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Journal of Photochemistry and Photobiology A: Chemistry 153 (2002) 41–53

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Direct and sensitized (energy and electron transfer) geometric isomerization of stilbene within zeolites: a comparison between solution and zeolite as reaction media

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Received 23 May 2002; received in revised form 18 July 2002; accepted 20 July 2002

Dedicated to Professor W. Adam on the occasion of his 65th birthday.

Abstract

The *trans*- and *cis*-stilbenes upon inclusion in NaY zeolite are thermally stable. Direct excitation and triplet sensitization results in geometric isomerization and the excited state behavior under these conditions are similar to that in solution. Upon direct excitation, a photostationary state consisting of 65% *cis* and 35% *trans* isomers is established. Triplet sensitization with 2-acetonaphthone gave a photostationary state consisting of 63% *cis* and 37% *trans* isomers. These numbers are similar to the ones obtained in solution. Thus, the presence of cations and the confined space within the zeolite have very little influence on the overall chemistry during direct and triplet sensitization. However, upon electron transfer sensitization with *N*-methylacridinium (NMA) as the sensitizer within NaY, isomerization from *cis*-stilbene radical cation to *trans*-stilbene occurs and the recombination of radical ions results in triplet stilbene. Prolonged irradiation gave a photostationary state (65% *cis* and 35% *trans*) similar to triplet sensitization. This behavior is unique to the zeolite and does not take place in solution. Steady state fluorescence measurements showed that the majority of stilbene molecules are close to the *N*-methylacridinium sensitizer. Diffuse reflectance flash photolysis studies established that independent of the isomer being sensitized only *trans* radical cation is formed. Triplet stilbene is believed to be generated via recombination of stilbene radical cation and sensitizer radical anion. One should be careful in using acidic HY zeolite as a medium for photoisomerization of stilbenes. In our hands, in these acidic zeolites isomerization dominated the photoisomerization.

Keywords: Electron transfer; Geometric isomerization; Stilbene

1. Introduction

The utility of zeolites for stabilizing ionic species such as radical cations and carbocations and for promoting separation of ion pairs is now well-recognized [1–18]. A number of early studies demonstrated that stable radical cations could be thermally generated by inclusion of aromatic and alkene substrates in zeolites [2–4]. In other cases, more reactive radical cations have been generated photochemically by either one- or two-photon processes within X and Y zeolites [5–9]. A variety of studies have focused on using the zeolite environment to control charge separation efficiency and have demonstrated that radical ion pairs are significantly longer-lived in a zeolite channel or cage than in solution, thus, illustrating the potential for modulation of the energy-wasting back electron transfer step [10,11]. In addition to increasing the charge separation efficiency, the zeolite environment can change the reactivity of the radical ions and allow for reaction pathways that are not favored in solution. Early work by Bauld used zeolites as a photocatalysts for the radical ion mediated dimerization of alkenes [12]. A number of more recent studies have focused on photosensitized electron transfer chemistry of arylalkenes and have shown that there are important differences in reactivity for zeolite-included radical cations [13–18]. For example, we have shown that substituted styrene radical cations in NaX lead to cyclobutane dimers in ratios that are substantially different from those obtained in solution, presumably due to the

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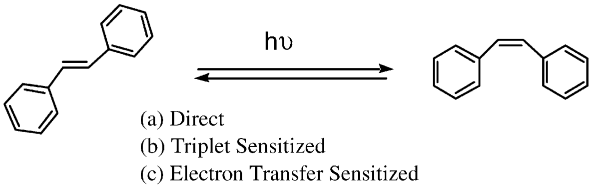
PII: S1010-6030(02)00300-3

constraints imposed by the restricted space available in the zeolite framework [13]. Similarly, 1,1-diarylethylene radical cations yield products derived from hydrogen abstraction and reaction with superoxide anion in Y zeolites, by contrast to results in solution where addition of the radical cation to ground state alkene is favored [14]. Photooxidations involving stilbene radical cations generated via excitation of charge transfer complexes or dye sensitization also exhibit different reactivity patterns in a zeolite environment [15].

In our continuing efforts to understand the effects of the zeolite environment on radical cation reactivity, we have examined the photosensitized electron transfer chemistry of stilbene in NaY zeolite. The electron transfer chemistry of both *cis*- and *trans*-stilbene has been extensively studied in solution, and leads to a concentration dependent one way *cis*–*trans* isomerization and, in the presence of oxygen, to oxidative cleavage to benzaldehyde [19]. Transient spectroscopy experiments have shown that both *cis* and *trans* radical cations are configurationally stable on a microsecond timescale, leading to the conclusion that the *cis*–*trans* isomerization occurs via reversible addition of radical cation to alkene to form an acyclic dimer radical cation that reverts to reactants with loss of stereochemistry [19]. Two diffuse reflectance flash photolysis studies have shown that direct excitation of either stilbene isomer in zeolites results in formation of the *trans* radical cation [5,8b], although the direct excitation results have been shown to be complicated by direct photochemical interconversion of *cis* and *trans* isomers [5]. By contrast, the photosensitized electron transfer chemistry of *cis*-stilbene using 2,4,6-triphenylpyrylium cation encapsulated in HY zeolite has been reported to lead to clean one-way isomerization [16]. In addition to the photochemically induced isomerization of stilbenes within zeolites, thermal isomerization of one way *cis* to *trans* isomerization of stilbene catalyzed by protons within acidic zeolites has also been reported [20].

Based on the earlier results, it is unclear whether the stilbene radical cation does undergo isomerization in zeolite, and if so by what mechanism (unimolecular versus reversible dimer formation). The selective generation of stilbene radical cations via photosensitized electron transfer in non-acidic zeolites should in principle allow one to resolve these questions since both direct photoisomerization and competing thermal acid catalyzed chemistry can be avoided. We have now studied the photosensitized electron transfer chemistry of both *cis*- and *trans*-stilbene in Y zeolite using the ionic sensitizer, *N*-methylacridinium salt, and a combination of product studies, fluorescence and diffuse reflectance transient spectroscopy. The results described in this report lead to the conclusion that the *cis* radical cation undergoes rapid unimolecular isomerization in Y zeolite, by contrast to the results in solution.

In addition to examining the photosensitized electron transfer reactions, we have also investigated the influence of cations upon the direct and triplet sensitized isomerization of stilbenes. This work was prompted by the recent discovery that the geometric isomerization of *cis*-1,2-diphenylcyclopropane to its *trans* form is prevented within Y zeolites. In this system, cation complexation is believed to provide a barrier for rotation in the excited state [21]. A decade ago, one of the authors established that direct excitation of stilbene results in *cis*–*trans* isomerization of stilbene within X and Y zeolites but not within the narrow channels of ZSM-5 [22]. This observation has been confirmed recently by Ellison and Thomas through careful lifetime measurements of *trans*-stilbene included in NaY and ZSM-5 [23]. Although the exact lifetimes of the excited singlet state of *trans*-stilbene in the two studies differ the general conclusions remain the same. Reported lifetime by (Tulane) group is more in agreement with that of *trans*-stilbene included in NaY co-adsorbed with solvents (hexane and water). The results presented here show that geometric isomerization of *cis*- and *trans*-stilbenes occur readily within NaY upon direct excitation, triplet sensitization and electron transfer sensitization (Scheme 1). Of these reactions, only the electron transfer sensitized isomerization within NaY zeolite shows features that are different from those in solution.



Scheme 1.

