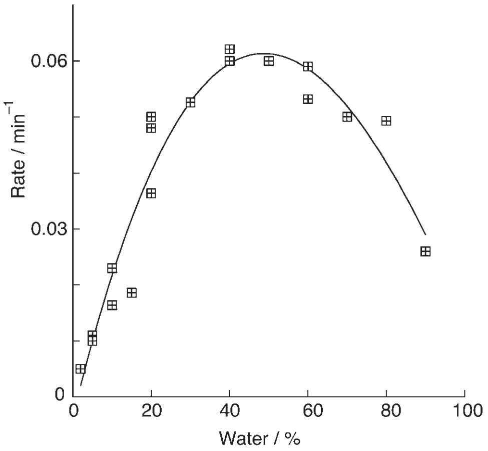

Figure 4. Observed rate constants of **Ct** as a function of the percentage of water in the solvent mixture.

In Figure 4, a further decrease in the water concentration leads to a decrease of the observed rate constant. Below a 50% water concentration, the hydration reaction cannot again be the rate-determining step, because immediately after dissolution there is no flavylium cation, that is, the hydration is instantaneous on the experiment timescale. In addition, the ring-opening/closure (**Cc**–**B** equilibrium) usually occurs on the sub-second timescale in water and there is no evidence for this to be different in these solvent mixtures. This trend of the observed rate can only be explained if the *cis–trans* isomerization is slower in ethanol than in water. This could be due to a higher dipole moment of *trans*-chalcone, associated with a stronger stabilization of this form relative to the *cis* isomer, upon increasing the water content of the mixture. However, because the thermal equilibrium leads to quantitative formation of the *trans* isomer, for the whole range of water concentrations studied, there is no additional evidence to support this preferential stabilization of the *trans* form by the increase in the polarity of the medium. On the other hand, taking into account that the twisted intermediary state for a *cis–trans* isomerization involving an asymmetrically substituted olefin should be of zwitterionic type,[33,34] the respective process should be much more favored in polar solvents like water, as has been found in the case of asymmetrically substituted azobenzenes.[34]

Photochemistry: Figure 5 shows the photochemical behavior of compound **1** at room temperature in ethanol/water 80:20 (v/v) and in absolute ethanol. Irradiation of *trans*-chalcone gives rise to the formation of **Cc** in fast equilibrium with **B**. In both cases, a photostationary state is reached, due to the thermal reaction as well as to the photoreactivity of the **Cc** species. The photochemical conversion of **Ct** into **Cc** is larger in absolute ethanol, and the respective quantum yield is also higher (see Figure 5 and Table 2).

Table 2 shows that the quantum yield of **Ct** photoisomerization decreases with increasing water content. The percentage of *trans* isomer at the photostationary state follows the inverse trend. These results clearly point to a polarity effect on the stabilization of the *trans*-chalcone form relative to the *cis*-chalcone form. With the increase in polarity, the initial state (*trans*-chalcone) is stabilized relative to the final state (*cis*-chalcone) and the *trans–cis* photoconversion is consequently reduced. This interpretation is in agreement with the predictions of molecular orbital calculations (Figure 6) for the relative energies and dipole moments of the *cis*- and *trans*-chalcones in the first singlet excited state.

However, the predictions for the ground state contradict the observed increase of the *cis–trans* thermal-isomerization

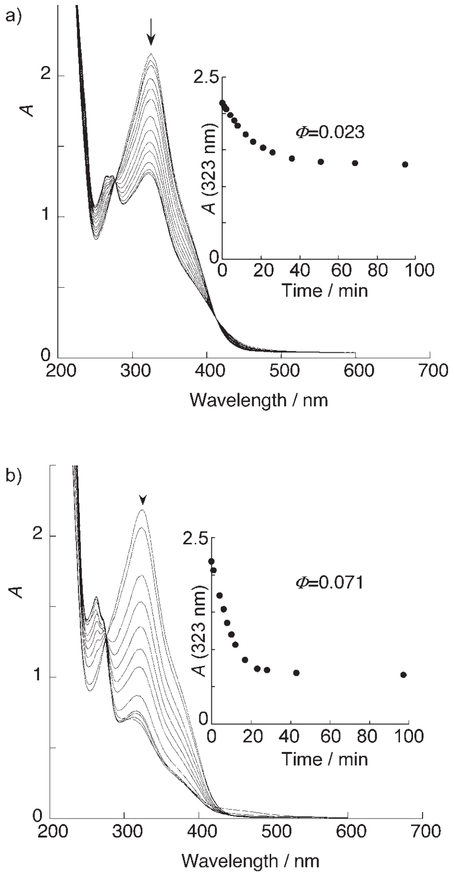

Figure 5. Spectral modifications upon irradiation at $\lambda = 313$ nm of **1** at room temperature in a) ethanol/water 80:20 (v/v) and b) in absolute ethanol.

Table 2. Quantum yield for the *trans–cis* photoisomerization (ϕ_{tc}) and the percentage of *trans*-chalcone in the final photostationary state (PSS).

