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Kinetic Studies of Solvent and Pressure Effects on Thermochromic Behavior of 6-Nitrospiropyran

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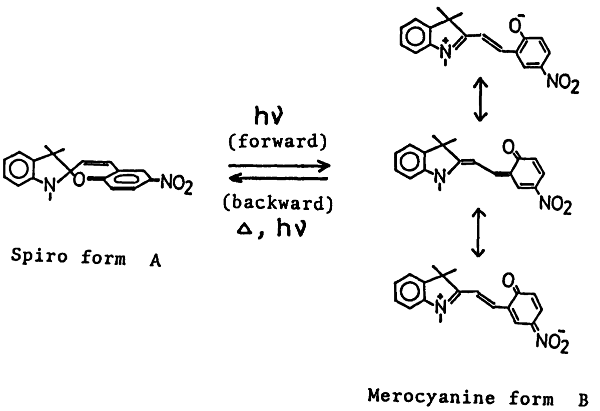
The thermal conversion of 6-nitrospiropyran from a merocyanine form to a spiro form was studied in various solvents and under high pressures. The rates of the thermal conversions were remarkably retarded in polar solvents, and a Kirkwood plot of the rate constants showed a large downward deviation as the solvent polarity increased. The rate constants (on a logarithmic scale) were linearly related to Kosower's *Z*-values. The values of the activation volumes were positive and divided into two groups: $\Delta V^{\neq}\approx 10\,\text{cm}^3\,\text{mol}^{-1}$ (in nonpolar solvents) and $\Delta V^{\neq}\approx 20\,\text{cm}^3\,\text{mol}^{-1}$ (in polar solvents). These findings suggest that for the reaction in polar solvents, specific interactions are operating and that the thermal conversion proceeds *via* a transition state which is much less polar than the initial state.

The photochromism and thermochromism of 1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (6-nitrospiropyran) have been recognized as the equilibrium between stable colorless and metastable colored forms (Scheme 1).[1]



Scheme 1.

The absorption of light transforms the colorless form **A** having reciprocally orthogonal indoline and pyran rings into the colored form **B** having the structure of a merocyanine dye. This merocyanine form is considered as characterized by the coplanarity of the molecular skeleton. In the dark, form **B** thermally isomerizes to form **A**.[1] However, in spite of the fact that there have been some studies regarding the thermochromism of 6-nitrospiropyran, the mechanism of the thermal conversion (**B**→**A**) in relation to the polarity of the transition state has not been well established yet.

Very recently, we reported[2] that in the isomerization of 4-dimethylamino-4′-nitroazobenzene (NDAAB), the activation volumes ($\Delta V^{\neq}<0$) tend to negatively increase with an increase in the solvent polarity. This trend regarding the pressure effect is just the reverse of that for some ionic reactions such as Menschutkin reactions.[3] We suggested, therefore, that this might be due to the dipole induced by polar solvents. Form **B** in Scheme 1 is electronically similar to *trans*-push-pull azobenzenes in the sense that the conjugation band shows remarkable shifts.[4] Therefore, it is of great interest to investigate the kinetic solvent effects of 6-nitrospiropyran and to compare these with those of push-pull azobenzenes such as NDAAB.

This work has been undertaken from such a point of view and a discussion regarding the electronic structure of the transition state is presented.

Experimental

Reagent. 1′,3′,3′-Trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (6-nitrospiropyran) was purchased from Tokyo Chemical Industry Co. and was used as received; mp 179—180 °C (lit,[5] 179—180 °C).

Solvents. All the chemicals were of reagent grade. Hexane, cyclohexane, dioxane, and benzene were purified by drying over sodium wire and distillation. Chloroform, acetone, and acetonitrile were dried over calcium chloride, calcium sulfate, and calcium hydride, respectively, and distilled. *N,N*-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were dried over molecular sieves (Type 4A) and calcium hydride, respectively, and distilled under reduced pressure.

Apparatus and Procedure. The high-pressure techniques and procedures for kinetic measurements were the same as those described elsewhere.[2] The sample solution (*ca.* $10^{-4}\,\text{mol}\,\text{dm}^{-3}$) was irradiated with a Toshiba H400-P mercury arc through an interference filter (Toshiba UV-D33D) to produce **B**. The thermal return was monitored by the change in the maximum absorption in the vicinity of 600 nm (**B**) by means of a Hitachi 139 spectrophotometer.

