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NMR Observation of Indanyl Carbenium Ion Intermediates in the Reactions of Hydrocarbons on Acidic Zeolites

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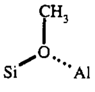
Abstract: In situ ^{13}C MAS–NMR was used to study the reactions of [α-^{13}C]styrene, [β-^{13}C]styrene, and [α-^{13}C]-α-methylstyrene on the acidic zeolites HZSM-5, HY, and H-mordenite. Neither the methylphenylcarbenium ion nor the dimethylphenylcarbenium ion were observed as persistent species by NMR, even at low temperatures. However, styrene reacted on zeolite HY to form an appreciable yield of the 3-methyl-1-phenylindanyl cation, and this cation was stable up to ca. 323 K. The mechanism by which this cation formed was apparently hydride transfer from neutral 1-methyl-3-phenylindan to transient (i.e., not observed) methylphenylcarbenium ion. The analogous 3,3-dimethyl-1-phenylindanyl cation did not form as a persistent species when α-methylstyrene was adsorbed on HY; we attribute this negative result to the relative difficulty of intermolecular methyl transfer vs hydride transfer. Styrene dimers cracked on HZSM-5 at ca. 433 K to form a significant yield of the 1-methylindanyl cation, which was stable indefinitely in the zeolite at 298 K. Further heating converted this cation into naphthalene, the ultimate product of dimerization, cracking, skeletal isomerization, and dehydrogenation. A very low yield of the analogous 1,3,3-trimethylindanyl cation formed in the reactions of α-methylstyrene on HZSM-5; we attribute the disparity in yields between the less bulky and more bulky cation to the steric effect of the pore size. The yields of both methylindanyl cations on zeolite HY were very low or negligible. This observation may reflect the fact that HZSM-5 is a slightly stronger acid than HY. The above results are introduced and discussed in the context of our recently proposed reclassification of typical zeolites as strong acids rather than superacids. We also show that the observation of indanyl cations but not simple phenylcarbenium ions as persistent species in high concentration is an expected consequence of the relative acid strengths of the zeolites and carbenium ions. The principal components of the ^{13}C chemical shift tensor of the charged carbon of the 3-methyl-1-phenylindanyl cation were $\delta_{11} = 310$, $\delta_{22} = 286$, and $\delta_{33} = 68$ ppm; for the 1-methylindanyl cation these values were $\delta_{11} = 359$, $\delta_{22} = 320$, and $\delta_{33} = 76$ ppm.

Introduction

The reactions of hydrocarbons in acidic zeolites are frequently assumed to be analogous to those in superacid solutions, and thus descriptions of these reactions make use of free carbenium ion and carbonium ion intermediates.[1–3] Yet, a recent theoretical study has questioned whether free carbonium ion intermediates occur in hydrogen exchange reactions,[4] and in situ spectroscopic evidence for carbenium ion intermediates has been fragmentary and contentious.[5–7] The results of a number of spectroscopic and theoretical studies suggest several alternatives to free, charged species as persistent intermediates in zeolite catalyzed reactions. Kazansky,[8] Bosácek,[9] this group,[10–13] and others[14–16] have described bound alkoxy species such as **1**–**3**. These intermediates can be viewed as "incipient carbenium ions" that have forsaken their freedom for the stabilization provided by covalent attachment to the conjugate base site of the zeolite. That such species are not free is hardly unexpected; many primary and other simple carbenium ions have never been isolated in condensed media, including superacid liquids and solids at low temperature, and it would be very surprising if such species persisted as free cations in a zeolite.



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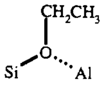

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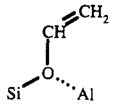

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Hydrogen bonding also gives rise to persistent intermediates other than free cations. A ^1H NMR study[17] showed that benzene undergoes hydrogen exchange through a persistent π-bonded complex. Of course, a cation transition state or transient intermediate may still exist on the reaction coordinate for this process, but the cation does not form to an appreciable equilibrium concentration as some views of zeolite acidity would require. A recent spectroscopic and theoretical study[18] showed that acetonitrile is not protonated in HZSM-5 as it is in superacids. Proton

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(1) Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. *New Solid Acids and Bases*; Kodansha: Tokyo, Elsevier: Amsterdam, 1989; Chapter 1.

(2) Campbell, I. M. *Acidity and Properties of Major Industrial Acids*; Chapman & Hall: London, 1992; Chapter 7.

(3) Gates, B. C. *Catalytic Chemistry*; Wiley & Sons: New York, 1991; Chapter 5.

(4) Kramer, G. J.; van Santen, R. A.; Emeis, C. A.; Nowak, A. K. *Nature* **1993**, *363*, 529–531.

(5) Biaglow, A. I.; Gorte, R. J.; White, D. *J. Chem. Soc., Chem. Commun.* **1993**, 1164–1166.

(6) Buzek, P.; Schleyer, P. v. R.; Vancik, H.; Mihalic, Z.; Gauss, J. *Angew. Chem.. Int. Ed. Engl.* **1994**, *33*, 448–451.

(7) Fărcaşiu, D. *J. Chem. Soc., Chem. Commun.* **1994**, 1801–1802.

(8) Kazansky, V. B. *Acc. Chem. Res.* **1991**, *24*, 379–383.

(9) Bosácek, V. *J. Phys. Chem.* **1993**, *97*, 10732–10737.

(10) Haw, J. F.; Richardson, B. R.; Oshiro, I. S.; Lazo, N. D.; Speed, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2052–2058.

(11) Murray, D. K.; Howard, T.; Goguen, P. W.; Krawietz, T. R.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 6354–6360.

(12) Murray, D. K.; Chang, J-W.; Haw, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 4732–4741.

(13) Lazo, N. D.; White, J. L.; Munson, E. J.; Lambregts, M.; Haw, J. F. *J. Am. Chem. Soc.* **1990**, *112*, 4050–4052.

(14) Stepanov, A. G.; Zamaraev, K. I.; Thomas, J. M. *Catal. Lett.* **1992**, *13*, 407–422.

(15) Malkin, V. G.; Chesnokov, V. V.; Paukshtis, E. A.; Zhidomirov, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 666–669.

(16) Aronson, M. T.; Gorte, R. J.; Farneth, W. E.; White, D. *J. Am. Chem. Soc.* **1989**, *111*, 840–846.

(17) White, J. L.; Beck, L. W.; Haw, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 6182–6189.

(18) Haw, J. F.; Hall, M. B.; Alvarado-Swaisgood, A. E.; Munson, E. J.; Lin, Z.; Beck, L. W.; Howard, T. *J. Am. Chem. Soc.* **1994**, *116*, 7308–7318.

