Photochemical and Thermal Behavior of Styrenes within Acidic and Nonacidic Zeolites. Radical Cation *versus* Carbocation Formation

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Laser flash photolysis of a series of substituted styrenes embedded within the cavities of the large pore zeolite NaY leads to the formation of the corresponding styrene radical cation. The reactivity and spectra of these radical cations embedded within NaY are examined and compared to the reactivity of the same radical cations in solution. It is found that for the highly reactive parent styrene radical cation the zeolite framework provides a strong stabilizing effect. For the 4-methoxy-substituted styrene radical cation the zeolite framework plays less of a role in stabilizing the radical cation as compared to the reactivity of the same radical cation in acetonitrile solution. Rigorous analysis of the thermal stability of 4-methoxystyrene, 4-methylstyrene, and anethole in the zeolite micropores was carried out using two sources of NaY zeolite (Aldrich and The PQ Corporation). It was found that the thermal stability was surprisingly dependent on the source of the NaY zeolite. 4-Methoxystyrene, 4-methylstyrene, and anethole were thermally stable in NaY (Aldrich) but rapidly dimerized in NaY (PQ) upon incorporation with dichloromethane. We observed the formation of the same type of dimers not only for 4-methoxystyrene but also for 4-methylstyrene and anethole. In addition, 4-methoxystyrene was incorporated into a series of different acid zeolites (HZSM-5, HMordenite, HBeta, and HY) varying in the shape and size of their micropores where rapid thermal protonation occurs. Dimerization of the thermally formed 4-methoxyphenethyl cation with a neutral molecule of 4-methoxystyrene took place within all the acid zeolites examined. The generation of this secondary 1,3-bis(4-methoxyphenyl)-1-butylium ion was clearly observed in the medium pore ZSM-5. This carbocation was found to be thermally unstable in the acidic environment provided by the four acidic zeolites and underwent a proton and hydride transfer to form the more stable allylic 1,3-bis(4-methoxyphenyl)buten-1-ylium cation. In the large round cavities of HY a competing cyclization reaction took place which led to the formation of the 3-methyl-5-methoxy-1,4methoxyphenylindanyl cation.

Introduction

Our current knowledge of the chemistry of organic compounds is largely based on understanding the reactive intermediates which are involved in the transformation of starting materials to products. The reactive intermediate generated from a given compound may vary with the operating mechanism and the conditions under which the reaction is carried out. Recently, a large amount of work has focused on the photochemistry of styrene derivatives and it has been found that irradiation of substituted styrenes leads to the formation of two different types of cationic reactive intermediates depending on the conditions employed. Using laser flash photolysis, researchers have been able to study the reactivity of phenethyl carbocations generated by photoprotonation of the corresponding styrene derivative when the photolysis was carried out in nonnucleophilic fluorinated alcohols such as 2,2,2-trifluoroethanol and 1,1,1,3,3,3hexafluoro-2-propanol.¹ On the other hand, the corresponding styrene radical cations have been generated by direct photoionization of the styrene derivative when the laser photolysis was carried out in water or acetonitrile.² These studies have led to a deeper insight on the reactivity of both carbocations and radical cations under solvolytic conditions. A large amount of information on carbocations has also been obtained by studying these species in strong acidic media such as concentrated H_2SO_4 and magic acid solutions. Under these harsh conditions many carbocations are sufficiently stable for their spectral properties to be obtained.³

Zeolites are microporous crystalline aluminosilicates made up of $[SiO_4]^{4-}$ and $[AIO_4]^{5-}$ tetrahedra.⁴⁻⁶ The tetrahedra are arranged in a three-dimensional array, which gives the zeolite its open framework structure. The framework geometry of zeolites consists of pores and channels whose size and shape vary widely among different types of zeolites. Zeolites are often classified by their pore size.⁷ For example, ZSM-5 has a pore containing 10 oxygen atoms and is classified as a medium pore zeolite whereas Beta has a pore containing 12 oxygen atoms and is known as a large pore zeolite.⁸ For every aluminum present in the framework there is a net negative charge which must be compensated by a charge balancing cation. These charge-balancing cations are often Na⁺ or other alkali earth metals. Brönsted acid sites can be easily introduced into the framework by exchanging the Na⁺ cations with protons. These acidic solids have been the subject of extensive research due to their catalytic ability.⁸

Zeolites have proven to be good hosts for the study of cationic intermediates presumably due to the stabilization provided by the internal electrostatic fields within the voids of the microporous solids⁹ and to the confined environment, which provides protection of the cationic center from nucleophilic species.¹⁰ Owing to the need to generate thermally the

