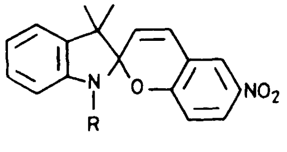
Effect of the Phase Transition of a Bilayer Membrane on the Thermal Decolouration of a U.V.-irradiated Indolinospirobenzopyran

Takahiro Seki* and Kunihiro Ichimura

Research Institute for Polymers and Textiles, 1-1-4 Yatabe-Higashi, Tsukuba, Ibaraki 305, Japan

The kinetic parameters for the thermal decolouration of u.v.-irradiated spiropyran derivatives incorporated in a bilayer vesicle membrane were affected by the crystal to liquid crystal phase transition.

The photochromic behaviour of spiropyrans in solutions,[1] polymer films,[2] monolayers,[3] and Langmuir–Blodgett multilayers[4] have been extensively investigated. It is known that for spiropyrans embedded in polymer films,[2] the photochromism is largely dependent on the dynamics (rigidity) of the matrices around the spiropyran molecules. A large number of double-chain amphiphiles form bilayer membranes in water which show a sharp fluidity change at the crystal to liquid crystal phase transition temperature (T_c).[5] In the crystalline phase (below T_c) the bilayers form with the all-*trans* chains closely packed, and in the liquid crystalline phase (above T_c) the membrane fluidity increases and the chains resemble liquid hydrocarbons with several *gauche* bonds.[6] It is therefore of interest to study the kinetics of the photochromic reactions of spiropyrans when incorporated in a bilayer membrane with respect to the change in fluidity. Spiropyrans have been embedded in bilayers in order to explore the molecular mobility[7] and to attempt to construct a photoresponsive transport system.[8] However, no attempt seems to have been made to investigate the dependence of the photochromic process upon the physical state of the membrane. In this communication we report some preliminary results on the regulation of the thermal decolouration of the compounds (**1**) and (**2**) [the thermal isomerization of u.v.-irradiated merocyanine (PMC) to the original spiropyran] by making use of the phase transition of a dioctadecyldimethylammonium bromide ($2C_{18}N^+2C_1$) bilayer vesicle membrane.[†]



(**1**) R = Me
(**2**) R = $[CH_2]_{17}Me$

[†] Compound (**1**) was purchased from Tokyo Kasei Co. and (**2**) was prepared in our laboratory according to the method of Gruda and Leblanc.[9] $2C_{18}N^+2C_1$ was purchased from Sogo Pharmaceutical Co.

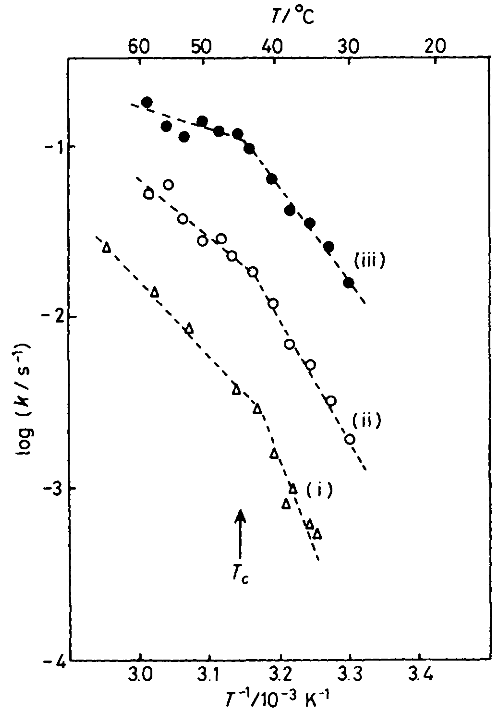


Figure 1. Arrhenius plots for the thermal decolouration rate of (**1**) and (**2**) incorporated in a $2C_{18}N^+2C_1$ bilayer vesicle membrane. $[2C_{18}N^+2C_1] = 6.0 \times 10^{-3}$ M, $[(\mathbf{1})] = [(\mathbf{2})] = 3.0 \times 10^{-5}$ M. (i) (**1**); (ii) (**2**), slow reaction; (iii) (**2**), fast reaction.

Table 1. Kinetic parameters for the isomerisation of (**1**) and (**2**).

Amphiphile	Spiropyran	T/°C	E_a/ kcal mol^{-1}	$\Delta S^\ddagger$/ cal mol^{-1} K^{-1}
$2C_{18}N^+2C_1$[a]	(**1**)	35[b]	35.1	40.5
		50[c]	21.8	−1.3
	(**2**)	35[b]	26.0	19.1
			33.1	38.3
		50[c]	10.5	−30.2
			16.7	−13.9
CTAB[d]	(**1**)	35	19.2	−10.3
	(**2**)	35	19.2	−1.9

[a] Conditions are as shown in Figure 1. [b] Below T_c. [c] Above T_c. [d] $[\mathrm{CTAB}] = 1.0 \times 10^{-2}$ M, $[(\mathbf{1})] = [(\mathbf{2})] = 5.0 \times 10^{-5}$ M.

