Unusual Reverse Photochromic Behavior of Indolinobenzospiropyran 6-Carboxylates in Aqueous Binary Solvents

Sam-Rok Keum,* Se-Jung Roh, Sang-Eun Kim, Sung-Hoon Lee, Chul-Hee Cho, Sung-Hoon Kim,† and Kwang-Nak Koh‡

*Department of New Material Chemistry, Korea University, Jochiwon 339-700, Korea. *E-mail: keum@korea.ac.kr*
†Department of Dyeing and Finishing, Kyungpook National University, Daegu 702-701, Korea
‡Department of Pharmacy, Pusan National University, Busan 609-735, Korea
Received September 14, 2005

Key Words : Thermo- and photochromic molecules, Aqueous binary solvent mixtures, Normal and reverse photochromism

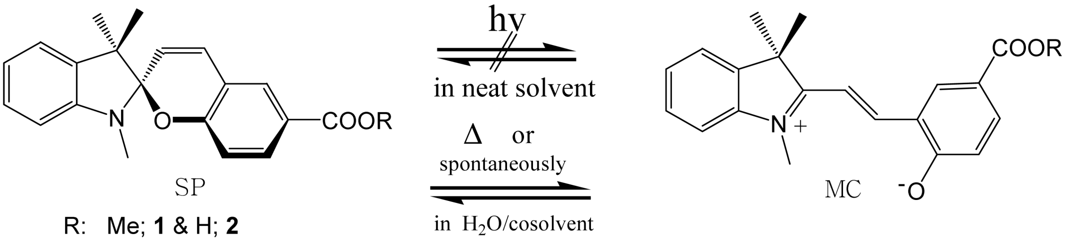
Thermo- and photochromic indolinobenzospiropyran dyes recently have become important in connection with the rapid development of information recording systems, such as high-density optical data storage, optical switching, displays and non-linear optics.[1] These molecules are known to be in equilibrium with their metastable colored forms. The absorption of ultraviolet light shifts the equilibrium towards the merocyanine colored form (MC), while the reverse process shifting them toward the colorless form (SP) is induced by visible light, heat, or can occur spontaneously (*normal photochromism*).[2,3]

The color of the MC form as well as the rate of rearrangement back to the SP form are both dependent on the polarity of the solvent. The stabilization of the MC form in polar solvents leads to it having a larger energy of activation and a slower MC↔SP transition as compared to that in non-polar solvents. Occasionally, the merocyanine form is further stabilized by factors such as hydrogen bonding,[4] combination with a crown ether or cyclodextrin[5] and complexation with a metal.[6] Thus, the initially colorless solutions of spiropyrans become deeply colored upon the spontaneous formation of the merocyanine (*reverse photochromism*).[7]

Continuing our previous works on the solvatokinetic and solvatochromic behaviors of spiropyran derivatives in various neat organic solvents, we examined the photochromic behaviors of spiropyran derivatives in binary aqueous solvent media. Since merocyanine dyes in solution usually exist in dipolar ionic forms, their preferential solvation[8] in binary mixtures was expected to affect their photophysical behavior. Although many studies have been conducted on the photochromic behaviors of spiropyran derivatives in various neat organic solvents,[2,3] to the best of our knowledge, no papers have previously been published on the photochromic behaviors of spiropyrans in aqueous binary solvent systems. Herein, we describe the unusual photochromic behaviors of indolinobenzospiropyran 6-carboxylates **1-2** in aqueous binary solvent media, as depicted in Scheme 1.