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SCHEME 1



carbocation upon adsorption of a neutral precursor, studies involving the stability of carbocations within zeolites have focused on acidic zeolites.¹¹ In some cases, carbocations have been found to be sufficiently stable in acid zeolites to obtain their spectral properties by conventional techniques.¹²⁻¹⁶ It has recently been suggested that the acidity of zeolites compares better to 70% aqueous solutions of H₂SO₄ than to that of superacid media as some researchers have postulated.¹¹ Therefore, it is not only the extreme acidity of zeolites but other special properties of the internal voids, in terms of polarity, mobility restriction, presence of acid sites, that makes these solids very appropriate to stabilize positively charged reaction intermediates.^{17,18} When a positively charged species is incorporated inside the voids of these solids, the whole lattice of the zeolite acts as a counteranion, insulating and protecting the carbocation from attack by external nucleophiles.¹⁹ Stabilization has been found to be dramatic in many cases in which the tight fit between the organic guest and the zeolite occurs.²⁰ These appropriate characteristics combined with the wide range of crystalline structure and the possibility to introduce active sites have made zeolites the host of choice for many studies of organic cations.

Organic radical cations formed within the zeolite framework have been the subject of much interest.²¹⁻²⁸ Electron acceptor sites may be present within the zeolite framework, and therefore, zeolites have been established as convenient host materials to promote the formation of radical cations.¹⁸ Spontaneous radical cation formation and/or precursor decomposition has been reported upon the incorporation of several organic guests into Na⁺-exchanged zeolites.²⁹⁻³² However, it is now accepted that acid sites in these solids are related to their electron acceptor ability. Recent studies have supported that Brönsted acid sites of zeolites can also be responsible for the thermal radical cation formation, thus implying that the H⁺-form of zeolites could exhibit a dual behavior as acid and oxidizing solids.^{8,10,33,34} On the other hand, a few examples of organic radical cations within the zeolite framework generated by photolysis or pulse radiolysis have also been reported; however, radical cations of styrenes in zeolites have never been studied.^{29,33-39}

It is, therefore, of interest to determine which is the prevalent pathway when both processes, either protonation or single electron abstraction, Scheme 1, can occur concurrently.^{40,41} As previously mentioned, C=C double bonds, and in particular simple styrenes, are suitable probe molecules to establish the nature of the actual intermediate (e.g., a radical cation or a carbocation) generated within zeolite media. In this study two complementary strategies have been devised: either timeresolved diffuse-reflectance techniques for the Na⁺-form of the large pore Y zeolite where radical cation intermediates appear as short-lived transients, and conventional diffuse reflectance for acid zeolites, where thermally generated carbocations appear as persistent, long-lived species.

Results and Discussion

Radical Cation Generation. The free diffusion of 20 mg of anethole in dichloromethane, CH_2Cl_2 , with 600 mg of dehydrated NaY (Aldrich), led to the incorporation of 5 mg of



Figure 1. Transient diffuse reflectance spectrum after 266 nm excitation of an O₂ purged (A) and vacuum-sealed (B) sample of anethole incorporated with NaY (Aldrich). Spectra were recorded (\bullet) 1.6 μ s, (\blacksquare) 4.8 μ s, (\blacklozenge) 24 μ s, and (\blacktriangle) 75 μ s after the laser pulse. The samples were prepared using CH₂Cl₂ as the carrier solvent.

anethole into the framework of the Y faujasite (average loading level: 1 anethole/10 supercages). Once the incorporation procedure was complete, the sample was thoroughly washed with CH₂Cl₂ and dried under vacuum. Throughout the incorporation procedure the bulk sample remained white, showing no obvious signs of styrene decomposition (vide infra differences in the NaY samples). The laser photolysis experiments were performed on the same day as sample preparation. Laser flash photolysis of the anethole-NaY complex under an atmosphere of oxygen led to the transient reflectance spectrum shown in Figure 1A. The spectrum shows two strong absorption bands, one centered at 620 nm and the other at 400 nm, and is almost identical to that observed for the anethole radical cation in solution.^{2,42} On the basis of this similarity, the intermediate generated upon 266 nm excitation of anethole encapsulated within NaY can be confidently identified as the anethole radical cation, $R_1 = OCH_3$ and $R_2 = CH_3$, formed by photoionization of anethole, eq 1. The assignment of the two reflectance bands



to one species is in agreement with the observation that both the 400 nm and the 620 nm bands decay with identical kinetics. The decay was fit to a double-exponential expression where the fast component was analyzed for the decay of the radical cation embedded within the framework of NaY and was on the order of $4 \times 10^4 \text{ s}^{-1}$.

