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^{27}Al and ^{13}C NMR Relaxation Studies of Aminoalanes

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Introduction

The chemical reactivity of organoaluminum compounds toward amines is well established,[1] with the chemistry of compounds containing Al−N bonds presently receiving considerable attention, primarily due to their possible use as AlN precursors in advanced materials applications.[2] Recently, we reported the synthesis; characterization; and ^{1}H, ^{13}C, and ^{27}Al NMR chemical shift data for the three series $[Me_2AlR']_2$,[3] $[R_2AlNMe_2]_2$,[4] and $Me_3Al{\cdot}R'H$,[3] where R′ = NMe_2, NEt_2, NPr^n_2, NPr^i_2, NBu^n_2, NBu^i_2, NC_4H_8, NC_5H_{10}, NC_6H_{12}, $NC_5H_{11}N$, NPh_2, and $NBzl_2$, and R = Me, Et, Pr^n, Bu^n, and Bu^i. The ^{1}H and ^{13}C NMR chemical shifts for R′ are comparable to those of the parent secondary amines. However, the ^{1}H and ^{13}C NMR chemical shifts and line widths for the R resonances are influenced by the electronegativity and quadrupole moment of the ^{27}Al atom, particularly in the C-1 position. The ^{27}Al NMR chemical shifts fall in a narrow range, typical of tetracoordinate aluminum,[5,6] for all three series. However, as discussed below, within each series the ^{27}Al NMR half-height line width, $\nu_{1/2}$, varies for each compound, dependent upon the R or R′ group. This suggests that the steric nature or size of the R or R′ group may directly affect the solution dynamic properties of the above compounds. Such a variation in ^{27}Al NMR line width with molecular size has been established for alkylaluminum compounds.[6−10] The solution structural and dynamic properties of trialkylaluminum compounds have, in fact, been extensively investigated by a variety of NMR techniques,[11] primarily to determine the extent of dimerization of R_3Al.[12] In addition, NQR[13] and solid-state NMR relaxation studies[14] have been reported. However, to our knowledge, no such studies have been reported for aminoalanes other than an NQR measurement for $[Me_2AlNMe_2]_2$.[13]

In the present report, ^{27}Al and ^{13}C NMR relaxation studies were conducted to determine the role of the R or R′ group in each series in governing the dynamic properties of these compounds in solution. The results obtained are compared with available data for ^{27}Al and ^{13}C NMR relaxation in alkylaluminum compounds.

Experimental Section

All compounds used in this study were synthesized and characterized as previously reported.[3,4] A Vacuum Atmospheres Model HE-43 Dri-Lab equipped with a Model HE-493 Dri-Train was used for the storage and handling of all reagents and for solution preparation. All NMR studies were conducted in NMR tubes (Wilmad, 10 mm, Pyrex) equipped with screw tops containing a PTFE insert to exclude moisture and air. The ^{13}C and ^{27}Al NMR spectra were obtained on a Nicolet 300 MHz FT NMR spectrometer operating at 75.4 and 78.2 MHz, respectively. NMR measurements at 22 °C were conducted on 0.40 M solutions of $Me_3Al{\cdot}R'H$ and $[Me_2AlR']_2$ in benzene-d_6, while variable temperature measurements on $[R_2AlNMe_2]_2$ employed toluene-d_8 as a solvent. The ^{27}Al NMR spectral acquisition parameters were optimized to prevent distortion of the base line and to allow proper phasing of the signal for accurate half-height line width measurement. In each case, an ^{27}Al NMR background signal was obtained and subtracted from the compound signal. The ^{27}Al NMR resonances were best represented by a Lorentzian line shape, and $\nu_{1/2}$ was obtained from a nonlinear least squares iterative calculation. The ^{27}Al NMR chemical shifts were externally referenced to $[Al(H_2O)_6]^{3+}$. The ^{13}C NMR T_1 measurements were performed using the standard inversion recovery method with three-parameter fitting of the data.[15] Ten delay times were used in the determination of each T_1 value. The ^{13}C NOE measurements utilized standard ^{13}C decoupling techniques.[16]

