Preparation and NMR Characterization of Carbenium Ions on Metal Halide Powders

Teng Xu, Paul D. Torres, Larry W. Beck, and
James F. Haw*

*Laboratory for Magnetic Resonance and Molecular Science
Department of Chemistry, Texas A & M University
College Station, Texas 77843*

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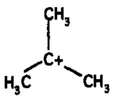
We report that a wide variety of carbenium ions and related electrophilic species can be prepared by the direct contact of suitable precursors with metal halide powders at reasonable temperatures and in the absence of solvent, permitting direct measurement of the principal components of the ^{13}C chemical shift tensors.

The Friedel−Crafts alkylation and acylation reactions, first reported in 1877,[1] are among the most important in chemistry. The generalized reaction, as surveyed in Olah's books[2,3] and elsewhere,[4] proceeds on a wide variety of catalysts; the most familiar is $AlCl_3$, but other metal halides including $ZnCl_2$ are valued for their lower activity and sometimes greater selectivity. Metal halide powders or molten salts are also employed as catalyst components in several continuous processes,[5] and Drago has described acid catalysts based on oxide supports treated with aluminum chloride.[6]

Figure 1 a−c shows ^{13}C NMR spectra[7] obtained with cross polarization (CP) and magic angle spinning (MAS) at various temperatures and spinning speeds following adsorption[8] of *tert*-butyl-α-^{13}C chloride on aluminum chloride powder at 233 K. These spectra show, unambiguously, that the product was uncoordinated *tert*-butyl carbenium ion **1**.



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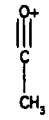

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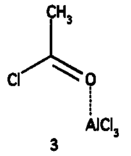

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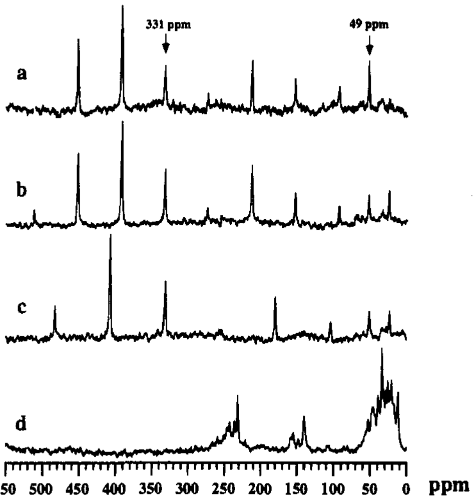

Figure 1. ^{13}C MAS NMR 50.1 MHz spectra of *tert*-butyl-α-^{13}C chloride on $AlCl_3$. CP spectra a, b, and c show cation **1** formed from the adsorption of ca. 0.05 mmol/g at 233 K: (a) acquired at 233 K with a spinning speed of 2.50 kHz; (b, c) acquired at 173 K with spinning speeds of 2.50 and 3.00 kHz, respectively. These spectra show the isotropic peak for the labeled carbon at 331 ppm, its associated spinning sidebands, and a small natural abundance methyl signal at 49 ppm. (d) Another sample was prepared at 298 K with a higher loading (0.8 mmol/g), and the Bloch decay spectrum showed other carbenium ion products (see text).

The isotropic ^{13}C shifts for the labeled carbon, 331 ppm, as well as the methyl groups, visible at natural abundance at 49 ppm, are within several parts per million of those seen in previous superacid solution reports,[9] and the exceptionally large chemical shift anisotropy is characteristic of carbenium ions with localized charges.[11] Cation **1** was indefinitely persistent on $AlCl_3$ or $AlBr_3$ between 173 and 233 K and reacted only upon warming to 273 K or above. Figure 1d shows a ^{13}C spectrum obtained after treating $AlCl_3$ with a greater loading of *tert*-butyl-α-^{13}C chloride at 298 K. The products apparently included methyl-substituted cyclopentenyl and cyclohexenyl carbenium ions as suggested by the diagnostic shifts for the terminal (230−260 ppm) and central (140−160 ppm) allylic carbons.[12]

