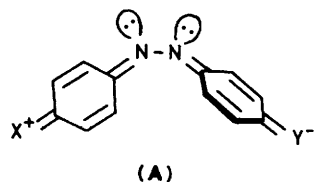


A Volumetric Study on the Thermal *cis*-to-*trans* Isomerization of 4-(Dimethylamino)-4'-nitroazobenzene and 4,4'-Bis(dialkylamino)azobenzenes: Evidence of an Inversion Mechanism¹

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The reaction volume (ΔV) for the thermal *cis*-to-*trans* isomerization of 4-(dimethylamino)-4'-nitroazobenzene in various solvents has been obtained by means of the photostationary state and capillary method. It has been shown that the activation volume (ΔV^\ddagger) is closely related to the reaction volume in each solvent. Substantial kinetic pressure and solvent effects have been observed for 4,4'-bis(dimethylamino)azobenzene, 4,4'-bis(diethylamino)azobenzene, and 4,4'-(dipyrrolidin-1-yl)azobenzene. The π - π^* conjugation band of the *trans*-isomers of these compounds shows a remarkable solvatochromic shift, and logarithms of kinetic constants in various solvents are satisfactorily correlated with the Taft π^* scale, which represents solvent polarity-polarizability interactions. From McRae's formula, it has been deduced that the interaction between the solvent dipole and the solvent-induced dipole has an important influence on the behaviour of these 'push-pull' and 'push-push' azobenzenes. The results afford unequivocal evidence that the isomerization proceeds *via* a coplanar inversion transition state which is electronically similar to the *trans*-isomer.

It is accepted that the thermal *cis*-to-*trans* isomerization of most azobenzenes proceeds *via* an inversion transition state. In 1971, Whitten and co-workers² reported very large kinetic solvent effects on the isomerization rate of 4-(diethylamino)-4'-nitroazobenzene (1) and suggested a rotational transition state (A) in which the original π -bond is ruptured

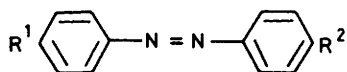


heterolytically. On the basis of a correlation of the free energy of activation with Kosower's Z values³ and other solvent polarity parameters,⁴ they suggested that the degrees of charge transfer in the transition state and in the Frank-Condon excited state are similar.

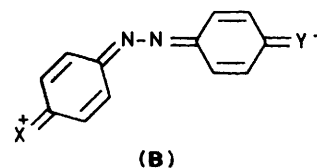
Asano *et al.*^{5,6} measured the isomerization rate of 4-(dimethylamino)-4'-nitroazobenzene (2) under high pressures, and estimated the activation volume (ΔV^\ddagger). They found $\Delta V^\ddagger \approx 0$ in hexane and $-20 \text{ cm}^3 \text{ mol}^{-1}$ in benzene. According to their view, this large difference affords unequivocal evidence

for a change in mechanism, *i.e.* from inversion in hexane to rotation in benzene, since only heterolytic scission should give rise to great enhancement of the dipole moment, and this in turn would cause stronger solvation in the transition state and a decrease in the volume of the system. Thereafter they^{7,8} estimated ΔV^\ddagger for various types of azobenzenes in various solvents and found that ΔV^\ddagger varies in the range 0 to $-30 \text{ cm}^3 \text{ mol}^{-1}$. They interpreted the results in terms of a competitive inversion-rotation mechanism, the degree of contribution depending on the nature of substituents and on solvent polarity.

On the other hand, Andersson⁹ has investigated the reaction of compound (2) in the vapour phase, and concluded on the basis of the Kirkwood plot that the inversion mechanism is involved in isomerization in solution as well as in the vapour phase. Marcandalli *et al.*¹⁰ have studied the isomerization of 4'-substituted 4-diethylaminoazobenzenes, and found that substitution in the 4'-position leads to a rate increase, regardless of the nature of the substituents. This is in accord with our previous results^{11,12} and those of Talaty and Fargo.¹³ They also found that the rate constants expressed on the logarithmic scale in various solvents are well correlated by the Taft π^* scale¹⁴ of solvent polarity for 'push-pull' as well as 'push-push' azobenzenes. They explained the results in terms of a highly dipolar transition state, stabilized through coplanar resonance structures such as (B).



