

Evidence of an Inversion Mechanism for the Thermal *cis*–*trans* Isomerization of Push–Pull Azobenzenes. A Volumetric Study

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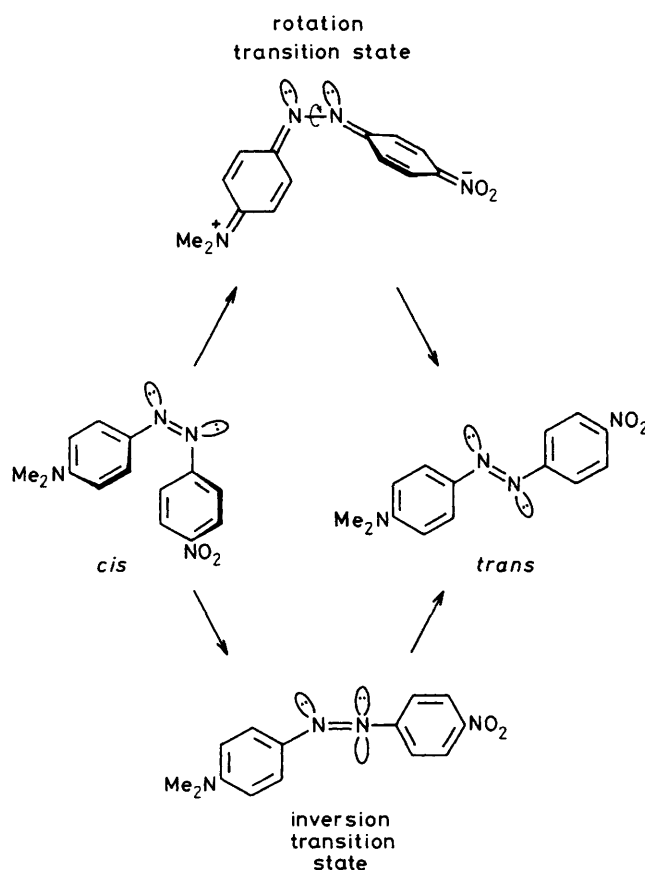
The partial molar volumes of *trans*-4-dimethylamino-4'-nitroazobenzene in solvents of different polarities are linearly related to the activation volumes in the same solvents for the thermal *cis*–*trans* isomerization of this species, which affords unequivocal evidence for an inversion transition state.

For most azobenzenes, the inversion mechanism has generally received recognition. However, the mechanism for push–pull azobenzenes such as 4-dimethylamino-4'-nitroazobenzene (NDAAB) is still a subject of debate. Whitten *et al.*^{1–3} found a very large kinetic solvent effect for push–pull azobenzenes and suggested a rotation mechanism in such a way that the –N=N– π -bond ruptures heterolytically to produce a dipolar transition state. Asano *et al.*^{4–6} studied the kinetic pressure effects and found that the activation volume ΔV^\ddagger decreased with an increase in solvent polarity and electron-donating power of the push-substituents. They have explained these findings in terms of the inversion–rotation competition mechanism. Recently, the inversion theory has been revived through mechanistic studies in the vapour phase⁷ and in various solvents.⁸ We have also undertaken a kinetic investigation of the solvent, substituent, and pressure effects of this reaction and have concluded that the observed results are

more consistent with the inversion mechanism rather than the rotation or inversion–rotation competition mechanism.⁹

In spite of apparently contradictory conclusions, there exists an agreement that activated complexes of this type of azobenzenes are more polar than the *cis*-isomers. A point in dispute is as follows: according to the inversion theory, a large polarity change occurs on proceeding from the initial to the inversion transition state, while according to the rotation theory, the polarity change in the inversion mechanism is, if any, very small. However, kinetic studies on the solvent, substituent, and pressure effects have not eliminated either of these mechanisms. Therefore, more convincing evidence of the mechanism of the isomerization is required.

