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Photochromism in Cucurbit[8]uril Cavity: Inhibition of Hydrolysis and Modification of the Rate of Merocyanine−Spiropyran Transformations

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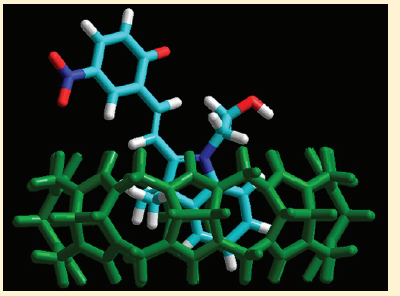
Supporting Information

ABSTRACT: The effect of inclusion complex formation on the photochromic behavior of a spirobenzopyran dye and its merocyanine isomer was studied in aqueous solution using cucurbit[8]uril (CB8) as a host. The merocyanine (MC) and protonated merocyanine (MCH^+) were the most stable forms both in water and inside the cavity of CB8. The equilibrium constant of 1:1 complexation with CB8 was found to be 1.7×10^5 and 2.0×10^6 M^{-1} for the former and latter species, respectively. The encapsulation led to significant change in the rate of the photoinduced and thermal photochromic transformations and hindered the hydrolysis of MC. The effect of CB8 on the reaction kinetics strongly altered with pH. The transition from the spiropyran form to *trans*-MC in a thermal reaction had 33 kJ mol^{-1} lower activation energy and more than 5 orders of magnitude smaller Arrhenius pre-exponential factor in CB8 than in water.



1. INTRODUCTION

Organic photochromic compounds have been receiving considerable attention because of their versatile applications in optical information storage, logic gates, molecular machines, ophthalmic lenses, photoresponsive materials, and ion sensors.[1−6] The reversible transformation between two isomers of these molecules has a great potential to be used in neurobiology,[7] biomedical imaging, photocontrol of protein activity, and transport through biological membranes.[8] Switching of fluorophores by light-induced structural change of a photochrome can offer the opportunity to achieve subdiffraction-limit resolution in the imaging of cellular structures.[9−11] Biomacromolecules functionalized by photoresponsive moieties are of substantial interest in a broad range of biomedical fields.[12]

The majority of the novel applications require systems with aqueous solubility, which can be achieved by modification of photochromes with hydrophilic functional groups.[13] This approach usually involves tedious multistep covalent syntheses and a time-consuming purification procedure.[14,15] An alternative, more efficient strategy is the solubilization by self-assembly with surfactants,[16] vesicles,[17] bile salt aggregates,[18] or cyclodextrins.[17,19−23] Photochromic compounds form inclusion complex with cyclodextrins, but the binding constants are only about $(2−3) \times 10^3$ M^{-1}. Cucurbiturils, a family of pumpkin-shaped cavitands comprised of glycoluril units linked by a pair of methylene groups, usually show a stronger binding propensity.[24−26] Because of the considerable negative charge density of the ureido carbonyl groups and the inner surface of the hydrophobic cavity,[27] these macrocycles preferentially bind cationic compounds and serve as versatile receptors for redox active substrates.[28] The confinement in cucurbiturils enhances photostability,[29,30] facilitates stereoselective photodimerization,[31−34] and effectively disrupts the intermolecular forces responsible for the aggregation.[35,36]

We have shown that the inclusion in cucurbit[7]uril is a powerful tool to modify photophysical properties,[37,38] promote tautomerization,[39] impede nucleophilic addition,[40] and inhibit photooxidation.[29] The objective of the present work is to reveal how the encapsulation in cucurbit[8]uril (CB8) influences the kinetics of the color change and the stability of a photochromic dye (Scheme 1), *N*-(2-hydroxyethyl)-3′,3′-dimethyl-6-nitrospiro [2*H*-1-benzopyran-2,2′-indoline] (SP).[3] This type of dye has usually been studied in organic solvents or organic solvent−water mixtures, but very little information is available on their reactions in aqueous medium. Shiraishi and co-workers recently showed that SP isomerizes to colored merocyanine (MC) in a thermally induced process in methanol:water 1:1 v/v mixture because the highly polarized MC form is stabilized by hydrogen-bonding interactions.[41] Upon irradiation with visible light, MC is converted into SP, even in aqueous medium. Stafforst and Hilvert found a fast hydrolysis of peptide-substituted MC yielding Fischer's base and 4-nitrosalicylaldehyde under physiological conditions (Scheme 1).[13] Since the decomposition seriously limits the utility of this photochrome in water, it is important to examine whether the inclusion in CB8 cavity hinders hydrolysis, alters photochromic behavior, or enhances solubility in water.