Photoionization of anethole must be accompanied by the ejection of an electron into the zeolite framework. Electrons within the pores of faujasites typically complex with Na⁺ counterions to generate Na_4^{3+} ions that have absorption in the



Figure 2. Transient diffuse reflectance spectrum after 266 nm excitation of an O₂ purged sample of 4-methoxystyrene incorporated with NaY (Aldrich). Spectra were recorded (\oplus) 0.4 μ s, (\blacksquare) 1.3 μ s, (\blacklozenge) 4.8 μ s, and (\blacktriangle) 14 μ s after the laser pulse. The sample was prepared using CH₂Cl₂ as the carrier solvent.

500 nm region, eq 2.43,44 We investigated the possibility that

$$e^{-} + 4Na^{+} \rightarrow Na_{4}^{3+}$$
(2)

we could observe such a sodium complex by carrying out the photolysis of the anethole-NaY complex in the absence of oxygen. Figure 1B shows the transient diffuse reflectance spectrum generated upon 266 nm excitation of anethole in NaY under reduced pressure (0.005 Torr). Additional absorption in the 500 nm region is clearly seen in the spectrum and has a maximum at \sim 520 nm. The decay of this transient was found to be 1.5×10^6 s⁻¹, which is much faster than the decay of the anethole radical cation. The transient reacted very rapidly with oxygen as seen by its complete quenching upon the addition of oxygen to the sample. We therefore assign this transient species to the Na4³⁺ complex generated when the electron is ejected from anethole into the zeolite framework. The fact that we simultaneously observe both the radical cation of anethole and the trapped electron provides compelling evidence that photoionization is occurring in the large pore Na⁺-form Y zeolite upon 266 nm laser excitation.

A sharper absorption band in the 380-400 nm region is observed upon going from a vacuum to an O₂ environment. Such narrowing has been observed before for diffuse reflectance studies in zeolites.¹³ In the present work, the small change in the maximum may be due to the presence of the radical anion of the styrene produced by trapping of the photoejected electron by neutral 4-methoxystyrene. A similar process has been observed in the formation of the pyrene radical anion upon photoionization of pyrene in zeolites.⁴⁵

These results established that styrene type radical cations can be readily generated and observed in the zeolite framework using time-resolved diffuse reflectance and encouraged us to attempt to generate radical cations of other styrene derivatives in NaY. In particular, this would allow us to address questions concerning how the zeolite framework influences the lifetime of the photogenerated radical cations with decreasing thermodynamic stability. Thus we examined the photolysis of 4-methoxystyrene, 4-methylstyrene, and styrene incorporated in NaY. In all cases, incorporation procedures involved using CH₂Cl₂ as the carrier solvent, and the samples remained colorless throughout sample preparation. The photolysis experiments were carried out within 24 h of sample preparation.

Laser photolysis of 4-methoxystyrene incorporated within NaY under an atmosphere of oxygen led to the transient diffuse reflectance spectrum shown in Figure 2. The spectrum shows strong bands centered at 600 and 360 nm that are consistent with assignment of the transient to the 4-methoxystyrene radical cation,² $R_1 = OCH_3$ and $R_2 = H$, eq 1. The decay of the two



Figure 3. Transient diffuse reflectance spectrum after 266 nm excitation of 4-methylstyrene (A) and styrene (B) in O₂ purged NaY (Aldrich). Spectra were recorded (\odot) 0.28 μ s, (\blacksquare) 0.72 μ s, (\diamondsuit) 1.4 μ s, and (\blacktriangle) 6.0 μ s (4-methylstyrene) and (\odot) 0.28 μ s, (\blacksquare) 0.56 μ s, (\diamondsuit) 0.80 μ s, and (\bigstar) 6.0 μ s (styrene) after the laser pulse. The samples were prepared using CH₂Cl₂ as the carrier solvent.

