for p-NO_2 was noted previously. Although a firm conclusion cannot be drawn because of this uncertainty, a trend in the predicted direction is indicated by the results in Table II.

Hammett ρ as a Criterion of Selectivity. The Hammett ρ value has frequently been used as a selectivity parameter in discussions of the RSP. In general, higher ρ values are associated with lower reactivities in systems where the RSP is applicable. This is apparently the case for reaction of the methyl phenyl sulfates with the normal nucleophiles.[6]

At first glance the α nucleophiles would appear to follow the RSP as well, since these have associated higher reactivities than the normal nucleophiles but have lower ρ values. However, our discussion has shown that the lower ρ value for the α nucleophile is not brought about by the motion A → B corresponding to lower selectivity but rather by a change in transition-state character dominated by anti-Hammond effects. This obviously brings into question the use of ρ as a selectivity parameter. In principle it would be valid to use ρ for systems which can be represented by two-dimensional diagrams but not for systems in which anti-Hammond effects are believed to be important.

Conclusion Concerning Validity of the RSP. The overall conclusion that may be drawn from this study is that the RSP will hold whenever (and only whenever) "perpendicular" or "anti-Hammond" effects are absent or when they are of subordinate importance. When this is so, any valid measure of transition-state structure should reflect the RSP, but not otherwise. In that sense, the RSP should be understood as a rule of restricted applicability.

Experimental Section

Materials. The aryl methyl sulfates were prepared according to previously described procedures.[7] The methanol used in the kinetics was spectroquality Fisher reagent grade. Methanolic stock solutions of hydrogen peroxide were prepared from 30% Anachimia reagent grade solution, and the solutions were standardized iodometrically. Solutions of sodium methoxide were obtained by dissolving clean sodium metal in dry methanol and standardized by titration with 0.100 N HCl.

Kinetic Procedures. Kinetic data were obtained spectrophtometrically by using a Bausch and Lomb SP505, a Unicam SP800B, or a Beckman 25 spectrophotometer fitted with thermostated cell blocks. The reactions were followed either by repeated scanning between 220 and 370 nm or at a constant wavelength (λ_{max} for $ArOSO_3^-$). Details of treatment of the kinetic data are given elsewhere.[37]

In a typical run the reaction medium was prepared by addition of aliquots of methanolic solutions of hydrogen peroxide and sodium methoxide and completing volume up to 3.00 mL with methanol. The reaction was started by adding 50 μL of an ethereal 3.60×10^{-3} M stock solution of the substrate to the H_2O_2/MeONa/MeOH solution contained in the cuvette at constant temperature.

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Registry No. m-NPMS, 66735-53-3; p-BPMS, 66735-54-4; PMS, 66735-55-5; p-MPMS, 46231-81-6; p-NPMS, 38319-17-4; HOOH, 7722-84-1.

Mechanistic Study of Thermal Z–E Isomerization of Azobenzenes by High-Pressure Kinetics

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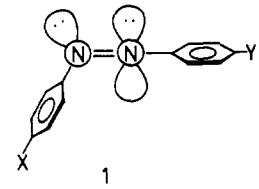
Abstract: Pressure effects for the thermal Z–E isomerization of several azobenzenes were measured in various solvents. The activation volumes for 4-(dimethylamino)-4′-nitroazobenzene indicate that the reaction mechanism changes from inversion in n-hexane to rotation in benzene and other relatively polar solvents. The same change in mechanism takes place in the case of 4-anilino-4′-nitroazobenzene when the solvent is changed from benzene to acetone; for 4-methoxy-4′-nitroazobenzene and unsubstituted azobenzene, the reaction mechanism does not change greatly with solvent polarity. The activation enthalpy for azobenzene was redetermined; the result suggests that the original dipole moment is reduced by about 40% in the activation step.

