Pergamon

Tetrahedron 54 (1998) 15667–15672

TETRAHEDRON

# Influence of Cations in Faujasite Zeolites in *cis-trans* Isomerization of 4-Bromophenyl Styryl Sulfone

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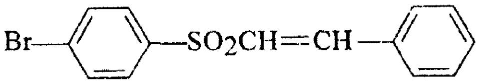
Received 29 July 1998; revised 5 October 1998; accepted 22 October 1998

*Abstract* : Cation-exchanged faujasites are used in controlling the photostationary ratio in *cis-trans* isomerization of 4-bromophenyl styryl sulfone. The predominance of the *cis*-isomer in zeolites with larger cations is attributed to the smaller cage size. © 1998 Published by Elsevier Science Ltd. All rights reserved.

## INTRODUCTION

Photochemical reactivities and photophysical properties of organic molecules are considerably altered when they become part of an organized system and it is then possible to control, tune and achieve selectivity.[1] In this context, the internal structures (cages and pores) of zeolites can play a considerable role and have therefore attracted recent attention.[2] Two types of zeolites, pentasil and faujasite, are commonly employed in photoreactions of several organic compounds. These two types of zeolites have fundamentally different void space topologies. While silicalite belonging to the former type contains interconnected near- circular zig-zag channels and elliptical straight channels, with diameters of 5.4Å and 5.75Å respectively, the latter contains a much larger cage (inner diameter ~12Å) and window (~7.4Å). In an earlier report,[3] a silicalite was employed to control composition of the photostationary state in the 3,4-dimethylbenzophenone sensitized *cis-trans* isomerization of stilbene and the authors have established conversion of *cis*-stilbene into *trans* in >90% yield. The *trans*-isomer is included readily into the channels of the silicalite while both the *cis*-isomer as well as the sensitizer are poorly included. It is thus possible to convert the *cis*-isomer completely into the *trans*-isomer. As faujasite has not been employed in such isomerization studies, we report herein the use of faujasite zeolites to control the photostationary state in *cis-trans* isomerization of 4-bromophenyl styryl sulfone (**1**). Unlike the stilbene example cited above, the *cis*-isomer in the present work is included inside the cage more readily while the *trans*-isomer prefers to stay outside. This is the first report of cation-exchanged faujasites being successfully used for *cis-trans* isomerization, providing some strikingly different results.



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*PII:* S0040-4020(98)00980-6

## RESULTS AND DISCUSSION

Results obtained on irradiation of *trans*-4-bromophenyl styryl sulfone in isotropic media and also as a slurry in the various zeolites are presented in Table 1. An increase in the irradiation time causes a gradual increase in the conversion of *trans*- into its *cis*-isomer and after an hour the isomer distribution remains constant indicating the attainment of photostationary state. Irradiation of the pure *trans*-isomer in hexane as well as in methanol gives a photostationary mixture richer in the *cis*-isomer (65%). The same ratio of products is also obtained when the pure *cis*-isomer is irradiated. Unlike the direct irradiation, isomer distribution in the photostationary state is significantly different in the benzophenone-sensitized irradiation (Table 1).

Table 1. Isomer Distribution in the Photostationary State of *trans*-4-Bromophenyl Styryl Sulfone[a,b]

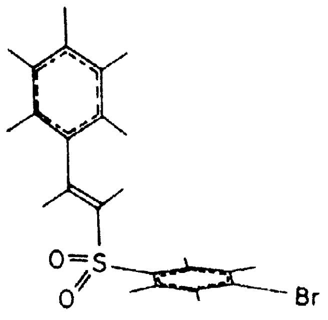
| Reaction conditions | % of *cis*-isomer | % of *trans*-isomer | Reaction conditions | % of *cis*-isomer | % of *trans*-isomer |
|---|---|---|---|---|---|
| Hexane | 65 | 35 | NaY | 76 | 24 |
| Methanol | 67 | 33 | KY | 56 | 44 |
| Methanol/Benzo-phenone | 94 | 6 | RbY | 90 | 10 |
| | | | CsY | 94 | 6 |
| LiY | 75 | 25 | TlY | 68 | 32 |

[a] Irradiated for 2 h.
[b] The same ratio is also obtained when the pure *cis*-isomer is irradiated.

