Photochemistry of Stilbene Adsorbed on Silica Gel and NaX Zeolite. A Diffuse Reflectance Laser Flash Photolysis Study¹

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Diffuse reflectance laser flash photolysis (266, 308, or 355 nm) of either cis- or trans-stilbene (St) adsorbed on silica gel or included in NaX zeolite leads to the formation of the *trans*-St radical cation with λ_{max} at 475 nm at high laser powers. At low laser intensities trans-St also yields radical cation while cis-St photocyclizes to give dihydrophenanthrene with λ_{max} at 450 nm. In contrast to the results for irradiation of stilbene alone on solid supports, irradiation of the cis-St/TNM charge transfer complex on silica or zeolite leads to a mixture of both *trans*- and *cis*-St⁺⁺ (λ_{max} at 510 nm), demonstrating that the *cis* radical cation is stable with respect to isomerization on these two solids. This result, in combination with product studies which demonstrate that there is substantial *cis-trans* isomerization within a single laser pulse, leads to the conclusion that the formation of *trans*-St⁺⁺ following laser irradiation of *cis*-St occurs via *cis*-*trans* isomerization followed by photoionization of trans-St. Laser irradiation of St or pyrene on NaX zeolite results in strong transient signals in the 500-600 nm region due to trapped electrons, in addition to the signals due to radical cations. The effects of both water and oxygen on the trapped electron and radical cation have been examined. The trapped electron can be photobleached with a second 532 nm laser pulse. The bleaching does not lead either to trapping of the electron by ground state aromatic to give its radical anion or to recombination with the radical cation to regenerate the starting material. This suggests that irradiation leads to a redistribution of the electron to other zeolite sites.

Introduction

The potential of porous solid supports such as zeolites, silica, alumina, and clays for controlling the photochemistry and photophysics of adsorbed organic molecules has attracted considerable attention during the past decade.^{3–8} Many of these studies have demonstrated that the product distributions obtained in porous solids are frequently very different from those in solution. These effects generally result from restrictions to the mobility of either the excited states or the intermediates derived from them. The development of diffuse reflectance flash photolysis techniques by Wilkinson and co-workers has facilitated the direct time-resolved study of these excited states and reactive intermediates in opaque solids.^{9–13} The technique has now been applied to excited states, free radicals, and radical ions in a variety of systems.^{14–22}

A number of recent studies have demonstrated the feasibility of generating radical cations on solid supports by electron transfer quenching of an excited donor or acceptor with a ground state molecule,^{15,17,23,24} by direct photoionization of adsorbed aromatics,16,19-22 or by excitation of charge transfer complexes.20 For example, photoionization of anthracene and pyrene in X and Y zeolites occurs via both one- and two-photon processes.¹⁹ Both the radical cation and the trapped electron (Na_4^{3+}) are readily detectable by time-resolved diffuse reflectance methods. The photoionization of stilbene and several other diphenylpolyenes has also been examined on solid supports.^{16,21} On alumina the diphenylpolyene radical cations are long-lived (milliseconds) and decay almost exclusively by radical cation-electron recombination.¹⁶ Diphenylpolyene radical cations trapped within the channel structure of pentasil zeolites are much more stable and are generated simply by room temperature inclusion of the polyenes in thermally activated zeolite.²⁵ Although this procedure does not generate stable radical cations in the larger

cavities of either X or Y zeolites, the stilbene (St) radical cation has been produced by photoionization in NaX zeolite.²¹ In this case both cis- and trans-stilbene yielded the trans radical cation. This is in contrast to results in solution where it has now been established that the cis-stilbene radical cation is stable with respect to unimolecular isomerization on a microsecond time scale.²⁶ In this experiment the radical cation was generated by photoinduced electron transfer from biphenyl to singlet 9,10dicyanoanthracene, followed by secondary electron transfer from cis- or trans-stilbene. This method has the advantage of eliminating possible complications due to generation of the trans radical cation from cis-St⁺⁺ via bimolecular dimerization or electron transfer reactions. In contrast to its thermal stability in solution, cis-St⁺⁺ has recently been shown to undergo photochemical isomerization, although trans-St*+ does not.27 Note, however, that rapid thermal isomerization of cis-St*+ has been observed in micellar solution.²⁸

We have now examined the photochemistry of both cis- and trans-stilbene and their charge transfer complexes with tetranitromethane on silica and in NaX zeolite using both steady state and transient techniques. These results are of particular interest given recent observations of the importance of methoxysubstituted stilbenes in the photoreversion of lignin-rich wood pulps.²⁹ Our results demonstrate that *trans*-St⁺ produced following direct excitation of cis-St results from rapid cis-trans photoisomerization within a single laser pulse, followed by photoionization via excited trans-St, and not from rapid cistrans isomerization of the initial radical cation. This conclusion is supported by the fact that cis-St++ can be readily generated by excitation of the tetranitromethane complex and is stable with respect to isomerization under these conditions. Two-laser experiments demonstrate that the trapped electron produced by photoionization of trans-St in NaX is efficiently bleached by 532 nm excitation and leads to redistribution of the electron to other zeolite sites.

