Dyes and Pigments 80 (2009) 149–155

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Flash photolysis and stopped flow studies of the 2′-methoxyflavylium network in aq. acidic and alkaline solution

Vesselin Petrov, Raquel Gomes, A. Jorge Parola, Fernando Pina*

REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

ARTICLE INFO

Article history:
Received 21 May 2008
Received in revised form 9 June 2008
Accepted 10 June 2008
Available online 25 June 2008

Keywords:
Flavylium
2-Phenyl-1-benzopyrylium
Flash photolysis
Stopped flow
Photochemistry
Chalcones

ABSTRACT

The rate and equilibrium constants of the network of chemical species involving the dye 2′-methoxyflavylium tetrafluoroborate were characterized using stopped flow and flash photolysis in both acidic and alkaline aqueous solution. The *trans*-chalcone is the thermodynamic stable species in acidic solutions $2 < pH < 7$; irradiation of trans-chalcone at low pH leads to the corresponding coloured flavylium cation. The system reverts to its initial state in a few hours, in the dark. The kinetics of the various steps in the system were determined; flash photolysis revealed that the rate determining process of flavylium formation is the ring closure to give the corresponding hemiketal. In alkaline medium the ionized *trans*-chalcone is the stable form and clear evidence for the existence of a hemiketal species was obtained. A write-read-erase cycle can be performed with this compound.

1. 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 network of chemical reactions of flavylium compounds is well established and with the exception of those bearing a methyl substitution in position 4 (where hydration and subsequent reactions are not observed in water) [3] follow a common pattern reported in Scheme 1 [4].

The initial interest on the synthetic flavylium chemistry was due to the fact that these compounds follow the same general network of chemical reactions of anthocyanins, the ubiquitous colorants of plants and fruits, Scheme 1 [4a–c]. It is worth of note the seminal work of McClelland and co-workers on the hydration of flavylium ions. They were able to clarify by means of stopped flow experiments, many kinetic details of Scheme 1, contributing in this way to the understanding of the anthocyanins chemistry. More recently, the multistate nature of these networks exhibiting different chemical structures that can be reversibly inter-converted by external stimuli, as pH variations or light, has been an additional incentive to the study of these molecules [4d]. Systems capable of write-read-erase, or even mimicking the elementary behaviour of neurons based on synthetic flavylium compounds were recently reported [5–7].

One fascinating aspect of flavylium compounds is the possibility of tuning not only the pH dependent mole fraction distribution of the several forms (states), but also the rates of inter-conversion between the states, simply by modifying the nature and position of the substituents [8]. In particular the existence or not of a *cis*–*trans* isomerization thermal barrier is a crucial factor to define the behaviour of the multistate system and its potential domain of applications [8c]. As an example, while optical memories should be based on the existence of the barrier, in ophthalmic lens the lack of barrier is welcome [9].

It is a matter of fact that most of the research carried out to get more insight on the kinetics and the thermodynamics of Scheme 1 was made in acidic medium. This is probably a consequence of the analogy with anthocyanins, which are not stable in basic medium. Moreover the photochromic properties of the network occur essentially in acidic medium. However, the exploitation of the network in basic medium is also useful to potential applications and may contribute to the overall comprehension of the system.

The photochromic properties of the network arise from the photoisomerisation of the *trans*-chalcone to the *cis*-chalcone followed by a fast ring closure to give the species **B2** and a subsequent dehydration to produce the coloured flavylium cation. The photochemical products are not thermodynamically stable at the pH values where the photochemical reaction takes place (where the

---

* Corresponding author. Tel.: +351 212948355; fax: +351 212948550.
E-mail address: fjp@dq.fct.unl.pt (F. Pina).

0143-7208/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2008.06.005

trans-chalcone is the dominant species) and the system reverts back to the initial state with a rate that depends on the magnitude of the *cis–trans* isomerization thermal barrier.

Less attention has been paid to the role played by the hemiketal species **B4**. This species can appear upon a pH jump from acidic solutions ($\mathbf{AH}^+$) to less acidic or basic pH values, but usually its concentration is very small and can be neglected [4b,c]. In this work we report on the network properties of the new compound 2′-methoxyflavylium, extend the chemical treatment of the system to the basic region and give an experimental evidence for the existence of the hemiketal **B4** in basic medium. The possibility of using 2′-methoxyflavylium to carry out a write-read-erase cycle is also discussed.

2. Experimental

2.1. General for synthesis

All reagents and solvents used were of analytical grade. ^{1}H NMR spectra were run on a Bruker AMX 400 instrument operating at 400.13 MHz. Field Desorption mass spectra were run on a Micromass GCT apparatus, and elemental analysis was obtained on a Thermofinnigan Flash EA 1112 Series instrument.