Results

The wavelengths at the maximum absorption of **B** of 6-nitrospiropyran and first-order rate constants in various solvents are given in Table 1, together with the activation parameters. The pressure dependence of the rate constants was treated by a quadratic equation (Eq. 1). The rate constants under high pressures and the activation volumes ($\Delta V^{\neq}$) at atmospheric pressure were estimated according to Eq. 2 and are given in Table 2.

TABLE 1. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE THERMAL CONVERSION OF 6-NITROSPIROPYRAN (PROBABLE ERRORS IN PARENTHESES)

	Solvent	Kosower's Z-values[a)]	$\lambda_{\max}$	$10^3\,k/\mathrm{s}^{-1}$						Ea	$\Delta S^{*}_{303\,\mathrm{K}}$
		kJ mol^{-1}	nm	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	kJ mol^{-1}	J K^{-1} mol^{-1}
1	Hexane	252	620, 565	28.1 (1.3)	47.7 (0.2)	78.4 (0.3)	130 (1)			76.4 (0.5)	−22.3 (1.6)
2	Cyclohexane	262	615, 585	20.8 (0.3)	37.6 (0.4)	73.1 (0.1)	105 (2)			83.0 (4.0)	−2.1 (13.2)
3	Dioxane	—	590	32.8 (0.1)	56.6 (0.4)	96.6 (0.1)	153 (1)			77.4 (0.8)	−17.6 (2.8)
4	Benzene	261	600	42.6 (0.1)	66.2 (1.8)	123 (1)	166 (1)			70.6 (3.9)	−38.6 (12.8)
5	Chloroform	264	580		21.9 (0.2)	40.0 (0.4)	79.1 (0.2)	137 (1)		95.9 (1.7)	36.6 (5.7)
6	Acetone	275	565		7.22 (0.04)	12.5 (0.2)	27.2 (0.1)	48.6 (0.2)		101 (4)	43.3 (11.7)
7	DMF	287	560		1.55 (0.07)	3.21 (0.02)	5.49 (0.02)	10.1 (0.1)		96.2 (2.3)	15.9 (7.7)
8	Acetonitrile	298	555		2.99 (0.09)	5.61 (0.02)	11.8 (0.1)	22.3 (0.1)		105 (2)	50.4 (6.7)
9	DMSO	298	550			0.997 (0.009)	1.92 (0.01)	3.56 (0.02)	6.53 (0.04)	101 (1)	21.2 (1.2)

a) Values taken from Ref. 18.

TABLE 2. RATE CONSTANTS AND ACTIVATION VOLUMES FOR THE THERMAL CONVERSION OF 6-NITROSPIROPYRAN AT 30 °C (PROBABLE ERRORS IN PARENTHESES)

	Solvent	$10^3\,k/\mathrm{s}^{-1}$						ΔV^{*}
	p/kg cm^{-2} [a)]	1	100	200	400	800	1200	cm^3 mol^{-1}
1	Hexane	78.4 (0.3)			64.6 (0.1)	58.5 (0.3)	53.1 (0.3)	12.8
2	Cyclohexane	73.1 (0.1)	69.9 (0.2)	68.4 (0.2)	63.2 (0.2)			9.4
3	Dioxane	96.6 (0.1)			84.1 (0.1)	71.2 (0.1)	62.4 (0.1)	9.8
4	Benzene	123(1)		118(3)	113(1)	110(1)		6.5
5	Chloroform	40.0 (0.4)			31.4 (0.1)	27.0 (0.1)	22.6 (0.4)	15.1
6	Acetone	12.5 (0.2)			9.61 (0.02)	7.33 (0.05)	5.88 (0.05)	19.5
7	DMF	3.21 (0.02)			2.45 (0.02)	2.06 (0.02)	1.72 (0.02)	17.5
8	Acetonitrile	5.61 (0.02)			4.18 (0.02)	3.17 (0.02)	2.60 (0.01)	21.2
9	DMSO	0.997 (0.009)			0.791 (0.010)	0.670 (0.002)	0.577 (0.003)	15.6

