Photoinduced Electron Transfer Reactions within Zeolites: Detection of Radical Cations and Dimerization of Arylalkenes[1]

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Abstract: Photosensitized electron transfer reactions between excited singlet acceptors and arylalkenes included within NaX zeolites have been studied using a combination of product studies, fluorescence spectroscopy, and diffuse reflectance laser flash photolysis. Steady-state and time-resolved fluorescence quenching of cyanoaromatic and ionic sensitizers by arylalkenes demonstrates that singlet quenching occurs predominantly by a static process. Diffuse reflectance flash photolysis studies indicate that quenching of singlet cyanoaromatic sensitizers by *trans*-anethole and 4-vinylanisole occurs via electron transfer and yields relatively long-lived radical cations. Signals due to trapped electrons (Na_4^{3+}) are also observed, suggesting that photoionization of the cyanoaromatic sensitizer occurs in competition with electron transfer quenching of the excited singlet by the alkene. The long lifetimes of the radical cations indicate the utility of the zeolite environment for controlling the energy-wasting back electron transfer step. Photosensitized electron transfer reactions of five alkenes (*trans*-anethole, 4-vinylanisole, phenyl vinyl ether, and two indenes), using both ionic and cyanoaromatic sensitizers, lead to predominantly dimeric cyclobutane products as in solution. However, the dimer ratios are substantially different with the cis/syn cyclobutanes formed preferentially in the zeolite reactions, presumably as a result of constraints imposed by the restricted space of the zeolite supercage. In fact the zeolite environment is more important in determining the geometry of the dimeric products than is the method (direct or sensitized photocycloaddition vs radical ion initiation) for their generation.

Zeolites have recently been shown to stabilize organic radical cations and carbocations and to promote separation of charged ion pairs.[2−20] For example, inclusion of a variety of aromatic compounds in zeolites leads to direct formation of stable radical cations and carbocations at Lewis and Brønsted acid sites.[7−11] Transient absorption studies indicate that photoionization of aromatic substrates also occurs readily in many zeolites by either one- or two-photon processes; again the observed radical cations are considerably longer-lived than in solution.[12−20] Excitation of charge transfer complexes between pyridinium acceptors and arene donors in zeolites generates radical ion pairs that are orders of magnitude longer-lived than in solution, demonstrating the substantial potential of the zeolite cage for controlling back electron transfer.[4] Related experiments indicate that efficient charge separation is also achieved upon photoinduced electron transfer between ruthenium donors and pyridinium acceptors in the presence of zeolites; in these experiments the pyridinium acceptor is included in the zeolite and the size of the donor restricts it to the solution phase.[3] These results suggest that the confined space of the zeolite interior should provide an ideal environment for carrying out photosensitized electron transfer

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(1) NRCC-40871.

(2) (a) Ledney, M.; Dutta, P. K. *J. Am. Chem. Soc.* **1995**, *117*, 7687. (b) Borja, M.; Dutta, P. K. *Nature*, **1993**, *362*, 43.

(3) (a) Yonemoto, E. H.; Kim, Y.; Schmehl, R. H.; Wallin, J. O.; Shoulders, B. A.; Richardson, B. T.; Haw, J. F.; Mallouk, T. E. *J. Am. Chem. Soc*. **1994**, *116*, 10557. (b) Brigham, E. S.; Snowden, P. T.; Kim, Y. S.; Mallouk, T. E. *J. Phys. Chem*. **1993**, *97*, 8650.

(4) (a) Yoon, K. B.; Park, Y. S.; Kochi, J. K. *J. Am. Chem. Soc*. **1996**, *118*, 12710. (b) Yoon, K. B.; Huh, T. J.; Kochi, J. K. *J. Phys. Chem*. **1995**, *99*, 7042. (c) Sankararaman, S.; Yoon, K. B.; Yabe, T.; Kochi, J. K. *J. Am. Chem. Soc*. **1991**, *113*, 1419. (d) Yoon, K. B.; Hubig, S. M.; Kochi, J. K. *J. Phys. Chem*. **1994**, *98*, 3865.

(5) (a) Werst, D. W.; Tartakovsky, E. E.; Piocos, E. A.; Trifunac, A. D. *J. Phys. Chem*. **1994**, *98*, 10249. (b) Werst, D. W.; Piocos, E. A.; Tartakovsky, E. E.; Trifunac, A. D. *Chem. Phys. Lett*. **1994**, *229*, 421. (c) Piocos, E. A.; Werst, D. W.; Trifunac, A. D.; Eriksson, L. A. *J. Phys. Chem*. **1996**, *100*, 8408. (d) Barnabas, M. V.; Trifunac, A. D. *Chem. Phys. Lett*. **1992**, *193*, 298.

(6) Roth, H. D.; Weng, H.; Zhou, D.; Lakkaraju, P. S. *Acta Chem. Scand.* **1997**, *51*, 626.

(7) Ramamurthy, V.; Caspar, J.; Corbin, D. *J. Am. Chem. Soc.* **1991**, *113*, 594.

(8) Caspar, J. V.; Ramamurthy, V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 600.

(9) Liu, X.; Iu, K.-K.; Thomas, J. K.; He, H.; Klinowski, J. *J. Am. Chem. Soc.* **1994**, *116*, 11811.

(10) (a) Garcia, H.; Garcia, S.; Perez-Prieto, J.; Scaiano, J. C. *J. Phys. Chem.* **1996**, *100*, 18158. (b) Fornes, V.; Garcia, H.; Jovanovic, S.; Marti, V. *Tetrahedron*, **1997**, *53*, 4715. (c) Cozens, F. L.; Garcia, H.; Scaiano, J. C. *Langmuir*, **1994**, *10*, 2246.

(11) Corma, A.; Fornes, V.; Garcia, H.; Marti, V.; Miranda, M. A. *Chem. Mater.* **1995**, *7*, 2136.

(12) Lednev, I. K.; Mathivanan, N.; Johnston, L. J. *J. Phys. Chem.* **1994**, *98*, 11.

(13) Hashimoto, S. *Chem. Phys. Lett.* **1996**, *252*, 236.

(14) Hashimoto, S.; Mutoh, T.; Fukumura, H.; Masuhara, H. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3653.

(15) Liu, X.; Iu, K.-K.; Thomas, J. K. *J. Phys. Chem.* **1994**, *98*, 13720.

(16) Liu, X.; Iu, K.-K.; Thomas, J. K. *J. Phys. Chem.* **1994**, *98*, 7877.

(17) Iu, K.; Thomas, J. *J. Phys. Chem.* **1991**, *95*, 506.

(18) Mao, Y.; Thomas, J. K. *J. Phys. Chem.* **1995**, *99*, 2048.

(19) Cozens, F. L.; Bogdanova, R.; Regimbald, M.; Garcia, H.; Marti, V.; Scaiano, J. C. *J. Phys. Chem. B* **1997**, *101*, 6921.

(20) Gessner, F.; Scaiano, J. C. *J. Photochem. Photobiol. A: Chem.* **1992**, *67*, 91.