Results and Discussion

The ^{27}Al NMR chemical shifts for all three series occur in the range 150−180 ppm, indicative of tetracoordinate aluminum.[5,6] However, there is a large variation in the half-height line width, $\nu_{1/2}$, within each series. In general, $\nu_{1/2}$ increases in each series as the R or R′ groups become larger or more sterically demanding. Similarly, for the alkylaluminum compounds, R_6Al_2, in toluene-d_8 solution, $\nu_{1/2}$ (Hz) varies as R = Me (850); Et (2550); Pr^n (6300); Pr^i (5900); Bu^n (7800); and Bu^i (6300).[6] Complexation of Et_6Al_2 with several types of Lewis base donors has been shown to cause an increase in the ^{27}Al line width.[7−9] The line width of the aluminum NMR resonance was found in general to increase as the size of the donor molecule increased. This may be due to an increase in

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the rotational correlation time of the molecule or possibly due to steric effects on the symmetry of the molecular electric-field gradient about the aluminum nucleus. The ^{27}Al $\nu_{1/2}$ values (Hz) for the series $Me_3Al\cdot R'H$ increase in the following order at 22 °C: Me_2N (990) < Et_2N (1610) < C_4H_8N (1700) < Pr^i_2N (1760) < $C_5H_{10}N$ (2190) < $C_6H_{12}N$ (2280) < Pr^n_2N (2560) < Bu^i_2N (2690) < $NC_5H_{11}N$ (2850) < Bu^n (3300). Molar volumes for the adducts were determined by density measurements for the liquid adducts and estimated from the densities of Me_6Al_2 and R'H for the solid adducts. A plot of $\nu_{1/2}$ versus molar volume shows a linear dependence with $r = 0.82$. However, the line width values for the branched-chain amines Pr^i_2NH and Bu^i_2NH seem anomalous. As seen from the above $\nu_{1/2}$ values, $\nu_{1/2}$ for the ^{27}Al NMR resonance of $Me_3Al\cdot NPr^i_2H$ is significantly less than that of $Me_3Al\cdot NPr^n_2H$, although from density measurements the two adducts have almost the same molar volume. The same observation also holds for the $Me_3Al\cdot NBu^i_2H$ and $Me_3Al\cdot NBu^n_2H$ adducts. r increases to 0.93 with exclusion of the $Me_3Al\cdot NPr^i_2H$ and $Me_3Al\cdot NBu^i_2H$ data points. Recent correlations of ^{13}C NMR chemical shift data with amine cone angle data for the $Me_3Al\cdot R'H$ adducts indicate that there may be significant conformational changes occurring upon adduct formation for the sterically demanding secondary amines.[17] A more linear variation of $\nu_{1/2}$ with molar volume occurs for the $[Me_2AlR']_2$ series, where $\nu_{1/2}$ values (Hz) for the ^{27}Al NMR resonances at 22 °C increase in the order Me_2N (640) < C_4H_8N (1280) < Et_2N (1370) < $C_5H_{10}N$ (1560) < Pr^i_2N (1590) < $C_6H_{12}N$ (2500) < $NC_5H_{11}N$ (2550) < Pr^n_2N (3500) < Bu^i_2N (4500) < Bu^n_2 (5000). ($r = 0.987$, excluding the Pr^i_2N derivative.)

For the $[R_2AlNMe_2]_2$ series, where R = Me, Et, Pr^n, Bu^n, and Bu^i, the half-height line widths (Hz) for the ^{27}Al NMR resonances at 22 °C in toluene-d_8 solution increase in the order Me (730) < Et (1240) < Pr^n (2380) < Bu^i (2900) < Bu^n (3620). A plot of $\nu_{1/2}$ versus the molar volume of the aminoalane indicates no linear correlation, but suggests that substitution of the alkyl group on the aluminum atom has an additional effect on the ^{27}Al NMR relaxation rate. Larger R groups would be expected to lower the electric-field symmetry about the aluminum atom, thus increasing quadrupolar relaxation.[7] To determine the principal contributions to the ^{27}Al quadrupolar relaxation, variable temperature ^{27}Al NMR line width and ^{13}C NMR T_1 and NOE data for the NMe_2 group were obtained for the $[R_2AlNMe_2]_2$ series.

