Hydrogen–Deuterium Exchange between $LiBH_4$ and $LiBD_4$. Isotope Effects on the ^1H and ^{11}B Nuclear Magnetic Resonance Spectra of Species $LiBH_nD_{4-n}$

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Summary Isotope effects on the ^{11}B–H coupling constant and on the ^1H and ^{11}B chemical shifts are observed in the n.m.r. spectra of the mixture of species, $LiBH_nD_{4-n}$ (n = 0—4), produced by H–D exchange between $LiBH_4$ and $LiBD_4$.

The addition of tetrahydrofuran to a mixture of $LiBH_4$ and $LiBD_4$ (H : D = 2 : 1) yielded a solution (*ca.* 3·5M in boron) which exhibits the ^{11}B (15·09 MHz) and ^1H (100 MHz) n.m.r. spectra shown in Figures 1 and 2. Clearly these are not the spectra of the initial components, but rather the superposition of spectra due to a mixture of species: BH_4^-, BH_3D^-, $BH_2D_2^-$, BHD_3^-, and BD_4^- resulting from H–D exchange. In the above solution, the first three of these species predominate.

Analysis of the ^{11}B spectrum is given in Figure 1, where the larger splitting is due to $J(^{11}B–H)$ (81·5 Hz for $LiBH_4$) and the smaller to $J(^{11}B–D)$ (12·5 Hz for $LiBH_3D$). The centres of the resonances of $LiBH_nD_{4-n}$ are seen to occur at successively higher field as n decreases from 4 to 2. In fact, resonances for $LiBH_3D$ and $LiBH_2D_2$ occur *ca.* 0·13 and 0·27 p.p.m. respectively upfield from $LiBH_4$.

The ^1H n.m.r. of the solution is affected by the natural occurrence of two isotopes of boron: ^{11}B (80·2%, $I = {}^3/_2$, yielding the quartet shown in Figure 2A—2D (in order of low to high field), and ^{10}B (19·8%, I = 3), yielding a less intense septet. H–D coupling (^2H, I = 1, and J_{H-D} 1·6 Hz for $LiBH_3D$), together with isotope effects are responsible for the fine structure apparent in the peak and at least portions of the spectra of BH_4^- (singlet), BH_3D^- (1 : 1 : 1 triplet) and $BH_2D_2^-$ (1 : 2 : 3 : 2 : 1 quintet)

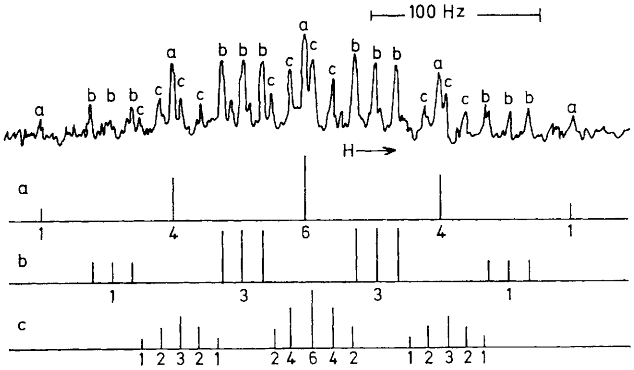

Figure 1. ^{11}B n.m.r. spectrum of the mixture of species $LiBH_nD_{4-n}$. a = $LiBH_4$, b = $LiBH_3D$, c = $LiBH_2D_2$.

can be observed. The centres of the ^{1}H resonances of the species $LiBH_nD_{4-n}$ occur to higher field as n decreases from 4 to 2. Such a trend is consistent with the majority of previously recorded deuterium isotope effects on ^{1}H chemical shifts.[1] It is also clear from Figure 2 that the four members of the quartet are not identical. The change in the relative positions of the component multiplets corresponds to a decrease in the absolute value of $J(^{11}B\text{–}H)$ as n decreases in $LiBH_nD_{4-n}$. The congestion of the multiplets and the resulting overlap limits the accuracy with which the above effects can be measured. Nevertheless it is estimated that the $LiBH_3D$ resonance occurs *ca.* 0·011 p.p.m. upfield of $LiBH_4$ and $|J(^{11}B\text{–}H)|$ in $LiBH_3D$ is *ca.* 0·4 Hz less than that in $LiBH_4$. Isotope shifts in the ^{1}H n.m.r. of an aqueous solution of partially deuteriated potassium hydroborates have been reported previously.[2] The authors, however, reported that (unlike the present result) the four members of the quartet were equivalent.

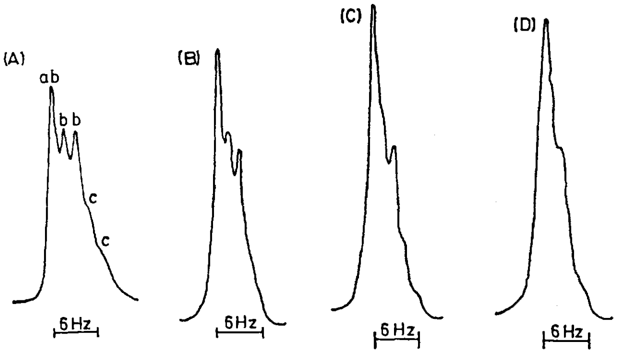

FIGURE 2. ^{1}H n.m.r. spectrum of the mixture of species $Li^{11}BH_nD_{4-n}$, showing individual components of the quartet. Only the ^{11}B quartet is shown here; the ^{10}B septet is omitted. Each member of the quartet A—D was run under slightly different conditions. Adjacent members of the quartet are separated by $J(^{11}B\text{–}H)$ (*ca.* 81 Hz).

We believe the present work contains the first observation of an isotope shift in a ^{11}B n.m.r. spectrum and is the first report of a secondary isotope effect on a coupling constant $J(^{11}B\text{–}H)$, thus adding to the limited data regarding isotope effects on coupling constants at present available in the literature.[3]

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