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Thermal *Z–E* Isomerization of Azobenzenes. The Pressure, Solvent, and Substituent Effects

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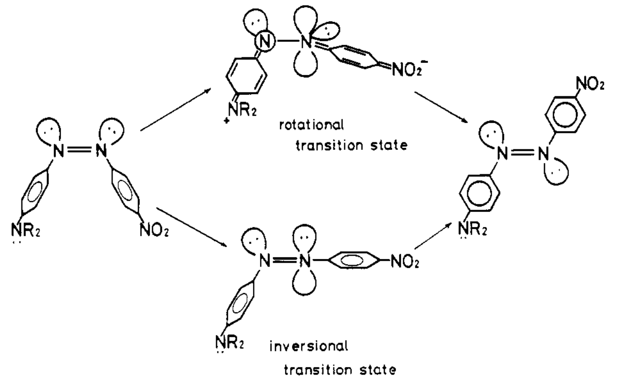
The rates of thermal *Z–E* isomerization of 4-(dimethylamino)-4′-nitroazobenzene were measured in a variety of solvents, and the Kirkwood plot revealed that the rate constant increase is much larger in polar solvents than expected from the continuum theory. The result can be reasonably explained by the intervention of rotational isomerization which proceeds via a highly polar transition state. The large negative activation volumes support it. It is also shown that a strong electron-donating dialkylamino group makes the rotational transition state stable enough to compete with the inversional one without assistance from the electron-attracting substituent. On the contrary, an electron-attracting group like nitro increases the stability of the inversion transition state more than that of the transition state for the rotational isomerization.

The mechanism of thermal *Z–E* isomerization of azobenzenes continues to attract the attention of many investigators. When the azobenzene bears no substituents or when electronic push–pull interactions between substituents are not possible, the experimental[1–5] and theoretical (CNDO/2 calculation[6,7]) results obtained so far are in accordance with the inversion mechanism. In this mechanism, one of the nitrogen atoms undergoes rehybridization to sp-hybrid state during activation.[3] The experimental evidence for this mechanism includes (a) the facility of the isomerization around a nitrogen–nitrogen and a carbon–nitrogen double bond compared with a carbon–carbon double bond, (b) very slight solvent dependence of the reaction rate,[1] (c) polarity decrease during activation,[2,3] (d) activation volumes that are close to zero,[4] (e) the same activation enthalpies in a cholesteric and isotropic solvents,[5] and (f) facile isomerization of the azobenzene unit fixed as a part of a ring system.[4] On the other hand, when the compound is push–pull substituted, namely, when it has strong electron-donating and electron-attracting substituents in 4- and 4′-positions, respectively, some experimental evidence favors the dipolar rotational transition state where the nitrogen–nitrogen π-bond is heterolytically ruptured and the rotation around the remaining σ-bond takes place. In 1972, Whitten and his co-workers[8] reported that the isomerization rate of 4-(diethylamino)-4′-nitroazobenzene, hereafter referred to as NEt_2-NO_2-AB, was strongly dependent upon the solvent polarity. In their recent investigations,[9,10] they examined the relations between the free energy of activation and a few empirical solvent polarity parameters, i.e., Kosower's *Z*, Taft's π^*, and Winnik's P_y[11] values. In each case, rough correlation was found. They also studied the absorption maxima of (*E*)-NEt_2-NO_2-AB in various solvents and showed that E_{max} for the π–π^* transition is, too, correlated with $\Delta G^{\ddagger}$. These findings were interpreted as the indications of the dipolar character of the activated complex, and they supported the rotation mechanism.

Scheme I



However, when the experiment was extended to the high-pressure condition, kinetic evidence that requires some modification of this simple picture was obtained.[3] Pressure effects on the isomerization rate of 4-(dimethylamino)-4′-nitroazobenzene, NMe_2-NO_2-AB, revealed that the reaction is greatly accelerated by increasing pressure in polar solvents as expected from the rotation mechanism (electrostriction), but in hexane, the acceleration was nominal. The activation volume in hexane was close to zero, while in polar solvents, the value was around −20 mL/mol or more. These results strongly indicate that the polarity of the activated complex is large in polar solvents but there is little polarity difference between the activated complex and the *Z* isomer in hexane. Therefore, we proposed a reaction scheme shown below.