2.1.1. Synthesis of 2′-methoxy-2-phenyl-1-benzopyrylium tetrafluoroborate

2′-hydroxy-2-phenyl-1-benzopyrylium tetrafluoroborate was prepared according to a procedure adapted from Katritzky [10]. Salicylaldehyde (1 ml, 9.5 mmol) and 2′-methoxyacetophenone (1.5 ml, 10.8 mmol) were dissolved in 10 ml of acetic acid and 2 ml of HBF_4. Ten milliliters of acetic anhydride were then added dropwise and the temperature of the reaction mixture rose. The reaction mixture was stirred overnight. By the following day, ethyl acetate was added and a brownish solid precipitated. The solid was filtered off, carefully washed with diethyl ether and dried (1.92 g, 5.9 mmol); yield: 62.0%. ^{1}H NMR (D_2O/DCl, p*D* ≈ 1.0, 400.13 MHz) δ (ppm): 9.55 (1H, d, $^3J = 9.1$ Hz), 9.08 (1H, d, $^3J = 9.1$ Hz), 8.54 (1H, dd, $^3J = 8.5$ Hz, $^4J = 1.2$ Hz), 8.42–8.34 (3H, m), 8.02 (1H, t, $^3J = 7.4$ Hz), 7.91 (1H, td, $^3J = 7.9$ Hz, $^4J = 1.3$ Hz), 7.44 (1H, d, $^3J = 8.6$ Hz), 7.34 (1H, t, $^3J = 7.6$ Hz), 4.17 (3H, s, OCH_3). MS-FD: *m*/*z* (%): 237.100 $[M]^+$ (100). EA calculated for $C_{16}H_{13}BF_4O_2\cdot1.7H_2O$: C 54.18, H 4.66; found: C 54.21, H 5.37.

2.2. General for measurements

Solutions were prepared using Millipore water. The pH of solutions was adjusted by addition of HCl, NaOH or universal buffer of Theorell and Stenhagen [11] and was measured in a Radiometer Copenhagen PHM240 pH/ion meter. UV–vis absorption spectra were recorded in a Varian-Cary 100 Bio spectrophotometer or in a Shimadzu VC2501-PC.

2.3. Irradiation experiments

Quantum yields were determined by irradiation at 436 nm, using a medium pressure mercury arc lamp and the excitation bands were isolated with interference filters (Oriel). Actinometry was made using the ferrioxalate system [12]. The flash photolysis and stopped flow experiments were performed as previously described [13]. Nanosecond laser flash photolysis experiments were run on a LKS.60 Nanosecond Laser Photolysis Spectrometer from Applied Photophysics.

3. Results and discussion

The thermodynamic equilibrium and the pseudo-equilibrium when ***B4*** *is formed*: The network of chemical reactions reported in Scheme 1 can be summarized by the following set of equations.

In acidic media,

$$\mathbf{AH}^+ + 2H_2O \leftrightharpoons \mathbf{B2} + H_3O^+ \qquad K_{h2} \tag{1}$$

$$\mathbf{AH}^+ + 2H_2O \leftrightharpoons \mathbf{B4} + H_3O^+ \qquad K_{h4} \tag{2}$$

$$\mathbf{B2} \leftrightharpoons \mathbf{Cc} \qquad K_t \tag{3}$$

$$\mathbf{Cc} \leftrightharpoons \mathbf{Ct} \qquad K_i \tag{4}$$

Eqs. (1)–(4) can be substituted by a single acid-base equilibrium [4], as shown by Eq. (5):

$$\mathbf{AH}^+ + 2H_2O \leftrightharpoons \mathbf{CB} + H_3O^+ \qquad K'_a \tag{5}$$

where $[\mathbf{CB}] = [\mathbf{B2}] + [\mathbf{B4}] + [\mathbf{Cc}] + [\mathbf{Ct}]$ and $K'_a = K_{h4} + K_{h2} + K_{h2}K_t + K_{h2}K_tK_i$.

Extension to basic media can be made through Eqs. (6) and (7).

$$\mathbf{Cc} + H_2O \leftrightharpoons \mathbf{Cc}^- + H_3O^+ \qquad K_{Cc} \tag{6}$$

$$\mathbf{Ct} + H_2O \leftrightharpoons \mathbf{Ct}^- + H_3O^+ \qquad K_{Ct} \tag{7}$$

Eqs. (6) and (7) can also be substituted by a single acid-base equilibrium as shown in Eq. (8)

$$\mathbf{Ct} + \mathbf{Cc} + H_2O \leftrightharpoons \mathbf{CB}^- + H_3O^+ \qquad K''_a \tag{8}$$

where $[\mathbf{CB}^-] = [\mathbf{Cc}^-] + [\mathbf{Ct}^-]$ and $K''_a = K_{h2}K_t(K_{\mathbf{Cc}} + K_{\mathbf{Ct}}K_i)/K'_a$

The formation of the ionized species displaces the equilibrium towards $\mathbf{Cc}^-$ and $\mathbf{Ct}^-$ at sufficiently basic medium and the system can be viewed as a diprotic acid whose ionizations constants are K'_a and K''_a, Eqs. (5) and (8).

The mole fraction of each species can be easily calculated according to Eq. (9)

$$\frac{[\mathbf{AH}^+]}{C_0} = \frac{[\mathbf{H}^+]^2}{D};\quad \frac{[B_2]}{C_0} = \frac{K_{h2}[\mathbf{H}^+]}{D};\quad \frac{[B_4]}{C_0} = \frac{K_{h4}[\mathbf{H}^+]}{D};\quad \frac{\mathbf{Cc}}{C_0} = \frac{K_{h2}K_t[\mathbf{H}^+]}{D}$$

