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Solid State ^{13}C NMR Can Distinguish between Bronsted and Lewis Acid Adducts of Amines

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ABSTRACT

The solid ^{13}C NMR spectra of solid complexes of phenethylamine with $SnCl_4$, Me_3SnCl, $AlCl_3$, and HCl are presented and discussed as a means of distinguishing between Bronsted and Lewis acid adducts of alkyl amines. Solution ^{13}C NMR results are discussed in terms of species present in complex equilibria and their detection using the two NMR methods.

INTRODUCTION

The ability of amines to form either Bronsted adducts or Lewis acid adducts is a cornerstone of much of the chemistry of amines [1]. The stability of these adducts has additionally provided important insights into the nature of the bonding with regard to electronic and steric effects [2]. In many instances, either the Bronsted or the Lewis acid derivative is prepared or studied independently. However, most catalytic processes on surfaces involve complex mixtures of both species and therefore appropriate characterization is very important in determining active sites, catalytic efficiency and other reaction parameters.

The various physical methods that have been used to characterize Bronsted and Lewis acid adducts have had varying success on solid surfaces [3]. The application of ^{13}C NMR to the chemisorption of amines (n-butylamine and pyridine) on alumina and silica-alumina has provided some insights into these interactions. In particular, for pyridine, ^{13}C NMR chemical shifts are valuable for distinguishing between the adducts, but on balance the differentiation for the stronger bases, the aliphatic amines, is not as clear [4]. More recent studies suggest that ^{15}N NMR could likely provide the desired characterization of Lewis and Bronsted sites, [5] however this would require ^{15}N enrichment. It is more desirable to have a useful method for ^{13}C NMR since enrichment would likely not be required and there is a significant value in probing the same kinds of interactions with multiple "nuclear spin labels" [5c].

A ^{13}C NMR study of amine borane adducts in solution by Wrackmeyer and coworkers led us to believe that it would be possible to use ^{13}C chemical shifts as a general method for distinction between Bronsted and Lewis acids [6]. We now describe our ^{13}C NMR results that demonstrate that, with the suitable choice of amine, clear differentiation of acid alkyl amine adduct type is possible in the solid state.

RESULTS AND DISCUSSION

The phenethylamine adducts were prepared from $SnCl_4$, Me_3SnCl, $AlCl_3$, and HCl. The ^{13}C NMR spectra of these compounds were determined as solids at both 25 MHz and 75.5 MHz using cross polarization with magic angle spinning (CPMAS). Solution spectra were obtained in DMSO and diglyme solvent. The solid CPMAS spectra are shown in Figure 1) and Table 1 records the chemical shift values of the solid and solution data. The ^{13}C NMR spectrum of the borane adduct was described earlier by Wrackmeyer and coworkers [6].

We found that either Bronsted or Lewis acid adduct formation has an appreciable (3–7ppm) shielding effect on the beta carbon in the solid spectra relative to the amine. For the solution spectra, a

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This paper is dedicated to Professor Herbert C. Brown on the occasion of his 80th birthday.

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TABLE 1 ^{13}C NMR Spectral Data[a] for Adducts of N-Phenethylamine

Solid State

Amine Compound	*C1*	*C2 C3 C4*[b]	*Ca*	*Cb*
$SnCl_4$	138(80)	128.0(80)	45.9(207)	35.1(135)
Me_3SnCl	138(80)	128.0(80)	45.2(*)	37.3(180)
$AlCl_3$	138(91)	128.0(171)	47.0(*)	33.0(140)
HCl	138(60)	128.0(171)	42.0(225)	33.5(117)

Solution Compound	*C1*	*C2*	*C3*	*C4*	*Ca*	*Cb*
Free Amine	140.0	128.7	128.3	126.0	43.6	40.2
BH_3	138.6	128.5	128.5	126.3	49.4	34.3
HCL	137.6	128.6	128.6	126.6	40.2	33.0
$SnCl_4$[c]	137.4	128.6	128.6	126.7	40.0	32.9
$SnCl_4$[d]	135.8	127.5	127.3	125.4	40.0	32.0
Me_3SnCl	138.9	128.5	128.3	126.1	42.3	37.7
$AlCl_3$	137.5	128.6	128.6	126.7	40.0	32.9
HC1+Amine[f]	138.9	128.6	128.4	126.2	41.7	36.2

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^{13}chemical shifts in ppm with respect to TMS and linewidths in Hz given in parentheses. A * indicates a very broad signal and the linewidth could not be determined accurately.