bands followed the same kinetics and was fit to a double exponential expression where the fast component was analyzed for the decay of the radical cation within NaY and was on the order of $1.6 \times 10^6 \text{ s}^{-1}$. Figure 3 shows the transient diffuse reflectance spectra of the radical cations generated upon photoionization of 4-methylstyrene, $R_1 = CH_3$ and $R_2 = H$, and parent styrene, $R_1 = H$ and $R_2 = H$, eq 1. In both cases, the λ_{max} of the transients at ca. 350–360 nm and ca. 600 nm are in accordance with the spectra of the appropriate radical cation,² indicating that the NaY framework clearly acts as a highly polar, solid matrix for the generation and detection of these reactive cationic species. Additional absorption near 500 nm is also observed in these spectra. Absorption near this region has been observed upon the generation of styrene radical cations in solution, and attributed to the presence of "dimer" radical cations produced by addition of the radical cation to the neutral styrene.^{2,46} Such a process may take place rapidly in zeolites, especially under conditions where a radical cation is generated in a doubly occupied cavity.

The traces for the decay at 600 nm of the photogenerated 4-methoxy, 4-methyl, and unsubstituted styrene radical cations are shown in Figure 4. These traces do not follow simple firstorder behavior, but each can be adequately fit to an expression for two consecutive first-order decays. While the long-lived component for the 4-methoxystyrene radical cation is more pronounced than that for the 4-methyl and the unsubstituted derivatives, the rate constants calculated from the decays of each radical cation, summarized in Table 1, are remarkably similar.^{19,47} In particular, a factor of about 4 separates the rate constant for the highly unstable parent radical cation from that of the stabilized 4-methoxystyrene radical cation when the radical cations are generated in the confined environment of the zeolite. This contrasts sharply with results in homogeneous solutions, such as AcN, where the difference in reactivity is greater than $10^{6.2}$ It is also interesting that the observed decrease in the range of reactivity in the zeolite can be mostly attributed



Figure 4. Transient decay kinetics generated upon 266 nm excitation for 4-methoxystyrene (\blacksquare), 4-methylstyrene (\bigcirc), and styrene (\bigcirc) within NaY (Aldrich). The normalized traces were monitored for the 600 nm band under an atmosphere of oxygen.

 TABLE 1: First-Order Rate Constants for the Decay at 600

 nm of Substituted Styrene Radical Cations in NaY and in

 Acetonitrile (AcN)

	NaY (k_{obs}/s^{-1})		
substituted styrene	fast	slow ^a	$\operatorname{AcN}^{b}(k_{obs}/s^{-1})$
styrene 4-methylstyrene 4-methoxystyrene anethole	$\begin{array}{c} 4.5 \times 10^{6} \\ 2.6 \times 10^{6} \\ 1.4 \times 10^{6} \\ 4.5 \times \end{array}$	$0.5 \times 10^{6} \\ 0.4 \times 10^{6} \\ 0.1 \times 10^{6} \\ 10^{4}$	c,d 3×10^{8} 1.3×10^{5} 4×10^{4}

^{*a*} Fast and slow refer to the fast component and the slow component, respectively, obtained by fitting the decay traces to a double first-order exponential expression. ^{*b*} Taken from reference 2. ^{*c*} Too fast to be directly measured. ^{*d*} The estimated value by extrapolation of the 4-Me and 4-MeO data is $5 \times 10^{10} \text{ s}^{-1}$.

to the effect of the zeolite environment on the reactivity of the less stable radical cation.¹⁹ Thus, while the decay of anethole and 4-methoxystyrene radical cations in NaY is similar to their decay in AcN, the more unstable parent styrene radical cation is about 4 orders of magnitude less reactive in the zeolite compared to AcN. These results suggest that the kinetic stabilizing effect of the zeolite framework is far more effective for the more unstable cationic species and that for slightly stabilized radical cations the zeolite framework is no more effective than solvents such as acetonitrile. The stabilizing effect of the zeolitic media on short-lived photogenerated radical ion pairs has been already noted,⁴⁸ but the modulation in this effect depending on reactivity of the species is remarkable. In addition, since the stabilized 4-methoxystyrene radical cation and the parent styrene radical cation have very similar absolute reactivities in the zeolite, the thermodynamic stability of the radical cation does not seem to be a major factor in determining the relative reactivity of the radical cations. The large kinetic stabilizing effect of the zeolite framework to the less stable radical cations may be due to the limiting amount of reactive species found within the cavity. Thus the rate determining step may be due to the availability of a nucleophile (or some other quenching agent) and not due to the inherent stability of the radical cation.