In Scheme I the inversional and rotational isomerizations are competing. In the absence of solvational stabilization of the rotation transition state, the inversion route is predominant. When the solute–solvent interactions lower the energy of the dipolar transition state, the rotational route becomes predominant. In the intermediate case, the two reactions proceed at somewhat comparable rate.

This conclusion was challenged recently, however.[12] Andersson measured the isomerization rate of NMe_2-NO_2-AB in the vapor phase at 185–275 °C and estimated the rate constant at 25 °C by the Arrhenius equation. The value was close to the one obtained by means of the Kirkwood plot where ln *k* is plotted against $(\epsilon - 1)/(2\epsilon +$

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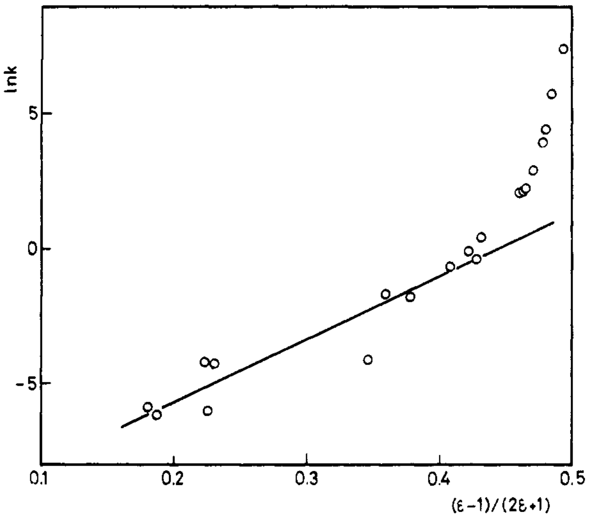

Figure 1. The Kirkwood plot for the *Z*–*E* isomerization of 4-(dimethylamino)-4′-nitroazobenzene at 25 °C.

1) (ε, dielectric constant). The roughly linear correlation between these two quantities, including the value in the vapor phase, was interpreted as an indication of one common reaction mechanism, i.e., inversion, because the lack of solvational stabilization of the dipolar transition state in the vapor phase should favor the inversion at the nitrogen atom. His plot included, however, only the rate constants in nonpolar and moderately polar solvents. The solvent with the highest dielectric constant was ethanol. The values in methanol and dipolar aprotic solvents like dimethyl sulfoxide were not included.

In this paper, first we will show that the Kirkwood plot becomes nonlinear when the values in polar solvents are included and, therefore, the rotational mechanism must be operative. Secondly, we will discuss the relative importance of electron-donating and electron-attracting substituents in lowering the energy of the rotational transition state.

Results and Discussion

Table I. First-Order Rate Constants for the *Z*–*E* Isomerization of 4-(Dimethylamino)-4′-nitroazobenzene in Various Solvents at 25 °C

solvent	ε[a]	k, s^{-1}
pentane	1.836	0.00271 ± 0.00015
hexane	1.89	0.00201 ± 0.00010
p-dioxane	2.209	0.0142 ± 0.0004
CCl_4	2.228	0.00236 ± 0.00013
C_6H_6	2.275	0.0108 ± 0.0011
Et_2O	4.325	0.0152 ± 0.009
$CHCl_3$	4.806[b]	0.180 ± 0.002[c]
C_6H_5Cl	5.621	0.163 ± 0.001
THF	7.58	0.510 ± 0.003
CH_2Cl_2	8.90	0.90 ± 0.02[d]
o-$C_6H_4Cl_2$	9.93	0.692 ± 0.003
1,2-dichloroethane	10.36	1.48 ± 0.02[d]
cyclohexanone	18.3[b]	8.35 ± 0.13[d]
i-PrOH	19.92	8.22 ± 0.18[d]
acetone	20.70	9.57 ± 0.15[d]
EtOH	24.55	17.87 ± 0.04
MeOH	32.70	51.2 ± 0.7
N,*N*-dimethylformamide	36.71	83.2 ± 1.45
Me_2SO	46.6	298 ± 7.7
formamide	111.0[b]	1640 ± 7.0

[a] Dielectric constant at 25 °C. [b] At 20 °C. [c] Reference 13. [d] Reference 3.

