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Synthesis of the heptamethylbenzenium cation in zeolite-β: *in situ* NMR and theory

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We synthesized the heptamethylbenzenium cation on zeolite-β by co-feeding excess methanol and benzene into a flow rector at 250 °C. Experimental isotropic ^{13}C chemical shifts are in excellent agreement with theoretical (GIAO-MP2/tzp/dz) values calculated for the theoretical (B3LYP/6-311G*) structure of the cation. These results, along with a previous study of the pentamethylbenzenium cation on HZSM-5, afford an example of zeolite topology controlling the substitution pattern of persistent carbenium ions.

KEY WORDS: zeolite solid acids; persistent carbenium ions; *in situ* NMR; GIAO; theoretical calculations; methanol conversion.

1. Introduction

In situ NMR [1,2] has identified several types of carbenium ions that are indefinitely persistent on acidic zeolite catalysts. Cyclopentenyl cations, typified by the 1,3-dimethylcyclopentenyl cation **1**, were first identified on zeolite HY [3] and have been extensively studied on zeolite HZSM-5 [4–7]. The indanyl cation **2** was synthesized on zeolite HZSM-5 [8]. Tao and Maciel [9] prepared the trityl cation, $(C_6H_5)_3C^+$, on HY.

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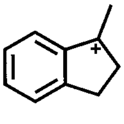

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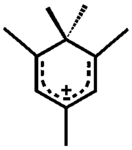

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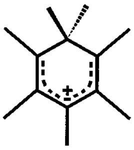

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More recently we used a pulse-quench reactor to prepare the 1,1,2,4,6-pentamethylbenzenium cation **3** in zeolite HZSM-5 by the reaction of an excess of methanol with either benzene or toluene [10]. The essential feature of the pulse quench reactor that was necessary for observation of cation **3** was the use of gas flow as in a conventional catalytic reactor; the gas flow stream carried the co-product water away, which would otherwise have hydrolyzed the cation in a reverse reaction to generate methanol and tetramethylbenzene. The assignment of the NMR spectrum to cation **3** was established in part by the use of theoretical chemistry. We optimized the structure of this cation using density functional theory at the B3LYP/6-311G** level and then modeled the ^{13}C chemical shifts using the GIAO-MP2 method [11]. Excellent agreement was observed between the theoretical shifts and those measured for the reaction product in zeolite HZSM-5. Cation **3** has an unusual substitution pattern—ring positions 3 and 5 are not substituted. This was reflected experimentally in the observation that the signal due to those carbons did not survive in a dipolar dephasing (interrupted decoupling) experiment. Also this assignment was consistent with the theoretical shifts. In our paper reporting the synthesis of cation **3** [10], we speculated that this unusual substitution pattern was the result of steric constraints in zeolite HZSM-5. We concluded that even in the more spacious channel intersections of HZSM-5, complete methylation of the aromatic ring to form the heptamethylbenzenium cation **4** would be precluded.

In the present contribution we test that conclusion by using similar methods to synthesize a benzenium cation in zeolite H-β. The BEA topology of H-β also features intersecting channels, but these are 12-ring channels compared with the smaller 10-ring channels of HZSM-5 (MFI topology). As we hoped, the reaction of benzene with excess methanol in a flow reactor produced the heptamethylbenzenium cation **4** as confirmed by *in situ* NMR measurements on the quenched catalyst, as well as theoretical calculations. This is an excellent example of how different zeolite frameworks can stabilize carbenium ions with subtly different structures.

2. Experimental

2.1. *Materials and reagents*

Zeolite-β (Si/Al = 13) was obtained from Zeolyst International and pressed into pellets. Zeolite HZSM-5

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(Si/Al = 19, 30% alumina binder) was obtained from UOP. Benzene-$^{13}C_6$ was obtained from Cambridge Isotopes Inc. and methanol-^{13}C was obtained from Isotec. Two solutions were prepared for this study; in each case one of the labeled compounds was mixed with the other compound at natural abundance, to a final concentration of 1 mol benzene to 10 mol methanol.

