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A Kinetic Study of the Thermal Conversion of 1′,3′,3′-Trimethylspiro-[2*H*-1-benzopyran-2,2′-indoline]-8-carboxylic Acid

Yoshimi Sueishi, Masanobu Ohcho, Shunzo Yamamoto, and Norio Nishimura*
Department of Chemistry, School of Science, Okayama University, Tsushima, Okayama 700

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Synopsis. The rate of the thermal conversion of 1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline]-8-carboxylic acid (8-COOH-SP) from its spiro form to its merocyanine form has been measured in several solvents at high pressures. Small solvent- and pressure-dependencies of the rate were observed. These results suggest that the electronic structure of the transition state of this reaction is nonpolar and that it is similar to that previously observed for the thermal conversion of so-called 6-nitrospiropyran from its merocyanine form to its spiro form.

It is a matter of interest, when an isomerization is accompanied by a π- or σ-bond fission, what kind of bond fission (homolytic or heterolytic?) is involved. Hitherto, we have investigated the cis-trans thermal isomerizations of azobenzenes,[1–3] acetylindigos,[4] and formazans[5] from such a point of view. The isomerization of the so-called spiropyrans has attracted much attention because of their reversible photochromic and thermochromic behavior. In a previous paper,[6] we have studied the solvent and pressure effects on the rate of the thermal conversion of 1′,3′,3′-trimethyl-6-nitro[2*H*-1-benzopyran-2,2′-indoline](6-NO_2-SP) and suggested that the observed results are more consistent with the mechanism involving the homolytic fission of the C_{spiro}–O bond than with that involving the heterolytic fission (Scheme 1). In contrast to 6-NO_2-SP, it was shown[7] that the spiro (SP) form of 8-COOH-SP is less stable than its merocyanine (MC) form; an intramolecular hydrogen bonding for the latter may be responsible for this. Therefore, the SP form thermally isomerizes to the MC form. In spite of this, it seems natural to consider that the thermal isomerizations of the two compounds proceed via the same reaction path or the same type of transition state. In order to confirm our previous view, we have now examined the kinetic solvent and pressure effects on the thermal conversion (SP→MC) of 8-COOH-SP.

Experimental

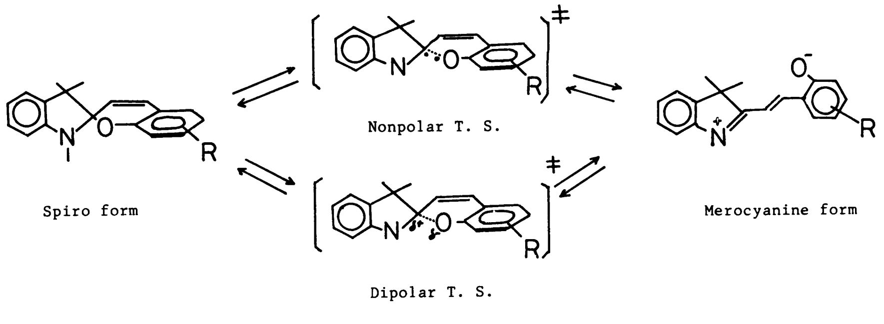
Materials. The 8-COOH-SP was generously supplied by Nippon Kanko Shikiso Kenkyusho (Japanese Research Institute for Photosensitizing Dyes, Co., Ltd.), and it was recrystallized from acetone: mp 244—245 °C (lit,[7] 245 °C). The reagent-grade solvents were purified and distilled in the usual manner.

Apparatus and Procedure. The high-pressure apparatus and procedure for the kinetic measurements were identical with those described elsewhere.[6] The solvents were deaerated by means of N_2 bubbling. The sample solution (ca. 10^{-4} mol dm^{-3}) was irradiated with a 650W projection lamp through a filter of a $CuCl_2$ solution. The absorption maximum (λ_{max} 530 nm) was monitored by means of a Hitachi 139 spectrophotometer, and the absorbance was recorded as a function of the time.

Results and Discussion

It was found that the first-order kinetics holds for this reaction. The rate constants obtained in several solvents and at various pressures are given in Table 1, together with the activation parameters. In such nonpolar solvents as hexane, the solubilities are very poor; this made the estimation of the rate constant impossible in nonpolar solvents.

