# Solvent and Pressure Dependence of the Energy Profile for the Thermal Fading of a Merocyanine Formed from a Spironaphthoxazine

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Activation volumes, activation enthalpies and activation entropies were measured for the thermal fading of a merocyanine formed from a spironaphthoxazine in methyl acetate and ethanol. All of the activation parameters clearly demonstrated that the energy profile was different in these two solvents.

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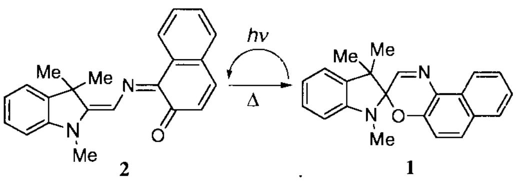
Spirooxazines are known to be photochromic, i.e., they are converted to colored merocyanines under the irradiation of UV light and the merocyanine thermally returns to the original spiro species in the dark. Although various studies have been published on the photochemical ring-opening processes and structures of merocyanines,[1–4] relatively little is known about the thermal ring closure process. As a part of our dynamic route studies of solution reactions,[5] we measured kinetic effects of pressure on the fading of a merocyanine **2** formed from 1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3'-[3*H*]naphth[2,1-*b*][1,4]oxazine] **1** (Scheme 1) in ethanol and methyl acetate and the results are going to be reported in this letter.



**Scheme 1.**

The spironaphthoxazine **1** was a commercial product (Aldrich) and used without further purification. High-pressure setup was similar to the one reported earlier.[6] Solution of **1** was kept in a quartz inner cell which is connected to a pressure-transmitting device and set in the center of a high-pressure optical vessel. The merocyanine **2** was photochemically generated in situ and its decay was followed spectrophotometrically. At all of the conditions studied, the reaction followed the first-order rate law.

The observed rate constants are plotted against pressure in Figure 1. As can be seen clearly from the Figure, the reaction was slower in ethanol and the pressure dependence of the rate was qualitatively different in these two solvents. Namely, in methyl acetate, the reaction was slightly accelerated with increasing pressure at atmospheric pressure ($\Delta V^{\neq} = -1$ to $-3$ cm$^3$ mol$^{-1}$). At higher pressures, however, a pressure increase resulted in small but clear retardations ($\Delta V^{\neq} = 1$ to $2$ cm$^3$ mol$^{-1}$). In ethanol, on the other hand, the reaction was characterized by modest positive activation volumes ($\Delta V^{\neq} = 3$ to $8$ cm$^3$ mol$^{-1}$) throughout the whole pressure range studied. The activation enthalpies and activation entropies at various pressures estimated from the results in Figure 1 are listed in Table 1. Obviously, the reaction was slower in ethanol because of a larger activation enthalpy. These results demonstrate unequivocally that the reaction mechanism is sensitive to the nature of the solvent and pressure.

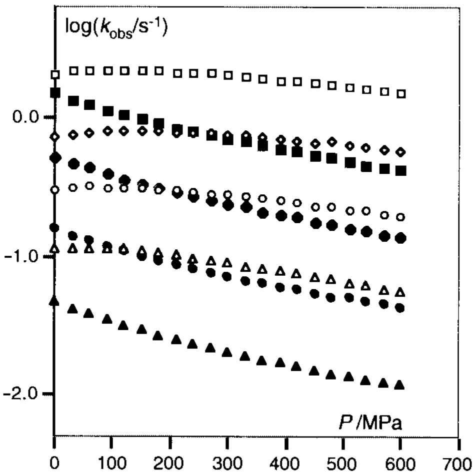
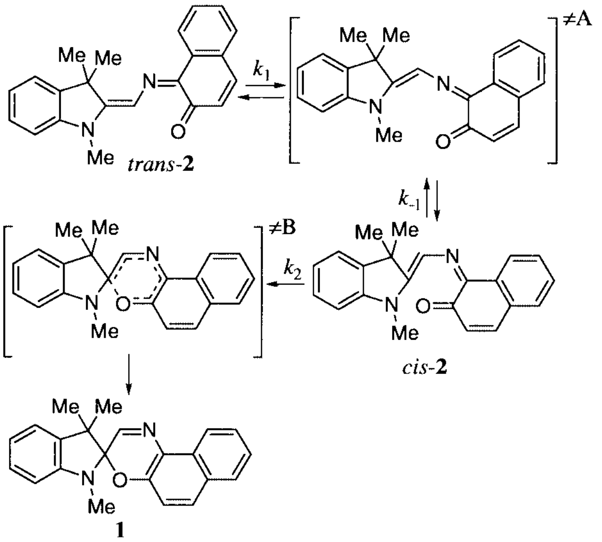


**Figure 1.** Pressure effects on the fading rate of a merocyanine **2** formed from a spirooxazine **1** in methyl acetate and ethanol. (open symbols: methyl acetate, filled symbols: ethanol). □ ■; 35 °C, ◇ ◆; 25 °C, ○ ●; 15 °C, △ ▲; 5 °C.