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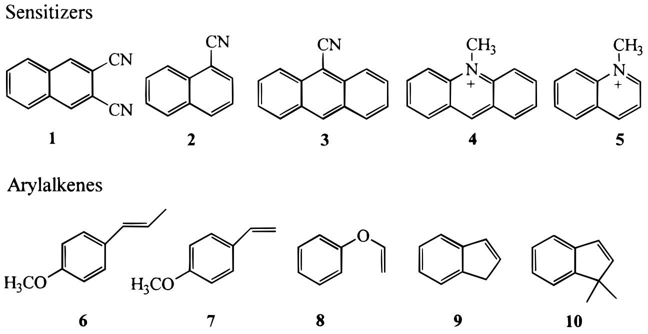
Chart 1



reactions, and in particular for overcoming the limitation of rapid back electron transfer that decreases the efficiency of singlet sensitized electron transfer reactions in solution. This aspect of zeolite chemistry has received little attention. There are recent examples of the photosensitized electron transfer isomerization and dimerization of aryl alkenes in zeolites.[21−24] In these examples the triphenylpyrylium sensitizer was synthesized within the cavities of acidic HY zeolite. The use of zeolites as catalysts for thermal electron transfer cycloaddition chemistry has also been investigated.[25]

Previous research from one of our laboratories has shown that double loading techniques can be used to place two dissimilar molecules near one another within a zeolite.[26] Results presented herein on the dimerization of arylalkenes unequivocally establish that this is a viable approach for conducting photoinduced electron transfer reactions within zeolites and clearly demonstrate that the use of “designer” zeolite hosts is not essential. The approach that we have taken also avoids the use of acidic zeolites which can complicate the chemistry via proton transfer pathways. Photosensitized electron transfer reactions between a series of sensitizers and arylalkenes included in zeolites have been studied by a combination of fluorescence spectroscopy, diffuse reflectance flash photolysis,[27,28] and product studies. The radical cation mediated dimerization of arylalkenes has been extensively investigated in solution and provides an excellent model for examining the effects of the zeolite on photosensitized electron transfer chemistry.[25,29−31] The sensitizers used include several cyanoaromatic and ionic sensitizers and are shown in Chart 1 along with the arylalkene donors. We have used only NaX zeolites to avoid complications from the thermal generation of carbocations at Brønsted acid sites.[32] This zeolite is a crystalline aluminosilicate with large 13 Å cages that are connected tetrahedrally to adjacent cages by 7.4 Å channels. Our results demonstrate the advantages of the zeolite medium for controlling both the efficiency of radical ion formation and modulating the product ratios.

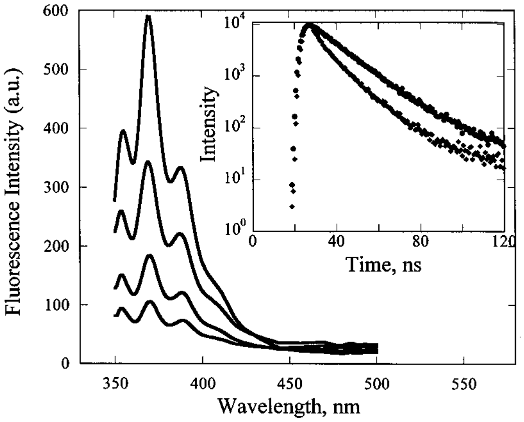


Figure 1. Steady-state fluorescence spectra for samples of 2,3-dicyanonaphthalene/NaX for four different loadings of *trans*-anethole. Loading levels (top to bottom) were 0, 34, 83, and 110 μmol/g *trans*-anethole. The inset shows fluorescence decay traces for the samples with 0 and 110 μmol/g *trans*-anethole.

Results and Discussion

Fluorescence Spectroscopy. Fluorescence spectra for the sensitizers on NaX zeolite were similar to those obtained in solution. For example, 2,3-dicyanonaphthalene (**1**) shows a structured emission with λ_{max} values of 353, 369, and 386 nm on NaX (Figure 1) as compared to 342, 359, and 376 nm in acetonitrile.[33] The spectrum is unchanged in the presence of arylalkenes, but the fluorescence intensity is substantially reduced, as shown in Figure 1 for three different loadings of *trans*-anethole (**6**). The total fluorescence intensity decreases with increased loading of **6** with approximately 75% quenching for the highest loading.

The fluorescence lifetimes for **1** in NaX (10 μmol/g) in the presence and absence of **6** were measured by single photon counting. The fluorescence data gave reasonably good fits to a single exponential with lifetimes of ∼14 ns for a nitrogen-purged sample of **1** alone and 5.1 ns for an aerated sample. The measured lifetime did not vary with sample loading (within the 3−30 μmol/g range), with excitation wavelength or with the solvent (diethyl ether or dichloromethane/hexane mixtures) used to prepare the sample. The fluorescence lifetimes in the presence of **6** were slightly shorter, with values of 12, 11.5, and 11 ns measured for 34, 83, and 110 μmol/g loadings. Note that a value of 11 ns indicates approximately 35% quenching of the excited singlet which is much less than the value of 75% quenching obtained from the steady-state fluorescence intensity measurements for the same sample. Representative decays for **1** alone and in the presence of 110 μmol **6** are shown in the inset of Figure 1.

Qualitatively similar results were obtained for the various other sensitizer/arylalkene combinations used in the present work. For example, NaX/1-cyanonaphthalene/phenyl vinyl ether, NaX/9,10-dicyanoanthracene/4-vinylanisole, and NaX/*N*-methylacridinium/4-vinylanisole combinations all gave results

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(21) Corma, A.; Fornes, V.; Garcia, H.; Miranda, M. A.; Primo, J.; Sabater, M.-J. *J. Am. Chem. Soc.* **1994**, *116*, 2276.

(22) Corma, A.; Fornes, V.; Garcia, H.; Miranda, M. A.; Sabater, M. J. *J. Am. Chem. Soc.* **1994**, *116*, 9767.

(23) Fornes, V.; Garcia, H.; Miranda, M. A.; Mojarrad, F.; Sabater, M.-J.; Suliman, N. N. E. *Tetrahedron* **1996**, *52*, 7755.

(24) Cano, M. L.; Corma, A.; Fornes, V.; Garcia, H.; Miranda, M. A.; Baerlocher, C.; Lengauer, C. *J. Am. Chem. Soc.* **1996**, *118*, 11006.

(25) Bauld, N. L. *Adv. Electron Transfer Chem.* **1992**, *2*, 1.

(26) (a) Pitchumani, K.; Gamlin, J. N.; Ramamurthy, V.; Scheffer, J. R. *Chem. Commun.* **1996**, 2049. (b) Leibovitch, M.; Olvsson, G.; Sundarababu, G.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1996**, *118*, 1219.

(27) Wilkinson, F.; Kelly, G. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press Inc.: Boca Raton, 1989; Vol. I, Chapter 12.

(28) Wilkinson, F.; Willsher, C. J. *Tetrahedron* **1987**, *43*, 1197.

(29) Johnston, L. J.; Schepp, N. P. *Adv. Electron Trans. Chem.* **1996**, *5*, 41.

(30) Mattes, S. L.; Farid, S. *Org. Photochem.* **1983**, *6*, 233.

(31) Lewis, F. D. In *Photoinduced Electron Transfer;* Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, Chapter 4.1.