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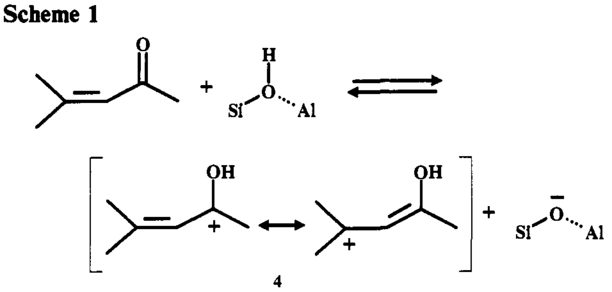
Scheme 1



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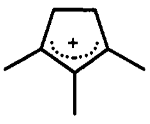
transfer at high temperature from the zeolite to acetonitrile was proposed to occur in a hydrogen bonded complex with little analogy to solution superacid chemistry.

But some experimental evidence has suggested that the carbenium ion picture is a good model for other persistent species. Adsorbates with certain functional groups can exhibit large ^{13}C chemical shift changes upon adsorption in acidic zeolites, and these are reminiscent of protonation shifts in solution. We recently reported a study of mesityl oxide on zeolites of various acid strengths (Scheme 1).[19] The ion **4** is indeed a (resonance-stabilized hydroxy) carbenium ion, but its extent of formation in zeolite HZSM-5, as measured by the ^{13}C shifts, was equivalent to only 70% H_2SO_4. Thus, although **4** is technically a carbenium ion, its observation was actually consistent with other observations that zeolites are not sufficiently strong acids to protonate weakly basic hydrocarbons to a significant equilibrium concentration without alkoxy formation. Furthermore, **4** is stabilized by hydrogen bonding to the conjugate base site.

The strongest direct evidence for the formation of persistent carbenium ions in the reactions of hydrocarbons in zeolites has been the observation of alkyl substituted cyclopentenyl cations such as **5**.[10,20] These ions formed from the reactions of propene and ethylene through mechanisms that were complex but previously well characterized in H_2SO_4 solutions.[21] Recently we reported the formation of cyclopentenyl ions like **6** through more straightforward reactions of cyclic alcohols and olefins.[22]



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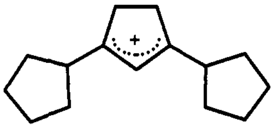

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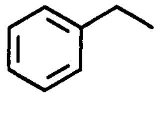
In that investigation, we explained the persistence of cyclopentenyl cations but not cyclohexenyl or simple allylic cations in terms of our measurement of zeolite acid strength. The five-membered ring in the cyclopentenyl cations locks the delocalized system into planarity and makes these ions especially stable.[23] This stability was quantified as the concentration of H_2SO_4 required to achieve equal concentrations of the cation and its corresponding diene. The substituted cyclopentenyl ions were much weaker acids than the zeolites, whereas those carbenium ions whose acidities are much stronger than 70% H_2SO_4 either transferred the proton back to the zeolite or rearranged to form the less acidic cyclopentenyl ions.

We were concerned that the cyclopentenyl cations were the only well established class of persistent cations in zeolites, so we set out to identify a second and more interesting class. Of the olefins that might be expected to yield persistent carbenium ions in superacidic zeolites, styrene and α-methylstyrene are compelling precursors. Yet neither the methylphenylcarbenium ion (**7**) nor the dimethylphenylcarbenium ion (**8**) persists in 100% H_2SO_4. **8** requires 30% oleum (SO_3/H_2SO_4),[24] and the observation of **7** at all was a triumph of superacid solution chemistry.[25]



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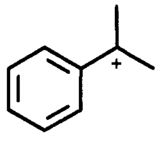

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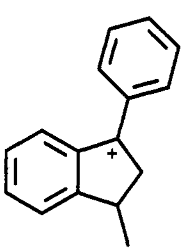
In the present work, neither ion persisted in zeolites HZSM-5 or HY, even when great care was taken to minimize oligomerization reactions. However, the 3-methyl-1-phenylindanyl cation (**9**) formed readily in zeolite HY during the reaction of styrene. Hydride transfer to a transient **7** was invoked to explain the formation of **9**; the analogous 3,3-dimethyl-1-phenylindanyl cation (**10**) did not form during the reaction of α-methylstyrene, and we explain this by the relative difficulty of hydride vs methyl transfer.



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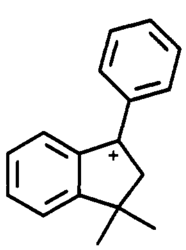

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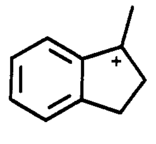
Styrene dimers readily cracked at 373 K to yield the persistent 1-methylindanyl cation (**11**) on HZSM-5. Our inability to detect **11** on HY may reflect the small differences in acid strength between these materials, as the acid strength of **11** is ca. 78% H_2SO_4.[26] Upon further heating, **11** converted to naphthalene; thus **11** is a true reaction intermediate. The analogous 1,3,3-trimethylindanyl cation (**12**) derived from α-methylstyrene formed to a very small extent. The relative extent of formation for **11** vs **12** on zeolite HZSM-5 reflects the fact that the intermediate **11** can fit in ZSM-5 more easily than **12**.



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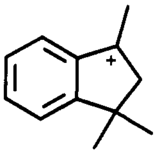

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Thus, the indanyl cations are established as a class of persistent intermediate species in acidic zeolites, but the results presented are further evidence for classifying zeolites as strong acids but not superacids. We suggest that this view of acid strength could be applied predicably to discover other classes of persistent cations. The cumulative evidence of this and other studies would suggest that reactions in acidic zeolites proceed through a continuum of reaction mechanisms with bound species and minor charge separation on one extreme and free or weakly ion paired cations on the other.

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[19] Xu, T.; Munson, E. J.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 1962–1972.

[20] Oliver, F. G.; Munson, E. J.; Haw, J. F. *J. Phys. Chem.* **1992**, *96*, 8106–8111.

[21] Pines, H. *The Chemistry of Catalytic Hydrocarbon Conversions*; Academic Press: New York, 1981; Chapter 1.

[22] Xu, T.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 7753–7759.

[23] Deno, N. C. In *Carbonium Ions*; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1970; Vol. 2, Chapter 18.

[24] Olah, G. A.; Pittman, C. U.; Waack, R.; Doran, M. *J. Am. Chem. Soc.* **1966**, *88*, 1488–1495.

[25] Olah, G. A.; Porter, R. D.; Kelly, D. P. *J. Am. Chem. Soc.* **1971**, *93*, 464–466.

[26] Deno, N. C.; Groves, P. T.; Jaruzelski, J. J.; Lugasch, M. N. *J. Am. Chem. Soc.* **1960**, *82*, 4719–4723.

