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Kinetics of thermal bleaching reaction of the photomerocyanine form of spironaphthooxazine

Tae-Wook Shin [a], Young-Shik Cho [b], Young-Duk Huh [b], Kap Duk Lee [a],
Wongkang Yang [a], Jeunghee Park [c], In-Ja Lee [a,*]

[a] *Department of Chemistry, Dongguk University, Kyongju-Si, Kyongpook 780-714, South Korea*
[b] *Department of Chemistry, Dankook University, Seoul 140-714, South Korea*
[c] *Deparment of Chemistry, Korea University, Jochiwon, Chungnam 339-700, South Korea*

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Abstract

The thermal bleaching reactions of photomerocyanine (PMC) form of spironaphthooxazine (SNO) were investigated in various temperatures and solvents using laser flash photolysis. The thermal decay rate of PMC for SNO markedly decreases as temperature decreases and generally increases with solvent polarity. The solvent effect on the rate constant was well explained by using the π^*-scale. The activation energy and activation entropy also increase with the solvent polarity and the isokinetic relation has been observed. The combined results are interpreted in terms of dissociation of solvated PMC complex and/or ordered solvent structure around PMC molecules. Based on the experimental results, the potential energy surface along the reaction path in the ground state has been proposed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Spironaphthooxazine; Photomerocyanine; Thermal decay; Solvent effect

1. Introduction

Thermochromism and photochromism of spiropyrans (SP) and spirooxazines (SO) have been the subject of great interest in last few decades due to their applications in various fields, such as display system, optical switching and non-silver high-resolution photography [1–4]. SO are of particular interest among spiro compounds due to their relatively high photostability [2,5]. Colorless SO experiences heterolytic cleavage of C–O spirobond of oxazine ring upon ultraviolet irradiation to give a colored open form, photomerocyanine (PMC) (Scheme 1). Then the open form PMC tends to revert to the colorless SO either upon heating or by irradiation with visible light [2,5].

PMC form of unsubstituted spironaphthooxazine (SNO) exhibit positive solvatochromism [6–8] and its rate constants of the thermal ring closure increase as the solvent polarity increases [6,7]. However, in solutions the absorption maximum of SNO having NO_2 group or electron-donor substituents show negative solvatochromism and its thermal bleaching rate decreases as the solvent polarity increases [7]. Based on these results, it was concluded that PMC form of substituted-SNO has bipolar structure contrary to the quinoid form of unsubstituted SNO.

In this study, we present extended kinetic data of the thermal decay reaction of PMC form of unsubstituted SNO in various solvents. Because the rate of the thermal bleaching reaction varies only by a factor of few times from solvent to solvent and its rate constant k is $\sim 1\ \mathrm{s}^{-1}$ at 25°C, we followed the rate measurements by laser flash photolysis method. The solvent effects on the activation parameter for the thermal decay are estimated by analyzing the experimental data and have been utilized to propose the potential energy surface along the reaction path in the ground state.

2. Experimental

2.1. Materials

The 1,3-dihydro-1,3,3-trimethyl-spiro[2H-indol-2,3′-[3H]-naphth[2,1-b][1,4]oxazine] (SNO) was purchased from Tokyo Kasei Industry and used without further purification. SNO was dissolved in various spectroscopic grade solvents (Aldrich) and the sample concentration was 2.0×10^{-4} M in all solvents.

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* Corresponding author.
E-mail address: lij@mail.dongguk.ac.kr (I.-J. Lee).

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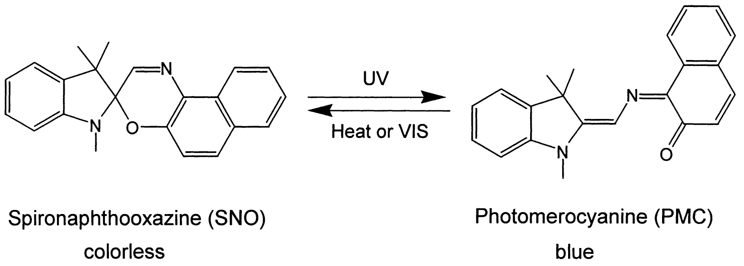

Scheme 1.

