TEMPERATURE DEPENDENCE OF THE PMR SPECTRA OF Al(BH$_4$)$_3$·O(C$_2$H$_5$)$_2$, AND QUADRUPOLE RELAXATION OF BORON AND ALUMINUM NUCLEI

G. N. Boiko

Investigations of aluminum borohydride (I) [1, 2] and its complexes [3-6] by the NMR method have not led to definite confirmation of the bridge structure of these molecules, proposed on the basis of spectrochemical and x-ray structural analyses. Despite the differences in the form of the absorption lines, the NMR spectra of borohydride compounds indicate the equivalence of all the hydrogen atoms in the BH$_4$ groups and imply rapid (on the NMR time scale) proton exchange between the bridge and end positions. Several proton exchange mechanisms have been suggested as explanations of the equivalence of the H atoms in (I): quantum mechanical tunneling [1], tautomerization [7], transition of Al(BH$_4$)$_3$ molecules from one structural form to another [2], rotation of the borohydride groups [8], etc.

To determine the nature of chemical exchange in borohydride systems, I investigated the NMR-$^1$H, $^1$H-$^{27}$Al, and $^1$H-$^{11}$B spectra of solutions of Al(BH$_4$)$_3$·O(C$_2$H$_5$)$_2$ in toluene and ether at concentrations in the range 0.5 - 4 M at temperatures from 30 to -110°C. The spectra were measured by means of an RYa-2305 (60 MHz) spectrometer with a special device for double resonances of $^{11}$B and $^{27}$Al. The NMR-$^1$H and $^{11}$B spectra of Al(BH$_4$)$_3$·O(C$_2$H$_5$)$_2$ at 25°C are given in [3, 6].

Figures 1 and 2 show typical changes in the $^1$H-$^{11}$B and $^1$H-$^{27}$Al spectra of protons of BH$_4$ groups when the specimens are cooled. With a decrease in temperature the lines of the quartet $^1$H-$^{27}$Al become broader (Fig. 1) and converge, and at -80°C a single signal without a fine structure is observed. Under these

![Fig. 1. $^1$H-$^{27}$Al spectra of a 0.5 M solution of the etherate of (I) in toluene (left-hand side experiment, right-hand side calculation).](image1)

![Fig. 2. $^1$H-$^{11}$B spectra of a 0.5 M solution of the etherate of (I) in toluene (left-hand side experiment, right-hand side calculation).](image2)
conditions, the spectrum of $^1\text{H} - {^{11}\text{B}}$ displays sharp contraction of the initial broad line to a singlet (Fig. 2). Similar changes are observed in the spectra of solutions of $\text{Al(BH}_4\text{)}_3 \cdot \text{O(C}_2\text{H}_5\text{)}_2$ in ether when cooled to $-110^\circ\text{C}$. The broadening of the lines and the disappearance of the fine structure is not due to deterioration of the spectrometer's resolution as a result of an increase in viscosity or of crystallization, because the solvent proton signals remain narrow throughout the temperature range. An increase in the complex concentration in the solution or of the viscosity of the solvent leads to faster spectral changes.

The symmetrical narrowing of the lines in the $^1\text{H}$ and $^1\text{H} - {^{11}\text{B}}$ spectra, and the nature of the disappearance of the fine structure in the $^1\text{H} - {^{27}\text{Al}}$ spectra, do not agree with retardation of bridge and end proton exchange. It was postulated that a decrease in temperature leads to complication of the proton spectra structure and to broadening of the spectral region. In fact we observe averaging of $\text{H} - \text{B}$ and $\text{H} - \text{Al}$ spin–spin interaction, and the single signal exhibited by the spectra in the range from $-80$ to $-100^\circ\text{C}$ indicates equivalence of the borohydride protons in $\text{Al(BH}_4\text{)}_3 \cdot \text{O(C}_2\text{H}_5\text{)}_2$.

The fact that we cannot distinguish between the bridge and end atoms of H indicates the low-energy barrier of the exchange process and the need to investigate the NMR spectra of borohydride compounds at lower temperatures.