Interest in the mechanism of thermal Z–E isomerizations of azobenzenes has recently revived. The majority of the new studies have been kinetic,[1,3-7] but molecular orbital calculations[1,8] and thermochemical measurements[2] have also been made. The inversion mechanism is accepted for most cases;[7,9] in this pathway, the double bond between the nitrogen atoms remains intact, but one of them undergoes rehybridization from sp^2 to sp in the transition state **1**. However, for push–pull substituted azobenzenes



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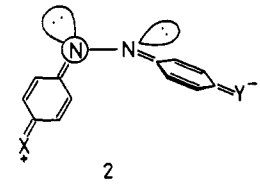

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(i.e., which have strong electron-donating and -attracting substituents in the 4- and 4′-positions, respectively) considerable dependence of the rate constant on the solvent polarity was observed; in such instances, a rotation mechanism via the dipolar transition state **2** is postulated.[10] Since **1** and **2** greatly differ in their polarities, the activation volume,[11] obtained from the pressure effects on the rate constant, is expected to provide unequivocal evidence for the operating mechanism. In the inversion mechanism, neither bond formation nor bond scission occurs during activation, and the polarity of the Z isomer may be only

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Table I. First-Order Rate Constants (k, s^{-1}) for the Isomerization of (*Z*)-4-(Dimethylamino)-4'-nitroazobenzene at Various Pressures

		P, bar							
solvent	*T*, °C	1	300	600	900	1200	1500	1800	2100
hexane	40	0.0106	0.0111	0.0113	0.0103	0.0106	0.0109	0.0112	0.0119[a]
carbon tetrachloride	40	0.0124	0.0138	0.0152	0.0166	0.0175	0.0185	0.0198	
dioxane	40	0.0468	0.0604	0.0738	0.0836	0.0978			
benzene	40	0.0429	0.0540	0.0662	0.0789	0.0917	0.107		
chloroform	15	0.080	0.107	0.144	0.183	0.229	0.277	0.334	0.400
dichloromethane	25	0.90	1.24	1.62	2.09	2.56	3.15	3.76	4.47
1,2-dichloroethane	25	1.48	2.05	2.68	3.45	4.36	5.43	6.36	7.65
cyclohexanone	25	8.35	10.4	12.7	15.3	17.7	20.6	24.1	
2-propanol	25	8.22	10.7	13.6	16.2	19.3	22.4	26.0	30.9
acetone	25	9.57	13.2	17.3	21.8	26.8	32.5	38.2	45.4
methanol	25	57.4	73.0	88.0	102				

[a] From ref 12.

Table II. First-Order Rate Constants (10^3k, s^{-1}) for the Isomerization of (*Z*)-4-Anilino-4'-nitroazobenzene at Various Pressures

		P, bar							
solvent	*T*, °C	1	300	600	900	1200	1500	1800	2100
benzene	40	6.95	7.45	7.93	8.40	8.72	9.10		
acetone	25	98.4	124	150	178	204	235	267	300

Table III. First-Order Rate Constants (10^4k, s^{-1}) for the Isomerization of (*Z*)-4-Methoxy-4'-nitroazobenzene at Various Pressures

		P, bar							
solvent	*T*, °C	1	300	600	900	1200	1500	1800	2100
hexane	25	1.91	1.88	1.85	2.02	1.92	2.00	2.06	2.07
benzene[a]	25	2.32		2.47					
dichloromethane	25	6.03	6.39	6.77	7.10	7.36	7.74	8.00	8.29
1,2-dichloroethane	25	6.83	7.27	7.73	7.95	8.32	8.56	8.89	9.11
acetone	25	5.52	6.00	6.38	6.62	6.81	7.11	7.44	7.63
methanol	20	2.87	3.02	3.19	3.28	3.43	3.55	3.63	3.74

[a] The rate constants at other pressures are 2.37×10^{-4} s^{-1} (200 bar), 2.45×10^{-4} s^{-1} (400 bar), and 2.50×10^{-4} s^{-1} (700 bar).

Table IV. First-Order Rate Constants (10^5k, s^{-1}) for the Isomerization of (*Z*)-Azobenzene at Various Pressures

		P, bar							
solvent	*T*, °C	1	300	600	900	1200	1500	1800	2100
hexane[a]	60	12.3	12.8	13.3	13.3	14.0	14.3	14.6	14.8
benzene[a]	60	10.0		9.9		10.6		10.7	11.0
cyclohexanone	50	3.12	3.15	3.15	3.30	3.30	3.24	3.31	3.33
methanol[a]	65	8.65		8.85		8.95		9.12	9.09

[a] From ref 7.

partially lost (vide infra); therefore, the pressure dependence of the rate constant will be small. On the contrary, in the rotation mechanism, the original π electrons are transferred toward the pulling group and the newly formed positive charge center is stabilized by the pushing group. This results in great enhancement of the dipole moment, and this in turn causes stronger solvation in the transition state and a decrease in the volume of the system.