2. Results

2.1. Product studies

Photochemical product studies for direct excitation, triplet sensitization and electron transfer sensitization of *trans*- and *cis*-stilbenes included within NaY were carried out. Direct irradiations were performed with a 450 W medium pressure mercury lamp with appropriate Corning glass filters to isolate the desired irradiation wavelength. Although both hexane slurry and solid state irradiations were conducted, product formation was much faster under slurry conditions. Therefore, only the results of slurry irradiations are reported in Tables 1 and 2. Both *trans*- and *cis*-stilbenes were thermally stable within NaY zeolites. Upon direct excitation ($\lambda > 300$ nm) under nitrogen saturated conditions a photostationary state consisting of 65% *cis* and 35% *trans* was established in about 12 h (Table 1). This ratio is similar to the one obtained in hexane under the same conditions. This established that geometric isomerization in the excited singlet state within NaY (hexane slurry) is identical to the one that occurs in solution. As would be expected, under oxygen saturated conditions both oxidation products and phenan-

Table 1
A comparison of the products of direct and triplet sensitized irradiations of stilbene in solution and NaY zeolite

Condition	Starting isomer	*cis*:*trans* ratio	Remarks
Direct irradiation, hexane (>300 nm); nitrogen	*trans* or *cis*	65:35	
Direct irradiation, NaY/hexane, >300 nm; nitrogen	*trans* or *cis*	64:36	87% Recovery
Direct irradiation, hexane (>300 nm); oxygen	*trans* or *cis*		Prolonged irradiation yields phenanthrene as the only product
Direct irradiation, NaY/hexane, >300 nm; oxygen	*trans* or *cis*		Prolonged irradiation yields phenanthrene along with oxidation products
Fluorenone sensitized, dichloromethane, >350 nm	*trans* or *cis*	90:10	
Fluorenone sensitized, NaY/hexane, >350 nm	*trans* or *cis*	86:14	
2-Acetonaphthone sensitized, dichloromethane, >350 nm	*trans* or *cis*	72:18	
2-Acetonaphthone sensitized, NaY/hexane, >350 nm	*trans* or *cis*	63:37	
4-Aminobenzophenone sensitized, dichloromethane, >350 nm	*trans* or *cis*	57:43	
4-Aminobenzophenone sensitized, NaY/hexane, >350 nm	*trans* or *cis*	55:45	

For direct irraditions, 300 mg of activated NaY and 3 mg of stilbene were used (1 molecule per 10 supercages). The samples were irradiated with a 450 W medium pressure mercury lamp with 280 nm cut-off filters. The sensitizer was maintained at 1 molecule per 10 supercages and stilbene at 1 molecule per 5 supercages. NaY was activated at 500 °C prior to loading with sensitizer and stilbene.

threne were obtained as the final products. No dimers were detected at the loading levels used in our experiments (1 molecule per 10 supercages).

Triplet sensitization was conducted with fluorenone, 2-acetonaphthone and 4-aminobenzophenone as triplet sensitizers (Table 1). No thermal reaction occurred when stilbene and the above sensitizers were co-adsorbed within NaY. Excitation of the sensitizer was achieved with light of $\lambda > 350$ nm. After 40 h of irradiation, a photostationary state was reached from either *trans*- or *cis*-stilbene (loading levels: sensitizer, 1 molecule per 10 supercages and stilbene, 1 molecule per 5 supercages). The *cis*:*trans* ratios within zeolites are similar to that in solution suggesting that the photochemical behavior of *trans*- and *cis*-stilbene triplets is the same in both solution and zeolites [24,25]. Previously 4-aminobenzophenone has been used as a triplet sensitizer for stilbene isomerization within H^+ exchanged Y, mordenite, ZSM-5 and beta zeolites [26]. In our hands, conversion of *cis*- to *trans*-stilbene occurred when this sensitizer was included in HY, H-mordenite and H-beta and kept in the dark over night. No such thermal reaction occurred when *cis*-stilbene was stirred with HZSM-5 in hexane, presum-

Table 2
Electron transfer sensitized irradiation of stilbene within NaY zeolite[a,b,c]

Sensitizer and medium	Starting isomer	Photoproduct *trans*:*cis*	Remarks
N-Methylacridinium iodide/acetonitrile, >420 nm, 15 h	*cis*	99:1	
N-Methylacridinium exchanged/NaY/hexane, >420 nm, 40 h[a]	*cis*	31:69	90% Recovery; 10% products with long retention times also formed
N-Methylacridinium exchanged/NaY/hexane, >420 nm, 40 h[a]	*trans*	35:65	90% Recovery; 10% products with long retention times also formed
N-Methylacridinium exchanged/NaY/hexane, no irradiation, kept in dark for 12 h[a]	*cis*	Only *cis*	95% Recovery, no thermal reaction
Triphenylpyrrilium exchanged HY/hexane, no irradiation, kept in dark for 12 h[d,e]	*cis*	98:2	76% Recovery; *cis* was converted to the *trans* by thermal reaction
Triphenylpyrrilium exchanged HY/methylene chloride, no irradiation, kept in dark for 12 h	*cis*	*cis* in supernatant	Most of stilbene remained in supernatant
HY/methylene chloride, no irradiation, kept in dark for 12 h[f]	*cis*	66:33	50% Recovery; *cis* was converted to the *trans* by thermal reaction
HY/hexane, no irradiation, kept in dark for 12 h[f]	*cis*	75:25	50% Recovery
NaY/hexane, no irradiation, kept in dark for 12 h[f]	*cis*	Only *cis*	95% Recovery, no thermal reaction

[a] The sensitizer was kept at 1 molecule per in 100 supercages and stilbene at 1 molecule per 10 supercages. The NMA-NaY sample was dried at 100 °C prior to use.

[b] All irradiations were conducted with 450 W medium pressure mercury lamp with 380 nm cut-off filter.

[c] Mass balance was estimated using tetradecane as the internal standard.

[d] TPP-HY was activated at 100 °C, 300 mg of zeolite and 3 mg of *cis*-stilbene were stirred in solvent for 12 h and extracted with methylene chloride–acetonitrile.

[e] When unactivated TPP-HY was used (300 mg of zeolite and 3 mg of *cis*-stilbene) no stilbene was incorporated in the zeolite using either hexane or methylene chloride as solvent.

[f] HY was activated at 500 °C, 300 mg of zeolite and 3 mg of *cis*-stilbene were stirred in solvent for 12 h and the sample was extracted with methylene chloride–acetonitrile.

ably due to the fact that *cis*-stilbene does not fit in the channels of ZSM-5.

Electron transfer sensitization studies within NaY were conducted with *N*-methylacridinium salt (NMA), 9-cyanoanthracene (9-CA) and triphenylpyrylium salt as sensitizers. The results with 9-cyanoanthracene were not reproducible from one experiment to the next and the mass balance was poor. Therefore, product studies for this sensitizer were not pursued further. Triphenylpyrylium included Y zeolite was prepared and characterized as reported in the literature [16]. Unfortunately, HY zeolite had to be used for this purpose. The *cis*-stilbene was isomerized to