[b] In the solid state identification of specific signals for aromatic C2, C3 and C4 is not possible.

[c] In DMSO-d6 solution.

[d] In diglyme solution with 5% $CDCl_3$.

[e] In $CDCl_3$ solution.

[f] N-Phenethylamine.HCl : N-Phenethylamine ratio = 1:1.

similar effect is observed (2.5–8 ppm). The alpha carbon effects, however, more strongly depend upon the type of adduct and to some degree whether the result is obtained in the solid state or in solution. For the solid compounds, we found deshielding effects (1.6–3.4 ppm) for Lewis acid adducts but a shielding effect (1.6 ppm) for the Bronsted acid adduct. This often leads to greater differences between the alpha and beta carbons for the Lewis acid adducts (13.4 ppm avg) than for the corresponding carbons in the protonated species (7.9 ppm avg). In solution this same trend is observed for the BH_3 (deshielding 5.8 ppm) and HCl (shielding 3.4 ppm) compounds. However, caution must be applied in the general use of in solution data due to reactions or decompositions which we discuss below.

These differing trends in nuclear shielding reflect composites of electronic and steric effects. In general, only the carbons alpha and beta to the nitrogen are significantly modified by complexation to the nitrogen. The beta carbons are always more shielded (gamma effect) and this has been related to charge effects with modelling to semiempirical charge calculations [7]. For the alpha carbon, there are contributions from both electronic and steric effects. Increased steric effects around the nitrogen can influence the shielding of the carbon alpha to the nitrogen.

In a series of aliphatic amines of varying steric requirements, it is observed that for small or moderately sized groups protonation results in increasing shielding for the alpha carbon atom relative to the amine. However, when the steric requirements of the amine are significantly greater, as, for example, isopropyl or tert-butylamine, protonation results in a deshielding effect compared to the amine.

In the systems we are concerned with the steric requirements of the base are kept constant and we vary the steric requirements of the reference acid. As has been so clearly demonstrated in the classic studies of steric effects using addition compounds, increases in the steric requirements of either component should result in similar steric effects [8]. To the extent that ^{13}C chemical shifts monitor these same steric changes, the effects we note are comparable.

Accordingly, for reaction of phenethylamine (and presumably other amines) with an acid considerably larger than a proton, that is, a Lewis acid, the chemical shift of the alpha carbon differentiates between these complexes and those formed with a proton. This is most clearly demonstrated by the solid CPMAS behavior and is also evident in some but not all of the solution data.

A caveat is in order since the direction of the effect is different for aromatic amines. Protonation of N, N-dimethylaniline leads to a more deshielded methyl carbon resonance than complexation with either borane or $AlCl_3$ relative to the free amine [9].