(32) We and others have found that even NaY and NaX zeolites are slightly acidic. Of the two NaX was found to be less acidic. Therefore, most of the studies are carried out in NaX. (a) Jayathirtha Rao, V.; Perlstein, D. L.; Robbins, R. J.; Lakshminarasimhan, P. H.; Grey, C. P.; Ramamurthy, V. *Chem. Commun.* **1998**, 269. (b) Scaiano, J. C.; Kaila, M.; Corrent, S. *J. Phys. Chem.* **1997**, *101*, 8564.

(33) Brancaleon, L.; Brousmiche, D.; Johnston, L. J. *J. Photochem.* **1998**, submitted for publication.

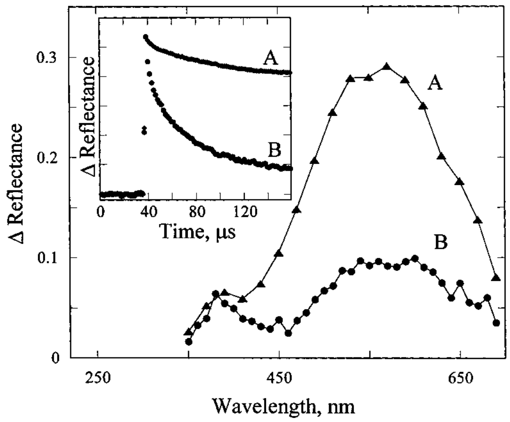

Figure 2. Transient spectra measured after 266-nm excitation of samples of 2,3-dicyanonaphthalene (10 μmol/g) in NaX prepared using hexane (A) or 15% dichloromethane/hexane (B) as solvent. The inset shows normalized decay traces measured at 560 nm under conditions A and B.

that were similar to those described above. The sensitizer fluorescence emission was quenched much more than the excited singlet lifetime. In these experiments the sensitizer loading level was maintained at 50 μmol/g (one molecule per eight supercages) and the loading level of the alkene quencher was varied between 0.25 and 2 molecules per supercage. At the highest loading level examined the emission was quenched by 80%, whereas the lifetime was reduced by ~20%. The combined results of the steady-state and time-resolved fluorescence measurements for a number of sensitizer/alkene combinations indicate that the singlet quenching process has a substantial static component, since the decrease in intensity for a given donor loading is much larger than would be expected on the basis of the change in the fluorescence lifetime.

Diffuse Reflectance Laser Flash Photolysis: Sensitizers and Arylalkenes Alone. Control experiments in which samples of either sensitizer or arylalkene alone were excited at 266 or 355 nm were carried out prior to studying mixed samples. Unless otherwise noted the concentration of sensitizer used was approximately 10 μmol/g, which corresponds to a loading of 1 molecule per 40 supercages. Excitation of nitrogen-purged samples of **1** on NaX prepared using diethyl ether or hexane gave strong signals with λ_{max} at ~560 nm (Figure 2A), which were efficiently removed by purging the sample with oxygen. These results are consistent with photoionization of the substrate to give electrons that are trapped by Na^+ to give Na_4^{3+} (eq 1),

$$\mathbf{1} \xrightarrow{h\nu} \mathbf{1}^{\bullet+} + e^- \xrightarrow{4Na^+} Na_4^{3+} \qquad (1)$$

as observed upon excitation of a wide variety of aromatics.[12−17,19,20] Although the facile photoionization of a dicyanoaromatic is somewhat surprising, these results are in agreement with our recent observations of photoionization of **1** in acetonitrile at high laser energies.[33] Samples of **1** on NaX prepared using dichloromethane/hexane solvent mixtures showed quite different results: the yield of trapped electron was substantially lower and there was an additional weak signal at 380 nm (Figure 2B). Similar results could be obtained by taking a sample prepared with hexane and then purging it with nitrogen that had been bubbled through dichloromethane. The 380-nm signal is assigned to the 2,3-dicyanonaphthalene radical cation, by analogy with our recent observation of this species in acetonitrile (λ_{max} 380 nm)[33] and in agreement with matrix spectra for cyanonaphthalene radical cations.[34] The signal is relatively weak and cannot be detected in the presence of the large trapped electron signals, as in Figure 2A. Normalized traces showing the decay of the trapped electron signal at 560 nm under the conditions used to obtain the spectra shown in Figure 2, parts A and B, are shown in the inset of Figure 2. In addition to the large decrease in signal intensity in the presence of dichloromethane, there is also much more rapid decay of the trapped electron under these conditions.

The above results are consistent with trapping of both the initial photoejected electron and Na_4^{3+} by residual dichloromethane that is not removed from the zeolite using our sample preparation technique. This is in good agreement with the use of chlorinated solvents as electron scavengers in both laser photoionization and pulse radiolysis studies in solution.[35,36] The use of dichloromethane is advantageous for removing trapped electron signals which can easily obscure weaker signals. Although the trapped electron also reacts with oxygen, this is less desirable for studies involving bimolecular electron transfer quenching of relatively long-lived singlet excited states. In some cases the relatively small, trapped electron signals observed for samples containing residual dichloromethane can be further reduced by oxygen purging. This suggests that some of the electrons may be trapped in sites that are accessible to oxygen but not to dichloromethane. The yield of the trapped electron also varied with the water content of the zeolite, consistent with recent pulse radiolysis studies that demonstrate that electrons are trapped by water to give short-lived hydrated electrons in fully hydrated NaX and NaY zeolites.[37,38]

Direct 355-nm excitation of both 1-cyanonaphthalene (**2**) and 9-cyanoanthracene (**3**) on NaX also provided evidence for photoionization to give trapped electrons (560 nm), as well as weaker signals in the 450-nm region. For **3**, a fraction of the 450-nm signal was removed by purging the sample with oxygen, while the remainder was unaffected by oxygen. This suggests that both triplet and radical cation contribute to the 450-nm signal, consistent with reported spectra for 9-cyanoanthracene triplet and radical cation in solution and in a matrix, respectively.[39,40] For **2**, the 450-nm signal was unaffected by oxygen and is assigned to radical cation. These results demonstrate that photoionization is a general phenomenon for cyanoaromatics in NaX zeolite.

Direct excitation of several substituted styrenes, including **6** and **7**, in NaY zeolite has recently been shown to generate the respective arylalkene radical cations.[19] We also observe radical cation formation upon 266-nm excitation of **6** and **7** in NaX (10 μmol/g), as shown in the inset of Figure 3 for an oxygen-saturated sample of **6** prepared using dichloromethane/hexane as solvent. Although the trapped electron is not observed under these conditions, even for nitrogen saturated samples, it is formed when diethyl ether is used as the solvent for sample preparation. These results are consistent with the literature results for **6**/NaY samples prepared using dichloromethane for which only very weak and short-lived trapped electron signals were detected.[19] As expected, 355-nm excitation (the wavelength used for excitation of the sensitizer/arylalkene samples

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(34) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.

(35) Brede, O.; David, F.; Steenken, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 23.

(36) Workentin, M. S.; Johnston, L. J.; Wayner, D. D. M.; Parker, V. D. *J. Am. Chem. Soc.* **1994**, *116*, 8279.