The volume profile along the reaction co-ordinate is expected to be very different for the two routes, which are shown in Scheme 1. For rotation, the volume profile would have a deep minimum, since an extremely dipolar structure accompanied by heterolytic π -bond fission is assumed for the transition state. For inversion, the electronic distribution of the π -electrons in the transition state may become similar to that of the *trans*-isomer as a result of restoration of the coplanarity (which is possible for inversion only).^{8–10†} Hence, the activation volume, which is very solvent-dependent,^{6,9} may be correlated to the partial molar volume \bar{V} of the *trans*-isomer in the same solvent. The partial molar



Scheme 1

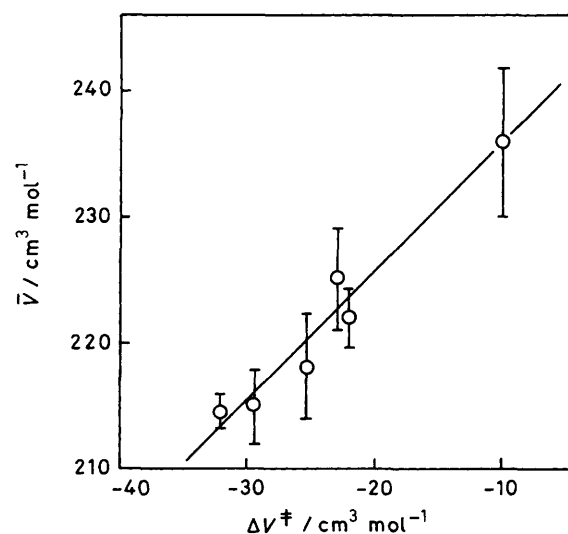


Figure 1. Partial molar volumes, \bar{V} , of *trans*-NDAAB vs. activation volumes, ΔV^\ddagger , for *cis*–*trans* isomerization of NDAAB in solvents of different polarities at 298.2 K.

† The effects of substituents on the dipole moments of azobenzenes have been discussed in detail in ref. 10.

Table 1. The partial molar volumes, \bar{V} , of *trans*-NDAAB and *trans*-DAAB at 298.2 K, and the volume of activation, ΔV^\ddagger , for *cis*-*trans* isomerization.

Solvent	NDAAB		DAAB	
	$\bar{V}/\text{cm}^3 \text{mol}^{-1}$	$\Delta V^\ddagger/\text{cm}^3 \text{mol}^{-1} \text{a}$	$\bar{V}/\text{cm}^3 \text{mol}^{-1}$	$\Delta V^\ddagger/\text{cm}^3 \text{mol}^{-1} \text{b}$
CCl ₄	236.1 ± 5.8	-10.2(298.2)	201.8 ± 2.0	-2.5(343.2)
Benzene	225.2 ± 3.7	-22.8(298.2)		
Toluene	221.9 ± 2.5	-22.1(298.2)	200.2 ± 1.7	-0.1(343.2)
Dioxane	217.9 ± 4.1	-25.3(298.2)		
CHCl ₃	214.8 ± 3.1	-29.5(298.2)	199.7 ± 1.5	-1.9(330.2)
Chlorobenzene	214.5 ± 1.2	-31.9(298.2)		
MeCN	185.1 ± 3.9	^c	194.8 ± 1.4	-3.6(323.2) ^d

^a Estimated by the method reported in ref. 9. ^b Cited from ref. 9. ^c The rate was too rapid to follow. ^d In MeOH.

volumes at infinite dilution of *trans*-NDAAB and *trans*-*p*-dimethylaminoazobenzene (DAAB) were estimated by density measurements in solvents of different polarities (Table 1). A Kyoto Denshi digital precision density meter DA-101B was used. The temperature was controlled within (25 ± 0.001) °C. For DAAB, both \bar{V} and ΔV^\ddagger are virtually solvent-independent.⁹ However, \bar{V} is linearly related to ΔV^\ddagger for NDAAB (Figure 1). This strongly supports the inversion mechanism, namely, the solvent dependency of ΔV^\ddagger is related to that of \bar{V} . This relationship between \bar{V} and ΔV^\ddagger cannot be explained in terms of the rotation or inversion-rotation competition mechanism. Reasons why the ΔV^\ddagger value of push-pull azobenzenes strongly depends on the solvent polarity have been suggested,⁹ but have not been substantiated to date.

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