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Experimental Section

Materials. The silica gel and NaX zeolite used were Aldrich Davisil 634 (480 m²/g; 60 Å pore diameter, 100–200 mesh) and BDH 13X molecular sieves, respectively. Both *cis*- and *trans*-stilbene (St), biphenyl (Aldrich), and potassium dichromate (Fisher) were used as received. Pyrene (Aldrich) was recrystallized twice from benzene. Tetranitromethane (TNM) (Aldrich) was purified by extraction of the impurities into distilled water, followed by drying over anhydrous sodium sulfate.³⁰ Spectrophotometric grade hexane (Photorex Reagent) containing 0.005% water was used.

Sample Preparation. The procedure used for preparation of silica gel and zeolite samples was similar to that described previously.¹⁸ Silica gel and zeolite were activated for 16 h at 200 and 500 °C, respectively, under air and then cooled to room temperature in a desiccator. The solid (3 g) was added to 20 mL of a hexane solution of the additive, and the resulting slurry was stirred for 50 min. The amount of material adsorbed was typically 80-90% or more than 99% for silica gel or zeolite, respectively, based on UV analysis of the supernatant hexane. The hexane solution was removed, and the residual solvent was evaporated under vacuum for 4 h at room temperature. Samples were then stored in a desiccator until used. Samples dried at either room temperature or at 90 °C gave similar results. In general, fresh samples were made the day before the laser experiments were carried out, although no difference was observed for samples that had been prepared 2 weeks earlier. For the time-resolved experiments the samples were contained in 3 \times 7 or 7 \times 7 mm² quartz cells and were purged with oxygen or nitrogen for 40 min before laser excitation in the case of oxygenated or oxygen-free experiments. For all experiments the samples were shaken or moved to provide a fresh surface for every laser shot. The spectra and kinetic traces at low laser power required 16 shots for each point.

Diffuse Reflectance Laser Flash Photolysis. The diffuse reflectance laser flash photolysis apparatus has been described previously.¹⁸ For most of these experiments the second (532 nm), third (355 nm), or fourth harmonic (266 nm) of a Lumonics HY750 Nd:YAG laser (10 ns/pulse) was used for sample excitation. A mean pulse power of 28 mJ was measured for the fourth harmonic from the YAG laser using a chemical actinometer. This value, in combination with the area of the beam (0.5 cm²), gives an estimate of \leq 56 mJ/cm² for the mean value of the laser power per pulse at the highest power used for our experiments. The laser intensity was attenuated with an aqueous solution of K2Cr2O7 for dose dependence measurements. A Lumonics EX-530 excimer laser (308 nm, ≤40 mJ/ pulse, 8 ns/pulse) and a Nd:YAG-pumped Lumonics HD-500 dye laser (stilbene 420 dye, 18 mJ/pulse) were also used in some experiments. For the two-laser experiments, both laser beams were aligned at approximately 45° to the front face of the sample and on the opposite side from the monitoring beam.

The diffuse reflectance laser flash photolysis data are reported as 1 - R as defined below, where J_0 is the initial reflected

$$1 - R = (J_0 - J_t) / J_0$$

light from the sample before the laser pulse and J_t is the reflected light at time t after laser excitation. The value 1 - R is a linear function of the amount of transient present, when 1 - R < 0.1.¹³ This simplified kinetic analysis has been shown to be applicable to systems that have a concentration profile which decreases exponentially with penetration depth.¹³

Steady State Measurements. Diffuse reflectance spectra were measured using a Cary 3 UV-visible single monochro-



Figure 1. Steady state absorption at 306 nm as a function of the cumulative incident laser energy for 266 nm irradiation of aerated samples of (1) *trans*-St (4.1×10^{-5} mol/g) and (2) *cis*-St (4.7×10^{-5} mol/g) on NaX zeolite. Insert: an expansion of the data for early irradiation times.

mator spectrophotometer equipped with a diffuse reflectance accessory. The reflectance spectra were recorded using PTFE reference disks as a white standard, without correcting for variations from 100% reflectance for the PTFE sample. Reflectance spectra were obtained for both stilbene-impregnated samples and the pure zeolite or silica powder and were converted to the Kubelka-Munk remission function. The difference between the two was used to characterize the ground state absorption of the samples. For the steady state photolysis experiments samples contained in $3 \times 10 \text{ mm}^2$ quartz cells were irradiated with the expanded Nd:YAG laser beam. The laser beam was expanded so that it was as large as the sample area to be irradiated and then passed through a scattering filter. The light exposure was measured using the *cis*-*trans* isomerization of stilbene in hexane as a chemical actinometer.