The electronic absorption spectra of the spiropyran carboxylates **1-2** showed no absorbance in the visible region on irradiation in neat solvents, whereas, they unexpectedly showed chromotropism in aqueous binary solvent mixtures such as water/methanol, water/DMSO, water/acetonitrile, etc. The UV-Vis. spectral changes for the SP → MC conversion of SP-**1** in water-methanol solvent mixtures (50/50 v/v %) are shown in Figure 1, as a representative example. Initially, the water-methanol solution of SP-**1** has an absorption band only in the 300 nm region. However, the colorless solution becomes spontaneously deeply colored upon the ring-opening reaction of SP-**1** to MC-**1**. MC-**1** has a strong absorption at 522 nm in 50/50% aqueous methanol. Reproducible results for the ring-opening reaction of spiropyran to merocyanine were obtained through the development of a protocol that maximized the formation of the colored form, as indicated by the solid line in Figure 1. The colored merocyanine solutions revert to the colorless spiropyran state upon their exposure to visible light of the appropriate wavelength.

In addition to its major absorption at 500-550 nm, SP-**2** has an extra absorption band in the 400-450 nm region in aqueous binary solvent mixtures. This extra absorption band is probably due to the proton transferred MC form (MCH^+-COO^-). The proton might migrate from the 6-substituent COOH to the oxygen atom of the phenoxide anion in aqueous solvents, since the COOH group is more acidic than the OH group of the phenyl ring. This was confirmed by the UV-Vis spectral behavior of spiropyran both in HCl/aqueous



Scheme 1

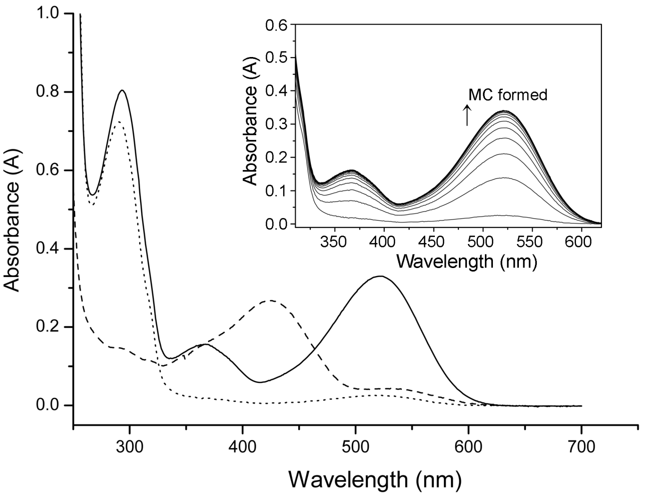


Figure 1. UV-Vis spectra for SP-**1** and SP-**2** in 50% aqueous methanol in the equilibrium state at ambient temperature. The solid (SP-**1**) and dashed (SP-**2**) lines refer to the merocyanine formed when the ring-opening reaction is completed, and the dotted line refers to the colorless SP form induced by visible light. The inset shows the UV-Vis spectral scans for the ring opening reaction of SP-**1** in binary aqueous solvents (MeOH/H_2O = 50/50 v/v %, every 5 min).

methanol and TEA/aqueous methanol, as reported earlier.[9]

A particular case[10] of the reverse photochromic behavior in neat organic solvents was reported in the case of spiropyrans bearing substituents such as the –COOH or –OH groups at the C8 position.

The rate of the spontaneous ring-opening reaction to the colored MC ring (SP → MC) was measured in binary aqueous solvents for **1**-**2**. The coloration rates of the colorless SP form obeyed good reversible first-order kinetics for all substrates examined in this work. The rate constants were independent of the initial spiropyran concentration in the range of 10^{-4} M to 5×10^{-5} M. The observed spectrophotometric data and derived first-order rate constants for the SP↔MC conversion in the binary aqueous solvents are listed in Table 1. The kinetics of the dark conversion of SP to MC show the strong influence of the medium.

