

# N-Alkyltrilium Cations in Zeolites: A Study Using Theoretical Chemistry and in Situ NMR with the Pulse-Quench Reactor

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Stepanov and Luzgin recently applied solid-state NMR with magic-angle spinning (MAS) to the reactions of acetonitrile with olefins or alcohols in zeolite HZSM-5 at 296 K and observed signals they assigned to *N*-alkyltrilium cations (*Chem. Eur. J.* **1997**, 3, 47). Here we report strong verification of their assignment and show that these cations can also form in catalytic flow reactors. We used the recently developed pulse-quench reactor to contact acetonitrile and either *tert*-butyl alcohol or isobutylene for several seconds at temperatures up to 433 K followed by a rapid thermal quench.  $^{13}\text{C}$  and  $^{15}\text{N}$  MAS NMR measurements were performed at 77–298 K to identify the species present in the zeolite and to permit determination of the principal components of the chemical shift tensors. We optimized the geometry of the *N*-*tert*-butylacetoneitrilium cation and acetonitrile using density functional theory at B3LYP/DZVP2 and then calculated theoretical chemical shift tensors using the GIAO-MP2 level of theory and two basis set schemes. Essentially quantitative agreement was obtained between theoretical and experimental  $^{13}\text{C}$  principal components for the nitrile carbon tensor, and the agreement for the  $^{15}\text{N}$  tensor was almost equally good.

There has been much recent progress in the development of in situ NMR<sup>1,2</sup> and its application to the study of reaction mechanisms in zeolite catalysis. Traditional in situ experiments require adsorbing one or more reagents onto a catalyst and then sealing the sample in a magic-angle spinning (MAS) rotor. Spectra can then be acquired as the sample is progressively heated in the NMR probe. Such methods have been used to identify a variety of reactive intermediates in zeolites including framework alkoxy species,<sup>3</sup> persistent cyclopentenyl<sup>4</sup> and indanyl<sup>5</sup> carbenium ions, and oxonium<sup>6</sup> ions. Recently, Stepanov used similar NMR methods in a very creative way to make the first identification of *N*-alkyltrilium cation intermediates, e.g. **1**, in zeolites.<sup>7</sup> Stepanov reacted acetonitrile with either an olefin (oct-1-ene) or alcohol (*tert*-butyl alcohol) to give cation intermediates which upon subsequent reaction with water afforded *N*-alkylamides as in the Ritter reaction well-known in solution chemistry.

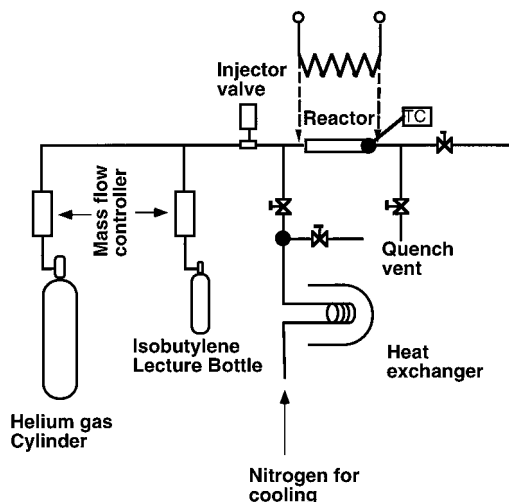
Very recently, we developed the pulse-quench catalytic reactor, which permits NMR studies of catalyst samples prepared under actual reaction conditions.<sup>8</sup> The pulse-quench reactor operates with pulsed introduction of one or more reactants and continuous removal of products. An essential feature of this reactor is that the sample temperature can be reduced very rapidly (quenched) to preserve a catalyst sample prepared under transient conditions at much higher temperatures. Using the pulse-quench reactor, we studied the mechanism of methanol-to-gasoline chemistry on zeolite HZSM-5 by  $^{13}\text{C}$  MAS NMR with a time resolution as short as 200 ms.<sup>9</sup> Product removal by gas flow is also a significant feature of the pulse-quench system, and this was central to our observation of the hydrolytically unstable pentamethylbenzenium cation, which was trapped in the channel intersections of HZSM-5 during alkylation of

benzene or toluene with methanol.<sup>10</sup> This species could not be observed using traditional in situ methods, because the coproduct of the alkylation reaction, water, does not escape the sealed rotor.

As an early application of the pulse-quench reactor, we were drawn to Stepanov's report of *N*-alkyltrilium cations.<sup>7</sup> This synthetic target presented several instrumental challenges and opportunities for the further development of the reactor. We easily reproduced Stepanov's observation of cation **1** by co-injecting acetonitrile and *tert*-butyl alcohol onto a zeolite HZSM-5 bed at 433 K and allowing reaction to occur for 8 s prior to a rapid quench to 298 K. We also modified the quench reactor to permit quasi-continuous injection of gases and then synthesized **1** by co-introduction of acetonitrile- $^{15}\text{N}$  and isobutylene. In the latter experiments, we were able to obtain **1** with sufficient selectivity to permit measurement of the principal components of the  $^{13}\text{C}$  and  $^{15}\text{N}$  chemical shift tensors of the nuclei linked by the triple bond.