Results

Steady State Photolysis of Stilbene Adsorbed on Silica and NaX Zeolite. Spectra of *cis*- and *trans*-St adsorbed on silica gel at concentrations of $10^{-7}-10^{-6}$ mol/g are similar to the absorption spectra of the corresponding isomers in hexane solution. The maximum for the lowest energy transition is at 282 nm for *cis*-St as compared to 276 nm in hexane solution. The vibrational structure in the spectrum for *trans*-St is less well resolved on silica than in hexane solution, and at loadings greater than 1.6×10^{-5} mol/g an additional shoulder appears in the 350-450 nm region. This concentration corresponds to 0.2 molecule per nm², i.e., approximately 10% of monolayer coverage.

Aerated samples of trans- or cis-St included in NaX were irradiated at room temperature with the expanded 266 nm beam from a pulsed YAG laser. The changes in the reflectance spectra were typical of those for cis-trans isomerization in liquid solution and reflect the longer wavelength absorption and higher extinction coefficient for the trans isomer. Longer irradiation times resulted in significant deviation from the isosbestic points at 238 and 262 nm and the appearance of an additional long wavelength absorption in the 350 nm region. Figure 1 shows the Kubelka-Munk function of the reflectance at 306 nm vs light exposure for trans- and cis-stilbene samples with concentrations of 4.1×10^{-5} and 4.7×10^{-5} mol/g, respectively. This wavelength corresponds to the largest difference in extinction coefficient for the two isomers. The results indicate that under these experimental conditions an absorbed energy of approximately 7 mJ/cm² (\sim 8 shots with the expanded laser beam)



Figure 2. Transient spectra obtained by 266 nm irradiation of aerated samples of (1) *trans*- and (2) *cis*-St on silica gel $(1.1 \times 10^{-6} \text{ mol/g})$ using (a) full laser power and (b) 9.6% laser power.

is sufficient to convert either *cis*- or *trans*-St to 50% of the photostationary state isomer composition. The slower conversion of either *cis*- or *trans*-St to the product absorbing at longer wavelength required exposures of \sim 500 mJ/cm².

Irradiation of *cis*- and *trans*-St adsorbed on silica gel at concentrations of 2.8×10^{-6} and 3.2×10^{-7} mol/g, respectively, resulted in qualitatively similar results to those outlined above for the zeolite samples. The energy required for 50% photo-isomerization increased to 17 mJ/cm².

Diffuse Reflectance Laser Flash Photolysis. Stilbene on Silica Gel. Figure 2 shows transient spectra obtained by 266 nm excitation of aerated silica gel samples of cis- and transstilbene $(1.1 \times 10^{-6} \text{ mol/g})$ at high and low laser power. The spectra measured at full laser intensity (Figure 2a) are very similar for the two isomers and have λ_{max} at 475 nm with a weak broad absorption in the 700 nm region, consistent with the known spectrum for *trans*-St⁺⁺ in solution^{26,27} and in zeolites.²¹ However, spectra recorded after most of the radical cation has decayed are different for the two isomers. Thus, the trans-St sample shows an additional long-lived residual absorption in the 320 nm region while cis-St has a weak absorption at 450 nm, as well as the 320 nm band. Transient spectra for cisand trans-St samples were also measured at low laser power, as shown in Figure 2b. Although the spectra are much noisier under these conditions, irradiation of trans-St still clearly gives radical cation. However, cis-St gives a broad absorption centered at approximately 450 nm that still has not decayed after 700 μ s. This species is the same as that observed after the radical cation has decayed in the experiment at full laser intensity. It is identified as 4a,4b-dihydrophenanthrene formed by cyclization of cis-stilbene, as previously observed in solution.7,31

The intensity of the transient absorption at 475 and 700 nm was measured as a function of the laser intensity for silica gel



Figure 3. Signal intensities at 475 (\Box) and 700 nm (\blacktriangle) as a function of the laser power for 266 nm irradiation of aerated samples of (a) *trans-* and (b) *cis-*St on silica gel (1.1 × 10⁻⁶ mol/g). The data at 700 nm have been normalized to the 475 nm signal intensity.

samples with a 1.1×10^{-6} mol/g loading of *cis*- or *trans*-St. The normalized data are shown in Figure 3 and indicate that the signal intensity does not depend linearly on the laser dose, particularly at low excitation energies. The laser intensity dependence is identical within experimental error at the two wavelengths for *trans*-St. However, there are marked differences between the two wavelengths for *cis*-St.

Both *cis*- and *trans*-St on silica were also excited at 355 nm under air; in this case substantially higher concentrations (2.5×10^{-4} and 1.6×10^{-5} mol/g) were required to have sufficient absorption for the transient experiments. The results were similar to those obtained for 266 nm excitation at low laser intensity (i.e., Figure 2b); that is, 355 nm excitation of *trans*-St produces radical cation whereas *cis*-St gives primarily dihydrophenanthrene along with minor amounts of *trans*-St⁺. It is important to note that there is no evidence for the formation of *cis*-St⁺ at 510 nm^{26.32} upon excitation of either *cis*- or *trans*-St under any of our experimental conditions.