Experimental Section

Catalyst Preparation and Reagents. Zeolites HZSM-5 (framework Si/Al = 21) and NH_4Y (framework Si/Al = 2.5, N_2 surface area greater than 800 m^2/g) were obtained from UOP Corp. The crystallinity and morphology of the HZSM-5 sample were verified by X-ray diffraction and electron microscopy. The acid site concentration in the HZSM-5 and HY samples was independently checked by several methods including elemental analysis for aluminum, ^{27}Al and ^{29}Si MAS–NMR, quantitative proton NMR, and ^{13}C NMR titrations. H-mordenite was obtained from Shell. Catalysts were activated at 673 K by a procedure described elsewhere[10] and were used within 1 day of activation. [α-^{13}C]styrene (99% ^{13}C), [β-^{13}C]styrene (99% ^{13}C), and [α-^{13}C]-α-methylstyrene (99% ^{13}C) were obtained from Isotec. Styrene (99%), α-methylstyrene (99%), and toluene (99%) were obtained from Aldrich.

Sample Preparation for in Situ MAS-NMR. All the samples were prepared using the shallow bed CAVERN device[27] to ensure a homogeneous distribution of adsorbates on zeolites. Typically, 0.20–0.35 g of zeolite was loaded into a shallow bed CAVERN and activated in vacuo to final pressures of less than 5×10^{-5} Torr. The reactant loadings were typically less than 0.4 equiv on zeolite HY and less than 0.9 equiv on zeolite HZSM-5. The three adsorbates, [α-^{13}C]styrene, [β-^{13}C]styrene, and [α-^{13}C]-α-methylstyrene, were each studied after adsorption at room temperature and following adsorption at reduced temperatures. Liquid nitrogen (77 K), liquid nitrogen/pentane (143 K), and liquid nitrogen/acetone (203–223 K) cold baths were used for adsorptions at cryogenic temperatures. Shallow bed CAVERNs were cooled, and at least 0.5 h was allowed for the catalyst temperature to equilibrate prior to adsorption. The sample was loaded into the rotor after adsorptions, and the rotor was capped. These steps were performed at the temperature of adsorption or lower to avoid warming the samples. The rotor was then transferred to the NMR probe, which had already been cooled to the desired temperature. ^{13}C NMR spectra were then acquired as the probe temperature was raised to progressively higher temperatures.

NMR Spectroscopy. In situ ^{13}C solid state NMR experiments were performed with magic angle spinning (MAS) on a home built spectrometer operating at 50.1 MHz or a Chemagnetics CMX-360 MHz spectrometer operating at 90.5 MHz. Hexamethylbenzene (17.4 ppm) was used as an external chemical shift standard, and all chemical shifts are reported relative to TMS. Chemagnetics-style pencil probes spun 7.5 mm zirconia rotors at 1–6 kHz with active spin speed control.

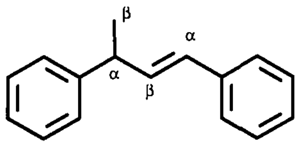
The exact experimental protocol differed from run to run, but in most cases the temperature was raised incrementally, and a variety of ^{13}C spectra were obtained at each temperature. These included the following: cross polarization[28] (CP, contact time = 2 ms, pulse delay = 1 s, 800 transients); cross polarization with interrupted decoupling[29] (contact time = 2 ms, pulse delay = 1 s, 800 transients, dipolar dephasing time of 50 μs); single pulse excitation with proton decoupling (pulse delay = 4–8 s, 200 transients); and single pulse with no proton decoupling (pulse delay = 4–8 s, 200 transients). A different protocol was used in some cases to better characterize the carbenium ions: after heating at a given temperature, the sample was returned to 298 K, and up to 40,000 scans were acquired. This protocol was especially important for measuring chemical shift anisotropy using slow spinning speeds.

Ex Situ Identification. Samples were prepared for ex situ analysis by GC-MS using methods described in ref 19.

Results

Even relatively simple oligomerization reactions on zeolites produce several major products and thus lead to ^{13}C MAS spectra that are initially challenging to assign. In order to identify the neutral dimeric and trimeric compounds present without resort to NMR assignments, we extracted samples with toluene and analyzed them by GC-MS. We have good confidence in this method for zeolite HY, which has a pore size of ca. 0.74 nm, but less confidence in extracts from HZSM-5, which has a channel diameter of ca. 0.55 nm. It must be emphasized that although this ex situ procedure is useful for identifying the major and minor neutral species in the zeolite and thus facilitating the NMR spectral assignments, such analysis cannot identify the carbenium ions that are the primary focus of this investigation.

Extraction showed that the products of styrene dimerization on zeolites at 298 K were identical to those in H_2SO_4 solution,[21,30–35] namely the linear dimer **13** and roughly equal amounts of *cis*- and *trans*-1-methyl-3-phenylindan (**14**).



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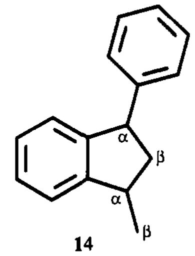

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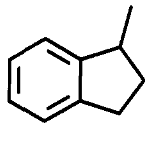
The labels α and β on these structures designate the ^{13}C labeled carbons derived from the corresponding isotopomer of styrene, and these designations are important for understanding the NMR spectra. Small amounts of trimers were also observed by GC-MS. Ex situ analysis also showed that heating to higher temperatures formed 1-methylindan (**15**) and a small amount of naphthalene. The dimers **16** and **17** were identified in extracts of samples derived from the reactions of α-methylstyrene.



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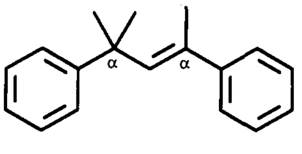

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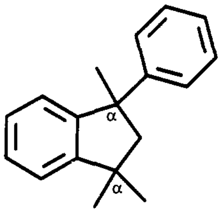

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Table 1 compares isotropic ^{13}C chemical shifts for products in (or on) the zeolites with solution values. These data are also tabulated for all of the cations considered in this investigation; solution values only are presented for the cations that did not form in the zeolites. Further evidence for the assignments of the spectra included the expected response to interrupted decoupling (spectra not shown).

In Situ Studies of Styrene. Figure 1 shows ^{13}C MAS spectra (both CP and Bloch decay) from a study in which [α-^{13}C]styrene was adsorbed on zeolite HZSM-5 and allowed to react as the temperature was raised. At 223 K, most of the adsorbate was unreacted styrene, although a small amount of the dimers **13** and **14** had formed. There was no evidence of the methylphenylcarbenium ion **7**. As the temperature was raised to 298 K, much of the styrene reacted to form the dimer **14**, but some unreacted styrene persisted even at this temperature. The signal for unreacted [α-^{13}C]styrene clearly showed spinning sidebands due

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(27) Munson, E. J.; Murray, D. K.; Haw, J. F. *J. Catal.* **1993**, *141*, 733–736.

(28) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569–590.

(29) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854–5856.