2. EXPERIMENTAL SECTION

SP (TCI) was used without further purification. High-purity cucurbit[8]uril, kindly provided by Dr. Anthony I. Day, was dried in high vacuum for several days prior to use. The pH of the

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solutions, adjusted with HCl or KOH, was measured with Consort C832 equipment. The glass electrode was calibrated at pH 4, 7, and 10 with buffer standards. The UV−visible absorption spectra were recorded on a Unicam UV 500 or a Hewlett-Packard spectrophotometer. Corrected fluorescence spectra were obtained on a Jobin-Yvon Fluoromax-P photon-counting spectrofluorometer. Photoirradiations were performed using 150 W xenon lamp and monochromator in 1 × 0.4 cm quartz cell. The whole solutions were exposed to light. The temperature of the samples was controlled with a Julabo thermostat. The experimental data were analyzed by the ORIGINPRO8 software.

3. RESULTS AND DISCUSSION

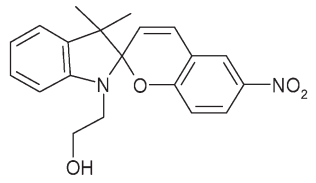
The Effect of pH Variation. Despite the hydroxyethyl moiety, which was introduced to enhance hydrophilicity, SP crystals could not be dissolved in water. However, after storing in the dark for 2 days in 4.3 mM HCl solution, SP was dissolved, resulting in a yellow solution, the absorption spectrum of which corresponded to that of the protonated merocyanine (MCH^+) form of similar compounds.[14] Acid-promoted thermal transformation of SP to MCH^+ occurred (Scheme 2), and the product became much more soluble in water due to its ionic character. MCH^+ is thermodynamically more stable than SP because of the more efficient stabilization of the cationic species by hydrogen bonding.[41] The increase of the polarity in a series of organic solvents was also found to promote the formation of the merocyanine form.[42]

The inset in Figure 1 shows the variation of the absorption spectrum upon addition of KOH. The gradual disappearance of the MCH^+ absorption, which is accompanied by the rise of a band with a maximum at 505 nm, is attributed to the formation of MC via the deprotonation of the phenolic OH-group of MCH^+. In the presence of CB8, a higher pH was needed to bring about spectral changes. The negative logarithm of the equilibrium constant of the proton dissociation from MCH^+ (pK_a) was calculated by nonlinear least-squares fit of the Boltzmann function (eq 1) to the experimental data.

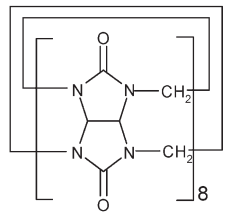
$$A = \frac{A_0 - A_\infty}{1 + \exp[(\mathrm{pH} - \mathrm{p}K_a)/P]} + A_\infty \quad (1)$$

where P denotes a fitting parameter, and A_0 and A_∞ are the absorbances at low and high pH, respectively. The analysis of the pH dependence of the absorbances in Figure 1 provided pK_a = 4.52 in water and 5.60 in CB8 cavity. The acidity diminution of 1.08 pH unit upon confinement in CB8 originated from the preferential binding of MCH^+ cation promoted by ion−dipole

Scheme 1



N-(2-hydroxyethyl)-3',3'-dimethyl-6-nitro-spiro[2H-1-benzopyran-2,2'-indoline] (SP)



Cucurbit[8]uril (CB8)