Somewhat different results were obtained following 266 nm excitation of nitrogen-purged samples of trans-St. In this case there was a reasonably strong signal at 360 nm, in addition to radical cation at 475 nm. The 360 nm signal decayed much more rapidly than the radical cation and had a half-life of ~ 13 μ s. The signal was efficiently quenched by oxygen. The transient is assigned to triplet stilbene, based on its reaction with oxygen and its spectral similarity to stilbene triplet in solution at low temperature.^{33,34} The same 360 nm transient was also observed for nitrogen-purged samples of cis-St, although its intensity was considerably weaker. Significant variations in the relative yield of triplet and radical cation were observed for samples prepared at different times, probably indicating that either one or both of these transients are particularly sensitive to the sample preparation technique. This may be caused by differences in stilbene distribution or by the presence of water or residual solvent and was not investigated in further detail.

Stilbene in NaX Zeolite. Transient diffuse reflectance spectra obtained at three different times after 266 nm excitation of *trans*-St included in NaX (2×10^{-5} mol/g) under air are shown in Figure 4. In addition to *trans*-St⁺, there is clearly a second species at 550 nm that decays more rapidly and has absorption



Figure 4. Transient spectra obtained (1) 0.5, (2) 10, and (3) 600 μ s after 266 nm excitation of an aerated sample of *trans*-St on NaX zeolite (2 × 10⁻⁵ mol/g). Insert: transient spectrum obtained by subtraction of the 0.5 and 3 μ s data.



Figure 5. Decay kinetics measured at (a) 540 and (b) 700 nm after 266 nm irradiation of a sample of *trans*-St on NaX zeolite $(2.3 \times 10^{-5} \text{ mol/g})$ under (1) nitrogen, (2) air, and (3) oxygen.

characteristics consistent with the known spectrum for trapped electrons (Na4³⁺) in X and Y zeolites.¹⁹ A comparison of the transient decays at 540 nm and at 700 nm under nitrogen, oxygen, and air is shown in Figure 5. The rapid decay of the 540 nm signal in the presence of oxygen further confirms its assignment to the trapped electron. The intensity of the radical cation signal at 700 nm is substantially weaker for an oxygen-purged sample, although the decay kinetics do not change dramatically. Analogous results in terms of transient spectra and kinetics were obtained upon 308 nm excitation of *trans*-St in NaX and 266 nm excitation of samples of *cis*-St in NaX. As observed previously, no signals due to *cis*-St^{•+} at 510 nm were detected.²¹



Figure 6. Normalized transient spectra measured 0.5 μ s after 355 nm irradiation of aerated samples of TNM and (1) *trans*- and (2) *cis*-St on silica gel. Insert: normalized decay kinetics at 475 (O) and 510 (\blacktriangle) nm for the TNM-*cis*-St sample.

There was no evidence for the formation of triplet stilbene at 360 nm upon excitation of either *cis*- or *trans*-St on NaX. Since the radical cation had still not completely decayed on our longest time scale (0.8 ms), it was not possible to provide any clear evidence for the formation of dihydrophenanthrene for this support. Low dose experiments aimed at detecting *cis*-St⁺⁺ were not attempted since *cis*-*trans* isomerization was more difficult to eliminate on the zeolite than on silica and since the zeolite results are complicated by the presence of signals due to the trapped electron which overlap with those of *cis*-St⁺⁺.

The relative signal intensities at 475 and 540 nm for stilbene-NaX samples were somewhat variable from one sample to the next. Two experiments were carried out to test whether or not this was due to varying amounts of coadsorbed water. In one case two identical stilbene samples were prepared except that water-saturated hexane was used for sample preparation for one and dry hexane for the other. In the second case a sample was prepared under dry conditions, and then half was stored in a dessicator and the other half was equilibrated with water vapor before the laser flash experiments. For both methods the signal intensity at both 475 and 540 nm was substantially higher for the dry sample than for the wet one. This indicates that water affects the yields of both the trapped electron and the radical cation. The effects of water on the trapped electron were examined in more detail for samples of pyrene on NaX, as discussed below.

