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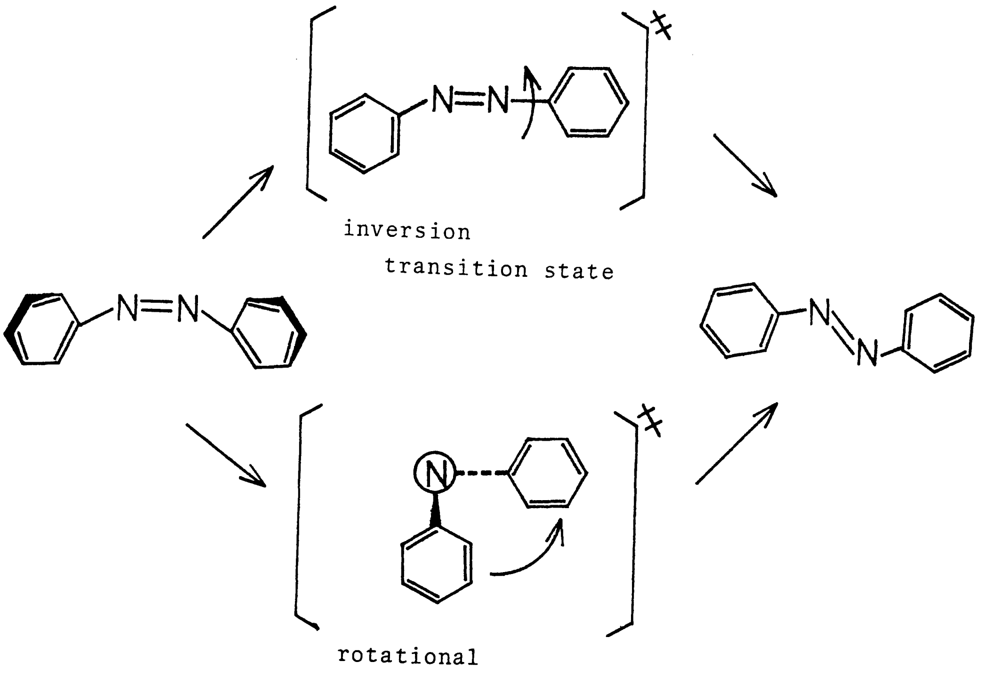
ON THE ROTATION VERSUS THE INVERSION MECHANISM IN THE THERMAL ISOMERIZATION OF CIS-AZOBENZENES

Seiji SHINKAI,* Yumiko KUSANO, Kazuyoshi SHIGEMATSU, and Osamu MANABE
Department of Industrial Chemistry, Faculty of Engineering,
Nagasaki University, Nagasaki 852

The thermal cis-to-trans isomerization of an azobenzene covalently-bridged to azacrown ether occurs via the inversion mechanism, and the rotational mechanism is not allowed owing to the rigid ring structure. By using the "standard" azobenzene, it was demonstrated that the thermal isomerization of most cis-azobenzenes occurs via the inversion mechanism, the activation parameters being subject to a good $\Delta H^{\neq}$ - $\Delta S^{\neq}$ compensation relationship.

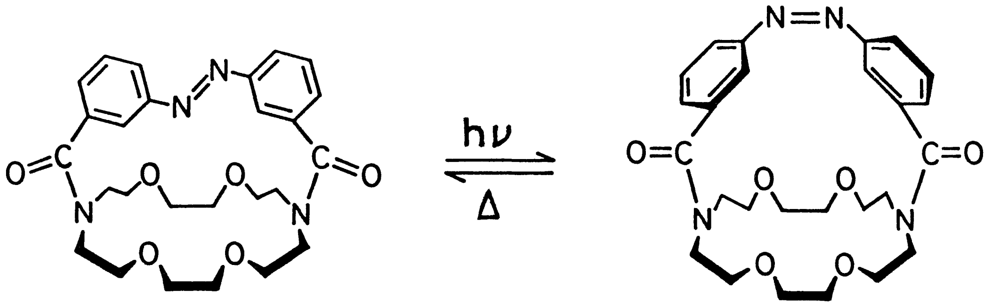
The thermal isomerization of cis-azobenzenes to trans-azobenzenes has been a controversial problem. Two opposing mechanisms have been proposed: the reaction may proceed either via the rotational mechanism involving the rotation about the N=N bond or the inversion mechanism involving the flip-flop inversion of one of the nitrogen atoms.