Solvent Effects. First-order rate constants for the isomerization of NMe_2-NO_2-AB at 25 °C and 1 bar were measured in twenty different solvents with various dielectric constants (from 1.836 for pentane to 111 for formamide). The values are listed in Table I and the Kirkwood plot is shown in Figure 1 where the line was drawn according to the result of the linear regression analysis performed on the basis of twelve data points from pentane to 1,2-dichloroethane. The values for NEt_2-NO_2-AB reported by Whitten and his co-workers[10] give a similar plot. The two sets of data show the same tendency, i.e., the rate constant increases moderately in relatively nonpolar solvents but it starts to deviate upward in the solvents with a dielectric constant of around 10. The rate constant in formamide, 1640 s^{-1}, is ca. 500 times as large as the extrapolated value, 3.3 s^{-1}, from the line for nonpolar solvents. These results clearly indicate that the *Z*–*E* isomerization can not be purely inversional in all of the solvents. Furthermore, even the modest rate increase in relatively nonpolar solvents corresponds to the fairly large charge separation in the activated complex as discussed by Whitten.[10,14] The Kirkwood plot suggests that the rotational mechanism becomes energetically competitive with the inversion route in dichloromethane or 1,2-dichloroethane, and the former mechanism dominates the latter in acetone and other polar solvents. Although the line was drawn for the twelve points, they may better be considered to consist a part of a nonlinear correlation. This again suggests the gradual shift of the mechanism. This discussion is in accordance with the results of high-pressure experiments. Some newly determined rate constants at various pressures and temperatures are given in Table II. Table III lists the activation volumes at zero pressure estimated either by eq 1 or 2. Equation 1 was used when

$$\ln \frac{k_p}{k_1} = a + bP \qquad (1)$$

$$\ln \frac{k_p}{k_1} = aP + \frac{bP}{1 + cP} \qquad (2)$$

the pressure effect was small and eq 2 was shown to be superior to the widely used quadratic equation.[13] As in eq 3, activation volume may be divided into two contributions, one from the changes in the size and shape of the reactants and the other from the changes in thermal motions of reactants and solvent molecules.[13] The first

$$\Delta V^{\ddagger} = \Delta V^{\ddagger}_{\text{int}} + \Delta V^{\ddagger}_{\text{therm}} \qquad (3)$$

contribution is usually referred to as intrinsic activation volume, and it is considered to be relatively insensitive to pressure. Since the reaction under discussion is unimolecular, the second contribution, thermal activation volume, mainly reflects the electrostrictive volume change during activation and is pressure dependent. From the rate constants in Table II, the intrinsic activation volume in methanol can be estimated as −7.1 mL/mol according to eq 4[16] where *B* is the Tait equation parameter of the

$$-\frac{RT}{P-1} \ln \frac{k_p}{k_1} = \Delta V^{\ddagger}_{\text{int}} - \frac{\kappa}{P-1} \ln \frac{B+P}{B+1} \qquad (4)$$

solvent and $\Delta V^{\ddagger}_{\text{int}}$ and κ are the parameters to be adjusted. Therefore, it may be a reasonable estimation that the contraction in thermal volume is around 20 mL/mol in

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(14) The slope for NMe_2-NO_2-AB is 23.5 (r = 0.950) while Whitten reported 33.9 (r = 0.945) for NEt_2-NO_2-AB.

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Table II. First-Order Rate Constants (k, s^{-1}) for the *Z–E* Isomerization of 4-(Dimethylamino)-4′-nitroazobenzene at Various Pressures in Several Solvents