Theoretical chemistry has proven to be very useful as an aid in the assignment of exotic species proposed from NMR studies of catalysis.<sup>1,11,12</sup> We optimized the geometry of **1** using density functional theory at B3LYP/DZVP2 and then calculated theoretical chemical shift values using the GIAO-MP2 level of theory<sup>13</sup> and two basis set schemes. This level of theory has repeatedly proven to be reliable for  $^{13}\text{C}$  shifts of carbenium ions and other challenging cases, and we were not disappointed here—theory and experiment agree very closely not only for the isotropic  $^{13}\text{C}$  shift of **1** but also for the principal components of the chemical shift tensor. Somewhat to our surprise, the calculated  $^{15}\text{N}$  shift tensors were also in very good agreement with experiment, especially when the basis set on nitrogen was augmented with diffuse functions. We consider the agreement between theory and experiment to be indisputable evidence of Stepanov's assignment.

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**Figure 1.** Schematic of the pulse-quench catalytic reactor in the configuration used to react acetonitrile and isobutylene. Labeled acetonitrile (either  $1\text{-}^{13}\text{C}$  or  $^{15}\text{N}$ ) was introduced using a pulse injection valve, and unlabeled isobutylene was introduced using a mass flow controller. For the reactions using *tert*-butyl alcohol, this reagent was introduced using a second pulse injection valve (not shown).

## Methods Section

**Catalyst Preparation and Reagents.** Zeolite HZSM-5 (Si/Al = 21) pellets that contain 30% alumina binder were obtained from UOP Corp. Acetonitrile- $1\text{-}^{13}\text{C}$  (99%  $^{13}\text{C}$ ) and acetonitrile- $^{15}\text{N}$  (99%  $^{15}\text{N}$ ) were obtained from Cambridge Isotopes. *tert*-Butyl alcohol (99%), 2-propanol (99.5%), *n*-pentene (99%), and isobutylene (99%) were purchased from Aldrich.

**Sample Preparation for MAS NMR.** We used our recently developed pulse-quench reactor<sup>8</sup> to prepare samples for MAS NMR studies. The pulse-quench reactor employed is essentially a fixed bed microflow reactor. Helium was used as the carrier gas, the flow rate of which was 600 sccm (standard cubic centimeters per minute). The catalyst was activated by heating at 573 K for 1 h under flowing He in the reactor immediately prior to use. Acetonitrile and *tert*-butyl alcohol were introduced in pulse mode by the use of injection valves as in ref 9. Figure 1 shows the configuration of the reactor for pulsed injection of acetonitrile followed by quasi-continuous introduction of isobutylene. One essential feature of the pulse-quench reactor is that the temperature of the catalyst bed can be rapidly lowered to ambient temperature a short time after reactant introduction.

After thermal quench, the reactor was sealed off and removed to a drybox under a nitrogen atmosphere with an  $\text{H}_2\text{O}$  concentration of less than 0.3 ppm. The catalyst was packed into a 7.5 mm MAS rotor, and the rotor was sealed off with a Kel-F endcap. At no time was any of the samples exposed to atmospheric moisture.

**NMR Spectroscopy.**  $^{13}\text{C}$  and  $^{15}\text{N}$  solid-state NMR experiments were performed with magic-angle spinning on a modified Chemagnetics CMX-300 MHz spectrometer operating at 75.4 MHz for  $^{13}\text{C}$  and 30.4 MHz for  $^{15}\text{N}$ . Hexamethylbenzene (17.4 ppm) and glycine- $^{15}\text{N}$  (−347.6 ppm) were used as external chemical shift standards for  $^{13}\text{C}$  and  $^{15}\text{N}$ , respectively.  $^{13}\text{C}$  chemical shifts are reported relative to TMS and  $^{15}\text{N}$  chemical shifts relative to nitromethane. Chemagnetics-style pencil probes spun 7.5 mm zirconia rotors at 1–6.5 kHz with active spin speed control ( $\pm 3$  Hz).

The  $^{13}\text{C}$  experiments we performed included cross-polarization (CP, contact time = 2 ms, pulse delay = 1 s, 2000 transients), cross-polarization with interrupted decoupling (contact time = 2 ms, pulse delay = 1 s, 2000 transients, dipolar

dephasing time of 50  $\mu\text{s}$ ), and single-pulse excitation with proton decoupling (Bloch decay, pulse delay = 10 s, 4000 transients). In the case of  $^{15}\text{N}$  experiments, cross-polarization spectra were obtained with a pulse delay of 1 s and contact time of 2 ms, and typically 4000 scans were averaged.  $^{15}\text{N}$  Bloch decay spectra (10 s pulse delay, 4000 scans) were also obtained.