Nerbonne and Weiss[1)] argued for the rotational mechanism on the basis of the activation parameters in cholesteric liquid crystal solvent, whereas Ljunggren and Wettermark[2)] and Haberfield et al.[3)] argued for the inversion mechanism on the basis of the theoretical calculation and the enthalpy of solvent transfer, respectively.

Nishimura et al.[4] also supported the inversion mechanism on the basis of substituent and solvent effects. Here, we wish to report a new, unambiguos method to distinguish between the rotational and inversion mechanisms on the basis of a $\Delta H^{\ddagger}$-$\Delta S^{\ddagger}$ compensation relationship.

We synthesized an azobenzene-bridged crown ether (1).[5] Since two benzene rings are covalently-linked to the crown ether ring, the thermal cis-to-trans isomerization via the rotational mechanism is highly unlikely. The CPK model building suggests that the rotational transition state requires either an extreme steric hindrance between the azobenzene and the crown ether ring or a highly distorted conformation of the crown ether. On the other hand, the inversion of the azo-linkage occurs smoothly without requiring the steric distortion of the crown ether. It is presumed, therefore, that the rotational isomerization of cis-(1), if it were possible, would proceed via an energetically-unfavorable transition state, resulting in an extremely large free-energy of activation. We observed that cis-(1) is isomerized in the dark to trans-(1) quantitatively and the first-order rate constant ($k = 1.56 \times 10^{-5}\ s^{-1}$ at 40°C in benzene) is comparable with that of an analogous azobenzene, 3,3'-bis(morpholinocarbonyl)azobenzene (2) ($k_1 = 6.28 \times 10^{-6}\ s^{-1}$ at 40°C in benzene). The finding unambiguously indicates that the thermal isomerization of cis-(1) proceeds via the inversion mechanism.



trans-(1) cis-(1)

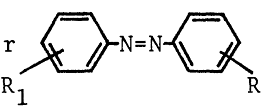
We determined the activation parameters about several azobenzene derivatives (Table). Most importantly, we found that the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for (1)-(4) (see Table) are subject to a compensation relationship (Figure). The plots are expressed by Eq. (1) with an excellent correlative coefficient (r=0.999).

$$\Delta H^{\ddagger}(\mathrm{cal\ mol^{-1}}) = 359\,\Delta S^{\ddagger}(\mathrm{eu}) + 26.3 \times 10^{3} \qquad (1)$$

The result clearly supports that the thermal isomerization of (1)-(4) occurs via a single mechanism[6] (i.e., inversion mechanism).

Previously, Nerbonne and Weiss[1] argued for the rotational mechanism. Their proposal is based on the finding that the Arrhenius plot for the thermal isomerization of cis-azobenzene in a liquid crystal does not yield a single straight-line slope for the cholesteric and isotropic phases. We found, however, that all the activation parameters obtained by them (half-filled circles in Figure) are also included in the line expressed by Eq. (1). Adding their data to ours, we obtained

Table. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the thermal isomerization for



a)

Material No.	R_1	R_2	Solvent	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ eu
1			benzene	18.2	-22.6
2	3-MC[d)]	3'-MC	benzene	23.0	- 9.3
2	3-MC	3'-MC	o-DCB[b)]	11.8	-39.0
3	4-MC	4'-MC	o-DCB[b)]	12.3	-39.3
4	H	H	hexane	7.1	-55.0
4	H	H	CB[b)]	7.6	-52.6
4	H	H	o-DCB[b)]	3.3	-63.0
5	4-NMe_2	4'-NO_2	hexane	3.4	-56.7
5	4-NMe_2	4'-NO_2	benzene	0.1	-63.9
5	4-NMe_2	4'-NO_2	dioxane	15.2	-15.8
5	4-NMe_2	4'-NO_2	benzene:dioxane[c)]	14.5	-18.5

[a)] Photoisomerization of (1)-(4) was carried out with a 500W high-pressure Hg-lamp and that of (5) with a 150W tungsten-lamp. [b)] o-DCB and CB denote o-dichlorobenzene and chlorobenzene, respectively. [c)] 1:1 in vol.
[d)] MC denotes morpholinocarbonyl (-CON⌒O).