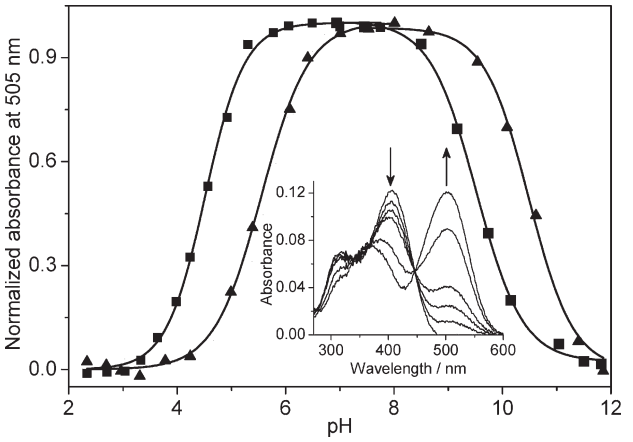
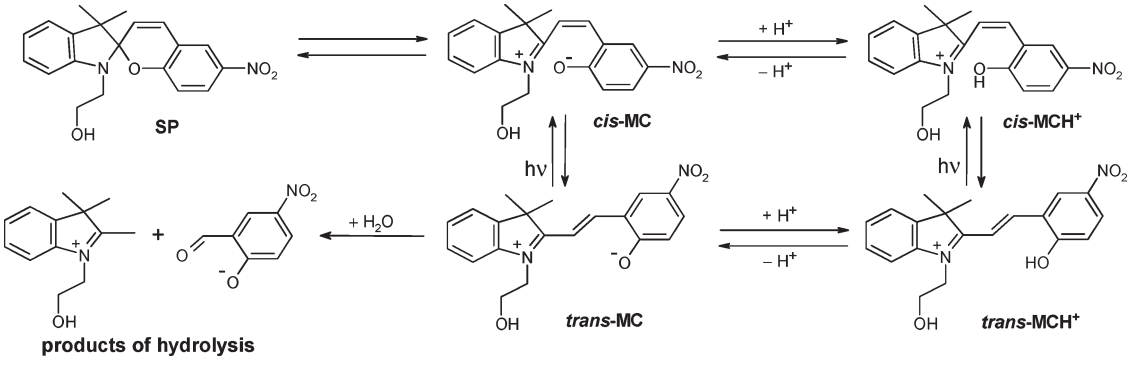


Figure 1. Effect of pH on the normalized absorbance of 6.6 μM MCH^+ solution in the presence of 77.5 μM CB8 (▲) and in water (■). The inset displays the absorption spectra in water at pH 2.3, 3.6, 4.0, 4.2, 4.9, and 7.8.

