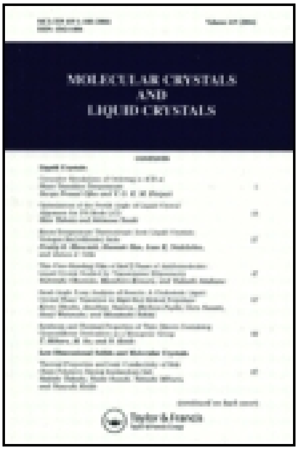

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Photoisomerization of Azobenzene in Zeolite Cavities

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Cis- and *trans*-azobenzenes adsorbed in NaY, Na-mordenite, and Na-ZSM-5 were irradiated using 313- and 254-nm lights. The *cis-trans* isomer ratio in the photostationary state produced in the zeolites was compared with that in cyclohexane. It was found that Na^+ in the cavities did not significantly affect the ratio although for stilbene a drastic change in the ratio was caused most likely by electrostatic interaction between the carbon-carbon double bond and Na^+. For azobenzene it seems probable on the basis of the results obtained by semiempirical molecular orbital calculation (AM1) that Na^+ interacts with a lone pair of one of the two nitrogen atoms, but not with the π-orbital of the nitrogen-nitrogen double bond.

Keywords: Photoisomerization; Azobenzene; Zeolite; Effect of Metal Ions; Adsorption Site

Introduction

Cis-Trans isomerization of arylalkenes is one of the most important photochemical reactions in organic synthesis and in biochemical processes. Therefore, photoisomerization in solution has already been studied extensively from the point of view of the mechanisms and potential energy surfaces related to the excited states.[1] Moreover, many attempts to regulate *cis-trans* photoisomerization have been made particularly for azobenzenes because of their well-known organic photochromic molecule, for example using supramolecular systems,[2] polymeric matrix,[3] and polymeric chains.[4] Intrazeolite photochemistry is also likely to become an attractive research field,[5] due to the considerable potential of zeolites as unique new photochemical reaction vessels to control the reactivity of guest molecules.[6] We have investigated the mechanism and potential energy surface for the photoisomerization of stilbene (**St**) in zeolite Y, and found the isomerization to be significantly effected by metal ions such as Na^+ and K^+ in the cavities.[5c] In order to establish the *cis-trans* photoisomerization mechanism in zeolite cavities, we have examined the effects of Na^+ and the cavity size on the photoisomerization of azobenzene (**AB**) in NaY (pore size: 7.4 Å), Na-mordenite (Na-MOR: 7.0 x 6.5 Å), and Na-ZSM-5 (5.3 x 5.4 and 5.1 x 5.5 Å), by analysis of the *cis*/*trans* (*c*/*t*) isomer ratio in the photostationary state (PSS) and by semiempirical molecular orbital calculation (AM1 method). Although there have been a few investigations of the photochemistry of **AB** in zeolite cavities,[7—9] this paper reports here for the first time our findings that the *c*/*t* ratio in PSS for **AB** depends on the cavity size and the amount of **AB** loaded in the cavities, but not on the interaction with Na^+. This results is quite different from that for **St** reported previously.[5c]

Experimental

Materials. *Trans*-azobenzene (*t*-**AB**) was purchased from Nacalai Tesque and recrystallized using ethanol and benzene. *Cis*-azobenzene (*c*-**AB**) was obtained by irradiation of *t*-**AB** in cyclohexane using a high-pressure mercury lamp (Riko UVL-400HA) and purified by means of flash column chromatography on silica gel using hexane as an eluent.