However, when irradiated as a slurry in LiY and NaY zeolites, the *trans*-isomer gives a greater proportion of the *cis*-isomer (76%). Surprisingly with KY zeolite less of the *cis*-isomer is obtained (56%). With RbY and CsY zeolites, the *cis*-isomer is the predominant one (>90%), which is comparable with that of benzophenone-sensitized irradiation. Though this may indicate contribution from the heavy atom effect, there will be a much more significant role from the cage effects also.

On stirring as a hexane slurry, it has been observed that while the *trans*-isomer remains essentially (>95%) in the hexane portion, the *cis*-isomer forms an inclusion complex much more readily as evidenced by its absence in the hexane portion. This observation is perplexing, because in earlier studies[3] with stilbene, the *trans*-isomer is included into the channels of silicalite more readily than the *cis*-isomer. To understand this interesting observation, the molecular models of *cis*- and *trans*-isomers of (**1**) were analysed using the software "INSIGHT-II (BIOSYM)-Builder and Discover Molecules", and the observed molecular dimensions for the most stable conformations of *cis*- and *trans*- isomers of (**1**) are presented in Table 2.

trans



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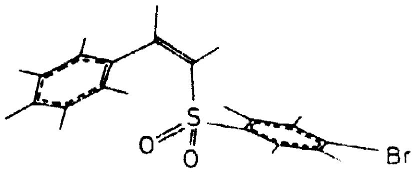
cis



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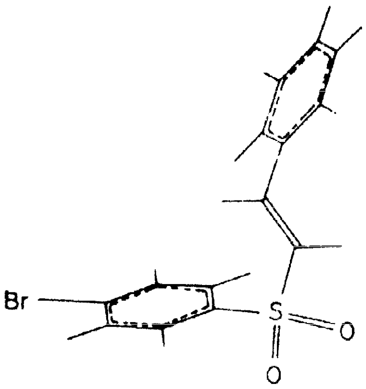

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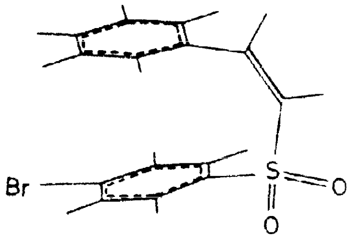

2

Table 2. Molecular Dimensions for the Most Stable Conformations of *cis*- and *trans*- Isomers of (**1**)

| | X-axis (Å) | Y-axis (Å) | Z-axis (Å) | | X-axis (Å) | Y-axis (Å) | Z-axis (Å) |
|---|---|---|---|---|---|---|---|
| *trans*-1 | 9.28 | 8.81 | 5.26 | *cis*-1 | 11.73 | 7.14 | 4.44 |
| *trans*-2 | 6.98 | 8.38 | 8.50 | *cis*-2 | 7.95 | 5.66 | 6.31 |

The data in Table 2 reveal that the *trans*-isomer is bulky enough at least as far as two axes are concerned, pointing out clearly that the penetration is difficult. Though the cage is large enough to accommodate the molecule, the smaller window does not allow the molecule to squeeze in. On the other hand the *cis*-isomer can enter more readily into the cage. Single crystal X-ray diffraction studies[4] on pure *cis*- and *trans*-4-bromophenyl styryl sulfones also confirm the molecular dimensions presented in Table 2.

The slightly higher yield of the *cis*-isomer during isomerization in LiY and NaY compared to isotropic media reveals that the cage effect is also present in LiY and NaY. However, due to the smaller cation size, the cage size is not reduced to that extent to hold the *cis*-isomer and hence, it is likely that some of the *cis*-isomer escapes out of the cage. The fact that nearly 75% of the reaction mixture is still inside the cage (revealed by the analysis of zeolite portion) indicates that despite the reduced cage effect, the stronger electrostatic field present in LiY and NaY may have contributed to retaining the *cis*-isomer inside the cage. Though the cage effect may be more with KY compared to LiY and NaY, the decreased electrostatic field effect probably reduces the importance of the cage effect in KY. In fact, the percentage of *cis*-isomer falls even below the level of solution irradiation.

The importance of size effects in controlling the product distribution is demonstrated by studies with CsY and RbY and also with NaY activated at different temperatures. It is clear from the data, that in zeolites with bulkier cations such as CsY and RbY, the reduced cage volume would result in a tighter fit of the *cis*-isomer inside the cage. This results in selective sequestering of the *cis*-isomer from the mixture, after irradiation. Thus, while the bulk solvent has the *trans*-isomer, the zeolite interior holds the *cis*-isomer tightly. With smaller cations, the *cis*-isomer may not be tightly held and hence, on irradiation can undergo isomerization to the *trans*-isomer which can escape the cage into the bulk solvent because it is not tightly held in the cage. But with tight packing, as with larger cations the chances of escape are significantly reduced as there is little free space available for rotation. This makes the *cis*-isomer in CsY and RbY less reactive towards isomerization.