Influence of the NaY Source. Early in our study we found that sample preparation was critical and that we obtained different results depending on the source of NaY. The zeolitestyrene samples prepared using NaY Si:Al = 2.4 (Aldrich) remained white throughout the sample preparation procedure. To test that the styrenes were not reacting upon incorporation into the zeolite micropores, we carried out rigorous product analysis using 4-methoxystyrene. The complete incorporation of 40 mg of 4-methoxystyrene into the NaY faujasite (800 mg) was accomplished using hexane as the carrier solvent. The sample was thoroughly dried under vacuum in the usual way, and once prepared, the sample was left under vacuum for a period of 1 day. After this time the 4-methoxystyrene was reextracted from the zeolite using CH_2Cl_2 as the solvent. According to GC analysis the only compound retrieved from the zeolite was 4-methoxystyrene in greater than 95% purity. To test further for the stability of 4-methoxystyrene within the Na⁺-form of Y zeolite, the sample was allowed to remain under vacuum for a period of 1 week and then was reextracted from the zeolite. GC analysis showed that 4-methoxystyrene was still the major compound (85%); however, a new peak which had a longer retention time (12.5 min) than that of 4-methoxystyrene (4.3 min) and accounted for 10% of the organic matter was clearly observed.

The same sample preparation procedure with 4-methoxystyrene was followed using NaY Si:Al = 2.6 purchased from the PQ corporation. In this case, very different results were obtained. When 4-methoxystyrene dissolved in either CH₂Cl₂ or hexane was mixed with the activated NaY (PO) zeolite, the solid turned light purple immediately as the organic mixture came into contact with the zeolite. Diffuse reflectance spectroscopy showed the presence of a weak band at 585 nm accompanied with an intense absorption at 280 nm owing to unaltered starting 4-methoxystyrene. The characteristic 585 nm absorption is consistent with the results attained using acid zeolites (vide infra). The purple color was persistent and remained during the sample preparation procedure. Once the incorporation procedure was finished, no 4-methoxystyrene could be recovered from the zeolite upon extracting out the organic material using CH₂Cl₂ as the solvent. Two products (ratio 10:1) were extracted according to GC analysis, and the retention time of the major peak (12.5 min) was identical to that of the minor product extracted from the Aldrich sample after 1 week. The new compounds formed upon incorporation of 4-methoxystyrene into NaY (PQ) were examined and identified using GC, GC/MS, and ¹H NMR as trans and cis isomers of 1,3-dianisyl-1-butene formed by the acid-catalvzed dimerization of 4-methoxystyrene within the zeolite voids, eq 3.



These results therefore indicate that dimerization of 4-methoxystyrene does occur on both Na⁺-form of the Y faujasites but with enormously different rates. We also confirmed by GC/ MS and ¹H NMR that 4-methylstyrene and anethole undergo rapid dimerization upon incorporation in the NaY sample from PQ.

The observed dimers upon incorporation of 4-methoxystyrene into the Y faujasite are consistent with a mechanism involving carbocation intermediates^{49,50} since the intermediacy of radical cations would lead to a different dimer distribution.³⁰ In fact, the dimerization reaction of the 4-methoxystyrene radical cation with its neutral precursor has been shown to yield high concentrations of the dihydronaphthalene, 1,2-dihydro-7-methoxy-1-(4'-methoxyphenyl)naphthalene and the cyclobutane, *trans*-1,2-bis(4-methoxyphenyl)cyclobutane.⁵¹ These products are clearly not observed in the product mixture extracted from the zeolites, which indicates that the major path of decomposition does not involve radical cation intermediates.

We checked the acidity of the NaY sample from PQ by IR spectroscopy following the standard pyridine adsorptiondesorption method.⁵² In this technique, pyridine vapors (5 Pa) are adsorbed onto dehydrated zeolites and the presence of pyridinium ions (Brönsted sites) or pyridine adducts (Lewis sites) are determined by their characteristic aromatic vibration bands at 1550 and 1450 cm⁻¹, respectively. Using this technique, no Brönsted acid sites could be observed and only very weak Lewis sites were titrated after evacuation of the pyridine at 150 °C for 1 h. This corresponds to the minimum outgassing temperature that can be used in the pyridine method in order to avoid the interference of physisorbed pyridine. In addition, the sensitivity of the pyridine adsorption-desorption method is estimated to 1 mmol of pyridine, while differences in the population of active sites can be smaller than this. The fact that weak Lewis acid sites are present in NaY (PQ sample) was confirmed by measuring the amount of ammonia (1.39 mmol g^{-1}) adsorbed onto a dehydrated sample at 100 °C. In addition, the crystallinity of the PQ sample determined by XRD was found to be 100%. In spite of the fact that we have not been able to measure differences in the acidity of the samples by state-of-the-art techniques in zeolite chemistry, it is clear that minor differences in the Si:Al ratio or in the crystallinity lead to large differences in their catalytic behavior for the dimerization of 4-methoxystyrene. In this regard, it has been reported that the dimerization of the parent unsubstituted styrene by zeolite does not require the presence of strong acid sites.⁵⁰ Even the ability of neutral silanol groups to catalyze olefin polymerization has been recently advanced.53-55