(37) Liu, X.; Zhang, G.; Thomas, J. K. *J. Phys. Chem.* **1995**, *99*, 10024.

(38) Takatani, S.; Fukumura, H.; Masuhara, H.; Hashimoto, S. *J. Phys. Chem. B* **1997**, *101*, 3365.

(39) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180.

(40) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

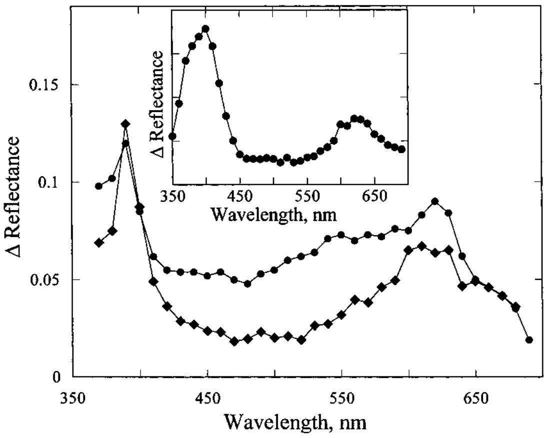

Figure 3. Transient spectra measured after 355-nm excitation of 2,3-dicyanonaphthalene (10 μmol/g) plus *trans*-anethole (52 μmol/g) in NaX under nitrogen (●) and oxygen (◆). The inset show the spectrum obtained by direct 266-nm excitation of an oxygen-saturated sample of 10 μmol *trans*-anethole in NaX.

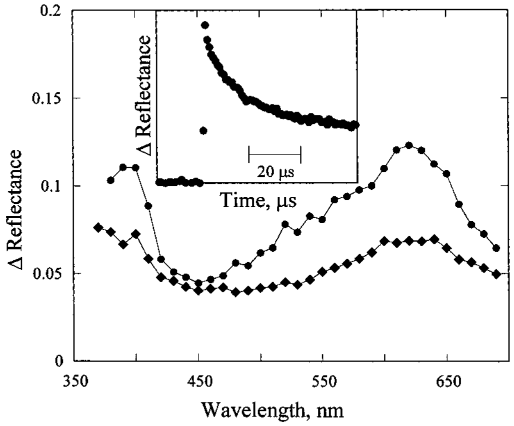

Figure 4. Transient spectra measured 0.6 μs after 355-nm excitation of nitrogen-purged samples of 2,3-dicyanonaphthalene (10 μmol/g) plus *trans*-anethole (◆, 32 μmol/g; ●, 190 μmol/g) in NaX. The inset shows the decay of the signal at 610 nm for the sample with the higher *trans*-anethole loading.

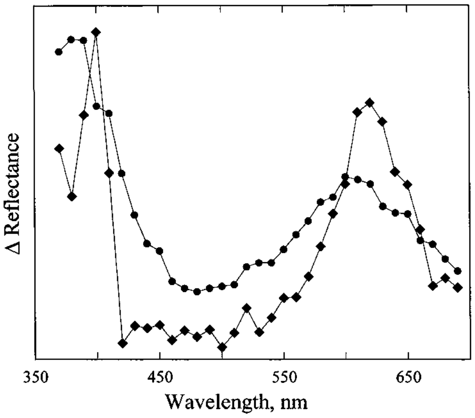

Figure 5. Transient spectra measured after 355-nm excitation of samples of 1-cyanonaphthalene (9 μmol/g) plus *trans*-anethole (56 μmol/g) on NaX (■) and 4-vinylanisole (73 μmol/g) on NaX (●). The maximum Δ reflectance values are 0.06 and 0.15 for *trans*-anethole and 4-vinylanisole, respectively.

as discussed below) of samples of either **6** or **7** in NaX did not yield any significant transients.

Sensitizers plus Arylalkenes. Transient spectra measured after 355-nm excitation of a nitrogen-purged sample of **1** and **6** in NaX (10 and 52 μmol/g, respectively) prepared using dichloromethane/hexane show absorption maxima at 620 and 390 nm, with a broad weaker absorption between 500 and 600 nm, as shown in Figure 3. The latter is removed by purging the sample with oxygen, consistent with its assignment to trapped electrons, Na_4^{3+}. Under oxygen the remaining transient has maxima at 390 and 620 nm (Figure 3), in good agreement with the solution spectrum for the *trans*-anethole radical cation[35,41] and with spectra obtained by photoionization on zeolites (ref 19 and Figure 3, inset). Note that the relative intensities of the 390- and 620-nm peaks are different in the photosensitization and photoionization experiments. This is the result of contributions from residual trapped electron at 620 nm and bleaching of the sensitizer and/or fluorescence correction at 390 nm for the photosensitization experiment. The photoionization spectrum is in good agreement with those observed in solution.[29,35] As noted above, neither trapped electron nor radical cation signals are observed upon 355-nm excitation of **6** alone on NaX. This demonstrates that the excited sensitizer decays by two pathways, namely electron transfer from arylalkene to generate a radical ion pair (eq 2) and photoionization to give trapped electron, as observed upon excitation of the sensitizer alone (eq 1). Although the radical anion of **1** has

$$\mathbf{1} + \mathbf{6} \xrightarrow{h\nu} \mathbf{1}^{\bullet-} + \mathbf{6}^{\bullet+} \qquad (2)$$

been characterized in solution, it has weak absorptions that overlap those of the trapped electron and the *trans*-anethole radical cation, and is not observable in oxygen-saturated samples.[33] Use of samples prepared from diethyl ether gave much larger trapped electron signals, in agreement with results noted above for excitation of **1** alone.

The yield of radical cation increases with increased loading of **6**, as shown in Figure 4 for samples containing 35 and 190 μmol/g arylalkene. Note that the higher loading corresponds to approximately one alkene per two supercages. These results are completely consistent with the fact that the steady state fluorescence data indicate that these loadings correspond to ~35 and >80% quenching of the singlet sensitizer. The *trans*-anethole radical cation is relatively long-lived in the zeolite with complex decay kinetics and half-lives in excess of 10 μs, as shown in Figure 4, inset. The kinetics do not change appreciably with loading, at least over the range that we have examined. Note that the decay traces are usually measured for nitrogen-purged samples, for which there is some residual trapped electron signal that overlaps the radical cation absorption and influences the kinetics. The relatively long lifetimes and strong radical cation signals indicate that back electron transfer is several orders of magnitude slower in the zeolite than for the same singlet ion pairs in solution, where $k_{-\mathrm{et}}$ values of 10^9 s^{-1} and low cage escape yields are typical.[42] These results are in good agreement with other examples, illustrating the ability of zeolites to stabilize radical ion pairs and overcome the limitation of back electron transfer.[4,5,21,22]

The generality of the above results was evaluated by generating $\mathbf{6}^{\bullet+}$ by photoinduced electron transfer using sensitizers **2** and **3** (Figure 5). The results were qualitatively similar to those discussed above for **1**, in that the long wavelength band of the radical cation was clearly visible. For **2**, the 390-nm band was also detected, although the ratio of the 620/390 nm signals was different from that shown in Figure 1. This we