Let us make a closer examination of the cause of averaging of the $\text{H} - \text{B}$ and $\text{H} - \text{Al}$ spin–spin interaction with a decrease in temperature. It is known that the fine structure in NMR spectra depends on the dynamic state of the interacting nuclei and may disappear if chaotic transitions of the spin states arise in one of the nuclei. For nuclei with spin $I > \frac{1}{2}$ (like $^{11}\text{B}$, $^{10}\text{B}$, $^{27}\text{Al}$, $^{14}\text{N}$, etc.), interaction of the quadrupole moments of these nuclei with the fluctuating electric field gradients is a very powerful relaxation mechanism in solutions. In this case the spin–lattice relaxation time can be expressed as

$$\frac{1}{T_1} = \frac{3}{40} \cdot \frac{2I + 3}{I^2(I - 1)} \cdot \left(1 + \frac{5}{3} \xi \right) \cdot \left(\frac{e^2Q}{\hbar}\right)^2 \cdot \tau_c,$$

where $\tau_c$ is the molecular rotation correlation time (it depends on the viscosity and temperature $\tau_c \sim \eta/T$), $I$ is the nuclear spin, $eq$ denotes the electric field gradients created at the nucleus by the electron density distribution over the bonds and by the external charges, $e^2Q/\hbar$ is the nuclear quadrupole bond constant (QBC), and $\xi$ is the electron environment asymmetry parameter; with axial symmetry $\xi = 0$, usually $1 \geq \xi \geq 0$.

From Eq. (1) it follows that a decrease in temperature leads to an increase in $\tau_c$, which induces more effective relaxation of the B and Al nuclei and therefore disintegration of the fine structure in the proton spectra. Thus these changes in the NMR spectra qualitatively agree with the influence of quadrupole relaxation of B and Al nuclei on the resonance of $^1\text{H}$ directly linked with these nuclei. To confirm that this assumption was correct, I compiled a program and theoretically calculated the dependence of the line shape in the proton spectra on the rate of quadrupole relaxation of B and Al nuclei. All such calculations are performed on the assumption that for nuclei with spin $I > \frac{1}{2}$ the principal relaxation mechanism is quadrupole interaction. The correctness of this assumption has been corroborated by investigations of the line width in the spectra of various compounds of boron [9], nitrogen [10], aluminum [11], etc. The calculation was based on the theory [12] of the effect of spin motion on multiplet structure in NMR spectra. For the cases in question spin motion is due to quadrupole relaxation of the nuclei. The NMR–$^1\text{H}$ spectra of (I) and its complexes are interesting because the line shape in the proton spectra is simultaneously influenced by quadrupole relaxation of B and Al nuclei. Calculation of such systems is difficult, but the use of $^1\text{H} - {^{11}\text{B}}$ and $^1\text{H} - {^{27}\text{Al}}$ double resonance enables one to eliminate the effect of one of the nuclei and to use the above theory.

Using the program I calculated the temperature dependence of the $^1\text{H} - {^{11}\text{B}}$ and $^1\text{H} - {^{27}\text{Al}}$ spectra. I introduced a correction for the line width in absence of the effect of quadrupole relaxation, for which I took the line halfwidth of the $\text{CH}_3$ group of the solvent molecule ($\sim 1.5$ GHz). Since the broadening of the resonance line of protons of the BH$_4$ groups in the temperature range investigated is considerably greater than 1.5 GHz, this assumption did not introduce a major error into the calculation. In all cases I obtained satisfactory agreement between the experimental and calculated spectra (see Figs. 1 and 2). From the calculation of the spectra I determined the quadrupole relaxation time of B and Al. The activation energies of molecular rotation of the complexes in the solutions were determined from the slope of the straight lines obtained by plotting log $T_1$ vs $1/T$ (Fig. 3). For all the solutions investigated these graphs were linear in a wide range of temperatures and concentrations. This shows that quadrupole relaxation of B and Al nuclei is largely governed by rotation of all the molecules of the complex, and that intramolecular proton exchange apparently does not induce changes in the electric field gradients in these nuclei.