Scheme 2. Reactions in Water



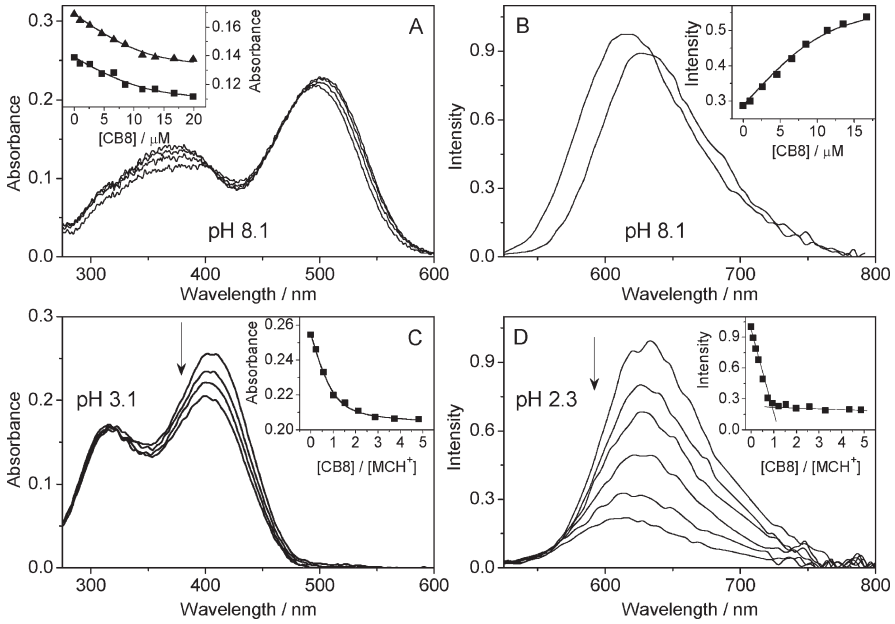


Figure 2. Variation of absorption and fluorescence in aqueous solution upon addition of CB8. (A) [MC] = 11.8 μM; [CB8] = 0, 2.6, 6.6, 19.9 μM; pH 8.1; optical path, 1 cm; inset, absorbance at 531 (▲) and 372 nm (■). (B) [MC] = 10.8 μM; [CB8] = 0 and 20 μM; pH 8.1; excitation at 450 nm; inset, fluorescence intensity at 580 nm. (C) [MCH^+] = 2.8 μM; [CB8] = 0, 1.6, 2.8, and 13.3 μM; pH 3.1; optical path, 5 cm; inset, absorbance at 405 nm. (D) [MCH^+] = 24.3 μM; [CB8] = 0, 4.6, 7.7, 12.4, 17.8, and 137 μM; pH 2.3; excitation at 350 nm; inset, fluorescence intensity at 632 nm. The lines in the insets represent the fitted function.

interactions with the carbonyl groups on the CB8 portal. The decrease of the positive charge density of the guest upon deprotonation weakened the interaction with the partial negative charge of the carbonyl-fringed portal, leading to smaller stability for the MC−CB8 complex. Above pH 8, MC absorption irreversibly decreased due to hydrolysis (Scheme 2). As seen in Figure 1, enhanced resistance against decomposition was found in the presence of 77.5 μM CB8.

Determination of the Equilibrium Constants for the Binding to CB8. The results of spectrophotometric and fluorescence spectroscopic studies confirmed the encapsulation of MCH^+ and MC in CB8. Titration with CB8 at pH 8.1 brought about slight hypsochromic displacement in the first and a hypochromic effect in the second absorption bands of MC (Figure 2A). A concomitant small rise of the fluorescence intensity and a blue-shift of the fluorescence maximum were also observed (Figure 2B). These changes were evidence of MC binding to CB8. The results could be described well by assuming complex formation with 1:1 stoichiometry. The following function gave the relationship between the absorbance at a particular wavelength (A_λ) and the total concentration of the host compound ($[CB8]_0$):[43]

$$A_\lambda = A_0 + \frac{A_\infty - A_0}{2}\left\{1 + \frac{[CB8]_0}{[Dye]_0} + \frac{1}{K[Dye]_0} - \left[\left(1 + \frac{[CB8]_0}{[Dye]_0} + \frac{1}{K[Dye]_0}\right)^2 - 4\frac{[CB8]_0}{[Dye]_0}\right]^{1/2}\right\} \quad (1)$$

where K represents the binding constant, and A_∞ and A_0 denote the absorbance of the fully complexed and free dye, whose initial concentration is $[Dye]_0$. The fluorescence intensity data presented in Figure 2B was fitted with an analogous function. For the equilibrium constant of MC confinement in CB8, $K = 1.7 \times 10^5$ M^{-1} was calculated by the global analysis of the absorption and fluorescence titrations. When the experiments were performed with MCH^+ solutions at pH 3.1, the intensity of the first absorption band decreased with growing CB8 concentration and fluorescence quenching accompanied by a blue-shift of the fluorescence maximum occurred (Figure 2C,D). The analysis of the absorbances provided 2.0×10^6 M^{-1} for the equilibrium constant of MCH^+ encapsulation in CB8. Unfortunately, the structure of the complexes could not be determined by NMR spectroscopy because of the low solubility.

The fluorescence maximum of the MC−CB8 complex had about 10 nm blue-shift compared to that of MC (Figure 2B) due to the low polarity of CB8 cavity. Interestingly, the fluorescence spectrum of MCH^+ solution (Figure 2D) corresponded to that of MC. This implies that MCH^+ rapidly loses a proton in the singlet-excited state because of the acidity enhancement upon light absorption. Such behavior has been observed for 2- and 3-cyanophenols.[44] When MCH^+ is excited, the increase of CB8 concentration causes fluorescence quenching. The less polar microenvironment in CB8 decelerates the deprotonation of the complexed MCH^+ in the excited state, allowing more efficient competition for radiationless deactivation. As a result, less singlet-excited MC−CB8 complex is produced. Consequently, significantly weaker fluorescence is emitted in the presence of CB8 than in water.

When the titrations with CB8 are repeated at 24.3 μM MCH^+ concentration, the absorbance and fluorescence intensity changes level off at equimolar MCH^+:CB8 solution (Figure 2D), corroborating the 1:1 stoichiometry of binding under our experimental conditions.