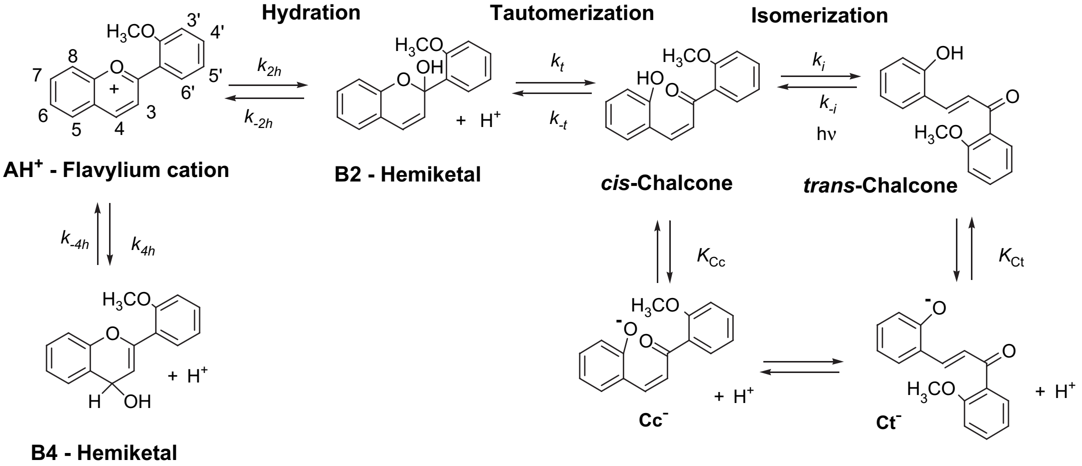
$$\frac{[\mathbf{Ct}]}{C_0} = \frac{K_{h2}K_tK_i[\mathbf{H}^+]}{D};\quad \frac{[\mathbf{Cc}^-]}{C_0} = \frac{K_{\mathbf{Cc}}K_{h2}K_t}{D};\quad \frac{[\mathbf{Ct}^-]}{C_0} = \frac{K_{\mathbf{Ct}}K_{h2}K_tK_i}{D}$$

$$\begin{aligned} D &= [\mathbf{H}^+]^2 + K'_a[\mathbf{H}^+] + K_{\mathbf{Cc}}K_{h2}K_t + K_{\mathbf{Ct}}K_{h2}K_tK_i \\ &= [\mathbf{H}^+]^2 + K'_a[\mathbf{H}^+] + K'_aK''_a \end{aligned} \tag{9}$$

In this approach $\mathbf{B2}^-$ and $\mathbf{B4}^-$ have not been considered, because their formation is expected to occur at extremely basic pH values and in the case of $\mathbf{B2}^-$ it would immediately give rise to $\mathbf{Cc}^-$ by a simple electronic rearrangement, and by consequence their concentrations are negligible.

The spectral variations of the equilibrated solutions of 2′-methoxyflavylium are reported in Fig. 1. For all the pH range three absorption spectra are observed which can easily be attributed to the flavylium cation ($\mathbf{AH}^+$), *trans*-chalcone (**Ct**) and ionized *trans*-chalcone ($\mathbf{Ct}^-$), $pK'_a = 1.60 \pm 0.05$ and $pK''_a = 8.60 \pm 0.05$.

In the cases, as in the present compound, where the *trans–cis* isomerization is slower than all the other processes, a



Scheme 1.

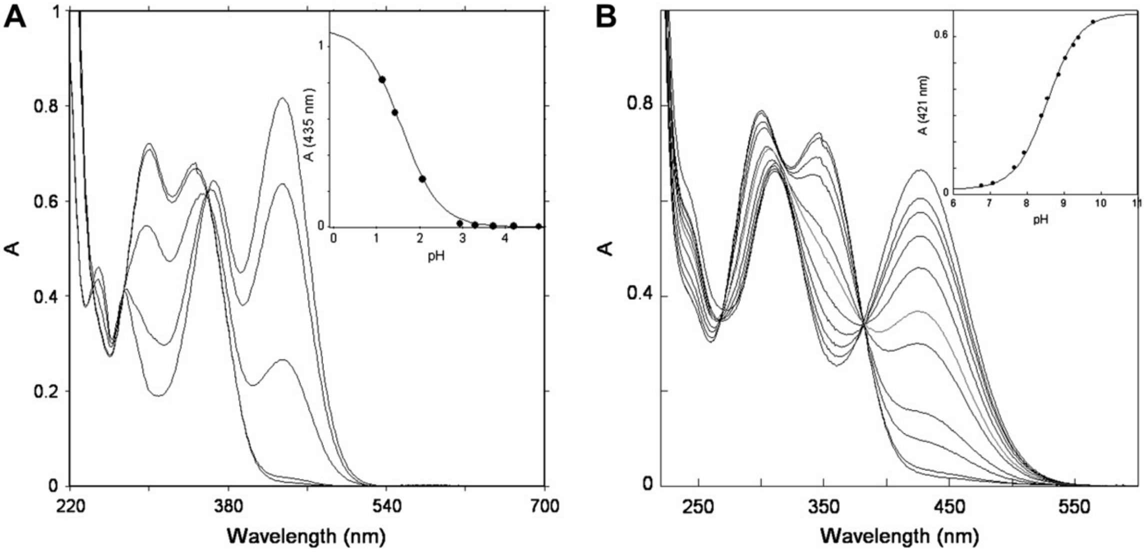


Fig. 1. Absorption spectra of dark equilibrated solutions (1 day) of the compound 2′-methoxyflavylium 4×10^{-5} M as a function of pH: (A) acidic p$K'_a = 1.60$, (B) basic media inflection point at p$K''_a = 8.60$.