Inclusion of AB into Zeolite Cavities. Zeolite (1 g) was activated at 500 °C using an electric furnace for more than 15 h, and cooled to room temperature in a desiccator. The activated zeolite was added into a solution including 5—20 mg **AB** in 50 ml anhydrous cyclohexane and kept in the dark for more than 15 h. After filtration and washing with *cyclohexane, the zeolite sample was dried under vacuum.*

Irradiation of Zeolite Sample. A zeolite sample (20 mg for NaY, 40 mg for Na-MOR, and 100 mg for Na-ZSM-5) including **AB** was left between two Pyrex plates (size, 76 x 26 mm or 100 x 100 mm). The sample was irradiated at room temperature through a Hoya U-340 glass filter (313 nm band pass) using a high-pressure mercury lamp. For 254-nm irradiation, two quartz plates and a low-pressure mercury lamp (Riko UVL-160LA) were used. The *cis*- and *trans*-isomers produced were extracted with 1 ml CH_2Cl_2 and analyzed using a JASCO Finepak SIL packed column attached to an HPLC, hexane/ethyl acetate (90/10) as an eluent, and a 271-nm light to detect the isomers.

MO Calculation. Geometry optimization for **AB** and the complexes which interacted with Na^+ was carried out using the AM1 method in MOPAC 97 installed in CSC Chem3D Ver. 4.5 for Windows.

Results and Discussion

c/t Isomer Ratio in PSS.

a. In Solution: Effect of Concentration. As can be seen from Table 1, when a 313-nm light was used for **AB**, the *c/t* ratio depended on the initial concentration in cyclohexane; *c/t* = ca. 80/20 for 2 x 10^{-4} M and ca. 55/45 for 1 x 10^{-2} M. This suggests that in lower concentrations production of *c*-**AB** proceeds efficiently, while it is suppressed in higher concentrations. The effect of concentration probably indicates that in higher concentrations a unimolecular isomerization process from *t*-**AB** to *c*-**AB** competes with a bimolecular process, which prefers to form *t*-**AB**. For example, more selective deactivation to *t*-**AB** might occur through an excimer and exciplex of **AB**. This mechanism can be supported by our finding that the irradiation of *c*-**AB** using a 254-nm light, which can more selectively excite *c*-**AB**, yielded *t*-**AB** as the major isomer regardless of the initial concentration: *c/t* = 10/90 for 2 x 10^{-4} M and 15/85 for 1 x 10^{-2} M.

Table 1. *Cis/trans* Isomer Ratio of Azobenzene in Photostationary State (PSS) in Cyclohexane and Zeolites NaY and Na-MOR

Wavelength[a] /nm	Amount[b]	*cis/trans* Isomer Ratio in PSS C_6H_{12}[d]	NaY (7.4 Å)[e]	Na-MOR (7.0 x 6.5 Å)[e]
254	2 x 10^{-4} M	10/90		
	1 x 10^{-2} M	15/85		
313	2 x 10^{-4} M	80/20		
	1 x 10^{-2} M	55/45		
254	6.9 x 10^{-5} mol/g		20/80	
313	3.4 x 10^{-5} mol/g		75/25	
	6.9 x 10^{-5} mol/g		80/20	
	1.4 x 10^{-4} mol/g		80/20	
254	Saturated[c]			20/80
313	Saturated[c]			50/50

[a] Effective excitation wavelength. [b] Concentration of *c*- and *t*-**AB** in cyclohexane and amount of *t*-**AB** loaded in 1 g zeolite. [c] Cavities of Na-MOR were saturated by *t*-**AB**. [d] In cyclohexane. [e] Pore size.

b. In Zeolite:

i. Effect of Amount loaded. The *c/t* ratio of **AB** adsorbed in NaY in PSS on excitation using a 313-nm light seemed to change depending on the amount loaded in the cavities: namely, loading of a larger amount of *t*-**AB** tended to make formation of *c*-**AB** inefficient. However, we noticed incidentally that the *cis*-to-*trans* thermal isomerization rate increased in the samples of NaY containing larger amounts of *t*-**AB**.[10] Therefore, we finally determined that the *c/t* ratio in PSS was an almost constant 80/20 in the samples loaded with between 1.4 x 10^{-4} mol/g and 3.4 x 10^{-5} mol/g. Hence, we have concluded that there is no significant difference in between the photochemical behavior of **AB** in solution and that in NaY. However, this result is markedly different from that for **St** reported previously.[5c]