Inhibition of Hydrolysis by CB8. The effect of the inclusion in CB8 on the kinetics of MC hydrolysis was studied at pH 8.5 by

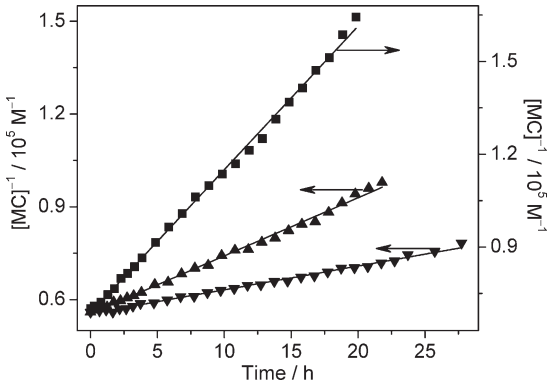


Figure 3. Reciprocal MC concentration as a function of reaction time at pH 8.5 in the case of 0 (■), 0.77 (▲), and 1.42 (▼) CB8:MC molar ratios. The lines show the fitted functions.

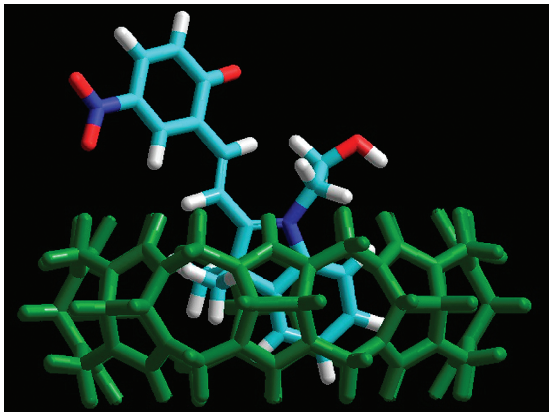


Figure 4. Energy-minimized structure of *trans*-MC−CB8 complex.

the detection of the absorption at 505 nm. MC concentration was calculated using a molar absorption coefficient of $\varepsilon(505\text{nm}) = 18\,100\ M^{-1}\ cm^{-1}$. For MCH^+, $\varepsilon(405\text{nm}) = 18\,400\ M^{-1}\ cm^{-1}$ was obtained. As shown in Figure 3, linear correlations appear between the reciprocal MC concentration and the reaction time. This indicates that the disappearance of MC follows second-order kinetics. For the apparent rate constants, $k = 1.29$, 0.52, and $0.21\ M^{-1}\ s^{-1}$ are obtained from the slopes in the case of 0, 0.77, and 1.42 CB8:MC molar ratios, respectively. The more than 6-fold decrease in k values close to 1:1 molar ratio implies strong binding of MC to CB8. Inclusion complex formation inhibits the base-catalyzed hydrolysis of MC. The acceleration of the decomposition with growing pH reflects the important role of OH^- in the process. Quantum chemical calculations with RM1 semiempirical method using HyperChem 8.0 program give the energy-minimized structure shown in Figure 4. A similar result is obtained for MCH^+−CB8 complex. The dimethylindoline moiety is embedded in the cavity of CB8, whereas the alkene moiety is located in the vicinity of the carbonyl-rimmed portal. The electrostatic repulsion with the high electron density of the carbonyl oxygens of the macrocycle hinders the approach of anions to the alkene moiety. Therefore, the inclusion complex formation protects the double bond against the OH^--catalyzed hydrolysis.

Effect of CB8 on the Kinetics of Photochromic Reactions. The inclusion in CB8 altered the rate of both the thermal and