Tetranitromethane-Stilbene Complexes. Coadsorption of tetranitromethane (TNM) and cis- or trans-stilbene on either silica gel or NaX results in the appearance of an additional long-wavelength absorption in the 350-450 nm region that is not observed for either of the two components alone. This is consistent with our observation of characteristic charge transfer complex absorption for stilbene and tetranitromethane in dichloromethane solution and with literature results for other aromatic/ tetranitromethane complexes.³⁵⁻³⁸

Diffuse reflectance spectra recorded after 355 nm excitation of aerated samples of *cis*- and *trans*-St (3×10^{-6} and 4×10^{-6} mol/g) plus tetranitromethane (7×10^{-5} mol/g) on silica gel are shown in Figure 6. Both show a strong band at 475 nm due to *trans*-St^{•+}. However, the spectrum for the *cis* isomer shows an additional band at 510 nm that is consistent with formation of *cis*-St^{•+} upon excitation of the complex. The yield of *cis*-St^{•+} was always substantially less than that of *trans*-St^{•+} and decreased with lower concentrations of stilbene. Only *trans*- St^{++} was formed by either 266 or 308 nm excitation of *cis*- or *trans*- St in the presence of TNM, presumably due to substantial absorption of the incident light by uncomplexed stilbene.

Although the absorption by uncomplexed stilbene at 355 nm is quite low at the loadings employed in the above experiments, we were concerned that the observed formation of *trans*-St⁺⁺ could be due to direct excitation of stilbene. In order to minimize this problem, the *cis*-St-TNM complex on silica was also excited at 420 nm, where absorption by uncomplexed St (or TNM) is much lower. For a sample containing 1.6×10^{-6} and 2.4×10^{-4} mol/g of *cis*-St and TNM, 420 nm excitation produced only *trans*-St⁺⁺. In contrast, a shoulder due to *cis*-St⁺⁺ was observed for a sample containing 1.8×10^{-5} and 4.5×10^{-5} mol/g of *cis*-St and TNM, respectively.

The decay traces at 475, 510, and 700 nm measured after 355 nm excitation of a *cis*-St/TNM sample are identical after normalization (Figure 6, insert), indicating that the two isomers have similar lifetimes under these conditions. The radical cation decay occurs over a period of $\sim 10 \ \mu$ s and is not single exponential. The decay of *trans*-St⁺⁺ is considerably more rapid under these conditions than when the same intermediate is produced by direct photoionization.

Very similar results to those described above for silica gel samples have been obtained upon diffuse reflectance flash photolysis of TNM—and *cis*- or *trans*-St—complexes included in NaX zeolite under air using 355, 266, or 308 nm excitation. As described above for the complexes on silica gel, a shoulder at 510 nm due to *cis*-St⁺ was only detected following 355 nm excitation of the *cis*-St/TNM complex.

Pyrene on NaX Zeolite. Diffuse reflectance flash photolysis (308 nm excitation) of nitrogen-purged samples of pyrene in NaX (8.3×10^{-6} mol/g) produces the transient spectrum shown in Figure 7a. Pyrene triplet (415 nm) and radical cation (450 nm) are both clearly visible, in addition to a broad signal due to the trapped electron at 550 nm, in good agreement with previous results for this system.¹⁹ Under air the transient spectrum consists of only Py⁺⁺ and Na₄³⁺ (Figure 3b). A spectrum recorded at low laser intensity (0.7% of full laser power) under a nitrogen atmosphere showed triplet pyrene (415 nm with a weaker band at 510 nm) with a weak band due to radical cation at 450 nm and little or no absorption due to the trapped electron.

The effect of water was also examined for pyrene on NaX samples. Comparison of a dry sample to one that had been equilibrated with water-saturated air at room temperature indicated that the trapped electron decayed more rapidly for the wet sample. Effects on the radical cation absorption were much more modest.

Two Laser Flash Photolysis. Several two-laser flash photolysis experiments^{39,40} were carried out for samples of both stilbene and pyrene on solid supports. These were designed to test whether excitation of the trapped electron resulted in its recapture by either radical cation or ground state precursor. In one experiment the trapped electron was generated by 308 nm excitation of trans-St on NaX zeolite and was then excited after a $1-2 \mu s$ delay by a second 532 nm laser pulse. This led to efficient bleaching of the transient absorption at 550 nm by the second laser. The 475 and 700 nm signals also decreased, although by a much smaller amount (70, 30, and 20% at 550, 475, and 700 nm, respectively). Because both stilbene radical cation and radical anion absorb in the same region, it is difficult to establish whether any of the photobleaching of the trapped electron yields stilbene radical anion. Therefore, the same experiment was repeated with a sample of trans-St plus biphenyl $(7 \times 10^{-6} \text{ and } 7.5 \times 10^{-5} \text{ mol/g}, \text{ respectively})$. Note that



Figure 7. (a) Transient spectra obtained by one (1, 308 nm) and two laser (2, 308 + 532 nm) irradiation of a nitrogen-purged sample of pyrene on NaX zeolite (8.3×10^{-6} mol/g). (b) Decay kinetics measured at (1) 450, (2) 415, and (3) 550 nm for two laser irradiation of the same sample.

biphenyl does not absorb significantly at 308 nm so there are no complications due to its direct excitation. In this case the 550 nm signal was also bleached efficiently, but there was no evidence for formation of biphenyl radical anion at 655 nm^{32} as a result of bleaching of the trapped electron.