2.2. Kinetic study

In the thermal bleaching experiments of PMC, SNO was transformed to PMC by a single pulse irradiation of 337 nm light (1.4 mJ, 600 ps) from a pulsed N_2 laser (Laser Photonics LN-1000). A yellow He–Ne laser (594 nm, Edmund G3941) was used as a probe beam, which is right angle to the UV light from the N_2 laser. In order to prevent the photo-isomerization reaction of PMC to SNO due to the He–Ne laser, the light intensity of the He–Ne laser was reduced to $\sim$10 nW/cm^2 using the neutral density filters. Before the UV irradiation, the sample was thermally equilibrated for 30 min at the desired temperatures. After the thermal equilibrium, a function generator (Wavetek 145) triggers the N_2 laser to produce the PMC form and then the sync out from the laser triggers an oscilloscope (HP54600B) to display the signal. Upon the irradiation by the UV light of N_2 laser, the absorption of PMC appeared and thus, decreased the transmitted probe beam intensity. The change in the probe beam intensity was detected using PMT (R928) and displayed by the oscilloscope. The data displayed on the oscilloscope were transferred to IBM-compatible PC and analyzed in the PC.

The sample cell made of quartz was placed in the specially designed cell holder and then attached to the cold head of the cryostat (Janis, RGD-210). The temperature of the sample was maintained within ±0.1°C of the desired temperatures using the cryostat and temperature controller (Lakeshore Model 330).

3. Results and discussions

Dilute solutions of unsubstituted SP and SO are colorless or slightly colored in organic solvents. Upon UV irradiation, the closed SO (or SP) shows positive photochromism, i.e., the colorless SO (or SP) is converted to blue PMC that reverts to SO (or SP) in the dark. The thermal back reaction of PMC is known to follow the first-order reaction in solutions [5,7] while it deviates from the first-order reaction in amorphous solids [9,10]. In this study, the thermal decay reaction of PMC form of unsubstituted SNO has been extensively studied at several temperatures in various solvents.

3.1. Kinetics of thermal bleaching reaction

The thermal decay rates of PMC form produced upon ultraviolet exposure were measured at more than four temperatures in a wide range of solvents. The solvents include carbon tetrachloride (CCl_4), toluene, 1,4-dioxane, tetrahydrofuran (THF), chloroform, benzene, acetone, acetonitrile, 1-butanol, 2-propanol, ethanol and methanol. The representative thermal decay curves in chloroform and 1-butanol are presented in Figs. 1A and 2A, respectively. As indicated in the figures, the decay rate has been markedly slowed down as the temperature is lowered and it is slower in 1-butanol than in chloroform at the same temperature. The thermal back reaction may finally stop at -60°C [2].

The integrated form of the first-order rate law is

$$[\mathrm{PMC}] = [\mathrm{PMC}]_0\, \mathrm{e}^{-kt}$$

Here, k is the rate constant and $[\mathrm{PMC}]_0$ and [PMC] are the concentrations of PMC present at right after UV irradiation and at time t, respectively. From Figs. 1B and 2B, the first-order plot of Figs. 1A and 2A, it is easily seen that the thermal decay reaction of PMC form well follows the first-order reaction. The rate constants of the thermal bleaching reactions obtained at several temperatures for various solvents are listed in Table 1. From these data it is evident that the rate constant increases with temperatures in a given solvent and is generally larger in the polar solvents than in the nonpolar solvents within the aprotic solvents.

The variation of rate constants with temperatures is represented for the several solvents as the Arrhenius plot in Fig. 3. The activation energy E_a and the pre-exponential factor A for the thermal bleaching reaction of PMC are estimated from the slope and the intercept of the Arrhenius plot, respectively, and are summarized in Table 2. The fact that the activation energy is generally larger in polar solvents than in nonpolar solvents indicates that the rate of the thermal decay reaction in polar solvent is more sensitive on the temperature than those in nonpolar solvents. As illustrated in Tables 1 and 2, it is interesting that fast reaction has high activation energy.

