Mechanism of *Cis*-to-*Trans* One Way Isomerization of Stilbene and Formation of Its Stable Dimer Cation Radicals in Zeolite Cavities

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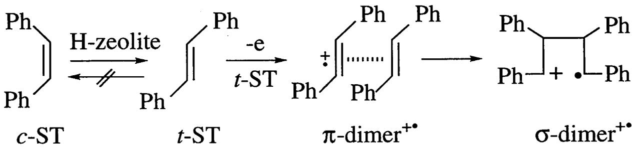
(Received June 17, 1997; CL-970462)

Cis-to-*trans* one way isomerization of stilbene in the first case catalyzed by proton, and then, secondly through electron transfer, occurred in acidic zeolites without light, suggesting that dimer cation radicals with charge transfer interaction between *trans*-stilbene and its cation radical may be formed in H-ZSM-5, whereas 1,4-dimer cation radicals of stilbene may be produced in H-mordenite.

Cation and anion radicals, generated by photoinduced electron transfer reaction, have produced many interesting addition reactions, while their reactivities have attracted much attention in kinetic studies using time-resolved techniques because they are short-lived species in solution.[1] However, it was recently found that cation radicals trapped in zeolite cavities can be long-lived and occasionally stable species.[2,3] In order to obtain deeper insights into the reactivities of ion radicals in zeolite cavities,[4,5] we have studied the reaction behavior of *cis*- (*c*-ST) and *trans*-stilbene (*t*-ST) in zeolite Y, mordenite, and ZSM-5 cavities under conditions without light, by means of diffuse reflectance, Raman, and ESR spectra. We report here that it has been found that *cis*-to-*trans* one way isomerization of *c*-ST through proton addition-elimination and electron transfer processes occurs in acidic zeolite cavities such as H-Y, H-mordenite, and H-ZSM-5. In addition, we suggest that the reactivities of monomer cation radicals of *c*-ST and *t*-ST (*c*-ST$^{+\bullet}$ and *t*-ST$^{+\bullet}$, respectively) depend on the size of the zeolite cavities, where *t*-ST$^{+\bullet}$ reacts with *t*-ST to form a dimer cation radical with charge transfer interaction (π-dimer$^{+\bullet}$) in H-ZSM-5 and a 1,4-dimer cation radical (σ-dimer$^{+\bullet}$) in H-mordenite (Scheme 1).



Scheme 1.

Anhydrous cyclohexane solutions (100 mL) of *c*-ST and *t*-ST (1 mM) were mixed with zeolites (1 g) activated at 500 °C for 20 h before use, and stirred under nitrogen for 48 h. After the zeolite samples were filtered and washed with cyclohexane, the stilbenes included into zeolite cavities were analyzed by means of the spectral techniques mentioned above, while the filtrates were examined by high-performance liquid chromatography (HPLC). When zeolite Na-Y (Tosoh; pore size, 7.4 Å)[6] was used, the Raman spectra measurement showed that neutral *c*-ST and *t*-ST employed as starting materials were adsorbed within the supercage of Na-Y without undergoing any reaction.[7] For H-Y (Tosoh, 7.4 Å), only neutral *t*-ST was observed in the supercage of H-Y, regardless of the starting olefin used. In the cases of Na-Y and H-Y, trace amounts of stilbenes were detected in the filtrates. These results indicate that *cis*-to-*trans* one way isomerization of *c*-ST occurred when it was adsorbed into the supercage of H-Y, similar to the case of Ca-Y.[8] It should be noted that *cis*-to-*trans* one way isomerization of *c*-ST is catalyzed by neutral and ion radical species in solution,[9-11] but not by proton. However, a mechanism for proton-catalyzed isomerization generating a carbocation as an intermediate was proposed recently for Ca-Y though unsupported by experimental data.[8] To elucidate the mechanism of *cis*-to-*trans* one way isomerization of *c*-ST in H-Y, we studied the reaction behavior of *cis*- and *trans*-α,α'-dimethylstilbene in the zeolite (*c*- and *t*-DMST, respectively) because it has been found that DMST cation radicals do not isomerize.[12,13] When *c*- and *t*-DMST were stirred with H-Y under similar conditions, the olefins isomerized both ways. Accordingly, it is likely that the one way isomerization of *c*-ST proceeds through the addition-elimination reaction of proton in the supercage.