R ¹	R ²
(1) NEt ₂	NO ₂
(2) NMe ₂	NO ₂
(3) [CH ₂] ₄ N	[CH ₂] ₄ N
(4) NMe ₂	NMe ₂
(5) NEt ₂	NEt ₂
(6) NMe ₂	H
(7) NEt ₂	MeO



We have previously examined substituent, solvent, and pressure effects on the isomerization rates of various types of azobenzene.^{12,15} We found no fundamental distinction between push-pull azobenzenes and other kinds. We considered that resonance stabilization in the transition state through a coplanar conformation (sterically impossible for *cis*-isomers) played the most important role in determining the rate. For push-pull azobenzenes in particular, the contribution of the

dipolar structure (B) is responsible for the rate increase and for the large negative ΔV^\ddagger values in polar solvents. It seems, however, that a discussion based on kinetic pressure, substituent, and solvent effects does not necessarily afford conclusive and unequivocal evidence for the mechanism in dispute.

In preliminary communications, we have shown that the partial molar volume of *trans*-(2) is linearly related to ΔV^\ddagger ,^{1a} and that ΔV^\ddagger is also well correlated with ΔV^{1b} in some solvents of different polarities. We considered that these findings supported the inversion mechanism, since the electronic structure of the inversion transition state would be similar to that of the *trans*-isomer.

In this paper, we discuss the proposed mechanisms more comprehensively. The main results that should be kept in mind are as follows: (i) ΔV^\ddagger is well correlated with ΔV in various solvents; (ii) the interaction between solvent dipole and solvent-induced solute dipole plays an important role; and (iii) even for push-push azobenzenes, for which the transition state (A) is least likely, the rate is substantially increased by external pressure.

Experimental

Materials.—4,4'-Di(pyrrolidin-1-yl)azobenzene (3). 1-Chloro-4-nitrobenzene was added to an excess of pyrrolidine to give quantitatively 1-nitro-4-(pyrrolidin-1-yl)benzene; this was recrystallized from acetone. The subsequent procedure is similar to that of Shine and Chamness.¹⁶ A mixture of ethanol (200 cm³), 12M-NaOH (12 cm³), and 1-nitro-4-(pyrrolidin-1-yl)benzene (6 g) was heated to boiling in a three-neck flask (500 cm³) equipped with a reflux condenser. Zinc dust (12 g) was added in small portions. Boiling was continued for 30 min after the addition was complete; the hot solution was filtered and filtrate neutralized with cold aqueous acid. The precipitate was dissolved in benzene and the product (3) was separated, purified by column chromatography, and recrystallized from chloroform-hexane; yield ca. 10%, m.p. 269–270 °C, δ_H (CDCl₃) 1.90–2.20 (m, 8 H), 3.18–3.60 (m, 8 H), 6.60 (d, *J* 8.6 Hz, 4H), and 7.81 (d, *J* 8.6 Hz, 4 H).

Other materials were used as supplied. Reagent-grade solvents were purified, dried, and distilled in the usual way.

Kinetic Measurements.—The high-pressure vessel used for the disubstituted azobenzenes was the same as reported previously.¹⁷ A sample solution was loaded into the (Teflon) inner cell. High pressure, generated by a plunger-pump, was measured with a Haise Bourdon gauge. After irradiation with a 650 W tungsten lamp for about 1 min, the light was cut off by a shutter, and the change in the absorbance at or near the absorption maximum of the *trans*-isomer was monitored with a Hitachi 139 spectrophotometer. The *cis* \rightleftharpoons *trans* reaction was repeated several times in the same solution, and the rate constant was estimated by first-order analysis. In order to avoid adventitious contamination by acid, which might affect the rate, small amounts of piperidine (0.3%) were added to the solution in every run.

Spectral Measurements.—The absorption spectra were recorded with a Hitachi 228 double-beam spectrophotometer. Spectra in the visible region for the push-push azobenzenes consisted of a few bands, attributed to a normal vibrational structure. Band separation was achieved by taking fourth-order derivatives by means of an integrated computer program; and the positions of the 0–0 bands were determined.

Partial Molar Volume of *trans*-(1).—A Kyoto Denshi DA-101B digital precision density meter placed in a thermostatically

controlled air-box was used. The temperature around the measurement cell was regulated to within 25 ± 0.001 °C by circulating doubly thermocontrolled water. Solutions of various molalities were prepared and their densities were measured. Partial molar volumes at infinite dilution in various solvents were estimated in the usual manner.

Volume of Reaction.—The *trans-cis* photostationary state was reached on irradiation of a solution of (2) in a high-pressure vessel (see Figure 2 of ref. 17) with visible light. The vessel was made of stainless steel, and fitted with two cells (for sample and reference solutions) and a stop-valve. The cells were equipped with sapphire windows in the horizontal direction for spectral measurements, and with one window in the vertical direction for irradiating the solution. The sample and the reference solutions were brought to the required pressure, and then the stop-valve was closed. The vessel was separated at the stop-valve from the pump system and brought into the cell compartment of a Hitachi 100-50 double-beam spectrophotometer. A projection lamp set vertically was used for irradiation. After the photostationary state was attained, the absorbance at the maximum absorption of the *trans*-isomer was measured at various pressures. Since the absorbance due to the *cis*-isomer could be neglected at this wavelength,² the *trans*:*cis* molar ratio could be estimated. The reaction volumes in various solvents were estimated from the pressure dependence of the molar ratio. When the excitation light was cut off, *cis*-to-*trans* isomerization started and the change in absorbance was recorded, from which the kinetic data were obtained.