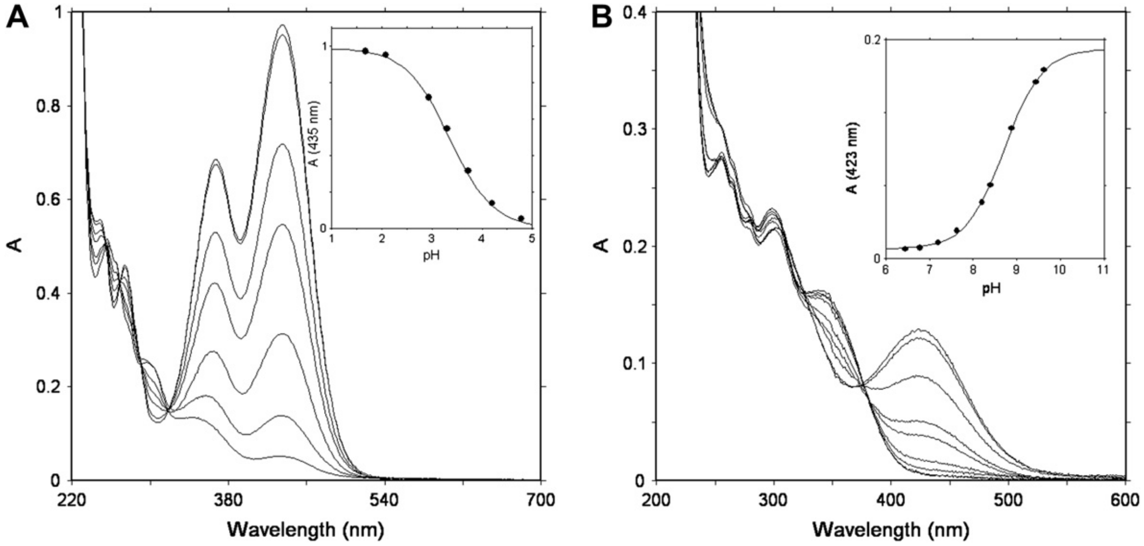


Fig. 2. Spectral variations after ca. 1 min upon a pH jump from the stock solutions of the compound 2′-methoxyflavylium 4×10^{-5} M at pH = 1 to the desired pH values: (A) acidic (p$K^{\wedge}_a = 3.35$); (B) basic (p$K_{obs} = 8.70$).

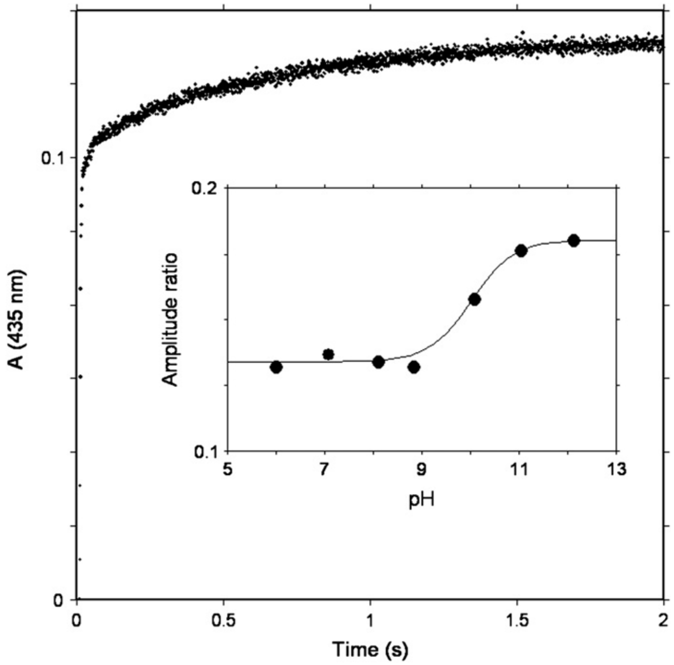


Fig. 3. Stopped flow trace of the reverse pH jump for a pseudo-equilibrated solution at pH = 12.2 to pH = 1.0 (ratio [$\mathbf{Cc}^-$]/[**B4**] = 0.18); inset: pH dependence of the ratio of the amplitudes of both exponentials (slower/faster) when pH jumps are carried out from the basic region to pH = 1.0.

Table 1
Thermodynamic constants for the compound 2′-methoxyflavylium in aqueous solution, at 295 K

K_{h2} (M)	K_t	K_i	$K_{\mathbf{Cc}}$ (M)	$K_{\mathbf{Ct}}$ (M)
$(4.00 \pm 0.08) \times 10^{-4}$	0.12 ± 0.02	$(5 \pm 1) \times 10^2$	$(1.9 \pm 0.2) \times 10^{-8}$	$(2.5 \pm 0.3) \times 10^{-9}$

pseudo-equilibrium state can be defined considering all the equations of the set with exclusion of those involving the formation of the *trans*-chalcone. In the cases where the formation of **B4** is significant the treatment of the system should take into account that this species is a kinetic product that was proved to disappear through $\mathbf{AH}^+$ [4c]. According to the results previously obtained by McClelland for the analogous compound 4′-methoxyflavylium, if a pH jump from 1 ($\mathbf{AH}^+$) to moderately acidic pH values is carried out, water attacks position 2 of the flavylium cation leading to **B2** in competition with the attack to position 4 forming **B4**. On the other hand **B2** equilibrates with **Cc** in a sub-second time scale and by consequence the pseudo-equilibrium is established between the three species **B4**, **B2** and **Cc**. Usually the concentration of **B4** is very small in moderately acidic medium. In the case of the compound 4′-methoxyflavylium it is 0.3% [4c] and in the present compound we were not able to detect its formation unless as a kinetic product at basic pH values, see below [4c].