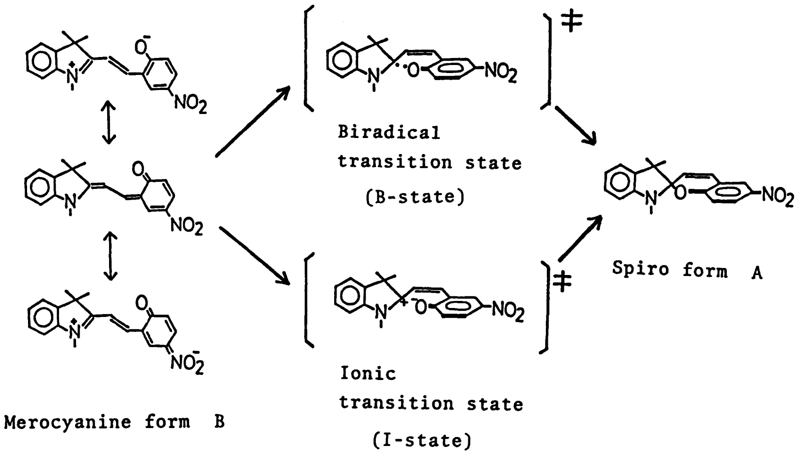
a) 1 kg cm^{-2} = 0.9807 × 10^5 Pa.

$$\ln k = a + bp + cp^2 \qquad (1)$$

$$\Delta V^{*} = \left(\frac{\partial \ln k}{\partial p}\right)_{T,\,p=1} \approx -bRT \qquad (2)$$

Discussion

Regarding the thermal conversion (**B**→**A**) of 6-nitrospiropyran, there are a few reports.[1)] For example, Metras *et al.*[6)] reported that the competitive ring-closure reaction takes place *via* either of the two conformational isomers. Meanwhile, Arnaud *et al.*[7)] inferred the existence of four conformational isomers, and pointed out that a rapid equilibrium is established among them at room temperature and that the thermal conversion from **B** to **A** proceeds from one of them. A similar discussion has been presented by Tamagake *et al.*[8)] who suggested eight possible conformational isomers. On the other hand, Flannery, Jr.[9)] suggested that a rate-determining step (in polar solvents) is the dissociation of a dimer or of



Scheme 2.

a solute-solvent complex.

As far as we examined the electronic spectrum and the time-dependence of its intensity in the dark, any evidence to support the above suggestions has not been found. The visible absorption spectra in alkanes consist of two bands (Table 1). From the temperature dependence of the intensities of these bands, Heiligman-Rim *et al.*[10] concluded that the bands could be ascribed to two different conformational isomers, not to the vibrational structure for a single species. In fact, the relative rate of the disappearance of these bands at any time was constant, indicating that a rapid equilibration between the two isomers had been attained before the ring-closure reaction (**B**→**A**) occured. Judging from the spectral shifts of merocyanine dyes,[11] the band in the vicinity of 620 nm in alkanes could be ascribed to the conformational isomer that dominantly exists in polar solvents (the structure has not been clarified yet). However, even if the reaction proceeds from one of the conformational isomers, there are two possible routes (Scheme 2): One involves the homolytic fission of the bond between the spiro C atom and the pyran oxygen to produce a biradical transition state (B-state) and the other involves a heterolytic fission to produce an ionic transition state (I-state). Since the thermal conversion from **B** to **A** is a Cyclization reaction, it is natural to assume these cyclic transition tates. In the transition state, the delocalization of the π-electrons, substantiated in form **B**, becomes impossible since the indoline and pyran parts of the molecule are reciprocally orthogonal. Accordingly, the I-state must be zwitterionic such as the products of the Menschutkin reaction.[3] In order to clarify which of these routes is more consistent with the experimental observations, we have examined the kinetic solvent and pressure effects regarding the thermal conversion.