	solvent (T, °C)				
P, bar	hexane (40)	hexane (55)	hexane (70)	benzene (70)	methanol (25)
1	0.0107 ± 0.0005	0.0450 ± 0.0010	0.159 ± 0.004[a]	0.578 ± 0.016	51.2 ± 0.7
300	0.0110 ± 0.0004	0.0453 ± 0.0011	0.171 ± 0.002	0.700 ± 0.013	67.3 ± 1.5
600	0.0119 ± 0.0008	0.0463 ± 0.0010	0.182 ± 0.002	0.829 ± 0.011	86.5 ± 1.7
900	0.0124 ± 0.0006	0.0476 ± 0.0008	0.194 ± 0.004	0.960 ± 0.014	105 ± 3.5
1200	0.0128 ± 0.0005	0.0506 ± 0.0008	0.207 ± 0.003	1.122 ± 0.026	124 ± 4.4
1500	0.0132 ± 0.0006	0.0531 ± 0.0010	0.218 ± 0.005	1.283 ± 0.036	147 ± 4.4
1800	0.0133 ± 0.0002	0.0556 ± 0.0011	0.227 ± 0.004	1.455 ± 0.051	173 ± 4.4
2100	0.0135 ± 0.0003	0.0586 ± 0.0014	0.236 ± 0.003	1.657 ± 0.036	203 ± 9.8
2400		0.0604 ± 0.0009			

[a] At 50 bar.

Table III. Activation Volumes at Zero Pressure for the *Z–E* Isomerization of 4-(Dimethylamino)-4′-nitroazobenzene

solvent	T, °C	$\Delta V_0^{\ddagger}$, mL/mol	ref
hexane	40	−3.02 ± 0.33	this work
	55	−3.68 ± 0.24	this work
	70	−6.76 ± 0.31	this work
CCl_4	40	−10.91 ± 1.32	3
C_6H_6	30	−23.81 ± 3.27	15
	40	−22.00 ± 0.68	3
	70	−19.36 ± 0.63	this work
$CHCl_3$	15	−25.90 ± 0.88	3
	25	−24.99 ± 0.25	13
CH_2Cl_2	25	−28.61 ± 0.65	3
1,2-dichloroethane	25	−27.74 ± 0.97	3
cyclohexanone	25	−20.19 ± 1.30	3
i-PrOH	25	−26.89 ± 2.48	3
acetone	25	−29.62 ± 0.57	3
MeOH	25	−27.17 ± 1.67	this work

Table IV. Apparent Thermal Activation Volumes and Calculated Electrostrictive Activation Volumes (mL/mol) for the Isomerization of (*Z*)-4-(Dimethylamino)-4′-nitroazobenzene

solvent	$(\Delta V^{\ddagger}_{\text{therm}})_{\text{app}}$	$\Delta V^{\ddagger}_{\text{el}}$
acetone	−23	−35
1,2-dichloroethane	−21	−89
CH_2Cl_2	−22	−121
C_6H_6	−17	−91

methanol at ordinary temperatures. As discussed above, this thermal volume change results mainly from increase in the electrostriction of solvent molecules during activation. The electrostrictive volume contraction of continuous medium caused by a dipole (dipole moment μ) in the center of a spherical cavity (radius r) is given by eq 5. For

$$\Delta V_{\text{el}} = -\frac{N_0\mu^2}{r^3}\frac{3}{(2\epsilon + 1)^2}\frac{\mathrm{d}\epsilon}{\mathrm{d}P} \qquad (5)$$

the activation process in the present reaction, we will get eq 6. If we assume that the isomerization in methanol is

$$\Delta V^{\ddagger}_{\text{el}} = -N_0\left[\frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} - \frac{\mu_{\text{cis}}^2}{r_{\text{cis}}^3}\right]\frac{3}{(2\epsilon + 1)^2}\frac{\mathrm{d}\epsilon}{\mathrm{d}P} \qquad (6)$$

purely rotational, we will be able to estimate $\Delta V^{\ddagger}_{\text{el}}$ values for hypothetical pure rotation in other solvents by comparing $[1/(2\epsilon + 1)^2]\mathrm{d}\epsilon/\mathrm{d}P$ values. The results are given in Table IV with the apparent thermal activation volume, $(\Delta V^{\ddagger}_{\text{therm}})_{\text{app}} = \Delta V_0^{\ddagger} + 7$, for several solvents. The larger difference between these two quantities in less polar solvents is a good qualitative indication of the importance of inversion in nonpolar media. From the slope of the line in Figure 1, the "average" value for $(\mu_{\ddagger}^2/r_{\ddagger}^3 - \mu_{\text{cis}}^2/r_{\text{cis}}^3)$ in nonpolar media can be calculated. For NMe_2-NO_2-AB, this is 9.67×10^{-13} erg and if the same value is true in methanol, it predicts that the $\Delta V^{\ddagger}_{\text{el}}$ is only −1.6 mL/mol. The value is much smaller than the "experimental" −20 mL/mol, again strongly suggesting that the polarity of the activated complex varies with the solvents.