ii. Effect of Cavity Size. When the cavities of Na-MOR were saturated by *t*-**AB** and the zeolite sample was irradiated using a 313-nm light, the *c*/*t* ratio became ca. 50/50 in PSS, as can be seen in Figure 1. This value clearly indicates that cavities smaller than those in NaY does not favor *trans*-to-*cis* photoisomerization of **AB** probably due to the steric effect. In Na-ZSM-5, which has the smallest cavities in the zeolites used, no isomerization occurred from *t*-**AB** to c-**AB**, most likely because the spaces were too small.

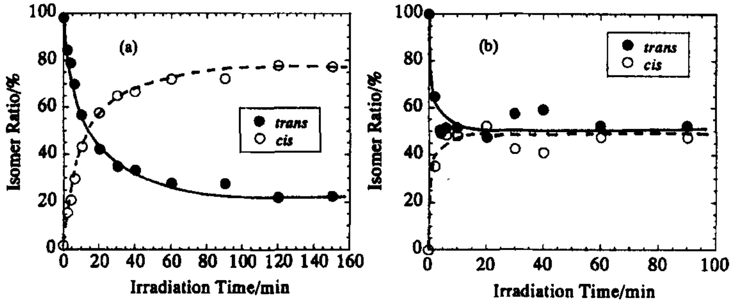
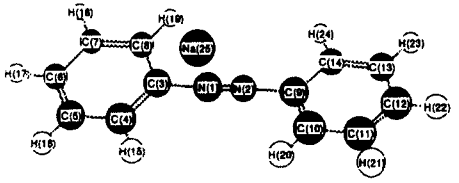


Figure 1. Plot of composition of **AB** adsorbed in the zeolite cavities, obtained by irradiation using a 313-nm light vs. irradiation time: (a) in NaY (1.4 x 10^{-4} mol/g) and (b) in Na-MOR (saturated).

iii. Effects of Metal Ion and Excitation Wavelength. It is noteworthy that in both cyclohexane and the zeolites the *c*/*t* ratio for **AB** in PSS depended on excitation wavelength and on the initial amount, but not on interaction with Na^+. Excitation using a 254-nm light promoted formation of *t*-**AB**, and a 313-nm light promoted formation of *c*-**AB**. The ratio in the zeolites did not become the same as that in cyclohexane; however, this is presumably due to the amount loaded and the cavity size as mentioned above.

MO Calculation using the AM1 Method. In order to predict which site in **AB** interacts with Na^+ in the zeolite cavities, geometry optimization for **AB**/Na^+ complex was carried out using the AM1 method as shown in Figure 2. The results of the calculation clearly indicate that for both *c*- and *t*-**AB** Na^+ interacts with a lone pair of one of the two nitrogen atoms, but not with the π-orbital of the nitrogen-nitrogen double bond as suggested in the case of **St**. The distance between Na^+ and the nitrogen atom was calculated to be 3.07 Å for *t*-**AB** and 2.88 Å for *c*-**AB**. Comparison of this result with the distance between Na^+ and one of the carbon atoms comprising the ethylene bond for **St** (3.66 Å for *t*-**St** and 4.05 Å for *c*-**St**), suggests that **AB** is probably adsorbed in NaY more strongly than **St**. However, as described above, the *c*/*t* ratio in PSS observed in NaY was extremely similar to that yielded in cyclohexane. Therefore, we have concluded that photoisomerization in zeolite cavities depends on the adsorption site in guest molecules.



∠C9-N2-N1-Na = 16°
∠C8-C3-N1-Na = 51.4°
∠C10-C9-N2-N1 = 46.7°
∠N2-N1-Na = 33.8°
∠C3-N1-Na = 54.1°
N1-Na = 3.07 Å

Figure 2. Optimized structure of *t*-AB/Na^+ complex calculated using the AM1 method.

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