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^{1}H and ^{27}Al NMR Study of $Li[AlH_4]$ + Ti Compounds in Solution

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A broad sextet signal in the ^{1}H NMR spectrum of $Li[AlH_4]$ in THF-d_8, centered at 2.75 ppm with J/Hz = 176, was assigned to the signal from $[AlH_4]^-$. Also investigated were the reactions of $Li[AlH_4]$ with $TiCl_3$ or $Ti(OBu)_4$ in THF.

Alkali metal tetrahydroaluminate $M[AlH_4]$ (or alanate), especially the ether-soluble Li salt, has been widely used in synthetic chemistry as a reducing agent since its discovery by Finholt et al.[1] In 1997, Bogdanović et al. revived the less common sodium salt ($Na[AlH_4]$) as a solid-state hydrogen storage material by discovering that certain transition-metal compounds, notably titanium(III) trichloride ($TiCl_3$) and titanium(IV) tetrabutoxide ($Ti(OBu)_4$), enhanced the thermolysis of solid $Na[AlH_4]$ (Ti-doped alanates)[2,3] (See Ref. 4 for the latest development of "light element hydrogen storage materials" initiated by Bogdanović's work.). In the course of our studies of the reaction mechanism[5] and electrochemical properties[6,7] of alanates we found that although Al NMR studies have been reported,[8,9] no ^{1}H NMR spectra from $[AlH_4]^-$ are available except for two in which the information given is so vague that the precise position of signals cannot be obtained due to the low magnetic field and sensitivity of the equipment at that time.[10,11] In the present Short Article, we report the ^{1}H NMR spectrum of $[AlH_4]^-$, made possible by the remarkable progress in NMR spectrometry. We have also investigated the reaction of $Li[AlH_4]$ with $TiCl_3$ and $Ti(OBu)_4$ in THF solution in order to obtain some insight in understanding the reaction mechanism of alanates in solid and solution states.

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Experimental

$Li[AlH_4]$, $Li[AlD_4]$, $Na[AlH_4]$, $Li[BH_4]$ (the latter three are for comparison), THF-d_8(99.5%D), $TiCl_3$, and $Ti(OBu)_4$ were purchased from Aldrich. THF-d_8, $TiCl_3$, and $Ti(OBu)_4$ were used without further purification. Hydrides were purified by recrystallization from dried diethyl ether ($Li[BH_4]$, $Li[AlH_4]$, and $Li[AlD_4]$) or from dried THF ($Na[AlH_4]$). Tetramethylsilane (TMS) was used as an internal reference for ^{1}H. The outer tube of a coaxial double NMR tube was filled with a D_2O solution of $Al(NO_3)_3$ as an external reference for ^{27}Al. Air- and oxygen-sensitive substances such as $Li[AlH_4]$ were handled in a glove box filled with purified Ar in which oxygen concentration and dew point were maintained below 1 ppm and 178 K, respectively. The concentration of the salts in THF was 0.3 mol dm^{-3}. The NMR spectra were taken at 23 °C with a JEOL JNM-AL400 spectrometer ($\nu(^{1}H)$/MHz = 399.65).

In order to investigate the reaction between alanate and Ti species we measured the ^{27}Al and ^{1}H NMR spectra of the supernatant solutions formed after the reaction of $Li[AlH_4]$ with $TiCl_3$ or $Ti(OBu)_4$ in THF.

Results and Discussion

Figure 1 shows the ^{27}Al spectrum of $Li[AlH_4]$ in THF-d_8. A sharp quintet signal appears at 98.4 ppm against $Al(NO_3)_3$(aq) with the coupling constant J/Hz = 174. That the proton-decoupling measurement unifies the signal into a singlet testifies to the Al–H bond. The result agrees well with precedent studies.[8–11]

Figure 2 shows the ^{1}H NMR spectra of $Li[AlH_4]$, $Li[AlD_4]$, and $Na[AlH_4]$ in THF-d_8 as well as of the THF-d_8 solvent without solute. Two strong peaks at 1.7 and 3.6 ppm are obviously from the light hydrogen THF in THF-d_8 contained as an impurity. Other impurities in THF-d_8 appear at around 0.9, 1.3, and 2.5 ppm, among which the last one is HDO and reacts with $[AlH_4]^-$ when the solute is added. Comparing Figure 2 (b: $Li[AlD_4]$) and (c: $Li[AlH_4]$) and considering $I = 5/2$ for ^{27}Al, one finds that the broad sextet signal spreading from 1.7 to 3.8 ppm are from the protons in $[AlH_4]^-$. A waveform separation with six equivalent Gauss functions, as drawn with the gray lines in Figure 2c, indicates that, for $Li[AlH_4]$, the sextet centers at 2.75 ppm with the coupling constant J/Hz = 176 and the full width at half maximum (FWHM)