A flat cell (ca. 1 600 cm³) equipped with a capillary tube (diam. 0.533 mm) and a vacuum stirrer was kept in a thermostat. The capillary was calibrated with mercury, and the temperature was regulated to within 25 ± 0.001 °C. After the solution had been loaded, it was irradiated from both sides of the cell with projection lamps. The temperature rose a little owing to absorption of light energy. After the light was turned off, the meniscus fell quasi-exponentially with time. The position of the meniscus was read every 10 s. A correction due to Newtonian cooling was made by following the temperature decrease with a thermistor immersed in the solvent used.

Results

The first-order rate constants for *cis*-to-*trans* isomerization of compound (2) in various solvents and at various pressures are given in Table 1. The photostationary *trans*:*cis* concentration ratios at various pressures are given in Table 2. It can be seen that the rate constants as well as the molar ratios depend markedly on external pressure and solvent polarity. The first-order rate constants for the isomerization of 4,4'-bis(dimethylamino)azobenzene (4), 4,4'-bis(diethylamino)azobenzene (5), and the dipyrrolidinyl derivative (3) were also estimated at various pressures and in various solvents (Tables 3 and 4).

Discussion

Volume Profile for the Isomerization of (2) in Various Solvents.—In the preliminary communication,^{1a} we showed that the partial molar volumes of *trans*-(2) (V_{trans}) in solvents of different polarities are linearly related to the activation volumes in the same solvents for thermal isomerization. If it is assumed that the partial molar volume of the *cis*-isomer (V_{cis}) does not change from solvent to solvent, the solvent dependence of ΔV^\ddagger is considered to be a reflection of that of V_{trans} . We concluded, therefore, that this relationship is in favour of the single-inversion mechanism, and against the rotation or the inversion-rotation competition mechanism. However, the volume profile of this reaction, if known, might well afford more convincing

Table 1. First-order rate constants ($10^3k/s^{-1}$) for the *cis*-to-*trans* thermal isomerization of 4-(dimethylamino)-4'-nitroazobenzene at various pressures, at 298.2 K

Solvent	$p/kg\text{ cm}^{-2}$							
	1	150	200	300	400	450	600	1 000
CCl ₄	2.96			3.38			3.72	4.32
Toluene	10.9	13.6		14.5			17.0	22.0
Benzene	12.3		14.1		17.1		18.7	
Dioxane	14.6	17.2		19.1		20.6	22.8	
Chlorobenzene	162			232			282	341
Chloroform	173			236			299	362

Table 2. Photostationary molar ratios ($[trans]/[cis]$) at various pressures, at 298.2 K

Solvent	$p/kg\text{ cm}^{-2}$							
	1	150	200	300	400	600	1 000	
CCl ₄	2.09	2.29		2.48		2.58	2.83	
Toluene	1.72	2.05		2.29		2.48	2.68	
Benzene	1.88		2.24		2.50	2.63		
Dioxane	1.42		1.70		1.85	1.90		
Chlorobenzene	2.22		2.92		3.36	3.78		
Chloroform	3.46			5.10		5.84	6.99	

Table 3. First-order rate constants for disubstituted azobenzenes at 313.2 K and 1 bar

Solvent	$10^2k/s^{-1}$		
	(4)	(5)	(3)
Hexane	0.353 ± 0.008	0.582 ± 0.003	0.422 ± 0.004
CCl ₄	0.371 ± 0.003	0.847 ± 0.006	0.607 ± 0.003
Toluene	0.491 ± 0.002	1.07 ± 0.01	0.906 ± 0.005
CH ₂ ClCH ₂ Cl	1.09 ± 0.01	2.78 ± 0.01	2.19 ± 0.02
CH ₃ CN	1.25 ± 0.01	3.13 ± 0.01	2.34 ± 0.01
(CH ₃) ₂ SO	1.77 ± 0.01	4.27 ± 0.02	2.86 ± 0.01

Table 4. First-order rate constants ($10^2k/s^{-1}$) for the isomerization of (3) at various pressures, at 313.2 K

Solvent	λ_{max}/nm^a	$p/kg\text{ cm}^{-2}$			
		1	400	800	1 200
Hexane	457	0.442	0.438	0.456	0.465
CCl ₄	470	0.607	0.620	0.637	0.648
Toluene	480	0.906	0.932	0.969	1.00
CH ₂ ClCH ₂ Cl	490	2.19	2.30	2.45	2.60
CH ₃ CN	488	2.34	2.42	2.48	2.52
(CH ₃) ₂ SO	499	2.86	2.90	2.95	3.02

^a π - π^* conjugation 0-0 band.

justification for the mechanism. However, the isolation of the *cis*-isomer has not been accomplished yet, and no reaction volume has been reported.