(30) Bertoli, V.; Plesch, P. H. *J. Chem. Soc.* **1968**, 1500–1516.

(31) Risi, P. J.; Gauvin, D. *Can. J. Res. (B)*, **1936**, *14*, 255.

(32) Corson, B. B.; Dorsky, J.; Nickels, J. E.; Kutz, W. M.; Thayer, H. I. *J. Org. Chem.* **1954**, *19*, 17–26.

(33) Calder, I. C.; Lee, W. Y.; Treloar, F. E. *Aust. J. Chem.* **1969**, *22*, 2689–2691.

(34) Taylor, A. R.; Keen, G. W.; Eisenbraun, E. J. *J. Org. Chem.* **1977**, *42*, 3477–3480.

(35) Corson, B. B.; Heintzelman, W. J.; Moe, H.; Rousseau, C. R. *J. Org. Chem.* **1962**, *27*, 1636–1640.

Table 1. Isotropic ^{13}C Chemical Shifts (δ) of Carbons Derived from C_α of the Precursor[h]

	δ (ppm)					δ (ppm)	
	zeolite		solution		carbenium		
neutral compds	C-1	C-3	C-1	C-3	ions	zeolite C-1	solution C-1
styrene[a]	137		136		cation **7**[c]		233
dimer **13**[b]	128	45	129	43	cation **8**[d]		254
dimer **14**	50	39			cation **9**	221	225[f]
α-methylstyrene[a]	141		142		cation **11**	251[e]	252[g]
dimer **16**		39			cation **12**	252	252[g]
dimer **17**[b]	51	43	51	43			
naphthalene[a]	129		128				

[a] Solution values are from ref 36. [b] Solution values are from ref 37. [c] Reference 25. [d] Reference 38. [e] On zeolite HZSM-5. [f] This is the ^{13}C chemical shift of 1-aryl-1-(4′-methylphenyl)-1-ethyl cation reported in ref 39, a model compound for cation **9**. [g] This is the ^{13}C chemical shift of 1,3-dimethylindanyl cation reported in ref 40, a model compound for cations **11** and **12**. [h] Solution values are from the literature and zeolite values are from HY unless noted otherwise.

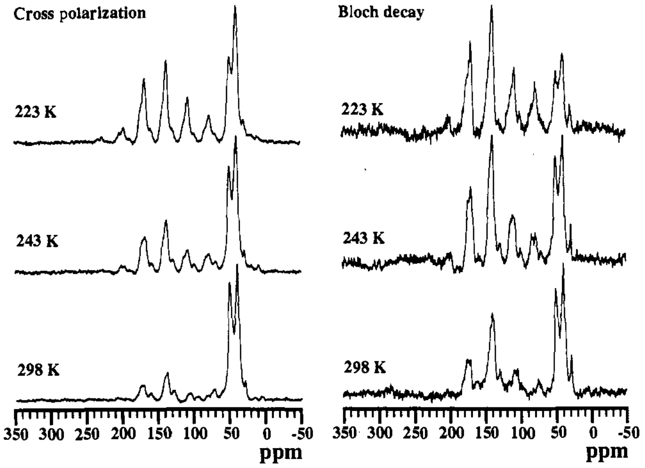

Figure 1. In situ 90.5-MHz ^{13}C MAS–NMR studies of the reactions of [α-^{13}C]styrene on zeolite HZSM-5 following adsorption at 213 K. Both Bloch decay and CP spectra are shown. The spectra at 223 K show the unreacted styrene (137 ppm) and **14** (50 and 39 ppm). Several orders of spinning sidebands associated with the unreacted styrene were seen. A small amount of ethylbenzene (29 ppm) was also formed at this temperature. Upon raising the temperature through 243 to 298 K, a large amount of **14** formed at the expense of styrene. A weak resonance at 128 ppm in both the CP and Bloch decay spectra indicates the existence of **13**.

to unaveraged chemical shift anisotropy, so the styrene must have been in a restricted environment. We speculate that it was trapped in the channels by dimer molecules and was thus unable to assume a favorable orientation for oligomerization reactions.

Figure 2 shows ^{13}C MAS Bloch decay spectra of [α-^{13}C]styrene on zeolite HY at low temperature. The larger pore size and hence freer mass transport in this zeolite was reflected in the fact that more than 90% of the styrene reacted at 223 K. The products at this temperature were primarily the dimers **13** and **14**. Those assignments of the carbons derived from C_α are in Table 1; the major C_β assignments are C_{Me} of **13** and **14,** 20 ppm; C_2 of **14**, 42 ppm; C_2 of **13**, 135 ppm.

The most interesting feature in Figure 2 is the isotropic peak in the C_α spectrum at 221 ppm and its associated spinning sidebands. This chemical shift is in excellent agreement with the solution values for diphenylmethylcarbenium ions.[39,41–43] This peak was very reproducible. The products in Figure 2 were stable indefinitely at room temperature. The only possible assignments for this ion are resonance stabilized carbenium ion **9** or hydroxy carbenium ions (cf. Scheme 1); the latter possibility can be excluded, because no oxygen was present in the adsorbate. The peak at 29 (C_α) and 15 ppm (C_β) combined with the GC-MS data for the extracts shows that a near stoichiometric amount of ethylbenzene formed with the carbenium ion.

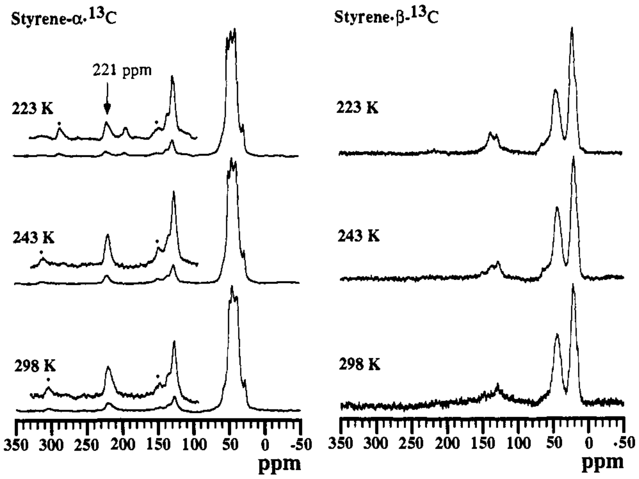

Figure 2. In situ 50.1-MHz ^{13}C MAS–NMR studies of the reactions of [α-^{13}C]styrene and [β-^{13}C]styrene on zeolite HY following adsorption at 213 K; only the Bloch decay spectra are shown, and asterisks denote spinning sidebands associated with the 221 ppm resonance. The conversion of styrene (137 ppm in α-^{13}C and 128 ppm in β-^{13}C) was almost complete even at 223 K. The products were **13** (45 and 128 ppm in α-^{13}C, 20 and 142 ppm in β-^{13}C), **14** (50 and 39 ppm in α-^{13}C, 42 and 20 ppm in β-^{13}C), and some ethylbenzene (29 ppm in α-^{13}C and 15 ppm in β-^{13}C). A downfield shift at 221 ppm in the α-^{13}C spectra indicates the formation of cation **9**. The spectra at higher temperatures show similar features.