In the preliminary communication,[12] it was reported that the isomerization rate of 4-(dimethylamino)-4'-nitroazobenzene (hereafter referred to as NMe_2-NO_2-AB) in benzene was accelerated by increasing the external pressure and that in *n*-hexane was affected little; this was taken as evidence for a change of mechanism with solvent, i.e., from inversion in *n*-hexane to rotation in benzene. In this paper, the kinetic pressure effects on the isomerization rates of several azobenzenes in several solvents are presented and their mechanistic implications discussed.

Results

The first-order rate constants for the isomerization of NMe_2-NO_2-AB in various solvents at atmospheric and at high pressures are given in Table I; some of these results are illustrated in Figure 1. It can be seen in Figure 1 that the pressure effect is nominal in *n*-hexane, that it becomes appreciable in carbon tetrachloride, and that a strikingly large acceleration is realized in other solvents. The acceleration is larger in 1,2-dichloroethane than in the more polar solvents cyclohexanone and methanol. When the electron-donating group is changed from dimethylamino to anilino or methoxy, the rate enhancement with solvent polarity and with external pressure becomes less evident, as can be seen from Tables II and III; when all of the substituents are removed, the acceleration with pressure becomes very small, especially in polar solvents (Table IV).

Discussion

The Isomerization of Push–Pull Substituted Azobenzenes. From the results in Tables I–IV, the activation volumes at atmospheric pressure were estimated according to eq 2.[13] The values are listed

$$\ln k = a + bP + cP^2 \quad (1)$$

$$\Delta V^{\ddagger} = -RT\left(\frac{\partial \ln k}{\partial P}\right)_{T,P=1} = -(b + 2c)RT \approx -bRT \quad (2)$$

in Table V. The activation volumes for NMe_2-NO_2-AB clearly show that the transition-state polarity increases markedly when the solvent is changed from *n*-hexane to carbon tetrachloride, benzene, and chloroform. This can be most reasonably explained by the two competing reaction paths discussed above. This view

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(13) When the pressure effect was small, the third term in eq 1 was omitted.

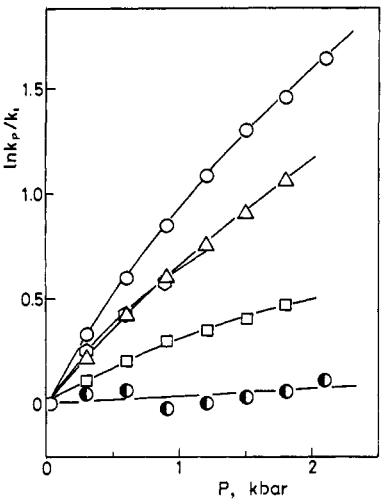
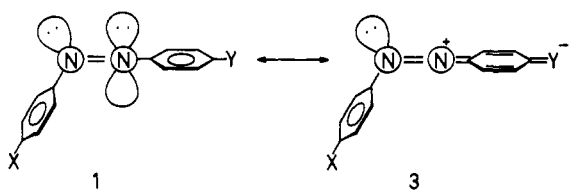


Figure 1. Pressure effects on the isomerization of (*Z*)-4-(dimethylamino)-4′-nitroazobenzene: (○) 1,2-dichloroethane; (△) cyclohexanone; (□) methanol; (◫) carbon tetrachloride; (◐) hexane.

Table V. Activation Volumes for the Thermal *Z*-*E* Isomerization of Azobenzenes in Various Solvents

	activation volume, mL/mol (*T*, °C)			
solvent	azobenzene	MeO-NO_2-AB	PhNH-NO_2-AB	NMe_2-NO_2-AB
hexane	−3.3 (60)	−1.2 (25)		−0.7 (40)
carbon tetrachloride				−9.5 (40)
dioxane				−22.4 (40)
benzene	−1.2 (60)	−2.6 (25)	−6.5 (40)	−20.5 (40)
chloroform				−24.5 (15)
dichloromethane		−4.9 (25)		−25.5 (25)
1,2-dichloroethane		−5.1 (25)		−26.2 (25)
cyclohexanone	−0.8 (50)			−18.2 (25)
2-propanol				−20.3 (25)
acetone		−7.9 (25)	−17.9 (25)	−25.3 (25)
methanol	−0.7 (65)	−4.3 (20)		−21.6 (25)