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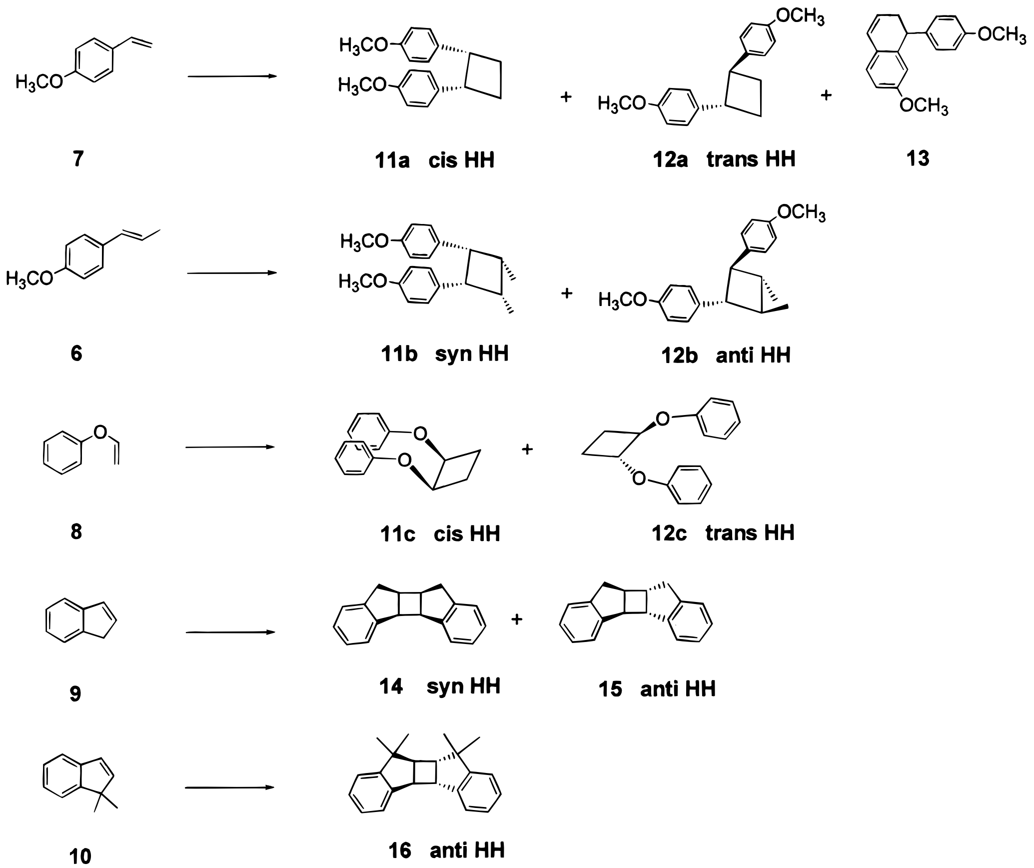
(41) Johnston, L. J.; Schepp, N. P. *J. Am. Chem. Soc.* **1993**, *115*, 6564.

(42) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794.

Scheme 1



attribute to contributions from either trapped electrons or radical anion at longer wavelengths and differences in the sensitizer bleaching at short wavelength. For **3**, the UV band of the radical cation is not observed due to bleaching of the sensitizer, which starts to interfere at ~450 nm. In addition to the 620-nm band of the radical cation there is a second transient between 440 and 500 nm that reacts with oxygen. This is consistent with formation of 9-cyanoanthracene radical anion, although we cannot exclude some contribution from triplet.

4-Vinylanisole radical cation was also formed by excitation of either **1** or **2** in NaX in the presence of **7** (Figure 5). In this case the radical cation has $\lambda_{\max}$ at ~370 and 610 nm, in good agreement with both solution spectra[41] and the spectrum for the same radical cation generated by photoionization in NaY.[19] The radical cation decays somewhat more rapidly than that from **6**, although the kinetics are still nonexponential, as discussed below. The spectrum in Figure 5 also shows a small shoulder at 410 nm that may be due to the sensitizer radical cation. Transient spectra on zeolites were not examined for the other three alkenes, **8**−**10**. Solution spectra indicate that both the phenyl vinyl ether and indene radical cations have relatively weak absorptions between 400 and 700 nm and are unlikely to be good candidates for transient work on zeolites.[43] Measurements at shorter wavelength are complicated by sensitizer bleaching as noted above.

Product Studies. Having established the formation of alkene radical cations within a zeolite, we proceeded to examine the products of radical cation initiated dimerization of **6** and **7** as well as phenyl vinyl ether (**8**), indene (**9**), and dimethylindene (**10**) (Scheme 1). The aims of this study were to show that the radical cations generated by photosensitization are reactive within the constrained environment of a zeolite and to examine the influence of the zeolite cavity on the geometry of the dimers. The photocycloaddition and photoinduced electron transfer chemistry of all the alkenes has been investigated in solution, and the literature results provide useful background information to aid in understanding their behavior within the constrained spaces of a zeolite.[44−47] All five alkenes were found to undergo thermal dark reactions within NaY as well as within triphenylpyrylium entrapped HY zeolite. Therefore, our studies were conducted within NaX zeolites. Both ionic and neutral sensitizers were used. *N*-Methylacridinium and *N*-methylquinolinium salts[48] were introduced into NaX zeolite by ion exchange, while the neutral sensitizers were added to NaX by physisorption from solution. The sensitizer loading in all our experiments was approximately one sensitizer molecule per eight supercages (50 μmol/g). Independent of the sensitizer, the alkenes showed similar behavior, suggesting that a single mechanistic pathway is involved in all cases.

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[43] Lew, C. S. Q.; Brancaleon, L.; Johnston, L. J. Unpublished results.

[44] Lewis, F. D.; Kojima, M. *J. Am. Chem. Soc.* **1988**, *110*, 8664.

[45] Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1994**, *116*, 6895.

[46] (a) Draper, A. M.; Ilyas, M.; de Mayo, P.; Ramamurthy, V. *J. Am. Chem. Soc.* **1984**, *106*, 6222. (b) Tojo, S.; Toki, S.; Takamuku, S. *J. Org. Chem.* **1991**, *56*, 6240. (c) Mattes, S. L.; Luss, H. R.; Farid, S. *J. Phys. Chem.* **1983**, *87*, 4779. (d) Kuwata, S.; Shimemitsu, Y.; Odaira, Y. *J. Org. Chem.* **1973**, *38*, 3803. (e) Evans, T. R.; Wake, R. W.; Jaenicke, O. In *Exciplex*; Gordon, M.; Ware, W. R., Eds.; Academic Press: New York, 1975; p 345. (f) Farid, S.; Hartman, S. E.; Evans, T. R. In *Exciplex*; Gordon, M.; Ware, W. R., Eds.; Academic Press: New York, 1975; p 327. (g) Mattay, J.; Vondenhof, M.; Denig, R. *Chem. Ber.* **1989**, *122*, 951.

[47] (a) Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499. (b) Yasuda, M.; Pac, C.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 502. (c) Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* **1973**, 677. (d) Metzner, W.; Wendisch, D. *Liebigs Ann. Chem.* **1969**, *730*, 111. (e) Bowyer, J.; Porter, Q. N. *Aust. J. Chem.* **1966**, *19*, 1455.

