Anal. Calcd for $C_{18}H_{16}$: C, 93.05; H, 6.95. Found: C, 92.86; H, 6.76.

1,4-Dihydrotriphenylene (2) (R_f 0.28): 425 mg (47%) (67% of **2** was isolated by column chromatography from the crude products of the metal–ammonia reduction of **1** using 2.5 mmol of lithium per 1 mmol of substrate); mp 203–204 °C (ethanol); NMR ($CDCl_3$) δ 3.80 (s, 4 H), 6.1 (br s, 2 H), 7.5–7.8 (m, 4 H), 7.9–8.1 (m, 2 H), 8.6–8.9 (m, 2 H); mass spectrum, *m/e* 230 (M^+).

Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.32; H, 6.18.

Finally, elution with benzene gave recovered triphenylene (15 mg, 2%).

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Registry No. **1**, 217-59-4; **2**, 39935-60-9; **3**, 114249-91-1; **4**, 114221-72-6; **5**, 5981-10-2; *cis*-**6**, 99144-04-4; *trans*-**6**, 99144-01-1; **7**, 114221-73-7; **8**, 114221-74-8; NH_3, 7664-41-7; Li, 7439-93-2.

Kinetic Effects of Pressure on Thermal *Z–E* Isomerization of a Stilbazolium Betaine. Dependence of Activation Volume on Reaction Conditions

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Stilbazolium betaines continue to attract attention because of their extreme solvatochromism.[1] 1-Methyl-4-(4-hydroxystyryl)pyridinium betaine (**1**) has been studied especially extensively. The *Z–E* photoisomerization and thermal isomerization of **1** and its conjugate acid were first confirmed by Steiner and his co-workers.[2] Their study revealed that thermal *Z–E* isomerization of **1** takes place relatively slowly in water. Rotation about the central carbon–carbon bond in its quinoid form **2** is the only plausible route in this isomerization (Scheme I); this reaction provides us with an opportunity to examine whether the solvent molecules recognize the oxygen and nitrogen atoms as independent charge centers in the *Z* configuration and whether the formal charge disappearance in the activation step results in a large positive activation volume. If this turns out to be the case, it may be taken as yet another fact supporting the rotational mechanism of *Z–E* isomerization of aminoazobenzenes. Large *negative* activation volumes were previously interpreted to be the result of electrostriction of solvent caused by intramolecular charge separation during the activation step.[3] This paper describes the kinetic effect of pressure on the thermal *Z–E* isomerization of **1** and its dependence on the reaction conditions.

Experimental Section

Materials. 1-Methyl-4-(4-hydroxystyryl)pyridinium betaine was prepared as described.[4] After several recrystallizations from water, the blue-red crystals were dried in vacuo.

Anal. Calcd for $C_{14}H_{13}ON \cdot {}^1/_2H_2O$: C, 76.34; H, 6.41; N, 6.36. Found: C, 76.43; H, 6.57; N, 6.52.

Water was deionized and distilled. Methanol was used after distillation from magnesium.

Kinetic Measurements. To 10 mL of a (1–1.4) × 10^{-4} mol L^{-1} solution of **1** was added 1 mL of 1 × 10^{-3} mol L^{-1} hydrochloric acid, and the mixture was diluted to ca. 30 mL. After irradiation by a UV lamp (Toshiba FL20S-BLB), the solution was basified by adding 10 mL of 0.1 mol L^{-1} sodium hydroxide solution and diluted to 50 mL. It was transferred to a modified hypodermic syringe. The syringe was connected to a sampling valve and pressurized in a thermostated pressure vessel. Samples were withdrawn at regular intervals after the compression heat was dissipated. The reaction was followed by monitoring the absorption increase in the visible region.[2] Measurements were made at every 30 MPa up to 210 MPa. It was confirmed that the reaction rate was independent of the base concentration; the reproducibility of the rate constant was 2–4%.

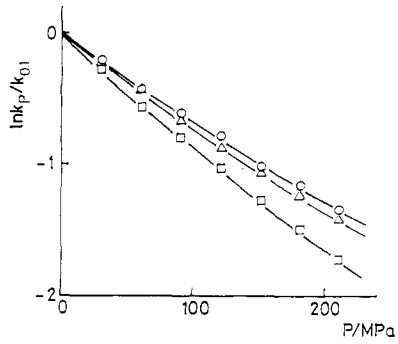

Figure 1. Effect of pressure on the isomerization rate of (*Z*)-1-methyl-4-(4-hydroxystyryl)pyridinium betaine in water and aqueous methanol at 25 °C: (○) water; (△) 20 wt % methanol; (□) 40 wt % methanol.

Scheme I

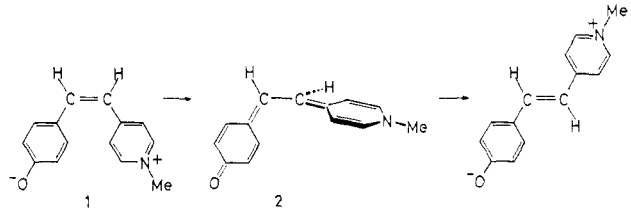

Table I. First-Order Rate Constants ($10^5k/s^{-1}$) and Activation Volumes ($cm^3\ mol^{-1}$) for *Z–E* Isomerization of 1 in Water

	T/°C				
P/MPa	10	15	25	35	45
0.1	0.499	1.17	5.74	24.6	101
30.0		0.967	4.64	20.2	81.7
60.0		0.779	3.73	16.7	65.0
90.0		0.661	3.12	13.7	55.7
120.0		0.534	2.61	11.5	46.2
150.0		0.419	2.04	9.86	39.8
180.0		0.335	1.79	8.09	33.9
210.0			1.48	7.10	29.8
$\Delta V_0^{\ddagger}$		16.5 ± 0.4[a]	17.7 ± 1.4	18.1 ± 1.7	20.0 ± 1.2

[a] The pressure independence of the activation volume was assumed in the calculation.

