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PRESSURE DEPENDENCE OF THE PHOTOSTATIONARY trans/cis CONCENTRATION RATIO OF 4-DIMETHYLAMINO-4'-NITROAZOBENZENE. A NEW METHOD OF EVALUATING THE REACTION VOLUME

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A simple method of obtaining the reaction volume by means of the photostationary state method has been proposed. The reaction volume for the cis-to-trans thermal isomerization of 4-dimethylamino-4'-nitroazobenzene in some solvents was found to be well correlated to the corresponding activation volume.

It is generally recognized that the activation volume ($\Delta V^{\ddagger}$) affords valuable information about the transition state and hence the reaction mechanism for any reaction. With the development of high pressure techniques, the estimation of $\Delta V^{\ddagger}$ became rather routine work for kineticists. Very recently, Yoshimura et al.¹⁾ found that $\Delta V^{\ddagger}$ was well correlated to the reaction volume (ΔV) for 1,3-dipolar cycloaddition reactions, and pointed out the importance of drawing the volume profile as well as the energy profile in order to determine the mechanism. However, in contrast to the vast accumulation of the $\Delta V^{\ddagger}$ data, comparatively a little amount of the ΔV data are available up to date.

In this letter, we wish to report a convenient method of evaluating ΔV for the thermal cis-to-trans isomerization of 4-dimethylamino-4'-nitroazobenzene (<u>1</u>) from the pressure dependence of the photostationary trans/cis ratio. When trans-<u>1</u> was irradiated with a projection lamp under various pressures, the photostationary state was attained within 2 min. It was found that the ratio remarkably depended on the applied pressure. The data are given in Table 1.

Table 1. Pressure Dependence of the Photostationary trans/cis Ratio of <u>1</u>

	P/kg cm^{-2} a)					$\Delta V/cm^3\ mol^{-1}$	$\Delta V^{\ddagger}/cm^3\ mol^{-1}$
Solvent	1	150	300	600	1000		
CCl_4	2.09	2.29	2.48	2.58	2.83	-12.2	-10.3
Toluene	1.72	2.05	2.29	2.48	2.68	-24.3 b)	-22.0
$CHCl_3$	3.46	5.10		5.84	6.99	-32.2	-30.4

a) 1 kg cm^{-2} = 0.9807 bar. b) This value may be compared with the one 24.0 ±3.2 $cm^3\ mol^{-1}$ obtained by dilatometric method.

The simplest kinetic mechanism consistent with the pressure dependence is depicted by Scheme 1. This scheme is virtually the same as that suggested by Zimmerman et al. for azobenzene.[2)] By using the Förster cycle and thermodynamic parameters, the free energy change for the isomerization is given by

$$\Delta G = \Delta G^{*} - (E_t - E_c) - T(\Delta S - \Delta S^{*}) \qquad (1)$$

where the asterisk refers to the excited state. According to Scheme 1, the trans/cis molar ratio in the photostationary state (r_e) can be given by

$$r_e = \frac{k_1k_2k_{-3} + k_4(k_2k_{-3} + k_{-1}k_{-2} + k_{-1}k_{-3})/I}{k_{-1}k_{-2}k_3} \qquad (2)$$

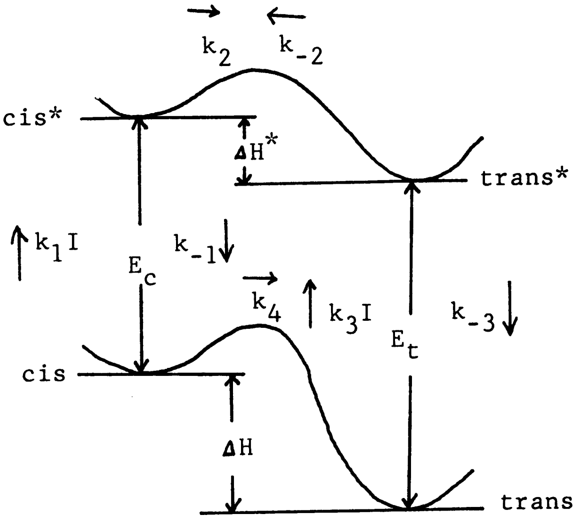
where I denotes the light intensity. We found that the ratio decreased with increasing the light intensity to reach a constant value as expected from Eq. 2. In this case, r_e is given by

$$r_e = \text{const} \times K^{*} \qquad (3)$$

where $K^{*} = k_2/k_{-2}$. If the 2nd and 3rd terms in Eq. 1 are independent of pressure, as usually be assumed in the Förster cycle,[3)] then it follows from Eqs. 1 and 3:

$$\Delta V = \left(\frac{\partial \Delta G}{\partial p}\right)_T = \left(\frac{\partial \Delta G^{*}}{\partial p}\right)_T = -RT\left(\frac{\partial \ln r_e}{\partial p}\right)_T \qquad (4)$$

The reaction volumes extrapolated to p = 0 were estimated from the quadratic regression equation and are given in Table 1, together with the $\Delta V^{\ddagger}$ values cited from Ref. 4. A good correlation between $\Delta V^{\ddagger}$ and ΔV, and the numerical agreement of the ΔV value in toluene with the one obtained dilatometrically suggest strongly the validity of the proposed method of estimating the reaction volume of 1. The above correlation affords strong evidence in favor of the inversion mechanism we have proposed[4)] and against the rotational one[5,6)] because of the small difference between $\Delta V^{\ddagger}$ and ΔV. Details will follow.



Scheme 1.

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