Bull. Chem. Soc. Jpn., 62, 1777—1780 (1989)

Thermal Isomerization of 1′,3′,3′-Trimethyl-8-nitrospiro-[2*H*-1-benzopyran-2,2′-indoline]-6-carboxylic Acid

Norio Nishimura,* Jun'ichi Miyake, and Yoshimi Sueishi
Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700

(Received January 5, 1988)

The rates of thermal isomerization of 1′,3′,3′-trimethyl-8-nitrospiro[2*H*-1-benzopyran-2,2′-indoline]-6-carboxylic acid (6-COOH-8-NO_2-SP) from its spiro form (SP) to its merocyanine form (MC) have been measured in some solvents and at high pressures. The equilibrium constants between these isomers at atmospheric pressure and at 30 °C are in the range of 0.25 to 2.52 depending on solvents. The activation volumes are 0.2—3.4 $cm^3 mol^{-1}$, while the reaction volumes are −7.9—−22.3 $cm^3 mol^{-1}$. Thus the volume profile was found to have a maximum, as predicted previously.

Thermochromic materials have attracted attention for many years. Recently, interest has been stimulated due to their practical applications to thermal copies, optical switches and displays. Spiropyrans belong to the most important class of the organic photochromic compounds which are used as light-sensitive materials. In spite of their practical interests, a little work focused on the mechanism of the photo and thermal isomerization of spiropyrans between SP and MC has been done.[1-5]

Recently we have studied the solvent and pressure effects on the rate of thermal conversion of 1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (6-NO_2-SP)[6] from MC to SP, and of 1′,3′,3′-trimethyl-spiro[2*H*-1-benzopyran-2,2′-indoline]-8-carboxylic acid (8-COOH-SP)[7] from SP to MC. The role of solvent-induced solute (MC) dipole has been discussed. The volume profile predicted with the help of these compounds has a maximum which is rarely found in chemical reactions. It has been concluded that these compounds probably isomerize via the same reaction path, i.e., via a transition state involving homolytic bond fission or bond formation, rather than via a heterolytic transition state.

The present work has been undertaken to ascertain if such a maximum really exists in the volume profile. We have used 6-COOH- 8-NO_2-SP for which SP and MC are in thermal equilibrium in the dark, and this made the estimation of equilibrium constant possible at any temperatures and pressures. The kinetic and thermodynamic quantities for the isomerization reaction are presented and the energy and volume profiles drawn.

Experimental

Materials. Utilizing the Reimer-Tiemann reaction, 3-formyl-4-hydroxybenzoic acid was prepared according to the method of Wynberg:[8] 4-hydroxybenzoic acid (0.1 mol) was refluxed for an hour with water (90 cm^3), KOH (1 mol), and chloroform (0.125 mol). After acidification and ether extraction, a brown solid 3-formyl-4-hydroxybenzoic acid was obtained. Nitration of this compound was carried out at temperatures between −5 and −10 °C. The precipitate, 3-formyl-4-hydroxy-5-nitrobenzoic acid, was recrystallized from 2-propanol; mp 217—219 °C. Equimolar amounts of this compound and 1,3,3-trimethyl-2-methylene indoline were dissolved into ethanol and the solution was refluxed for two hours. A dark precipitate 6-COOH-8-NO_2-SP was collected and dried. This compound is sparingly soluble in most solvents, and no further purification has been tried. However, its ^{1}H NMR spectrum in DMSO-d_6 showed that this compound is clearly an isomeric mixture of SP and MC in solution; δ=1.12, 1.25 (s, 3′-CH_3), 2.67 (s, $\rangle$N-CH_3) for SP; δ=1.74 (s, 3′-CH_3), 3.91 (s, $\rangle$N-CH_3) for MC. For spectral assignments, a report of Toppet et al. was referred.[9] Solvents used are of reagent grade and purified and dried in the usual manner.