2.2. *Catalysis*

Experiments were performed using a pulse quench reactor [12] with a motor-driven syringe pump as described previously [13]. For each experiment a bed consisting of 0.3 g of catalyst was activated at 400 °C in the reactor under 600 sccm He flow for 2 h immediately prior to use. This carrier gas feed rate was also used during introduction of the methanol/benzene solutions. The catalyst bed was equilibrated at 250 °C and then 100 μl of methanol/benzene solution was delivered at a rate of 50 μl min^{-1} to form reaction products in the zeolite. Immediately upon completion of solution introduction, the catalyst temperature was quenched to ambient. The reactor was then sealed off and transferred into a glove box filled with nitrogen. Catalyst pellets were ground and transferred to either a 7.5-mm or 5-mm MAS rotor (as dictated by spinning speed requirements) which were sealed with Kel-F end-caps.

2.3. *NMR spectroscopy*

^{13}C solid state NMR experiments were performed with magic angle spinning (MAS) on a Varian Infinity plus 300 MHz spectrometer operating at 75.4 MHz for ^{13}C. Hexamethylbenzene (17.4 ppm) was used as an external ^{13}C chemical shift standard. Chemagnetics-style pencil probes were used. Typical ^{13}C experiments included: cross polarization (CP, contact time = 2 ms, pulse delay = 1 s, 4000 transients) and cross polarization with interrupted decoupling (contact time = 2 ms, pulse delay = 1 s, 4000 transients, dipolar dephasing time of 50 μs).

2.4. *Theoretical methods*

We optimized the geometry of the heptamethylbenzenium cation **4** using density functional theory. We used the B3LYP hybrid exchange-correlation functional [14] and the 6-311G* basis set [15]. The minimum energy geometry has one of the hydrogens of the methyl in the 5 position eclipsing the ring, whereas the other two are above and below the ring, giving C_1 symmetry. In order to make the NMR calculations (see below) tractable, we rotated the methyl group 90° to give the molecule C_s symmetry. The change in energy associated with this rotation is negligible.

We then calculated the ^{13}C isotropic chemical shifts using the GIAO method at the MP2 level [11]. We and others have previously found that GIAO-MP2 calculations with Ahlrichs' polarized triple-zeta basis set on C (tzp) and a double-zeta basis set on H (dz) [16] give good predictions of carbon chemical shifts in carbenium ions. Unfortunately, due to program limitations we were not able to treat the entire molecule at this level. Instead, we performed one calculation in which the ring carbons were represented by tzp, the methyl carbons were represented by dzp, and all hydrogens were treated with the dz basis set. We then did a second calculation in which tzp was used on methyl carbons, dzp on ring carbons, and dz on hydrogens. The results reported are those for which the carbons under consideration were treated at tzp; thus all the ring carbon results are from one calculation, while the methyl carbon shifts are from a second calculation. The values are reported relative to those of TMS, calculated at the GIAO-MP2/tzp/dz//B3LYP/6-311G* level of theory. All of the calculations were done with Gaussian98 [17]. The GIAO-MP2/tzp/dz ^{13}C chemical shifts for the pentamethylbenzenium cation **3** discussed here for comparison are from our earlier work [10]. In that case the full GIAO-MP2 calculation was tractable with C_s symmetry imposed.

3. Results

3.1. *NMR experimental evidence*

Figure 1 reports representative ^{13}C CP/MAS NMR spectral results for the products in zeolite-β following reaction of benzene-$^{13}C_6$ and excess methanol in the quench reactor as described above. The spectra are essentially identical with or without dipolar dephasing, indicating that all carbon atoms are either mobile or substituted so as to not have any directly attached hydrogens. Mobile species could include unreacted benzene, methylbenzenes that readily tumble in the spacious channels of β, or methyl groups which undergo internal rotation. For the results in figure 1, only the ring carbons were labeled with ^{13}C, and there is no evidence from the spectra for label exchange between ring and methyl positions here. Thus, methyl groups are not visible in figure 1.

The most intense signals in figure 1 are at 130 and 139 ppm, and these are in good agreement with the ^{13}C shifts of neutral methyl benzenes, especially xylenes and toluene. For example, the shift of the substituted ring carbon of toluene is 138 ppm, and the remainder cluster near 128 ppm. The shoulder near 132 ppm suggests that more highly substituted methylbenzenes (durene, hexamethylbenzene) are also present. Four less intense signals in figure 1 have remarkable chemical shifts: 199, 191, 152 and 58 ppm. These are assigned below to the heptamethylbenzenium cation **4**, and it is central to this contribution to establish that the results are not consistent with the pentamethylbenzenium cation **3**. Using methods identical