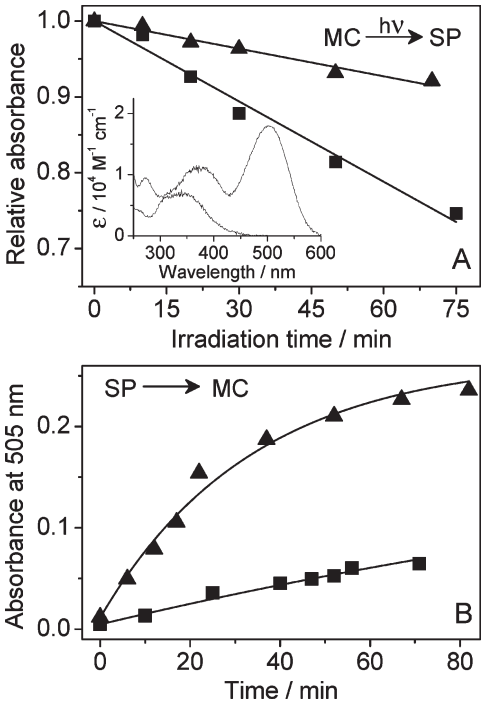


Figure 5. (A) Relative absorbance variation of 17 μM MC at 505 nm upon irradiation with 505 nm light in water at pH 7.2 (■) and in the presence of 20.5 μM CB8 at pH 8.5 (▲). Inset: absorption spectrum of MC and SP in water. (B) Rise of absorbance at 505 nm due to MC formation from 13 μM SP in the dark in water at pH 7.2 (■) and in 20.5 μM CB8 solution at pH 8.3 (▲).

photochemical processes (Figure 5). Irradiation of 17 μM MC solution at pH 7.2 with 505 nm light brought about a gradual disappearance of the MC absorption. Complete photoisomerization to colorless SP was achieved and the characteristic orange-red color of MC solution totally vanished (inset in Figure 5A). The photoinduced reaction proceeded via two main steps. The conformational transition to *cis*-MC was followed by ring closure.[45,46] For the closely related *N*-methyl derivative, Görner demonstrated that the trans−cis photoisomerization occurs predominantly from the singlet-excited state via an intermediate possessing perpendicular conformation.[47] A large range of isomers is possible for the MC and MCH^+ forms.[48] The trans and cis species in Scheme 2 denote the distributions of different isomers with dominating trans or cis characters. The two predominant ground-state isomers probably have trans−trans−cis and trans−trans−trans conformations, as suggested for a closely related *N*-methyl derivative.[49] The structure of these isomers is shown in the Supporting Information. Addition of CB8 in 1.6-fold excess barely modified the shape of the spectra but significantly decelerated the photoinduced SP formation. Under identical irradiation conditions, the plot of the relative absorbance variation as a function of time showed about 3-fold slower reaction rate for the MC−CB8 complex compared to that found for the free MC. The strong host−guest interactions stabilized *trans*-MC−CB8 and sterically hindered the isomerization preceding the formation of the closed SP form.

The kinetics of the back reaction was affected by CB8 in the opposite way (Figure 5B). SP reverted to *trans*-MC in the dark 6.4 times more rapidly inside CB8 macrocycle than in water. The process followed first-order kinetics with rate constants of 4.9×10^{-4}

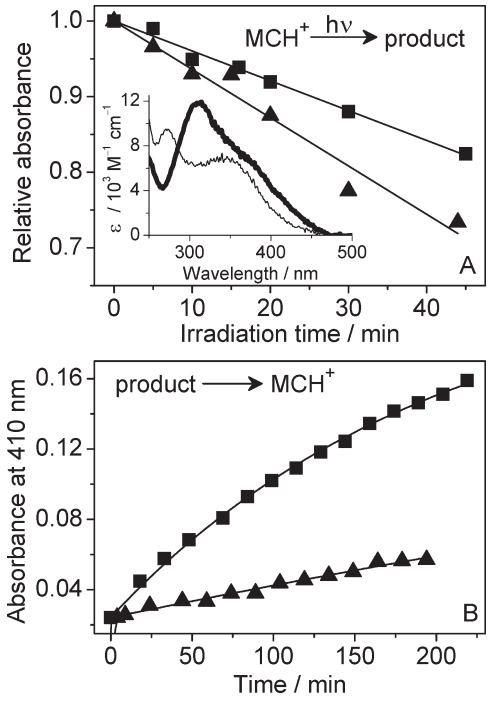


Figure 6. (A) Relative absorbance change in the course of photolysis with 410 nm light at pH 2.35 at 0 (■) and 9.8 (▲) CB8:MCH$^+$ molar ratios. Inset: absorption spectrum of photoproducts in water (thin line) and in 126 μM CB8 solution (heavy line). (B) Back formation of MCH$^+$ in the dark at 0 (■) and 3.6 (▲) CB8:MCH$^+$ molar ratios (pH 2.35).