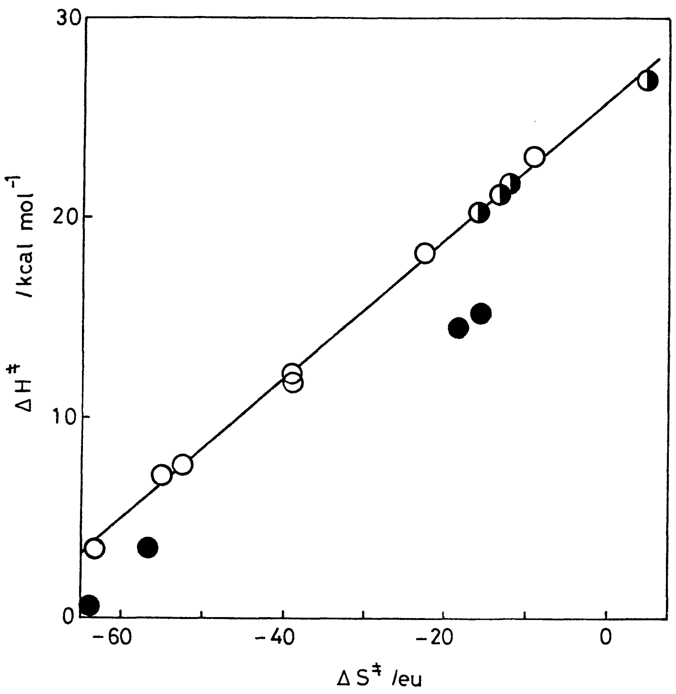


Figure. $\Delta H^{\ddagger}$-$\Delta S^{\ddagger}$ Compensation relationship. Half-filled circles are the data cited from Ref. 1. Filled circles are the data for 4-dimethylamino-4'-nitroazobenzene

Eq. (2) (r=0.999), which is essentially equivalent to Eq. (1).[7]

$$\Delta H^{\ddagger}(\mathrm{cal\ mol^{-1}}) = 348\ \Delta S^{\ddagger}(\mathrm{eu}) + 25.8 \times 10^{3} \qquad (2)$$

Presumably, a break point in their Arrhenius plot reflects the influence of a phase transition of the liquid crystal on the inversion mechanism but not on the rotational mechanism.

Very recently, Asano[8] reported on the basis of the pressure effect that a push-pull-substituted azobenzene (5) (see Table) may proceed via the rotational mechanism. We found that the activation parameters for (5) (filled circles in Figure) clearly deviate from Eq. (2): in dioxane, for example, 4.8 kcal mol^{-1} downward from the linear relationship. In extrathermodynamic relationships, a $\Delta H^{\ddagger}$ - $\Delta S^{\ddagger}$ compensation relationship is valid as evidence for a single reaction mechanism, whereas a deviation from the linearity does not become "direct" evidence for a change in the reaction mechanism.[6] Therefore, one cannot ascribe readily the deviation of the plots for (5) to the involvement of the rotational mechanism. However, when considering the present results together with those of the pressure effect reported by Asano,[8] the deviation is most probably due to the rotational mechanism (at least partially). In order to further specify the origin of the deviation, one has to make another "standard" azobenzene derivative, the thermal isomerization of which occurs only via the rotational mechanism.

In conclusion, the present study demonstrated that (i) the thermal isomerization of cis-azobenzenes without push-pull substituents occurs via the inversion mechanism, and (ii) the activation parameters are subject to a $\Delta H^{\ddagger}$ - $\Delta S^{\ddagger}$ compensation relationship.

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