Water %	% *trans*-chalcone in PSS	ϕ_{tc}
0	0.30	0.071
5	0.46	0.050
10	0.52	0.032
20	0.61	0.023
35	0.68	0.010
50	0.72	0.008
60	0.66	0.006

rate with the increase in polarity. Because in the ground state, the *cis* isomer is predicted to have a higher energy and dipole moment, it is expected that an increase in polarity would stabilize the *cis* isomer and decrease the rate of *cis–trans* interconversion, the opposite of the observed behavior. A way to reconcile the contradictory results can be envisaged if the polarity effect in the ground state is strictly kinetic, that is, if the main effect on the rate constants originates from the stabilization of the intermediary twisted state. The twisted intermediary state is known to have a zwitterionic nature in the case of isomerizations of asymmetrically substituted double bonds containing conjugated electron acceptor and donor groups that can participate in a push–pull mechanism, like in the case of push–pull azobenzenes.[34] Such is also the case of the 9-hydroxychalcones resulting from the ring opening of flavylium salts, which always contain an electron-withdrawing carbonyl group at position 2 and an electron-donating hydroxyl group in position 9 (see Scheme 1), conjugated through the phenyl ring and the isomerizing double bond. The zwitterionic intermediary state is expected to be strongly stabilized with the increase of the water concentration of the mixture.

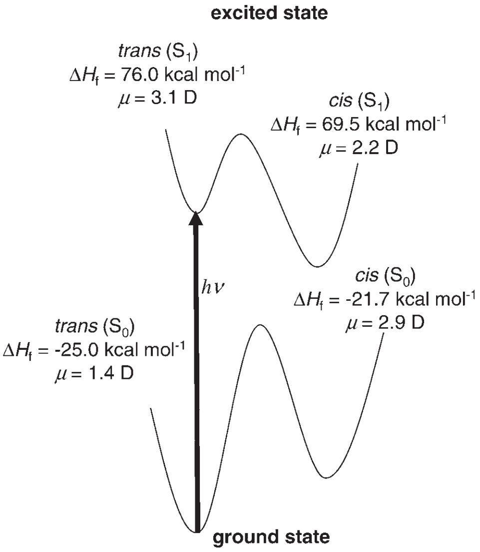

Figure 6. Calculated heats of formation (ΔH_f) and dipole moments (μ) of the ground and first singlet excited states of the *cis* and *trans* isomers of 9-hydroxy-4′-iodo-8-methoxychalcone.

In summary, the results from the photoisomerization study point to the existence of a small barrier in the first excited state and consequent control of the extent of the photoisomerization by the relative energy of the two isomers. In contrast, there is a large barrier in the ground state, and the isomerization rate would be controlled by the energy of the zwitterionic intermediate.

Conclusion

One consequence of this work is to point out that less water in the system, that is, inclusion of flavylium salts in a more or less organic environment, leads to a more efficient hydration step. This has important implications on the models developed so far to explain the copigmentation mechanism in plants. In fact, because lowering of the dielectric constant of the medium surrounding the flavylium cation results in a loss of color (owing to speeding up the hydration reaction, probably due to the loss in stability of the charged species relative to the neutral species), a competitive stabilizing effect must be present in the copigmentation interaction to explain the observed color stability in nature. Recently, the presence of charge-transfer interactions between organic copigments and flavylium salts has been proposed to participate in the mechanism in copigmentation,[35] and it would be worth looking into the effect of different media on these interactions.

On the other hand, less water in the system clearly increases the barrier for *trans–cis* isomerization of the chalcones in the ground state, a result expected from the predictable effect of the solvent polarity on the stability of the zwitterionic twisted intermediary state; an identical effect was observed for the *cis–trans* isomerization of push–pull azobenzenes.[34] In the case of the 4′-iodo-8-methoxyflavylium salt (**1**) studied here, it seems clear from the solvent effect on the *trans–cis* photoisomerization quantum yield that the excited-state potential-energy curve connecting the two isomers is significantly affected. If equilibrium between the two isomer populations is attained in the excited state, it is reasonable to assume that the ratio of the isomer concentrations in the excited state ([*cis**]/[*trans**]) will be related to their relative stability. In this case, the solvent effect will be greater in the isomer with the higher dipole moment, usually the *trans* isomer, due to its more extended conformation. The increase in solvent polarity will tend to lower the *trans–cis* photoisomerization quantum yield because it will shift the excited-state equilibrium towards the more stable form, namely, *trans*-chalcone.

A final remark relates to future applications of these compounds supported in different media (e.g., polymer hydrogels)[36] in which water concentration can be controlled. Less water in the system clearly increases the barrier for *trans–cis* isomerization of the chalcones in the ground state whereas it destabilizes the *trans* form in the excited state. Both of these changes are desirable improvements in the properties of these compounds with respect to applications in the field of photochemical memories, because it increases both the ground-state *trans*-chalcone metastability at acidic pH values and the photochemical quantum yield for the *trans–cis* photoisomerization.

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