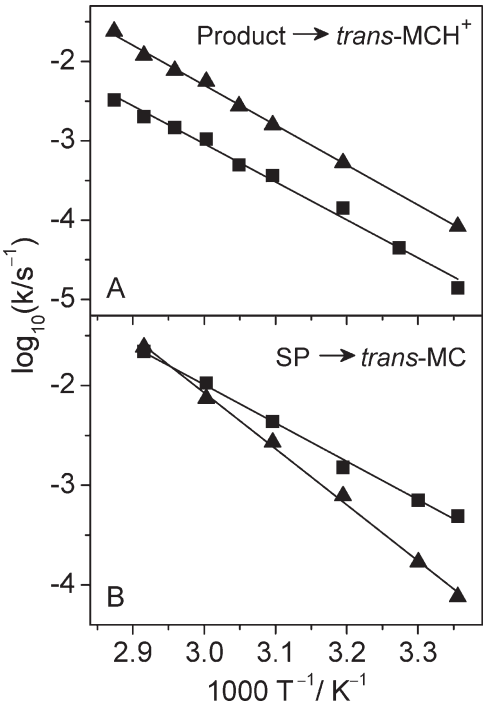


Figure 7. Arrhenius plots of the rate constants of the thermal back reactions in the presence (▲) and absence (■) of CB8 at (A) pH 2.7 and (B) 7.7.

and 7.6 × 10^{-5} s^{-1} in the presence of 21 μM CB8 and in water, respectively. The faster reaction in CB8 is probably due to the less polar microenvironment in the CB8 cavity. The acceleration of the SP → *trans*-MC conversion with decreasing solvent polarity has been observed for other spirobenzopyrans.[50]

When MCH$^+$ is photolyzed with 410 nm light at pH 2.35, the product has significantly different absorption spectrum in the presence of CB8 and in water (inset of Figure 6A), indicating that the initially formed *cis*-MCH$^+$ cannot react further in a ring closure process within the host. The spectrum of the photoproduct in water corresponds to that of SP, but the large stability of the *cis*-MCH$^+$−CB8 complex prevents deprotonation of the dye inside the host. As a consequence, SP−CB8 cannot be formed because the closure of the spiro ring requires deprotonation. Since CB8 preferentially binds cationic species,[24] the loss of proton is not favored for MCH$^+$−CB8, and the photoirradiation results in *cis*-MCH$^+$−CB8 product. In water, the initially formed *cis*-MCH$^+$ can lose a proton, allowing spiro ring formation. Since SP is produced via three steps, its formation in water is slower than the simple isomerization to *cis*-MCH$^+$ in CB8.

Both *cis*-MCH$^+$−CB8 and SP are formed in reversible processes. In the dark, they are converted back to the most stable MCH$^+$ conformation in first-order reactions, whose rate constants are 1.4 × 10^{-5} and 8.3 × 10^{-5} s^{-1} for the complexed and free dyes, respectively (Figure 6B).

Temperature Dependence of the Photochromic Reactions. To understand why the confinement in CB8 accelerates the thermal back reaction in alkaline medium but diminishes its rate in acidic solution, temperature-dependent measurements were performed. The Arrhenius plots of the rate constants are presented in Figure 7, and Table 1 summarizes the activation energies (E_A) and pre-exponential factors (A). It is important to note that E_A and A values are empirical parameters, which are related only indirectly to the enthalpy and entropy of activation for the elementary processes. Since all of the photochromic transformations are multistep reactions, it is not justified to employ the Eyring−Polanyi equation of the transition state theory. At pH 2.7, the cis−trans isomerization of MCH$^+$ in CB8 macrocycle and the transformation of SP to *trans*-MCH$^+$ in water have similar activation energies, 92 and 96 kJ mol^{-1} for the former and latter processes, respectively. This may indicate that the opening of the spiro ring has small activation energy and the cis−trans isomerization is the rate-determining step in water. The almost 30-fold smaller A factor of the cis−trans isomerization of MCH$^+$ in CB8 makes the back formation of *trans*-MCH$^+$ significantly slower in CB8 than in water.