Procedure. High pressure techniques and procedures for kinetic measurements were almost the same as those described before.[10] A sample solution (ca. 10^{-4} mol dm^{-3}) flushed with nitrogen gas was irradiated for a few seconds with a projection lamp. The thermal return from SP to MC was followed by monitoring the change in the absorbance in the vicinity of 560 nm using a Hitachi 139 spectrophotometer. The half life of the reaction was of the order of 10^3 s, and the absorbance at $t=\infty$ was estimated so that the first-order plot produced a best straight line. The photo and thermal isomerizations could be carried out reproducibly, and the apparent first-order rate constants (see Eq. 2 below) agreed within 5% error.

Results

Although conformational problems[3-5,11] remain for MC, the thermal equilibrium of 6-COOH-8-NO_2-SP between SP and MC can simply be represented as

$$\mathrm{SP} \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{MC} \qquad (1)$$

Upon irradiation of the visible light, the equilibrium shifts to SP, and it returns to the original state in the dark.

In order to determine the concentrations of the isomers, it is necessary to know the molar absorptivity of MC. First, the equilibrium constant at 25 °C in DMSO-d_6 was estimated by means of ^{1}H NMR technique; the ratio of the integrated intensities of 3′-methyl protons in MC snd SP was regarded as the equilibrium constant (K=2.83 at 25 °C). From this

Table 1. Equilibrium Constants of 6-COOH-8-NO_2-SP between MC and SP at Various Pressures and Volumes of Reaction

Solvent	λ_{max}/nm	K (30 °C)						ΔV°	ΔV_{solv}	$10^{11}q_p$[a]	ΔV_{solv}[b]
	p/kgf cm^{-2}[c]	1	200	400	600	800	1200	cm^{3}mol^{-1}	cm^{3}mol^{-1}	Pa^{-1}	cm^{3}mol^{-1}
$CHCl_3$	573	0.250		0.312		0.383	0.454	−15.6	−30.6	15.9(30 °C)	−32.5
1,2-Dichloroethane	566	0.299		0.389		0.484	0.571	−18.6	−33.6	12.1(30 °C)	−24.7
Acetone	565	0.314		0.431		0.546	0.653	−22.3	−37.3	6.02(35 °C)	−12.3
DMSO	555	2.52	2.62	2.80	2.84			−7.9	−22.9	1.2[d]	−1.8

a) Original q_p-values (Refs. 14,15) calculated on the basis of the Tait-type equation, $q_p=A/(B+p)$, are about twice as large as ours. We have estimated $(\partial\varepsilon/\partial p)_{T,p=0.1\ \mathrm{MPa}}$ from the quadratic regression equation, $\varepsilon=ap^2+bp+c$. b) Calculated by using Eq. 7. c) 1 kgf cm^{-2}=9.81×10^4 Pa. d) Estimated by assuming $(\partial\varepsilon/\partial p)=$ 3×10^{-8} Pa^{-1} (see text).

K-value and the absorbace at 555 nm (λ_{max} of MC), the molar absorptivity was estimated to be 33000 dm^3 mol^{-1} cm^{-1}. This value could be used for other solvents without substantial danger, since the spectral shapes in the visible region in different solvents are almost the same.

It was found that the return rate follows the first-order kinetics, as expressed by Eq. 2.

$$\mathrm{d}[\mathrm{MC}]/\mathrm{d}t = k_{obsd}([\mathrm{MC}]_\infty - [\mathrm{MC}]) \quad (2)$$

where $[\mathrm{MC}]_\infty$ is the concentration of MC at equilibrium and k_{obsd} ($=k_f+k_b$) is the apparent rate constant. The equilibrium constant K is given by

$$K = [\mathrm{MC}]_\infty/[\mathrm{SP}]_\infty = k_f/k_b \quad (3)$$

Using K and k_{obsd}, k_f and k_b were calculated. These values at various pressures and temperatures are given in Tables 1—3.