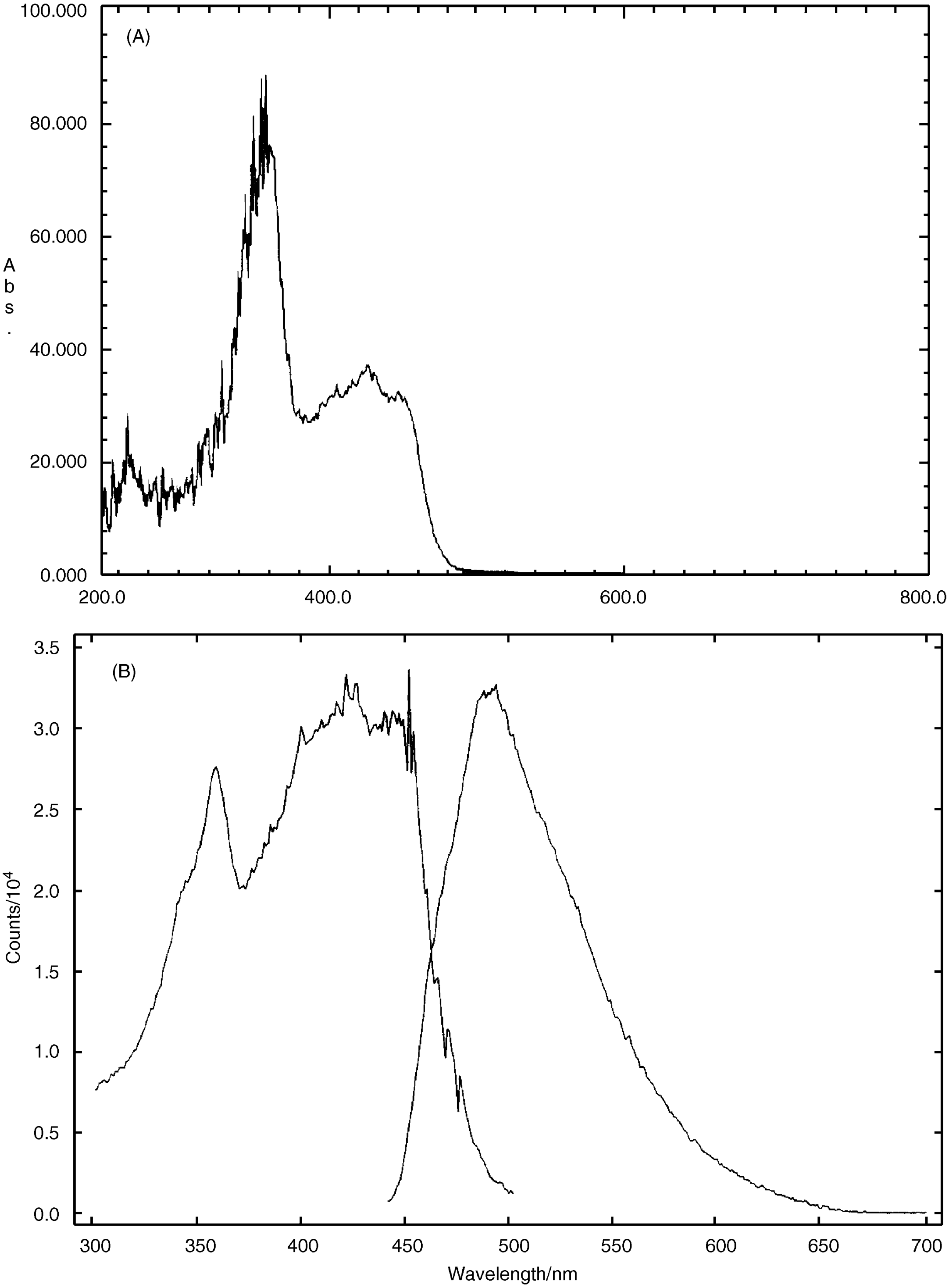


Fig. 1. Diffuse reflectance (A), and emission and excitation (B) spectra of *N*-methylacridinium/NaY. For the emission spectrum, the excitation was kept at 420 nm and the excitation spectra was recorded by monitoring emission at 520 nm.

the *trans* isomer thermally at room temperature in both HY and triphenylpyrylium incorporated HY (Table 2). Because of this complication, no further experiments were performed with this sensitizer. *N*-Methylacridinium iodide, a well-known electron transfer sensitizer, was exchanged into NaY by stirring in acetonitrile. The diffuse reflectance and fluorescence emission and excitation spectra shown in Fig. 1 are in agreement with that of *N*-methylacridinium salt. For product studies, the sensitizer was kept at a loading level of 1 molecule per 100 supercages and stilbene at 1 in 10 supercages. Both *cis*- and *trans*-stilbenes were thermally stable within *N*-methylacridinium exchanged NaY. In solution, excitation of *N*-methylacridinium iodide in the presence of *cis*-stilbene results in quantitative formation of *trans*-stilbene. However, excitation of *N*-methylacridinium iodide in the presence of *trans*-stilbene results in no change. We were surprised to find that sensitization by *N*-methylacridinium (>380 nm) within NaY zeolite resulted in different behavior (Table 2). In about 40 h, a photostationary state was reached from either *cis*- or *trans*-stilbene to give a mixture consisting of both *trans* and *cis* isomers (Table 2). The mass balance monitored with an external standard (hexadecane) indicated that only 10% of stilbene gave other products. However, continued irradiation resulted in oxidation and high molecular weight products (uncharacterized). From the product studies, it is clear that interconversion between *cis*- and *trans*-stilbene occurs upon electron transfer sensitization within NaY.

2.2. Fluorescence quenching

Fluorescence quenching studies were carried out to confirm that excited *N*-methylacridinium was quenched by both *cis*- and *trans*-stilbene. The sensitizer concentration was maintained at 1 in 10 supercages and the stilbene loading varied from 1 in 40 to 1 in 1 supercages. The fluorescence intensity decreased with increasing loading of stilbene for both *cis* and *trans* isomers; representative results are shown in Fig. 2 for quenching of *N*-methylacridinium with *cis*-stilbene. The fluorescence intensity decreases with increasing loading of stilbene, with 80% reduction at a loading level of 1 molecule per 10 supercages. Qualitatively similar results were obtained for *trans*-stilbene. Consistent with the steady state results, the fluorescence lifetime of *N*-methylacridinium also decreased with increased stilbene loading (Table 3). The decay of *N*-methylacridinium showed a two component decay with lifetimes of 26–38 ns (major; >90%) and 9–13 ns for a range of loadings of *cis*- and *trans*-stilbene (0 to 1 stilbene per supercage). The decay of *N*-methylacridinium within NaY in the absence of quencher also showed a two