For the reactions in solution, the activation enthalpy is expressed as $\Delta H^{\ddagger} = E_{\mathrm{a}} - RT$. Because $k = (k_{\mathrm{B}}T/h) \times \mathrm{e}^{-\Delta G^{\ddagger}/RT}$ and $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, rate constant k is

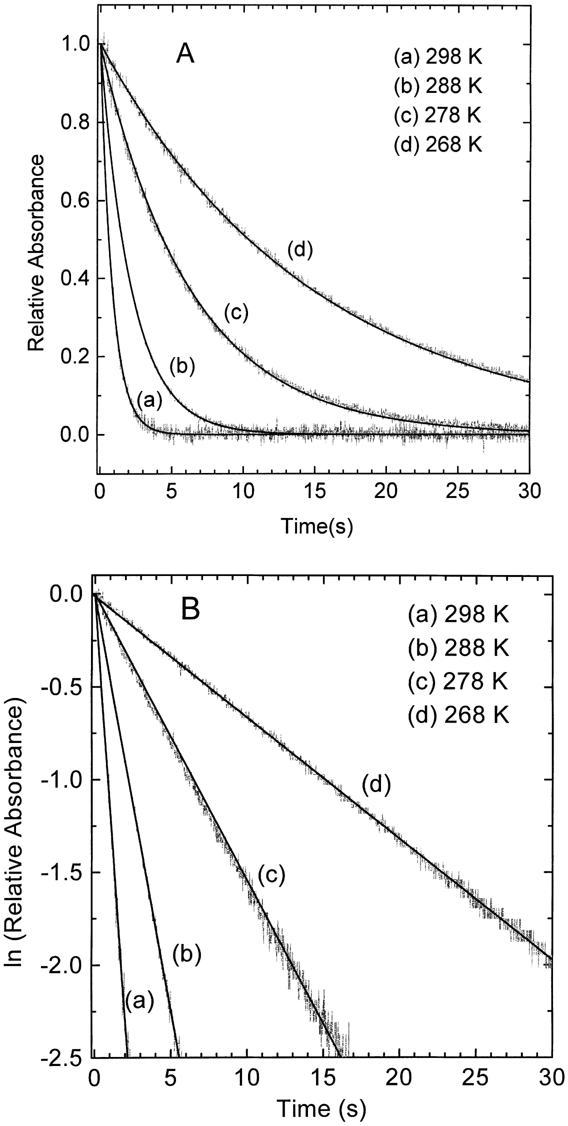

Fig. 1. Thermal decay curves of PMC for SNO in chloroform solution. The concentration of SNO is 2.0×10^{-4} M. (A) plot of absorbance vs. time, (B) first-order plot of (A). The noisy lines are experimental data and the smooth solid lines are fits to the first-order reaction.