Table 1. The absorption maxima and observed rate constants for the ring-opening reaction of SP-carboxylates in aqueous solvent mixtures

Compd	Solvent Ratio	Water / MeOH		Water / CH_3CN		Water / DMSO	
		λ_{max} nm	k_{obs} [b]	λ_{max} nm	k_{obs} [b]	λ_{max} nm	k_{obs} [b]
SP-**1**	30:70	528	13.1	540	9.09	548	–
	50:50	521	6.71	530	3.95	529	16.7
	60:40	517	4.37	526	3.11	524	7.06
	70:30	513	1.41	521	1.25	518	5.75
SP-**2** [a]	50:50	425 (542)	2.27	425 (541)	5.36	422 (552)	0.92
	60:40	422 (536)	2.19	423 (544)	3.12	421 (543)	1.14
	70:30	422 (533)	3.94	419 (537)	2.84	418 (536)	1.57
	80:20	418 (528)	1.48	420 (533)	2.34	417 (533)	2.25

[a]Values in parenthesis denote absorbance maxima in basic media. [b]Values of data (s^{-1}) × 10^{-1}

The formation of the colored MC form of SP-**1** & **2** in the thermal equilibrium state was varyng the water content of the aqueous methanol solvents.

The concentrations of the MC species in the thermal equilibrium state increased as the water content of the binary solvent mixtures increased. Both the stability of the MC form and the transition energy E_T were found to increase with increasing water content of the binary solvent mixtures. This may imply that the MC form has lower polarity in the excited states than it does in the ground state, and that the same effects contribute to the solvation of both of these states. In addition, the larger amounts of MC species were formed as the polarity of the binary solvent mixtures increased and the slower reactions of SP molecules were detected. This may implicate that this reversible reaction involves an unknown intermediate (X).[11]

Now, the question arises as to what factors are responsible for the difference between the neat and aqueous mixed solvents. It is inescapable to assume that hydrogen bonding by water plays an important role in the kinetic behavior of SP carboxylates in aqueous solvent mixtures. Solvation by water molecules via hydrogen bonding could be responsible for the stabilization of the MC species, along with its concomitant effect on the kinetics of thermal coloration.

We believe that this is the first report on the reverse photochromism of spiropyrans in aqueous binary solvent systems.

Acknowledgements. This work was supported in part by grant No. (R01-2003-000-10248-0) from the Basic Research Program of the Korea Science & Engineering Foundation (S.R.K.) and in part by the Brain Korea 21 project.

References

1. (a) Crano, J, C.; Guglielmetti, R. J. *Organic Photochromic and Thermochromic Compounds*; Plenum press: New York and London, 1999; p 11. (b) *Photochromism: Molecules and Systems*; Durr, H.; Bouas-Laurent, H., Eds.; Elsevier: 1992.
2. Swansberg, S.; Buncel, E.; Lemieux, R. P. *J. Am. Chem. Soc.* **2000**, *122*, 6594.
3. (a) Choi, H. B.; Ku, B. S.; Keum, S. R.; Kang, S. O.; Ko, J. J. *Tetrahedron* **2005**, *61*(15), 3719. (b) Keum, S. R.; Ku, B. S.; Shin, J. T.; Ko, J. J.; Buncel, E. *Tetrahedron* **2005**, *61*(28), 6720.
4. Suzuki, T.; Lin, F.-T.; Priyadashi, S.; Weber, S. G. *J. Chem. Soc. Chem. Comm.* **1998**, 2685.
5. Inouye, M.; Ueno, M.; Kitao, T. *J. Am. Chem. Soc.* **1990**, *112*, 8977.
6. Miyashita, A.; Iwamoto, A.; Kuwayama, T.; Shitara, H.; Aoki, Y.; Nihira, H. *Chem. Lett.* **1997**, 965.
7. Sunamoto, J.; Iwamoto, K.; Akutagawa, M.; Nagase, M.; Kondo, H. *J. Am. Chem. Soc.* **1982**, *104*(18), 4904.
8. Reichardt, C. *Solvents Effects in Organic Chemistry*; Verlag Chemie: 1979.
9. Keum, S. R.; Lee, K. B.; Buncel, E. *Tet. Lett.* **1994**, *35*(7), 1015.
10. Inoue, E.; Kokado, H.; Shimizu, I.; Kobayashi, H.; Takahashi, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*(7), 1951.
11. Song, X.; Zhou, J.; Li, Y.; Tang, Y. *J. Photochem. Photobiol. A* **1995**, *92*, 99.