The pseudo-equilibrium in acidic medium can be accounted for by Eqs. (10) and (11).

$$\mathbf{AH}^+ + 2H_2O \leftrightharpoons \mathbf{CB}^{\wedge} + H_3O^+ \qquad K^{\wedge}_a = K_{h2} + K_{h4} + K_{h2}K_t \tag{10}$$

where

$$[\mathbf{CB}^{\wedge}] = [\mathbf{B2}] + [\mathbf{B4}] + [\mathbf{Cc}] \tag{11}$$

In basic medium the pseudo-equilibrium is established in a different way. In first place the formation of the species results from the attack of the hydroxyl ion to positions 2 and 4 rather than water and by consequence the proportions of **B2** and **B4** formed immediately after the pH jump are different. Secondly **B4** tends to live more time than in acidic medium because the rate of flavylium formation necessary to consume **B4** is slower due to the low proton concentration. In other words **B4** is formed and kinetically trapped at basic pH values. Conversely all **B2** and **Cc** formed are transformed into $\mathbf{Cc}^-$ if the pH is sufficiently high. The experience indicates that **B4** cannot be neglected in these cases, unless for the flavylium compounds bearing hydroxyl substituents

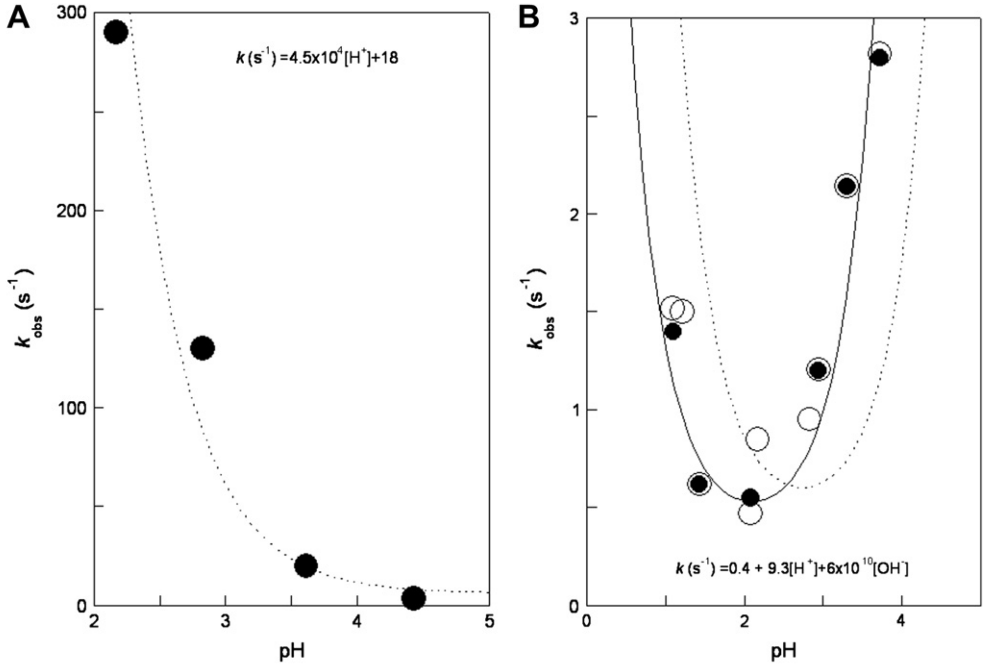


Fig. 4. (A) Rate constants of the faster process of the reversed pH jumps monitored by stopped flow; (B) the same as in (A) for the slower process (○); rate of the ring closure k_{-t} occurring upon flash photolysis of the pseudo-equilibrium state of the compound 2′-methoxyflavylium (●); for comparison purposes the rate constants for identical process in the compound 4′-methoxyflavylium are represented (traced line).

Table 2
Kinetic constants for the compound 2′-methoxyflavylium in aqueous solution, at 295 K

k_{h2} (s^{-1})	k_{-h2} ($M^{-1}\,s^{-1}$)	k_t (s^{-1})	k_{-t} (s^{-1})	k_i (s^{-1})	k_{-i} (s^{-1})	k'_{h2}/k'_{h4}
18 ± 9	$(4.5 \pm 0.9) \times 10^4$	0.05 ± 0.01	0.40 ± 0.06	$(1.3 \pm 0.1) \times 10^{-4}$	$(2.5 \pm 0.7) \times 10^{-7}$	0.18 ± 0.02

because in these cases formation of the quinoidal base is more efficient than hydroxylation to give **B4** (or **B2**). In summary there is a change of the regime of the pseudo-equilibrium in basic media according to Eqs. (12) to (14) and Eq. (3).

$$\mathbf{AH}^+ + OH^- \rightarrow \mathbf{B4} \qquad k'_{h4} \tag{12}$$

$$\mathbf{AH}^+ + OH^- \rightarrow \mathbf{B2} \qquad k'_{h2} \tag{13}$$

$$\mathbf{Cc} + H_2O \leftrightharpoons \mathbf{Cc}^- + H_3O^+ \qquad K_{Cc} \tag{14}$$

After the pH jump to basic medium both hemiketal species are formed with a ratio $[\mathbf{B2}]/[\mathbf{B4}] = k'_{h2}/k'_{h4}$, followed by the equilibrium between **B2** and **Cc**. For more basic pH values **Cc** deprotonates to $\mathbf{Cc}^-$, and a pseudo-equilibrium occurs between $\mathbf{Cc}^-$ and **B4**, see below.

