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The Prediction of Persistent Carbenium Ions in Zeolites

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One of the most exciting and fundamental developments in heterogeneous catalysis has been the rapid progress in the characterization of persistent carbenium ions and related charged species on solid acids by NMR.[1] Recent work has made it clear that a wide variety of electrophilic species can be prepared as long-lived species on metal halide powders,[2] and one can draw analogies between these materials and liquid superacids.[3] This comparison is much more challenging for persistent carbenium ions on zeolites, the most important solid acid catalysts.[4,5] While previous reports have recognized that the persistent carbenium ions observed in zeolites are among the more easily prepared cations in acidic solutions and other low nucleophilic environments, there has been no previous attempt at a quantitative understanding of persistent carbenium ion formation in the context of the gas-phase properties relevant to zeolite catalysis.

Here we focus on cations that can in principle or in fact be formed by protonation of an olefinic or aromatic hydrocarbon. There have been many published attempts to observe persistent carbenium ions including the isopropyl, allyl, *tert*-butyl, and styryl cations in acidic zeolites—most of these attempts were either completely unsuccessful or resulted in larger persistent cations formed by oligomerization and secondary reactions.

Persistent carbenium ions derived from olefins that have been convincingly characterized in zeolites are of three types: Cation **1b** (Figure 1) is the simplest example of the indanyl cations shown to persist in a zeolite.[6] The parent olefin of **1b** is **1a**, 1-methylindene. Indanyl cations were synthesized in acidic zeolites by dimerization of styrene followed by straightforward rearrangements and eliminations. Cation **2b** is an example of the alkyl-substituted cyclopentenyl cations which very commonly form in acidic zeolites.[7−10] Cylopentenyl cations have been synthesized in zeolites by the extensive reaction of simple olefins including propene, the more straightforward reactions of cyclopentene or cyclopentanol, and very complex reactions such as the conversion of methanol to hydrocarbons on zeolites. **2b** can formally be obtained by protonation of 1,3-dimethylcyclopentadiene, **2a**. Finally, cation **3b** is the first benzenium-like species identified in a zeolite;[11] it was synthesized by the extensive alkylation of benzene with methanol. Protonation of **3a**, 1,5,6,6-tetramethyl-3-methylenecyclohexa-1,3-diene, a known compound, would also produce **3b**. A fundamental question is why these species are observed in zeolites, while the many other carbenium ions mentioned above are not.

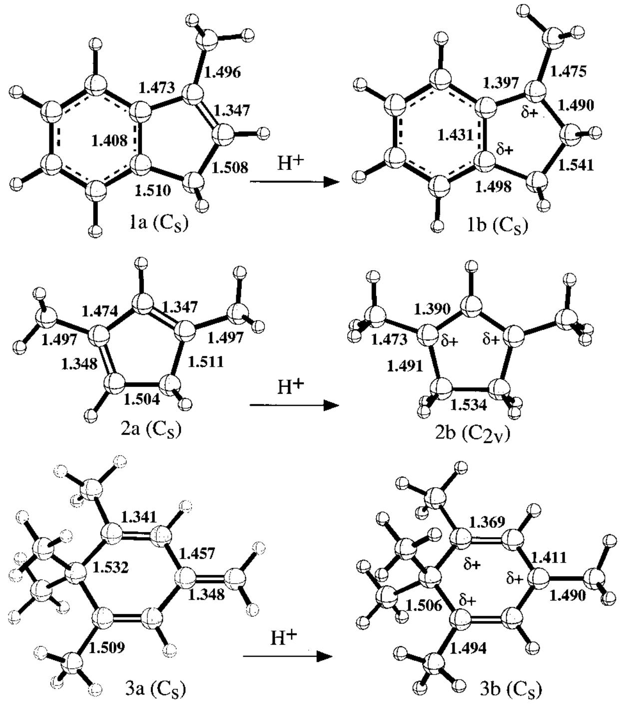

Figure 1. B3LYP/TZVP optimized geometries of olefins **1a**−**3a** and corresponding carbenium ions **1b**−**3b**. Selected bond distances (Å) and point group symmetries are indicated. Distances related by symmetry are not shown. Bond orders are graphically shown only for the parent olefins, for which the assignment is unambiguous. The positively charged carbons (determined by a Mulliken population analysis) of the carbenium ions are labeled.