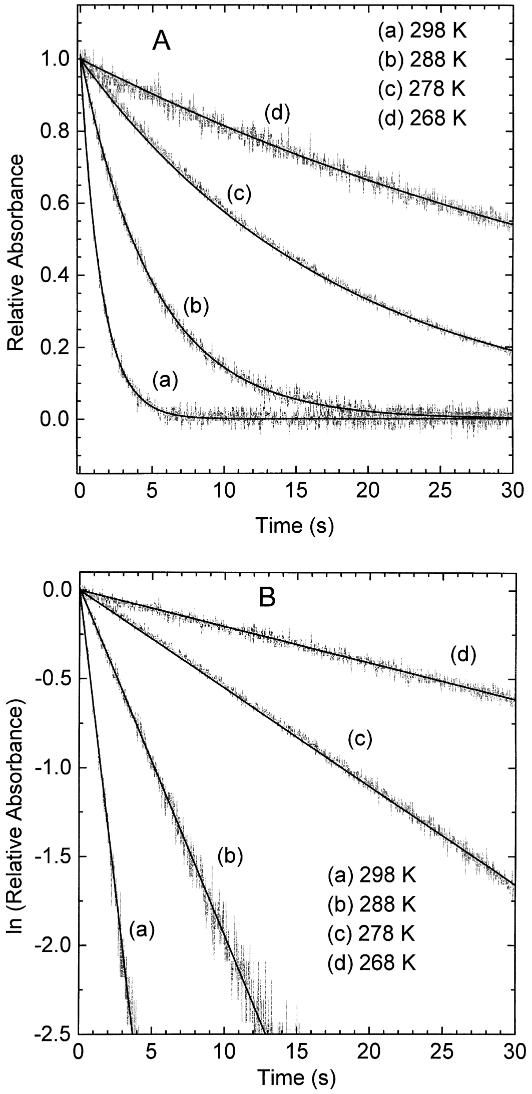

Fig. 2. Thermal decay curves of PMC for SNO in 1-butanol solution. The concentration of SNO is 2.0×10^{-4} M. (A) plot of absorbance vs. time, (B) first-order plot of (A). The noisy lines are experimental data and the smooth solid lines are fits to the first-order reaction.

expressed as

$$k = \frac{\mathrm{e} k_\mathrm{B} T}{h}\, \mathrm{e}^{\Delta S^{\ddagger}/R}\, \mathrm{e}^{-E_\mathrm{a}/RT} \qquad (1)$$

Here, k_B is the Boltzmann constant and T is the temperature. The activation enthalpy and activation entropy at 298 K obtained using these relationships are also listed in Table 2. Table 2 shows that in the polar solvents $\Delta S^{\ddagger}$ is positive and the activation energy is about 80 kJ/mol. The case in nonpolar solvents such as benzene and toluene is quite different, i.e., $\Delta S^{\ddagger}$ is negative and activation energy ≈60 kJ/mol. The differences in $\Delta S^{\ddagger}$ and E_a with the solvent polarity will be discussed later in detail.

The Gibbs function of activation $\Delta G^{\ddagger}$ at 298 K has been measured using $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ and independently by using $\Delta G^{\ddagger} = -RT\ln(kh/k_\mathrm{B}T)$. The $\Delta G^{\ddagger}$ obtained by the two methods are coincident with each other and indicated also in Table 2. Regardless of the solvent polarity, $\Delta G^{\ddagger}$, a function of temperature, is shown to be similar in most of the solvent.

3.2. Solvent effects on the thermal back reaction

In order to quantitatively determine the solvent effect on the thermal decay reaction of PMC, the several solvent polarity scales have been applied. Among them, the π^*-scale is observed to be best in explaining the behavior of thermal reaction of PMC. The relationship between the π^*-scale and

Table 1
Rate constants (s^{-1}) of thermal decay reaction of PMC for SNO in various solvents

Solvent	Temperature (K)								
	298	293	288	283	278	273	268	263	258
Carbon tetrachloride	3.3076		1.0012		0.2701		0.0789		0.0263
Toluene	0.3687	0.2379	0.1332	0.0926	0.0558	0.036	0.0230		
THF	0.8174		0.2864		0.1189		0.0443		
Chloroform	1.1730	0.7332	0.4515	0.2517	0.1542	0.0963	0.0604		
Benzene	0.4787	0.3087	0.2105	0.1306	0.0753				
Acetone	1.7496		0.5909		0.1685		0.0321		
Acetonitrile	2.2575	1.2783	0.7173	0.4193	0.1995		0.0498		
1-Butanol	0.6777		0.1935		0.0559		0.0173		
2-Propanol	0.7411		0.2071		0.0553		0.0152		0.0047
Ethanol	0.6962	0.3461	0.1754	0.0959	0.0535	0.0264			
Methanol	0.6470	0.3167	0.1740	0.0800	0.0431	0.0213			
	298	295	292	288					
1,4-Dioxane	0.8654	0.6562	0.5054	0.3621					

the rate constant of the thermal bleaching reaction can be expressed as [11,12]

