Mechanism of Thermal Isomerization of Azobenzene in Zeolite Cavities

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The life time of *cis*-azobenzene in zeolite supercage is twenty times longer than that in benzene at room temperature. The kinetic studies indicate that the thermal isomerization proceeds through inversion mechanism. Activation parameters show that the zeolite nanospace gives the same environment as that of gas phase.

The *cis*-to-*trans* photoisomerization of azobenzene (AB) is used for switching a function of molecule, such as artificial enzyme[1] and probing the microenvironments of compound such as polymer and clay.[2] Recently there were papers concerning that zeolite nanocavities are promising photochemical reaction vessels, which can control the photoreactivities of guest organic molecules.[3,4] We have already reported photochemical behavior of stilbene such as isomerization and oxidation in zeolite cavity.[5] Hoffman and Lei reported photoisomerization and photocyclization of AB in zeolite microenvironment.[6,7] However, no clear understanding has yet emerged as to the effect of the zeolite nanospaces on the mechanism. AB has been well-studied in solution because of its importance as a photochromic molecule. In this paper we report that the isomerization proceeds through inversion mechanism judging from activation parameters of AB in zeolite microenvironment.

The experimental procedure for the preparation of the azobenzene incorporated into zeolite Y (Faujasite) is the same as that in our previous paper.[5] *cis*-Azobenzene (*c*-AB) was prepared by column chromatographic separation of irradiated sample of *trans*-AB (*t*-AB). The Raman spectra confirmed that *t*-AB, starting material, was adsorbed into the supercages of zeolite Na-Y (NaY) and K-Y (KY) without any change. After the photo- and thermal reactions, AB was extracted with CH_2Cl_2 from zeolite and [*c*-AB]/[*t*-AB] were determined by HPLC. Only isomerization occurred without giving any by-products. For kinetic measurements, *c*-AB adsorbed zeolite sample was prepared with cyclohexane solution of *c*-AB and an activated zeolite. Samples were thermostated without light. Figure 1 shows disappearances of [*c*-AB] at various temperatures. The decrease of *c*-AB proceeds with a first order kinetics. The isomerization rate constant was obtained from [*c*-AB] by HPLC. As intensities of Raman band of *t*-AB in cyclohexane are linearly correlated with the concentration of *t*-AB determined by HPLC, we apply Raman spectra to in situ analysis. The growth of Raman intensity gives us a first order rate constant. These two different methods gave similar rate constants. Figure 2 shows Arrhenius and Eyring plots for rate constants obtained from HPLC and Raman. Table 1 shows activation parameters for the thermal isomerization of AB in various media. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in Y zeolite are bigger than that in benzene[8] and polycarbonate film.[9] The value in zeolite is close to that in vapor phase.[11]

There are two papers about isomerization of AB in zeolite cavity.[6,7] They reported on a spectroscopic investigation of photoisomerization of AB. But they only observed photo-reversibility of spectra. There were no data about *c*-AB in zeolite cavity. We studied these behavior by means of HPLC and Raman. *c*-AB which we introduced into zeolite cavity was stable at least for two thousands hours at room temperature. The life time of *c*-AB is twenty times longer than that in benzene. *c*-AB is stabilized in microenvironment of the zeolite cavity. *c*-AB ultimately isomerized to *t*-AB. In the presence of proton, *c*-AB can easily give a cyclized compound such as benzo[*c*]cinnoline (BC) in solution. Photolysis of AB in H-zeolite led to the formation of BC and benzidine.[12] We could not observe any cyclization products in NaY and KY, in which all the Brønsted acid sites could not be replaced by alkali metal.

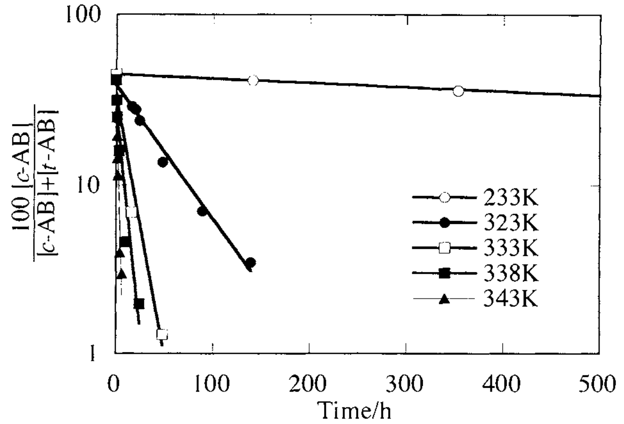

Figure 1. First-order plots for disappearance of [*c*-AB] at various temperature.