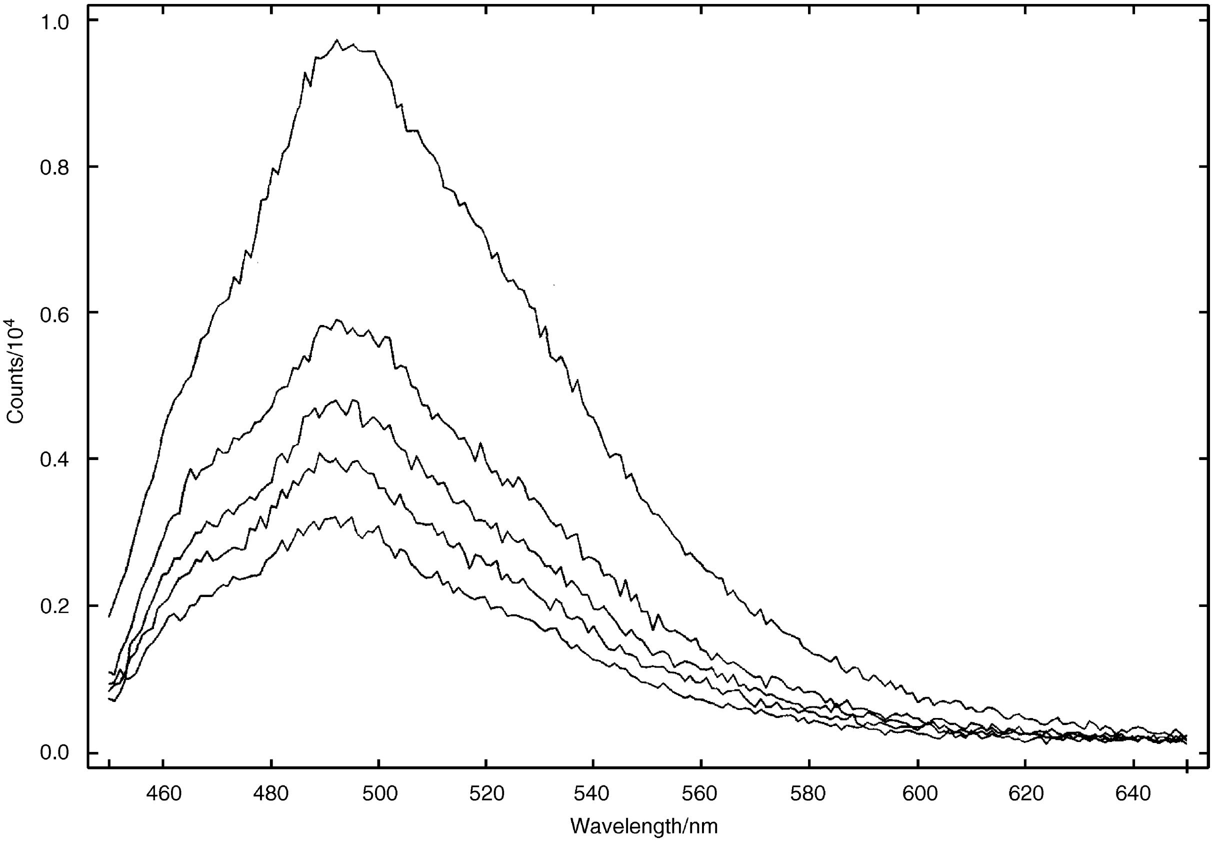


Fig. 2. Steady state fluorescence spectra for samples of *N*-methylacridinium/NaY for five different loading levels of *cis*-stilbene. Loading levels from top to bottom: 0, 0.1, 0.2, 0.5 and 1 molecule of *cis*-stilbene per supercage. Sensitizer was kept at 1 molecue per 10 supercages.

Table 3
Excited singlet state lifetime of *N*-methylacridinium (NMA) exchanged NaY as measured by single photon counting[a,b]

Loading level of NMA	Loading level of *cis*-stilbene	Fluorescence lifetime of the sensitizer, τ_1 and τ_2 (ns)	
1 in 10 cages	None	37.8	12.6
1 in 10 cages	1 in 20 cages	33.2	15.5
1 in 10 cages	1 in 10 cages	34.3	13.9
1 in 10 cages	1 in 5 cages	29.3	12.0
1 in 10 cages	1 in 2 cages	29.1	11.4
1 in 10 cages	1 in 1 cage	25.8	10.8

[a] Lifetime data could only be fitted with a double exponential decay.

[b] The samples were dried on a vacuum line (10^{-3} Torr) and used as solids.

component decay with a major component of 38 ns which is close to the lifetime in acetonitrile (36 ns) and a second 13 ns component. For the same loading level of 1 in 10 supercages, the lifetime decreased only by 11% which is much less than the 80% steady state fluorescence quenching noted earlier. The combined fluorescence and lifetime results indicate that quenching of *N*-methylacridinium excited singlet occurs by both static and dynamic mechanisms, the former being the dominant one.

2.3. Diffuse reflectance flash photolysis

Transient spectra were measured after 355-nm laser excitation of both 9-CA and NMA in the presence of *cis*- and *trans*-stilbene. Representative spectra are shown in Fig. 3 for NMA; the spectra obtained in the presence of the *cis* and *trans* isomers are identical, with λ_{max} at 490 nm, consistent with the formation of the same radical cation from both isomers. The transients obtained from *cis*- and *trans*-stilbene decayed with similar complex kinetics over a period of ∼150 μs. A comparison of the spectra obtained for NMA/*cis*-stilbene in the presence of oxygen and nitrogen is shown in Fig. 4A and B. The spectrum for a nitrogen-purged sample shows additional longer wavelength absorption due to the sensitizer radical, which in solution has a broad absorption centered at 500 nm [27]. Excitation of NMA alone in NaY also gave weak signals consistent with reduction of the sensitizer, presumably by direct electron transfer from the zeolite, as has been observed recently for chloranil in zeolites [28]. Control experiments in which both *cis*- and *trans*-stilbene were excited directly at 355 nm in NaY in the absence of sensitizer were carried out. In each case, only very weak signals were obtained (Fig. 4C for *cis*-stilbene), as a result of the minimal stilbene absorption under these conditions. This confirms that direct photoionization of stilbene does not contribute significantly to the transient spectra obtained in the presence of NMA.

Since there is some overlap of the sensitizer radical and the stilbene radical cation spectra in the 500 nm region, a similar set of experiments was carried out using 9-CA as the sensitizer; this gave virtually identical results to those presented earlier for NMA. Excitation of oxygen-purged samples of *cis*- and *trans*-stilbene yielded similar spectra with λ_{max} at 485 nm (Fig. 5). The sensitizer radical anion is rapidly scavenged by oxygen and does not contribute to the transient spectrum. Note that the small shift in absorption maximum from that obtained with NMA may reflect some contributions from the NMA sensitizer radical.

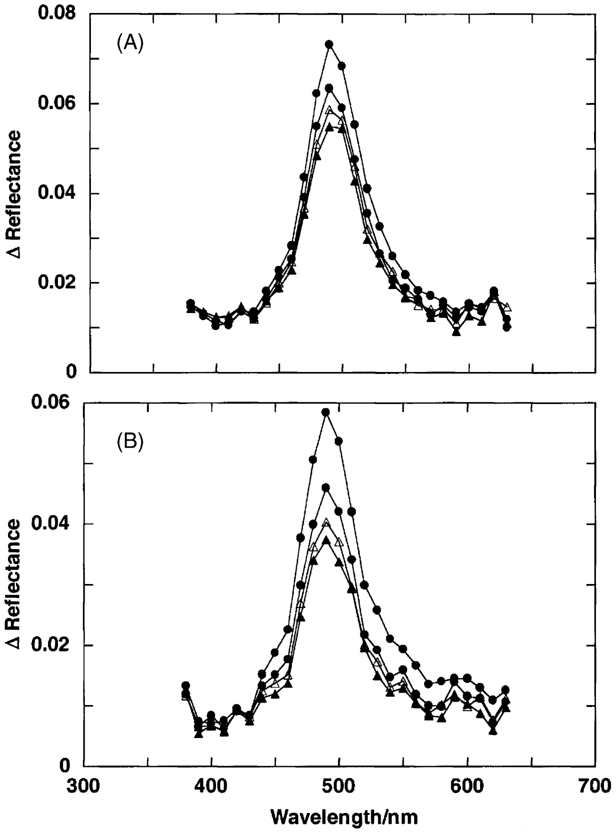


Fig. 3. Transient spectra measured following 355 nm excitation of oxygen-purged samples of *N*-methylacridinium/NaY in the presence of *cis*-stilbene (A) and *trans*-stilbene (B). Spectra were recorded at delays of 2, 5, 10 and 14 μs after the laser pulse and the stilbene loading was 1 molecule per 15 supercages.

The earlier results indicate that a single radical cation is observed upon sensitization of either *cis*- or *trans*-stilbene with NMA and 9-CA within zeolites. In acetonitrile the *cis* and *trans* radical cations have quite distinct spectra with λ_{max} at 508 and 472 nm, respectively [19]. By analogy with these results, the transient obtained in NaY (485 nm) is most consistent with formation of the *trans* radical cation. This also agrees with previous observations for the direct photoexcitation of stilbene on silica gel and in zeolites. There is no evidence in any of the photosensitization results for the formation of the *cis* radical cation which, by analogy with spectra in solution, should absorb beyond 500 nm [19].