The spectral variations concerning the pseudo-equilibrium are reported in Fig. 2.

As in the case of the thermodynamic equilibrium, the pseudo-equilibrium can be accounted for by the existence of a diprotic species with $\mathrm{p}K^{\wedge}{}_{a} = 3.35 \pm 0.05$ and an inflection point at pH = 8.70 ± 0.05. In the first equilibrium, Fig. 2A, the flavylium cation pseudo-equilibrates with a mixture of the hemiketals (basically **B2**) and *cis*-chalcone, as reported in previous work for the analogue 4′-methoxyflavylium [4c], while in the second pseudo-equilibrium **B4** is maintained as a kinetic product and thus the inflection point can be assigned to the formation of $\mathbf{Cc}^-$ from **Cc** in fast equilibrium with **B2**, the respective $\mathrm{p}K_{obs}$ being given by Eq. (15).

$$\frac{K_{\mathbf{Cc}}K_t}{1 + K_t} = 10^{-8.70} \tag{15}$$

3.1. *Reverse pH jumps*

Reverse pH jumps consist on acidifying a pseudo-equilibrated solution at a given pH and monitoring subsequent spectral changes by stopped flow [3,9]. This procedure has been used in acidic media, but can also be extended to the pseudo-equilibrium in basic solutions. In order to perform this kind of experiments pseudo-equilibrated solutions were prepared from the stock solution at pH = 1.0 by addition of base. These solutions should be used immediately before formation of significant amounts of **Ct** or $\mathbf{Ct}^-$. When the initial pH of the stopped flow experiment is neutral or moderately acidic the equilibrium constant obtained from the ratio of the amplitudes of the two processes is $K_t = 0.12 \pm 0.02$ [14]. The biexponential characteristics of the traces at low pH values are explained by a faster reaction where $\mathbf{AH}^+$ appears from **B2** dehydration, followed by formation of more $\mathbf{AH}^+$ at the expenses of **Cc** disappearance (through **B2**).

When the same back pH jump is carried out from sufficiently basic solutions, the biexponential nature of the traces is explained as follows: (i) a faster process due to the formation of $\mathbf{AH}^+$ from **B4** followed by (ii) a slower process resulting from the formation of more flavylium cation from $\mathbf{Cc}^-$ in a sequence of events: protonation to give **Cc** (very fast), ring closure to form **B2** and finally dehydration to give $\mathbf{AH}^+$. The ratio of the amplitudes is given by Eq. (16), because all $\mathbf{Cc}^-$ at this pseudo-equilibrium results from **B2** formed in competition with **B4**, during the initial pH jump prior to the back one followed by stopped flow, see Fig. 3.

$$\frac{[\mathbf{Cc}^-]}{[\mathbf{B4}]} = \frac{k'_{h2}}{k'_{h4}} = 0.18 \pm 0.02 \tag{16}$$

The inset of Fig. 3 is compatible with the existence of a first regime where the ratio of the amplitude of the two exponentials is K_t and a second regime where the ratio of the amplitudes is given by Eq. (16). The change of regime starts to occur at pH = 9, when the hydroxyl concentration becomes high enough to favour Eqs. (12) and (13) over Eqs. (1) and (2).

The data from Figs. 1–3 allows to obtain all the equilibrium constants of the network, see Table 1. The value of $K_{\mathbf{Cc}}$ was obtained from Eq. (15), using the value of K_t obtained from reverse pH jumps.

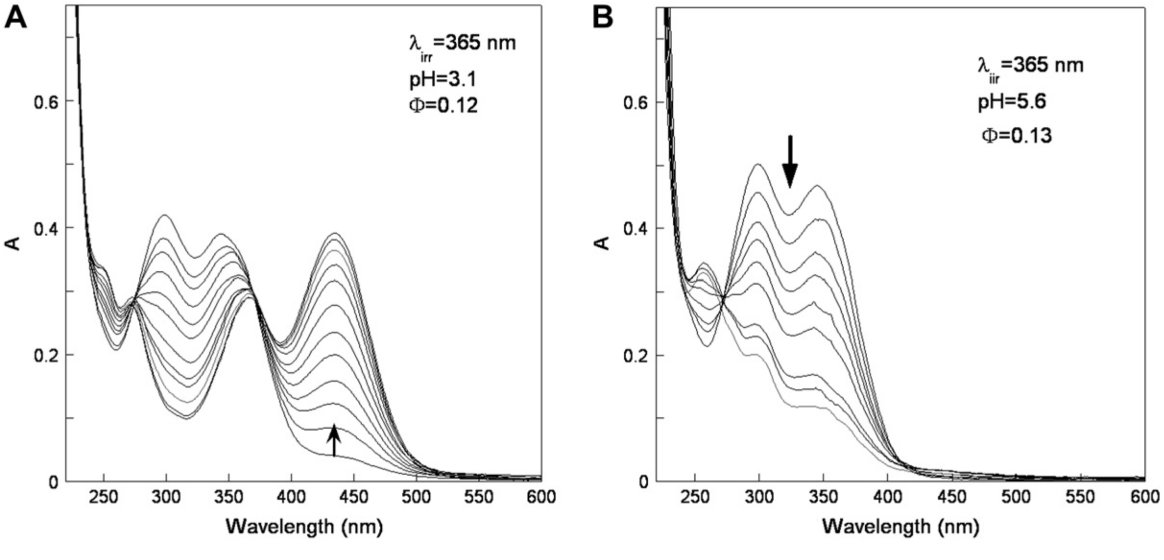


Fig. 5. Spectral variations of the compound 2′-methoxyflavylium 3.3×10^{-5} M, upon irradiation at 365 nm at pH = 3.1 (A) and at pH 5.6 (B).