Solvent Effects. Figure 1 shows an Ea *vs.* $\Delta S^{\neq}$ plot. Though Ea and $\Delta S^{\neq}$ do not necessarily line up in the order of the dielectric constants of the solvents and a scatter is observed, it could be said that the linear free energy relationship[12] roughly holds. If the reaction of this system proceeds by a competitive mechanism[6] and the mechanism continuously varies with solvent polarities,[9] the Ea–$\Delta S^{\neq}$ plot might be curved. From the plots, such an indication is not observed.

On the basis of the Kirkwood treatment,[13] the dielectric influence of solvents on the rate constants for unimolecular reactions is given by

$$\ln k = \ln k_0 + \frac{N}{RT}\left(\frac{\mu_{\neq}^2}{r_{\neq}^3} - \frac{\mu^2}{r^3}\right)\left(\frac{\varepsilon-1}{2\varepsilon+1}\right), \tag{3}$$

where notations have their usual meanings. If the $(\mu_{\neq}^2/r_{\neq}^3-\mu^2/r^3)$-term is independent of the solvent polarity, a linearity between $\ln k$ and $(\varepsilon-1)/(2\varepsilon+1)$ is expected and the slope can be regarded as a measure of the change in the dipole moment upon activation. As shown in Fig. 2, the linearity is poor. Very recently, a similar nonlinear behavior of the Kirkwood plot was reported by Asano and Okada[14] for the thermal *cis*-to-*trans* isomerization of NDAAB: The plot becomes nonlinear when the points for all polar solvents are included. Asano and Okada interpreted this in terms of a mechanism change from inversion to rotation. According to our view,[2] however, such a behavior is not due to the intervention of a competitive reaction but arises due to the neglect of the induced dipole in the polar solvents. The solvent-induced dipole moment is not involved in the Kirkwood treatment.

Recently, ^{1}H- and ^{13}C-NMR spectroscopy have been applied to the problem of the electronic structure of the molecules having a conjugation system. For instance, on the basis of the ^{1}H-NMR spectral shifts in various solvents, Mottaleb and Kader[15] interpreted their shifts as an indication of a solvent-induced change in the electronic structure. Moreover, in a

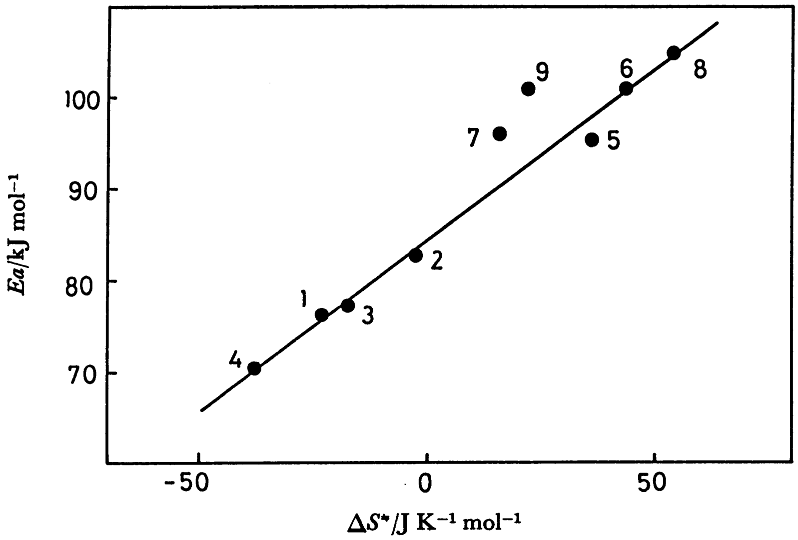


Fig. 1. Ea-ΔS^{*} relationship for the thermal conversion of 6-nitrospiropyran at 30 °C; correlation coefficient r 0.964.