The archetypal Friedel-Crafts acylation reaction involves acetyl chloride and $AlCl_3$ catalyst. Figure 2 shows ^{13}C MAS spectra from a series of experiments in which either acetyl-*1*-^{13}C chloride or acetyl-*2*-^{13}C chloride were adsorbed onto $AlCl_3$ powder at room temperature. The isotropic shifts observed, 152 and 14 ppm, are in excellent agreement with previous reports of the acylium ion **2** in superacid solutions[13] and a solid state study of a stoichiometric salt.[14] The principal components of the ^{13}C chemical shift tensor (Table 1) reflect the axial symmetry of the linear cation, and the values of the isotropic shifts can be rationalized from the structurally analogous acetonitrile. ^{13}C Bloch decay (BD) spectra showed small peaks due to mobile species that did not cross polarize efficiently; these were the precursor complex **3** (210 and 38 ppm)[14] and a small amount of acetic acid.

Even acetone showed appreciable shifts following contact with metal halides, the magnitude of which correlates with the

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* Author to whom correspondence should be addressed.

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[7] The ^{13}C MAS NMR spectra were acquired with active spin speed control; 800−2000 scans were averaged for cross polarization experiments with contact times of 2−4 ms and pulse delays of 4−10 s. The Bloch decay spectra were acquired with 200−800 scans and pulse delays of 10−50 s.

[8] Typically 1.4 g of freshly opened, anhydrous $AlCl_3$ (Strem Chemical) was loaded into a modified ultrashallow bed CAVERN (for a similar device, see: Munson, E. J.; Murray, D. K.; Haw, J. F. *J. Catal.* **1993**, *141*, 733−736) inside the dry box. The CAVERN was evacuated for ca. 12 h under vacuum, and the final pressure was less than 10^{-4} Torr. After adsorption, the sample was packed into a 7.5-mm NMR rotor and capped inside the drybox. An alternate CAVERN design (Munson, E. J.; Ferguson, D. B.; Kheir, A. A.; Haw, J. F. *J. Catal.* **1992**, *136*, 504−509) was used for the adsorption of *tert*-butyl-α-^{13}C chloride at 233 K. After adsorption, the rotor was capped and transferred into a precooled NMR probe.

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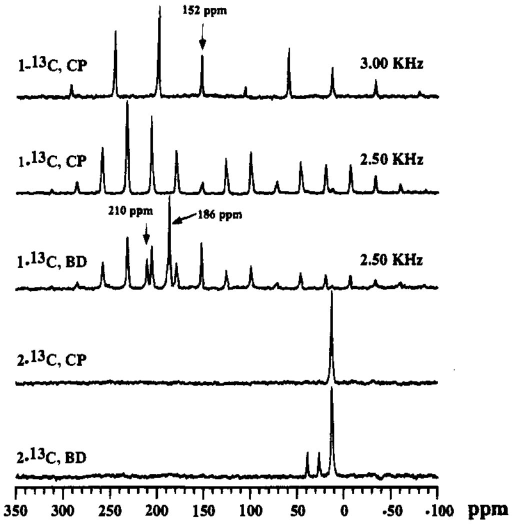
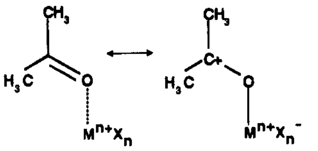


Figure 2. ^{13}C MAS NMR 75.4 MHz spectra of acetyl chloride on $AlCl_3$ (0.4 mmol/g. Spectra derived from both acetyl-*1*-^{13}C chloride and acetyl-*2*-^{13}C chloride are shown, and all the spectra were acquired at 298 K. The 152 ppm (1-^{13}C) and 14 ppm (2-^{13}C) isotropic resonances indicate the formation of acylium cation **2**. See text for other details.