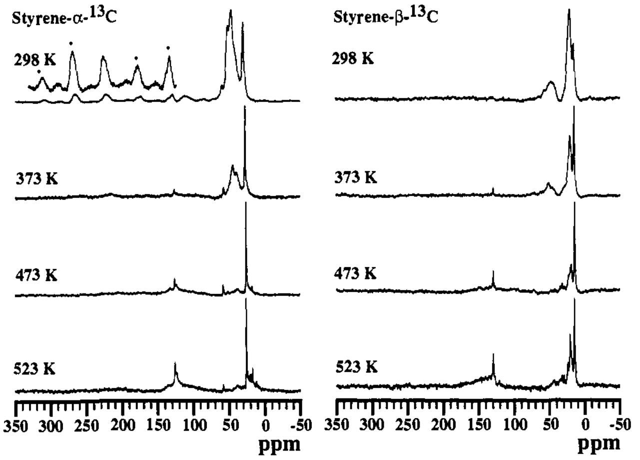

Figure 3. In situ 90.5-MHz ^{13}C MAS–NMR studies of the reactions of [α-^{13}C]styrene and [β-^{13}C]styrene on zeolite HY following adsorption at 298 K; only the Bloch decay spectra are shown, and asterisks denote the spinning sidebands of the 221 ppm resonance. The spectra at 298 K show **14** (39 ppm in α-^{13}C and 42, 20 ppm in β-^{13}C), ethylbenzene (29 ppm in α-^{13}C and 15 ppm in β-^{13}C), and **9** (221 ppm). **9** and **14** readily decomposed upon heating. The final products at 523 K were mostly ethylbenzene and naphthalene (129 ppm in the spectra of both isotopomers). The formation of coke was indicated by the humps in the 110–140 ppm regions for both isotopomers.

Figure 3 shows high temperature studies of [α-^{13}C]styrene and [β-^{13}C]styrene on zeolite HY. The spectra at 298 K are different from those in Figure 2, because secondary reactions were favored by performing the adsorption without a cryogen bath, and the yields of the carbenium ion **9** and ethylbenzene were higher. The relative integrated signal intensity for the 221 ppm peak and its sidebands indicates that 16% of the dimers were ionized, and this works out to 0.01 equiv relative to the number of acid sites. Heating these samples to 523 K produced mixtures of ethylbenzene, naphthalene, and other aromatics, but no additional carbenium ions were observed.

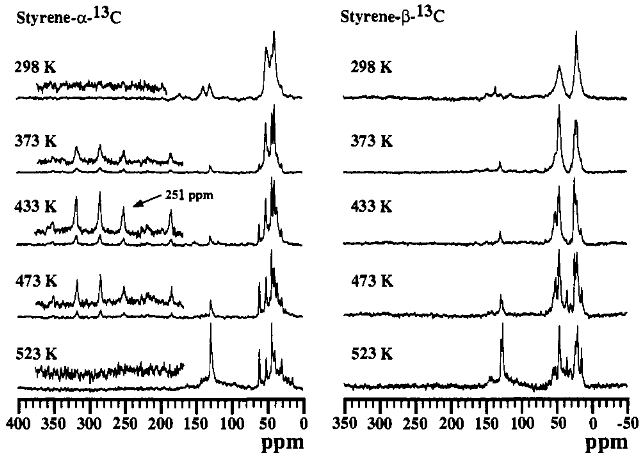

Figure 4. In situ 90.5-MHz ^{13}C MAS-NMR studies of the reactions of [α-^{13}C]styrene and [β-^{13}C]styrene on zeolite HZSM-5 following adsoption at 298 K. Only the Bloch decay spectra are shown. The spectra at 298 K show the formation of a small amount of **13** (128 ppm in α-^{13}C) and **14** (50 and 39 ppm in α-^{13}C, 42 and 20 ppm in β-^{13}C). The α-^{13}C spectra acquired at 373, 433, and 473 K show a resonance at 251 ppm as well as the associated spinning sidebands; this indicates the formation of 1-methylindanyl cation (**11**). The complexity in the aliphatic regions (10–50 ppm) in the spectra of the both isotopomers implies that cracking reactions were important at high temperatures. The resonances at 129 ppm reflect the formation of naphthalene.

Figure 4 shows high temperature studies of [α-^{13}C]styrene and [β-^{13}C]styrene on zeolite HZSM-5. Cracking of dimers began at 373 K, and a new carbenium ion with an isotropic ^{13}C shift of 251 ppm formed. The intensity of this signal decreased at higher temperatures coincident with the formation of naphthalene. The chemical shift of 251 ppm is in good agreement with that for methylindanyl cation;[40] therefore, this resonance was assigned to **11**. In a duplicate experiment with [α-^{13}C]styrene on HZSM-5, the sample was heated to 433 K for 0.5 h, and quantitative Bloch decay spectrum (not shown) was acquired. The integrated intensity of the 251 ppm peak and its spinning sidebands indicates that 21% (0.21 equiv) of the acidic sites of HZSM-5 were charge compensated by carbenium ion **11**.

α-Methylstyrene. No carbenium ions were observed in the low temperature studies of α-methylstyrene dimerization; Figure 5 shows a representative result for zeolite HY. In this case the reactant was stable at 153 K and formed the linear dimer **16** at 193 K which cyclized to **17** as the temperature was raised to ambient. The cations **8** and **10** did not form in this experiment, and they did not form in analogous experiments with H-mordenite or HZSM-5 or when [α-^{13}C]-α-methylstyrene and $^{13}CH_3Br$ were coadsorbed on HY.

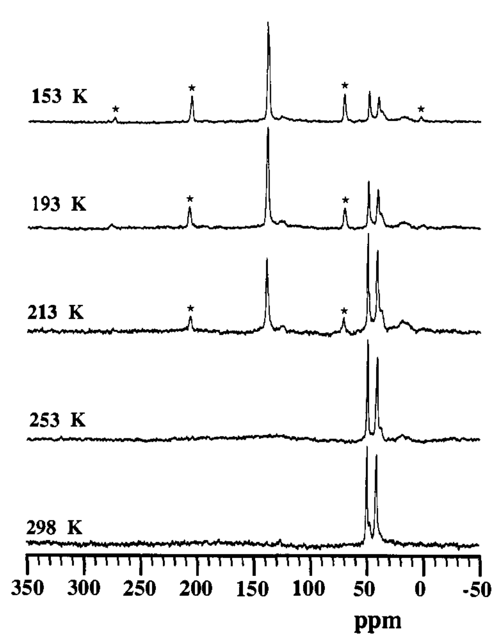

Figure 5. In situ 50.1-MHz ^{13}C MAS-NMR studies of the reactions of [α-^{13}C]-α-methylstyrene on zeolite HY following adsorption at 143 K (Bloch decay spectra are shown). The spectrum at 153 K shows unreacted α-methylstyrene (141 ppm) and **17** (51 and 43 ppm). The conversion of α-methylstyrene to **17** was complete upon raising the temperature to 253 K.