In hexane, we would expect quite a small solvational stabilization for the dipolar transition state and, therefore, the enthalpy of activation will be higher for rotation than for inversion. If this is the case, partial shift of the mechanism from inversion to rotation would be expected at higher temperatures. The results in Table III bear this out. The activation volume at 70 °C, −6.76 mL/mol, indicates a modest polarity increase in the activation step at this temperature. To the contrary, in benzene, where a large acceleration by pressure is observed, the activation volume tends to become less negative with increasing temperature and this might be taken as an indication of lower activation enthalpy for rotation in benzene.

From these analyses, it can be reasonably concluded that the isomerization of NR_2-NO_2-AB proceeds via the inversion route in hexane and in the vapor phase, but in methanol and other polar solvents, it isomerizes through the dipolar rotational transition state. In the solvents with intermediate polarity, the proportion of the two reactions are supposed to depend strongly on the solvational ability of the solvent molecules. Next, we will discuss the question of which substituent plays a more important role in stabilizing the rotational transition state.

Substituent Effects. As can be seen in the foregoing discussion, the contribution from the rotation mechanism can be detected effectively by measuring the activation volume. Therefore, we undertook the kinetic experiments for 4-(diethylamino)azobenzene, NEt_2-AB, 4-(dimethylamino)-4′-chloroazobenzene, NMe_2-Cl-AB, sodium 4-[[*p*-dimethylamino)phenyl]azo]benzenesulfonate, NMe_2-SO_3-AB (methyl orange), and 4-nitroazobenzene, NO_2-AB, in several solvents up to 2.1 kbar. The results are shown in Tables V and VI. The activation volumes at zero pressure are given in Table VII. Table VII also includes the recalculated values for 4-methoxy-4′-nitroazobenzene, MeO-NO_2-AB.[3] The activation volumes for NO_2-AB clearly show that the nitro group on one of the para carbons is not enough to make the rotational transition state energetically competitive with the inversional state even in methanol. The addition of a methoxy group facilitates the isomerization but the effect is modest, and the polarity increase of the transition state is not high enough to result in large negative activation volumes. Since the rate constant for the unsubstituted azobenzene in heptane was calculated to be 2.4×10^{-6} s^{-1} at 25 °C based on the results by Halpern and his co-workers,[1] the nitro group seems to increase the rate ca. 11 times. Therefore, the lowering of the energy of the inversion transition state by the introduction of the nitro group amounts to only a few kilocalories/mole at most. The diethylamino group gives a

Table V. First-Order Rate Constants ($k \times 10^5$, s^{-1}) for the *Z–E* Isomerization of 4-Nitroazobenzene and 4-(Diethylamino)azobenzene in Various Solvents

	NO_2-AB		NEt_2-AB				
P, bar	hexane 25 °C	methanol 25 °C	hexane 25 °C	benzene[a] 25 °C	acetone 25 °C	ethanol 20 °C	methanol 20 °C
1	2.74 ± 0.10	6.30 ± 0.18	4.33 ± 0.03	5.20 ± 0.07	6.57 ± 0.12	3.72 ± 0.17	6.25 ± 0.24
300	2.82 ± 0.07	6.84 ± 0.09	4.73 ± 0.07		6.91 ± 0.17	3.79 ± 0.03	7.84 ± 0.25
600	2.92 ± 0.05	7.11 ± 0.17	4.57 ± 0.06	5.43 ± 0.02	7.25 ± 0.12	3.80 ± 0.06	9.60 ± 0.20
900	3.06 ± 0.12	7.32 ± 0.26	4.72 ± 0.03		7.32 ± 0.06	3.80 ± 0.03	11.5 ± 0.8
1200	3.20 ± 0.03	7.87 ± 0.19	4.74 ± 0.07			3.94 ± 0.04	13.7 ± 1.3
1500	3.31 ± 0.18	7.91 ± 0.32	4.65 ± 0.10			3.94 ± 0.22	18.3 ± 1.0
1800	3.57 ± 0.05	8.43 ± 0.34	4.92 ± 0.04			3.97 ± 0.11	22.3 ± 1.2
2100	3.67 ± 0.12	8.50 ± 0.32	5.33 ± 0.05			4.47 ± 0.14	27.0 ± 1.1