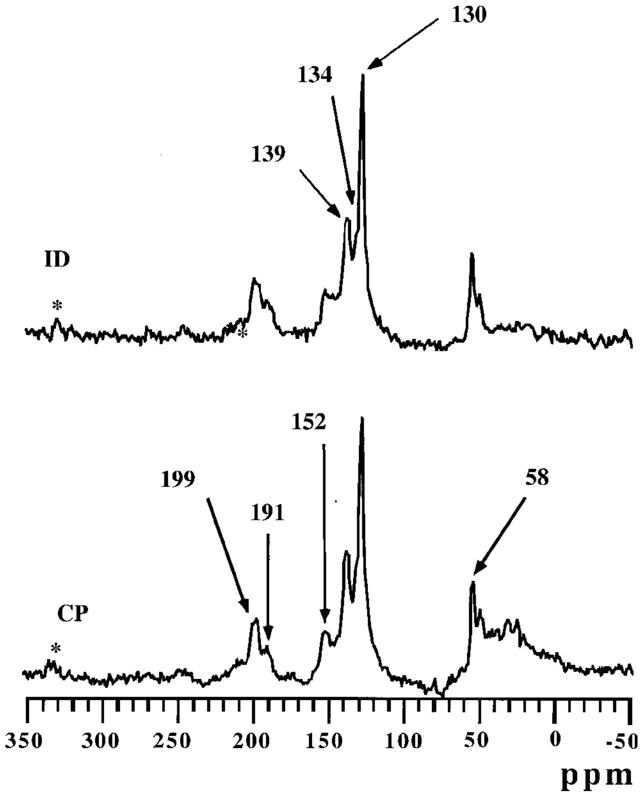

Figure 1. Selected 75.4 MHz ^{13}C MAS spectra of the ring carbons of the heptamethylbenzenium ion **4** (199, 191, 152 and 58 ppm) on zeolite H-β. Signals between 130 and 139 ppm are due to the ring carbons of neutral aromatic compounds. Benzene-$^{13}C_6$ and an excess of methanol were flowed onto the catalyst bed with helium flow and allowed to react at 250 °C before quench. Both cross polarization (CP) and interrupted decoupling (ID) spectra are shown. ∗ denotes spinning sideband.

to those used for figure 1, we reacted benzene-$^{13}C_6$ and excess methanol in zeolite HZSM-5 and obtained the ^{13}C NMR spectra in figure 2. This result is identical to our earlier paper [10]; here we focus on several similarities and differences between figures 1 and 2. On HZSM-5 (figure 2) we see a signal at 206 ppm instead of that at 199 ppm (figure 1, zeolite-β). The 152-ppm signal in figure 1 (H-β) is not seen in figure 2 (HZSM-5). Both figures show signals at ∼190 ppm and sharp signals at 58 ppm. Thus, two very distinct differences are apparent in the two figures—the signal at 152 ppm in figure 1 (for which no comparable feature is resolved in figure 2), and the signal at 199 ppm (figure 1) or 209 ppm (figure 2).

For completeness, we also reacted unlabeled benzene and excess methanol-^{13}C in H-β to obtain products in the zeolite with labeled methyl groups; that result is reported in figure 3, which is not nearly so informative as with labeled ring carbons. The most intense signals are from unreacted methanol (50 ppm) and dimethylether (60 ppm). Figure 1 told us that the reaction products in H-β included a variety of methylbenzenes, and this is reinforced by the upfield signals in figure 3. This region is too poorly resolved to provide any definitive assignment information, but methyl signals are present over a broad range (for this functional group), and this range does include all of the chemical shifts expected for cation **4** on the basis of either solution state experiments or theoretical calculations (see below).