[48] (a) Krohnke, F.; Honig, H. L. *Chem. Ber.* **1957**, *90*, 2215. (b) Yoon, U. C.; Quillen, S. L.; Mariano, P. S.; Swanson, R.; Stavinoha, J. L.; Bay, E. *J. Am. Chem. Soc.* **1983**, *105*, 1204.

Table 1. Product Distribution upon Photoinduced Electron Transfer Sensitized Dimerization of Alkenes Included within NaX Zeolites[a−d]

trans-anethole (**6**)	HH-syn[e] **11b**	HH-anti[e] **12b**
acetonitrile, PET sensitizer[f,g]	4	96
NaX, 1-cyanonaphthalene[g]	66	33
NaX, 9-cyanoanthracene[g]	45	55
NaX, *N*-methylquinolinium	55	45

phenyl vinyl ether (**8**)	HH-cis **11c**	HH-trans **12c**
acetonitrile, PET sensitizer[f]	55	45
NaX, 9-cyanoanthracene	65	35
NaX, 1-cyanonaphthalene	55	45
NaX, *N*-methylquinolinium	63	37
NaX, *N*-methylacridinium	70	30

1,1-dimethylindene (**10**)	anti HH **16**
acetonitrile, PET sensitizer[f]	>95 (only)
NaX, 1-cyanonaphthalene	>95 (only)
NaX, *N*-methylacridinium	>95 (only)
Na X[h]	>95 (only)

[a] See Scheme 1 for structure of products. All yields are based on GC and do not include the unreacted alkene. [b] Loading level: sensitizer, 1 molecule per 8 supercages; alkene, 0.5−2 molecules per supercage. The ratio of the dimers did not vary with the loading level of the alkene. [c] All zeolite irradiations (450-W medium-pressure mercury lamp with Pyrex filter) were conducted as a hexane slurry (5 mL) under nitrogen atmosphere and conversions were kept below 30%. Reported yields are based on GC analyses. [d] The dimers were not interconverted in the conversion range reported here. When independently tested, only the *cis*-dimer of phenyl vinyl ether rearranged to the trans isomer within NaX. [e] HH, head−head HT, head−tail. [f] PET sensitizers include 9-cyanoanthracene, 1-cyanonaphthalene, and *N*-methylacridinium iodide. All three sensitizers gave essentially the same product distribution. [g] Isomerization of the alkene occurred and the reaction was complicated by oxidation. [h] Direct excitation (>300 nm) in the absence of sensitizers.

Table 2. Photodimerization of Indene: Influence of Zeolite on Product Distribution[a]

	dimer		dimer	
conditions	syn HH (**14**)	anti HH (**15**)	syn HT	anti HT
NaX, oven, 500 °C (thermal)[b]				
NaX[c]	35	59	6	
NaX, 1-cyanonaphthalene[d]	45	50	5	
NaX, 9-cyanoanthracene[d]	51	45	3	
NaX, *N*-methylacridinium[d]	35	60	5	
NaX, *N*-methylquinolinium[d]	38	58	4	
NaX, 4-methoxyacetophenone[e]	68	27	4	
NaX, 4-aminoacetophenone[e]	70	26	3	
1-cyanonaphthalene, CH_3CN[f]	1	96		2
N-methylacridinium iodide, CH_3CN[f]		96		4
4-aminoacetophenone, CH_3CN[g]	2	85	5	8
4-methoxyacetophenone, CH_3CN[g]	3	84	5	8
CH_3CN[h]	74	12	5	6

[a] Conditions as noted in Table 1. [b] Test for dark reaction, absent. [c] Direct excitation in NaX. [d] PET sensitized reaction, hexane slurry. [e] Triplet sensitized reaction in hexane slurry. [f] PET sensitized reaction in solution in the absence of zeolite. [g] Triplet sensitized reaction in the absence of zeolite, for comparison. [h] Direct excitation in the absence of zeolite, for comparison.

Table 3. Photodimerization of 4-Vinylanisole: Influence of Zeolite on Product Distribution[a,b]

conditions	**11a** (cis HH)	**12a** (trans HH)	**13**
NaX, oven, 500 °C (thermal)[c]			
NaX[d]			
NaX, 9,10-dicyanoanthracene	78	14	7
NaX, 9-cyanoanthracene	66	26	7
NaX, 1-cyanonaphthalene	57	28	14
NaX, *N*-methylquinolinium	58	30	12
NaX, *N*-methylacridinium	58	23	19
acetonitrile, PET sensitizer[e]	4	90	6

[a] Conditions as noted in Table 1; see Scheme 1 for structures of products. [b] The dimer distribution is based on GC analysis of the dimers alone. The oxidation products anisaldehyde and 4-methoxyphenylacetaldehyde always accompanied the dimers and their yields are not included in the calculation. [c] Control dark reaction; alkene is stable within NaX. [d] Stability of alkene upon direct excitation; alkene is stable within NaX upon irradiation above 350 nm. [e] PET sensitizers include 9-cyanoanthracene, 1-cyanonaphthalene, and *N*-methylacridinium iodide.

Product studies were conducted by irradiating a nitrogen-saturated hexane slurry of NaX containing alkene and sensitizer. In all five cases, loading levels were such that all alkene molecules remained within the zeolite (see Table 1). In addition, the conversions were kept low (<25%) to minimize complications due to over-irradiation. The dimer product distributions obtained by photosensitized electron transfer for the five alkenes in both zeolites and acetonitrile solution are summarized in Tables 1−3. The tables also include the results of direct excitation and triplet sensitization. Of the alkenes investigated, the two indenes (**9** and **10**) yielded only dimeric products, with no side products detected by GC. With both **6** and **7**, oxidation of the alkene was also observed and could not be eliminated even under nitrogen-saturated conditions. This may be due to the fact that adsorbed oxygen cannot be completely removed by bubbling nitrogen through the samples. Photooxidation of a number of alkenes and alkanes within zeolites has recently been observed.[49,50]

Since one of the main aims of the study is to establish the feasibility of PET sensitization within zeolites, it is important to minimize any contributions from direct excitation of the alkene. Appropriate filters were used to reduce the amount of light absorbed by the alkenes. More importantly, **8** is known to dimerize only under electron transfer conditions; direct excitation is reported to yield only polymer.[46d] Furthermore, for **7** only oxidation products could be observed upon direct irradiation in NaX, thus confirming that the dimeric products in the sensitized experiments arise via an electron transfer route. While contributions due to dimerization from the excited singlet state of the alkene could not be completely ruled out at the wavelengths used for the 1-cyanonaphthalene and *N*-methylquinolinium salt sensitized reactions (>320 nm), with all other sensitizers the dimerization observed within NaX must result from photosensitization. Since all the sensitizers used in this study have triplet energies well below those of the alkenes,[51] we conclude that electron transfer is the primary step in the dimerization process.