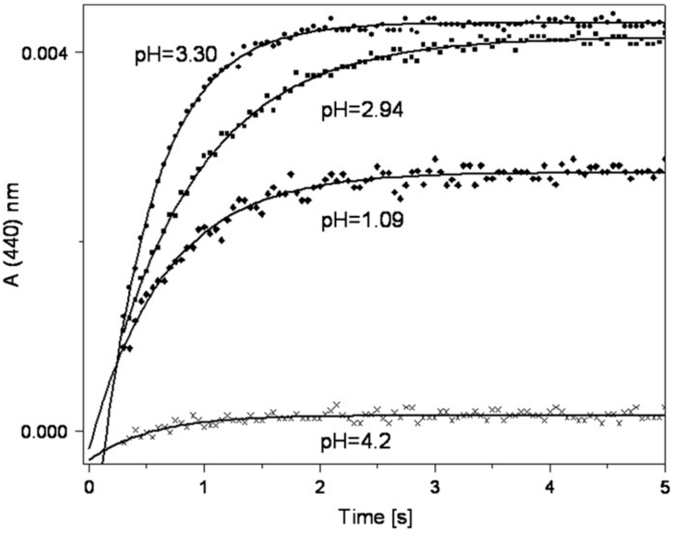
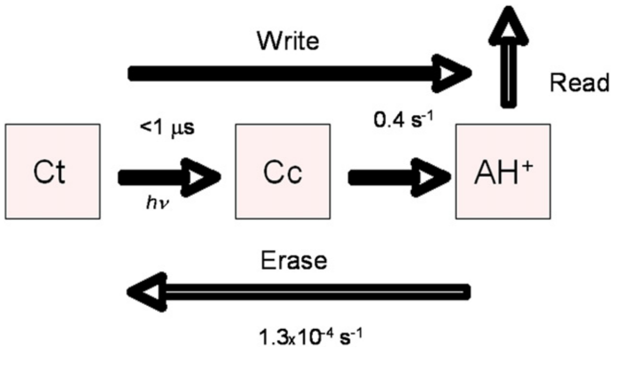


Fig. 6. Transient absorption traces obtained by flash photolysis of the compound 2′-methoxyflavylium at 440 nm.

The value of $K_{\mathbf{Ct}}$ was obtained from Eq. (8). The values of $pK_{\mathbf{Cc}}$ and $pK_{\mathbf{Ct}}$ are close to pK_{obs} (Fig. 2B) and pK''_a, respectively, showing that at basic pH values, **Cc**/**Cc**$^-$ predominates in the pseudo-equilibrium and **Ct**/**Ct**$^-$ in the final equilibrium.

3.2. Kinetics

The stopped flow experiments reported in Fig. 3 were extended to different pH values and the rates of the fast and slow processes represented as a function of pH as shown in Fig. 4. The rate of the faster process, Fig. 4A, corresponding to the formation of **AH**$^+$ from **B2**, can be fitted with the following expression $(4.5\times10^4[\mathbf{H}^+]+18)\ s^{-1}$, allowing to obtain $k_{-h2}=(4.5\pm0.9)\times10^4\ M^{-1}\ s^{-1}$ and $k_{h2}=18\pm9\ s^{-1}$ from which $K_{h2}=4.0\times10^{-4}$ M, in accordance with the value reported in Table 1. The slower process can be attributed to the tautomerization and exhibits a dependence on pH, Fig. 4B, according to $(0.4+9.3[\mathbf{H}^+]+6\times10^{10}[OH^-])\ s^{-1}$. A similar dependence was previously reported by McClelland [4c,10] in the case of the parent compound 4′-methoxyflavylium, traced line of Fig. 4B, and was interpreted as a catalytic effect of both proton and hydroxyl ions on the kinetics of ring opening and closure. Due to the lack of accumulation of **B2**, the rate of the reaction, k_t[**B2**], is negligible in this process and its kinetics should be controlled by the ring closure, allowing to calculate $k_{-t}=0.40\pm0.06\ s^{-1}$; from the equilibrium constant $K_t=0.12\pm0.02$, the rate constant $k_t=0.05\pm0.01\ s^{-1}$ can then be obtained.



Scheme 2.

The rate constants of the slower process leading to the formation of *trans*-chalcone and ionized *trans*-chalcone according to the pH follow a first order kinetic process, the respective rate constants being reported in Table 2.

3.3. Photochemistry

The photochemical products from irradiation of the compound 2′-methoxyflavylium are dependent on the pH of the solutions, see Fig. 5. At pH = 3.1, irradiation of the **Ct** form leads to the flavylium cation while at pH = 5.8 a mixture of **B** and **Cc** is formed. The quantum yield for the photochemical reaction is $\Phi=0.12$ at pH = 3.1, and $\Phi=0.13$ at pH = 5.6. These values are the same within experimental error (estimated 10%), a result that is expected because the photochemical step is the same in both cases and the system possesses a *cis*–*trans* isomerization thermal barrier.