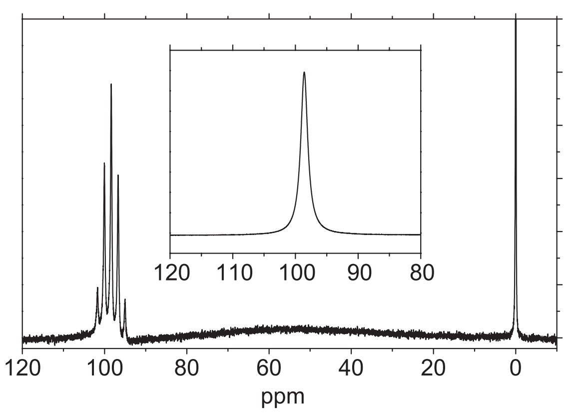

Figure 1. ^{27}Al NMR spectrum of 0.3 M $Li[AlH_4]$ in THF-d_8 with $Al(NO_3)_3$(aq) as a reference. The inset is the spectrum taken with ^{1}H-decoupling.

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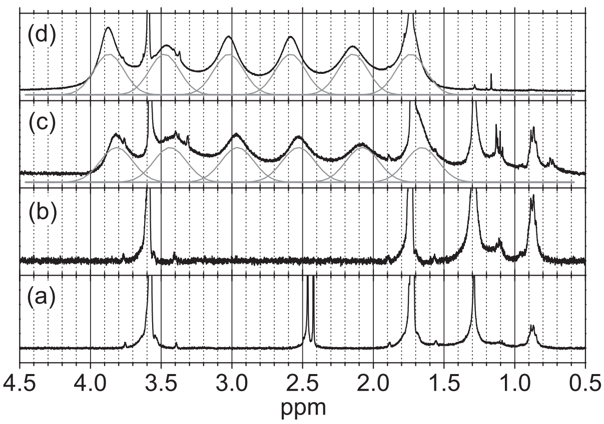

Figure 2. ^{1}H NMR spectra of (a) THF-d_8 (solvent without solute), (b) Li[AlD_4], (c) Li[AlH_4], and (d) Na[AlH_4] in THF-d_8 with TMS as a reference.

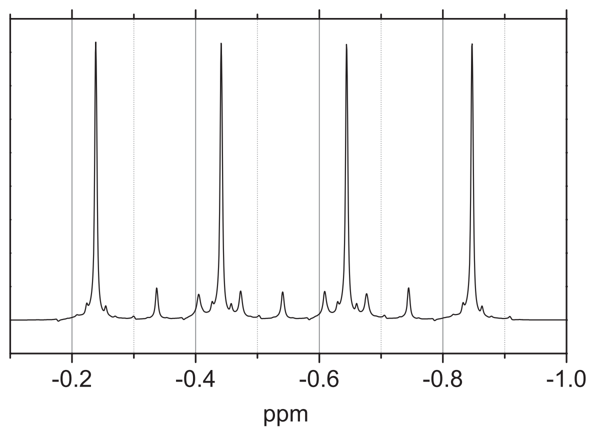

Figure 3. ^{1}H NMR spectrum of Li[BH_4] in THF-d_8.

W/Hz = 108. For Na[AlH_4], the sextet shifts slightly to higher field and centers at 2.81 ppm with J/Hz = 171. The coincidence in these coupling constants with ^{27}Al (J/Hz = 174) evidences that the sextet stems from ^{1}H bonded to Al. Let us compare this result of $[AlH_4]^-$ with $[BH_4]^-$. The ^{1}H NMR spectrum of Li[BH_4] in THF, Figure 3, exhibits a strong quartet (^{11}B, $I = 3/2$, J/Hz = 81) and a weak septet (^{10}B, $I = 3$, J/Hz = 27), both centered at −0.54 ppm. FWHM of the quartet is W/Hz = 2.1 which is 1/50 of that of $[AlH_4]^-$. The narrow signals suggest a highly symmetric shape of $[BH_4]^-$ in THF, which stands in contrast to solid Li[BH_4] where the $[BH_4]^-$ moiety is strongly distorted.[12] The difference in line width between $[AlH_4]^-$ and $[BH_4]^-$ indicates that the longitudinal relaxation time $T_1 \gg J^{-1}$ for $[BH_4]^-$ whereas $T_1 \approx J^{-1}$ for $[AlH_4]^-$.[13] This must be related to the fact that the quadrupole moment Q of ^{27}Al ($0.15e \times 10^{-28}\,m^2$) is about four times larger than that of ^{11}B ($0.04e \times 10^{-28}\,m^2$).