[a] The rate constants at other pressurs are 5.34 ± 0.03 (200 bar), 5.41 ± 0.02 (400 bar), and 5.49 ± 0.05 (700 bar).

Table VI. First-Order Rate Constants ($k \times 10^5$, s^{-1}) for the *Z–E* Isomerization of Some Disubstituted Azobenzenes

	NMe_2-Cl-AB			NMe_2-SO_3-AB		
P, bar	hexane 20°C	ethanol 20 °C	methanol 20 °C	ethanol 25 °C	methanol 25 °C	water 25 °C
1	3.28 ± 0.15	5.14 ± 0.25	6.16 ± 0.21	8.92 ± 0.29	11.0 ± 0.3	15100 ± 200
300	3.40 ± 0.13	5.34 ± 0.15	6.70 ± 0.41	9.01 ± 0.75	13.1 ± 0.5	18600 ± 600
600	3.42 ± 0.09	5.30 ± 0.28	7.66 ± 0.26	9.20 ± 0.15	16.8 ± 0.3	22800 ± 400
900	3.45 ± 0.07	5.29 ± 0.22	8.53 ± 0.19	9.52 ± 0.60	20.7 ± 0.2	27600 ± 800
1200	3.52 ± 0.04	5.29 ± 0.15	9.60 ± 0.46	10.06 ± 0.22	25.1 ± 0.6	32800 ± 900
1500	3.57 ± 0.06	5.36 ± 0.25	11.32 ± 0.24	10.68 ± 0.48	30.1 ± 0.4	39100 ± 700
1800	3.60 ± 0.09	5.52 ± 0.29	12.46 ± 0.55	10.88 ± 0.04	37.1 ± 0.6	44800 ± 1400
2100	3.75 ± 0.10	5.51 ± 0.23	15.49 ± 0.62	10.78 ± 0.56	45.6 ± 0.5	52200 ± 1900

Table VII. Activation Volumes at Zero Pressure for the *Z–E* Isomerization of Some Substituted Azobenzenes

	$\Delta V_0^{\ddagger}$, mL/mol				
solvent	NO_2-AB	NEt_2-AB	MeO-NO_2-AB[a]	NMe_2-Cl-AB	NMe_2-SO_3-AB
hexane	−3.67 ± 0.23	−1.68 ± 0.46	−1.18 ± 0.43	−1.14 ± 0.09	
C_6H_6		−1.73 ± 0.29	−2.64 ± 0.28		
CH_2Cl_2			−5.30 ± 0.39		
1,2-dichloroethane			−6.44 ± 0.98		
EtOH		−1.61 ± 0.42		−0.66 ± 0.16	−2.73 ± 0.28
MeOH	−3.48 ± 0.26	−17.55 ± 0.24[b]	−4.63 ± 0.47	−10.49 ± 0.45	−17.20 ± 1.26
H_2O					−17.95 ± 0.41

[a] Recalculated from the rate constants in ref 3. [b] *k* at 1.2 kbar is omitted in the calculation.