is supported by the fact that the pressure effect tends to decrease when the solvent polarity is further increased. The activation volumes in cyclohexanone, 2-propanol, and methanol are all less negative than the ones in 1,2-dichloroethane and dichloromethane. Similar solvent dependences of activation volume were reported for some ionic reactions such as Menschutkin reactions[14,15] and a [$_\pi$2 + $_\pi$2] cycloaddition.[16] Since large, negative activation volumes were obtained in various types of solvents, there seems to be no single important solute–solvent interaction mechanism, e.g., charge-transfer interaction, that stabilizes the rotational transition state specifically. The results for PhNH-NO_2-AB and MeO-NO_2-AB indicate clearly the importance of the electron-donating substituent. Although the methoxy group is one of the archetypal π donors, a clear-cut change in mechanism to rotation did not take place even in methanol. The results are compatible with the inversion mechanism if we consider the contribution from a polar structure, **3**. On the other hand, the results for PhNH-



NO_2-AB indicate that the reaction proceeds via the rotation mechanism at least in acetone. The intrinsic activation volume (vide infra) for this compound was similar to the one for NMe_2-NO_2-AB, suggesting the same mechanism for both azobenzenes. Judging from the activation volumes, however, the polarity of the transition state **2** is lower in PhNH-NO_2-AB, and in benzene the inversional and the rotational rates seem to be comparable.

Since solvent polarity is known to increase with pressure, there might be some cases in which pressure itself causes a change in mechanism. However, so far as we have examined, there was no evidence for such a change, probably because of the relatively low upper pressure limit (≤2.1 kbar).

The Intrinsic Activation Volume and Its Implication. Activation volumes can be divided into two terms, i.e., the structural or intrinsic term and the solvent term.

$$\Delta V^{\ddagger} = \Delta V^{\ddagger}_{int} + \Delta V^{\ddagger}_{solv} \quad (3)$$

This division is, of course, an artificial one, but it is widely used in discussions of activation volumes of ionic reactions. For example, it is customarily said that in S_N1 reactions the intrinsic activation volume is positive because of the bond scission, and the solvent volume change is negative because of the increasing solute–solvent interactions in the activation step. As can be seen from this example, the latter is usually understood as the volume change of the solvent molecules during activation and the former term includes all of the rest of the activation volume, which may consist of the change in the van der Waals volume, the void volume, which inevitably exists around the van der Waals spheres,[17] and, in addition, the volume created by internal rotations and vibrations. In 1963, Brower[18] tried to make use of this bisection to estimate the transition-state polarity in some bimolecular nucleophilic substitutions. The division of the activation volume was effected by assuming that the intrinsic activation volume does not vary with the charge type of the reaction and that the observed activation volumes for reactions between neutral and anionic reactants consist solely of the intrinsic volume change. Several methods of estimating the intrinsic activation volume have been devised since then.[14,19-21] Two of them[14,19] utilize activation volume solvent dependence. They require pressure effect measurements in solvents with various polarities and, of course, the same reaction mechanism in all of the solvents. This prerequisite is not met in the present reaction. A few years ago, one of the present authors[20] proposed a method based on the pressure dependence of the activation volume. Its basic idea is that, first, the activation volume can be expressed as

$$\Delta V^{\ddagger} = \Delta V^{\ddagger}_{int} + \Delta n^{\ddagger}(V_{solv} - V_{bulk}) \quad (4)$$

where V_{solv} and V_{bulk} are molar volumes of solvent in a solvation sphere and in bulk, respectively, and $\Delta n^{\ddagger}$ is the solvation number change for the activation step, and second, the solvent molecules in the solvation sphere behave as if they are under extra internal pressure, δP. In other words, V_{solv} at the external pressure P can be given by

$$V_{solv} = V_1\left(1 - C \ln \frac{B + P + \delta P}{B + 1}\right) \quad (5)$$

where V_1 is the molar volume of the bulk solvent at 1 bar and B and C are the Tait equation parameters.[22] From eq 4 and 5 the following is obtained, if we assume that δP is smaller than B.[24]

$$-RT\left(\frac{\partial \ln k}{\partial P}\right)_T = \Delta V^{\ddagger}_{int} + \Delta n^{\ddagger} C V_1 \ln \frac{B + P}{B + P + \delta P} \approx \Delta V^{\ddagger}_{int} + \Delta n^{\ddagger} C V_1 \frac{\delta P}{B + P} \quad (6)$$