2.4. Computational studies

To examine the role of cation binding to stilbene during the isomerization process we have computed the

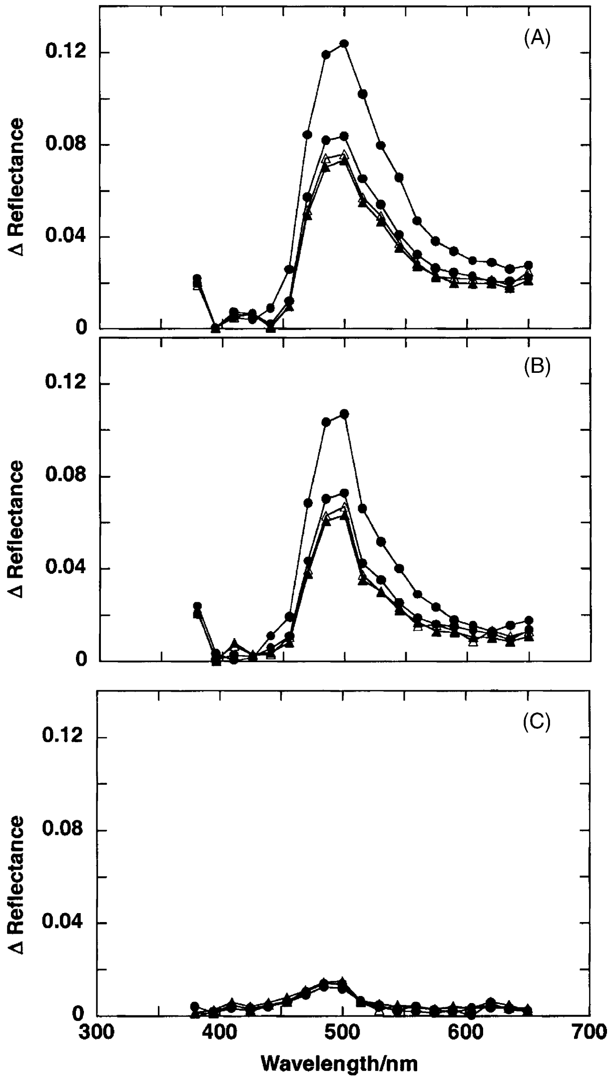


Fig. 4. Transient spectra measured following 355 nm excitation of nitrogen (A) and oxygen-purged (B) samples of *N*-methylacridinium/NaY in the presence of *cis*-stilbene (1 molecule per 15 supercages) and an oxygen-purged sample of *cis*-stilbene in NaY (C) (1 molecule per 15 supercages). Spectra were recorded at delays of 3, 6, 11 and 15 μs after the laser pulse.

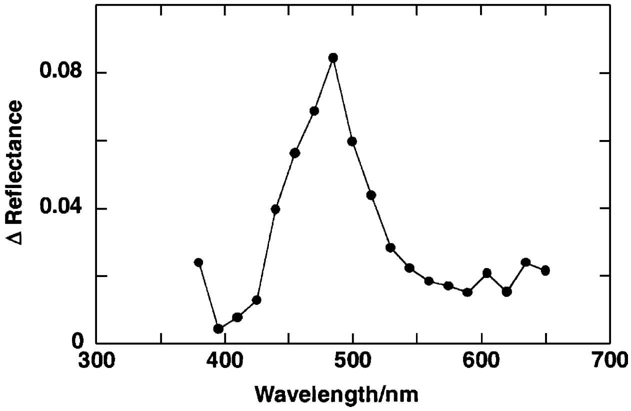


Fig. 5. Transient spectra measured 4 μs after 355 nm excitation of an oxygen-purged sample of 9-cyanoanthracene/NaY in the presence of *cis*-stilbene (1 molecule per 15 supercages).

binding energies of alkali ions to *cis*-stilbene. We believe that the alkali ion will bind to only one of the two phenyl rings in *trans*-stilbene and this type of complexation would be expected to have at most a minimal effect on the isomerization process. On the other hand, co-operative binding of the cation to both phenyl groups is likely for *cis*-stilbene and may selectively restrict the conversion of *cis*-stilbene to *trans*. Computational studies have indicated that this type of binding is favored in *cis*-1,2-diphenylcyclopropane. Consistent with the computational results, *cis*-1,2-diphenylcyclopropane failed to isomerize to the *trans* isomer within Y zeolites [21]. We have computed the binding energies of alkali ions to *cis*-stilbene and compared the data with that of *cis*-1,2-diphenylcyclopropane. The interaction energies computed at ab initio levels (HF, MP2 and B3LYP) for alkali cation binding to *cis*-stilbene and *cis*-1,2-diphenylcyclopropane are provided in Table 4. The energies of cation binding to two benzene molecules in sandwich geometries are also included for comparison. The most significant results from the computational studies are as follows: (a) the complexation energies for cation binding to *cis*-1,2-diphenylcyclopropane are similar to those for cation complexation with two free benzene units (sandwich structure); (b) binding to *cis*-stilbene is of much lower energy than to the earlier two systems. For example, the binding energies (MP2 level) of Na$^+$ ion to two benzene rings, *cis*-1,2-diphenylcyclopropane and *cis*-stilbene are −56.2, −53.9 and −47.5 kcal/mol, respectively. While the interaction in still quite substantial, the magnitude of binding energy in the case of *cis*-stilbene is presumably not

Table 4
Interaction Energies (kcal/mol) of alkali metal cations flanked by two aromatic rings in various molecules

Metal ion (M$^+$)	Bz···M$^+$···Bz	*cis*-Diphenylcyclopropane			*cis*-Stilbene		
	MP2	HF	MP2	B3LYP	HF	MP2	B3LYP
Li	−81.1	−63.48	−75.82	−66.83	−56.80	−67.93	−57.63
Na	−56.2	−47.08	−53.87	−49.67	−41.55	−47.54	−41.60
K	−32.3	−28.24	−32.57	−29.17	−23.84	−40.05	−22.17
Rb	−27.7	−23.49	−28.22	−23.10	−19.39	−23.09	−17.14
Cs	−22.6	−15.01	−22.66	−18.03	−14.58	−17.95	−12.12

For Li and Na, a 6-31G* basis set is employed. K, Rb and Cs are treated with Hay–Wadt's ECP with explicit valence functions with a six-term polarization.

large enough to overcome the effect of solvation of cations by zeolite framework. The reduced binding energy of *cis*-stilbene relative to *cis*-1,2-diphenylcyclopropane would then account for the observed difference in photochemical behavior between the two systems within NaY zeolite. In this context, one should note that during the geometry optimization a C_s symmetry constraint was imposed for *cis*-1,2-diphenylcyclopropane, while *cis*-stilbene was optimized in a C_2 symmetric form. We have tried optimizing the *cis*-stilbene with C_{2v} symmetry. Frequency calculation revealed that the higher energy symmetric form is a transition state (presumably between two C_2 symmetric systems). Subsequently, we lowered the symmetry from C_{2v} to C_2, which eventually resulted in the C_2 symmetric minima. In the case of DPCP, a minimum with the C_s symmetry was identified, which is the highest possible symmetry for this structure.

