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Synthesis of a Benzenium Ion in a Zeolite with Use of a Catalytic Flow Reactor

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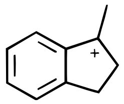
The observation and mechanistic significance of carbenium ions in acidic zeolites is one of the central problems in heterogeneous catalysis.[1−3] Early speculation included suggestions of superacidic zeolites and carbenium intermediates of all types. It is now generally recognized that zeolite acid strength is more in line with conventional strong acids, and the characterization of a long-lived, free carbenium ion within a zeolite is a rare achievement. Previously, only three types of long-lived carbenium ions have been unambiguously identified in zeolites, mostly by ^{13}C solid-state NMR with magic angle spinning.[4−9] In 1989 Haw et al. identified alkyl-substituted cyclopentenyl cations similar to **1** which formed in the low-temperature reactions of propene on zeolite HY.[4] Cyclopentenyl cations have since been shown to form on several zeolites from a variety of olefins and their precursors.[5,6,9] In 1994 Xu and Haw[7] identified several indanyl cations, including **2**, which formed from styrene on zeolite HZSM-5. In 1995 Tao and Maciel[8] synthesized the trityl cation, $(C_6H_5)_3C^+$, in zeolite HY from the Friedel−Crafts reaction of CCl_4 and benzene. Cano et al. recently reported the synthesis of several trityl cation derivatives inside zeolites Y and β.[10] Previous NMR studies of carbenium ions in zeolites (and many similar, but unsuccessful, attempts) used sample preparation methods that differ in significant ways from the conditions used in catalytic flow reactors. In particular, the organic precursor(s) and the zeolite were invariably sealed such that nothing could escape the zeolite.

1



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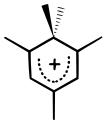

3

We prepared the benzenium cation **3** in zeolite HZSM-5 by a novel experimental procedure. The key to the preparation of **3** was the use of flow reactor conditions for sample preparation;[11] we pulsed an aromatic hydrocarbon and an excess of methanol onto a zeolite bed at 573 K with continuous He carrier gas flow, allowed them to react for 4 s, and then rapidly quenched the sample temperature to ambient. In a flow reactor, the coproduct (water) diffuses out of the zeolite crystallites and is swept out of the sample by carrier gas, leaving cation **3** trapped in the zeolite. Our various attempts to observe **3** in sealed MAS NMR rotors were uniformly unsuccessful; in the presence of water the equilibrium concentration of **3** in the zeolite is negligible.

We synthesized **3** in zeolite HZSM-5 a number of times, pulsing either benzene or toluene into the flow reactor with methanol, and we permuted the ^{13}C label in the reactants as an aid to spectral assignment. Representative ^{13}C MAS spectra showing **3** prepared from various precursors are summarized in Figure 1. Signals due to the cation were also enhanced by cross polarization (not shown). Verification of the identity of **3** was obtained with theoretical methods and by comparison with ^{13}C shifts of model carbenium ions such as heptamethylbenzenium ion.[12] We optimized the geometry of **3** at the B3LYP[13] level using the 6-311G** basis set[14] and the program NWChem.[15] GIAO-MP2[16] ^{13}C chemical shifts were determined with the tzp (C) and dz (H) basis sets[17] by using ACES II.[18] The C_s form of **3** is shown in Figure 2. The C_s conformer is less than 0.1 kcal/mol above that of the C_1 global minimum; these structures are interconverted by rotation of methyl group C-7. Differences in other internal coordinates between the two conformers are negligible. The GIAO-MP2 calculations were tractable only for the C_s conformer. The geminal methyl groups C-7 and C-8 are nonequivalent according to theory, but this is not observed experimentally due to dynamical averaging of these geminal methyl groups at 298 K. The agreement between the observed (Figure 1) and predicted shifts for **3** (caption to Figure 2) is at least as good as seen for other benzenium cations,[19] and given the exotic chemical shifts of benzenium cations, this agreement is powerful evidence for the proposed assignment.[20] The observed shifts are also in line with experimental values for heptaalkylbenzenium cations in solution.[12,21]

It is noteworthy that the formation of cation **3** occurs not by protonation, but rather by alkylation. This is consistent with our

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(11) In brief, samples were prepared by using a device we call a "pulse-quench catalytic reactor" that will be described in detail elsewhere. It is much like a standard benchtop flow reactor equipped for pulsed introduction of reagents, and differs primarily in the extensive use of computer-controlled valves to rapidly reduce the temperature of the gas flowing over the catalyst. A very rapid thermal quench is probably not essential for the observation of **3**, and we anticipate that replication of this result could be achieved by the diligent application of standard flow reactors. Quenched samples are sealed in the reactor, and transfer of the catalyst to MAS rotors is carried out in a glovebox; thus, once prepared, samples of zeolite containing **3** were not exposed to moisture.

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(20) Other evidence for the assignment is the result of dipolar dephasing experiments conducted at both ambient and low temperatures (not shown) which confirm that C-2, C-4, and C-6 are substituted. This result requires two substituents for sp^3-hybridized carbon C-2 (58 ppm).