slightly larger rate constant in hexane but the pressure effect shows the lack of polarity of the activated complex. This is fully in agreement with the results for NMe_2-NO_2-AB. As discussed earlier, the pressure effect shows little polarity increase in the reaction of this azobenzene in hexane despite the presence of push–pull interactions between the substituents. The activation volumes are similar in benzene, acetone, and ethanol for NEt_2-AB. However, in methanol, the results are different. The increase in pressure results in fairly large acceleration. The activation volume is −17.6 mL/mol. Although the value is ca. 10 mL/mol less negative than that for NMe_2-NO_2-AB, it shows that the polarity increase takes place during activation. This result strongly suggests that the lowering of the energy of the rotational transition state can be realized by a strong electron donor like a dialkylamino group without the assistance from a pulling group if the reaction medium has enough solvational ability. Such a substituent lowers the inversional activation energy too as can be seen from the rates in nonpolar solvents, but the interaction with the electron-deficient sp^2-hybridized nitrogen is stronger than that with the sp-hybridized nitrogen, and in the presence of strong solvation, the dipolar transition state becomes important. The lack of large acceleration for NEt_2-AB in methanol suggests, however, the energy lowering is not as large as in NMe_2-NO_2-AB. The results are similar in NMe_2-Cl-AB. The rate constant increases slightly with the medium polarity, and the pressure effect is relatively large in methanol. Since the activation volume in methanol is smaller compared with that for NEt_2-AB, the *p*-chloro substituent seems to act as a suppressor for the electron donation by the amino group, suggesting that the mesomeric interaction between the chlorine and the nitrogen atoms overwhelms the inductive interaction.

If the large negative activation volume for NEt_2-AB in methanol is the result of the intervention of the rotation mechanism, we can expect that strong acceleration is brought about by changing the solvent to the one with much higher polarity. The measurements in formamide were attempted but the catalyzed isomerization could not be suppressed by the addition of a small amount of piperidine.[17] This problem prevented us from using formamide as a reaction medium and we chose to use a water-soluble azo dye for the study in a highly polar solvent. Judging from its Hammett substituent constant, 0.09, the sulfonate group is almost neutral in terms of push–pull interactions. Therefore, the measurements were performed for NMe_2-SO_3-AB in basic media. As in NEt_2-AB and NMe_2-Cl-AB, the rate constant is in the order of 10^{-5} s^{-1} in ethanol, and the pressure effect is small. By changing the solvent to methanol, the reaction is accelerated somewhat and the pressure effect increases as observed for the other two azobenzenes. However, the most striking results were the rate constants in water. The value abruptly increases from 1.1×10^{-4} s^{-1} in methanol to 1.51×10^{-1} s^{-1} and the activation volume is as large as in methanol despite the large dielectric constant and its

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(17) The rate constant depended upon the concentration of piperidine even at 1.5 M. It was also found that the irradiation caused the increase in the rate constant.

Table VIII. Solvent Effects on the *Z–E* Isomerization Rate of 2,4-Dinitroazobenzene

solvent	k, s^{-1}
hexane	3.27 ± 0.44
C_6H_6	4.09 ± 0.37
$CHCl_3$	9.25 ± 0.48
CH_2Cl_2	7.78 ± 0.41
acetone	4.78 ± 0.14
EtOH	4.38 ± 0.48
MeOH	3.54 ± 0.49
formamide	7.08 ± 0.98

small pressure dependence. The $[1/(2\epsilon + 1)^2]d\epsilon/dP$ values are 9.15×10^{-7} bar^{-1} for methanol[18] and 1.48×10^{-7} bar^{-1} for water[19] at 25 °C. Therefore, though the presence of a negative charge on the sulfonate group makes a quantitative comparison difficult, we can reasonably expect that $\Delta V^{\ddagger}_{\text{therm}}$ would be larger in methanol if the reaction proceeds via the same transition state in both of the solvents. Almost the same activation volumes in the two solvents suggest that the rotation may not be predominant in methanol. This conclusion is in agreement with the slight acceleration observed when the solvent is changed from ethanol to methanol.