The experimental results lead us to believe that in the case of the heavier cation, the cation size effect (Lebensraum effect)[5] plays a major role in addition to some heavy atom effect. Support for this can be obtained by the use of NaY activated at different temperatures. With a lower activation temperature, the amount of water inside the cage is more, ensuring a tighter fit. This indeed is the case with NaY activated at 150 °C (>90% of the *cis*-isomer is formed). With an increase in activation temperature, the amount of the *cis*-isomer decreases progressively (Table 3).

When a mixture of known proportions of *cis*- and *trans*- isomers is stirred for 30 minutes with NaY zeolites (activated at various temperatures) the preferential inclusion of only the *cis*-isomer was observed. This selective inclusion of the *cis*-isomer is more pronounced as the activation temperature is decreased indicating that the presence of a small amount of water actually does not impede the inclusion of the *cis*-isomer while blocking the *trans*-isomer. The minor role of the heavy atom effect can also be evidenced from the lack of effect of TlY in controlling the photostationary state. The data in Table 1 show that the product ratio with TlY is the same as in irradiation in homogeneous solution. Possibly the *cis*-isomer has not gone fully into the cage due to the much larger cation size and the bulk of the isomerization may have happened on the surface itself.

Table 3. Effect of Activation Temperature[a] of NaY on the Isomer Distribution in the Photostationary State

| T (°C) | % of *cis*-isomer | % of *trans*-isomer | T (°C) | % of *cis*-isomer | % of *trans*-isomer |
|---|---|---|---|---|---|
| 150 | 91 | 9 | 400 | 81 | 19 |
| 250 | 84 | 16 | 500 | 76 | 24 |

[a] With unactivated NaY, isomer distribution is similar to that observed in the photolysis in homogeneous solution, indicating that the presence of large amount of water molecules block the penetration of both the *cis*- and *trans*-isomers into the supercage.

Thus the present study demonstrates the role of the cation-size effect in faujasite zeolite in controlling the isomer distribution in the photostationary state. Our inability to achieve 100% *cis*-isomer at the end of irradiation may be attributed to a small portion of the isomerization (of the substrate stuck on the surface) which can occur outside the zeolite. At this stage we are unable to explain how much is inside and how much is outside.

## EXPERIMENTAL

*trans*-4-Bromophenyl styryl sulfone[6] and the *cis*-isomer[7] were prepared according to literature procedures and were recrystallised from methanol. Faujasite NaY was obtained from Aldrich. The cations of interest were exchanged[8] into the NaY powder by stirring with the corresponding nitrate (10%) solution at 70 °C for about 12 h. The exchange was repeated at least four times. Each time, after exchange, the zeolite powder was washed repeatedly with distilled water and then dried. Based on an earlier literature report,[8] exchange levels are assumed to be between 62% to 84%. All these cation- exchanged zeolites were activated at 500 °C for about 10 h prior to use.

To a solution of the substrate (25 mg) in hexane/isooctane, 300 mg of the activated zeolite was added (after about 30 seconds of its removal from the furnace maintained at 500 °C). The slurry was then irradiated using a 125-W medium pressure mercury vapour lamp with magnetic stirring. After completion of irradiation, the hexane portion was filtered and analysed by HPLC (Shimadzu LC-8A modular HPLC system with reverse phase ODS column, UV-detector at 254 nm and methanol as the mobile phase). The zeolite portion was extracted with dichloromethane (20 mL) overnight and the concentrated extract was also analysed by HPLC. The data presented in Table 1 is from the combined hexane and zeolite portions (the hexane portion contained mostly the *trans*-isomer and the zeolite portion contained predominantly the *cis*-isomer. For example with RbY, out of a total of 90% *cis*-isomer, 88% was present inside the zeolite while only 2% remained in hexane. Similarly with CsY, out of a total of 94% *cis*-isomer, 93% remained in the zeolite portion. No *trans*-isomer was found inside the RbY and CsY zeolites).

*Acknowledgement*:

Financial assistance from UGC (Scheme No. F.12-57/93 (SR-I)), New Delhi is gratefully acknowledged.

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