On the other hand, it has been reported that one-electron oxidation of *t*-ST by Na-ZSM-5 (5.3 x 5.4 and 5.1 x 5.5 Å)[6] occurred to generate a radical species, originally ascribed to *t*-ST$^{+\bullet}$ stabilized in the zeolite cavities.[2] In our experiments, the reaction of *c*-ST and *t*-ST with H-ZSM-5 (Mizusawa Ind. Chem.) gave light yellow zeolite samples for both the olefins, as previously reported for *t*-ST.[2,3] Diffuse reflectance spectra of the samples were in close agreement with the spectrum reported by Ramamurthy et al. (Figure 1).[2] However, the difference in the absorption spectra between *t*-ST$^{+\bullet}$ and π-dimer$^{+\bullet}$ of *t*-ST is quite small, λ_{max}= ~485 and ~475 nm, respectively, as reported for pulse radiolysis of *t*-ST (0.1 M) in dichloroethane.[14] Therefore, it is difficult to distinguish clearly which species exists in the stilbene/H-ZSM-5 samples only on the basis of the diffuse reflectance spectra. By contrast, Raman spectra of the samples showed that the stable species adsorbed within the zeolite cavities is π-dimer$^{+\bullet}$, and not *t*-ST$^{+\bullet}$ (Figure 2). Although the Raman spectra shown in Figure 2 are similar to the spectrum initially assigned to *t*-ST$^{+\bullet}$ by Schneider et al.,[15,16] it was recently reassigned to a dimer cation radical of *t*-ST, probably π-dimer$^{+\bullet}$, based on the ratio of the Raman intensities at 1605 and 1565 cm^{-1}.[17] The ratio of the intensities is approximately 1 : 1 for *t*-ST$^{+\bullet}$ and much larger than unit for a dimer cation radical of *t*-ST. Similarly, the ESR spectrum observed for *t*-ST in H-ZSM-5 is in close agreement with that assigned to *t*-ST$^{+\bullet}$ in a CFCl$_3$ matrix.[18] However, based on the results of Raman spectra mentioned above we believe that the spectrum observed under the conditions is attributable to π-dimer$^{+\bullet}$, and not *t*-ST$^{+\bullet}$.

Moreover, weak hyperfine structure was also observed around 337 mT in the ESR spectrum for the dimer cation radical of *t*-ST, similar to the case of boric acid matrices, whereas *t*-ST$^{+\bullet}$ gave just a broad signal.

t-ST and *c*-ST were also oxidized in H-mordenite channels (Tosoh, 7.0 x 6.5 Å)[6] to ultimately give light violet zeolite samples after filtration. Raman spectra for both samples are very similar to those for the stilbene/H-ZSM-5 samples (Figure 2); therefore, the spectra are attributed to a dimer cation radical of *t*-ST, and not to *t*-ST$^{+\bullet}$. However, the samples gave a broad ESR signal, which is clearly different from that for the stilbene/H-ZSM-5 samples, attributed to π-dimer$^{+\bullet}$. In addition, it is worth noting that diffuse reflectance spectra recorded for the stilbene/H-mordenite samples resemble the spectrum of σ-dimer$^{+\bullet}$ of the stilbenes generated by γ-irradiation of tetraphenylcyclobutane in a solvent matrix (Figure 1).[14]

On the other hand, HPLC analysis of the filtrates for the H-ZSM-5 and H-mordenite samples (recovered stilbene, 0.8 mM) showed that *cis*-to-*trans* one way isomerization of *c*-ST also occurred. For zeolite Y and mordenite there are enough size of cavities in the zeolites in which *c*-ST can be included; therefore, the isomerization and the formation of the dimer cation radicals are likely to occur in the cavities. For H-ZSM-5, however, *c*-ST probably isomerizes first to *t*-ST on the surface of the zeolite through the carbocation and the cation radical of *c*-ST, because there are not spaces in the zeolite where *c*-ST can be adsorbed, followed by the inclusion of produced t-ST into the cavities.