All of these results unequivocally demonstrate that the crucial role in changing the mechanism of the *Z–E* isomerization from inversion to rotation is played by the electron-donating amino group, and the nitro group plays only a complementary role. In order to obtain further support for this conclusion, kinetic measurements for 2,4-dinitroazobenzene, $(NO_2)_2$-AB, were undertaken at atmospheric pressure. Because of the small change in absorption, the high pressure experiment could not be done with enough accuracy. The rate constants at 25 °C are given in Table VIII. Obviously, the second nitro group facilitates the isomerization a great deal. For example, in hexane, the rate constants are 2.74×10^{-5} s^{-1} for NO_2-AB and 3.27 s^{-1} for $(NO_2)_2$-AB. However, this extreme acceleration is not the result of the intervention of the rotation mechanism. As can be seen in Table VIII, the rate constant is nearly independent of the solvent polarity. The reaction proceeds at almost the same rate in both hexane and methanol, clearly denying the polarity increase in the activation step. The effect of the nitro group on the ortho carbon may be largely steric, namely, the substituent destabilizes the *Z* isomer by steric interactions with the ortho hydrogens of the other phenyl group. This view is supported by the examination of a CPK model of the molecule. The severe overlap of the oxygen atoms with the hydrogens in the *Z* isomer is completely relieved in the inversion transition state. Since the relief of the steric strain is also possible in the rotational transition state, again it can be concluded that the nitro group interacts more strongly with the sp hybridized nitrogen than with the sp^2 nitrogen.

Conclusion

The Kirkwood plot for the isomerization of (*Z*)-NMe_2-NO_2-AB shows a large upward deviation in polar solvents, and this deviation supports the change of the mechanism from inversion in nonpolar solvents to rotation in polar ones as previously proposed by the present authors. The large negative activation volumes for NEt_2-AB and NMe_2-SO_3-AB in methanol, and the rapid isomerization of the latter in water indicate that the presence of the dialkylamino group alone is sufficient to make the rotational isomerization competitive with the widely observed inversional isomerization.

Experimental Section

Materials. NEt_2-AB (mp 99–99.8 °C (lit.[20] 97.8 °C)), NMe_2-NO_2-AB (mp 234–235 °C (lit.[21] 232–234 °C)), and NMe_2-SO_3-AB (methyl orange) were commercial products and used after recrystallization. NO_2-AB (mp 138–139 °C (lit.[22] 135–135.2 °C)) was prepared from *p*-nitroaniline and nitrosobenzene. $(NO_2)_2$-AB (mp 119.8–121 °C (lit.[23] 116–117 °C)) was synthesized by the oxidation of 2,4-dinitrohydrazobenzene with yellow mercury(II) oxide in ethanol.[23] NMe_2-Cl-AB (mp 159.5–160 °C (lit.[22] 158–159 °C)) was prepared from *N,N*-dimethylaniline and 4-chloroaniline. All of the products were purified by recrystallization and column chromatography. The elemental analyses were satisfactory. Most of the solvents were spectrophotometric grade and used as received. Pentane, diethyl ether, chlorobenzene, *o*-dichlorobenzene, cyclohexanone, ethanol, and formamide were "guaranteed reagent grade" of Wako Pure Chemical Ind. and used after distillation, except formamide, which was used without further purification.

Kinetic Measurements. The isomerization was monitored by the absorbance change at or near the absorption maximum of the *E* isomer. The concentrations of all azobenzenes but $(NO_2)_2$-AB were in the range of $3{\sim}4 \times 10^{-5}$ M. For $(NO_2)_2$-AB, $8{\sim}10 \times 10^{-4}$ M solutions were used. Slow reactions were followed by a sampling technique[24] and rapid rates were measured by a flash spectroscopic method.[13] In the reactions with a half-life of a few minutes, a high-pressure optical cell which fits to a cell compartment of a double-beam spectrophotometer was used, and the reaction mixture was irradiated with a tungsten lamp.[25] In order to avoid catalysis by adventitious acidic impurities, piperidine (0.015–0.03 M) or sodium alkoxide (0.02–0.1 M) was added to the reaction mixtures for the azobenzenes with a dialkylamino group. In these concentration regions, the rates were independent of the base concentration within the experimental errors. The rates and the activation volume for NMe_2-SO_3-AB in water were slightly dependent upon the concentration of sodium hydroxide. The values in Tables VI and VII were obtained at $[OH^-] = 0.1$ M. The values at other concentrations were as follows: 0.147 s^{-1} (1 bar), –17.26 mL/mol (0.2 M) and 0.226 s^{-1} (1 bar), –21.06 mL/mol (0.02 M).

Registry No. NEt_2-AB, 2481-94-9; NMe_2-Cl-AB, 2491-76-1; NMe_2-SO_3-AB·Na, 547-58-0; NO_2-AB, 2491-52-3; NMe_2-NO_2-AB, 2491-74-9.

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