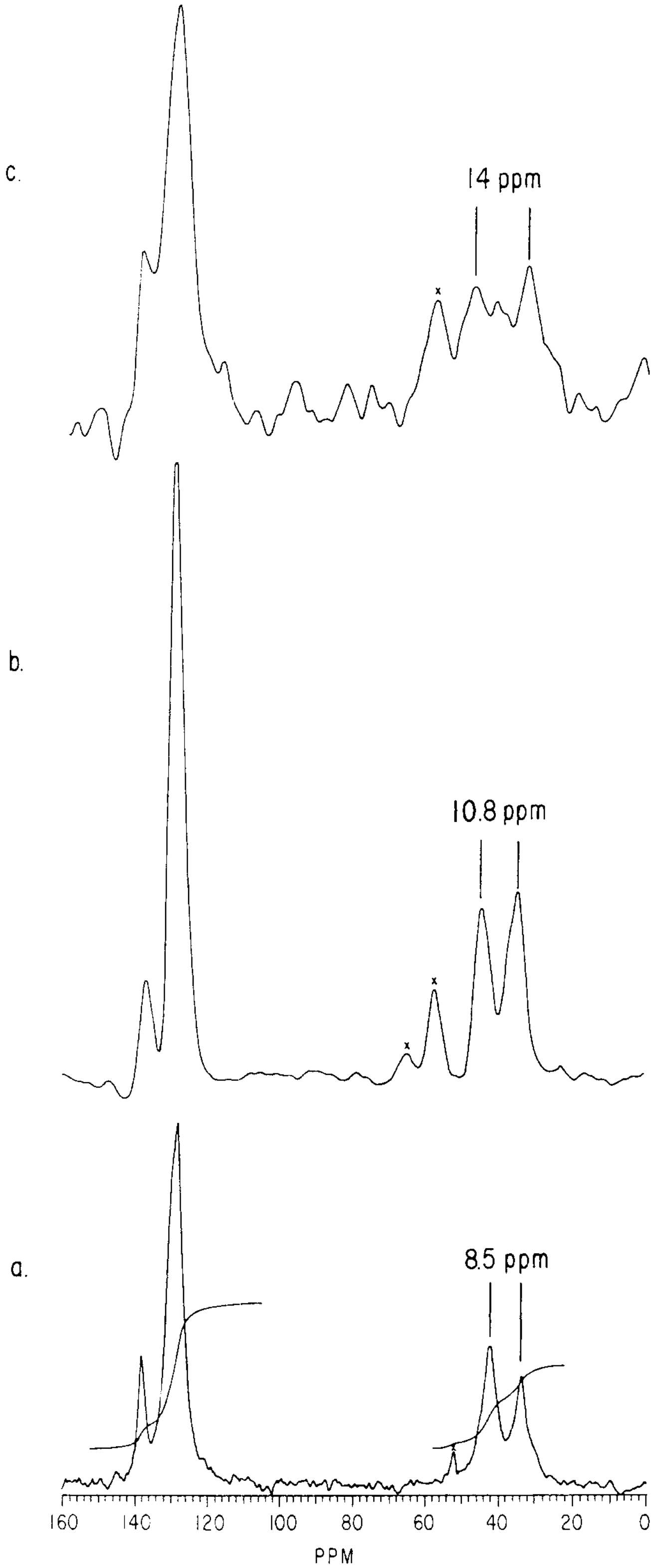

FIGURE 1 ^{13}CPMAS NMR Spectra of phenethylamine compounds: a) compound: with HCl, b) compound with $SnCl_4$, c) compound with $AlCl_3$. Difference between the chemical shifts of the alpha and beta carbons as indicated by arrows. Signals marked with x are spinning side bands.

While the steric effects of the reference acids BH_3 and $AlCl_3$ are greater than those of the proton, factors other than a simple steric correlation are likely to be important. Nevertheless, the essential point that ^{13}C NMR spectroscopy can be used to distinguish acid types is still valid. In many acid catalyzed processes on solid surfaces this methodology could provide distinction between either or both of these possible complexes. Indeed, we are pursuing such studies using metal exchanged clay catalysts with this very amine.

The comparison of the solid and solution chemical shift data provides insight on the species actually present when complex equilibria are possible. For example, the chemical shift values for the $SnCl_4$ amine compound in solution are nearly identical to those of the HCL amine compound. Quite likely the tin complex has reacted with solvent or an adventitious proton source to give the Bronsted adduct. Whatever equilibrium there is lies well on the side of the protonated form. In contrast, the chemical shift values for the Me_3SnCl compound in solution are midway between those of the free amine and the solid complex. In this case, the compound is likely partially dissociated in solution.

The question of what species are present in solutions bears directly on the strength of the bond as well as the competitive effect of solvent. When the chemical shift of the adduct is known from the solid state, the values obtained in solution provide insight into whether changes occur in solution. An application of this methodology should prove useful to determine the nature of species when various Lewis acids and amines are reacted in different solvents. Indeed, the complication of hydrolysis with adventitious water (or reaction with solvent) and subsequent protonation is always a concern. Our solution data in Table 1 indicate the likely importance of this process for $AlCl_3$, Me_3SnCl and $SnCl_4$ in DMSO, but the relative unimportance for the complexes with BH_3.