$2C_{18}N^+2C_1$ co-lypophilized with 0.5 mol% of (**1**) or (**2**) from chloroform solution under vacuum was sonicated above T_c (45 °C)[5] for 5 min in distilled water. The thermal decolouration rate constants were determined by following the decay of the visible absorption in the dark after u.v.-irradiation ($\lambda < 360$ nm, 500 W high pressure mercury lamp).

The spiropyran compounds, both in the original form and the ring-opened form (PMC), were practically insoluble in water and the visible absorption bands of PMC were detected only when a bilayer or a micelle forming amphiphile was present. This shows that most of the photochromic molecules are solubilized in molecular assemblies and those in the bulk make negligible contributions to the observed absorbances. A comparison of visible absorption maxima of PMC ($\lambda_{max.}$) in the bilayer was made with PMC dissolved in organic solvents. The $\lambda_{max.}$ values for the bilayer at 30 °C were 522 and 555 nm for (**1**) and (**2**), respectively, indicating that the microenvironment of the chromophore has a polarity ranging from methanol to acetone. The chromophore is probably located in the vicinity of the hydrophilic surface of the membrane.

Figure 1 shows the Arrhenius plots for the thermal decolouration rates of PMC of (**1**) and (**2**) in the bilayer vesicle. When (**2**) was employed, the reaction showed strong deviation from first-order kinetics and analysed as the sum of two exponential processes, a slow process and a fast one, see Figure 1. The deviation from first order kinetics is attributed to the distribution of the photochromic head group which may be either at the surface (slow process) or within (fast process) the membrane. A feature of the plots is that they have a clear break near 45 °C which corresponds to the T_c value of the sonicated $2C_{18}N^+2C_1$ vesicle.

The kinetic parameters calculated from the plots are summarized in Table 1 together with those of hexadecyltrimethylammonium bromide (CTAB) micellar systems. The kinetics above T_c in the bilayer systems are characterized by a relatively low activation energy (E_a = 10—22 kcal mol^{-1}; 1 kcal = 4.184 kJ) and a negative activation entropy, $\Delta S^\ddagger$. These values are qualitatively in agreement with those for CTAB micellar systems. In contrast, a higher activation energy (E_a = 26—36 kcal mol^{-1}) and positive $\Delta S^\ddagger$ are characteristic of bilayer systems below their T_c. Kinetic parameters are known to be dependent on the polarity of the medium.[1] This is not the critical factor in these systems because the $\lambda_{max.}$ value of PMC (522 nm) was identical below and above T_c in the $2C_{18}N^+2C_1$–(**1**) system. Therefore, we rationalise the kinetic parameters in terms of the fluidity of the bilayer matrix. The negative $\Delta S^\ddagger$ and relative small E_a values (less than 20 kcal mol^{-1}) for the system above T_c probably reflect the transition state of ring-formation from PMC to spiropyran.[1] The larger values of the kinetic parameters for the crystalline state of the bilayer (below T_c) presumably result from the extra energy required for the fluidization of the ordered amphiphilic molecules surrounding the photochromic chromophore during the isomerization, which is accompanied by a significant change in shape. Such fluidization of the matrix in the transition state accounts for the positive $\Delta S^\ddagger$ value.

In conclusion, it has been demonstrated that a bilayer membrane provides an effective medium for regulating the isomerization of a photochromic compound.

Received, 26th January 1987; Com. 089

References

1 J. B. Flannery, Jr., *J. Am. Chem. Soc.*, 1968, **90**, 5660.
2 G. Smets, *Adv. Polym. Sci.*, 1983, **50**, 17.
3 D. A. Holden, H. Ringsdorf, V. Deblauwe, and G. Smets, *J. Phys. Chem.*, 1984, **88**, 716; C. B. McArdle and H. S. Blair, *Colloid Polym. Sci.*, 1984, **262**, 481; E. E. Polymeropoulos and D. Möbius, *Ber. Bunsenges. Phys. Chem.*, 1979, **83**, 1215.
4 E. Ando, J. Miyazaki, K. Morimoto, H. Nakahara, and K. Fukada, *Thin Solid Films*, 1985, **13**, 21.
5 Y. Okahata, R. Ando, and K. Kunitake, *Ber. Bunsenges. Phys. Chem.*, 1981, **85**, 789.
6 J. F. Baret, 'Progress in Surface and Membrane Science,' eds. D. A. Cadenhead and J. F. Danielli, vol. 14, Academic Press, New York, 1981, pp. 291—351.
7 B. Nadolski, P. Uzański, and M. Kryszewski, *Makromol. Chem., Rapid. Commun.*, 1984, **5**, 327.
8 J. Sunamoto, K. Iwamoto, Y. Mohri, and T. Kominato, *J. Am. Chem. Soc.*, 1982, **104**, 5502.
9 I. Gruda and R. M. Leblanc, *Can. J. Chem.*, 1976, **54**, 576.