Very recently, we have proposed a convenient method of estimating ΔV .^{1b} When a solution of (2) was irradiated with a projection lamp under high pressure, the photostationary state was attained within 2-3 min. As shown in Table 2, the *trans*:*cis* molar ratio depends markedly on the applied pressure. If Scheme 1 is assumed,¹⁸ the molar ratio in the photostationary state is given by equation (1), where I denotes the light intensity.

$$[trans]/[cis] = \frac{k_1k_2k_{-3} + k_4(k_2k_{-3} + k_{-1}k_{-2} + k_{-1}k_3)/I}{k_{-1}k_{-2}k_3} \quad (1)$$

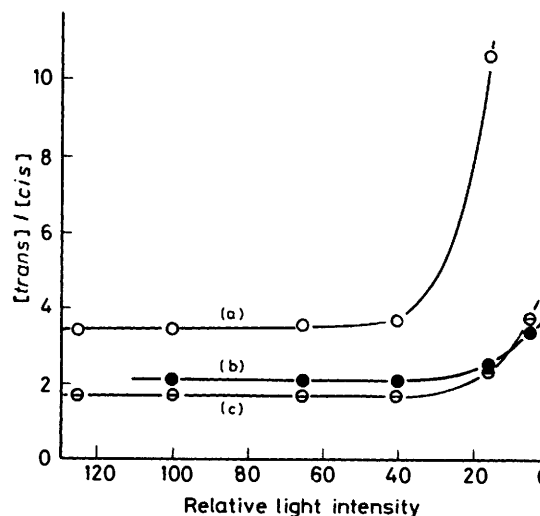
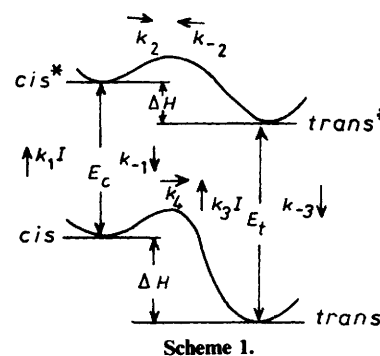
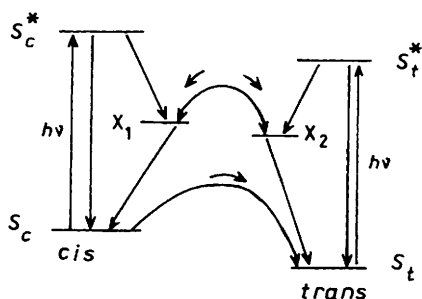
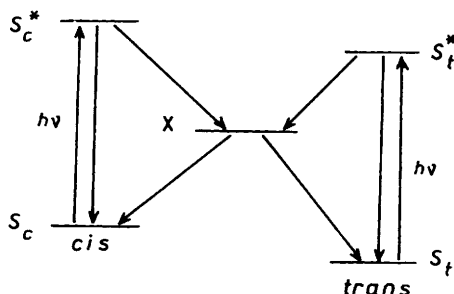


Figure 1. Photostationary state *trans*:*cis* molar ratios as a function of light intensity; solvents: (a) chloroform, (b) carbon tetrachloride, (c) toluene

Figure 1 shows the dependence of the ratio on I . It is seen that as I increases, the ratio decreases to reach a limiting value (R_∞), as expected from (1); see equation (2), where $k = k_1k_{-3}/k_{-1}k_3$, and $K^* = k_2/k_{-2}$ is the equilibrium constant for the photo-



Scheme 2.



Scheme 3.

$$R_{\infty} = k_1 k_2 k_{-3} / k_{-1} k_{-2} k_3 = kK^* \quad (2)$$

excited state. The energy diagram of compound (2) has not yet been established, and other models which can explain the pressure dependence are possible. Stegemeyer¹⁹ has developed simple models of *cis* \rightleftharpoons *trans* photoisomerizations in terms of two representative forms of different energy in the intermediate state: Scheme 2 involves an energy barrier between two intermediates, and Scheme 3 involves only one common intermediate. Stegemeyer pointed out that the main features of Scheme 1 are involved in Scheme 2. Indeed, if Scheme 2 is assumed, a similar pressure dependence on the *trans*:*cis* molar ratio can be derived, though a much more complicated treatment is required. Virtually the same scheme as Scheme 2 was suggested by Malkin and Fischer²⁰ for the photoisomerization of azobenzenes. However if Scheme 3, proposed by Yamashita *et al.*,²¹ is assumed, no pressure dependence can be expected. Therefore, even if we start from the simplest model (Scheme 1), the essential feature is accommodated.