As described above, direct evidence for radical cation formation has been obtained for **6** and **7** upon irradiation of three cyanoaromatic sensitizers within NaX. Although the conditions under which the laser experiments (solid samples) and product studies (slurry irradiations) are conducted are different, we believe that the conclusions drawn from the LFP experiments can be extended to the product studies. This is supported by the fact that several irradiations were carried out with solid samples and gave dimers in a ratio similar to that obtained in a slurry. The time required for achieving the same conversion for solid irradiations was much longer than that for

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(49) Frei, H.; Blatter, F.; Sun, H. *Chemtech* **1996**, *26*, 24.

(50) (a) Blatter, F.; Moreau, F.; Frei, H. *J. Phys. Chem.* **1994**, *98*, 13403. (b) Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1994**, *116*, 1812. (c) Sun, H.; Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1996**, *118*, 6873.

(51) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993.

the slurry irradiations and therefore the former were not pursued any further. The lifetimes of the radical cations observed in the transient experiments are consistent with the occurrence of a bimolecular process such as dimerization; the radical cations are sufficiently long-lived to be trapped by a neutral alkene in an adjacent cage to yield an adduct radical cation. The qualitative observation that 4-vinylanisole dimerizes more efficiently than *trans*-anethole is consistent with the shorter lifetime observed for the former during LFP conditions. This is also consistent with the known behavior in solution, where the rate constant for addition of the alkene radical cation to its precursor is ∼3 orders of magnitude lower for *trans*-anethole than for 4-vinylanisole.[44,45] It should be noted that the radical cations detected in the transient experiment may represent only a fraction of the reactive radical cations that lead to dimeric products. However, the relatively strong signals observed suggest that we are not detecting a minor fraction of the electron transfer events. The decay kinetics for the *trans*-anethole radical cation are independent of the loading level, at least over the range that we have examined, which indicates that reactions other than dimerization may contribute to the decay of this radical cation. The observation of dihydronaphthalene **13** (Scheme 1) as a product of 4-vinylanisole dimerization indicates that the adduct radical cation lives long enough to undergo rearrangement in competition with reduction to cyclobutane. It is clear that, at least in the case of 4-vinylanisole, back electron transfer from the sensitizer radical anion to either the monomer or adduct radical cations is considerably slower than in solution.

Finally it is of interest to examine the effect that the confined space of the zeolite has on the dimer geometry. Examination of Tables 1−3 reveals that for the same sensitizer, the ratios of dimers obtained within a supercage and in solution are different. Control experiments carried out with **8** and **9** established that the dimer ratio was independent of both the conversion (20−75%) and the loading level (0.25−2 molecules/supercage). Since in solution the cis HH dimer of **8** has been established to be less stable than the trans under PET conditions,[46c] both cis HH and trans HH dimers were synthesized, included within **3**−NaX and irradiated for the same length of time used for the alkene irradiations. To our surprise both dimers were stable. Similarly, irradiation (4 h) of syn HH indene dimer included within **2**−NaX gave only a small amount (∼4%) of indene. Although we did not independently examine the stability of the dimers from the other three alkenes, the dimer ratio was independent of the conversion (20−70%), indicating that decomposition of the dimer is not contributing to our observed dimer ratio. These observations support our conclusion that the observed dimer distribution during PET sensitization (tables) is a true reflection of the influence of the zeolite interior on the dimerization process.

The results presented in Tables 1−3 demonstrate that both cis/syn and trans/anti dimers are formed within the zeolite. We draw attention to the fact that the zeolite supercage favors a product (cis/syn isomer) that has a spherical shape more similar to the geometry of the supercage than the linear (elliptical) trans/anti isomer.[52] The adduct radical cations (either the long bond cyclobutane or 1,4-acyclic radical cations) would be expected to have closely similar size and shape to the product cyclobutanes. We propose that the elliptically or linearly shaped trans/anti isomer and its precursor radical cation are probably more readily accommodated in two cages, whereas the cis/syn isomer and its precursor can fit within a single supercage. On the assumption that the dimerization is likely to occur more readily within a single cage than between two cages, one would predict that the cis/syn isomer would be favored within zeolites. This prediction is consistent with the results for four different alkenes. However, 1,1-dimethylindene gives only the anti HH dimer; the behavior is unaltered from that in solution. In this case, formation of the syn isomer is sterically unfavorable both in solution and within zeolites. The influence of the zeolite supercage on the cyclization of the radical cations is similar to what we have observed earlier during the cylization of 1,4-diradicals generated during Norrish Yang Type II reactions.[53]

Examination of the photodimerization of indene under direct excitation, triplet sensitization, and electron transfer conditions provides additional support for the suggestion that the zeolite interior controls the nature of the dimer that is formed within a zeolite supercage. Indene has been investigated under all three conditions listed above in isotropic solution.[47] From the excited singlet state indene yields the syn HH dimer (**14**) and from the excited triplet state the anti HH dimer (**15**) is obtained as the major product. However, within NaX zeolite, both syn and anti HH dimers are formed (Table 2), independent of the method employed to initiate the reaction. This suggests that the nature of the reaction (direct or sensitized photocycloaddition vs radical ion mediated) does not control the dimer that is formed within a zeolite. Rather, the zeolite interior actively participates in controlling the geometry of the dimeric products.

Conclusions

The first examples of photosensitized electron transfer initiated dimerization of arylalkenes for independently loaded sensitizers and alkenes within nonacidic zeolites have been presented. The fluorescence data demonstrate that the excited singlet sensitizer is quenched by alkene via both static and dynamic processes with the former predominating. The flash photolysis data for several of the alkenes indicate that excited-state quenching leads to long-lived radical cations and illustrates the potential of the zeolite environment for controlling the rapid back electron transfer that limits the efficiency of singlet sensitized electron transfer chemistry in solution. Some photoionization of the cyanoaromatic sensitizers is also observed in the laser experiments, although this is unlikely to be important under steady-state irradiation conditions. Dimeric products are isolated from all the sensitizer/alkene irradiations in NaX, indicating that chemically reactive radical cations are produced in the photosensitized irradiations. Comparison of dimer ratios obtained in solution and in NaX illustrate the influence of the zeolite interior on the geometry of the final dimers.

Experimental Section

Materials. Zeolite NaX was obtained from Aldrich or BDH and was used as received. 1-Cyanonaphthalene, 2,3-dicyanonaphthalene, and 9-cyanoanthracene were obtained either from Aldrich or Kodak and recrystallized twice before use. *N*-Methylacridinium iodide and *N*-methylquinolium iodide were synthesized and purified according to a literature procedure.[48] 4-Vinylanisole, indene, and *trans*-anethole were obtained from Aldrich and were distilled once or passed through a short alumina column prior to use. Phenyl vinyl ether and dimethylindene were prepared following reported procedures.[48]

Sample Preparation. Sensitizers were incorporated into NaX by two procedures. The ionic sensitizers (**4** and **5**) were introduced by a cation exchange process. The cyanoaromatics (**1**−**3**) were introduced by inclusion from a hexane solution. For both procedures activated

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(52) Similar shape-selective arguments have been made previously: (a) Ramamurthy, V.; Sanderson, D. R. *Tetrahedron Lett.* **1992**, *33*, 2757. (b) Sundarababu, G.; Leobovitch, M.; Corbin, D. R.; Scheffer, J. R.; Ramamurthy, V. *Chem. Commun*. **1996**, 2159.