Solvent Effects. For the thermal conversion of 8-COOH-SP, there are two possible routes: the conversion via the C_{spiro}–O bond stretching to produce either homopolar or dipolar transition states (Scheme 1). If the conversion proceeds via the dipolar transition state, a very large kinetic solvent effect can be expected, as has been observed in Menschutkin reactions.[7] However, as may be seen in Table 1, no systematic solvent effects are observed. In DMSO, the rate is remarkably smaller than in other solvents. In spite of this, the activation energy is roughly compensated for by the activation entropy (Fig. 1). This suggests that a simple interaction mechanism[8] is involved in this reaction, too, as in the case of 6-NO_2-



Scheme 1.

Table 1. Rate Constants and Activation Parameters for the Thermal Conversion of 8-COOH-SP at 30 °C (Probable errors in parentheses)

Solvent	$10^3 k/s^{-1}$				ΔV^*	E_a [b]	$\Delta S^*_{303 K}$ [b]
P/kg cm^{-2} [a]	1	400	800	1200	cm^3 mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
Chloroform	60.8(0.2)	58.8(0.3)	58.5(0.4)	55.7(0.6)	1.2	88.1(0.7)	14.1(2.2)
Ethyl acetate	38.9(0.3)	36.7(0.2)	32.6(0.9)	30.2(0.8)	4.7	75.1(12.7)	−29.8(42.4)
Dichloroethane	48.1(0.2)	46.9(0.3)	45.9(0.9)	45.7(1.8)	2.1	89.6(0.4)	17.1(1.4)
Acetone	18.3(0.3)	17.9(0.2)	16.2(0.1)	14.6(0.1)	1.4	79.6(1.3)	−24.4(4.3)
Acetonitrile	27.2(0.2)	26.9(0.1)	26.4(0.4)	26.0(0.3)	0.8	78.9(3.4)	−23.7(0.9)
Dimethyl sulfoxide	1.45(0.01)	1.35(0.02)	1.30(0.01)	1.24(0.02)	4.6	104(1)	35.5(2.1)

a) 1 kg cm^{-2} = 0.9807 10^5 Pa. b) Estimated from the rate constants at 20—40 °C.

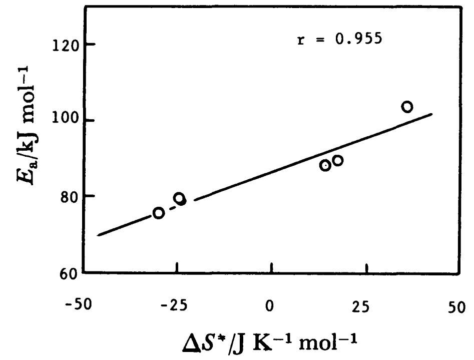


Fig. 1. $E_a-\Delta S^*$ relationship for the thermal conversion of 8-COOH-SP.

SP. In the present case, what kind of interaction is operative has not yet been clarified. However, it would be hard to explain the kinetic solvent effect, at least, in terms of solvent-polarity parameters or a special solvent-solute interaction, since the plots do not line up in the order of changing solvent polarities. As a whole, the above findings suggest that the nonpolar transition state is more likely than the dipolar or ionic one.

Pressure Effects. In order to confirm the above view, the rate was followed under high pressures. The pressure dependence on the rate constants was appoximated by a quadratic equation (Eq. 1), while the activation volume ($\Delta V^{\neq}$) at atmospheric pressure were estimated according to Eq. 2:

$$\ln k = a + bP + cP^2 \tag{1}$$

$$\Delta V^* = -RT(\partial \ln k/\partial P)_{T,P=1} \approx -bRT \tag{2}$$

If the reaction proceeds by the heterolytic mechanism, $\Delta V^{\neq}$ may be expected to be negative and its absolute value ($|\Delta V^{\neq}|$>20 cm^3 mol^{-1}) will decrease with an increase in the solvent polarities, as exemplified by Menschutkin reactions.[7] In the present case, however, the thermal conversion are slightly retarded by external pressures and the activation volumes take small positive values, virtually independent of the solvent polarity. This also supports the idea presented above.