A two-laser bleaching experiment was also carried out for pyrene on NaX, since in this case the spectra for the radical cation (450 nm), radical anion (490 nm), and trapped electron (550 nm) are better separated from each other. The second 532 nm pulse bleaches 70% of the Na₄³⁺ signal at 550 nm, 10% at 450 nm, and <5% at 415 nm (Figure 7b). A spectrum recorded after the second laser pulse indicates that most of the Na₄³⁺ signal has been removed (Figure 7a). There is no evidence for the production of either radical cation or anion as a result of bleaching of the trapped electron.

Discussion

Steady State Photolysis. Previous studies of the photochemistry of stilbene on both silica and alumina have indicated that the rate of cis-trans isomerization is considerably slower on solids than in solution.^{7,41} Despite this, our steady state irradiations of trans- and cis-stilbene included in NaX zeolite and adsorbed on silica gel demonstrate that cis-trans isomerization occurs rapidly on these solids using laser irradiation. For example, samples with loadings somewhat higher than those used for most of the laser flash photolysis experiments required only approximately 7 and 17 mJ to reach 50% of the photostationary state isomer composition for NaX and silica, respectively. The data presented in Figure 1 have not been corrected for factors such as changes in the depth of penetration of the analyzing beam as a function of the isomer composition. However, it is clear even from this qualitative data that substantial isomerization of either stilbene isomer will occur with a single pulse from the YAG laser, which had a maximum power of 56 mJ/cm² per pulse for the transient experiments reported herein.

Prolonged photolysis of either *cis*- or *trans*-St results in irreversible photochemistry that generates a new product with long wavelength absorption. These results are in agreement with Oelkrug's results for the photolysis of *trans*-St on alumina, in which a product with absorption in the 300-400 nm region was observed. It was suggested that this species was related to the formation of dihydrophenanthrene, which had earlier been characterized as the product of the reversible photocyclization of *cis*-stilbene in solution.^{7,31,42}

Diffuse Reflectance Laser Flash Photolysis of Stilbene. The transient spectra obtained by excitation of samples of either cis- or trans-St on silica at full laser power show absorption due to the *trans*-St radical cation with λ_{max} at 475 nm and a broad, weak absorption in the 700 nm region. The same results are obtained from the trans isomer at low laser intensity, but under these conditions cis-St gives a different transient with absorption at 330 and 450 nm which is very similar to the spectrum assigned to dihyrophenanthrene in solution.³¹ Additional long-lived signals in the 320 nm region are also observed upon excitation of trans-St; similar species have been observed upon irradiation of stilbene on alumina and, as noted above, have been preliminarily assigned to species related to photocyclization to dihydrophenanthrene.⁷ The absence of signals due to the cis-St radical cation under any of our experimental conditions (i.e., various excitation wavelengths and laser powers), in combination with the rapid cis-trans isomerization observed in the steady state irradiations, strongly suggests that the trans radical cation observed from cis-St arises via the following sequence: (1) photoisomerization of cis-St to the trans isomer and (2) photoionization of trans-St (eqs 1 and 2). An

$$cis-St \xrightarrow{hv}{hv} trans-St$$
 (1)

$$trans-St \xrightarrow[-e^-]{hv} trans-St^{\bullet+}$$
(2)

alternate explanation is that any cis-St^{*+} formed by photoionization of cis-St isomerizes to trans-St^{*+} sufficiently rapidly that it is not detected in our time-resolved experiments. This possibility can be ruled out since cis-St^{*+} can in fact be produced by excitation of the cis-St/TNM charge transfer complex on silica and under these conditions decays with similar kinetics to the *trans* radical cation.

The above explanation requires that cis-St not undergo photoionization upon direct excitation under our experimental conditions, in contrast to the results for the trans isomer. This raises two questions: (1) Is photoionization of trans-St monophotonic or biphotonic? (2) Why does cis-St not photoionize? With regards to the first question, previous results have indicated that the formation of stilbene radical cations in zeolites is monophotonic whereas both one- and two-photon routes have been suggested for the photoionization of anthracene and pyrene in zeolites.^{19,21} Experiments in which the dose dependence of the transient signals was measured as a function of laser energy were carried out in order to address these questions. For trans-St the plots of signal intensity vs laser dose are similar at both 475 and 700 nm and show some upward curvature at low laser intensity. Although this may indicate a biphotonic component to the photoionization process, the effect is not particularly large and is only obvious at low signal intensities where our data are least reliable. It is also possible that the upward curvature expected for a biphotonic process is offset by saturation of the ground state absorption which would lead to downward curvature in the plots. Given the number of possible factors that could affect the dose dependence data, it seems dangerous to draw any definite concusions with regards to the monophotonic versus biphotonic nature of the ionization process for *trans*-St.