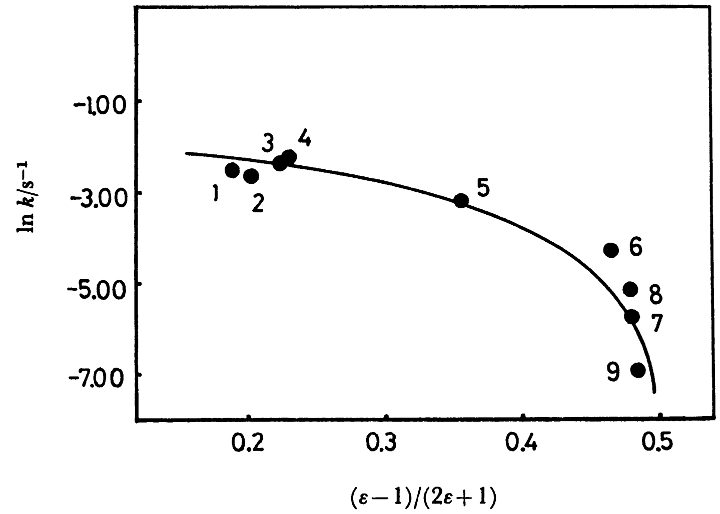


Fig. 2. The Kirkwood plot for the thermal conversion of 6-nitrospiropyran at 30 °C; correlation coefficient r −0.909.

theoretical investigation through the CNDO/S-CI method (including solvation for 4-[2-(1-methyl-4-pyridinio)ethenyl]phenolate which has a large π-electron system) Botrel *et al.*[16] showed a significant increase in the dipole moment with an increasing solvent polarity, and pointed out that it is important to take account of the change in the dipole moment induced by surrounding solvents. These are in accordance with our view.

In this connection, we considered that scales involving solute-solvent interactions at molecular levels would be better than a macroscopic dielectric constant in order to analyze the reaction-rate data. Whitten *et al.*[17] examined the relationship between the activation parameter $\Delta G^{\neq}$ of the thermal *cis*-to-*trans* isomerization of 4-diethylamino-4′-nitroazobenzene and the empirical scales (Koswer's Z-values, the Taft π^{*} parameter *etc.*), and have shown that they are linearly related (as a whole). We also have tentatively plotted ln k against Kosower's Z-values[18] (Fig. 3). Although a considerable scatter is observed (as in the case of azobenzenes shown in Ref. 17) the linearity is much improved over the Kirkwood plot. We could say, therefore, that for reactions where the change in the delocalization of π-electrons upon activation plays an important role, these empirical scales are better than the macroscopic ε-scale, although the choice of those scales is somewhat arbitrary.

In any case, the reaction rates were remarkably retarded in polar solvents (Table 1). If a biradical mechanism (Scheme 2) is assumed for the reaction, the transition state may be less polar than the initial one. This accounts for the above observations. On the contrary, if the reaction proceeds *via* the I-state,

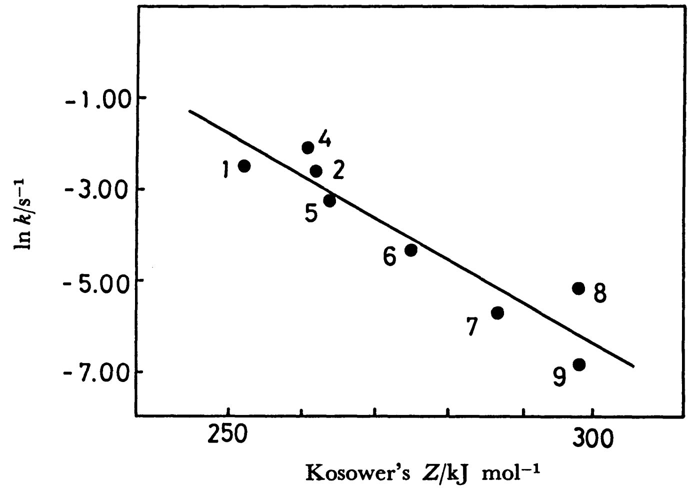


Fig. 3. ln k (at 30 °C) *vs.* Kosower's Z-values; correlation coefficient r -0.931.

an acceleration of the reaction rate is expected in analogy with the case of the Menschutkin reaction.[3] This is against the experimental observations.