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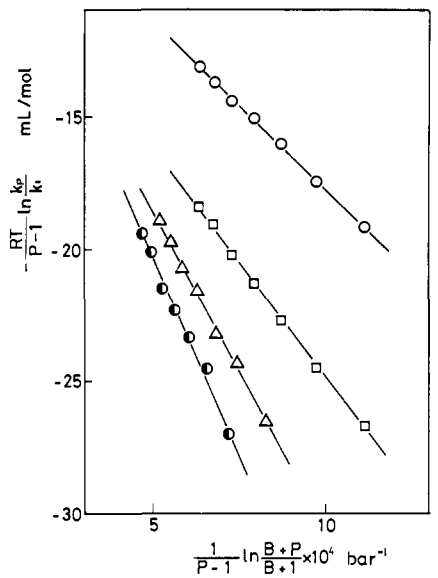

Figure 2. Estimation plots for intrinsic activation volumes: (○) PhNH-NO_2-AB in acetone; (□) NMe_2-NO_2-AB in acetone; (△) NMe_2-NO_2-AB in dichloromethane; (◐) NMe_2-NO_2-AB in 1,2-dichloroethane.

By integration of this equation from pressure = 1 to P, on the assumption that $\Delta V^{\ddagger}_{int}$, $\Delta n^{\ddagger}$, and δP are independent of pressure, the final expression

$$-\frac{RT}{P-1}\ln\frac{k_P}{k_1} = \Delta V^{\ddagger}_{int} - \frac{\kappa}{P-1}\ln\frac{B+P}{B+1} \qquad (7)$$

is reached, where κ stands for $\Delta n^{\ddagger} C V_1 \delta P$. Therefore, if the model is a good description of the system and the approximations are valid, the plot of the average activation volumes for the pressure range 1–P against $(1/(P-1))\ln[(B+P)/(B+1)]$ will yield a straight line, and the intrinsic activation volume will be obtained by extrapolating the line to infinite pressure. It was shown that the plot was linear in various ionic reactions, and the estimated $\Delta V^{\ddagger}_{int}$ values were reasonable, judging from the reaction mechanisms. They were also in fairly good agreement with the values estimated from the solvent effects on the activation volume where a comparison was possible. The plots for the present isomerizations are shown in Figure 2. The linearity is quite satisfactory; the correlation coefficients were 0.995 or more. The intrinsic activation volumes estimated by the extrapolation were −6.3 (CH_2Cl_2), −5.6 (CH_2ClCH_2Cl), and −7.5 (CH_3COCH_3) mL/mol for NMe_2-NO_2-AB and −5.3 mL/mol for PhNH-NO_2-AB in acetone. Two reasons are conceivable for these modest negative values. The first one is the destruction of the relatively bulky π electron cloud, and the second one is the restricted rotation of the phenyl groups in the transition state. The π electrons are transferred from the space between the two azo nitrogens toward the more electronegative oxygen atoms of the nitro group, and it may result in the decrease of the van der Waals volume. In the Z configuration, it is possible for the phenyl groups to interact not only with the π electrons but also with the nitrogen lone pairs, and the energy barrier between these two conformations amounts to only ca. 1 kcal/mol,[8] suggesting that the phenyl rings are twisting rapidly around the carbon–nitrogen single bond, creating a void space in the neighborhood of each ring. However, in transition state **2**, the rotational vibration is supposed to be severely restricted because of the overlap of the nitrogen 2p orbital with those of the phenyl carbons. This would result in the occupation of the original void space by the nearby solvent molecules. The relative importance of these two contributions is a question to be solved in the future.

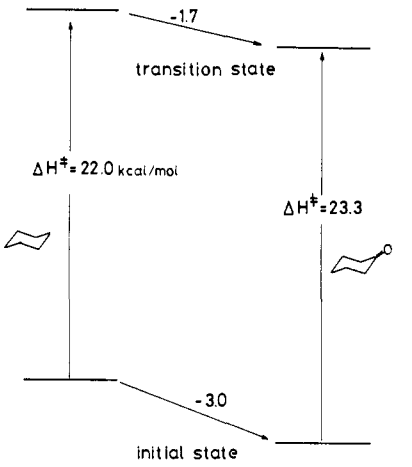

Figure 3. Relative enthalpies of the reactant and the activated complex in the isomerization of (*Z*)-azobenzene.