The Förster cycle for Scheme 1 is given by equation (3). If the

$$\Delta G = \Delta G^* - (E_t - E_c) - T(\Delta S - \Delta S^*) \quad (3)$$

generally accepted assumption $\Delta S - \Delta S^* = 0$ is valid, the reaction volume is given by equation (4).

$$\Delta V = (\delta \Delta G / \delta P)_T = (\delta \Delta G^* / \delta P)_T = RT(\delta \ln R_{\infty} / \delta P)_T \quad (4)$$

At first sight, one might think that the pressure dependence of the photostationary state composition can never lead to the estimation of ΔV , because the composition cannot represent the equilibrium constant for the ground-state *trans*/*cis*-isomers. Although some inevitable assumptions are involved in deriving equation (4), the foregoing treatment can be justified by the substantial pressure dependence of R_{∞} . The reaction and activation volumes extrapolated to zero pressure were calculated by means of a quadratic regression equation using the data in Tables 1 and 2; they are given in Table 5.

The volume of the system decreases as the dark reaction

Table 5. Activation and reaction volumes ($\text{cm}^3 \text{mol}^{-1}$) in various solvents for the thermal isomerization of (2)

Solvent	ΔV^{\ddagger}	ΔV°	ΔV^b	V_{trans}
CCl_4	-10.2	-12.2	-11.7 ± 25.5	236.1 ± 5.8
Toluene	-22.1	-24.3	-23.6 ± 5.5	221.9 ± 2.5
Benzene	-22.8	-26.0	-25.6 ± 8.9	225.2 ± 3.7
Dioxane	-25.3	-26.9	-27.9 ± 8.8	217.9 ± 4.1
Chlorobenzene	-31.9	-33.8		214.5 ± 1.2
Chloroform	-29.5	-32.2		214.8 ± 3.1

^a Photostationary method. ^b Capillary method.

Table 6. Activation volumes extrapolated to $p = 0$ for the isomerization of disubstituted azobenzenes at 313.2 K

Solvent	$\Delta V^{\ddagger} / \text{cm}^3 \text{mol}^{-1}$		
	(4)	(5)	(3)
Hexane	-4.8	-5.9	-2.2
CCl_4	-1.2	-1.9	-1.5
Toluene	-3.7	-3.5	-2.2
$\text{CH}_2\text{ClCH}_2\text{Cl}$	-5.6	-5.7	-3.9
CH_3CN	-4.7	-5.7	-2.5
$(\text{CH}_3)_2\text{SO}$	-3.1	-4.7	-1.2

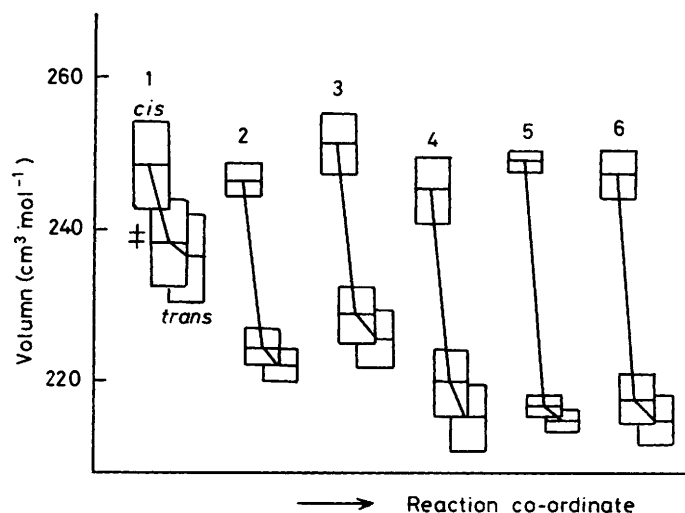


Figure 2. Volume profiles for the thermal *cis*-to-*trans* isomerization of (1) in various solvents: 1, carbon tetrachloride; 2, toluene; 3, benzene; 4, dioxane; 5, chlorobenzene; 6, chloroform

proceeds. Therefore, the dilatometric method was applied to estimate ΔV . When the sample solution was irradiated, a photostationary state was attained and the temperature of the solution became a little higher than that of the surroundings. The meniscus reading (r) as a function of time (t) after switching off the light source is given by equation (5), where A and B are