Principal components of chemical shift tensors were measured using the method of Herzfeld and Berger.<sup>14</sup> These are sorted such that  $\delta_{11} \geq \delta_{22} \geq \delta_{33}$ . The isotropic chemical shift is the average of those principal components,  $\delta_{\text{iso}} = 1/3(\delta_{11} + \delta_{22} + \delta_{33})$ . The chemical shift anisotropy (CSA) and asymmetry factor ( $\eta$ ) are defined by the following equations to conform with the convention in Duncan's compilation of CSA data.<sup>15</sup>

$$\text{for } |\delta_{11} - \delta_{\text{iso}}| \geq |\delta_{33} - \delta_{\text{iso}}|$$

$$\text{CSA} = 3/2(\delta_{11} - \delta_{\text{iso}}), \quad \eta = (\delta_{22} - \delta_{33})/(\delta_{11} - \delta_{\text{iso}})$$

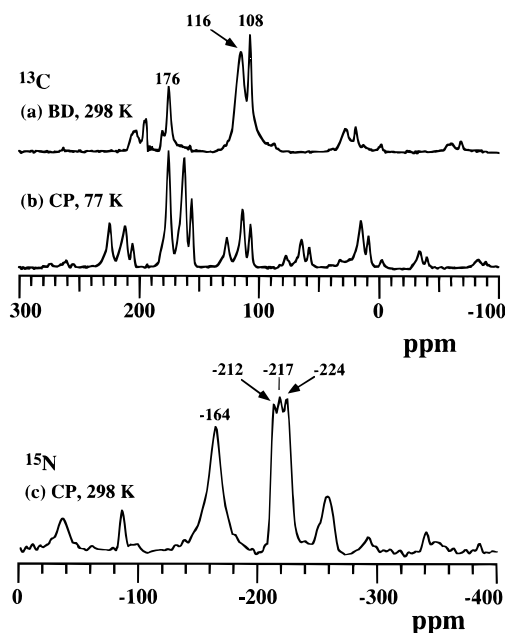
$$\text{for } |\delta_{11} - \delta_{\text{iso}}| \leq |\delta_{33} - \delta_{\text{iso}}|$$

$$\text{CSA} = 3/2(\delta_{33} - \delta_{\text{iso}}), \quad \eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{\text{iso}})$$

**Theoretical Details.** Structures of acetonitrile and the *N-tert*-butylacetoneitrilium ion were determined using density functional theory (DFT) using Becke's three-parameter hybrid method<sup>16</sup> together with the LYP correlation functional.<sup>17</sup> We used Godbout's DZVP2 basis set.<sup>18</sup> In the case of acetonitrile, we augmented the nitrogen basis set with one set of diffuse s and p functions. Frequency calculations were performed on both species at the same level of theory as the structure optimizations. All optimizations and frequency calculations were performed in Gaussian 94.<sup>19</sup> Chemical shieldings were determined using the gauge including atomic orbitals ansatz at both the GIAO-RHF and GIAO-MP2 levels of theory as implemented in ACES II.<sup>20</sup> For the chemical shielding calculations we employed Schafer's basis sets<sup>21</sup> with dz {31} on the H atoms and tzp {51111/311/1} (six Cartesian d orbitals) on the C and N atoms. We repeated the chemical shift calculations with the basis set for N augmented with s and p diffuse functions (tzp+). Calculated  $^{13}\text{C}$  chemical shifts are reported relative to C in tetramethylsilane, which has an absolute chemical shielding (in ppm) of 198.429 at MP2/tzp/dz and 192.630 at RHF/tzp/dz.  $^{15}\text{N}$  calculated chemical shifts are reported relative to experimental liquid nitromethane via a secondary calculated standard,  $\text{NH}_3$ . We do this by calculating the shielding of  $\text{NH}_3$  at the same level of theory as the molecules under study and referencing this to the gas-phase shift of  $\text{NH}_3$  relative to liquid nitromethane (−400.1 ppm).<sup>22</sup> The absolute shieldings (in ppm) of  $^{15}\text{N}$  in  $\text{NH}_3$  are 276.433 at GIAO-MP2/tzp+/tzp/dz, 256.827 at GIAO-RHF/tzp+/tzp/dz, 282.594 at GIAO-MP2/tzp/dz, and 267.996 at GIAO-RHF/tzp/dz.

## Results

**In Situ NMR.** Figure 1 is a diagram of the pulse-quench reactor in the configuration used to obtain some of the results reported in this investigation. This device is very much like a standard microreactor except that it is designed for the rapid switching of the gas stream flowed over the catalyst bed from helium to cryogenically cooled nitrogen, permitting a very rapid decrease in the catalyst temperature. The bed temperature decreases 50 K in the first 80 ms of a quench, a further 100 K drop occurs in the following 90 ms, and the catalyst temperature is at ambient or lower in less than 1 s. In the first applications of the pulse-quench reactor, the reagents injected onto the