Plots of signal intensity at 475 and 700 nm as a function of laser intensity for cis-St are also curved. Our postulated mechanism for the formation of trans-St*+ from cis-St is either a two- or three-photon process, depending on whether or not the photoionization of trans-St is mono- or biphotonic. In general, this is expected to result in substantial curvature for laser dose plots, although there are circumstances that result in linear behavior for multiphotonic processes.43 However, the signal at 475 nm is due to varying amounts of DHP (at low intensity) and trans-St⁺⁺ (at high intensity), and this, coupled with the question of ground state saturation effects, complicates the analysis. The signal at 700 nm is due only to radical cation, but at this wavelength the signal intensity is lower and the data are correspondingly less reliable. However, there is some indication of an induction period before the formation of any trans-St⁺ at this wavelength, as would be expected for a mechansim that requires cis-trans isomerization of stilbene prior to photoionization.

The apparent differences in photoionization efficiencies for cis- and trans-St can be explained on the basis of the behavior of their excited singlet states. In solution the fluorescence lifetime for cis-St is ~ 1 ps as compared to a lifetime of ~ 100 ps for trans-St.44,45 The much shorter lifetime for cis-St is partly a reflection of the additional chemical decay route that leads to photocyclization to dihydrophenanthrene with a quantum yield of 0.10.31 The lack of photoionization may simply mean that ionization cannot compete with the other rapid decay pathways for singlet cis-St. Alternatively, a biphotonic ionization process that involves absorption of a second photon by the first excited singlet state will also be very unlikely for singlet cis-St but much more feasible for the longer-lived trans-St singlet. The above rationalization is based on the solution lifetimes for cis- and trans-St. Although the reported lifetimes for trans-St on alumina (1-3.6 ns, depending on the activation temperature for)the alumina) are substantially longer than that in solution, it is reasonable to assume that the differences between the two isomers will be maintained on solid supports.7,16 In fact, the relative changes in fluorescence quantum yields and photoisomerization quantum yields for solution versus alumina indicate that the difference in lifetime for the two isomers may be greater on this solid than in solution.⁷ It is also possible that the higher oxidation potential for cis-St may be a factor (1.95 and 2.06 eV vs Ag/AgI in acetonitrile for trans- and cis-St, respectively)⁴⁶ in determining the relative photoionization efficiencies.

Excitation of both *cis*- and *trans*-St on NaX zeolite produces only the *trans* radical cation, presumably via a similar mechansim to that outlined above for the silica samples. In this case an additional broad absorption band due to electrons trapped as ionic sodium clusters is also observed. Similar absorptions have been produced by irradiation of other aromatics in NaY and NaX zeolites.¹⁹ The absorption due to the trapped electron decays rapidly in the presence of oxygen (see Figure 5), again in agreement with literature results. The yield of *trans*-St^{*+} is also affected by the presence of oxygen, although the decay kinetics change very little. This suggests that some radical cations react rapidly with O_2^{*-} produced by reaction of the trapped electron with oxygen, thus lowering the overall yield of radical cation. Further, the relative amounts of radical cation and trapped electron are sensitive to the amount of water present in the zeolite. The observed decrease in the yield of trapped electron in the presence of water may indicate that the nature and number of trapping sites are affected by coadsorbed water. The presence of water may also result in inclusion of the stilbene at sites that are further from the site for the trapped electron and may contribute to the observed variations.

The two-laser transient experiments indicate that the trapped electron generated by irradiation of St in NaX zeolite can be readily bleached by 532 nm irradiation. Although the bleaching is irreversible on the time scale of our transient experiments, there is no evidence that it leads either to the recombination of the electron and the radical cation or to capture of the electron by stilbene to give its radical anion. The latter conclusion is further substantiated by the experiment in which the trapped electron signal was bleached for a sample containing biphenyl without the concomitant formation of biphenyl radical anion. Similar results were also obtained when the trapped electron generated by photoionization of pyrene was bleached at 532 nm. This is a more conclusive experiment since the radical cation and anion spectra are better separated from the absorption due to the trapped electron in this sytem. These results suggest that irradiation of the trapped electrons leads to their redistribution to other sites that do not have detectable absorption within our spectral range or to dissolution of the ionic sodium cluster that is repsonsible for the visible absorption.