Carbenium Ion Generation. We had anticipated that the incorporation of 4-methoxystyrene into the acidic environment of H⁺ exchanged zeolites would lead to the rapid decomposition of the styrene by thermal protonation^{56,57} of the β -carbon to generate the 4-methoxyphenethyl carbocation. The possibility arose that if the sample was kept free of atmospheric water we would be able to observe the thermally stable carbocation within the strongly acidic and polar environment of the acid zeolite. The 4-methoxyphenethyl cation has been generated by photoprotonation of 4-methoxystyrene under solvolytic conditions and has an absorption maximum at 340 nm.¹ This cation is known to undergo a rapid dimerization reaction with the β -position of the alkene bond of 4-methoxystyrene to yield the 1,3-dianisylbut-1-ylium cation, characterized by a new absorption band shifted ~ 20 nm to longer wavelengths compared to the monomer 4-methoxyphenethyl cation.⁵⁸

Upon the incorporation of 4-methoxystyrene in H⁺-exchanged medium pore ZSM-5, the zeolite-styrene complex turned yellow immediately following the incorporation procedure. The ground state diffuse reflectance spectrum for the HZSM-5 4-methoxystyrene complex is shown in Figure 5A. This spectrum clearly shows a strong absorption band centered at 360 nm. This band is shifted exactly 20 nm to longer wavelengths with respect to the 4-methoxyphenethyl cation, $\lambda_{max} = 340$ and corresponds nicely to that of the 1,3-dianisylbut-1-ylium cation (spectrum A) generated by thermal protonation of 4-methoxystyrene in the acidic environment to yield the 4-methoxyphenethyl cation followed by its reaction with neutral 4-methoxystyrene, eq 3. The initially formed 4-methoxyphenethyl cation is too reactive to be observed under the conditions that the diffuse reflectance spectra are obtained.

After incorporation of 4-methoxystyrene into HZSM-5, the spectrum shown in Figure 5A progressively changed and after 72 h a very different diffuse reflectance spectrum shown in



Figure 5. Ground state diffuse reflectance spectra of 4-methoxystyrene incorporated in HZSM-5 recorded immediately after sample preparation (A) and after being stored 72 h at open ambient atmosphere (B).

Figure 5B was recorded. Quantitative electron pair resonance (EPR) spectroscopy established that the amount of radical ions at this stage was less than 10^{15} spin g⁻¹, which would correspond to less than 2×10^{-4} mg of radical cation/g of zeolite.^{59,60} These quantities are too low to account for the strong absorption bands. The peak at 360 nm is still clearly observable, but there is a much stronger absorption centered at 585 nm. This band is analogous to the absorption band centered at 500 nm for the unsubstituted 1,3-diphenylpropen-1-ylium cation in HZSM-5⁶¹ assuming a +10 nm shift for the methyl substituent on the allyl bridge and +25 nm shift for each 4-methoxy group.⁶² Therefore, the species responsible for the 585 nm band is thought to be due to the analogous 1,3-bis(4-methoxyphenyl)-2-buten-1-ylium cation (spectrum B). The first step in the generation of this allylic cation is also the dimerization reaction of the 4-methoxyphenethyl cation with 4-methoxystyrene to give the linear cation A.⁶³ Once this cation is formed within the zeolite it can undergo a hydride transfer from the linear dimer, resulting in equimolar formation of the allylic cation **B** and 1,3-dianisylbutane. The fact that both the linear dimer and its dihydro derivative are observed as reaction products upon adsorption of 4-methoxystyrene into acid zeolites (see Table 2) as well as detection of cation A lends support to our proposed reaction scheme,³² eq 4. Notably, the same absorption band, but



 TABLE 2: Products Formed upon Incorporation of 4-Methoxystyrene into HZSM-5, HMordenite, and HY Using Isooctane as the Carrier Solvent



^a Variable amounts of unidentified polymeric material was also extracted in the case of HMordenite and HY zeolites.