(53) Ramamurthy, V.; Corbin, D. R.; Johnston, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 3870.

zeolite was used. Zeolite NaX was activated by placing a known amount in a porcelain crucible in a preheated oven (~500 °C) for 10 h. The zeolite was cooled to room temperature and quickly transferred to a dry solvent in which further work up was carried out.

(a) Incorporation of *N*-Methylacridinium Iodide and *N*-Methylquinolium Iodide into NaX. To a 20-mL solution of dry acetonitrile containing 40 mg of the sensitizer was added 3 g of activated NaX, and the mixture was stirred for 24 h. The slurry was centrifuged, and the supernatant solution was discarded. To the solid was added 30 mL of dry acetonitrile, and the resulting mixture was stirred for a few hours and centriguged. The sequence was repeated five times, and the final solid was dried in an oven at ~100 °C. The NaX containing the sensitizer was characterized by diffuse reflectance and emission spectra. On the basis of the amount of the sensitizer that has remained within NaX (50 μmol/g), we estimate that there is one sensitizer molecule per eight cages.

(b) Incorporation of 1−3 within NaX. Known amounts of the aromatic sensitizer and activated NaX were stirred together in hexane for about 10 h. Since the sensitizers were not completely soluble a small amount of dichloromethane was added. In a typical procedure for samples prepared for product studies, 300 mg of activated NaX and 3 mg of the sensitizer were stirred in 15 mL of hexane and 3 mL of dichloromethane for 10 h. The slurry was filtered, washed with hexane, and dried on a vacuum line. The sample thus prepared contains approximately one molecule of the sensitizer in eight supercages. For fluorescence or flash photolysis experiments, a similar procedure was used; unless otherwise noted the solvent was 15% dichloromethane in hexane. The amount of sensitizer remaining in the solvent wash was quantified by UV−visible spectroscopy to obtain the loading level. Loading levels of approximately 10 μmol/g (one molecule per 40 cages) were used.

(c) Incorporation of Alkene into Sensitizer−NaX. To a slurry of hexane (10 mL) containing 300 mg of vacuum line dried sensitizer−NaX was added a known amount of alkene, and the mixture was stirred for 6 h. The slurry was filtered and washed with hexane. The hexane wash was collected and tested for remaining alkene. On the basis of a number of trials it was clear that 300 mg of sensitizer−NaX will take about 25 mg of the alkenes investigated herein. This corresponds to about 1.5 molecule per supercage. Various loading levels were used for both product studies and spectroscopic experiments, as noted in the text, tables, and figures. The zeolite thus prepared was dried on a vacuum line and used for further studies. Samples for fluorescence and flash photolysis work were prepared using a similar procedure but with the same solvent used to incorporate the sensitizer (i.e., 15% dichloromethane/hexane in most cases).

Irradiation and Product Analysis. Irradiations for product studies were conducted in a hexane slurry. Although irradiation of solid samples gave similar product distributions, conversions were low and prolonged irradiation times (10 h) were required to obtain yields that could be analyzed by GC. The zeolite prepared and dried as above was placed in dry hexane (5 mL) and irradiated with a 450-W medium-pressure mercury lamp under a nitrogen atmosphere. A Corning glass filter (CS-0.52) was used to cut off light below 340 nm. This ensured that the observed reaction is due to the sensitization process. Typical irradiation times varied between 3 and 6 h. Following irradiation the hexane was analyzed for the presence of reactants and products. In no case did we find either the reactant alkene or the product dimer in the hexane layer. The zeolite was extracted with either diethyl ether, dichloromethane, or tetrahydrofuran. This was achieved by stirring the zeolite with about 20 mL of the solvent for about 20 h. The solvent extract was analyzed by GC. The retention times for the dimers were known on the basis of analysis of authentic samples. The reported product distribution is based on the amount of the alkene reacted (~25%). The isolated yield of unreacted alkene and the product dimers was ~85%. Product dimers were characterized on the basis of comparison of NMR and mass spectra with authentic samples prepared by literature procedures.[44−47]

Control Experiments. (a) Stability of Alkenes. The five alkenes examined in this study underwent slow dark reaction in NaY zeolite. Therefore all studies were performed in NaX zeolite. The stability of the alkenes in NaX was tested by stirring 10 mg of alkene with 300 mg of activated NaX in hexane (10 mL) for 10 h. The zeolite was extracted with tetrahydrofuran, and GC analysis of the extract did not show the presence of either dimer or any other products.

(b) Stability of Dimers. Authentic dimers from each alkene were prepared by solution irradiation. The dimers were introduced into NaX and into **2**−NaX by a procedure similar to the incorporation of an alkene within a zeolite (described above). The zeolite containing the dimer was kept in the dark for several days and extracted with tetrahydrofuran. GC analysis did not indicate any change in the dimer ratio. Also no other products were detected, indicating that the dimers were stable within NaX and **2**−Na X.

(c) Stability of Dimers under Irradiation Conditions. The stability of the dimers under irradiation conditions was tested within **2**−NaX. Dimers of indene and phenyl vinyl ether prepared independently were incorporated within **2**−NaX. A slurry of the complex in hexane was irradiated for 5 h. Products were extracted and analyzed by GC. The indene dimer gave indene as a product in low yields but the ratio of the two dimers was not affected. The dimer of phenyl vinyl ether was stable under the irradiation conditions.

Studies within Triphenylpyrylium Entrapped Y Zeolite. HY zeolite entrapped with triphenylpyrylium was prepared and characterized according to a literature procedure.[24] The zeolite thus prepared was dried under vacuum at <100 °C and was used to sensitize the dimerization of **7**−**9**. These three alkenes (10 mg) were included within dry TPP−HY zeolite by stirring in hexane. Even during the stirring process the zeolite developed color, and extraction prior to irradiation gave products characteristic of an acid-catalyzed reaction. Therefore, this sensitizer and the procedure suggested to be useful for electron transfer reactions within zeolites could not be used for the alkenes studied in this work.

Fluorescence. Steady-state and time-resolved fluorescence measurements were carried out using a PTI system equipped with single photon counting capabilities. Samples were placed in quartz cuvettes at 45° to both excitation and emission beams. For the time-resolved measurements, the lamp profile was recorded using zeolite as scatterer with 340 nm excitation/emission; deconvolution and fittings were done using PTI software. The zeolite samples always showed a small fast component (<1 ns) at the beginning of the decay trace that was also present in unloaded zeolite (using 340/369 nm excitation/emission wavelengths). The remainder of the data gave reasonable fits to single-exponential kinetics for all the zeolite samples.

Diffuse Reflectance Laser Flash Photolysis. The flash photolysis system has been described in detail.[54] For these experiments a Lumonics Nd:YAG laser (10 ns/pulse; 266 nm, <30 mJ/pulse; 355 nm, <40 mJ/pulse) was used for sample excitation. Dry zeolite samples were contained in 3 × 7 mm^2 quartz cuvettes and were purged with nitrogen or oxygen before laser irradiation. The samples were moved and shaken frequently during the experiment to minimize problems related to product buildup.

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(54) Kazanis, S.; Azarani, A.; Johnston, L. J. *J. Phys. Chem.* **1991**, *95*, 4430.