Table VI. Temperature Effects on the Isomerization of (*Z*)-Azobenzene in Cyclohexanone at 1 Bar

T, °C	45	50	55	60	65
$10^5 k$, s^{-1}	1.74	3.12	5.38	9.36	16.5

Polarity of the Inversion Transition State. In the unsubstituted azobenzene, the activation energy increases, though slightly, with the solvent polarity.[25] This suggests that the initial polarity of *Z* isomer is lost at least partially in the transition state. Haberfield and his co-workers[2] discussed the matter in some detail. They measured the enthalpy of solvent transfer for (*Z*)-azobenzene, and by combining the value with the activation enthalpies calculated from the rate constants by Le Fèbre and Northcott,[26] they obtained the enthalpy of solvent transfer of the activated complex. The value was +1.7 kcal/mol for the transfer from cyclohexane to cyclohexanone, and the positive value was taken as evidence for the lack of polarity of the activated complex. It is unreasonable, however, to assume stronger solvation in cyclohexane for **1** because part of the original polarity must be retained druing activation. In fact, the activation volumes for the reaction were negative, as shown in Table V, indicating clearly that desolvation was not extensive. Since the activation enthalpy in cyclohexanone was calculated from the rate constants at 45 and 70 °C, and it is by far the largest value reported so far,[4,27] its redetermination was warranted. The newly determined rate constants are shown in Table VI. The activation enthalpy is 23.3 kcal/mol and the enthalpy of solvent transfer −1.7 kcal/mol, as can be seen from Figure 3. Judging from the ratio of the transfer enthalpies for the initial and the transition states, about 60% of the original polarity seems to be retained. The small negative activation volumes were probably brought about again by the restriction of thermal motions in **1**. Relatively large negative activation entropies[5] support this view.

Experimental Section

Material. The purities of all azobenzenes were checked by thin-layer chromatography. (*Z*)-Azobenzene was prepared according to Hartley;[28] mp 71.9–72.1 °C (lit. mp 71–72 °C). NMe_2-NO_2-AB was purchased from Tokyo Chemical Industry Co. and recrystallized (toluene); mp 234–235 °C (lit.[29] mp 232–234 °C). PhNH-NO_2-AB was prepared from diphenylamine and *p*-nitroaniline and purified by recystallization

(24) If we consider that V_{solv} is an average molar volume for all of the solvent molecules influenced by the solute electrostatic field, δP will be much smaller than B.[20] For example, in Menschutkin reactions the value was estimated[14] as ca. 310 bar, while the B values for organic solvents are about 1 kbar. In addition, $[1/(P-1)]\ln[(B+P)/(B+1)]$ is linearly proportional to the function obtained by integrating eq 6; therefore, the approximation adopted does not affect the result of the extrapolation to infinite pressure.

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(26) Le Fèbre, R. J. W.; Northcott, J. *J. Chem. Soc.* **1953**, 867.

(27) One exception was reported by Nerbonne and Weiss[5] for the isomerization in an anisotropic solvent. The enthalpy of activation in 1:1 mixture of 5α-cholestan-3β-yl acetate and 5α-cholestan-3β-yl nonanoate was 26.9 kcal/mol in the temperature range of the cholesteric phase; however, at higher temperatures the value was 21.1 kcal/mol, suggesting that the large activation enthalpy was the result of the anisotropy of the solvent.

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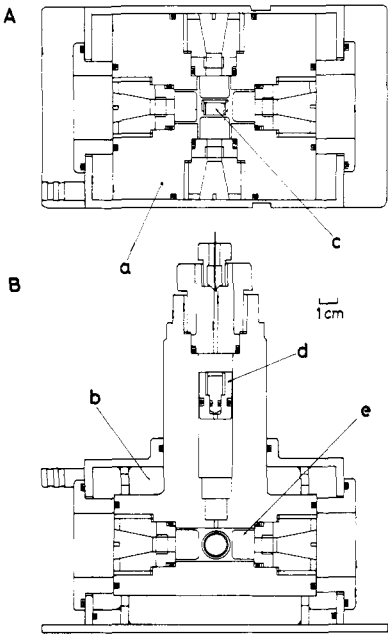

Figure 4. Cross sections of the high-pressure vessel: (A) top view; (B) side view; (a) pressure vessel; (b) water-circulating jacket; (c) inner sample cell; (d) liquid separation plunger; (e) quartz disk.