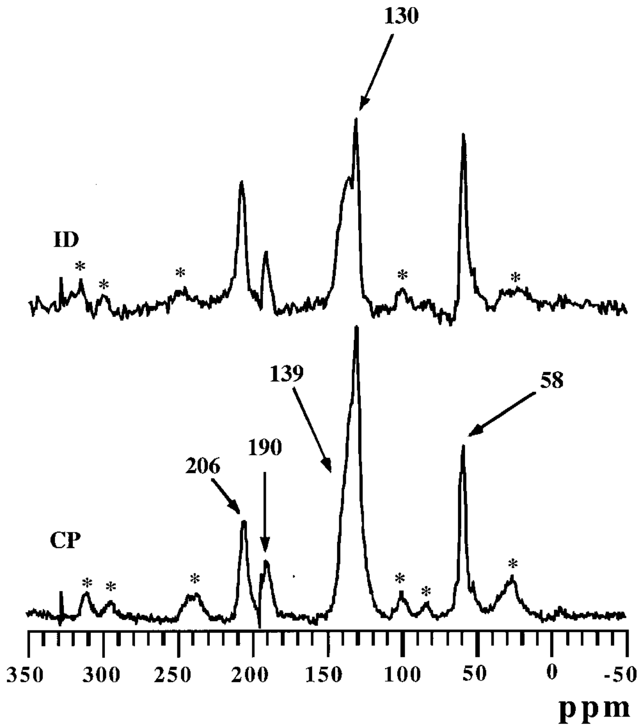

Figure 2. Selected 75.4 MHz ^{13}C MAS spectra of the ring carbons of the pentamethylbenzenium ion **3** (206, 190 and 58 ppm) on zeolite HZSM-5. Signals between 130 and 139 ppm are due to the ring carbons of neutral aromatic compounds, as well as one unresolved signal from the cation. Benzene-$^{13}C_6$ and an excess of methanol were flowed onto the catalyst bed with helium flow and allowed to react at 250 °C before quench. Both cross polarization (CP) and interrupted decoupling (ID) spectra are shown. ∗ denotes spinning sideband.

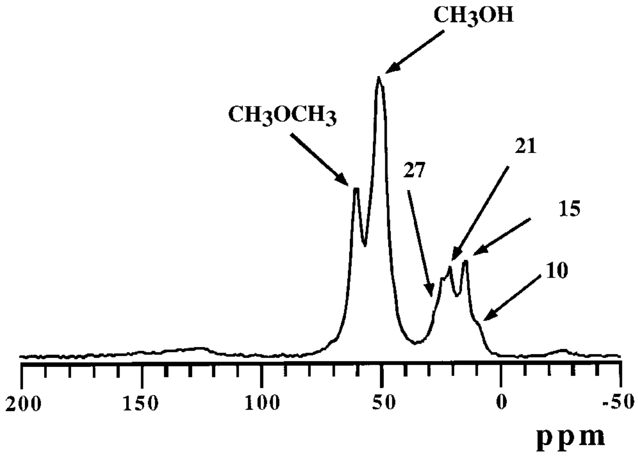

Figure 3. Selected 75.4 MHz ^{13}C MAS spectra of the methyl carbons from an experiment similar to that of figure 1. Signals from cation **4** are dominated by unreacted methanol, dimethylether, and neutral methylbenzenes adsorbed on zeolite H-β. Benzene and an excess of methanol-^{13}C were flowed onto the catalyst bed with helium flow and allowed to react at 250 °C before quench.

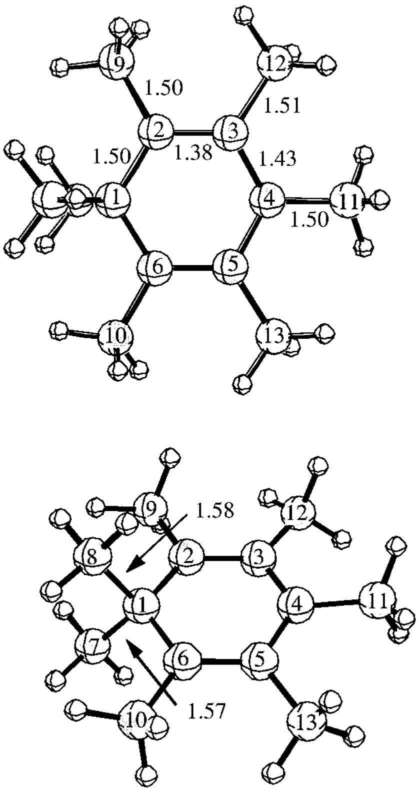

Figure 4. B3LYP/6-311G* optimized geometry of the heptamethylbenzenium cation **4**. Selected internal coordinates (in Å) are shown. The C-7 to C-1 to C-4 angle is 130.0°, the C-8 to C-1 to C-4 angle is 120.3°, and the C-7 to C-1 to C-8 angle is 109.7°. Thc MP2 isotropic ^{13}C chemical shifts are: C-1, 64 ppm, C-2 and C-6, 201 ppm, C-3 and C-5, 147 ppm, C-4, 190 ppm, C-7, 21 ppm, C-8, 25 ppm, C-9 and C-10, 24 ppm, C-11, 25 ppm, C-12 and C-13, 17 ppm.