$$r = A \exp(-k_{iso}t) + B \exp(-k_{therm}t) \quad (5)$$

constants, k_{iso} denotes the isomerization rate constant, and k_{therm} is the Newtonian cooling constant. The constants A and B were determined by changing their assumed values until the experimental points reproduced the most probable curve satisfying equation (5). The reaction volumes in various solvents were calculated from A , the initial concentration of the *trans*-isomer, and the extent of isomerization at the appropriate time;

they are given in Table 5. Those data involve large error limits. In particular, solubility is very poor in CCl_4 , and this produces a large uncertainty. In spite of this, the ΔV^\ddagger values estimated by these two independent methods agree fairly well. Figure 2 shows the volume profiles for the isomerization in solvents of different polarities: $V_{cis} (=V_{trans} - \Delta V)$ is virtually independent of solvents used and the activation volume is well correlated with the reaction volume.

In this connection, it is worth summarizing the rotation theory developed by Asano *et al.* for the thermal isomerization of push-pull azobenzenes,⁵⁻⁷ as follows. (1) An enhanced polarization due to heterolytic π -bond fission occurs only in the rotation transition state. (2) The activation volume is quite sensitive to polarity change during activation. (3) If the reaction takes place *via* the inversion transition state, an increase in the polarity is hardly to be expected. (4) An activation volume obtained from the pressure effect, therefore, will provide unequivocal evidence for the operating mechanism.

Subsequently, Asano *et al.*⁸ have examined the kinetic pressure effect for various kinds of azobenzenes in various solvents and have found that ΔV^\ddagger varies widely according to substituents and solvents. They have explained these observations in terms of a competitive rotation-inversion mechanism. Similar results have been obtained by us.¹⁵ However, our interpretation is quite different. If the competition mechanism is valid, the volume profile must have a minimum, the depth of which depends on the degree of contribution of the two extremes. This is contradicted by our results.

On the other hand, the volume profile for the single-inversion mechanism would be monotonic and ΔV^\ddagger and ΔV would vary according to solvent polarity, since the electronic structure of the intermediate and hence the degree of solvation would be similar to that of the *trans*-isomer. Therefore, the foregoing findings are clearly in favour of the single-inversion mechanism.

Role of Interaction between Solvent Dipole and Solvent-induced Dipole.—By applying Kirkwood's formula to the transition-state theory for this reaction, the expression (6) can be

$$\ln k = \ln k_0 + \frac{N_A}{RT} \left(\frac{\mu_\ddagger^2}{r_\ddagger^3} - \frac{\mu^2}{r^3} \right) \left(\frac{\epsilon - 1}{2\epsilon + 1} \right) \quad (6)$$

obtained for the rate constant in a medium of dielectric constant ϵ , where k_0 is the hypothetical rate constant in a condensed medium of $\epsilon = 1$, and μ and r denote the permanent dipole moment and the radius of the solute molecule, respectively.

Andersson⁹ measured the isomerization rate of compound (2) in the vapour phase and found that the k value extrapolated to 25 °C coincided with the value predicted by the Kirkwood plot. He therefore concluded that the inversion mechanism is involved. His view was challenged immediately by Asano and Yano⁸ who measured rates in solvents of a wide range of polarities (ϵ 2–110) and found that if polar solvents ($\epsilon > 10$) are involved, the Kirkwood plot becomes non-linear, deviating upwards. They explained the results in terms of the intervention of a highly dipolar rotational transition state in highly polar solvents. Thus they appear to believe, from the context, that inversion is predominantly involved in solvents of low dielectric constant such as benzene (ϵ 2.3) and dioxane (ϵ 2.2). They reported in the same paper large negative ΔV^\ddagger values ($\text{cm}^3 \text{mol}^{-1}$): -23.8 (benzene; 30 °C), -22.4 (dioxane; 40 °C), and -25.5 (CHCl_3 ; 25 °C). Hitherto, they have consistently advocated that such large negative ΔV^\ddagger values afford unequivocal evidence for the rotational transition state. According to our view, their interpretation seems to arise from the fact that they have overestimated the significance of the ΔV^\ddagger value on the one hand, and of the Kirkwood treatment on the other hand. Here, we wish to develop our view of these problems.