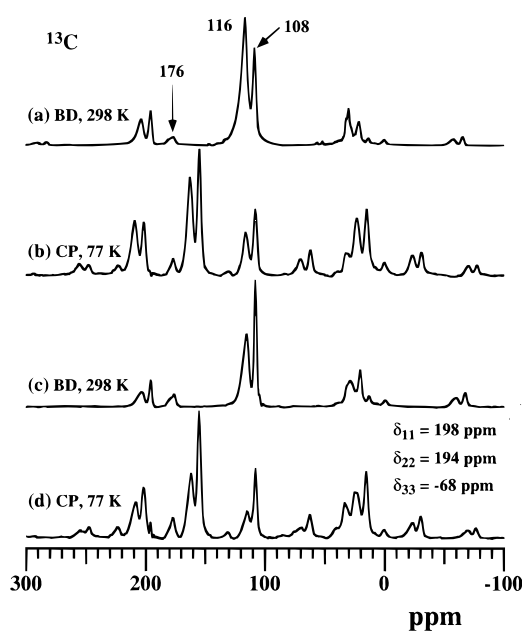


**Figure 2.** Selected 75.4 MHz  $^{13}\text{C}$  and 30.4 MHz  $^{15}\text{N}$  spectra showing products after reacting *tert*-butyl alcohol with acetonitrile in zeolite HZSM-5. The  $^{13}\text{C}$  sample (spectra a and b) and  $^{15}\text{N}$  sample (spectrum c) were prepared under identical conditions except the use of acetonitrile- $I$ - $^{13}\text{C}$  for the former and acetonitrile- $^{15}\text{N}$  for the latter. Isotropic shifts are indicated in the spectra, and all the other features are spinning sidebands. (a) Bloch decay (BD) spectrum showing  $^{13}\text{C}$  signals for **1** (108 ppm), *N*-*tert*-butylacetamide (176 ppm), and acetonitrile (116 ppm); (b) cross-polarization (CP) spectrum acquired at 77 K, showing the large chemical shift anisotropy for **1**; (c) CP spectrum showing  $^{15}\text{N}$  signals for **1** (-212 ppm), *N*-*tert*-butylacetamide (-217 ppm), and acetonitrile (-164 ppm). The  $^{15}\text{N}$  shift at -224 ppm is probably due to acetamide, which was formed by the hydrolysis of acetonitrile under the reaction conditions.

catalyst bed were liquids under laboratory conditions. To co-inject isobutylene for this investigation, the reactor was modified to permit quasi-continuous introduction of a reactive gas stream as well as computer-controlled injection of a pulse of acetonitrile.

For the reaction of acetonitrile with *tert*-butyl alcohol, samples were prepared by pulsing a mixture of *tert*-butyl alcohol (26  $\mu\text{L}$  or 1.4 equiv) and labeled acetonitrile (14.6  $\mu\text{L}$  or 1.4 equiv) into activated catalyst (0.35 g preactivation) at 433 K. The reaction was allowed to proceed for 8 s before a thermal quench to 298 K, followed by transfer of the catalyst bed to an MAS rotor under drybox conditions. Figure 2 reports representative results from experiments in which acetonitrile was labeled with either  $^{13}\text{C}$  or  $^{15}\text{N}$ . Figure 2a shows a  $^{13}\text{C}$  Bloch decay spectrum measured at 298 K. Three major isotropic peaks are observed: 116 ppm, unreacted acetonitrile; 108 ppm, cation **1**; and 176 ppm, *N*-*tert*-butylacetamide obtained by hydrolysis of **1**. The shoulder on the 176 ppm peak could represent acetamide formed by the direct hydrolysis of acetonitrile, a reaction in zeolites that has previously been characterized.<sup>23</sup> The formation of amides suggests that hydrolysis is competitive with desorption of water from the catalyst bed at 433 K. Figure 2b reports the  $^{13}\text{C}$  cross-polarization spectrum measured at 77 K for the sample discussed above. Spinning sidebands associated with all three species are more evident with these experimental conditions.

Figure 2c shows the  $^{15}\text{N}$  cross-polarization spectrum of a sample prepared using conditions otherwise identical to above except acetonitrile- $^{15}\text{N}$  was pulsed into the reactor. The resonance for unreacted acetonitrile (-164 ppm) is well-resolved, but the peaks for **1** (-212 ppm), *N*-*tert*-butylacetamide



**Figure 3.** The 75.4 MHz  $^{13}\text{C}$  spectra showing the formation of **1** by reacting isobutylene with acetonitrile- $I$ - $^{13}\text{C}$  in zeolite HZSM-5 at 353 K for 20 s. All the isotropic shifts are indicated in the spectra, and the rest are spinning sidebands. Spectra c and d were acquired following sample evacuation at 323 K in a shallow bed CAVERN to remove excess physisorbed acetonitrile (see Experimental Section). (a) Quantitative BD spectrum showing the resonances for **1** (108 ppm), unreacted acetonitrile (116 ppm), and a trace amount of *N*-*tert*-butylacetamide (176 ppm); (b) CP spectrum acquired at 77 K; (c) quantitative BD spectrum, showing that the physisorbed acetonitrile was removed by extended evacuation as indicated by the decrease in intensity of the 116 ppm peak; (d) CP spectrum acquired at 77 K, allowing accurate measurements of the principal components of  $^{13}\text{C}$  chemical shift tensors for **1** and chemisorbed acetonitrile.

(-217 ppm), and acetamide (-224 ppm) are closely spaced. These crowded spectra do not lend themselves to the measurement of principal components of chemical shift tensors, and we considered other experimental procedures for the synthesis and isolation of **1** as the dominant species in the zeolite.