**Table 1.** Activation enthalpies ($\Delta H^{\neq}$/kJ mol$^{-1}$) and activaton entropies ($\Delta S^{\neq}$/J K$^{-1}$ mol$^{-1}$) for the fading of **2** in methyl acetate and ethanol at various pressures.

| | Methyl acetate | | Ethanol | |
|---|---|---|---|---|
| *P* /MPa | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ |
| 0.1 | 66 | -26 | 81 | 22 |
| 150 | 68 | -19 | 82 | 22 |
| 300 | 71 | -8 | 83 | 22 |
| 450 | 74 | -1 | 84 | 22 |
| 600 | 76 | 5 | 84 | 20 |

In the merocyanine, eight geometrical isomers are conceivable about the C–C, C–N, and N–C bonds connecting the two ring systems. However, four of them with *cis*-conformation with respect to the central C–N bond are sterically crowded and their equilibrium concentrations would be negligibly low. According to the quantum mechanical calculations by Nakamura and his co-workers,[4] the most stable isomer was the one with a *tran-trans-cis* (TTC) conformation shown in Scheme 1. The CTC isomer was the second most stable with an energy ca. 8 kJ mol$^{-1}$ above the TTC. The TTT and CTT isomers were ca. 40 kJ mol$^{-1}$ less stable than the TTC. Therefore, **2** is expected to exist mostly as the TTC isomer. This expectation was confirmed by $^1H$ NMR spectra of **2** in methanol-$d_4$.[4] Although a zwitterionic structure can be drawn for **2**, the charges on the carbonyl oxygen and the relevant bond lengths supported a predominant contribution of a keto-structure to **2**.[4]



**Scheme 2.**

In order to form a spiro structure, two structural transformations shown in Scheme 2 must take place, i.e., a rotation around the central C–N bond followed by a ring closure. Since *cis*-**2** must be highly unstable, a steady state may be assumed and the observed rate constant would be given by eq 1.

$$k_{obs} = \frac{k_1 k_2}{k_{-1} + k_2} \qquad (1)$$

If ≠A is higher in its energy than ≠B, $k_{obs} \approx k_1$ and the activation volume would be a volume difference between ≠A and *trans*-**2**. If ≠B is higher, $k_{obs} \approx k_1k_2/k_{-1}$ and the activation volume would be a volume difference between ≠B and *trans*-**2**. The volume of ≠A is expected to be slightly smaller than that of *trans*-**2** because of the increased steric crowding[7] while ≠B is expected to show a larger partial molar volume than *trans*-**2** because solvent molecules which solvate the carbonyl group must be desolvated before the carbon–oxygen bond formation.[8] Slower reaction, positive activation volumes and larger activation enthalpies and activation entropies in ethanol are all in accordance with this consideration because the carbonyl group must be solvated strongly in ethanol and *trans*-**2** is more stabilized than in methyl acetate. These hydrogen-bonded solvent molecules will keep their ties to the oxygen atom during the first activation step to *cis*-**2**. However, they must be desolvated in the second step. Therefore, the energy of ≠B would be higher than that of ≠A in ethanol and this would result in a slower reaction with a positive activation volume and a positive activation entropy. In methyl acetate, solvation of the carbonyl group must be much more weaker and the first step may be rate-determining. The whole situation is schematically illustrated in Figure 2. The rate-determining step shifts from the first step in methyl acetate to the second step in ethanol. The inversion of the pressure effect in methyl acetate at around 100 MPa as well as larger activation enthalpies and activation entropies at higher pressures in the same solvent can be rationalized as indications of a pressure-induced enhancement of solvation of **2**. Measurements in other solvents are in progress and the results will be reported when they are completed.

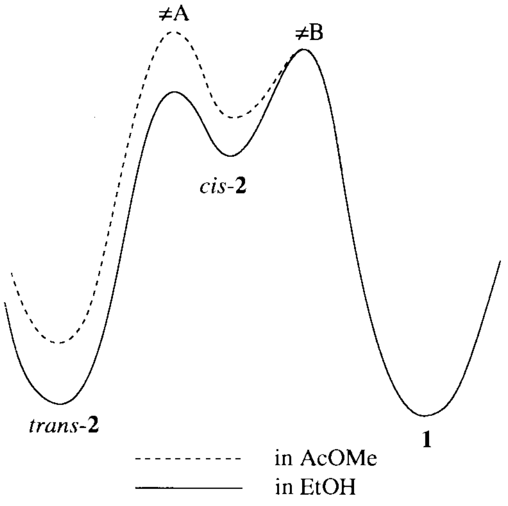


**Figure 2.** A schematic illustration of the energy profiles in ethanol and methyl acetate.

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