Interestingly, by the solid-state ^{1}H NMR, a sharp peak overlapping with a broad signal centered at around −50 ppm is observed in the solid Na[AlH_4].[14] This is in marked contrast with the weak signal located at 2.8 ppm in THF solution. Jensen et al.[14] attribute the sharp component to a "mobile hydrogen" present in the solid Na[AlH_4] as they observed that the sharp component increased when the solid Na[AlH_4] was doped with a catalytic amount of a Ti compound. The

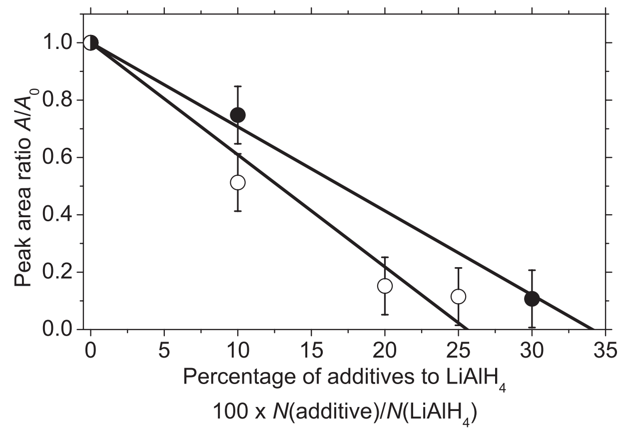

Figure 4. Variation in ^{1}H NMR peak area A from $[AlH_4]^-$ with the amount of $TiCl_3$ (filled circles) and $Ti(OBu)_4$ (open circles) relative to the amount of Li[AlH_4] where A_0 is the peak area measured when no additive was added.

circumstances around $[AlH_4]^-$ may be significantly different in the solid Na[AlH_4] compared to the situation in solution. Although Tarasov and Kirakosyan also observed a sharp signal in solid Li[AlH_4] and Li[AlD_4] using solid-state ^{1}H and ^{2}H NMR, they assigned the sharp component to organic solvent contamination.[15,16]

Figure 4 shows the variation in ^{1}H NMR peak area of $[AlH_4]^-$ with changing the amount of the Ti species added to Li[AlH_4] in THF. During the addition of the Ti species, gas evolved rigorously and dark solid precipitated. After waiting for a while, the supernatant solution was subjected to NMR spectroscopy. As shown in Figure 4, the peak area decreases linearly with the amount of the additives, implying that the ^{1}H signal from $[AlH_4]^-$, albeit broad, can be used for quantitative analysis. The lines intercept the abscissa at 34% and 26% for $TiCl_3$ and $Ti(OBu)_4$, respectively. This suggests the stoichiometric relations Li[AlH_4]:$TiCl_3$ = 3:1 and Li[AlH_4]:$Ti(OBu)_4$ = 4:1, obviously reflecting the initial valence of each Ti species. Unfortunately, from ^{1}H and ^{13}C NMR spectra we were not able to elicit clear information on what is formed after the reaction between Li[AlH_4] and the Ti species. For the solid Na[AlH_4], during the $TiCl_3$ doping process using a ball milling technique, Bellosta von Colbe et al. determined the reaction stoichiometry between Na[AlH_4] and $TiCl_3$ to be 3:1 and concluded that the Ti species was reduced to the zero-valent state after the doping process.[17] Although the situation in solution can be different from solid state and Li[AlH_4] may behave differently from Na[AlH_4], the present result suggests that alanate in THF also reduces Ti species into Ti^0 whatever the initial valence of Ti is.

^{27}Al spectra (Figure 5) indicate that a sharp singlet at 103 ppm and a doublet at 114 ppm (J/Hz = 349) appear with the increasing amount of $TiCl_3$ added to Li[AlH_4]. For the Li[AlH_4] + $AlCl_3$ system in THF, van Dijk and Smoorenberg, and Lefebvre and Conway assigned the singlet at 103 ppm (W/Hz = 5–20[8]/50[9]) and the doublet at 114 ppm (W/Hz = 203[8]/400[9] and J/Hz = 329[8]/330[9]) to $AlCl_4^-$ and $AlHCl_3^-$, respectively. The same species must be formed for the Li[AlH_4] + $TiCl_3$ system as well. When the counter anion of Ti species is not chlorine, a different feature appears (Figure 6).