The volume of activation could be explained in terms of the intrinsic volume alone. The stretching of the C_{spiro}–O bond upon activation must cause a small increase in volume. On the assumption that the stretching of the bond is 30%[9] of its original length, and that the thickness of the spiro ring is kept constant (34 nm),[10] the increment of the van der Waals volume due to the expansion of the ring is estimated to be 1.7 cm^3 mol^{-1}. Since the partial molar volume is about twice as large as its van der Waals volume,[11] $\Delta V^{\neq}$ would be about 3.4 cm^3 mol^{-1}. If this is compared with the experimental $\Delta V^{\neq}$- values, the homolytic fission is judge to be more likely.

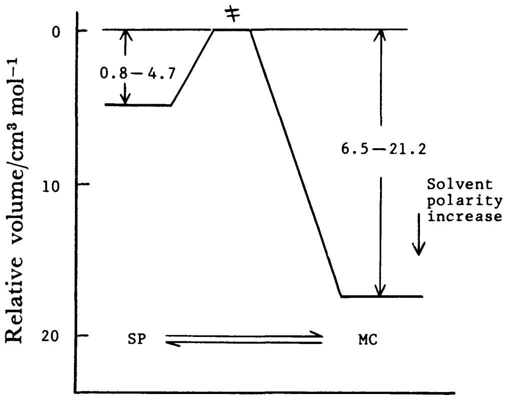


Fig. 2. Approximate volume profile for the SP⇄MC isomerization of spiropyrans.

Approximate Energy and Volume Profiles. For the MC→SP conversion of 6-NO$_2$-SP, the activation energies and activation volumes are in the ranges of 71—105 kJ mol^{-1} and 6.5—21.2 cm^3 mol^{-1} respectively in solvents of different polarities. It was found that there is a trend for both E_a and $\Delta V^{\neq}$ to be greater in polar solvents than in nonpolar solvents. In the case of the SP→MC conversion of 8-COOH-SP, the E_a's are in the range 75—104 kJ mol^{-1} and the $\Delta V^{\neq}$'s are 0.8—4.7 cm^3 mol^{-1}. In this case, no trend relating them to the solvent-polarity parameters could be observed. The above findings can be regarded as reasonable when one remembers the difference in the electronic structures between the MC and SP forms (Scheme 1).

Using the activation volume data of 6-NO$_2$—SP and 8-COOH-SP, we obtained the approximate volume profile shown in Fig. 2. Judging from the volume profile, the transition state is shifted to the SP form.

This implies that the bond breaking does not proceed very far at the transition state if the reaction is started from the SP form. The reverse is true if the reaction is started from the MC form.

It has been reported that some kinds of spiropyrans are in equilibrium with their MC form in solutions.[12] If we use such species and estimate ΔV and $\Delta V^{\neq}$, a more precise volume profile can be drawn. Along this line of thought, work is now under way.

A Comment on the Existence of Intermediates for the SP $\rightleftharpoons$ MC Isomerization. From the NMR study of some kinds of spiropyrans at various temperatures, to account for their experimental facts Toppet et al.[12] suggested that an open-ring cis-isomer exists as the intermediate for the SP$\rightleftharpoons$MC thermal isomerization (Scheme 2):

SP $\rightleftharpoons$ X(open-ring cis-isomer) $\rightleftharpoons$ MC trans-isomer

Scheme 2.

By using the picosecond-flash photolysis method, Krysanov and Alfimov[13] observed a transient spectrum with a very short lifetime during the photoisomerization of 6-NO_2-SP. They assigned the band peaking at 440 nm to the intermediate nonplanar cis configuration with the broken C–O bond of the pyran ring. This isomer corresponds to that suggested by Toppet et al.

Meanwhile, Inoue et al.[14] reported colorless intermediates were observed in the photo-decoloration process of 8-COOH-SP derivatives. They therefore considered that an energy minimum exists along the reaction coordinate. For unsubstituted 8-COOH-SP, however, they could not detect any such intermediate. It would be natural to assume the existence of such intermediate cis-isomer just after the breaking of the C_{spiro}–O bond. The intermediates observed by Inoue et al. are fairly stable and have activation energies as large as 80 kJ mol^{-1} for the reactions producing SP and MC isomers. Therefore, these can not correspond to the cis-isomer in Scheme 2. Incidentally, Zerbetto et al.[15] reported that no minimum was found in the ground-state potential curves computed by the NMDO method for the ring-opening reactions of chromens, which can be regarded as model compounds of spiropyrans. If we take these situations into account, it may be concluded that the transition state is involved in the formation process of X, followed by the rapid conversion to the MC trans isomer (Scheme 2).

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