Results and Discussion

The reaction follows a first-order rate law under all conditions studied and it was retarded greatly by increasing the pressure. For example, at 25 °C in water, the half-life was 3.35 h at 0.1 MPa and 13 h at 210 MPa. The rate constants in water are listed in Table I along with the

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Table II. First-Order Rate Constants ($10^5 k/s^{-1}$) and Activation Volumes ($cm^3\ mol^{-1}$) for Z-E Isomerization of 1 in Aqueous Methanol at 25 °C

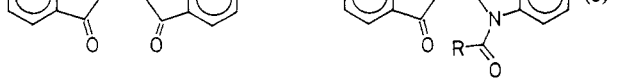
	P/MPa								
% MeOH	0.1	30.0	60.0	90.0	120.0	150.0	180.0	210.0	ΔV_0^*
20	18.4	14.5	12.0	9.49	7.64	6.40	5.35	4.46	19.1 ± 0.8
40	101	78.3	58.0	46.0	36.2	27.9	22.6	17.8	22.2 ± 0.8

activation volume at zero pressure estimated by eq 1[6] and 2. The values are in the range 16.5–20.0 $cm^3\ mol^{-1}$.

$$\ln k_P/k_{0.1} = aP + b \ln (1 + cP) \quad (1)$$

$$\Delta V_0^* = -(a + bc)RT \quad (2)$$

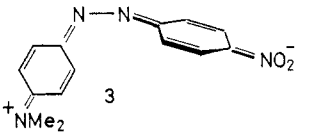
There are three probable factors that may cause an increase in partial molar volume in this reaction. The first two are the increase in the bond length in the central carbon–carbon bond and the increase in the freedom of motion. Both of them are expected because of the rupture of the central π-bond. The third factor is desolvation caused by the intramolecular neutralization of the opposite charges. A good example for the first and the second contributions is the isomerization of *N,N'*-diacylindigo dyes (eq 3).[7] In this isomerization, small positive (<4 $cm^3\ mol^{-1}$)



(3)

activation volumes were observed.[8] Since the reaction rate and the activation volume are almost independent of solvent polarity, the observed activation volumes must be the result of the first two contributions mentioned above. From these results, we can safely conclude that the major part of our activation volumes comes from desolvation caused by the charge neutralization in the activation step. In other words, the negatively charged oxygen and positively charged nitrogen atoms have their own solvation shell not only in the *E* but also in the *Z* configuration, and this solvational stabilization largely disappears in the transition state. The activation entropy calculated according to the Eyring theory (45 and 49 $J\ K^{-1}\ mol^{-1}$ at 0.1 and 180 MPa, respectively) is also in accordance with this conclusion. When solute–solvent interactions change greatly as in the present case, the accompanying volume change usually increases with rising temperatures. This is believed to derive mainly from the solvent polarity decrease by thermal expansion. The activation volumes in Table I clearly show this tendency. Furthermore, solvent effects on the rate and on the activation volume are also in accordance with desolvation in the activation step. If solvational stabilization is important in the *Z* configuration, the isomerization rate and its activation volume are expected to increase when less polar cosolvent is added to the reaction mixture. This assumption was examined by adding methanol at 25 °C. The results are shown in Table II. The rate constant increases from $5.74 \times 10^{-5}\ s^{-1}$ in water to 18.4 and $101 \times 10^{-5}\ s^{-1}$ in 20 and 40 wt % aqueous methanol, respectively; at the same time, the activation volume increased to 19.1 (20%) and 22.2 $cm^3\ mol^{-1}$ (40%), respectively. The larger retardation in less aqueous solvent can be seen in Figure 1. The short half-life prevented us from studying pressure effects in less polar solvents. However, the tendency is clear. All of the results obtained show the importance of desolvation in the activation step of the present isomerization.

In the *Z–E* isomerization of aminoazobenzenes, the strong solvational stabilization of a quinoid-type transition state such as **3** was proposed on the basis of a large negative activation volume and its dependence on temperature and solvent polarity.[3] If the strong solute–solvent interactions in the initial state disappear as the result of quinoid structure formation in the present inner salt, it is reasonable to assume an increase in solute–solvent interactions because of the appearance of formal charges in the rotational transition state of isomerization of aminoazobenzenes.



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Registry No. 1, 67106-80-3.

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(8) Relatively large activation volumes (8–9 $cm^3\ mol^{-1}$) observed for *N,N'*-dibenzoylindigos are attributable to face-to-face interactions of the aromatic rings in the initial state.

Efficient Optical Resolution of 2,2'-Dihydroxy-1,1'-binaphthyl and Related Compounds by Complex Formation with Novel Chiral Host Compounds Derived from Tartaric Acid

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Previously we reported that amide host compounds such as oxamide (**1**),[1,2] fumaramide (**2**),[3,4] methanetricarboxamide (**3**),[5] and 2,2'-biphenyldicarboxamide derivatives (**4**)[6] include a wide variety of organic compounds and form crystalline complexes of a stoichiometric host:guest ratio. Optical resolution of a guest compound by enantioselective inclusion is expected when an optically active amide host compound is used. We designed chiral amide host compounds, succinamide derivatives **7** and **10** and dioxolane-4,5-dicarboxamide **8**, by starting from the naturally occurring inexpensive chiral compound, (+)-tartaric acid.

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