The pressure dependence of the equilibrium constant was approximated by the following quadratic equation:

$$\ln K = ap^2 + bp + c \quad (4)$$

Discussion

The reaction volumes (ΔV°) at atmospheric pressure were estimated by

$$\Delta V^\circ = (\partial \ln K/\partial P)_T \cong -bRT \quad (5)$$

and they are given in Table 1. The activation volumes for the forward and backward reactions (Eq. 1) estimated by similar equations are given in Table 2. Using the data in Tables 1—3, $\ln K$, $\ln k_f$, and $\ln k_b$ were plotted against $1/T$ in accordance with the van't Hoff and Arrhenius equations (Fig. 1, r=0.998 each). From these plots, thermodynamic parameters were estimated and they are given in Table 4. The equilibrium constant in DMSO, compared with those in other solvents (Table 1) is greater by about a factor of ten, indicating the increased stabilization of MC relative to SP. The band in the visible region shifts to a shorter wavelength as the solvent polarity increases (blue shift). This inclination was also observed for 6-NO_2-SP.[6] There are some spiropyrans which exhibit

Table 2. Pressure Dependence of the Rate Constants for the Forward and Backward Reactions at 30 °C

Solvent	10^4k_f						$\Delta V^{\neq}$
	s^{-1}						cm^{3}mol^{-1}
P/kgf cm^{-2}	1	200	400	600	800	1200	
$CHCl_3$	3.52		3.45		3.38	3.28	1.0
$C_2H_2Cl_2$	2.07		2.11		2.09	2.04	−1.7(3.4)[a]
Acetone	1.87		1.85		1.82	1.76	0.2
DMSO	6.25	6.07	5.96	5.85			3.8
	10^4k_b						
	s^{-1}						
$CHCl_3$	14.1		11.1		8.83	7.22	16.2
$C_2H_2Cl_2$	6.93		5.44		4.33	3.58	16.7
Acetone	5.96		4.30		3.34	2.70	22.3
DMSO	2.48	2.32	2.13	2.06			11.5

a) Obtained by the linear regression equation.

Table 3. Temperature Dependence of K, k_f/s^{-1}, and k_b/s^{-1}

Solvent		25 °C	30 °C	35 °C	40 °C	45 °C
$CHCl_3$	K	0.275	0.256	0.228	0.210	0.192
	10^4k_f	1.64	3.08	6.29	10.3	16.8
	10^4k_b	5.95	12.0	27.6	49.1	87.2
DMSO	K	2.83	2.53	2.38	2.22	2.06
	10^4k_f	3.11	5.65	11.4	20.8	35.9
	10^4k_b	1.10	2.23	4.79	9.35	17.4

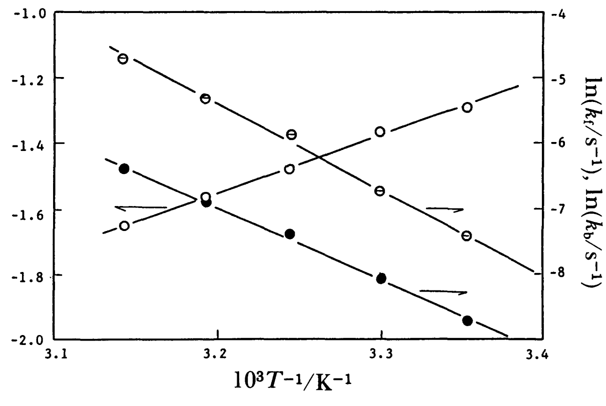
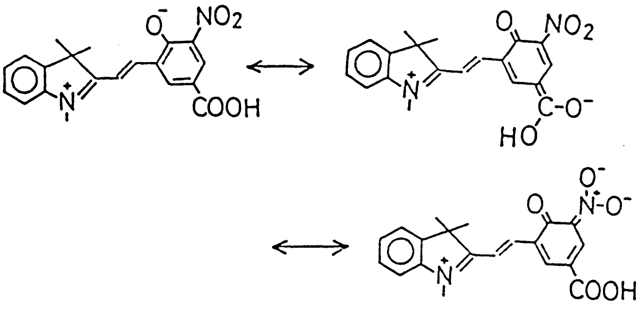


Fig. 1. The van't Hoff and Arrhenius plots for the thermal equilibration process of 6-COOH-8-NO_2-SP in $CHCl_3$: $\ln K$−1/T (○); $\ln k_f$−1/T (●); $\ln k_b$−1/T (⊖).