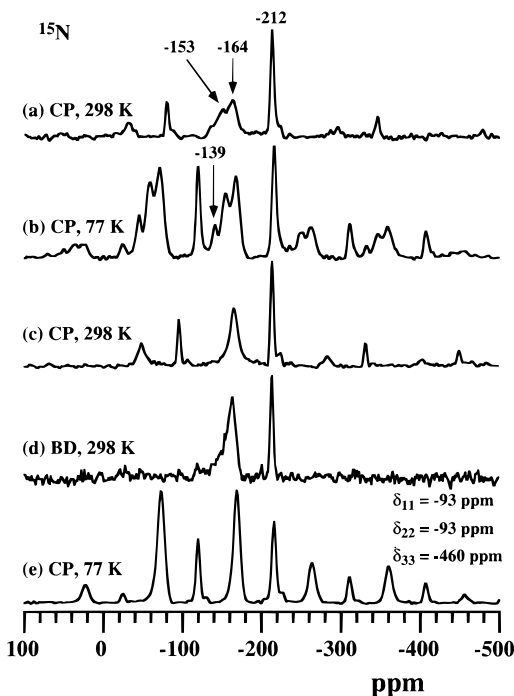
We verified that we could synthesize cations similar to **1** by co-injecting acetonitrile and olefins such as pent-1-ene that can be handled as liquids under laboratory conditions (spectra not shown). For comparison, Stepanov reacted oct-1-ene with acetonitrile to make acetonitrilium cations.<sup>7</sup> We synthesized **1** from acetonitrile and isobutylene using the device in Figure 1 and the following procedure. We first pulsed 30  $\mu\text{L}$  (2.6 equiv) of acetonitrile- $I$ - $^{13}\text{C}$  into activated zeolite HZSM-5 (0.40 g preactivation) at 353 K using He as carrier gas. Immediately following the pulse, the He carrier gas flow was stopped, and isobutylene was allowed to flow into the catalyst bed at 600 sccm. The reactions were stopped by thermal quench after flowing isobutylene for 20 s.  $^{13}\text{C}$  MAS spectra of a sample prepared using this procedure are summarized in Figure 3a,b. Only a trace of amide (176 ppm) was observed with this procedure, but there was quite a bit of unreacted acetonitrile (116 ppm), despite the use of an excess of isobutylene. To reduce the amount of acetonitrile, the sample in the sealed rotor was unpacked inside the drybox into a shallow bed CAVERN.<sup>24,25</sup> The CAVERN was attached to a vacuum line and evacuated for 2 h at 323 K so that the physisorbed acetonitrile was removed. The sample was then reloaded into the MAS rotor and sealed for further MAS NMR studies, which are shown in Figure 3c,d. Comparison of the  $^{13}\text{C}$  MAS spectra before and after evacuation shows that this procedure was partially suc-



**TABLE 1: Summary of Measured and Calculated  $^{13}\text{C}$  Chemical Shift Data for *N*-*tert*-Butylacetonitrilium Ion, **1**, and Acetonitrile,  $\text{C}_2\text{H}_3\text{N}$  ( $\delta$  Values in ppm)**

	basis sets for shifts	MP2						RHF					
		$\delta_{\text{iso}}$	$\delta_{11}$	$\delta_{22}$	$\delta_{33}$	CSA	$\eta$	$\delta_{\text{iso}}$	$\delta_{11}$	$\delta_{22}$	$\delta_{33}$	CSA	$\eta$
<b>1</b>	tzp/dz	108	198	198	-71	-269	0.00	125	224	224	-73	-297	0.00
	tzp+/tzp/dz	109	198	198	-71	-269	0.00	125	224	224	-73	-297	0.00
	exptl	108	198	194	-68	-264	0.02						
$\text{C}_2\text{H}_3\text{N}$	tzp/dz	118	218	218	-83	-301	0.00	128	244	244	-103	-347	0.00
	tzp+/tzp/dz	119	219	219	-83	-302	0.00	129	245	245	-103	-348	0.00
	exptl <sup>a</sup>	116	214	214	-85	-302	0.00						
	exptl <sup>b</sup>	117	216	216	-78	-293	0.00						
	exptl <sup>c</sup>	117	224	224	-96	-320	0.00						

<sup>a</sup> This work. Experimental shifts measured for acetonitrile in a zeolite at 77 K. Uncertainty in the experimental principal component data is generally less than 5 ppm. <sup>b</sup> Reference 26. <sup>c</sup> Reference 27.



**Figure 4.** The 30.4 MHz  $^{15}\text{N}$  spectra showing  $^{15}\text{N}$  signals for products from the reactions of acetonitrile- $^{15}\text{N}$  with isobutylene on HZSM-5. The sample was prepared under conditions identical to those used for Figure 3. Spectra c–e were acquired following sample evacuation at 323 K for 2 h in a shallow bed CAVERN. (a, b)  $^{15}\text{N}$  signals for **1** (–212 ppm), acetonitrile adsorption complex (chemisorbed) at –164 ppm, two types of physisorbed acetonitrile species at –153 and –139 ppm; (c, d) CP and BD spectrum, respectively, showing the removal of physisorbed species after extended pumping; (e) showing spectrum at 77 K, allowing measurement of the  $^{15}\text{N}$  principal component data both for chemisorbed acetonitrile and **1** after removal of physisorbed species.

cessful for removal of excess acetonitrile. Indeed, the resolution of the isotropic peaks and spinning sidebands in Figure 3d was sufficient for a determination of the principal components of the  $^{13}\text{C}$  chemical shift tensor on the nitrile carbon of **1**, and these are reported in Table 1.