Here we apply theoretical chemistry to explain the entirety of positive and negative observations of persistent carbenium ions from hydrocarbons on zeolites. Table 1 lists proton affinities (PA's) for a wide variety of olefins and aromatics. Experimental data[12] are presented when available. Theoretical PA's are presented when experimental data are unavailable, and for several of the smaller molecules to demonstrate the accuracy of the predicted values. The theoretical PA's are generally 1−2 kcal/mol less than the experimental measurements. For each case studied theoretically, optimized geometries were obtained by using density functional theory (DFT) with the B3LYP[13] hybrid exchange-correlation functional and the TZVP[14] basis set. Frequency calculations of all species were done to verify that the geometries were minima on the potential energy surface and to obtain zero-point and thermal corrections (298.15 K) for the determination of the PA. The frequencies were scaled by 0.95 to correct for anharmonicity. Single-point energies were then calculated at the MP4(SDTQ)/6-311+G* level with the B3LYP/TZVP geometries. We found that this extensive treatment of

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Table 1. Experimental and Theoretical Proton Affinities (kcal/mol) of Parent Hydrocarbons[a]

parent compound	exptl[b]	MP4/6-311+G*//B3LYP/TZVP[c]
benzene	179.3	178.3
propene	179.6	177.4
cyclopentene	183.0	181.3
allene	185.3	185.0
toluene	187.4	186.0
2-methylpropene	191.7	192.5
m-xylene	193.8	
styrene	200.3	
hexamethylbenzene	205.7	
α-methylstyrene	206.4	
1-methylindene (**1a**)*		209.8
1,3-dimethylcyclopentadiene (**2a**)*		215.6
1,5,6,6-tetramethyl-3-methylene-cyclohexa-1,3-diene (**3a**)*		227.4
pyridine*	222.0	219.1

[a] The PA for pyridine is also reported for comparison. An asterisk denotes compounds that persist as protonated species in acidic zeolites. [b] Experimental PA's from ref 12. [c] Electronic energy corrected for zero-point and thermal contributions.

electron correlation was necessary to obtain reasonably accurate predictions of the proton affinities. We used Gaussian94[15] for the DFT optimizations and frequency calculations, whereas the MP4 single points were obtained with MolPro.[16,17] Figure 1 reports theoretical geometries of olefins **1a**−**3a** and corresponding carbenium ions **1b**−**3b**, none of which have been previously studied theoretically.

Inspecting Table 1, one immediately understands why some carbenium ions persist in zeolites and others do not. The olefins which formally parent the persistent cations **1b**−**3b** are strong gas-phase bases, in one case having a predicted PA greater than that of pyridine, which is unambiguously protonated in typical acidic zeolites.[18] In contrast, all of the olefins which fail to yield persistent carbenium ions by protonation (without oligomerization) have lower proton affinities. For example, propene's PA value is more than 40 kcal/mol lower than that of olefin **2a**. Thus, when propene is adsorbed on zeolites[7] NMR spectra do not show the isopropyl cation, but rather a framework-bound alkoxy species and complex oligomerization and hydrogen transfer products, including **2b**. Cations **1b**−**3b** may be too large to approach the zeolite framework and form alkoxy species, and other cations sufficiently large to be persistent will probably have similar steric requirements.

Simply put, it appears that formation of a persistent carbenium ion in an unmodified zeolite requires that the parent compound have a PA of approximately 209 kcal/mol or more. The deprotonation energy of zeolite acid sites is in the range of 284−318 kcal/mol. Proton transfer and zwitterion formation can occur with an adsorbate PA of only ca. 209 kcal/mol due to the electrostatic stabilization provided upon ion-pair formation. The experimental PA's of azulene (221.1 kcal/mol) and 1,1-diphenylethylene (211.7 kcal/mol) indicate that these aromatic hydrocarbons also would form persistent carbenium ions in zeolites, suggesting new areas of experimental investigation. Protonation of the latter precursor would form the 1,1-diphenylethyl cation, which is similar to the trityl cation, known to form in zeolites by chloride abstraction.[19]

In summary, we have demonstrated that whether a given carbenium ion will persist in a zeolite can be predicted from the PA of the parent hydrocarbon. The persistent cations so far observed form from olefins with PA's similar to or higher than that of pyridine. Consideration of the PA's for a wide range of hydrocarbons suggests that few additional examples of such cations will be forthcoming, but guides us in the selection of possible targets. Coadsorption of solvents[20] or Lewis acids can modify the acid−base properties of zeolites. In this investigation, we have restricted ourselves to carbenium ions that persist indefinitely in unmodified zeolites at low or moderate temperatures. *Some* carbenium ions that are less stable than the limit reported here will doubtless have a transient existence as short-lived species in zeolites,[21] especially at higher temperatures.

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Supporting Information Available: Tables listing atomic coordinates for olefins **1a**, **2a**, and **3a** and carbenium ions **1b**, **2b**, and **3b** (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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