Figure 6. Ground state diffuse reflectance spectra of 4-methoxystyrene incorporated in HMordenite (A) and HBeta (B) recorded immediately after sample preparation.

appearing at 565 nm, is observed upon dissolving 4-methoxystyrene in concentrated sulfuric acid.

In order to unambiguously identify the 585 nm band as the 1,3-bis(4-methoxyphenyl)buten-1-ylium cation **B**, an alternative preparation of this cation was carried out in solution by dissolving the thermal labile hydroxy compound into an acidic TFE:AcOH solution. The addition of this allylic alcohol into the acidic solvent led to the formation of the allylic cation by loss of water, eq 5. The cation was sufficiently stable at room



temperature in the acidic environment for its absorption spectrum to be obtained. The absorption spectrum of the resulting cation **B** showed a strong band centered at 565 nm, which is in agreement with our identification of the 585 nm species within the zeolite micropores as the same cation.

When 4-methoxystyrene was incorporated into HMordenite or HBeta (Figure 6) by the same procedure as described for HZSM-5, the ground state reflectance spectra obtained are very similar to that shown in Figure 5B. In both cases, a small band centered at 360 nm and a much stronger band at 570 nm are observed. Thus, in these acidic zeolites both the 1,3-dianisyl-1-butylium **A** and the 1,3-bis(4-methoxyphenyl)-2-buten-1-ylium **B** cations are formed within zeolite environment.

Examination of the diffuse reflectance spectrum upon incorporation of 4-methoxystyrene into the large cavity HY zeolite also reveals the formation of both the 1,3-dianisylbut-1-ylium cation A and the 1,3-bis(4-methoxyphenyl)buten-1-ylium cation **B**, Figure 7A. However, we found that in this case, the diffuse reflectance spectrum was very sensitive to the adsorption procedure. Thus, by refluxing 4-methoxystyrene in CH₂Cl₂ the spectrum shown in Figure 7B is recorded. This band is consistent with the cyclized 3-methyl-1,4-methoxyphenylindanyl cation C formed after the initial dimerization step. 63,64 The initially formed carbocation has sufficient room in the tridirectional, large pore zeolite to undergo the cyclization reaction, which yields an unstable cyclohexadienyl cation. The cyclohexadienyl cation is not observed in the zeolite and is thought to undergo a rapid deprotonation to yield the neutral indane which then undergoes a hydride transfer to yield the 3-methyl-5-methoxy-1,4-methoxyphenylindanyl cation, eq 6. This reac-



tion mechanism is also supported by the observation of the indanic dimer in the reaction mixture after adsorption of 4-methoxystyrene in acid zeolites.

An analogous dimerization/cyclization reaction has been previously reported in the literature upon the incorporation of styrene into the large pore HY zeolite. The resulting 3-methyl-1-phenylindanyl cation was found to be sufficiently stable to be characterized by ¹³C NMR.⁶³

The major products obtained upon the incorporation of 4-methoxystyrene into HZSM-5, HMordenite, and HY are given in Table 2. For the zeolites examined, products derived from the dimerization reaction were found to include linear and cyclized products, together with 1,3-dianisylbutane. The major products observed upon incorporation of 4-methoxystyrene into the acidic zeolites agree with the carbocations observed by ground state diffuse reflectance for the zeolite complexes. In each case products derived from the initial attack of the 4-methoxyphenethyl cation to neutral 4-methoxystyrene are observed.⁶³ On the other hand the relatively poor mass balances, although not uncommon for product studies using microporous solids, reflects the presence on the solid of a large amount of unextractable organic material.

Conclusion

Radical cations of styrene derivatives are readily formed upon photoionization within the large pore NaY faujasite (Aldrich).



Figure 7. Ground state diffuse reflectance spectra recorded immediately after incorporation from a CH_2Cl_2 solution of 4-methoxy-styrene in HY stirring at room temperature (A) or at reflux temperature (B).

The reactivities of the 4-methoxy derivatives were found to be similar to those for the same radical cations in acetonitrile, but less stabilized 4-methyl and parent radical cations are remarkably long lived in the zeolite host where the rate constants of the 4-methoxy and unsubstituted derivatives vary by a factor of only 4. In contrast to the relatively high thermal stability of styrenes adsorbed on NaY (Aldrich), 4-methoxystyrene, 4-methylstyrene, and anethole were found to undergo a rapid dimerization reaction upon incorporation into NaY (PQ) zeolite.