Diffuse Reflectance Laser Flash Photolysis of TNM/St Complexes. Irradiation of TNM/aromatic charge transfer (CT) complexes in solution is well-known to result in rapid formation of a geminate radical ion pair, followed by rapid decomposition (<10 ps) of the tetranitromethane radical anion to give the trinitromethide anion plus NO₂.³⁵

$$[\operatorname{ArC}(\operatorname{NO}_2)_4] \xrightarrow{h\nu_{\operatorname{CT}}} [\operatorname{Ar}^{\bullet+}\operatorname{C}(\operatorname{NO}_2)_4^{\bullet-}] \xrightarrow{} [\operatorname{Ar}^{\bullet+}\operatorname{C}(\operatorname{NO}_2)_3^{-}\operatorname{NO}_2] (3)$$

The resulting ions either diffuse apart or undergo irreversible formation of a σ adduct.^{35–38,47} Irradiation of St/TNM charge transfer complexes on silica clearly leads to efficient generation of St⁺⁺ as shown in Figure 6. The observation of mixtures of both cis- and trans-St++ upon irradiation of the cis-St/TNM complex demonstrates that cis-St*+ is stable with respect to isomerization, at least on a time scale of tens of microseconds. The St radical cation decays considerably more rapidly when it is formed by irradiation of the CT complex rather than by photoionization. This rapid radical cation decay is most likely due to reaction with the trinitromethide anion. Alternatively, it is possible that the initial tetranitromethane radical anion does not undergo rapid decomposition on solid supports and that back electron transfer accounts for the decay of the radical cation. This seems considerably less plausible since it would require an increase of 5-6 orders of magnitude in the lifetime of the radical anion on solids as compared to solution, but our experimental data do not allow us to conclusively eliminate this possibility. Note that the kinetics for St++ decay in our experiments are comparable to those that have been measured for back electron transfer of geminate radical ion pairs produced by excitation of CT complexes in other zeolites.^{15,20} For example, the radical ions generated by excitation of naphthalene and anthracene with various acceptors have lifetimes in the range $1-10 \ \mu s.^{20}$

The spectrum shown in Figure 6 indicates that excitation of the *cis*-St/TNM complex yields predominantly *trans*-St⁺, even

after taking into account the fact that the extinction coefficient for trans-St⁺⁺ is approximately 3 times higher than that of cis-St⁺⁺ in solution.⁴⁶ The formation of the *trans* radical cation cannot be due to direct isomerization of an initially formed cis-St⁺⁺, given that the two have very similar lifetimes under these conditions and the relative contributions of each to the transient spectrum do not change with time. It is also unlikely that direct excitation of uncomplexed stilbene is responsible for the isomerization, particularly using 420 nm excitation. This leads to the conclusion that excitation of the CT complex provides an efficient route for cis-trans isomerization. One possible mechanism for this isomerization is back electron transfer within the geminate radical ion pair to give triplet stilbene, which then isometrizes. Based on the solution redox potentials of -0.03^{37} and 1.7 eV⁴⁶ vs SCE for TNM and cis-St, respectively, formation of triplet stilbene by back electron transfer is not energetically feasible in solution, although it is not clear how much these redox potentials will be modified on solid supports. Furthermore, as noted above, it is likely that decomposition of $C(NO_2)_4^{\bullet-}$ occurs much more rapidly than back electron transfer, based on the short lifetime of this species in solution. Therefore, back electron transfer does not seem to provide a reasonable explanation for the observation of high yields of trans-St⁺⁺ from the cis-St/TNM complex. Alternatively, isomerization of cis-St via its dimer radical cation as has been observed in solution⁴⁶ could provide a potential explanation for our observations, although the experimental data do not provide any evidence for this route.

Conclusions

Diffuse reflectance laser flash photolysis of either cis- or trans-stilbene adsorbed on silica gel or included in NaX zeolite gives strong transient signals due to the trans-St radical cation. By contrast, the irradiation of the cis-St/TNM charge transfer complex generates a mixture of both *cis*- and *trans*-St⁺. This result demonstrates that cis-St*+ is stable with respect to isomerization on both silica gel and in zeolites on the time scale of our diffuse reflectance experiments. Measurement of ground state spectra for laser-irradiated samples of cis- and trans-St on both supports indicates that *cis-trans* isomerization is sufficiently rapid that substantial isomerization occurs with a single laser pulse under the usual conditions of our transient experiments. This leads to the conclusion that the formation of trans-St*+ upon excitation of cis-St occurs via initial cistrans isomerization, followed by photoionization, and highlights the importance of working at low laser intensity for transient experiments on solid supports. Photoionization of cis-St appears to be much less efficient than that of trans-St, probably as a result of the shorter singlet lifetime for the former. At low laser intensities and/or long delay times after excitation dihydrophenanthrene formed by photocyclization dominates the transient spectra obtained from cis-St.

Samples of St on NaX zeolite also show strong transient signals in the 500 nm region due to the presence of the trapped electron, as noted in earlier work on the photoionization of other aromatics on X and Y zeolites.¹⁹ Irradiation of this transient with a second 532 nm laser pulse leads to nearly complete photobleaching. The bleaching does not lead to any detectable trapping of the electron by the ground state aromatic to give radical anion or to recombination with the radical cation to regenerate the starting material. This suggests that irradiation leads to a redistribution of the electron to other zeolite sites.

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