Figure 4 reports  $^{15}\text{N}$  spectra of cation **1** prepared from acetonitrile- $^{15}\text{N}$  and isobutene in the pulse-quench reactor as before. The spectra show little if any evidence of amides; the resonance of **1** is distinct at –212 ppm. Also present are several  $^{15}\text{N}$  resonances (between –153 and –164 ppm) for acetonitrile in various environments in the catalyst. The spectra in Figure 4c–e were measured following evacuation to remove some of the excess acetonitrile. These show only the acetonitrile resonance at –164 ppm. Figure 4e is a cross-polarization spectrum measured at 77 K; here one can see a number of

spinning sidebands for **1** clearly resolved from other features. The sideband intensities were used to determine the principal components of the  $^{15}\text{N}$  chemical shift tensor of **1** (Table 2).

**Theoretical Studies.** In several recent studies we have had good success using density functional theory at the B3LYP level to obtain geometries for subsequent chemical shift calculations. For example, the geometries of several benzenium ions at B3LYP were very similar to those at MP2, and the GIAO-MP2 chemical shifts calculated for the two geometries were also very similar.<sup>12</sup> We performed unconstrained optimizations of the geometries of cation **1** and acetonitrile at B3LYP/DZVP2. These structures are reported in Figure 5. Both species are minima in  $C_{3v}$  symmetry; therefore, all nuclei located on the symmetry axis are required to have axially symmetric chemical shift tensors with the unique component along this axis and the two identical components in a plane perpendicular to the axis. The calculated C–C and C $\equiv$ N bond distances—1.468 and 1.164 Å, respectively—in acetonitrile are in very close agreement with experimental gas-phase values<sup>29</sup> of 1.4617 and 1.1567 Å, respectively. Our calculations indicate the formation of a C–N single bond of typical length between C-2 of the *tert*-butyl group and acetonitrile. The angle between this bond and the three methyl groups attached to C-2 is 106.3°, very close to the tetrahedral angle. When acetonitrile reacts to form **1**, the C–C and C $\equiv$ N bond lengths are little changed; each lengthens by only ca. 0.01 Å. We did not attempt to model either the interaction of **1** with the zeolite or possible transition states leading to **1** from the reactants in contact with a model of a Brønsted site.

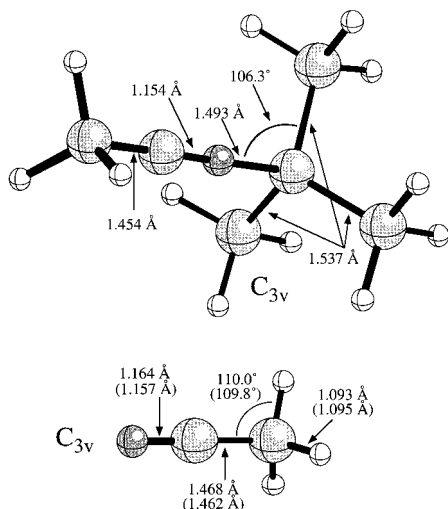
We used the geometries in Figure 5 in a series of GIAO chemical shift calculations that are reported in Table 1 ( $^{13}\text{C}$ ) and Table 2 ( $^{15}\text{N}$ ). Consistent with our previous computational studies of carbenium ions and related species, here we also observe large discrepancies between results obtained with neglect of electron correlation (RHF) and those obtained when correlation is treated at the MP2 level. We focus on the GIAO-MP2 results; first consider those for  $^{13}\text{C}$  of the nitrile carbon in acetonitrile and **1**. Not surprisingly, the  $^{13}\text{C}$  shift tensor was insensitive to addition of diffuse functions to nitrogen, and the agreement between experiment and theory is outstanding for both species. This is true not only for the isotropic shifts but also for the principal components of the  $^{13}\text{C}$  chemical shift tensors.

The  $^{15}\text{N}$  chemical shift tensor calculations were also in very good agreement with experiment, especially with the addition of diffuse functions to nitrogen. At GIAO-MP2/tzp+/tzp/dz, both acetonitrile and **1** yielded theoretical isotropic  $^{15}\text{N}$  shifts 10 ppm downfield of the experimental values, suggesting a systematic deviation. Good agreement was also obtained for the principal components.