$$\ln k = \ln k_0 + s(\pi^* - 0.133\delta)$$

Here s is a slope of plot for $\ln k$ vs. solvent polarity. And δ, the polarizability correction term, equals to 0.0 for nonchlorinated aliphatic solvent, 1.0 for aromatic solvent and 0.5 for polychlorinated aliphatic solvent. It is evident on the inspection of Fig. 4, the plot of $\ln k$ vs. π^*, that the kinetic behavior of PMC is different in three classes of the solvents, polychlorinated aliphatic solvents, alcoholic solvents and nonchlorinated solvents. Similar trend is also obtained for the plot of $\ln k$ vs. E_T (another solvent polarity scale). Some kind of specific solute–solvent interaction which may be present in polychlorinated solvents and alcoholic solvents might be responsible for the deviation from the linear relationship between $\ln k$ and π^*. The best fit to the experimental data for the nonchlorinated solvents was obtained with $s = 5.19$ ($n = 6$, $r = 0.995$).

Fig. 5 is a plot depicting isokinetic relationships for the thermal bleaching reaction of PMC for SNO using $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values obtained for various solvents. Regardless of the solvent characteristics, all data sit on the same line. This implies that there exists an isokinetic relation with the isokinetic temperature of 280.3 K [13]. The presence of the isokinetic relation does support the single reaction mechanism is operative for the thermal bleaching reaction in the series of the solvents. Although the rate constant

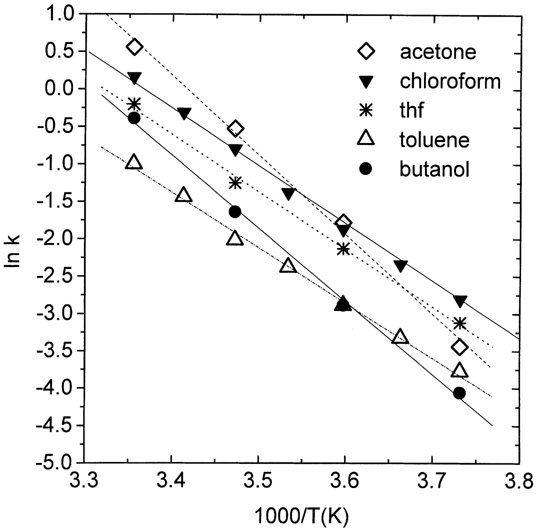

Fig. 3. An Arrhenius plot for the thermal bleaching reaction of PMC for SNO in selected solvents. Symbols represent experimental data and the lines are fit to the experimental data.

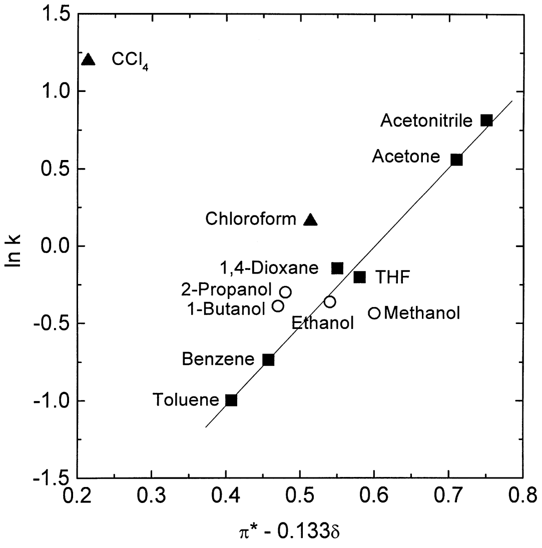

Fig. 4. Natural logarithm of the kinetic constants of the thermal bleaching reaction of PMC in various solvents as a function of $\pi^*-0.133\delta$ at 25°C. (▲), (○) and (■) represent polychlorinated aliphatic solvents, alcoholic solvents and nonchlorinated solvents, respectively. The solid line is a fit to the experimental data for the nonchlorinated solvents.