Table 4. Thermodynamic Quantities (303.2 K) for the Reaction SP $\rightleftarrows$ MC

Solvent	ΔH°	ΔS°	ΔV°	E_a	$\Delta S^{\neq}$	$\Delta V^{\neq}$	Remark
	kJ mol^{-1}	J mol^{-1} K^{-1}	cm^3 mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	cm^3 mol^{-1}	
CHCl$_3$	−14.5	−59	−15.6	92.9	−13.9	1.0	Forward
				107.4	45.1	16.2	Backward
DMSO	−12.0	−32	−7.9	98.1	8.7	3.8	Forward
				109.7	40.3	8.3	Backward

the red shift.[12] Although this band may be assigned to the conjugation band (intramolecular charge-transfer band) through one of the possible conformations of MC,[5] the blue shift is contrary to the general trend of the π-π^* transition which exhibits the red shift. Therefore, the ground state of MC must be more polar than the excited state. In fact, the dipole moments of 6-NO$_2$-SP in the ground and excited states are reported to be 12.7 and 3.5 Debye (1 Debye= 3.34×10^{-30} mC), respectively.[13] A substantial contribution of the following zwitterionic structures in the ground state may be responsible for the above findings.



The Volume of Reaction. Volume change accompanied by chemical reactions is conventionally divided into two terms: an intrinsic volume change (ΔV_{int}) and a volume change arising from reorganization of solvent molecules (ΔV_{solv}), i.e.,

$$\Delta V^\circ = \Delta V_{\text{int}} + \Delta V_{\text{solv}} \tag{6}$$

Recent theoretical approach to the partial molar volume developed by Yoshimura and Nakahara,[14] enables us to understand its significance at the molecular level. However, the separate estimations of ΔV_{int} and ΔV_{solv} are rather critical, and must be done with great care.

Walling and Naiman[15] estimated the activation volumes of the Claisen rearrangement reaction in several solvents, and found that they fell in the range of −10—−15 cm^{3}mol^{-1} with no obvious solvent dependence. They interpreted the results as consistent with rather tightly bonded cyclic transition state. This volume change could formally be ascribed to a 6-membered-ring-closure process. If we tentatively allot 15 cm^{3}mol^{-1} for ΔV_{int} in the present case, then the "relative" values of ΔV_{solv} could be calculated. They are given in the 3rd column from the right in Table 1.

On the basis of the Kirkwood equation, ΔV_{solv} could be given by Eq. 7.

$$\Delta V_{\text{solv}} = N_{\text{A}}\left(\frac{\mu_{\text{MC}}^2}{r_{\text{MC}}^3} - \frac{\mu_{\text{SP}}^2}{r_{\text{SP}}^3}\right) q_{\text{P}} \tag{7}$$

where q_{P} is defined by Eq. 8.

$$q_{\text{P}} = \frac{3}{(2\varepsilon+1)}\left(\frac{\partial\varepsilon}{\partial p}\right)_{T,p=0.1\,\text{MPa}} \tag{8}$$

Using available ε-p data,[16,17] q_{P}-values were estimated (Table 1). Then, likely μ and r values(μ_{MC}=15 Debye, μ_{SP}=3 Debye, r_{MC}=r_{SP}=0.4 nm) were substituted into Eq. 7, together with the q_{P}-values (Table 1). The discrepancy between the observed ΔV_{solv} (=ΔV°−ΔV_{int}) and calculated ΔV_{solv} becomes remarkable in the order chloroform <1,2-dichloroethane< acetone. This could be attributed to the enhanced polarization (increase of μ) within merocyanine molecule as the solvent polarity increases. Previously, we discussed this enhancement effect in some detail.[6,18,19] Unfortunately, no ϵ-p data are available for DMSO. However, judging from the $(\partial\varepsilon/\partial p)_T$-values for acetone and methanol[16,17] as polar solvents, $(\partial\varepsilon/\partial p)_T$-value for DMSO may not be far from 3×10^{-8} Pa^{-1}. Thus ΔV_{solv} in DMSO is presumed to be ca. −1.8 cm^3 mol^{-1}. It