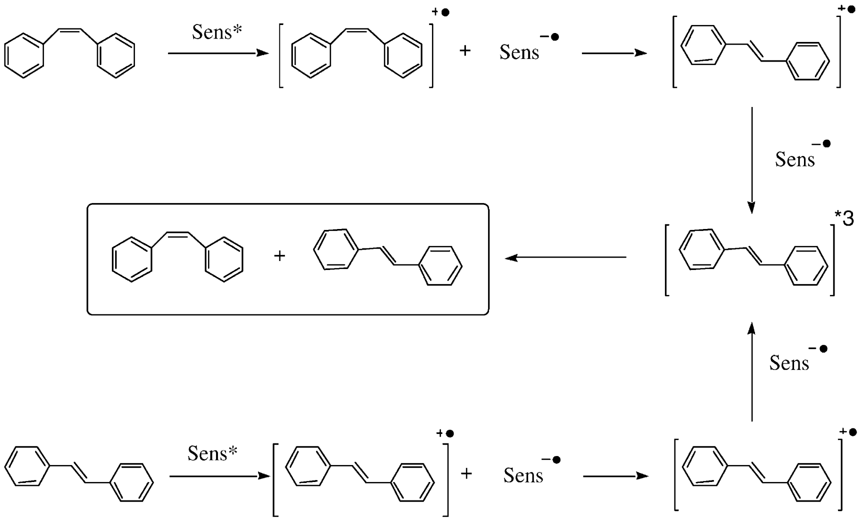
3. Discussion

The results described above lead to the following three observations, each of which is discussed in detail below: (a) while in solution electron transfer sensitization results in one-way *cis* to *trans* isomerization, within zeolites stilbenes undergo reversible *cis*–*trans* isomerization; (b) while in solution *cis*- and *trans*-stilbene radical cations do not interconvert, in zeolites only spectra corresponding to the *trans* radical cation are observed upon electron transfer sensitization. This suggests that the *cis* radical cation isomerizes to the *trans*, as discussed later; (c) while cation binding plays a significant role in the geometric isomerization of 1,2-diphenylcyclopropane, it has no effect on stilbene isomerization within zeolites.

The observation of the same radical cation upon photoinduced electron transfer from either *cis*- or *trans*-stilbene to sensitizers within NaY zeolite is surprising, based on results in solution where the isomeric radical cations have clearly distinguishable spectra [19]. The *cis* radical cation has an absorption that is red-shifted by ∼40 nm from the *trans* and both radical cations are configurationally stable on a microsecond timescale. The observation of only the *trans* radical cation in NaY suggests that the *cis*-stilbene radical cation may isomerize to *trans* rapidly in the zeolite. Although rapid isomerization of the *cis* radical cation is consistent with product studies in NaY which also show evidence for isomerization, there are a number of other possibilities that could explain the transient results. For example, previous studies have shown that only the *trans* radical cation is detected upon direct excitation of either *cis*- or *trans*-stilbene adsorbed on silica or included in NaX [5]. In this case, the formation of *trans*-stilbene radical cation upon excitation of *cis*-stilbene was hypothesized to occur via efficient *cis*–*trans* isomerization within a single laser pulse followed by photoionization of *trans*-stilbene. However, the control experiments noted earlier (excitation of stilbene in the absence of sensitizer) clearly demonstrate that the radical cations observed under photosensitized electron transfer conditions arise from excitation of the sensitizer not the stilbene. A second possibility is that the *trans* radical cation is formed by photoisomerization of an initially formed *cis* radical cation within the same laser pulse; *cis*-stilbene radical cation has been shown to undergo photochemical isomerization in solution although the *trans* radical cation does not photoisomerize [29]. This possibility is unlikely to account for the transient results since previous results using direct 266 nm photoionization to generate *trans*-stilbene radical cation in zeolites and on silica have shown that the radical cation does not have significant absorption at 355 nm [5]. Based on these studies, the extinction coefficient of the radical cation at 355 nm is more than 10 times lower than that at its visible absorption maximum for which an ε value of 59,600 in acetonitrile has been reported [19]. It is even less likely to play a role in the product studies where the light intensity is too low to allow for excitation of a short-lived radical cation before it decays via other routes.

On the basis of the earlier arguments, one can conclude that rapid unimolecular isomerization of the initial *cis*-stilbene radical cation is the most reasonable explanation for the transient results. Although *cis*-stilbene radical cation is configurationally stable in solution, a number of substituted *cis*-stilbene radical cations do undergo efficient isomerization in solution [30]. In this case, it has been argued that the increased isomerization reactivity of the substituted radical cations is related to changes in the separation and localization of the positive charge and the unpaired electron. It is possible that complexation of the radical cation by the zeolite environment has a similar effect. The *cis*-stilbene radical cation can be detected when generated by excitation of the tetranitromethane/stilbene charge transfer complex on silica, demonstrating that it does not isomerize rapidly on this support [5].

Based on the flash photolysis results one would expect *cis*-stilbene to give quantitatively the *trans* isomer and the *trans* isomer to be stable under the sensitization conditions. However, the results presented in Table 2 indicate that *trans*-stilbene does isomerize to the *cis* form and *cis*-stilbene does not isomerize quantitatively to the *trans* isomer. In fact, the same photostationary state (*cis*:*trans*, 35:65) is obtained upon prolonged irradiation for either isomer. Although this is unexpected based on the solution behavior of stilbene, analogous behavior has been observed for 4,4′-dimethoxy stilbene in solution. Upon electron transfer sensitization *trans*-4,4′-dimethoxy stilbene isomerizes to the *cis* isomer. Geometric isomerization of fumaronitrile sensitized by naphthalene and *trans*-4,4′-dimethoxy stilbene by 9-cyanoanthracene, and dimerization of 1,2-diphenylcyclopropenes upon 9,10-dicyanoanthracene sensitization have been established to proceed via the triplet state of the olefin generated via reverse electron transfer from the sensitizer radical anion to the olefin radical cation [31–34]. We believe that a similar process occurs in the case



Scheme 2.

of stilbene within NaY zeolite. While the diffuse reflectance flash photolysis unequivocally establishes the formation of *trans*-stilbene radical cation from *cis*-stilbene, the product studies show that the *trans*-stilbene radical cation give *cis*-stilbene. One mode by which this could occur is via formation of triplet *trans*-stilbene by reverse electron transfer as shown in Scheme 2. Under these conditions, the photostationary state will be determined by the decay ratio of the twisted triplet, in agreement with the fact that the same *cis*:*trans* ratio is obtained from both isomers via electron transfer sensitization. The *cis*:*trans* ratio for the electron transfer sensitization is similar to that obtained by triplet sensitization, which is also consistent with the proposed triplet pathway.

Combining the conclusions of the transient and product studies leads to the mechanism for isomerization shown in Scheme 2. Our transient studies do not provide direct evidence for the formation of triplet stilbene. The triplet has been shown to absorb at ∼360 nm which is relatively close to the excitation wavelength used in the present photosensitization studies. Furthermore, its lifetime is expected to be significantly shorter than that of the *trans*-stilbene radical cation which decays over a 150 μs times scale in NaY zeolite. For example, stilbene triplet has a lifetime of 0.1 μs in solution [25b] and ∼13 μs on silica [5]. Both the short triplet lifetime and the proximity of its absorption to the laser wavelength would make it difficult to detect stilbene triplet produced by recombination of stilbene radical cation and sensitizer radical anion within the zeolite.

Finally, it is of interest to compare the influence of the zeolite cations on the excited state behavior of *cis*-1,2-diphenylcyclopropane and *cis*-stilbene. Zeolite cations restrict the rotation of *cis*-1,2-diphenylcyclopropane to the *trans* form during both direct irradiation and triplet sensitization [21] whereas cations do not influence the behavior of *cis*-stilbene. As shown in Table 4, the cation binding energy to *cis*-stilbene is significantly smaller than that to *cis*-1,2-diphenylcyclopropane. The difference in the interaction energy of an alkali ion with various 1,2-diphenyls primarily arises from the ability of the molecular system to accommodate the alkali ion. If the geometrical perturbation accompanying alkali ion binding is minimal, the interaction tends to be stronger. The lighter cations such as lithium and sodium have the best possible interaction with two benzene molecules in the sandwich arrangement. In this case, the benzene molecules are not covalently connected and, thus, enjoy freedom for readjustment upon binding to the metal ion. The *cis*-1,2-diphenylcyclopropane is better suited to accommodate the alkali ion between the 1,2-diphenyl rings than is *cis*-stilbene (Fig. 6). The *cis*-stilbene in the minimum energy conformation has a C_2 symmetric arrangement, while in the alkali ion complex the preferred structure is C_{2v} symmetric. Reorganization and disrupted conjugation between the phenyl rings results in relatively weaker complexation with alkali ions (Fig. 7). The effect of alkali ion binding on the geometry of the parent systems and the positions of the alkali ion in the corresponding complexes can be gleaned from the optimized geometries provided in Figs. 6 and 7. The distance between the centers of the phenyl ring (R_2, Fig. 8) and the angle made by the phenyl rings to the C–C σ or π bond (A_1) serve as good indicators of the geometric distortion that accompanies complexation by alkali ions. Optimized molecular geometries (MP2 level) for the parent *cis*-1,2-diphenylcyclopropane and *cis*-stilbene and their complexes with alkali ions are provided in Table 5. It is noteworthy that co-ordination of Na^+ ion to *cis*-1,2-diphenylcyclopropane requires negligible distortion of the parent molecule. On the other hand, in the case of *cis*-stilbene distortion of the parent molecule must precede complexation. We believe that this difference translates into the observed photochemical behavior within zeolites. It is quite likely that *cis*-stilbene binds to the cation