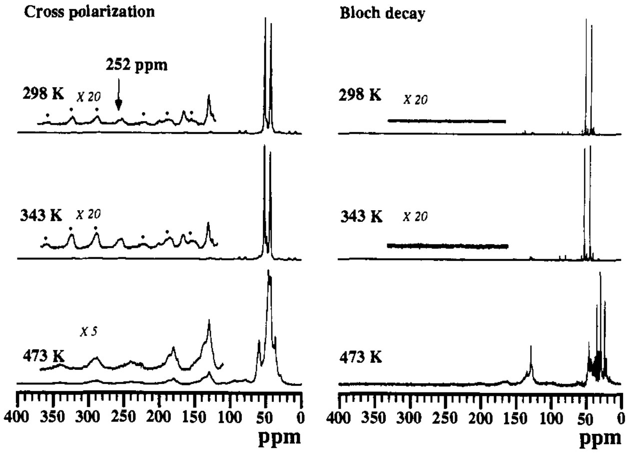

Figure 6. In situ 90.5-MHz ^{13}C MAS-NMR studies of the reactions of [α-^{13}C]-α-methylstyrene on zeolite HY following adsorption at 298 K; both the CP and Bloch decay spectra are shown, and asterisks denote spinning sidebands of the 252 ppm resonance. All the spectra were acquired at room temperature after heating at the indicated temperatures for 30 min. The CP and Bloch decay spectra were the average of 4000 and 200 scans, respectively. **17** (51 and 43 ppm) dominated the products below 343 K. A very small amount of indanyl cation **12** (252 ppm in the CP spectra) was detected. **12** decomposed completely after heating at 473 K. A mixture of hydrocarbons formed from cracking reactions at high temperatures.

Figures 6 and 7 show the high temperature reactions of [α-^{13}C]-α-methylstyrene on zeolites HY and HZSM-5, respectively. The major product on both zeolites at 298 K was the dimer **17**. This product cannot easily fit into the channels of HZSM-5, and we speculate that it formed outside the pores of the zeolite, perhaps by reacting at acid sites in pore mouths. Small signals corresponding to an isotropic peak at 252 ppm, and a number of spinning sidebands were seen when many scans were acquired using cross polarization to emphasize rigid species. This resonance indicates a very low yield of the cation **12**.

^{13}C Chemical Shift Anisotropies (CSA) of Cations 9 and 11. Figure 8 shows slow speed spectra of samples derived from [α-^{13}C]-styrene on zeolites HY and HZSM-5. The samples were prepared such that the yields of cations **9** (Figure 8a,b) and **11** (Figure

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(36) Breitmeier, E.; Haas, G.; Voelter, W. In *Atlas of Carbon-13 NMR Data*; Heyden & Son Ltd.; London, 1979.

(37) The ^{13}C chemical shift values of **13** (CAS registry No. 7302-01-4) and **17** (CAS registry No. 3910-35-8) in $CDCl_3$ were obtained from the SPECINFO database, which was produced by Chemical Concepts GmbH, P.O. Box 100202, W-6940 Weinheim, F.R. Germany.

(38) Olah, G. A.; Westerman, P. W.; Nishimura, J. *J. Am. Chem. Soc.* **1974**, *96*, 3548–3559.

(39) Brown, H. C.; Periasamy, M.; Perumal, P. T.; Kelly, D. P.; Giansiracusa, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 6300–6305.

(40) Olah, G. A.; Asensio, G.; Mayr, H. *J. Org. Chem.* **1978**, *43*, 1518–1520.

(41) Olah, G. A.; Liang, G. *J. Org. Chem.* **1975**, *40*, 2108–2116.

(42) Ancian, B.; Membrey, F.; Doucet, J. P. *J. Org. Chem.* **1978**, *43*, 1509–1518.

(43) Olah, G. A.; Surya Prakash, G. K.; Liang, G.; Westerman, P. W.; Kunde, K.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 4485–4492.

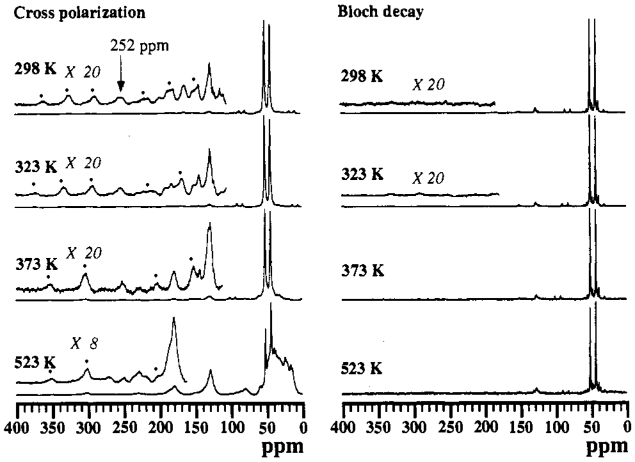
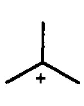


Figure 7. In situ 90.5-MHz ^{13}C MAS–NMR studies of the reactions of [α-^{13}C]-α-methylstyrene on zeolite HZSM-5 following adsorption at 298 K; both CP and Bloch decay spectra are shown, and the spinning sidebands of the 252 ppm resonance are indicated by asterisks. All the spectra were acquired at room temperature after heating for 30 min at the indicated temperatures. The CP spectra were the average of 2000 scans except for spectra at 298 and 323 K, which were the average of 10 000 and 20 000 scans, respectively. The Bloch decay spectra were the average of 200 scans except for the 298 and 323 K spectra, which were the average of 800 and 4000 scans, respectively. The dominant species at all the temperatures was **17** (51 and 43 ppm). A very small amount of indanyl cation **12** (252 ppm in CP spectra) was detected. The spinning speeds were intentionally varied and are listed below: 298 K, 3150 Hz; 323 K, 3800 Hz; 373 and 523 K, 4500 Hz.