Table 2
Thermodynamic parameters of thermal decay reaction of PMC for SNO at 25°C

Solvent	Parameter						
	π* [11]	E_a (kJ/mol)	$\Delta G^\ddagger$ (kJ/mol)	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J/K mol)	A (s^{-1})	ΔH [8] (kJ/mol)
Carbon tetrachloride	0.28	77.91	70.01	75.43	18.17	1.35×10^{14}	28.6
Toluene	0.54	61.46	75.45	58.99	−55.26	2.07×10^{10}	26.4
1,4-Dioxane	0.55	62.01	73.34	59.53	−46.33	6.34×10^{10}	26.3
THF	0.58	63.83	73.48	61.35	−40.70	1.18×10^{11}	23.8
Chloroform	0.58	66.52	72.59	64.04	−28.67	5.18×10^{11}	19.6
Benzene	0.59	62.88	74.81	60.40	−48.34	5.10×10^{10}	
Acetone	0.71	88.19	71.60	85.71	47.37	5.49×10^{15}	24.5
Acetonitrile	0.75	84.31	70.96	81.83	36.47	1.40×10^{15}	
1-Butanol	0.47	81.17	73.95	78.69	15.92	1.07×10^{14}	
2-Propanol	0.48	81.13	73.72	78.65	16.54	1.10×10^{14}	21.4
Ethanol	0.54	87.21	73.88	84.73	36.42	1.25×10^{15}	20.8
Methanol	0.60	92.10	74.06	89.62	52.22	8.63×10^{15}	20.4

of the thermal bleaching reaction has been classified into three classes, the reaction mechanism seems to be the same. Therefore, the difference in the activation energy, activation enthalpy and activation entropy in various solvents seems have their origin not in the reaction mechanism but in the interactions between the reaction species and solvent.

3.3. Thermal bleaching process

The earlier studies of the solvent effect on the λ_{max} of the absorption spectra reported that PMC for SNO shows positive solvatochromism [6–8], which is characteristic of compounds having a weakly polar ground state. Because this fact implies a small charge delocalizaion of PMC in the ground state, it was concluded that the structure of the PMC for SNO is predominantly quinoid form, in contrast with the PMC of nitro-substituted spiropyrans showing negative solvatochromism that implies a zwitterionic structure. Furthermore, the earlier kinetic study of the thermal decay of PMC for SNO showed that the rate constant increases when going from nonpolar to polar solvents [6,7]. This result was also interpreted as that the structure of PMC is quinoidal than zwitterionic.

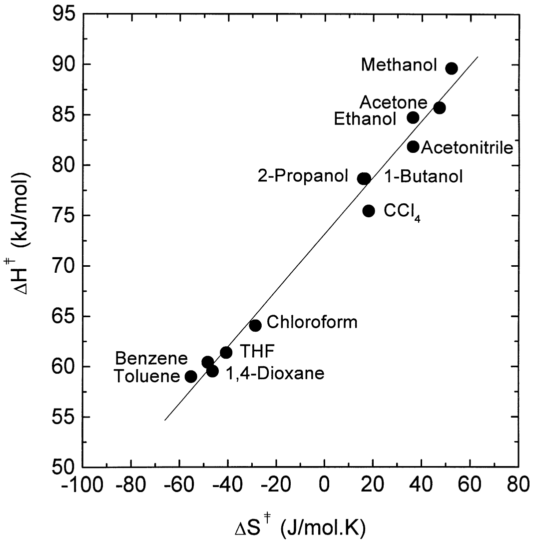

Fig. 5. A plot depicting isokinetic relationships for the thermal bleaching reaction of PMC for SNO. Symbols represent experimental data and the lines are fit to the experimental data. ($n = 12$, $r = 0.993$).

Our kinetic data listed in Table 1 also indicate that the rate constant increases with the solvent polarity. According to Table 2, however, it is evident that the activation energy as well as the thermal decay rate is larger in polar solvents than in nonpolar solvents. Because, for a series of kinetic study of a given reaction, it is general thought that the faster reaction corresponds to smaller activation energy and the slower reaction corresponds to higher activation energy, our data are somewhat surprising. According to Eq. (1), the fast reaction with large activation energy implies that the pre-exponential factor, e.g., the activation entropy must be large. Table 2 clearly shows that not only the rate constant but also the activation energy and the activation entropy increase in general as the solvent polarity increases. This fact indicates that the reason for the slow reaction in the nonpolar solvent is not due to the high activation energy but due to the negative value of the activation entropy.