Pressure Effects. The activation volume ($\Delta V^{\neq}$) is given (after differentiating Eq. 1 with respect to pressure) by,

$$\Delta V^{\neq} = \Delta V_0^{\neq} - N\left(\frac{\mu_{\neq}^2}{r_{\neq}^3} - \frac{\mu^2}{r^3}\right)\frac{3}{(2\varepsilon+1)^2}\left(\frac{\partial\varepsilon}{\partial p}\right)_T \qquad (4)$$

where $\Delta V_0^{\neq}$ is the difference in the intrinsic volume of a reaction molecule between the initial and the transition states. The second term represents the change in volume due to solvation or electrostriction. In our case, if the thermal conversion (**B**→**A**) proceeds *via* the cyclic transition state, it may safely be considered that the change in the intrinsic volume ($\Delta V_0^{\neq}$) accompanying cyclization upon activation is similar to the activation volume of the Claisen rearrangement reaction,[19] which is considered not to involve a volume change due to electrostriction. The reported activation volumes are about -15 cm^3 mol^{-1} for the Claisen rearrangement reaction.[19] If the reaction proceeds *via* the zwitterionic transition state, solvent may be constricted upon activation, as exemplified by the Menschutkin reaction.[3] Accordingly, the value for the activation volume ($\Delta V^{\neq}$) is large and negative, as expected from Eq. 4. On the contrary, if the biradical mechanism is assumed for the reaction, a positive activation volume is expected due to the release of electrostricted solvent molecules, as Stwart and Weale[20] reported for the reverse Menschutkin reaction ($\Delta V^{\neq}$=45 cm^3 mol^{-1}). As can be seen in Table 2, the activation volumes obtained are all positive and divided roughly into two groups: $\Delta V^{\neq}\approx 10$ cm^3 mol^{-1} (in nonpolar solvents) and $\Delta V^{\neq}\approx 20$ cm^3 mol^{-1} (in polar solvents). Therefore, the biradical mechanism is more favorable than the ionic one.

On the assumptions of the biradical mechanism and $\Delta V_0^{\neq}\approx -15$ cm^3 mol^{-1}, the activation volume can be estimated according to Eq. 4. In benzene, by substituting the numerical values (μ=12.7 Debye,[21] $\mu_{\neq}\approx 0$ Debye, r=4 Å (the distance between >N– and the nitro group), and $[3/(2\varepsilon+1)^2](\partial\varepsilon/\partial p)_T = 15\times10^{-11}$ Pa^{-1} at 30 °C[22]) into Eq. 4, the change in volume due to desolvation is calculated to be 23 cm^3 mol^{-1}. Therefore, the total volume change ($\Delta V^{\neq}$) is calculated to be 8 cm^3 mol^{-1}. Similarly, the activation volume in hexane ($[3/(2\varepsilon+1)^2](\partial\varepsilon/\partial p)_T = 19.4\times10^{-11}$ Pa^{-1} at 30 °C[22]) is estimated to be 14 cm^3 mol^{-1}. As may be seen in Table 2, these estimated values are approximately in accordance with the experimental ones. Similarly, the activation volume in acetone can be estimated as -7.7 cm^3 mol^{-1} ($[3/(2\varepsilon+1)^2](\partial\varepsilon/\partial p)_T = 4.82\times10^{-11}$ Pa^{-1} at 30 °C[22]). This value is extremely small compared with the observed one. The large discrepancy between the calculated and observed $\Delta V^{\neq}$-values in acetone may be ascribed to a change in the μ-term in Eq. 4 upon increasing the polarity of the solvent. In a previous section, we considered that the B-state is plausible and the extra dipole moment of form B with an ionic resonance structure is induced in polar solvents. The large positive $\Delta V^{\neq}$-value in acetone may be resposible for the increase in the dipole moment. The same trend has been observed for the thermal *cis*-to-*trans* isomerization of push-pull azobenzenes. The common situation is that a remarkable polarization through the delocalization of the π-electrons is considered to be substantiated both in the ground state (present case) and in the transition state (case of push-pull azobenzenes), and that the contribution of the polarized canonical resonance form is reinforced by polar solvents, in agreement with other evidence.[15,16] The large $\Delta V^{\neq}$-values in polar solvents can be qualitatively explained by this reasoning.

In conclusion, the kinetic solvent and pressure effects are in favor of the biradical mechanism *via* the less-polar transition state for the thermal conversion (**B**→**A**) of 6-nitrospiropyran and against the ionic one *via* the polar transition state.

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