By assuming that the relaxation of the ^{27}Al nucleus is due to quadrupolar interaction modulated by molecular reorientation,[7,11] then for extreme narrowing conditions where the molecular reorientation is defined by a single correlation time, τ_c, the quadrupolar relaxation rate[18] is given by

$$\frac{1}{T_{1Q}} = \frac{1}{T_{2Q}} = \left(\frac{3\pi^2}{10}\right)\left[\frac{2I+3}{I^2(2I-1)}\right]\left(1+\frac{\eta^2}{3}\right)\left(\frac{e^2qQ}{h}\right)^2\tau_c$$

Because the NQR data have been reported for $[Me_2AlNMe_2]_2$,[13] and a Lorentzian lineshape was found for the ^{27}Al NMR resonances, then the relationship between $\nu_{1/2}$ and τ_c for $[Me_2AlNMe_2]_2$ becomes

$$\frac{1}{T_{2Q}} = \pi\nu_{1/2} = 3.143 \times 10^{14}\tau_c$$

$\tau_c = 7.3$ ps for $[Me_2AlNMe_2]_2$ in toluene-d_8 solution at 22 °C. This value compares favorably with $\tau_c = 16.3$ ps for Et_6Al_2 in toluene-d_8 solution at 25 °C.[11] The $\nu_{1/2}$ values for $[Me_2AlNMe_2]_2$ were obtained from −80 to +80 °C, and τ_c was calculated as a function of temperature. A plot of ln τ_c versus $1000/T$ (Figure 1) indicates excellent Arrhenius behavior ($r = 0.999$). An E_a value of 10.0 kJ/mol was obtained. This value is in good agreement with $E_a = 12.5$ kJ/mol obtained for Et_6Al_2 from ^{13}C T_1 measurements.[11] For the other members of the series, Arrhenius behavior for the variation of $1/T_2$ with temperature was also observed: for R = Et, Pr^n, Bu^n, and Bu^i, $E_a = 9.5$, 10.1, 9.8, and 10.1 kJ/mol, respectively. In contrast, only non-Arrhenius behavior for the temperature dependence of ^{27}Al relaxation has been observed previously for alkylaluminum compounds,[7-11] possibly due to chemical exchange processes at higher temperatures.

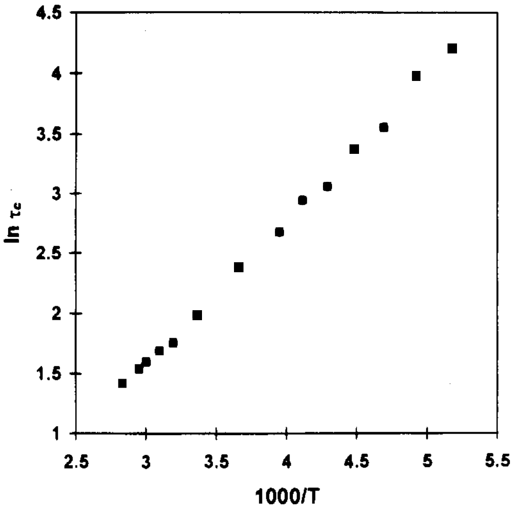

Figure 1. ln τ_c as a function of temperature for $[Me_2AlNMe_2]_2$.

To investigate more fully the concept of simple correlation time effects dominating ^{27}Al NMR relaxation in $[Me_2AlNMe_2]_2$, the ^{13}C T_1 and NOE values for the methyl carbon in the NMe_2 group were determined as a function of temperature from −60 to 60 °C. The NOE values vary from −1.96 at −60 °C, indicating full dipolar relaxation, to 1.28 at 60 °C. By assuming that the dipolar relaxtion rate of the ^{13}C methyl in the NMe_2 group is due only to directly bound protons and that extreme narrowing conditions apply with a single effective correlation time τ_c, then

$$\frac{1}{T_1^{DD}} = \left(\frac{\mu_o}{4\pi}\right)^2 \frac{n_H\gamma_H^2\gamma_C^2\hbar^2}{r_{CH}^6}\tau_c$$

where μ_o is the vacuum permeability, n_H is the number of protons directly bonded to the carbon atom, and r_{CH} is the bond length (109 pm).[11] $1/T_1^{DD}$ is calculated from

$$\frac{1}{T_1^{DD}} = \frac{1}{T_1^{obs}}\left(\frac{\text{NOE(obs)}}{1.99}\right)$$