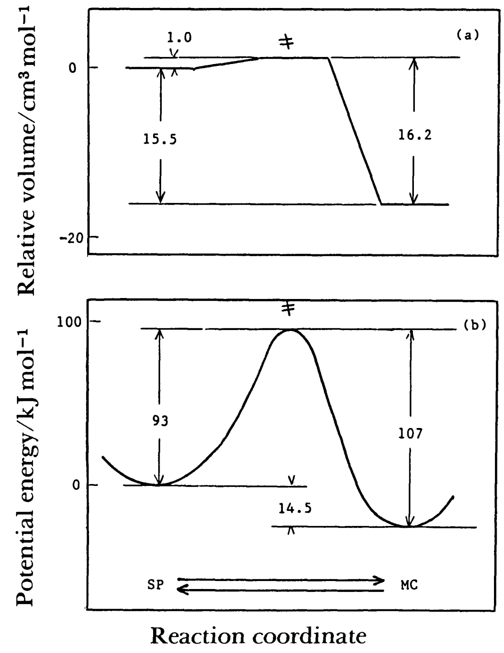


Fig. 2. Volume (a) and energy (b) profiles for the isomeric reaction of 6-COOH-8-NO$_2$-SP in CHCl$_3$.

could be said that the remarkable enhancement effect is involved in the case of DMSO, too.

Energy and Volume Profiles. In simple one-step reactions, the volume profiles are those having no extremum. This is in sharp contrast to the energy profile which has a maximum inevitably. According to le Noble,²⁰⁾ extrema are usually the rule for stepwise reactions. However, there are some exceptions: sigmatropic shifts such as the Claisen rearrangement show minina.²¹⁾ Diels-Alder reactions participated by maleic anhydride as a dienophile also show minima.²²⁻²⁴⁾ The reaction of *p*-methoxystyrene with TCNE is another example which involves minima in the volume profile.²⁵⁾ A maximum was observed in the degenerate Wagner-Meerwein shift²⁶⁾ and the amide rotation of dipeptides.²⁷⁾

The energy and volume profiles are shown in Fig. 2. The activation volumes for the forward reaction are positive and small, while the reaction volumes are negative (Table 2). Therefore, it is hard to imagine a dipolar transition state where the second term in Eq. 6 would overwhelm the first one. A transition state which involves a homolytic bond stretching may be acceptable; a small volume increment is expected in this process. Therefore, it could be said that the transition state is located near the initial state in the sense that the nuclei are near the initial positions.

If the data in Table 4 are inspected, one may notice that both ΔH° and ΔS° are smaller in $CHCl_3$ than in DMSO. The same is true for E_a and $\Delta S^{\neq}$, and ΔS° ($\Delta S^{\neq}$) and ΔV° ($\Delta V^{\neq}$) for the forward reaction. Although the reason is not clear, this compensation effect observed for $CHCl_3$ and DMSO are in line with the previous results.⁷⁾ It is notable that the entropy factor is as important as the enthalpy factor in determining the equilibrium. Leffler²⁸⁾ exemplified the compensation effect for a variety of reaction series, and for reactions in solvents of varying polarity. The existence of the isokinetic temperature predicted from the linear free energy relationship was demonstrated by us.²⁹⁾ Similarly, a rough linear correlation between $\Delta S^\circ(\Delta S^{\neq})$ and $\Delta V^\circ(\Delta V^\circ)$ was also reported,³⁰⁻³²⁾ and the reason discussed by Kondo and Tokura.³³⁾ Our results in this and previous investigations are in line with the findings of the above reports.

References

1) R.Heiligmen-Rim, Y. Hirshberg, and E. Fisher, *J. Phys. Chem.*, **66**, 2465 (1962).

2) J. Arnaud, G. Wippler, and F. Beaure D'augeres, *J. Chim. Phys.*, **64**, 1165 (1967).

3) I. Shimizu, H. Kadota, and E. Inoue, *Bull. Chem. Soc. Jpn.*, **42**, 1730 (1967).