The activation volume is usually divided into two terms: ΔV_{int}^\ddagger , the intrinsic volume change upon activation, and ΔV_{sol}^\ddagger , the volume change due to the change in solvation between the ground and transition states. From equation (6), equation (7) can be deduced. It is known that the $(\delta\epsilon/\delta P)_T/(2\epsilon +$

$$\Delta V_{sol}^\ddagger = -N_A \left(\frac{\mu_\ddagger^2}{r_\ddagger^3} - \frac{\mu^2}{r^3} \right) \frac{3}{(2\epsilon + 1)^2} \left(\frac{\delta\epsilon}{\delta P} \right)_T \quad (7)$$

$1)^2$ term generally decreases as solvent polarity increases. This is in agreement with the trend observed widely in Menschtukin reactions. However, in the Kirkwood treatment, the solvent molecules are regarded as a continuum, and specific solvent-solute interactions are neglected.

We have previously suggested that the upward deviation from the linear Kirkwood plot and the large negative values of ΔV^\ddagger in polar solvents might be due to the induced dipole in push-pull azobenzenes.¹⁵ In order to check this, McRae's formula (8) for frequency shift which arises from dipole

$$\Delta\nu = (AL + B) \frac{n^2 - 1}{2n^2 + 1} + C \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 1} \right) + F \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 1} \right)^2 \quad (8)$$

interactions was applied, where $\Delta\nu$ is the difference between absorption frequencies in solution and in the gas phase, $(AL + B)$, C , and F are constants independent of solvent properties, and n is the refractive index of solvents. In equation (8), the term C denotes the contribution from the interaction between permanent dipoles of solvent and solute molecules, and the term F represents the contribution from solvent dipole and solvent-induced dipole interaction, which may be regarded as the quadratic Stark effect.

On the basis of equation (8), we have estimated C and F . For compound (2) $C = -1712$ and $F = -1809 \text{ cm}^{-1}$; for (3) $C = -162$ and $F = -2836 \text{ cm}^{-1}$. The very small value of C for (3) comes from the fact that this substance has no permanent dipole moment. The magnitude of these F values indicates that this term cannot be ignored. Using the estimated values for $(AL + B)$, C , and F , the absorption frequencies (cm^{-1}) were calculated. In Figure 3, ν_{obs} is plotted against ν_{calc} for solvents of different polarities. A fairly good correlation is observed.

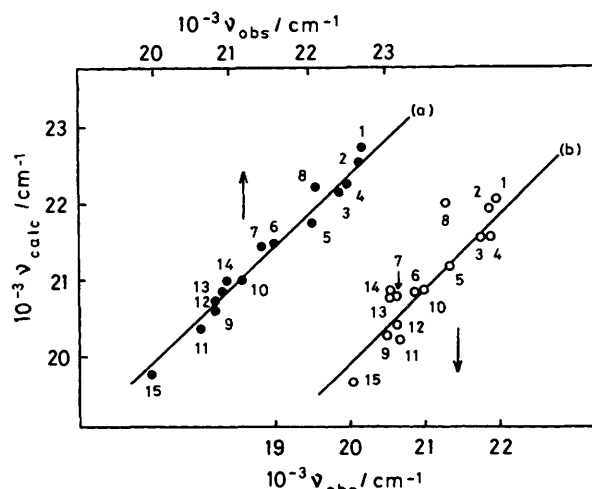


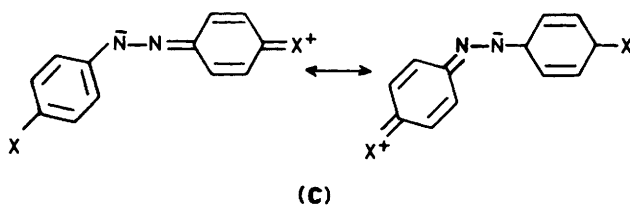
Figure 3. Plot of ν_{calc} vs. ν_{obs} for (a) *trans*-(1) and (b) *trans*-(3); solvents: 1, hexane; 2, heptane; 3, cyclohexane; 4, methylcyclohexane; 5, carbon tetrachloride; 6, toluene; 7, benzene; 8, diethyl ether; 9, chlorobenzene; 10, 4-methylpentan-2-one; 11, cyclohexanone; 12, ethyl benzoate; 13, propionitrile; 14, acetonitrile; 15, dimethyl sulphoxide

The foregoing findings suggest that a substantial polarization is induced in these kinds of azobenzene in polar solvents. In other words, μ_{trans} will become greater in polar solvents than in non-polar solvents. The same would be true for μ^\ddagger , by the reasoning already given. In deriving equations (6) and (7), the dipole moment in the transition state was tacitly assumed as constant, irrespective of solvent polarity. However, if the foregoing situation is taken into account, both the upward deviation from the linear Kirkwood plot and the large negative values of ΔV^\ddagger in polar solvents can be understood quite naturally. Experimental verification of such induction effects has been proceeding recently, and a theoretical treatment is being developed.^{22,23}