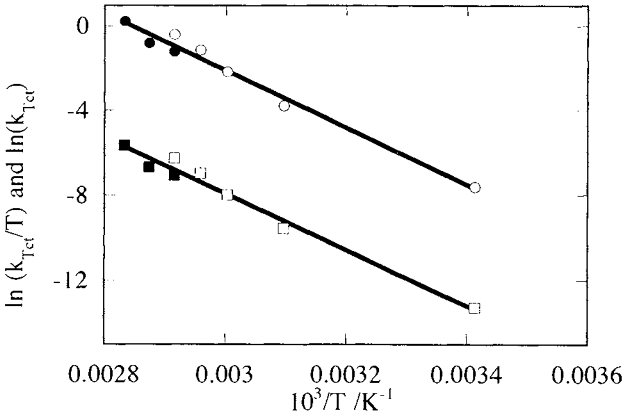

Figure 2. Arrhenius and Eyring plots for *cis*-to-*trans* thermal isomerization rate constant obtained by HPLC (□,○) and Raman (■,●).

There are two mechanisms for isomerization of AB. One is inversion mechanism; phenyl ring is swept though a planar transition state with a sp-hybridized N atom. The other is rotation mechanism; phenyl ring rotates about the N=N bond. Shinkai and Asano showed isokinetic plot for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$

Table 1. Activation parameters for the thermal isomerization of azobenzene in various media

	Benzene^a	NaY	KY	PC Film^b	Vapor Phase^c
$\Delta H^{\ddagger}$ / kcal mol^{-1}	21.7±0.4	26.9±1.5	28.0±1.9	14.9	27.6
$\Delta S^{\ddagger}$ / cal mol^{-1} K^{-1}	-12.0±1.3	2.2±4.6	7.1±5.9	-29.2	3.3
logA / s^{-1}	10.6	13.3±1.0	14.4±1.3	6.4	14.0
τ_{293K} / hr	110	2000	2000		

^{a}Reference 8. ^{b}Reference 9. ^{c}Reference 11.

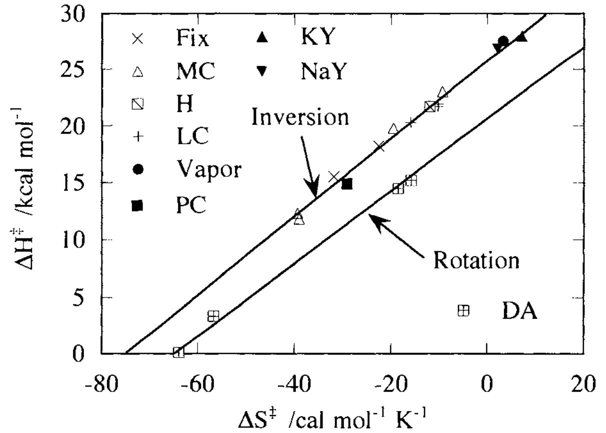

Figure 3. Isokinetic Plots for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

(Fix; azobenzene-bridged crown ether, MC; morpholinocarbonyl-azobenzene, DA; push-pull azobenzene, azobenzene in organic solvent (H) cited from ref. 13, in liquid crystalline solvent (LC) cited from ref. 8, in vapor phase (Vapor) cietd from ref. 11, in polycarbonate film (PC) cited from ref. 9, in zeolite (NaY, KY)).

(compensation rule) for isomerization of azobenzene.[13] The data for aza crown ether which cannot isomerize by rotation mechanism, set on the line for inversion mechanism. Weiss *et al.* studied liquid crystalline solvents as mechanistic probe for AB isomerization with an isokinetic plot.[8] Isokinetic plots treatment is best way to determine the isomerization mechanism for azobenzenes. We applied our data together with other 12 data sets for the isokinetic plots as shown in Figure 3 and found that these two points stood in the line for inversion mechanism. This indicates that the isomerization of AB in zeolite Y proceeds through inversion mechanism.

Obtained $\Delta H^{\ddagger}$ are slightly bigger than that in benzene and $\Delta S^{\ddagger}$ is positive and small, close to zero. Moreover, Raman spectrum of *t*-AB is identical to that of solid state of *t*-AB. These facts mean that azobenzene does not strongly interact with wall of zeolite cavity. But diffuse reflectance spectra of *t*-AB in NaY and KY showed that intensity ratio of n-π* and π-π* transition is different. It probably means that alkali metal can weakly interact with azobenzene. In the case of stilbene photoisomerization, we found that activation energy in zeolite was higher than that of solution because of interaction between stilbene and zeolite. There is possibility that microenvironment effect is a volume effect. Naito *et al.* estimated the volume for isomerization of AB is 0.12 nm^3 for inversion.[10] The volume of suparcage of Y zeolite is 0.83 nm^3 which is enough space for transition state of inversion.

In our experimental conditions, solvent molecules are not present in zeolite cavity but gas molecules are trapped and its motion is restricted. Thus, AB is supposedly surrounded by gas molecules which cannot stabilize the transition state of the isomerization. In solution, the interaction between an activated AB and solvent molecules can stabilize the transition state. So, the lifetime of *c*-AB in the cavity is twenty times longer than that in benzene. Obtained activation parameters are similar to that of gas phase as shown in Table 1. The zeolite nanospace gives the same environment as that of gas phase.

Zeolite nanospace can be useful environments for photochromic system because *c*-AB which is usually unstable could have a long life time. Studies of photochromic molecule in zeolite nanocavity are in progress. It is hoped that we will provide further evidence for the proposed microenvironmental effects.

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