8c,d) were appreciable. The relative sideband intensities were nearly identical in the CP vs Bloch decay spectra; the former were used in Herzfeld–Berger analyses[44] to determine the principal components of the chemical shift tensors for the three-coordinate carbons, and these are reported in Table 2. Anisotropic chemical shift measurements for carbenium ions are scarce. The principal component values for the *tert*-butyl cation (**18**)[45] and tropylium cation (**19**)[46] were reported in the literature, and we recently reported the values for cation **6**.[22]



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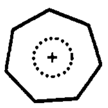

19

The localized cation **18** has a 450 ppm CSA and an asymmetry parameter (η) of 0, as it must for threefold symmetry. The delocalized allylic cation **6** has a CSA of 246 ppm and appreciable asymmetry; the CSA value is intermediate between the value for a localized charge (450 ppm)[45] and an olefinic carbon (ca. 141 ppm).[47] As shown in Table 2, the CSA values as well as the isotropic shifts reflect the degree of charge delocalization. Thus, the CSA of the tropylium cation **19** is significantly smaller than the phenylindanyl cation **9**, and the CSA of **9** is smaller than that of **11**.

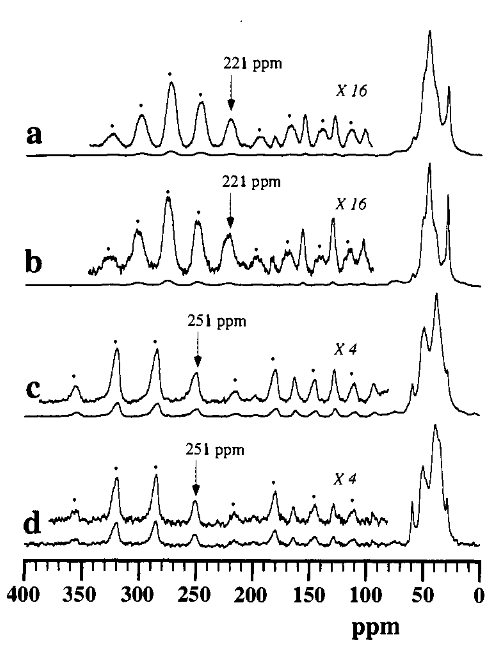

Figure 8. Selected 90.5-MHz ^{13}C MAS-NMR spectra showing some features of the 221 ppm (**9**) and 251 ppm (**11**) resonances. Adsorptions and spectral acquisition were performed at room temperature. Spectra a and b were acquired after adsorption without heating. Spectra c and d were acquired after the sample was heated at 433 K for 30 min. The spinning sidebands associated with the 221 and 251 ppm resonances are indicated by asterisks. (a) and (b): CP and Bloch decay spectra of [α-^{13}C]-styrene on HY, respectively, showing the spinning sidebands of 221 ppm resonance (2400 Hz spinning speed). (c) and (d): CP and Bloch decay spectra of [α-^{13}C]styrene on HZSM-5, respectively, showing the spinning sidebands of the 251 ppm resonance (3150 Hz spinning speed). Slow spinning speeds were used for maximum accuracy in the determination of the CSA data in Table 2.

Table 2. Summary of the Chemical Shift Anisotropies and Isotropic Peaks for *tert*-Butyl Cation **18**, Tropylium Ion **19**, Cyclopentenyl Cation **6**, and Indanyl Cations **9** and **11**

carbenium ions	principal components (ppm)			CSA (ppm)	η	isotropic peak (ppm)
	δ_{11}	δ_{22}	δ_{33}			
18[a]	450	450	0	450	0.0	300
11	359	320	76	263	0.2	251
6[b]	375	290	86	246	0.5	250
9	310	286	68	230	0.2	221
19[c]	280	168	22	203	0.8	157

[a] Reference 45. [b] Reference 22. [c] Reference 46.

Discussion

Simple Phenylcarbenium Ions. Neither **7** nor **8** were observed directly as persistent species at detectable concentrations in HZSM-5 or HY, in spite of our best efforts to adsorb very low loadings of olefins onto shallow catalyst beds at low temperature. Zeolite H-mordenite was also studied in the hope that the isolated channels[48] of this material would protect the simple cations from oligomerization, but this was without success. A second strategy to reduce mass transport, coadsorption of [^{13}C]methyl bromide, was similarly unsuccessful.

The simplest explanation for the failure to observe **7** and **8** and the presence of unreacted olefins in the zeolites at low temperature is that the zeolites studied here are not sufficiently strong acids to protonate styrene or α-methylstyrene to a measurable equilibrium concentration.

Phenylindanyl Cations. Dimerization of styrene occurred at low temperature to yield predominantly the neutral cyclic dimer **14** rather than a carbenium ion. The ion **9** was observed in appreciable yield when [α-^{13}C]styrene was adsorbed on zeolite HY and was accompanied by a near-stoichiometric amount of [α-^{13}C]ethylbenzene (Scheme 2). [β-^{13}C]Ethylbenzene was a coproduct of the corresponding reaction of the β-isotopomer of styrene. This strongly suggests that the phenylindanyl cation **9** formed as a secondary reaction through hydride abstraction from

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(44) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021–6030.

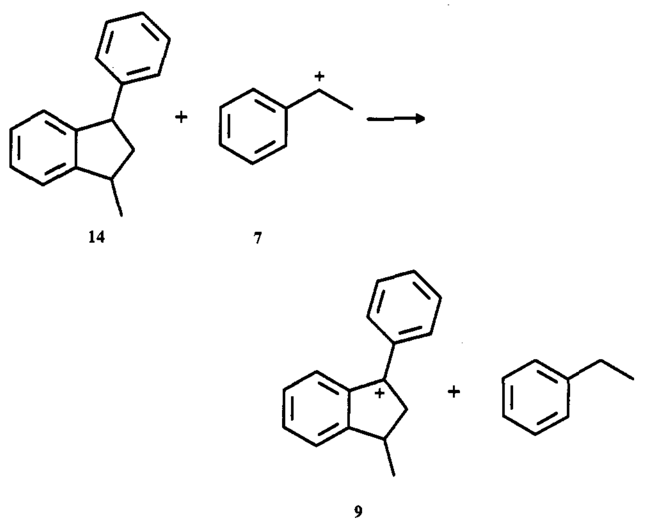
(45) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 201–208.

(46) Strub, H.; Beeler, A. J.; Grant, D. M.; Michl, J.; Cutts, P. W.; Zilm, K. W. *J. Am. Chem. Soc.* **1983**, *105*, 3333–3334.

(47) Duncan, T. M. *A Compilation of Chemical Shift Anisotropies*; The Farragut Press: Chicago, 1990; p c-4.

(48) Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry, and Use*; Wiley: New York, 1973; p 123.

Scheme 2



the dimer **14** by a transient (i.e., not observed) methylphenylcarbenium **7**. We infer the existence of **7** as a reaction intermediate but cannot say whether it exists in very low steady state concentration as a free carbenium ion or as an equivalent species stabilized by the zeolite.