4) S. A. Krysanov and M. V. Alfimov, *Laser Chem.*, **4**, 129 (1983).

5) K. Tamagake, Y. Kohno, Y. Shiota, and Y. Fujita, *Nippon Kagaku Kaishi*, **1984**, 82.

6) Y. Sueishi, M. Ohcho, and N. Nishimura, *Bull. Chem. Soc. Jpn.*, **58**, 2608 (1985).

7) Y. Sueishi, M. Ohcho, S. Yamamoto, and N. Nishimura, *Bull. Chem. Soc. Jpn.*, **59**, 3668 (1986).

8) H. Wynberg, *J. Am. Chem. Soc.*, **76**, 4998 (1954).

9) S. Toppet, W. Quintens, and G. Smets, *Tetrahedron*, **31**, 1957 (1975).

10) Y. Sueishi and N. Nishimura, *Bull. Chem. Soc. Jpn.*, **56**, 2598 (1983).

11) J. B. Flannery, Jr., *J. Am. Chem. Soc.*, **90**, 5660 (1968).

12) I. Ya. Kasparova, O. P. Shmakova, M. V. Mel'nik, B. M. Gutsulyak, and P. P. Kisilitsa, *Zh. Fiz. Khim.*, **60**, 504 (1986).

13) D. Lapienis-Grochowska, M. Kryszewski, and B. Nadolski, *J. Chem. Soc., Faraday Trans. 2*, **75**, 312 (1979).

14) Y. Yoshimura and M. Nakahara, *Ber. Bunsenges. Phys. Chem.*, **92**, 46 (1988), and references therein.

15) C. Walling snd M. Naiman, *J. Am. Chem. Soc.*, **84**, 2628 (1962).

16) H. Hartmann, A. Neumann, and G. Rinck, *Z. Phys. Chem. N. F.*, **44**, 204 (1965).

17) H. Hartmann and A. P. Schmidt, *Ber. Bunsenges. Phys. Chem.*, **72**, 875 (1968).

18) N. Nishimura, S. Kosako, and Y. Sueishi, *Bull. Chem. Soc. Jpn.*, **57**, 1617 (1984).

19) N. Nishimura, T. Tanaka, M. Asano, and Y. Sueishi, *J. Chem. Soc., Perkin Trans. 2*, **1986**, 1839.

20) W. J. le Noble, *Rev. Phys. Chem. Jpn.*, **50**, 207 (1980).

21) K. R. Brower, *J. Am. Chem. Soc.*, **83**, 4370 (1961).

22) R. A. Grieger and C. A. Eckert, *J. Am. Chem. Soc.*, **92**, 2918, 7149 (1970).

23) K. Seguchi, A. Sera, and K. Maruyama, *Bull. Chem. Soc. Jpn.*, **47**, 2242 (1974).

24) J. R. McCabe and C. A. Eckert, *Ind. Eng. Chem., Fundam.*, **13**, 168 (1978).

25) Y. Uosaki, M. Nakahara, and J. Osugi, *Int. J. Chem. Kinet.*, **15**, 805 (1983).

26) W. J. le Noble, S. Bitterman, P. Staub, F. K. Meyer, and A. E. Merbach, *J. Org. Chem.*, **44**, 3263 (1978).

27) H. Hauer, H. D. Ludemann, and R. Jaenicke, *Z. Naturforsch.*, **37**, 51 (1982).

28) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955), and references therein.

29) N. Nishimura, Y. Sueishi, and S. Yamamoto, *Chem. Lett.*, **1979**, 429.

30) K. J. Laidler and D. T. Y. Chen, *Can. J. Chem.*, **37**, 599 (1959).

31) L. G. Hepler, *J. Phy. Chem.*, **69**, 965 (1965).

32) S. D. Hamann snd M. Linton, *J. Chem. Soc., Faraday Trans. 1*, **1975**, 485.

33) Y. Kondo and N. Tokura, *Bull. Chem. Soc. Jpn.*, **42**, 1660 (1969).