Solvent and Pressure Effects on the Isomerization of Disubstituted Push-Push Azobenzenes.—Whitten and co-workers⁴ have examined the kinetic solvent effect in detail for compound (1). They presumed from a linear correlation of the rate of isomerization with the position of the π - π^* band (referred to as charge-transfer absorption by them) of the *trans*-isomer in different solvents that the degrees of charge transfer in the transition state for the isomerization and the excited state were similar. For disubstituted azobenzenes, heterolytic π -bond scission [e.g. (A)] in the transition state is least likely. Therefore, the smallest kinetic solvent effect and the smallest charge-transfer band shift could be expected. We have already shown¹⁵ that compound (4) exhibits kinetic solvent and pressure effects intermediate between these of 4-dimethylaminoazobenzene (6) and (2). In addition, the bathochromic shift was more remarkable for (4) than for (6).

In order to confirm that push-push azobenzenes generally show such behaviour, we have examined the kinetic solvent and pressure effects for compounds (5) and (3) (Tables 3 and 4), and estimated the ΔV^\ddagger values (Table 6). The magnitudes of the rate constants in every solvent are in the order: (4) < (3) < (5). This order agrees with that of the pK_a values of the *para*-substituted benzoic acids.²⁴ In any case, it has been clarified that these kinds of compound exhibit considerable kinetic pressure and solvent effects, as well as solvatochromic shifts. Since transition state (A) is least likely for push-push azobenzenes, the idea that (A) is responsible for the remarkable kinetic solvent and pressure effects is questionable.

In the inversion transition state, canonical resonance structures (C) are possible through the coplanar conformation.



Such partially dipolar resonance contributions for the *trans*-isomer are considered to be more remarkable in the Frank-Condon excited state than in the ground state. Hence we can naturally understand the fact that the greater the solvatochromic effect, the faster becomes the isomerization, even for push-push azobenzenes. However, the electronic structure (B) is impossible for these kinds of compound and this is presumably the reason that the foregoing effects are much less remarkable than those for 'push-pull' azobenzenes.

It will be instructive to examine the rate constant in terms of the π^* scale of solvent polarities. According to Marcondalli *et al.*,¹⁰ the rate constant for the isomerization can be given by equation (9), where s is a constant measuring the response of \ln

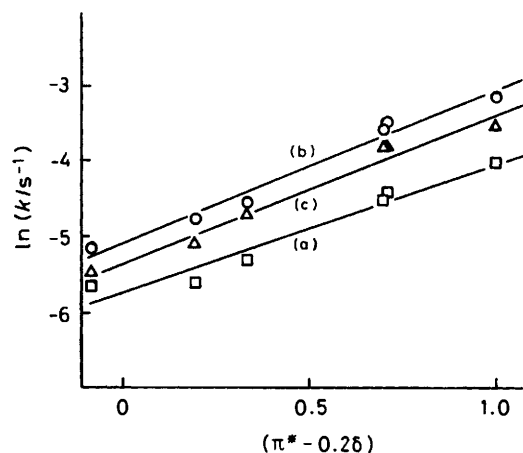


Figure 4. Rate constants (logarithmic scale) for the isomerization of (a) (1), (b) (3), and (c) (5) as a function of $(\pi^* - 0.28)$ at 313.2 K

$$\ln k_0 = \ln k + s(\pi^* - 0.28) \quad (9)$$

k to solvent polarity, and δ is a polarizability correction term, equal to 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatic solvents, and 1.0 for aromatic solvents. In Figure 4, $\ln k$ is plotted against $(\pi^* - 0.28)$. The s values for the linear plot are 1.69 for (4), 1.98 for (3), and 2.03 for (5). These values fall between those for (1) (10.6) and the methoxy-analogue (7) MeO-NEt₂-AB (0.88), but closer to the latter, as reasonably expected.

Conclusion

The thermal *cis*-to-*trans* isomerizations of push-pull and push-push azobenzenes are susceptible to kinetic solvent and pressure effects, but no essential difference in behaviour was observed between the two types. This leads to the conclusion that only one mechanism is involved. The main rate-controlling factor is resonance stabilization in the transition state through a planar conformation which is impossible for the *cis*-isomers and for transition state (A). Therefore, introduction of substituents of whatever type invariably accelerates the reaction and at the same time causes a solvatochromic shift. If 'push' and 'pull' substituents are introduced in the 4- and 4'-position, the rate is greatly enhanced, especially in polar solvents, owing to the addition contribution of (B). The volume profile indicates that the activation volume is close to the reaction volume in each solvent; thus the electronic structure of the activated complex is similar to that of the *trans*-isomer, having a planar conformation. It is concluded, therefore, that the present findings are in favour of the inversion mechanism and against the rotational one.

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Received 27th February 1986; Paper 6/410