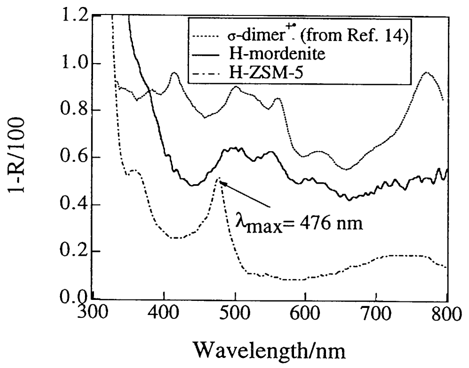


Figure 1. Diffuse reflectance spectra attributable to π- and σ-dimer cation radicals of stilbene, generated in H-ZSM-5 (SiO_2/Al_2O_3 = 30) and H-mordenite (SiO_2/Al_2O_3 = 16), respectively, and absorption spectrum for σ–dimer cation radical cited from reference 14.

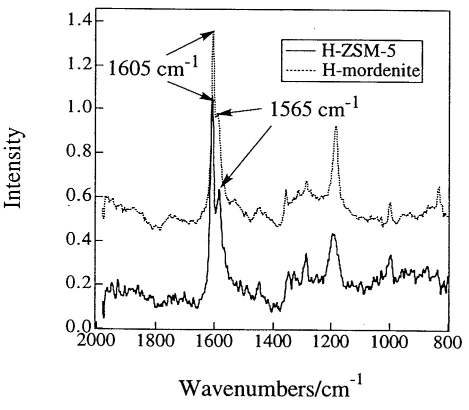


Figure 2. Raman spectra for stilbene dimer cation radicals produced from *t*-ST and *c*-ST within H-ZSM-5 (SiO_2/Al_2O_3 = 30) and H-mordenite (SiO_2/Al_2O_3 = 16). It is clear that the ratio of Raman intensities at 1605 and 1565 cm^{-1} is much larger than unit.

In control experiments, when Na-ZSM-5 (Mizusawa Ind. Chem.) and Na-mordenite (Mizusawa Ind. Chem.) were used instead of corresponding H-zeolites, no isomerization reaction occurred and no radical species was detected in the Na-zeolites. Furthermore, it was also found that H-ZSM-5 with the molar ratio of SiO_2/Al_2O_3 = 15 (N. E. Chemcat.) and 30 (Mizusawa Ind. Chem.), in contrast to that with the ratio of 150 (N. E. Chemcat.), has strong Lewis acid sites causing oxidation of the stilbenes, followed by formation of the π-dimer$^{+\bullet}$. From these results, there is no doubt that proton and a high amount of Al_2O_3 are essential for isomerization and oxidation of stilbenes.

Tojo et al. suggested that π-dimer$^{+\bullet}$ generated in solution should have a sandwich structure due to charge transfer resonance. Because of the limited space of the zeolite cavities, the structure of π-dimer$^{+\bullet}$ formed in H-ZSM-5 may differ from that in solution. Therefore, based on a recent theoretical study of the mobility of adsorbed molecules in silicalite[19] and X-ray powder diffraction study of *t*-ST in Na-ZSM-5,[20] we suggest that *t*-ST$^{+\bullet}$ probably interacts with *t*-ST at the intersection of the straight and zigzag channels. Finally, if the radical species stabilized in the mordenite is the σ-dimer$^{+\bullet}$, as we suggested, this is interesting because it is also a transient species in solution, decomposing readily to *t*-ST$^{+\bullet}$ and *t*-ST.[9,10]

The authors thank Mr. M. Murano for his assistance with the measurements and also gratefully acknowledge Prof. F. D. Lewis of Northwestern University for his helpful discussion.

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