Table 2 shows that in the polar solvents $\Delta S^\ddagger$ is positive and activation energy is ≈80 kJ/mol while in the nonpolar solvents $\Delta S^\ddagger$ is negative and activation energy is ≈60 kJ/mol. This fact may be qualitatively explained as follows. In benzene, $\Delta S^\ddagger$ of −48.35 J/K mol seems largely reflecting the formation of an ordered transition state, having orthogonal SNO geometry with C–O bond cleavage, from the open PMC form. In contrast, rather the higher activation energy in polar solvents seems to correspond to dissociation of a solvated PMC complex and/or destroy of the ordered solvent structure around PMC molecules, which are supported by the positive value of $\Delta S^\ddagger$.

Regarding on the solvatochromism, the conclusion that PMC for SNO shows positive solvatochromism was drawn

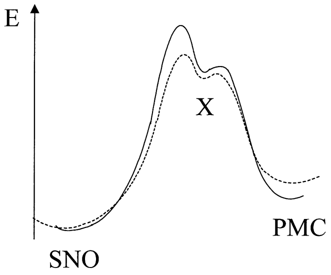

Fig. 6. Potential energy surface along the reaction path in the ground state for the nonpolar (dotted line) and polar solvents (solid line).

by using the broad unresolved absorption spectra of PMC isomers. Because PMC is present as a mixture of the several isomers and the amount and the kind of the PMC isomers present vary from solvent to solvent, the solvatochromism should be carefully analyzed. The apparent positive solvatochromism may not simply mean the red shift of the absorption spectra of one isomer of PMC. It may have contributions from the change in the kind and the amount of the isomers present whose absorption spectra are closely located.

In Ref. [8], the enthalpy changes of the thermochromic reaction SO (or SP) → PMC of several spiropyrans and spirooxazines in various solvents have been reported and some of them are listed in Table 2. The reaction enthalpy for all spirocompounds studied decreases as solvent polarity increases. Both the larger activation energy for the thermal decay reaction and the smaller enthalpy change for thermal SNO → PMC reaction in the polar solvents indicates that the open PMC for SNO is more polar than either one of the closed form SNO or the transition species. However, because the enthalpy change of the thermal SNO → PMC reaction do not depend on the solvent polarity as much as the nitro-substituted benzospiropyrans (NBSP), the PMC for SNO is not polar as much as PMC for NBSP.

From these discussions, the potential energy surface along the reaction path in the ground state is proposed. Although the relative stability of SNO in the polar solvent and nonpolar solvent is not clear, it is assumed in Fig. 6, that the potential energy of SNO is slightly lower in the polar solvents than in the nonpolar solvents. Because the primary photoproduct X [14], which experience the isomerization reaction to PMC even at 25 K, can be trapped at 25 K in the amorphous solid [15], X has been included in the potential energy surface diagram with negligibly small barrier for X → PMC reaction. Because the isokinetic relationship support the same reaction mechanism for all solvents studied, it is assume that the shape of the potential energy surface along the reaction path is similar both in the polar and nonpolar solvent. It is interesting that, although the relative stability of SNO in the polar and nonpolar solvent is not clear, the energy of the activated complex is lower in nonpolar solvent than in polar solvent.

In conclusion, the thermal bleaching reactions of PMC for SNO were investigated at several temperatures in various solvents using laser flash photolysis. The thermal decay rate of PMC for SNO, which is faster in the polar solvent, markedly decreases as the temperature decreases. Not only the rate constant but also the activation energy and activation entropy increase with the solvent polarity. The results are interpreted in terms of solvation of the polar species PMC and the dissociation of the solvated PMC complex and/or the ordered solvent structure around PMC molecules. Based on the results, the potential energy surface along the reaction path in the ground state has been suggested.

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