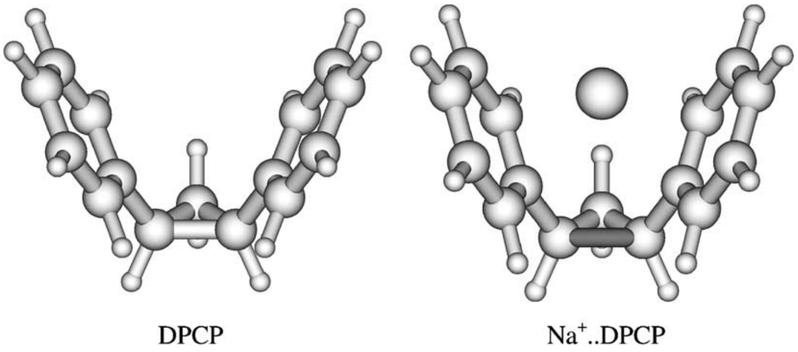


Fig. 6. MP2/6-31G* optimized geometry of *cis*-diphenylcyclopropane and its complex with Na^+ ion.

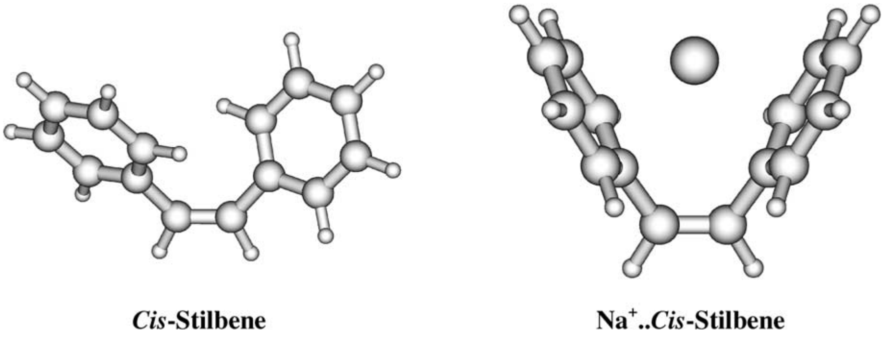


Fig. 7. MP2/6-31G* optimized geometry of *cis*-stilbene and its complex with Na^+ ion.

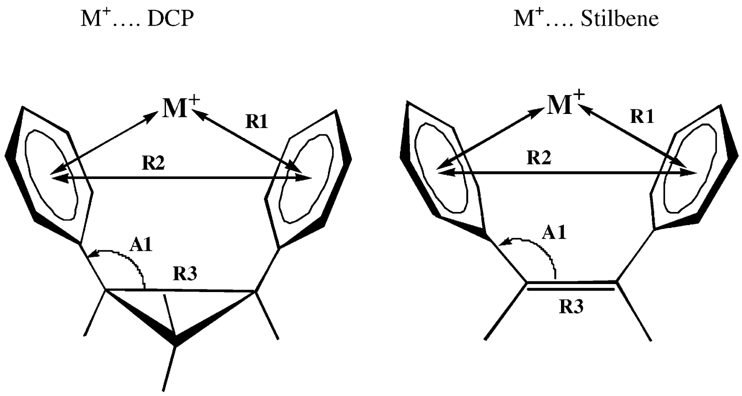


Fig. 8. Key geometrical parameters selected from the optimized molecular geometry (MP2) of alkali ion complexes of *cis*-1,2-diphenylcyclopropane and *cis*-stilbene.

Table 5
Key geometrical parameters (bond length (Å) and bond angles (°)) selected from the optimized molecular geometry (MP2) of alkali ion complexes of *cis*-1,2-diphenylcyclopropane and *cis*-stilbene[a]

Metal ion (M^+)	DCP system				Stilbene system			
	R1	R2	R3	A1	R1	R2	R3	A1
	–	4.36	1.54	119.5	–	4.85	1.35	126.7
Li	1.99	3.78	1.55	116.3	2.04	3.92	1.35	119.4
Na	2.46	4.28	1.54	118.8	2.45	4.32	1.35	121.6
K	3.10	4.61	1.53	120.9	2.85	4.63	1.34	123.5
Rb	3.10	4.76	1.52	122.0	3.11	4.78	1.34	124.5
Cs	3.46	4.90	1.52	123.1	3.91	4.92	1.34	125.6

The first row corresponds to the parent system without cation.

[a] Geometry optimizations have been performed at MP2 level with 6-31G* basis set for H, C, Li and Na. Hay–Wadt effective core potentials with valence functions are employed for the heavier metal ions such as K, Rb and Cs.

with one, rather than two, of its phenyl rings. The type II cation within a Y zeolite is bound to the six-membered oxygen rings of the zeolite framework and is likely to use the unexposed face to bind to the benzene ring. Unless such binding is weaker than diphenyl sandwich type binding, the alkali ion is unlikely to leave the oxygen ring. We believe that the computational data, after making allowance for counterion and solvation effects, are consistent with the photochemical observations.

4. Summary

Photoisomerization of *cis*- and *trans*-stilbenes included within NaY zeolite has been investigated. Direct excitation, triplet sensitization and electron transfer sensitization of either isomers resulted in geometric isomerization. Under conditions in which their photochemistry is examined both isomers of stilbene are thermally stable within NaY. Inclusion of *cis*-stilbene within HY zeolite (pure or impergnated with 2,4,6-triphenylpyrylium cation) resulted in thermal isomerization of *cis*- to *trans*-stilbene. Zeolite interior did not provide any restriction for rotation of the C=C bond in the excited state (excited singlet and triplet) or radical cation of stilbene. Although zeolite cations restrict the rotation of *cis*-1,2-diphenylcyclopropane to the *trans* form during both direct irradiation and triplet sensitization these cations do not influence the behavior of *cis*-stilbene. Recombination of *trans*-stilbene radical cation and sensitizer radical anion results in the formation of triplet *trans*-stilbene which isomerizes to both isomers. In solution, electron transfer sensitization results in one way isomerization from *cis* to *trans* where as in zeolite due to the involvement of triplet pathway two way isomerization occurs.

5. Experimental

5.1. Materials

Zeolite NaY (CBV-100) from PQ Corporation was used as received. HPLC grade hexane was used for all irradiations. Commercial samples of *trans*-stilbene, *cis*-stilbene, 9-cyanoantharcene, fluorenone, 2-acetonaphthone, 4-aminobenzophenone, chalcone and acetophenone were purified either by re-crystallization or distillation prior to use. *N*-Methylacridinium iodide was synthesized and purified according to a literature procedure [35]. HPLC grade hexane was used for all irradiations.