4-Methoxystyrene was also incorporated into a series of acid zeolites where rapid thermal protonation in the β -position occurred leading to the formation of three different carbocations. In the medium pore HZSM-5 the 1,3-dianisyl-1-butyl cation is clearly observable. Over time, this cation decays with the concomitant appearance of 1,3-bis(4-methoxyphenyl)but-1-ylium cation ($\lambda_{max} = 585$ nm), which is also observed after the adsorption of 4-methoxystyrene on HMordenite and HBeta. In HY a third carbocationic species is observed and is thought to be due to the 3-methyl-5-methoxy-1,4-methoxyphenylindanyl cation formed by a cyclization reaction. These different carbocations clearly demonstrate the ability of acid zeolites to control the products of a reaction by their shape-selectivity nature.

Experimental Section

The two types of nonacidic NaY faujasite were obtained from Aldrich (LZY52 molecular sieves, Si:Al = 2.4) and from PQ (Si:Al = 2.6) and were used as received. Both zeolites have previously been well characterized. The styrene derivatives were obtained from Aldrich and distilled prior to use. All solvents (hexane, dichloromethane, isooctane, and acetonitrile) were of the highest grade (OmniSolv, BDH) and used without further purification.

Ground state diffuse reflectance measurements of the dried samples were obtained using a Shimadzu UV-2101 PC scanning spectrophotometer. Kubelka—Munk equations F(R) were plotted as a function of wavelength. GC analysis was done using a Perkin Elmer autosystem GC with a DB5 15 meter column.

Time-resolved diffuse reflectance experiments were carried out using a nanosecond laser system similar to those previously described.⁶⁵ The excitation source was the fourth harmonic (266 nm, < 20 mJ, < 8 ns/pulse) from a Continuum NY61-10 YAG laser. The samples were contained in quartz cells constructed with 3 × 7 mm² tubing and were either evacuated under reduced pressure and sealed under vacuum or purged with oxygen for a minimum of 30 min prior to photolysis. The data analysis was based on the fraction of reflected light absorbed by the transient (reflectance change $\Delta J/J_o$) where J_o is the reflectance intensity before excitation and ΔJ is the change in the reflectance after excitation.

The guest-host samples were prepared with the utmost of care. The non-acidic zeolite was activated at 475 °C for at least 10 h before use. Typically 600 mg of zeolite was activated overnight and allowed to cool to room temperature in a dry environment. A solution of the organic styrene (about 20 mg) dissolved in the carrier solvent (20 mL of CH₂Cl₂ or hexane) was then rapidly added to the activated zeolite. The sample was magnetically stirred under an atmosphere of dry nitrogen for 1 h, after which time the sample was centrifuged and the solvent was decanted. Fresh solvent was added in order to wash the zeolite surface. The sample was stirred for another 30 min, centrifuged, and the solvent was decanted. The styrene-zeolite complex was then transferred to a desiccator and dried under vacuum of 0.005 torr for at least 5 h. Laser experiments were conducted on fresh samples generally the day of sample preparation.

The amount of organic material incorporated into the zeolite was calculated from the difference between the initial amount of the styrene and the amount that was recovered in the combined solutions measured by UV absorption. When hexane was used as the carrier solvent, it was found that >90% of the styrene was incorporated into the zeolite. The loading level was found to be much lower when CH_2Cl_2 was used as the carrier solvent, and in this case, about 25% of the styrene was incorporated.

Determination of the stability of the styrene upon incorporation was carried out by reextracting the incorporated material using CH₂Cl₂ as the solvent. The organic components were either extracted from the zeolite by continually washing the sample with fresh CH₂Cl₂ until no more organic compound was visible with UV absorption or the sample was extracted using a continuous solid-liquid extracting apparatus. The organic solution was analyzed by GC-MS (Varian Saturn 11, 35 m capillary column cross-linked 5% phenylmethylsilicone) and, after removal of solvent, by ¹H NMR (300 MHz, Varian Gemini).

The adsorption procedure for the acid zeolites was carried out by mixing a solution of 4-methoxystyrene (25 mg) in isooctane at 90 °C in the presence of the thermally dehydrated acid zeolite (1.0 g) for 1 h. After this time the solid was filtered, washed with fresh isooctane (10 ml), and submitted to solid liquid extraction using CH_2Cl_2 as solvent. The organic solution was analyzed by GC/MS (Varian Saturn 11, 35 m capillary column crosslinked 5% phenylmethylsilicone) and ¹H NMR.

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