3.2. Theoretical results

The optimized geometry of the heptamethylbenzenium cation is given in figure 4. Selected C–C bond lengths (in Å) are shown. The geometry of cation **4** is largely similar to that of cation **3** [10]; the bond lengths are the same within 0.01 Å. In both cases the bonds between C-2 and C-3 and between C-5 and C-6 are shorter, consistent with their expected double bond character. The bonds to C-1 have lengths indicative of single bonds. The most significant difference is in the angles C-7 and C-8, where methyls form with the ring. In the pentamethyl cation **3**, C-7 forms an out-of-plane angle of 66.1°, whereas the angle is 42.6° for C-8. In the heptamethyl cation **4** these angles are more similar: 50.0° for C-7 and 59.7° for C-8.

The predicted ^{13}C chemical shifts for the heptamethylbenzenium cation are reported in the caption of figure 4. Agreement between theory and experiment was as good for the heptamethyl cation **4** (figure 1) as was obtained previously [10] for the pentamethyl cation **3** (experimental results in figure 4). We focus first on C-2,6 and C-3,5. For cations **3** and **4**, theory predicts C-2,6 shifts of 209 and 201, respectively. Figure 1 shows a signal at 199 ppm that is in good agreement with the theoretical result for **4** but not for **3**. For C-3,5, theory predicts 147 ppm for cation **4** and 139 ppm for cation **3**. Thus, the 152 ppm signal in figure 1 is consistent with the theoretical result for the heptamethyl cation **4**, but not that for the pentamethyl cation **3**. For cation **3** we previously predicted a C-3,5 shift of 139 ppm [10]; this shift will not be resolved from those of the substituted ring carbons of the neutral methylbenzenes which dominate this spectral region in figure 2.

For C-4, theory predicts almost identical shifts for cation **3** (191 ppm) and cation **4** (190 ppm). Such a peak is seen experimentally in both figures 1 and 2. Theory also predicts near-identical shifts for the lone sp^3 hybridized ring carbon C-1, 65 ppm for **3** and 64 ppm for **4**. Here for cation **4**, as noted before for cation **3** [10], agreement is not so good—the experimental shift is 58 ppm in each case. The theoretical methyl shifts for cation **4** range from 17 to 25 ppm, and the experimental spectrum in figure 3 embraces all of the theoretical values.

4. Discussion

This study clearly shows that the benzenium cation formed from benzene and methanol on zeolite H-β is different from that formed on HZSM-5 under otherwise identical conditions. Using the same combination of experiment and theory that established the assignment of the pentamethyl cation **3** in HZSM-5 [10], we here establish the assignment of cation **4** in H-β. The largest discrepancy between theoretical and experimental ^{13}C shifts for cation **4** (6 ppm) was for C-1; for cation **3** we earlier reported a 7 ppm discrepancy for the analogous carbon. While we do not have an explanation for the theory's difficulty in modeling this shift, we note that this carbon is located in an environment with unusually strong steric clashes, and we had an even greater discrepancy of this sort for analogous dimethyl-substituted carbons on the heptamethylcyclopentenyl cation, which we synthesized in HSAPO-34 [18]. In any event, the ^{13}C shifts of **4** in the zeolite are also similar to those for this cation in superacid solution [19], and the discrepancy is thus more likely a limitation of the theoretical method than a consequence of the zeolitic environment. Overall, the agreement between theory and experiment is satisfactory, but it is necessary to note that chemical shifts calculated from this type of model may not always agree this well with experiment.

We have not here established or claimed any mechanistic significance for benzenium cations in zeolite catalysis. However, Mole and co-workers [20,21] reported that toluene is a "co-catalyst" for the conversion of methanol to hydrocarbons on zeolite HZSM-5, and they proposed a mechanism for this chemistry featuring somewhat different benzenium cation intermediates. We have recently verified the influence of toluene in methanol conversion on HZSM-5 [6] and established that methylbenzenes are reaction centers for methanol to olefin catalysis on HSAPO-34 [22]. Kolboe and Dahl [23,24] have proposed that methanol conversion on HZSM-5 and HSAPO-34 occurs on "hydrocarbon pool" species that could include carbenium ions.

5. Conclusions

We have shown that benzenium cations forming in aluminosilicate zeolites have degrees of methyl substitution controlled by the topology of the pore system. The heptamethyl cation **4** forms in zeolite H-β while zeolite HZSM-5 directs formation of the less bulky pentamethyl cation **3**. Further study of possible roles for benzenium cations in methanol to hydrocarbon reactions appears warranted.

Acknowledgments

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