5.2. Preparation of HY zeolite

Commercial NaY (40 g) was taken in 200 ml of water containing 4 g of ammonium acetate and stirred overnight at room temperature. The slurry was filtered over a sintered crucible and washed with 1 l of water. This procedure with ammonium acetate was repeated twice. After three runs, the solid was dried at 100–110 °C for 6 h. The dried white powder was activated at 500 °C for 6 h to give 35 g of HY.

5.3. Preparation of triphenylpyrylium incorporated HY zeolite

The earlier prepared HY zeolite (4 g), chalcone (1.64 g) and acetophenone (0.48 g) in 50 ml of octane were heated to ∼130 °C with vigorous stirring for 4 days. The color of the reaction mixture changed from pale yellow to dark yellow and finally to canary yellow. The solid material obtained was filtered and transferred to a solid–liquid extraction thimble and Soxhlett extraction was performed for 4 days at refluxing dichloromethane temperature. During this process, the solvent turned yellow and the zeolite turned light yellow. The triphenylpyrylium incorporated HY zeolite was characterized by diffuse reflectance and fluorescence emission spectra.

5.4. Preparation of *N*-methylacridinium incorporated NaY zeolite

To a 20 ml solution of dry acetonitrile containing 40 mg of *N*-methylacridinium iodide was added 3 g of activated (500 °C) NaY and the mixture was stirred for 24 h. The slurry was centrifuged and the supernatant was discarded. To the solid was added 30 ml of dry acetonitrile and the resulting slurry was stirred for a few more hours and centrifuged. The sequence was repeated five times and the final solid was dried at 100 °C. The NaY containing *N*-methylacridinium ion was characterized by diffuse reflectance and fluorescence emission spectra (Fig. 1). We estimate that these samples contain 1 molecule of *N*-methylacridinium ion per 10 supercages. By varying the amounts of *N*-methylacridinium iodide and NaY, NaY loaded with different amounts of the sensitizer was prepared.

5.5. Preparation of triplet sensitizer (fluorenone, 4-aminobenzophenone) incorporated NaY zeolite

In a typical procedure, 300 mg of activated NaY and 3 mg of the sensitizer were stirred in 15 ml of hexane for 10 h. The slurry was filtered, washed with hexane and dried on a vacuum line. The sample thus prepared contains approximately 1 molecule of the sensitizer in 10 supercages.

5.6. Incorporation of stilbene into electron transfer and energy transfer sensitizer incorporated NaY

To a slurry of hexane (10 ml) containing 300 mg of vacuum dried sensitizer-NaY, a known amount of stilbene (2–10 mg) was added and the sample was stirred for 6 h. The slurry was filtered and washed with hexane. The hexane wash was collected and tested for remaining olefin. The zeolite thus prepared was dried on a vacuum line and used for further studies.

5.7. Irradiation and analysis of products

Irradiations for product studies were conducted in hexane slurries. Although irradiation of solid samples gave similar product distributions, conversions were low and much longer irradiation times were required to obtain amounts that can be analyzed by GC. The zeolite prepared and dried as earlier was taken in dry hexane (5 ml) and irradiated with a 450 W medium pressure mercury lamp under a nitrogen atmosphere. Corning glass filters were used to obtain the required excitation wavelength. This ensured that the observed reaction was due to the sensitization process. Following irradiation the hexane was analyzed for the presence of reactants and products. Generally, we did not find stilbene or any other products in the hexane layer. The organic product was extracted by stirring the zeolite with about 20 ml of dichloromethane for about 20 h. To the solvent extract, a known amount of calibration compound (hexadecane) was added and the samples were analyzed by GC (SE-30 capillary column, 30 m × 0.25 mm; 0.25 mm film; 100–250 °C ramp at 5 °C/min). The *cis*- and *trans*-stilbenes were identified by comparison with authentic samples. Oxidation products were formed in varying amounts but were not characterized.

5.8. Thermal reaction within HY zeolite

The *cis*-stilbene (2 mg) was dissolved in 5 ml of hexane and to this HY (300 mg; activated at 500 °C overnight) was added. The slurry was stirred overnight and filtered. The supernatant hexane was analyzed by GC and the filtrate was extracted with acetonitrile–dichloromethane (10 ml) for 8 h. The solvent extract was analyzed by GC. Hexadecane was used as the calibration compound to determine the exact amounts of *cis*- and *trans*-stilbenes in the solution.

The earlier procedure was repeated with HY activated at 100 °C. However, under this condition >80% *cis*-stilbene remained in hexane solution and was not incorporated in the zeolite.

5.9. Thermal reaction within triphenylpyrylium incorporated HY zeolite

Two separate experiments were performed, one with dichloromethane as the solvent and the other with hexane. Dichloromethane was used as the solvent in the study reported in [16].

The *cis*-stilbene (2 mg) was dissolved in 5 ml of hexane (or dichloromethane) and to this triphenylpyrylium incorporated HY zeolite (100 mg; activated at room temperature at 10^{-3} Torr overnight) was added. The slurry was stirred overnight and filtered. The supernatant hexane was analyzed by GC and the filtrate was extracted with acetonitrile–dichloromethane (10 ml) for 8 h. The solvent extract was analyzed by GC. Hexadecane was used as the calibration compound to determine the exact amounts of *cis*- and *trans*-stilbenes in the solution.

5.10. Instrumentation

Absorption spectra were recorded on a Shimadzu 2101PC-UV-Vis spectrophotometer equipped with a diffuse reflectance accessory. The dry zeolite samples were packed into a 2 mm quartz cuvette (in a dry box) and sealed with Teflon tape. The reflectance spectra were converted to absorption by using a Kubelka–Munk program supplied with the instrument. The solution spectra were recorded in 10 mm quartz cells using solvent as the reference.

Emission spectra were recorded on an Edinburgh FS-900 CDT spectroflourimeter. Solid zeolite samples were taken in quartz ESR tubes placed in a quartz cylindrical Dewar and the emission collected at right angles was recorded. Lifetime measurements were carried out on an Edinburgh FL-900 CDT single photon counter using a hydrogen filled nanosecond flash lamp (40 kHz) as the light source. The lamp profile was collected with Ludox as the scattering medium. The observed decays were fitted using the exponential analysis program supplied with the instrument. The suitability of the fit was ascertained by a χ^2 value close to unity. The decays are multicomponent.

5.11. Diffuse reflectance laser flash photolysis

Samples of stilbene plus sensitizer were prepared using a similar procedure to that described earlier. Dry samples were loaded in 3 mm × 7 mm quartz cells, sealed with a septum and then purged with either oxygen or nitrogen for at least 20 min prior to laser irradiation. The laser flash photolysis system has been described previously [36]. For these experiments, a Lumonics HY750 Nd:YAG (355 nm; 10 ns/pulse; <30 mJ/pulse) was used for sample excitation. Zeolite samples were moved in the cell holder and shaken frequently in order to provide sample fresh surface and minimize complications due to product formation.

5.12. Computational details

The geometries of *cis*-1,2-diphenylcyclopropane, *cis*-stilbene and the sanwiched form with alkali metal cations ($M = Li^+, Na^+, K^+, Rb^+, Cs^+$) were optimized at both the second order Møller–Plesset (MP2) and hybrid HF-DFT (B3LYP) levels. The polarized 6-31G(d) basis set was used for C, H, Li and Na. For the heavier metal ions, the Hay–Wadt effective core potentials were used. The contraction scheme employed for the valence region was (5s5p)/[3s2p], augmented by a six-term d-polarization function. Thus, the valence basis is comparable to the 6-31G(d) basis used for the remaining atoms. The MP2 and B3LYP calculations were carried out using the Gaussian’94 suite of programs [37].

Acknowledgements

We thank S. Uppili for independently reconfirming observations made with electron transfer sensitizers and V.J. Rao for useful discussions. VR thanks the National Science Foundation (CHE-9904187 and CHE-0212042) for financial support.

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