It has been reported that both species can be detected by NMR spectroscopy at the same time in chloroaluminate molten salts. This is possible when the exchange is slow on the NMR time scale [9]. From our data, exchange in DMSO solution appears to be very rapid. Unfortunately, the melting point of DMSO is not favorable for low temperature studies. However, it would seem that with solvents closer in properties to the melts and more favorable melting points it should be possible to study the rates of exchange using dynamic NMR methods.

Finally, it is conceivable that such dynamic processes could be followed in the solid state by CPMAS. We have demonstrated that rapid solid state proton transfer between strong Bronsted acids on clays and ammonium compounds can be identified by CPMAS [10]. In previous work, we and others have used NMR spectroscopy to show that metal ion migration in solid clays is rapid [11]. Thus, it may be possible to monitor the solid state reversible reactions of Lewis and Bronsted acids in solid support catalysis.

EXPERIMENTAL

NMR Spectra. The solid state ^{13}C CPMAS spectra at 25 MHz were obtained on a modified Jeol 60FX with a Chemagnetics 2.35 T magnet equipped with a Chemagnetics probe. Kel-F rotors were used with spinning speeds of 2.5–3.5 kHz. The solid state ^{13}C CPMAS spectra at 75.5 MHz were obtained on a Varian XL 300 at 7.05 T equipped with a Doty probe. Sapphire rotors were used with spinning speeds of 5.5–9.5 kHz. The single pulse sequence used a contact time of 1 ms (unoptimized) and a recycle time of 4 seconds. The solution ^{13}C NMR spectra were obtained at 75.5 MHz using a Varian XL300 at 7.05 T and Waltz proton decoupling. All spectra are referenced to tetramethylsilane.

Materials. Solvents were distilled from CaH_2 before use and all the compounds used were commercially available.

$SnCl_4$. $H_2NCH_2CH_2C_6H_5$

To a stirred solution of phenethylamine (0.24 mL, 0.002 mol) in dry hexanes (10 mL) was added tin tetrachloride (0.22 mL, 0.002 mol). A white suspension formed, which was stirred for 2 hours. The solid was filtered off and dried in a vacuum. Yield (0.48 g, 0.0013 mol) 65%. The ^{13}C NMR spectra are displayed in the table.

$AlCl_3.H_2NCH_2CH_2C_6H_5$

A slurry of $AlCl_3$ (0.106 g, 0.008 mol) in methylene chloride (5 mL) was added to a solution of phenethylamine (0.1 mL, 0.0008 mol) in dry methylene chloride(10 mL). The resulting mixture was stirred overnight and the methylene chloride removed in vacuum to yield a colorless precipitate (0.180 g, 0.00071 mol) 85%. The ^{13}C NMR spectra are displayed in the table.

$Me_3SnCl.H_2NCH_2CH_2C_6H_5$

Trimethylchlorostannane (0.23 g, 0.0012 mol) in methylene chloride(5 mL) was added to phenethylamine (0.145 mL, 0.0012 mol) and stirred overnight. Dry hexanes (5 mL) were added, a white solid precipitated which was collected and dried in vacuum. Yield (0.31 g, 0.001 mol) 83%. In addition to the ^{13}C NMR spectral data displayed in the table,there was a signal at 2.63 ppm (methyl) with $J(^{117}Sn^{13}C) = 517.7$ Hz and $J(^{119}Sn^{13}C) = 543.3$ Hz.

$C_6H_5CH_2CH_2NH_3Cl$

Anhydrous HCl was passed through a solution of phenethylamine (0.3 mL, 0.0024 mol) in dry diethyl ether (20 mL) for 10 minutes at 0°C. The white precipitate was filtered off and dried in vacuum. Yield (0.31 g, 0.002 mol) 82%. The ^{13}C ^{N}MR spectra are displayed in the table.

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