**TABLE 2: Summary of Measured and Calculated  $^{15}\text{N}$  Chemical Shift Data for *N*-*tert*-Butylacetonitrilium Ion, **1**, and Acetonitrile,  $\text{C}_2\text{H}_3\text{N}$  ( $\delta$  Values in ppm)**

	basis sets for shifts	MP2						RHF					
		$\delta_{\text{iso}}$	$\delta_{11}$	$\delta_{22}$	$\delta_{33}$	CSA	$\eta$	$\delta_{\text{iso}}$	$\delta_{11}$	$\delta_{22}$	$\delta_{33}$	CSA	$\eta$
<b>1</b>	tzp+/tzp/dz	-205	-77	-77	-461	-384	0.00	-211	-70	-70	-493	-423	0.00
	tzp/dz	-198	-70	-70	-454	-384	0.00	-203	-62	-62	-485	-423	0.00
	exptl <sup>a</sup>	-215	-93	-93	-460	-367	0.00						
$\text{C}_2\text{H}_3\text{N}$	tzp+/tzp/dz	-146	10	10	-460	-470	0.00	-100	75	75	-449	-524	0.00
	tzp/dz	-139	21	21	-457	-478	0.00	-93	84	84	-446	-530	0.00
	exptl <sup>b</sup>	-167	-29	-46	-426	-389	0.07						
	exptl <sup>c</sup>	-156	6	6	-482	-489	0.00						

<sup>a</sup> This work. Experimental shifts measured for **1** in a zeolite at 77 K. Uncertainty in the experimental principal component data is generally less than 5 ppm. <sup>b</sup> This work. Experimental shifts measured for acetonitrile in a zeolite at 77 K. Uncertainty in the experimental principal component data is generally less than 5 ppm. <sup>c</sup> Reference 28.

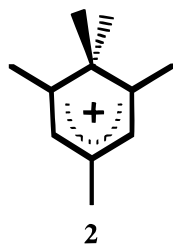


**Figure 5.** B3LYP/DZVP2 optimizations of **1** and acetonitrile. Selected distances (Å) and angles (deg) are shown. Microwave data for acetonitrile from ref 29 are shown in parentheses.

## Discussion

We have used the pulse-quench reactor to reproduce the essential features of Stepanov's study<sup>7</sup> of the intermediate formed by the reaction of acetonitrile and *tert*-butyl alcohol. We measured the principal components of the chemical shift tensors for that species and strongly verified Stepanov's assignment of the intermediate to cation **1** by comparison of experimental and theoretical chemical shift tensors.

We recently applied the pulse-quench reactor to the isolation and NMR characterization of a hydrolytically unstable pentamethylbenzenium cation **2** in zeolite HZSM-5.<sup>10</sup> This species was



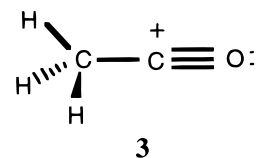
formed in the reactor by the reactions of benzene or toluene with excess methanol, but the cation could not be observed at all in a sealed MAS rotor. In a flow reactor, the coproduct of the alkylation reaction (water) is swept out of the catalyst bed and away from the benzenium cation, which is imprisoned in the channel intersections. Contact between water and the benzenium cation regenerates a neutral hydrocarbon, methanol, and an acid site, but otherwise no hydrolysis products not already

present under reaction conditions. In the present study the reactions of acetonitrile and *tert*-butyl alcohol in the pulse-quench reactor still led to the formation of amides in addition to **1**. Clearly, the hydrolysis of **1** must be competitive with the removal of water from the catalyst bed at 433 K, and amide formation appears to be essentially irreversible under these conditions.

To obtain spectra that were sufficiently uncluttered for sideband intensity measurements (required for calculation of the principal components of the shift tensors), we modified the quench reactor to admit isobutylene gas after a pulse of acetonitrile. In this case amide formation was negligible, but some unreacted acetonitrile was inevitably present. Some, but not all, of the excess acetonitrile could be removed in a subsequent evacuation step at 323 K. We speculate that the introduction of isobutylene into the zeolite at 353 K not only forms cation **1** but also blocks the zeolite channels by coke formation. Channel blockage would plausibly trap some unreacted acetonitrile in the zeolite.

We are encouraged by the fact that we were so readily able to use the pulse-quench reactor to reproduce a species originally observed by another research group,<sup>7</sup> but we also acknowledge that this is one case where the benefits of this reactor are not obviously superior to standard in situ NMR experiments using sealed rotors. Sealed rotor methods may sometimes provide a more uniform distribution of adsorbates, especially when the adsorption is done "shallow bed"<sup>24</sup> or if it is possible to heat the sample and promote a more uniform adsorbate distribution. A uniform distribution of acetonitrile and olefin or alcohol would tend to promote good selectivity for a product like **1**. Chromatographic and other effects may be operative in a flow reactor and contribute to differential spatial distributions of reactants.

The agreement between experimental and calculated chemical shift tensors for **1** is very satisfying. The GIAO-MP2 method has yielded satisfactory results for  $^{13}\text{C}$  shifts in a number of carbenium ions formed in various media. Furthermore, this method has also performed very well for  $^{13}\text{C}$  shifts of acylium ions including **3**, which is obviously analogous to acetonitrile.