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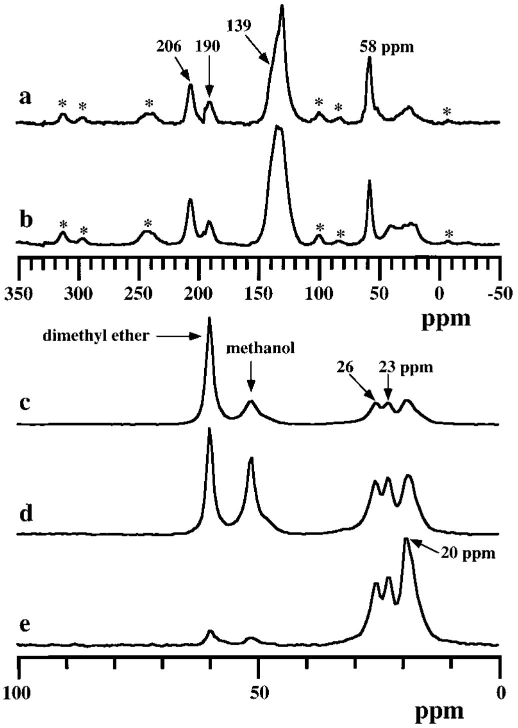

Figure 1. Selected 75.4 MHz ^{13}C MAS spectra of benzenium ion **3** (206, 190,139, 58, and incompletely resolved signals between 23 and 26 ppm) on zeolite HZSM-5 (Si/Al = 19). Signals near 20 ppm are due to the methyl carbons of neutral aromatic compounds, e.g., toluene and xylenes. Benzene or toluene and methanol were injected into the flow reactor as a pulse and allowed to react for 4 s at 573 K before quench: (a) 0.5 equiv of benzene-$^{13}C_6$ and 3 equiv of methanol-^{12}C; (b) 0.5 equiv of toluene-*ring*-$^{13}C_6$ and 2.5 equiv of methanol-^{12}C; (c) 0.5 equiv of benzene and 3 equiv of methanol-^{13}C; (d) 0.5 equiv of toluene and 2.5 equiv of methanol-^{13}C; and (e) 0.5 equiv of toluene-α-^{13}C and 2.5 equiv of methanol-^{12}C. 1 equiv on this catalyst corresponds to 0.58 mmol reactant/g of zeolite. An asterisk denotes spinning sideband.

recent observation that the benzenium ion $C_6H_7^+$ is not a stable state for benzene H/D exchange on acidic zeolites.[22] In the absence of water or another nucleophilic adsorbate, decomposition of **3** in the zeolite would require *methylation* of the conjugate base site on the zeolite framework. Therefore, the thermodynamic reference state for evaluating the stability of *gem*-dialkylbenzenium cations in zeolites is not a neutral complex of the proton form of the zeolite but rather of the methyl (methoxyl) form of the zeolite.

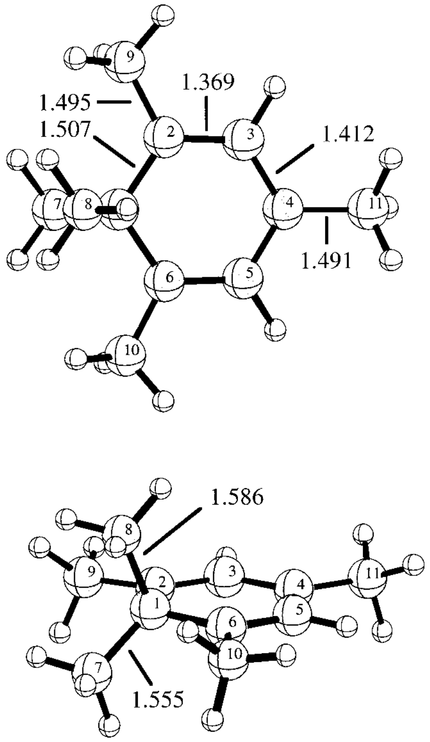

Figure 2. B3LYP/6-311G** geometry of **3** optimized in C_s symmetry. Selected internal coordinates are shown (in Å). The angle C-7 to C-1 to C-4 is 113.9°, C-8 to C-1 to C-4 is 137.4°, and C-8 to C-1 to C-7 is 108.7°. Theoretical ^{13}C isotropic chemical shifts are calculated at GIAO-MP2/tzp/dz and referenced to TMS at the same level of theory (absolute shielding = 198.8 ppm): C-1, 65 ppm; C-2 and C-6, 209 ppm; C-3 and C-5, 139 ppm; C-4, 191 ppm; C-7, 23 ppm; C-8, 35 ppm; C-9 and C-10, 28 ppm; C-11, 29 ppm.

A recent mechanistic study of the economically important process of toluene disproportionation in HZSM-5 proposed key roles for benzenium cations;[23] those cations were somewhat different from the cation reported here, but the observation of **3** suggests that theoretical and additional experimental studies of benzenium ion mechanisms in zeolite catalysis might be important. We believe that **3** forms in the channel intersections of HZSM-5, which are more spacious than the channels themselves, and that steric constraints account for the substitution pattern in which C-4 and C-6 are not alkylated.

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