Table 1. Arrhenius Parameters of the Thermal Back Reactions

	SP → *trans*-MC at pH 7.7		product → *trans*-MCH$^+$ at pH 2.7	
	E_A/kJ mol^{-1}	A/s^{-1}	E_A/kJ mol^{-1}	A/s^{-1}
in water	107	5.8 × 10^{14}	96	6.3 × 10^{12}
in CB8	74	3.4 × 10^{9}	92	2.2 × 10^{11}

At pH 7.7, the transition from SP to *trans*-MC is faster in the macrocycle below 339 K. Above this temperature the reaction is more rapid in water. The interactions with CB8 decrease E_A to 74 kJ mol^{-1} from the 107 kJ mol^{-1} value in water, and bring about more than 5 orders of magnitude A factor diminution (Table 1). Such a big A factor difference implies that the transition states have less degrees of freedom in CB8 in the case of all elementary reaction steps. The less polar microenvironment in CB8 may also

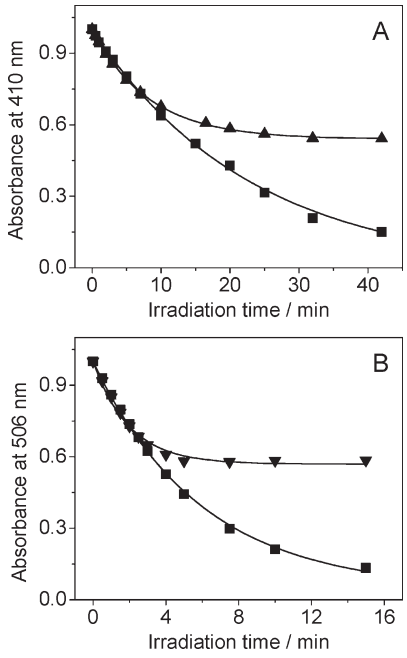


Figure 8. Effect of temperature variation on the photochemical decoloration kinetics in CB8 cavity for 15.7 μM *trans*-MCH$^+$ at 410 nm, pH 2.3, λ_{exc} > 430 nm (A) and 6.9 μM *trans*-MC at 506 nm, pH 7.7, λ_{exc} > 525 nm (B). Measurements at 288 K (■), 323 K (▼) and 343 K (▲).

contribute to the decrease of the Arrhenius parameters compared to those in water. Such a trend is expected on the basis of the data reported by Flannery.[51] For the SP → *trans*-MC thermal coloration E_A = 112 kJ mol^{-1} and $A = 1.7 \times 10^{14}$ s^{-1} was found in ethanol, whereas E_A = 87 kJ mol^{-1} and $A = 1.14 \times 10^{10}$ s^{-1} was obtained in benzene, indicating the diminution with decreasing solvent polarity.

The initial rate of the transformations of *trans*-MCH$^+$ and *trans*-MC induced by excitation in the lowest-energy absorption band is independent of the temperature in water and CB8 cavity alike. As representative examples, Figure 8 displays the absorbance diminutions during irradiation in CB8 at pH 2.3 and 7.7. It is apparent that the rate of photodecoloration does not vary with temperature at low conversion. The effect at longer irradiation times is due to the marked acceleration of the back reaction at higher temperatures (vide supra). The photoisomerization probably occurs in the singlet-excited state, where much smaller energy barriers are expected than in the ground state.[49,52]

4. CONCLUSIONS

The encapsulation in a macrocycle affects the photochromic behavior of a spirobenzopyran in a totally different manner for CB8 than previously found for cyclodextrins. In the latter host, SP is preferentially incorporated,[20] whereas CB8 produces the most stable complex with MCH$^+$ form. Inclusion complex formation with CB8 has three advantageous effects, which help to solve the problems limiting the applications of spirobenzopyrans in aqueous solution. The encapsulation not only improves the solubility and stability of the dye but also promotes the tuning of its photochromic behavior. These benefits and the remarkably strong binding of spirobenzopyran to cucurbit[8]uril may open up new possibilities in a wide variety of applications. Cucurbituril-type molecular containers have a great potential to be used for the development of a new generation of photoresponsive materials with unique properties. The photochromic behavior of the encapsulated dye can be adjusted by the variation of pH. The confinement in CB8 leads to the most substantial decrease in the Arrhenius parameters of the SP → *trans*-MC process, but the photoinduced isomerizations do not show temperature dependence.

■ ASSOCIATED CONTENT

Supporting Information. The structure of the trans−trans−cis and trans−trans−trans isomers are shown. This information is available free of charge via the Internet at http://pubs.acs.org.

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