(benzene–hexane) and column chromatography (silica gel/benzene–hexane); mp 162.2–163 °C (lit.[30] mp 162 °C). MeO-NO_2-AB was prepared by methylation of OH-NO_2-AB with methyl iodide and purified by column chromatography (silica gel/benzene) and recyrstallization (ethanol); mp 157.9–159 °C (lit.[31] mp 157.5–158 °C). The solvents used for the measurements were spectrophotometric grade, or reagent grade purified by distillations.

High-Pressure Kinetics. The reaction of azobenzene was followed by means of a high-pressure sampling technique.[32] In the push–pull substituted azobenzenes, a pressure vessel with four optical windows, illustrated in Figure 4, was used. It is made of 17-4PH stainless steel and equipped with a water-circulating jacket. The diameter of the windows is 8 mm. The sample solution was contained in the inner cell, which was similar to the one described by le Noble and Schlott.[33] The same solvent as the reaction mixture was used as the pressurizing fluid inside the optical vessel, and it was separated from the pressure-transmitting fluid, hexane, by a plunger in the upper cylinder. The pressure drop because of the friction was shown to be negligible (<0.7%) by the direct pressure measurement with a manganin coil in the sample room. The slower reactions were followed by means of a Shimadzu UV-180 double-beam spectrophotometer, and a tungsten projection lamp was the excitation light source. The experimental detail was described previously.[34] Fast decay times were measured by a flash spectroscopic technique. A xenon flash tube, a Jarrel-Ash grating monochromator, and a photomultiplier were attached to the windows of the pressure vessel. The monitoring light source was a stabilized halogen lamp. The light passed through the monochromator was introduced to the high-pressure cell. A two-cavity Ditric Optics interference filter was installed between the cell and the photomultiplier in order to eliminate the scattered flash light. The absorption maximum of the *E* isomer was monitored. The transient signals were recorded by a transient memory TM-1410 of Kawasaki Electronica Co. A high-speed signal averager, TMC-300 (Kawasaki Electronica), was used when S/N ratio improvement was necessary. The reproducibility of the rate constant was ±1–1.5%. In chlorinated hydrocarbons, the reaction was sometimes accelerated by adventitious acid. This undesired catalysis was prevented by adding small amounts of piperidine (ca. 10^{-3} M) to the reaction mixture. The addition of the base in other solvents did not produce any measurable change in the rate constant, except for PhNH-NO_2-AB; in this compound, it was found that piperidine catalyzed the reaction, and all of the measurements were done in the absence of the base.

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Registry No. (*Z*)-**1** (X = NMe_2; Y = NO_2), 73815-07-3; (*Z*)-**1** (X = anilino; Y = NO_2), 82248-50-8; (*Z*)-**1** (X = MeO; Y = NO_2), 20488-63-5; (*Z*)-**1** (X, Y = H), 1080-16-6.

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Rate Control by Restricting Mobility of Substrate in Specific Reaction Field. Negative Photochromism of Water-Soluble Spiropyran in AOT Reversed Micelles

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Abstract: The thermocoloration of a water-soluble spiropyran, 1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline]-6-sulfonic acid (**1**), which has been newly synthesized in this work, in the anionic AOT reversed micelles has been investigated in order to evaluate the effect of the reversed micelles in controlling the reaction rates or pathways by restricting the mobility of the substrates being situated in a specific reaction field. The probe **1** showed a negative photochromism in polar solvents such as water, MeOH, and EtOH as well as in the AOT reversed micelles. The thermocoloration rates of **1** were retarded by about 20 times in the 0.2 M AOT/0.6 M H_2O/hexane micelles compared with those in MeOH in which microscopic polarity was comparable to that in the interior core of the reversed micelles adopted. This was explicable in terms of the restriction in the internal rotation of the 2,3 σ bond of **1** during the thermocoloration accompanied by the cis–trans isomerization in a largely restricted field as provided by the reversed micelles. The extent of deceleration in the thermocoloration in the AOT reversed micelles was decreased by increasing the R ([H_2O]/[AOT]) value. The results obtained suggested a possibility that in the specific reaction field as provided by the reversed micelles, it may be possible to hold the labile substrate at the higher energy level by restricting the freedom of molecular motion.

Reversed micelles provide a unique field to solubilize ionic or polar solutes in apolar media and can control the reaction rate or pathway occurring in the interior core of micelles.[1] The system is roughly classified into two distinct categories:[2] (1) the catalysis

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