A plot of the natural log of the dipolar contribution to the spin−lattice relaxation rate for the methyl carbon in the NMe_2 group versus $1000/T$ is linear for $[Me_2AlNMe_2]_2$, as shown in Figure 2. ($r = 0.998$.) E_a is calculated to be 12.2 kJ/mol, in good agreement with the ^{27}Al NMR results. Using the above equation for ^{13}C dipolar relaxation, $\tau_c = 4.0$ ps at 22 °C. This τ_c value is slightly smaller than that obtained from the ^{27}Al NMR results ($\tau_c = 7.3$ ps) probably because of an additional relaxation

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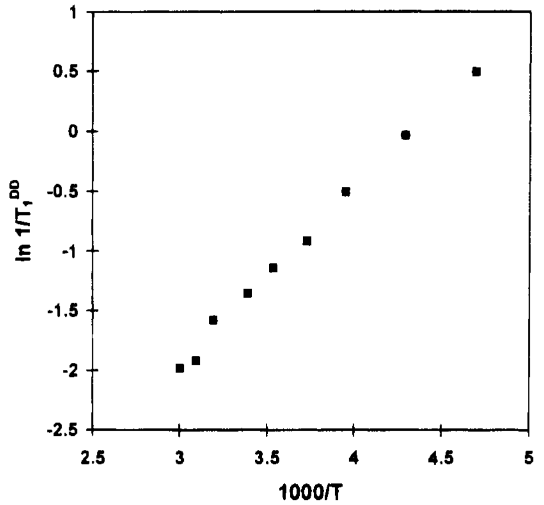

Figure 2. ln 1/T_1^{DD} as a function of temperature for the ^{13}C NMR resonance of NMe_2 in $[Me_2AlNMe_2]_2$.

contribution to the ^{13}C nucleus due to the rapid internal motion of the methyl groups.[11,14] For R = Me, Et, Pr^n, Bu^n, and Bu^i, the ^{13}C T_1 values for the methyl carbon in the NMe_2 group are 3.49, 2.10, 1.05, 0.80, and 0.86 s, respectively, at 22 °C. The corresponding NOE values for the methyl carbon are 1.80, 1.85, 1.80, 1.94, and 1.82, respectively. Thus, for the $[R_2AlNMe_2]_2$ series both the ^{27}Al and ^{13}C relaxation rates increase in the order Me < Et < Pr^n < Bu^i < Bu^n. There is a linear correlation between the $^{13}C(T_1^{DD})^{-1}$ for the NMe_2 group and the $^{27}Al(T_2)^{-1}$ ($r = 0.997$), indicating a single effective correlation time for molecular motion and relaxation for each member in the $[R_2AlNMe_2]_2$ aminoalane series.

In summary, ^{27}Al NMR relaxation data for the three series $Me_3Al{\cdot}R'H$, $[Me_2AlR']_2$, and $[R_2AlNMe_2]_2$ indicate that for each series the ^{27}Al NMR half-height line width, $\nu_{1/2}$, varies for each compound, dependent upon the R or R′ group. The data suggest a linear correlation of $\nu_{1/2}$ with molar volume for the $Me_3Al{\cdot}R'H$ and $[Me_2AlR']_2$ series. For the $[R_2AlNMe_2]_2$ series, substitution of R seems to have a complicated effect on the ^{27}Al NMR relaxation rate. However, the results of variable temperature ^{27}Al NMR relaxation and ^{13}C NMR T_1 and NOE studies suggest that there is a single effective molecular correlation time for each member in the $[R_2AlNMe_2]_2$ series.

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