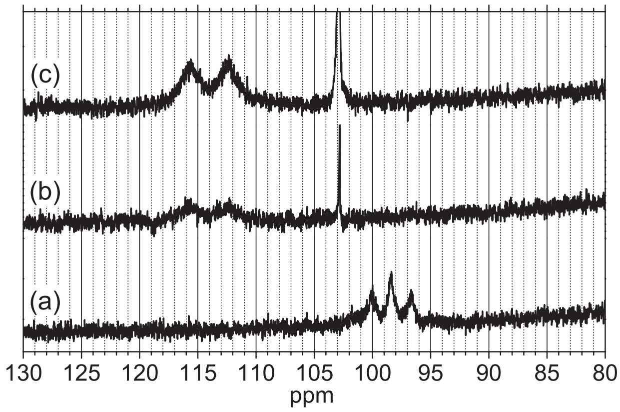

Figure 5. ^{27}Al NMR spectra of the supernatant THF solution of Li[AlH_4] to which (a) 30, (b) 40, and (c) 50 mol % of $TiCl_3$ was added relative to Li[AlH_4].

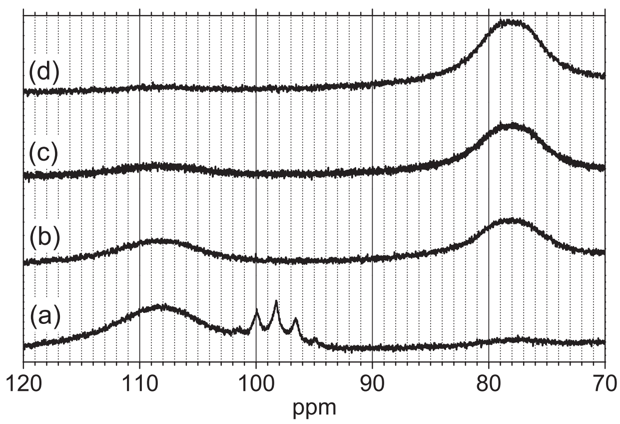

Figure 6. ^{27}Al NMR spectra of the supernatant THF solution of Li[AlH_4] to which (a) 25, (b) 30, (c) 40, and (d) 50 mol % of $Ti(OBu)_4$ was added relative to Li[AlH_4].

Near the 4:1 stoichiometric ratio of $Ti(OBu)_4$ (25 mol %) a broad peak centered at 108 ppm with $W/\mathrm{Hz} = 9.9 \times 10^2$ becomes prominent. With a further addition of $Ti(OBu)_4$ another broad peak at 78 ppm ($W/\mathrm{Hz} = 6.8 \times 10^2$) outstrips the peak at 108 ppm. The above-mentioned researchers assigned the peak at 108 ppm ($W/\mathrm{Hz} = 3000$[8]/1100[9]) to a pentacoordinate species $AlH_3\cdot 2THF$. Huet et al. observed that AlH_3 produced from the reaction between Li[AlH_4] and $AlCl_3$ in THF showed a signal at 115 ppm, while AlH_3 produced from Li[AlH_4] and H_2SO_4 showed a signal at 65 ppm.[18] For comparison, we measured the ^{27}Al NMR of AlH_3–dimethylethylamine (Aldrich) which exhibits a broad peak at 110 ppm with $W/\mathrm{Hz} = 1.5 \times 10^3$. The broad peak at 108 ppm in Figure 6 probably stems from the alane-related species (incidentally, as AlH_3 gives no distinct peak in ^{1}H NMR, it does not influence the peak area calculation in Figure 4.). The origin of the signal at 78 ppm is not clear.

For solid Na[AlH_4], Chaudhuri et al. proposed that highly diffusive alanes formed by Ti catalyst is the origin of the high reactivity of $TiCl_3$-doped Na[AlH_4].[19] We found that AlH_3 also catalyzes the electrochemical reaction of $[AlH_4]^-$ in THF and Et_2O.[7] Although we do not know why the AlH_3-related species seems to be present only in the $Ti(OBu)_4$-added solution and absent in the $TiCl_3$-added one, it is likely that the alanes play an important role in the reactions of alanates both in solid and in solution.

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