In order to get more insight, flash photolysis measurements were carried out, Fig. 6. The traces obtained at the absorption wavelength of **Ct** (not shown) show a bleaching immediately after the flash with no further modifications. This result is compatible with the existence of the thermal *cis*–*trans* isomerization barrier. At the absorption wavelength of the flavylium cation (440 nm), an increase in absorption follows the flash, according to a first order kinetic process, the respective rate constants showing a pH dependence which is coincident, within experimental error, with the ring closure constants taken from the reversed pH jump experiments, see Fig. 4B. This last result is an evidence for the fact that the rate determining process of the photochemical appearance of the flavylium cation is the ring closure to give the hemiketal **B2**.

The present system can be used as a temporary memory (Scheme 2). When **Ct** is irradiated, it leads to **Cc** in a very fast process, not observed with our nanosecond flash photolysis apparatus. The ring closure is the rate determining step to the formation of flavylium cation as reported in Fig. 4, with rate constant $0.40\ s^{-1}$. At pH = 3.1, the major species of the pseudo-equilibrium is **AH**$^+$ and a good signal (appearance of a visible colour) can be observed. The system reverts back to the initial **Ct** species with a rate constant $k_i=1.3\times10^{-4}\ s^{-1}$; the value of $k_{-i}=2.5\times10^{-7}\ s^{-1}$ can be calculated through the value of K_i, Table 2. Obviously, the kinetic constants imply that the time needed to operate the cycle is too long for practical applications, unless high temperatures are used that could lead to degradation. The parameters that control the kinetic barrier for *trans*–*cis* isomerization in 2′-hydroxychalcones have been discussed [8c], as well as those required for optimal optical memory performance [4d]. In particular, the barrier could be lowered by introducing electron donor groups, e.g., in position 7 or 5.

4. Conclusions

The synthesis and complete characterization of the new 2′-methoxyflavylium tetrafluoroborate, whose structure and chemical behaviour mimic those of natural anthocyanins, were described in this work. Using flash photolysis, stopped flow and absorption spectroscopy the rates and equilibrium constants of the various steps were determined. The ring closure of **Cc** to give hemiketal **B2** was found out to be the rate determining step of the flavylium formation. Clear evidence for the existence of the hemiketal **B4** species was obtained.

Acknowledgements

Portuguese FCT-MCTES and FEDER under project No. POCI/QUI/57735/2004, grants SFRH/BPD/18214/2004 (VP) and SFRH/BD/27282/2006 (RG) are acknowledged for financial support.

References

[1] Swain T. In: Harborne JB, Mabry TJ, Mabry H, editors. The flavonoids. London: Chapman and Hall; 1975. p. 1129.

[2] Markakis P, editor. Anthocyanins as food colors. New York: Academic Press; 1982.

[3] Pina F, Melo MJ, Santos H, Lima JC, Abreu I, Ballardini R, et al. New J Chem 1998;10:1093–8.

[4] (a) McClelland RA, McGall GH. J Org Chem 1982;47:3730–6;
(b) Brouillard JR, Dubois JE. J Am Chem Soc 1977;99:1359–64;
(c) McClelland RA, Gedge S. J Am Chem Soc 1980;102:5838–48;
(d) Pina F, Maestri M, Balzani V. Handbook of photochemistry and photobiology, vol. 3. ASP; 2003. p. 411–49, [chapter 9].

[5] Pina F, Melo MJ, Maestri M, Passaniti P, Balzani V. J Am Chem Soc 2000;122: 4496–8.

[6] Pina F, Lima JC, Parola AJ, Afonso CAM. Angew Chem Int Ed 2004;43:1525–7.

[7] Giestas L, Folgosa F, Lima JC, Parola AJ, Pina F. Eur J Org Chem 2005:4187.

[8] (a) Jimenez A, Pinheiro C, Parola AJ, Maestri M, Pina F. Photochem Photobiol Sci 2007;6:372–80;
(b) Melo MJ, Sousa M, Parola AJ, de Melo JS, Catarino F, Marçalo J, et al. Chem Eur J 2007;13:1417–22;
(c) Roque A, Lima JC, Parola AJ, Pina F. Photochem Photobiol Sci 2007;6: 381–5.

[9] (a) Bouas-Laurent H, Dürr H, editors. Photochromism: molecules and systems. Amsterdam: Elsevier; 1990;
(b) Crano JC, Guglielmetti R, editors. Organic photochromic and thermochromic compounds. New York: Plenum; 1999;
(c) Irie M. Photochromism: memories and switches. Chem Rev 2000;100: 1683–4.

[10] Katritzky AR, Czerney P, Levell JR, Du WH. Eur J Org Chem 1998:2623–9.

[11] Küster FW, Thiel A. Tabelle per le Analisi Chimiche e Chmico-Fisiche. 12th ed. Milano: Hoepli; 1982. p. 157–60. This universal buffer is prepared in the following way: dissolve 2.3 cm^3 of phosphoric acid (85% (w/w)), 7.00 g of monohydrated citric acid and 3.54 g of boric acid in some water, add 343 ml of 1 M NaOH and dilute with water until 1 dm^3.

[12] Hatchard CG, Parker CA. Proc R Soc A 1956;235:518–36.

[13] Maestri M, Ballardini R, Pina F, Melo MJ. J Chem Educ 1997;74:1314–6.

[14] It is assumed that the concentration of B4 in acidic medium can be neglected.