Table 1. Summary of the Isotropic Chemical Shifts (δ_{iso}), Principal Components (δ_{11}, δ_{22}, and δ_{33}), Chemical Shift Anisotropies (CSA), and Asymmetry Factors (η) of Cations **1**, **2**, and **4** on Metal Salts[10]

cation	salt	temp, K	δ_{iso}, ppm	CSA, ppm	η	δ_{11}, ppm	δ_{22}, ppm	δ_{33}, ppm
1	$AlBr_3$	173	330	414	0.00	468	467	54
2	$AlCl_3$	298	152	327	0.00	261	261	−66
4	$AlCl_3$	193	245	228	0.86	387	256	93
4	$ZnCl_2$	193	231	215	0.55	342	263	88

expected strength of the Lewis acid−base interaction. Figure 3 shows ^{13}C MAS spectra of acetone-*2*-^{13}C on various materials. Two isotropic peaks at 231 and 227 ppm were observed for acetone on $ZnCl_2$ powder, and appreciable chemical shift anisotropy was reflected in the sideband patterns at 193 K. The 231 ppm peak was in complete agreement with the shift observed for acetone diffused into ZnY zeolite.[15] A much greater shift, 245 ppm, was observed on $AlCl_3$ powder. For comparison, acetone has chemical shifts of 205 ppm in $CDCl_3$ solution,[16] 244 ppm in concentrated H_2SO_4,[17] and 249 ppm in superacid solutions.[18] We propose structure **4** for acetone on metal halide salts, and the relative contributions of the two canonical forms rationalize the dependence of the observed isotropic ^{13}C shift on the Lewis acidity of the metal halide.



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Acetone showed temperature-dependent dynamics on the metal halides; the broad sideband pattern seen on $AlCl_3$ below room temperature collapsed to a sharp resonance at 393 K, but the isotropic shift remained 245 ppm over the range of temperatures investigated. The acetyl chloride/$AlCl_3$ system exhibited more complex dynamics at higher temperature including irreversible changes (not shown). In some experiments, the adsorbate uptake exceeded monolayer coverage based on N_2 BET measurements. We have not characterized the detailed morphologies of these samples, but we anticipate a continuum between surface adsorption and stoichiometric compound formation in some cases. ^1H MAS experiments showed that the proton content of our $AlCl_3$ powder was low and could be further reduced by extended evacuation. By measuring the ^{31}P spectrum of adsorbed $P(CH_3)_3$, following the work of Lunsford and co-workers,[19] we established that Lewis sites greatly exceeded Bronsted sites on our $AlCl_3$ powder.

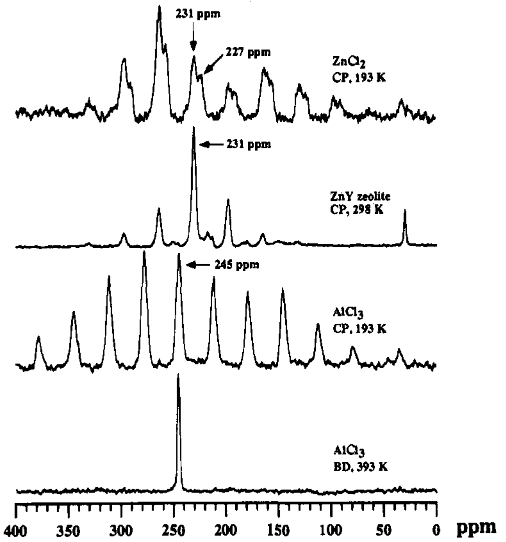

Figure 3. ^{13}C NMR 75.4 MHz spectra of acetone-*2*-^{13}C on various substrates. The loadings were 0.2−0.4 mmol/g.

We believe that significant progress in solid superacid chemistry awaits the application of NMR to adsorbates on a variety of metal halides, mixed salts, and salts treated with hydrogen halides.[20] The ease with which the data in Table 1 were acquired suggests that rapid progress can be made in the measurement of chemical shift principal component data for carbenium ions and other electrophilic species. Using cryogenic codeposition of alkyl halides and SbF_5, Yannoni was able to observe the *tert*-butyl and *sec*-butyl cations at low temperature.[21] In an analogous experiment, Buzek et al. were recently able to obtain the infrared spectrum of the allyl cation.[22] We are encouraged by the ease with which we were able to prepare the *tert*-butyl cation and plan on extending our observations to more challenging targets.

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