The placement of the positive charge on the carbon atom in **3** is based on our previous NBO calculations that show that the charge does indeed reside on this atom.<sup>11</sup> Our expectation was that cation **1** would be a particularly demanding challenge for the GIAO-MP2 methodology, especially for the  $^{15}\text{N}$  calculations

where we have far less experience. Indeed, the absolute accuracy obtained for  $^{15}\text{N}$  in **1** was not as good as that for the  $^{13}\text{C}$  shift, but we are still satisfied with the result. Gauss has extended GIAO chemical shift calculations to MP4<sup>30</sup> and coupled cluster treatments<sup>31</sup> and has demonstrated several demanding cases where the MP2 method is insufficient for treatment of correlation. On the basis of the present study alone, we are unable to predict the general applicability and accuracy of GIAO-MP2 shift calculations to problems in zeolite chemistry and catalysis. The  $^{15}\text{N}$  shifts of pyridine<sup>32</sup> and other nitrogen-containing molecules have been applied as acidity probes of catalysts. This suggests some further opportunities for comparison of experimental  $^{15}\text{N}$  shift tensors with theoretical tensors calculated at various levels of theory.

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## References and Notes

- (1) Haw, J. F.; Nicholas, J. B.; Xu, T.; Beck, L. W.; Ferguson, D. B. *Acc. Chem. Res.* **1996**, 29, 259–267.
- (2) Haw, J. F. In *NMR Techniques in Catalysis*; Bell, A., Pines, A., Eds.; Marcel Dekker: New York, 1994.
- (3) Haw, J. F.; Richardson, B. R.; Oshiro, I. S.; Lazo, N. L.; Speed, J. A. *J. Am. Chem. Soc.* **1989**, 111, 2052–2058.
- (4) Xu, T.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, 116, 7753–7759.
- (5) Xu, T.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, 116, 10188–10195.
- (6) Munson, E. J.; Haw, J. F. *J. Am. Chem. Soc.* **1991**, 113, 6303–6305.
- (7) Stepanov, A. G.; Luzgin, M. V. *Chem. Eur. J.* **1997**, 3, 47–56.
- (8) Haw, J. F.; Goguen, P. W.; Xu, T.; Skloss, T. W.; Song, W.; Wang, Z. *Angew. Chem.* **1998**, 37, 948–949.
- (9) Goguen, P. W.; Xu, T.; Barich, D. H.; Skloss, T. W.; Song, W.; Wang, Z.; Nicholas, J. B.; Haw, J. F. *J. Am. Chem. Soc.* **1998**, 120, 2651–2652.
- (10) Xu, T.; Barich, D. H.; Goguen, P. W.; Song, W.; Wang, Z.; Nicholas, J. B.; Haw, J. F. *J. Am. Chem. Soc.* **1998**, 120, 4025–4026.
- (11) Xu, T.; Torres, P. D.; Barich, D. H.; Nicholas, J. B.; Haw, J. F. *J. Am. Chem. Soc.* **1997**, 119, 396–405.
- (12) Xu, T.; Barich, D. H.; Torres, P. D.; Haw, J. F. *J. Am. Chem. Soc.* **1997**, 119, 406–414.
- (13) Gauss, J. *Chem. Phys. Lett.* **1992**, 191, 614–620.
- (14) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, 73, 6021–6030.
- (15) Duncan, T. M. *A Compilation of Chemical Shift Anisotropies*; Farragut Press: Chicago, 1990.
- (16) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648–5652.
- (17) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785–789.
- (18) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, 70, 560–571.
- (19) Gaussian 94, Revision E.2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.
- (20) ACES II, an ab initio quantum chemical program system. Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J.
- (21) Schafer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, 97, 2571–2577.
- (22) Jameson, C. J.; Jameson, A. K.; Oppenungu, Wille, S.; Burrell, P. M. *J. Chem. Phys.* **1981**, 74, 81–88.
- (23) Haw, J. F.; Hall, M. B.; Alvarado-Swaigood, A. E.; Munson, E. J.; Lin, Z.; Beck, L. W.; Howard, T. *J. Am. Chem. Soc.* **1994**, 116, 7308–7318.
- (24) Munson, E. J.; Murray, D. K.; Haw, J. F. *J. Catal.* **1993**, 141, 733–736.
- (25) Xu, T.; Haw, J. F. *Top. Catal.* **1997**, 4, 109–118.
- (26) Ripmeester, J. A.; Tse, J. S.; Davidson, D. W. *Chem. Phys. Lett.* **1982**, 86, 428–433.
- (27) Diehl, P.; Jokisaari, J.; Moia, F. *J. Magn. Reson.* **1982**, 49, 498.
- (28) Kaplan, S.; Pines, A.; Griffin, R. G.; Waugh, J. S. *Chem. Phys. Lett.* **1974**, 25.
- (29) Demaison, J.; Dubrelle, A.; Boucher, D.; Burie, J.; Typke, V. *J. Mol. Spectrosc.* **1979**, 76, 1–16.
- (30) Gauss, J. *Chem. Phys. Lett.* **1994**, 229, 198–203.
- (31) Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **1995**, 103, 3561–3577.
- (32) Haw, J. F.; Chuang, I.-S.; Hawkins, B. L.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, 105, 7206–7207.