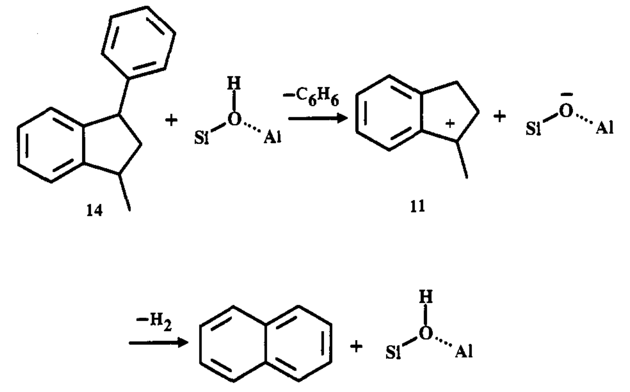
The phenylindanyl cation **10** should be at least as stable as **9** in zeolite HY, but it was never observed during the reactions of [α-^{13}C]-α-methylstyrene, nor was much [α-^{13}C]isopropylbenzene or [α-^{13}C]-*tert*-butylbenzene formed in these reactions. Hydride abstraction from the dimer **17** is not facile, and intermolecular methyl transfer is much more difficult than hydride transfer. Thus the reaction analogous to Scheme 2 did not occur in the reactions of α-methylstyrene *due to the differences in kinetic barriers*, in spite of the expected stability of the carbenium ion **10**.

Neither phenylindanyl cation accumulated in zeolite HZSM-5, in spite of the slightly higher acidity of this zeolite. This is certainly a consequence of the smaller channel sizes of HZSM-5. The cation **9** might fit in some locations in ZSM-5, but hydride abstraction from **14** by **7** is precluded by channel size.

Methylindanyl Cations. The styrene dimer **14** readily cracked with mild heating to form an appreciable amount of the 1-methylindanyl cation **11** on HZSM-5. Very low yields of the cation **12** were obtained when the dimer of α-methylstyrene was heated on HZSM-5 or HY. The low yield of **12** on HZSM-5 reflects the steric demands of the bulkier cation in the narrow zeolite channels. In the case of zeolite HY, we speculate that the very low yield of **12** and complete failure to detect **11** reflect the fact that HY is slightly less acidic than HZSM-5.

Implications for Zeolite Acid Strength. We have previously estimated that the acid strength of zeolite HZSM-5 is equivalent to that of ca. 70% H_2SO_4, while that of the HY sample used here is slightly lower, perhaps 65% H_2SO_4.[19] All of the observations in the present study are in reasonable agreement with this view. It is known that superacid solutions are required to stabilize the simple phenylcarbenium ions **7** and **8**,[24] and these cations did not form as persistent species in the zeolites. Deno's measurements of the equilibria for protonation of olefins in H_2SO_4 solutions showed that the cation **9** was half formed in 67–71% H_2SO_4.[49] Thus **9** is only slightly less stable than the trityl cation, which was half formed in 50% H_2SO_4.[50] Even without a phenyl substituent, the planarity of indanyl cations ensures their stability.[51] Deno determined that the cation **11** was half formed in 78% H_2SO_4.[26] Accepting all of the numbers in this paragraph uncritically does suggest an explanation for the appreciable, but incomplete, formation of **11** in HZSM-5 and its far lower yield in HY. *Although the above agreement may be a little too good to be true in an absolutely quantitative sense, all of the results of this study are in complete agreement with our view that zeolites are strong acids and not superacids. This realization is a powerful organizing principle for explaining and even predicting the occurrence or nonoccurrence of carbenium ions and other analogous species such as onium ions*[52,53] *as species at high equilibrium concentration in zeolites.*

Scheme 3



Implications for the Mechanism of Cracking Reactions on Zeolites. Textbook zeolite mechanisms make generous use of three-coordinate carbenium ion and five-coordinate carbonium intermediates based on the assumed analogy to superacid solution chemistry and the usual indirect evidence of product distributions and fates of labels. A recent communication[54] in this journal has seriously questioned the formation of carbonium ions in zeolites and invoked an alternate mechanism for acid catalyzed reactions of alkanes in zeolites. The present investigation did not treat the question of carbonium ions, but our revised view of acid strength must be considered in proposals for free carbonium ion mechanisms. Recent theoretical work[4] suggests that hydrogen scrambling in methane requires the participation of zeolite lattice oxygens, and this is consistent with our view that zeolites are not sufficiently strong acids to protonate an alkane to make a *free* carbonium ion.

Scheme 3 shows the species that we actually observed in the reaction by which styrene was converted to naphthalene on zeolite HZSM-5, and this could well be the clearest and most direct evidence for a free carbenium ion intermediate ever put forth for a zeolite catalyzed reaction. Not all reaction intermediates will be so cooperative as to persist at high concentrations long enough for their NMR spectra to be acquired, so free carbenium ions less stable than the indanyl cation **11** must surely be intermediates in some reactions in acidic zeolites. Scheme 2 certainly suggests the indirect detection of the less stable carbenium ion **7** through a hydride abstraction reaction, but this result is not definitive for a free ion.

It has previously been suggested that reactions on acidic catalysts might display a continuum of reaction mechanisms,[55] with free ions and stepwise reactions on one extreme and bound

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(49) Deno, N. C.; Groves, P. T.; Saines, G. *J. Am. Chem. Soc.* **1959**, *81*, 5790–5795.

(50) Deno, N. C.; Jaruzelski, J. J.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3044–3054.

(51) Olah, G. A.; Pittman, C. U. In *Advances in Physical Organic Chemistry*; Gold, V., Ed.; Academic Press: New York, 1966; pp 340–341.

(52) Munson, E. J.; Haw, J. F. *J. Am. Chem. Soc.* **1991**, *113*, 6303–6305.

(53) Munson, E. J.; Kheir, A. A.; Haw, J. F. *J. Phys. Chem.* **1993**, *97*, 7321–7327.

(54) Sommer, J.; Hachoumy, M.; Garin, F.; Barthomeuf, D. *J. Am. Chem. Soc.* **1994**, *116*, 5491–5492.

(55) Gates, B. C.; Kazer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw Hill: New York, 1979; p 28.

species and concerted processes on the other. Just as previous NMR studies[12] have clarified the bound methoxy groups at one end of the continuum, the present study has established the existence of free ions on the opposite extreme. This study has characterized a second class of persistent carbenium ions in zeolites, and these indanyl ions are both more interesting and mechanistically more significant than the previously characterized cyclopentenyl cations. Although the ultimate goal of zeolite mechanistic studies, characterization of the transition state and the influence of catalyst structure on its energy and geometry, will require a substantial theoretical effort, it is the belief of the authors that experimental characterization of the relatively stable species formed by pre-equilibria will continue to be an important contribution to this goal.

Acknowledgment. We acknowledge the support of U.S. Department of Energy (Grant No. DE-FG03-93ER14354).